WEATHERING OF THE GRANODIORITIC ROCKS
IN THE ROSE CANYON LAKE AREA, SANTA
CATALINA MOUNTAINS, ARIZONA

by

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ABSTRACT

The weathering of granodioritic rocks in subhumid environments results in mineralogical changes that are correlative with the chemical composition of surface water and ground water. The weathering of the granodioritic rocks near Rose Canyon Lake on the southwest flank of the Santa Catalina Mountains was considered in terms of reactants and products of the chemical equation:

The rock is a granodioritic gneiss, and the water is an acid carbon dioxide-charged solution that contributes hydrogen ions to the weathered material.

The residual constituents are grus, podzolic soil, and alluvium. In the transition from fresh rock to grus cohesive strength is lost because of the partial alteration of plagioclase feldspar to kaolinite; muscovite alters to illite, and both reactions cause gains in the amount of water and slight losses in silica, calcium, and sodium in the weathered material. In the upward transition from grus to soil, plagioclase

continues to alter to kaolinite, and illite alters to dioctahedral vermiculite. Most of the grus and soil contain less than 2 and 4 percent clay, respectively. The same minerals are present in the alluvial deposits as in the grus and soil.

Mobile constituents contribute to the dissolved solids in surface water and ground water; based on the length of time of water-rock contact, the occurrence of water is classed as direct runoff, base runoff, ephemeral springs, and perennial springs. The approximate length of time of water-rock contact in relation to mean dissolved-solids concentrations is several minutes to a few hours for 18 mg/l (milligrams per liter) in direct runoff, several hours to a few weeks for 43 mg/l in base runoff and ephemeral springs, and a few weeks to a few months for 73 mg/l in perennial springs. Precipitation, which contains about 5 mg/l dissolved solids, has a mixed cation-anion composition that changes instantaneously to a calcium sodium sulfate bicarbonate composition in the transition to direct runoff; dissolved-solids concentrations increase more than three times. Compositional changes in base runoff, ephemeral springs, and perennial springs occur at slower rates; in proportion the water acquires more sodium, bicarbonate, and silica than other constituents. In the transition from precipitation to perennial spring flow, silica, bicarbonate, and sodium increase 320, 27, and 18 times, respectively. Precipitation contributes about 40 percent of the dissolved solids to base runoff. About 30,

40, 50, and 60 percent of the bicarbonate, sodium, magnesium, and calcium, respectively, are contributed to base runoff from precipitation; however, more chloride, sulfate, and potassium are contributed by precipitation than leave the area by streamflow. Plagioclase feldspar (oligoclase), which weathers to kaolinite, is the only major mineral that alters significantly owing to weathering, and surface water and ground water are stable with respect to kaolinite.

Precipitation and direct and base runoff form a closed system with respect to dissolved carbon dioxide. Ephemeral and perennial springs depart from the closed-system relation because of their close association with decaying organic matter.

The rate of chemical denudation based only on the amount of dissolved constituents from weathering of the rock is 4.2 feet per 10^6 years (10 tons per square mile per year), which compares favorably with rates similarly calculated for other granitic terranes; this rate is about half that calculated using total dissolved solids uncorrected for contributions from precipitation. Chemical weathering seems ineffective as a cause of denudation based on the sizable contribution of dissolved constituents from precipitation and atmospheric-biospheric sources. The small amount of chemical weathering in fractures and cleavages of plagioclase, however, is sufficient to weaken the rock completely and thus to provide an abundant source of relatively unweathered detritus.

INTRODUCTION

Most of the previous studies of rock weathering have been focused on field and laboratory descriptions of the mineralogical and pedological changes that take place during the decay of rock materials or on studies and surveys of the mechanisms of such changes. Investigations of these types have been made by Merrill (1904), Polynov (1937), Goldich (1938), Jenny (1941), Wahlstrom (1948), Reiche (1950), Frederickson (1951), Keller (1957), Loughnan (1969), and Ollier (1969). Laboratory experimental studies of leaching of whole rock and specific minerals have been made by Pedro (1961), Marshall (1962), Pickering (1962), Correns (1963), and Huang and Keller (1969). The reports containing field and laboratory results describe changes in chemistry and mineralogy of the weathered rock but do not include studies of the relation between weathering and the soluble constituents removed by ground water and surface water. Although laboratory experimental studies have contributed much to the knowledge of the mechanism of chemical deterioration of rock minerals, laboratory conditions are artificial and may not duplicate the natural weathering environment. Only in recent years have investigations been made that relate the chemical content of surface water and ground water to specific

chemical changes caused by weathering (Feth; Roberson, and Polzer, 1964; Harriss and Adams, 1966; Wolff, 1967; Garrels, 1967; and Garrels and Mackenzie, 1967).

Purpose and Scope

The granodioritic rocks in the subhumid part of the Santa Catalina Mountains have a simple and uniform mineralogy, which makes them ideal for a study of weathering. This report describes the weathering and correlates the resultant chemical and mineralogical changes in the rock with the chemical composition of the surface water and ground water.

During the study, chemical and mineralogical analyses were made of the granodioritic rock to determine the type and composition of the parent minerals. X-ray and petrographic examinations were made of the weathered material in order to identify the clay minerals and other alteration and residual products of weathering. Chemical analyses of precipitation, surface water, and ground water were used to determine the amount and type of soluble chemical constituents that result from weathering of the rock. The theoretical stability of the rock minerals and alteration products was predicted from the chemical composition of the ground water and surface water and was compared to that of the actual minerals in the weathering profile. Chemical equations were postulated to explain the weathering and weathering products.

Location and Physiography

The Santa Catalina Mountains are in southeastern Arizona in the Basin and Range physiographic province (Fenneman, 1931) and characteristically rise abruptly from the basins. The Santa Catalina Mountains are northeast of Tucson (figs. 1 and 2) and are the northernmost range in a group of connected ranges that includes Tanque Verde Ridge and the Rincon Mountains. The Santa Catalina Mountains include about 200 square miles in Pima and Pinal Counties. The highest point is Mount Lemmon at an altitude of 9,157 feet above mean sea level, which is about 6,700 feet higher than Tucson.

The report area includes about 7 square miles near Rose Canyon Lake on the southwest flank of the Santa Catalina Mountains; it is bounded roughly on the north, east, and south by the Mount Lemmon Highway and extends about 2 miles southwest from the highway (fig. 1). Much of the area is characterized by gently sloping surfaces or benches that are deeply dissected by steep-walled canyons (fig. 3). Altitudes range from about 6,800 to 8,600 feet above mean sea level, and the prominent peaks are Rose Peak (altitude, 7,299 feet), Lizard Rock (altitude, 7,328 feet), Barnum Rock (altitude, about 7,920 feet), Green Mountain (altitude, 7,890 feet), Mount Bigelow (altitude, 8,560 feet), and Spencer Peak

Figure 2. --Area of report.

Figure 3. --Aerial view of part of the report area.

View looking southeast. Dissected bench in the Willow Canyon area is in the upper left part of the photograph; Spencer Canyon is in the foreground.

(altitude, about 8,160 feet). The area is drained mainly by the streams in Spencer, Palisade, Pine, Sycamore, Rose, and Willow Canyons. Most of the streams are ephemeral, and the duration of flow is dependent entirely on the amount of rainfall and snowmelt available.

Climate

Based on 4 years of record—from 1965 to 1968—at the Palisade Ranger Station, the mean annual temperature is 48.1°F, and the mean annual precipitation is 30.95 inches (U.S. Weather Bureau, issued annually). The maximum annual temperatures usually occur in June, and minimum temperatures usually occur in December and January; temperature extremes range from about 0°F to 85°F. December, January, February, July, August, and September have the largest amounts of precipitation—as much as 3 inches. June is the driest month, and precipitation usually is less than 0.20 inch.

About 85 percent of the precipitation is equally divided between summer (July to September) and winter (December to March), and the remaining 15 percent is about equally divided among the rest of the months. Occasionally, tropical storms move across the area in September and early October and deposit heavy amounts of rainfall. In general, summer precipitation is the result of convective thunderstorms, which are caused by moisture from the Gulf of Mexico. The convective thunderstorms generally occur in the afternoon or evening,

are localized and torrential in nature, and cause immediate runoff. Winter precipitation is the result of frontal storms that originate over the Pacific Ocean. The precipitation from frontal storms is more widespread than that from convective storms, is not as torrential, and may fall in the form of snow. As much as 24 inches of snow accumulates at the Palisade Ranger Station in February, and some snow cover is common during 4 months of the year. The precipitation from winter storms usually does not cause immediate runoff; however, the runoff is of longer duration than summer runoff.

Vegetation

The report area is in three major vegetation belts—the Montane Fir Forest in the higher altitudes, the Pine Forest in the middle altitudes, and the Pine-Oak Forest in the lower altitudes (Whittaker and Niering, 1965). The Pine Forest belt is the most widespread in the area. The principal vegetation types are given on the following page.

Trees

Acer grandidentatum

Abies concolor

Pseudotsuga

Pinus strobiformis

P. ponderosa

Quercus hypoleucoides

Q. rugosa

Shrubs

Jamesia americana

Yucca schottii

Herbs

Bromus richardsonii

Pteridium aquilinum

Thalictrum fendleri

Aquilegia chrysantha

Carex sp.

Galium asperrimum

Muhlenbergia virescens

M. emersleyi

Previous Work

This report contains the results of the first study of rock weathering in the Santa Catalina Mountains. Several reports concerning the structural geology and petrology of parts of the Santa Catalina Mountains are available, and four of these include all or part of the study area. Peirce (1958) interpreted the structure and petrography of the mountains north of the study area, and DuBois (1959) reviewed the general geology of the mountains and of the granitic-gneissic core and formally named the Catalina Gneiss. Pilkington (1962) reported on the structure and petrology of the mountains east of the study area. Waag (1968) made a detailed study of the structural geology in the Mount Lemmon and Mount Bigelow-Bear Wallow areas.

Methods

The geologic map (fig. 1) was prepared mainly to determine the variability of the mineralogical composition of the rock. Selected weathering profiles were described using the format of the U. S. Department of Agriculture (1951). Samples of unweathered rock and weathered material were collected for petrographic, chemical, X-ray, and particle-size analyses.

Chemical analyses were made on 31 surface-water and ground-water samples collected during the study. Field determinations of pH were made on most of the samples using a Beckman

Model N pH meter, and alkalinity measurements were made either at the time the samples were collected or in the laboratory at the end of the day. All samples were collected in polyethylene bottles, and often a second sample was filtered through 0.1 micron Millipore filter paper and acidified with concentrated hydrochloric acid to determine the total iron content.

Precipitation samples—9 of rain and 1 of snow—were collected at the Palisade Ranger Station. A 2-foot-square enclosure was installed at the station to collect the precipitation; the collecting surface is a 25- by 25-inch piece of corrugated fiberglass at the top of the enclosure, which is 5 feet above the ground. Precipitation drains from the fiberglass into a fiberglass-lined trough and flows through polyethylene tubing into a polyethylene bottle inside the enclosure. The collecting surface was covered between rains to eliminate inclusion of dry fallout in the sample.

Thin sections were made of 37 samples of unweathered rock and weathered material. The poorly consolidated material was impregnated with plastic—Laminac 4128 diluted with styrene—before the thin sections were cut. All the thin sections were etched with hydrofluoric acid and treated with sodium cobaltic nitrate to develop a yellow stain on the potassium feldspar (Bailey and Stevens, 1960).

Chemical analyses were made on 22 samples of unweathered rock and weathered material in the laboratory of the Geologic Division

of the U.S. Geological Survey, Washington, D. C. Rapid rock methods (Shapiro and Brannock, 1962) supplemented by atomic-absorption determinations were used in the analyses.

Most of the surface-water and ground-water samples and some of the precipitation samples were analyzed by Neil B. Carmony of the U.S. Geological Survey using methods described by Rainwater and Thatcher (1960). Personnel of the Soil and Water Testing Laboratory, Department of Agricultural Chemistry and Soils, University of Arizona, analyzed 14 water samples. All the samples were analyzed for the common ions silica, iron, calcium, magnesium, sodium, potassium, bicarbonate, sulfate, chloride, and fluoride. Donald W. Fisher of the Geological Survey in Washington, D. C., analyzed 4 rainwater samples; Mr. Fisher has modified some of the methods of Rainwater and Thatcher (1960) and has substituted additional methods to increase sensitivity for the determination of small amounts of constituents in rainwater.

A 2-gallon composite sample of rainwater was collected at the Palisade Ranger Station from July to October 1967, and 500 milliliters of the composite sample was added to 100-gram portions of 11 samples of unweathered and weathered rock; the water-rock mixtures were stored in polyethylene bottles. The water was allowed to remain in contact with the rock for about a year, and the mixtures were shaken

periodically. At selected intervals, the pH and specific conductance of each sample were measured.

Clay-sized material was separated from 62 samples of weathered material. Standard methods were used in the separation process, in the preparation of oriented clay-mineral slides, and in the ethylene glycol and heat treatment of the slides for identification by X-ray diffraction (Krumbein and Pettijohn, 1938; Warshaw and Roy, 1961; Brown, 1961). Powder photographs taken with 114.6 and 57.3 millimeter cameras were used to determine X-ray diffraction patterns from unoriented crystal planes, to substantiate diffractometer data, and to identify accessory minerals. A Norelco X-ray recording diffractometer and nickel-filtered copper $K\alpha$ radiation ($\lambda = 1.5418$ angstroms) were used for diffraction patterns. The same radiation was used for the powder photographs.

GEOLOGIC SETTING

The study area is in the granitic gneiss-gneissic granite part of the gneissic complex (DuBois, 1959) on the southwest flank of the Santa Catalina Mountains. The gneissic complex forms the core of the mountains and is bounded on the north and east by lower Precambrian to Cretaceous(?) sedimentary and metasedimentary rocks. The bounding rocks have been intruded by diorite and quartz diorite, which have been metamorphosed. Granitoid rocks are present in the western and northern parts of the mountains.

DuBois (1959) used the name Catalina Gneiss for the gneissic complex and divided it into three general groups—banded augen gneiss, augen gneiss, and granitic gneiss-gneissic granite. The banded augen gneiss crops out in the southern part of the Santa Catalina Mountains and grades northeastward into augen gneiss, which, in turn, grades northeastward into the granitic gneiss-gneissic granite in the higher altitudes. The contacts between the three groups are gradational, and the mineralogy of the groups is similar. The rock ranges from grano-dioritic to quartz monzonitic gneiss. In the eastern part of the fore-range of the Santa Catalina Mountains, Peterson (1968) further divided the banded augen gneiss into six units.

For purposes of this study, the granitic gneiss-gneissic granite was divided into three lithologic units—muscovite-biotite gneiss, muscovite-garnet gneiss, and a transitional unit (fig. 1). The transitional unit is a mixture of the muscovite-biotite gneiss and muscovite-garnet gneiss and may contain as much as 75 percent of either unit; if more than 75 percent of one lithologic unit is present in the mixture, the rock is mapped as that unit. This type of mapping is rather subjective, and in places rock-type percentages were difficult to estimate; therefore, most contacts are approximate.

The mineralogical and chemical differences between the units are small, and reactions to chemical weathering are the same. The muscovite-garnet gneiss, however, is somewhat more vulnerable to physical weathering and, as a result, is a weaker rock than the muscovite-biotite gneiss. Muscovite-biotite gneiss is relatively resistant and commonly underlies the prominent ridges and peaks, such as Rose Peak, Lizard Rock, and Barnum Rock (fig. 1). The muscovite-biotite gneiss grades into the transitional unit, which commonly bounds and underlies the erosional benches. The muscovite-garnet gneiss is exposed mainly in the Boy Scout Camp area, the Willow Canyon area, and in part of the area between Sycamore and Rose Canyons northeast of Rose Canyon Lake (fig. 1). In general the erosional benches are underlain by the muscovite-garnet gneiss.

Isolated blocks or slivers of muscovite-biotite gneiss commonly are included in the muscovite-garnet gneiss (fig. 4), which suggests that the muscovite-garnet gneiss has forcefully intruded the biotite gneiss. Matter (1969), however, presented chemical data from one pegmatite dike in the study area and concluded that the constituents in the dike were locally derived from the surrounding rock and were not intruded.

The areas that are underlain mainly by muscovite-garnet gneiss may correspond to the centers of domal upwelling, which are associated with the structural development of the mountains. South of Mount Bigelow, Waag (1968, p. 122) reported that a local upwelling in the gneiss caused a northward tectonic transport of the sediments of the Apache Group (Precambrian). The upwelling is centered in the area of the Boy Scout Camp (fig. 1), where the rock consists of more than 75 percent muscovite-garnet gneiss. The centers of upwelling may have been caused by the movement of heat and fluids upward into zones of weakness; heating of the overlying rocks and influx of material caused expansion, and a dome developed. This mechanism may explain the distribution of the muscovite-garnet gneiss and the possible intrusion of the muscovite-biotite gneiss by the muscovite-garnet gneiss (fig. 4). Data are insufficient to determine whether or not the Willow Canyon-Rose Canyon area, which is underlain by muscovite-garnet gneiss, is a center of upwelling.

A

Blocks of muscovite-biotite gneiss (dark gray) in muscovite-garnet gneiss. Rule in the photograph is 6 inches long.

B

Slivers of muscovite-biotite gneiss (dark gray) in muscovite-garnet gneiss. Rule in the photograph is 6 inches long.

Figure 4. -- Blocks and slivers of muscovite-biotite gneiss in muscovite-garnet gneiss at Girl Scout Spring.

The gneissic complex has been involved in at least two periods of metamorphism—the earlier in Precambrian time and the later in post-Cretaceous time (Peirce, 1958; DuBois, 1959; McCullough, 1963; Waag, 1968; Peterson, 1968). Potassium-argon age determinations suggest that the latest metamorphism was terminated in late Oligocene or early Miocene time (Damon, Erickson, and Livingston, 1963). During the latest period of deformation, feldspar porphyroblasts and pegmatite dikes, which parallel the planar and linear structures in the gneiss, formed as a result of metasomatic feldspathization. Post-deformation metasomatism formed crosscutting pegmatite dikes. The latest period of deformation formed joints and shears throughout the Catalina Gneiss of DuBois (1959); the joints and shears range from widely spaced joints and slight microscopic shearing of quartz and feldspar to closely spaced joints that grade into highly sheared zones. The shearing and jointing have placed the rock minerals in a reactive state by reducing the grain size and forming openings through which water may enter the rock. The main canyons in the study area have been eroded along a major northeast-trending nearly vertical system of joints.

The structural movements during and following metamorphism elevated the mountains with respect to the adjacent basins. The rocks in the mountains were eroded and deposited as alluvium in the basins. Detritus eroded from the Catalina Gneiss is present in the Tertiary and

Quaternary deposits in the northeastern part of the Tucson basin. The oldest of these deposits are of probable Oligocene to Miocene age and were originally named the Pantano Formation by Brennan (1957) and the type I and type II Rillito beds by Pashley (1966). Although Catalina Gneiss fragments are scarce in the type I Rillito beds, they increase in abundance in the type II and type III Rillito beds and in the overlying Fort Lowell Formation of Pleistocene age (Davidson, 1971), which indicates the time of emergence of the gneissic core of the mountains.

The time of stripping of the overlying rocks from the gneissic complex can be estimated from the relative abundance of limestone detritus in the Rillito beds; apparently, the limestone that originally capped the Santa Catalina Mountains was eroded in late Cenozoic time. In the Happy Valley area in the Rincon Mountains Harald Drewes (geologist, U.S. Geological Survey, oral commun., 1970) mapped Paleozoic limestone that metamorphosed to hornfels; the period of metamorphism terminated about 26 million years ago. Pebble counts show that limestone fragments average about 9 percent in the type I Rillito beds, about 13 percent in the type II Rillito beds, and less than 1 percent in the type III Rillito beds (Pashley, 1966). Drewes interprets the large limestone pebble count in the type II Rillito beds as the result of erosion of the limestone that capped the Santa Catalina and Rincon Mountains. The decrease in limestone detritus in the type III Rillito beds of probable Pliocene age indicates that most of the limestone cap

was removed from the mountains prior to the deposition of the type III Rillito beds. Therefore, the gneiss of the Santa Catalina Mountains was exposed to the agents of weathering and erosion between 3 and 12 million years ago.

The youngest sedimentary deposits in the basins surrounding the Santa Catalina Mountains, exclusive of the thin surficial deposits, are of Pleistocene age and are equivalent to the Fort Lowell Formation of Davidson (1971). The present-day topography of the Santa Catalina Mountains is the result of erosion of the detritus that forms the Fort Lowell Formation and to a minor degree the result of erosion of the detritus that forms the surficial deposits. Based on the age of the youngest part of the Fort Lowell Formation, the present topographic form of the mountains is at least 1 million years old.

ROCK WEATHERING

The weathering of the granodioritic rocks on the southwest flank of the Santa Catalina Mountains was considered in terms of reactants and products of the chemical equation:

The reactants are muscovite-biotite gneiss and muscovite-garnet gneiss, precipitation and snowmelt, and hydrogen ions contributed mainly by the dissociation of carbonic acid from the carbon dioxide that is dissolved in the water. The products are residual constituents—grus, podzolic soil, and alluvium—and mobile constituents—soluble material that has been derived from the weathering of the gneiss and has been dissolved and transported by surface water and ground water.

Reactants

Muscovite-Biotite Gneiss

The muscovite-biotite gneiss is light gray to white on fresh surfaces and light brown to light yellowish brown on weathered surfaces. The plagioclase and potassium feldspar are white, and the

quartz usually is colorless. Fresh biotite is dark greenish black to black, and the altered biotite is reddish copper owing to the presence of hematite. The muscovite-biotite gneiss is fairly even grained, and most crystals are less than 4 mm in diameter. Most of the unit exhibits cataclastic deformation, which ranges from faint foliation and slight shearing of quartz to strong foliation and nearly complete mylonitization of the rock.

In places, particularly where joints are widely spaced and the rock contains few pegmatite dikes, the muscovite-biotite gneiss weathers to rounded forms (fig. 5A). At the south margin of the area along the Mount Lemmon Highway northeast of Windy Point, weathering along the prominent joints has formed blocks and spires (fig. 6).

Mineralogical Composition. The essential minerals in the muscovite-biotite gneiss are quartz, potassium feldspar, and plagioclase. The principal accessory minerals are muscovite and biotite, and the minor accessory minerals are magnetite, garnet, zircon, apatite, clinozoisite, epidote, hematite, and rarely pyrite.

Quartz usually makes up from 30 to 40 percent of the rock; however, a few samples contained about 50 percent quartz (table 1). The quartz crystals show wavy extinction as a result of cataclastic metamorphism; a considerable amount of the quartz is shattered or sheared and forms a matrix for the feldspar (figs. 7 and 8B). Sutured boundaries are common on the quartz crystals.

A

Rounded forms developed by weathering and erosion of the muscovite-biotite gneiss along the Mount Lemmon Highway near Willow Canyon.

B

Slabby forms developed by weathering and erosion of the muscovite-garnet gneiss in Willow Canyon.

Figure 5. --Rounded and slabby forms developed by weathering and erosion of the muscovite-biotite gneiss and muscovite-garnet gneiss.

Figure 6. --Blocks and spires developed by weathering and erosion along prominent joints in the muscovite-biotite gneiss.

View along Mount Lemmon Highway northeast of Windy Point.

TABLE 1

MINERALOGICAL COMPOSITION OF UNWEATHERED ROCK
(VALUES IN PERCENT)

Minerals	Muscovite-biotite gneiss	Muscovite-garnet gneiss
Quartz		
Range	31.8-47.6	26.6-33.6
Mean	40.1	30.5
Potassium feldspar		
Range	11.0-28.6	13.0-23.2
Mean	17.6	16.9
Plagioclase		
Range	26.6-42.6	35.0-45.0
Mean	32.7	40.5
Muscovite		
Range	2.4-17.5	7.8-18.0
Mean	5.9	11.5
Biotite		
Range	0- 4.6	----
Mean	1.1	----
Biotite alteration products ^{1/}		
Range	1.4- 4.4	----
Mean	2.4	----
Other ^{2/}		
Range	.1- .4	.4- 1.0
Mean	.2	.6

^{1/} Includes mainly magnetite, hematite, a dark brown nearly opaque mineral, and rarely chlorite.

^{2/} Includes garnet, zircon, apatite, clinozoisite, epidote, and rarely pyrite.

Figure 7. --Feldspar porphyroblasts in a sheared quartz matrix
in the muscovite-biotite gneiss.

(Q, quartz; P, plagioclase; K, potassium feldspar; M,
muscovite)

A

Polarized light.

B

Center of A above. Polarized light.

A

B

Figure 7. --Feldspar porphyroblasts in a sheared quartz matrix in the muscovite-biotite gneiss.

Figure 8. --Plagioclase and potassium feldspar porphyroblasts in the muscovite-biotite gneiss.

(Q, quartz; P, plagioclase; K, potassium feldspar; M, muscovite; B, biotite and biotite alteration products)

A

Plagioclase porphyroblasts in a matrix of smaller crystals.
Polarized light.

B

Plagioclase and potassium feldspar porphyroblasts in a matrix of sheared quartz. Polarized light.

A

B

Figure 8. -- Plagioclase and potassium feldspar porphyroblasts in the muscovite-biotite gneiss.

Potassium feldspar generally makes up about 15 percent of the rock, but some samples contained more than 25 percent (table 1). The presence or absence of polysynthetic or gridiron twinning of microcline was used to differentiate orthoclase from microcline. Orthoclase is dominant over microcline and may be present as anhedral to subhedral porphyroblasts having definite boundaries (figs. 8B and 9) or as anhedral porphyroblasts having ragged boundaries (fig. 10). The effects of deuteric or hydrothermal type alterations on orthoclase are minor.

Plagioclase makes up from about 25 to 45 percent of the unit and is present as porphyroblasts (An_{15} to An_{20}), which may have formed by metasomatism (fig. 8A), and smaller interstitial crystals (An_{15} to An_{30}). Although some secondary sericite and epidote are present, deuteric or hydrothermal type alterations have not had much effect on the plagioclase. The ratio of plagioclase to orthoclase is 1:1 to 4:1; thus, the rock has a granodioritic to quartz monzonitic composition.

Muscovite generally makes up less than 5 percent of the rock, but some samples contained more than 15 percent (table 1). Muscovite crystals occur in scattered groups or in semialined stringers in the sheared matrix. Alteration is minor, although some crystal edges are serrated or finely broken. A small amount of very fine grained muscovite (sericite) has formed as a result of mild deuteric or hydrothermal type alterations of plagioclase feldspar.

Figure 9. --Feldspar porphyroblasts in a matrix of smaller feldspar crystals and sheared quartz in the muscovite-biotite gneiss.

Q, quartz; P, plagioclase; K, potassium feldspar; M, muscovite; B, biotite and biotite alteration products. Polarized light.

Figure 10. --Potassium feldspar porphyroblasts showing irregular boundaries and poikilitic texture, muscovite-biotite gneiss.

(Q, quartz; P, plagioclase; K, potassium feldspar)

A

Dark-gray material is potassium feldspar. Plain light.

B

Same view as A above. Polarized light.

0 1 mm

B

Figure 10. --Potassium feldspar porphyroblasts showing irregular boundaries and poikilitic texture, muscovite-biotite gneiss.

Biotite is less abundant than muscovite and generally does not make up more than 5 percent of the unit (table 1). Crystals usually are semialined in the sheared matrix and mark the foliation. Alteration is more pronounced on the biotite than on the other major minerals, and in nearly all samples of fresh rock the biotite has altered partially or completely to magnetite, hematite, and a nearly opaque dark-brown mineral. Some thin sections show minor amounts of chlorite after biotite. These secondary products probably are the result of the mild deuteric or hydrothermal type alterations and are not a result of weathering.

Garnet is a minor accessory mineral and was absent in most of the thin sections. In general the garnet is stable, but it is the source of a prominent limonitic stain in some slightly weathered rocks. Zircon and apatite are the most common of the other minor accessory minerals, which make up only a few tenths of a percent of the unit. Zircon crystals usually are euhedral and doubly terminated. Apatite occurs as lathlike or roughly rounded six-sided crystals.

Chemical Composition. The chemical composition of the muscovite-biotite gneiss is essentially the same as that of the muscovite-garnet gneiss, the difference being that the percentages of iron, magnesium, and calcium are slightly higher in the muscovite-biotite gneiss than in the muscovite-garnet gneiss. (See appendix A and table 2.) The two units are highly silicic in comparison with the average

TABLE 2

COMPARISONS OF AVERAGE CONCENTRATIONS OF CHEMICAL CONSTITUENTS IN
UNWEATHERED FELSIC ROCKS

Chemical constituent	Analyses of samples from the report area, in percent			Analyses of samples from other areas, in percent					
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
SiO ₂	73.6	74.2	73.9	73.86	74.57	69.15	66.88	70.7	76.37
Al ₂ O ₃	14.8	14.7	14.7	13.75	12.58	14.63	15.66	14.5	10.63
Fe ₂ O ₃	.64	.29	.49	.78	1.30	1.22	1.33	1.6	2.12
FeO	.31	.31	.31	1.13	1.02	2.27	2.59	2.0	1.22
MgO	.19	.10	.16	.26	.11	.99	1.57	1.2	.23
CaO	1.3	.71	1.1	.72	.61	2.45	3.56	2.2	1.30
Na ₂ O	4.3	4.3	4.3	3.51	4.13	3.35	3.84	3.2	1.84
K ₂ O	3.8	4.0	3.9	5.13	4.73	4.58	3.07	3.8	4.99
H ₂ O ⁻	.08	.03	.06	-----	-----	-----	-----	-----	.83
H ₂ O ⁺	.48	.66	.56	.47	.66	.54	.65	-----	
TiO ₂	.09	.05	.07	.20	.17	.56	.57	.5	.41
P ₂ O ₅	.04	.08	.06	.14	.07	.20	.21	.2	.21

TABLE 2—Continued

Chemical constituent	Analyses of samples from the report area, in percent			Analyses of samples from other areas, in percent					
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
MnO	0.07	0.12	0.09	0.05	0.05	0.06	0.07	0.1	0.25
CO ₂	<u>< .05</u>	<u>< .05</u>	<u>< .05</u>	<u>-----</u>	<u>-----</u>	<u>-----</u>	<u>-----</u>	<u>-----</u>	<u>.54</u>
Total	99.7	99.6	99.7	100.00	100.00	100.00	100.00	100.00	100.94

- (1) Average of four muscovite-biotite gneiss samples.
- (2) Average of three muscovite-garnet gneiss samples.
- (3) Average of columns (1) and (2).
- (4) Average of 48 alkali granite samples (Nockolds, 1954).
- (5) Average of 21 alkali rhyolite + rhyolite - obsidian samples (Nockolds, 1954).
- (6) Average of 121 adamellite (quartz monzonite) samples (Nockolds, 1954).
- (7) Average of 137 granodiorite samples (Nockolds, 1954).
- (8) Average of 250 quartzofeldspathic gneiss samples (Poldervaart, 1955).
- (9) Average of five arkose samples (Pettijohn, 1957).

compositions of quartz monzonite and granodiorite (table 2). The amount of silica is similar to that in alkalic granite, but the amounts and ratios of sodium to potassium are more representative of granodiorite. The iron content is smaller than that in most silicic rocks, and the percentages of calcium and magnesium, which are low for quartz monzonite or granodiorite, are about equivalent to those in rhyolite and arkose.

The chemical composition of the muscovite-biotite gneiss and of the muscovite-garnet gneiss does not match the chemical composition of most igneous rocks. Chemical changes caused by metasomatism may have altered the preexistent composition of the units, or the gneisses may have been derived from silicic sedimentary rocks.

Muscovite-Garnet Gneiss

The muscovite-garnet gneiss is an intimate mixture of muscovite-garnet gneiss and pegmatite. The unit generally is light gray to white because of the presence of feldspar; light-green muscovite and reddish-brown garnet are the main colored minerals. The texture ranges from aplitic to pegmatitic and may grade from one to the other in a few inches (fig. 11A) or may form fairly definite boundaries (fig. 11B). Feldspar crystals and muscovite books are as much as 2 inches in diameter in the pegmatite (fig. 11C). Shearing in the muscovite-garnet gneiss is similar to that in the muscovite-biotite

Figure 11.--Textural characteristics of the muscovite-garnet gneiss near Girl Scout Spring.

A

Gradation from aplitic to pegmatitic texture.

B

Relatively sharp boundaries between fine- and coarse-grained textures.

C

Large feldspar crystals and muscovite books in the pegmatitic rock.

A

B

C

Figure 11. --Textural characteristics of the muscovite-garnet gneiss near Girl Scout Spring.

gneiss (fig. 7). Although faint to strong foliation has developed in the dikes, the dikes usually are less sheared than the finer grained muscovite-garnet gneiss or the muscovite-biotite gneiss.

The muscovite-garnet gneiss weathers slabby because of the enclosed pegmatite dikes (fig. 5B). The dikes are more resistant to weathering than the finer grained muscovite-garnet gneiss and stand out in relief (fig. 12).

Mineralogical Composition. The essential minerals in the muscovite-garnet gneiss are the same as those in the muscovite-biotite gneiss—quartz, potassium feldspar, and plagioclase (table 1). The percentages of quartz and plagioclase are lower and higher, respectively, in muscovite-garnet gneiss than in muscovite-biotite gneiss, and the amount of muscovite is greater in the muscovite-garnet gneiss. The muscovite-garnet gneiss contains almost no biotite, and garnet usually makes up as much as 1 percent of the rock. The garnet crystals are reddish brown, subhedral to euhedral, and range from less than 0.1 mm to more than 2 mm in diameter. Other mineral inclusions are common in the garnet. Pilkington (1961) stated that the garnet in the Catalina Gneiss is a mixture of the end members almandine, spessartite, pyrope, and andradite.

Chemical Composition. The chemical composition of the muscovite-garnet gneiss is essentially the same as that of the muscovite-biotite gneiss, the difference being that the percentages of

A

B

Figure 12. --Differential weathering of pegmatite dikes (ledges) in muscovite-garnet gneiss near Willow Canyon.

Rule in upper photograph is 6 inches long.

iron, magnesium, and calcium are slightly lower in the muscovite-garnet gneiss than in the muscovite-biotite gneiss. (See appendix A and table 2.)

Precipitation

The precipitation in the study area has a mixed cation-anion composition and contains about 5 mg/l (milligrams per liter) of dissolved solids (table 3). Using the methods of Rainwater and Thatcher (1960), chemical analyses of five samples show that the precipitation is a calcium chloride bicarbonate type and that the concentrations of the main constituents vary greatly (appendix B). Using D. W. Fisher's (written commun., 1968) method for dilute waters, chemical analyses of four samples show that the precipitation is a sodium sulfate type and that there is less variance in the concentrations of the main constituents. The different results obtained using the two analytical methods may be caused by differences in the sensitivity of the methods, in the type of precipitation analyzed (winter or summer), in the amount of dry fallout in the sample, in the time of collection during the precipitation event, or in the composition of the precipitation in 1966 and 1967. All samples analyzed by methods of Rainwater and Thatcher (1960) were collected during 1966, whereas the samples analyzed by the modified methods of Fisher were collected during 1967. In addition to any differences in the chemical composition of precipitation with time,

TABLE 3

CHEMICAL COMPOSITION OF PRECIPITATION, PALISADE RANGER STATION AND TUCSON

[Analyses in milligrams per liter]

Constituents	Palisade Ranger Station								Tucson
	Analysis of four samples using methods for dilute waters by Fisher (written commun., 1968)			Analysis of five samples using methods by Rainwater and Thatcher (1960)			All samples		Analysis of pre- cipitation from July 1955 to June 1956 (data from Junge and Werby, 1958)
	Range	Median	Mean	Range	Median	Mean	Median	Mean	Mean
Silica (SiO ₂)	0.00-0.37	0.11	0.15	0.0-0.3	0.0	0.1	0.0	0.1	--
Aluminum (Al)	.00- .04	.02	.02	--	--	--	--	--	--
Calcium (Ca)	.18- .42	.30	.30	.0-1.6	.8	.7	.4	.5	1.22
Magnesium (Mg)	.02- .05	.03	.03	.0- .5	.0	.1	.0	.1	--
Sodium (Na)	.47- .92	.67	.68	.0- .8	.2	.4	.5	.5	.72
Potassium (K)	.07- .09	.08	.08	.2-1.8	.2	.5	.2	.3	.15
Ammonia (NH ₄)	.10- .40	.17	.28	--	--	--	--	--	--

TABLE 3—Continued

Constituents	Palisade Ranger Station								Tucson
	Analysis of four samples using methods for dilute waters by Fisher (written commun., 1968)			Analysis of five samples using methods by Rainwater and Thatcher (1960)			All samples		Analysis of pre- cipitation from July 1955 to June 1956 (data from Junge and Werby, 1958)
	Range	Median	Mean	Range	Median	Mean	Median	Mean	Mean
Bicarbonate (HCO ₃)	0.0 - 1.9	0.8	0.9	0.0- 6	0	1.4	0.0	1.2	--
Sulfate (SO ₄)	.50- 4.50	1.61	2.06	.0- 2.7	.4	.8	.5	1.3	1.48
Chloride (Cl)	.24- .49	.38	.37	.5- 3.0	2.0	1.9	.5	1.2	.17
Nitrate (NO ₃)	.25- 1.41	.81	.82	--	--	--	--	--	--
Dissolved solids	3.71- 7.25	4.97	5.22	3.4- 6.9	4.7	5.2	4.7	5.2	--
Specific conduct- ance (micro- mhos at 25° C)	7.3 -24.9	11.5	14.2	9 -18	13	13	13	14	--
pH	4.46- 6.06	5.34	5.30	4.8- 6.5	5.0	5.5	5.0	5.4	--

emanations from copper smelters may affect the chemical composition of the precipitation in the area; the smelter at San Manuel is about 20 miles north of the study area. Because of a copper strike, the copper smelters were not in operation from July 18, 1967, to March 28, 1968. Two samples collected before the strike contained considerably more sulfate than two samples collected during the strike (appendix B).

Table 3 gives a comparison of the analyses of precipitation sampled at the Tucson International Airport (Junge and Werby, 1958) and analyses of the precipitation sampled at the Palisade Ranger Station. The analyses for Tucson indicate that the precipitation is a calcium sulfate type. The differences in the dominant cations in the precipitation at the two stations probably are caused by the different climatic and geologic environments of the stations. The altitude of the Palisade Ranger Station is more than a mile higher than that of the Tucson station. The Palisade Ranger Station is surrounded by sodium-rich rocks, whereas the near-surface deposits surrounding the Tucson station are rich in calcium. Therefore, the cation composition of the precipitation probably is influenced by the composition of the airborne dust at the stations.

The precipitation in the study area generally contains about 5 mg/l of dissolved solids. The precipitation is acid, and pH values range from about 4 to 6. The chemical composition of precipitation

may affect the chemical composition of soil water and, therefore, the end products of weathering (Carroll, 1962, pl. 1).

In arid regions soil water is present only occasionally, and because of insufficient leaching there is little removal of the cations that are added by precipitation or that are derived from the weathering of minerals. Sodium may replace calcium and magnesium on exchange sites in montmorillonite, which, in addition to illite, generally is the principal clay mineral in arid regions. The presence of abundant sodium in soil water and on exchange sites causes the montmorillonite to become stable and resistant to breakdown by weathering.

In areas that receive medium to large amounts of precipitation and that have well-drained soil, the cations added by precipitation have little influence on the weathering process. The net reaction under humid conditions is the removal of cations from exchange sites and the substitution of hydrogen ions; the reaction is more effective as the acidity of the precipitation increases. Montmorillonite is unstable and kaolinite is stable. As Carroll (1962, pl. 1) pointed out, however, the exchange reactions are generalized, and no allowance has been made for the contribution of acid and carbon dioxide by soil organic matter or the complexing of cations by organic solutions.

The author has concluded that the cation composition of the precipitation has little effect on the weathering of minerals in the study area but that the dissolved carbon dioxide in the precipitation has a

significant effect on weathering; carbon dioxide is a principal source of hydrogen ions when dissolved in water, and precipitation and runoff form a closed system with respect to carbon dioxide. The soil atmosphere is a more potent source of carbon dioxide than precipitation, and soil water and ground water in contact with organic material contain greater amounts of dissolved carbon dioxide than surface water or precipitation.

Hydrogen Ions

The hydrogen ions (H^+) initiate the weathering of silicate minerals. These small cations penetrate the crystal structures and replace other cations, which, in some instances, causes an electrical imbalance. Eventual alteration to clay minerals results if the available water and leaching are sufficient to carry away the displaced cations.

The hydrogen ion, like all cations, is not in a free state in aqueous solutions but is hydrated (Mahan, 1965, p. 181). The hydronium ion is believed to be the stable state for hydrogen; however, this may be an oversimplification because there is some evidence that the hydronium ion may be further hydrated to form $H_9O_4^+$. In this report, H^+ will be used to refer to the form of hydrogen in aqueous solution regardless of the state of hydration.

The hydrogen-ion concentration is a measure of the acidity of a solution and is expressed as the pH—the negative logarithm of the hydrogen-ion concentration ($\text{pH} = -\log[\text{H}^+]$). pH is determined readily by measuring the electrical potential that develops between the hydrogen ions in solution and the appropriate electrodes that are placed in the solution.

In the study area the principal sources of H^+ are precipitation and organic material in the soil and the forest litter. The contribution of H^+ may be from carbonic acid formed from the solution of carbon dioxide in precipitation and soil water or directly from organic acids in the soil. Carbon-dioxide concentrations in the soil atmosphere caused by organic material may be 10 times that in the air (Bear, 1955, p. 205). The pH is about 4 in distilled-water leachates from decayed forest litter. Although the precipitation has pH values that range from about 4 to 6, the precipitation is very dilute and unbuffered, and the pH changes rapidly upon contact of the precipitation with rock and soil (Feth and others, 1964, p. 35).

Samples of unweathered and weathered material were mixed with rainwater in the laboratory, and the pH and specific conductance of the solutions were monitored with increasing time. The initial pH of the rainwater was 5.41, and the pH of the rainwater-soil and rainwater-rock mixtures ranged from 5.19 to 6.86 immediately after mixing. The effect of organic material in the soil or rock on the pH of

the water is shown by a direct relation between the pH of the mixtures and the value notation of the rock or soil color (Munsell Color Co., 1954); a similar relation exists between the pH of distilled-water slurries of soil or rock and the color value (fig. 13). The color value is a measure of the lightness or darkness of a color—a value of 0 is black, and a value of 10 is white. The color values for unweathered gneiss are about 8 and are as low as 2 for soil in which decayed organic material is abundant. Therefore, the color-value notation is a relative measure of the amount of organic material present because decayed organic material is the principal contributor of the dark color in the weathered material in the study area. A rock-rainwater mixture that has little or no organic matter has a pH of 7 or more because the hydrolysis between water and rock-forming minerals results in alkaline solutions. Stevens and Carron (1948) recorded an abrasion pH—the pH of a slurry as a result of pulverizing minerals in water—of between 7 and 11 for silicate minerals. Grant (1963) reported abrasion pH values that ranged from 5.0 in weathered rock to 9.3 in fresh rock. As the amount of organic material increases in the rock or soil, the contribution of H^+ becomes dominant over the high pH from hydrolysis of silicate minerals.

The surface water and ground water that drain the study area generally have a pH of from 5.5 to 7.5 (appendix C); in general the pH is the result of the interactions between the hydrolysis of silicate

Figure 13. --Value notations of rock and soil color versus initial pH of water-rock or water-soil mixtures.

minerals and the contribution of H^+ from organic material. Other possible sources of H^+ are strong mineral acids, acid clay, and living plants (Keller, 1957). Strong mineral acids, such as sulfuric acid, originate from the oxidation of pyrite and other sulfide minerals; however, sulfide minerals are rare in the unweathered rock and are not a major source of H^+ in the study area. Acid clay, which is a clay mineral that has a high percentage of H^+ in its cation sites, is a potential significant source of H^+ . Acid clay, when mixed with coarser fractions of nonclay-size minerals, exchanges H^+ for calcium and magnesium in the nonclay-size minerals. Acid clay as a source of H^+ was not evaluated in this study, but it probably is not a significant contributor because the percentage of clay is very low—usually less than 3 percent. Living plant rootlets exchange H^+ for soil cations, which the plant uses as nutrients, thereby creating a H^+ environment near the roots. Hydrogen ions so generated are available for alteration of nearby minerals in the soil and may contribute part of the acidity to the soil.

Products

Residual Constituents

The residual constituents result from the weathering of granodioritic rocks and include grus, podzolic soil, and alluvium. The principal mineralogical change during formation of the residual

constituents is the partial alteration of plagioclase to kaolinite, which causes physical disruption of the parent rock. Other significant mineralogical changes involve the alteration of muscovite to illite and illite to dioctahedral vermiculite.

Grus. Grus is defined as fragmental debris derived from the weathering of rocks, and, in this report, the term is applied to the weak slightly chemically weathered rock composed of angular and gritty material that has resulted from in situ weathering. Original rock textures and structures usually are preserved in grus.

Description and Distribution: In the study area the grus ranges from a fairly strong compact rock that breaks easily with a light blow of a hammer to a very weak and friable material that may be crushed easily with the fingers. The grus ranges from light gray or white to shades of yellowish brown and brown (fig. 14A). The light gray or white grus generally is not present in soil profiles, whereas the yellowish-brown and brown grus forms the C horizon in most profiles and occurs directly below the alluvial deposits. The feldspar in the grus commonly has a chalky or kaolinized appearance (fig. 14A), although less than 2 percent of the rock has been altered to clay minerals. Original rock textures and structures are preserved in the grus (fig. 14B) and can be traced into the soil zone, which indicates that there is very little volume change during weathering. In the transition

A

Hand specimens of fresh rock (left) and grus (center and right). Grus in the center is a fairly firm rock. The principal change from fresh rock to grus is the development of the chalky appearance of the feldspar. The grus on the right may be crushed easily by hand. Most of the plagioclase feldspar has been altered to fine sand and silt-size particles.

B

Thin soil (soil profile P-5) and grus developed on muscovite-garnet gneiss. Rock structures are well preserved. Sheet fractures are parallel to the surface and are present to a depth of about 2 feet. Pick handle is 18 inches long.

Figure 14. --A comparison of hand specimens of fresh rock and grus and a field exposure of grus.

from fresh rock to soil the bulk specific gravity of the grus decreases, and a value of 2.47 g/cm^3 (grams per cubic centimeter)—in fresh rock the value is about 2.70 g/cm^3 —was obtained for one grus sample having less than 2 percent clay. Grant (1963; 1964) used bulk specific gravity of weathered gneiss as an index of weathering of crystalline rocks in Georgia; he found a good indirect relation between bulk specific gravity and percent kaolinite in the weathered rock.

Rocks having strong foliation or closely spaced joints or shears tend to develop grus that spalls rock fragments. This phenomenon is particularly evident in artificial exposures, such as roadcuts, and causes the gneiss to appear to be more weathered than it is (fig. 15A). The deformation and fracturing of the gneiss (fig. 15B) as a result of cataclastic metamorphism accelerate the development of grus by reducing the grain size and providing channels for water to enter the gneiss. A rock that contains closely spaced joints and shears weathers more rapidly than a rock containing widely spaced joints or shears (fig. 16). Small amounts of weathering, chiefly hydrolysis of the silicate minerals, cause small amounts of expansion in the outer few millimeters of the rock; the expansion increases during cold weather because of the freezing and thawing of the enclosed moisture. The rock develops a thin rind of loose angular material (fig. 17), which eventually spalls from the surface of the exposure. The process is the same as that of spheroidal weathering, which develops concentric rinds

A

Exposure of grus in a roadcut on the Mount Lemmon Highway between Rose and Willow Canyons.

B

Closeup of exposure shown in A above.

Figure 15. --Development of grus caused by closely spaced shears.

Figure 16. --Differential weathering caused by the variation in the density of shears and fractures.

Exposure on Mount Lemmon Highway southeast of Spencer Peak.

Figure 17. --Rind of slightly weathered material on the surface of sheared rock.

Rule is 6 inches long. The exposure is on an unimproved road near the head of Sycamore Canyon.

or onionskins of slightly weathered rock on boulders. Large concentric rinds do not develop on the gneiss, however, because of its inherent weakness and lack of cohesive strength as a result of the cataclastic metamorphism.

In places grus has developed beneath fresher rock. Figure 18 shows an exposure of fresh muscovite-biotite gneiss, which is relatively free of closely spaced joints, resting in place on as much as 6 feet of grus. The situation seems anomalous until it is realized that the development of grus—or weathering in general—can occur only where moisture is present. The base of the fresh gneiss is at the top of the soil zone. The gneiss has been weathered to grus beneath the soil surface where moisture is retained. The fresh rocks on top of the grus may be exhumed core stones that formed beneath the soil in an earlier period of weathering or may be fresh-rock remnants formed at the ground surface by differential erosion. The rock near the widely spaced fractures weathered and was carried away, and the fresh boulders were preserved because weathering was greater in the widely spaced joints than on bare rock.

The thickest accumulations of grus are on the erosional benches at the base of the steep slope that continues to the crest of the Santa Catalina Mountains (fig. 1); here, the rocks receive more moisture than those in places farther from the slope break. The moisture is from runoff from the steep terrane above the break in slope. The

Figure 18. --Fresh muscovite-biotite gneiss in place on grus.

Gray rounded boulders are muscovite-biotite gneiss.
The exposure is on a fireroad 0.3 mile east of the
Palisade Ranger Station.

thick accumulations of grus on the benches are associated with remnants of alluvial deposits, which indicates that the areas near the slope break are sites of aggradation rather than erosion and, thus, are favorable for rock weathering and soil formation. The thickness and lateral extent of the grus are extremely variable. The grus commonly is from 2 inches to as much as a foot thick and is several feet thick near the break in slope. The grus is at least 15 feet thick in a roadcut near Willow Canyon (fig. 19).

Mineralogical Composition: The minerals in the grus are similar to those in slightly weathered gneiss. In the transition from rock to soil three of the five major minerals in the gneiss are altered in varying degrees. The principal alteration products are:

biotite $\longrightarrow$ magnetite + hematite

plagioclase $\longrightarrow$ kaolinite (also some sericite + epidote)

muscovite $\longrightarrow$ sericite $\longrightarrow$ illite $\longrightarrow$ vermiculite.

Significant physical changes accompany the mineralogical alterations in the weathering of rock to soil (table 4). Although biotite is the first mineral to exhibit alteration, some of the changes are not caused by weathering; nearly all the biotite in fresh rock showed some alteration to magnetite, hematite, and a brown opaque nonpleochroic mineral in thin sections. A small amount of chlorite was observed in some thin sections. The changes probably are the result of deuteric type

Figure 19. --Thick grus exposed in a roadcut along the Mount Lemmon Highway near Willow Canyon.

TABLE 4

SUMMARY OF PHYSICAL AND MINERALOGICAL CHANGES IN THE WEATHERING OF ROCK TO SOIL

Stage of weathering	Hand specimen	Thin section				Remarks
		Plagioclase	Biotite <u>1</u> /	Potassium feldspar	Muscovite	
1	Fresh rock: no obvious staining, except possibly around biotite	Essentially unaltered; cores of some crystals show slight deuteric-type alteration to sericite; some crystals are slightly fractured (figs. 7, 8, 9, and 20C)	Usually shows some alteration to magnetite, hematite, or a brown slightly pleochroic mineral	Unaffected	Unaffected	Mainly deuteric type alterations.
2	Slightly weathered rock: rock is firm, but very light-brown stain is noticeable; red hematite after biotite marks incipient weathering	Core of crystals shows alteration; fractured crystals more numerous	Considerable alteration to hematite	Unaffected	Generally unaffected, but edges of some crystals are crinkled	Incipient weathering.
3	Grus: shows obvious alteration on fresh surface; has a "kaolinized" appearance; light-brown stain is evident; rock can be broken with hands	Crystals "dusted" with reddish-brown kaolinite and iron oxides; all crystals show fractures; many partly filled with the alteration products (fig. 20B)	Nearly all altered to hematite	Unaffected	do.	Kaolinite, first clay mineral.
4	Grus: strong brown stain; original rock textures still evident, but rock crumbles easily with fingers	All crystals highly fractured; fractures widened by alteration and filled with clay skins; alteration products include kaolinite, sericite, and epidote	do.	Broadly fractured, but chemically unaltered	Commonly grades into sericite along edges; probable formation of illite from sericite	Development of clay skins; probably illite.

See footnotes at end of table.

TABLE 4—Continued

Stage of weathering	Hand specimen	Thin section				Remarks
		Plagioclase	Biotite ^{1/}	Potassium feldspar	Muscovite	
5	Grus: dark-brown stain and clay skins are evident; original textures still present, but rock crumbles very easily with fingers	Strongly altered to kaolinite and some sericite and epidote; only fragments of original crystals remain (figs. 20A and 21)	Nearly all altered to hematite	Fractured, but not chemically altered; fractures may contain clay skins (fig. 24)	Shows evidence of alteration to sericite and illite (figs. 20A and 21)	Clay skins abundant (fig. 21); illite, second clay mineral.
6	Soil: rock textures obliterated					Most significant change is the alteration of illite to vermiculite, third clay mineral.

^{1/} Essentially no biotite is present in muscovite-garnet gneiss. Garnet is the mafic mineral in this rock and normally shows very little indication of alteration.

alterations associated with metamorphism of the gneiss. Under weathering conditions, most of the remaining biotite is converted to hematite.

Plagioclase is the second mineral to show alteration. Plagioclase is unaltered in fresh rock (fig. 20C), except for minor changes in the cores of some crystals because of deuteric type alterations. Some crystals in fresh rock are slightly fractured; with increased weathering, fractures widen in the plagioclase, and kaolinite forms as an alteration product (fig. 20B). Because the fractured plagioclase makes up about one-third of the rock, the rock loses its cohesive strength and changes into friable grus. In the final transition from grus to soil the fractures in the plagioclase are widened and are filled with reddish-brown to brown clay; the crystals are altered to kaolinite and minor amounts of sericite and epidote (figs. 20A and 21).

Muscovite is the third mineral to show alteration by weathering; however, the muscovite is much more stable than the plagioclase. In the transition from grus to soil muscovite may grade into sericite along crystal edges, or the edges may become ragged and grade directly into clay (figs. 20A, 21, and 22). In the transition of muscovite to clay, sericite may not be microscopically obvious. Clay forms along the fractures in other crystals in the rock, particularly those in plagioclase feldspar, and with increased weathering forms clay skins.

Figure 20.--Transition of fresh rock to grus in soil profile P-7.

(Q, quartz; P, plagioclase; K, potassium feldspar; M, muscovite; B, biotite alteration products; ka, kaolinite; C, clay skins)

A

Grus, about 2 feet below the soil surface at the base of the B horizon. The plagioclase feldspar is completely dissected by fractures that are filled with clay skins or is altered to kaolinite. Muscovite shows evidence of alteration along the edges and in cleavage traces in the crystals. Polarized light.

B

Grus, 5 feet below soil surface. The plagioclase feldspar is completely dissected by fractures, causing the rock to lose its cohesive strength. Kaolinite has formed in the cores, and clay skins have formed in the fractures of the plagioclase. Clay skins also have formed in some of the large fractures in the rock. Polarized light.

C

Fresh muscovite-biotite gneiss, 12 feet below soil surface. Alterations are of the deuteric type and have affected the cores of some of the plagioclase feldspar (top center) and biotite. Plagioclase commonly is fractured. Polarized light.

Figure 20. --Transition of fresh rock to grus in soil profile P-7.

0 0.5 mm

Figure 21. --Weathered plagioclase feldspar crystal in grus near the base of the B soil horizon of soil profile P-7.

Only fragments of plagioclase remain within the boundaries of the former crystal. Kaolinite is the light-colored alteration product, and clay skins are the reddish-brown and light-yellowish-brown material filling fractures. Muscovite (M) has weathered to illite. Polarized light.

0 0.5 mm

Figure 22.--Muscovite altered to illite along boundaries and cleavage traces.

Muscovite is in center of photograph. Clay skins envelope all crystals and rock fragments. Polarized light.

Clay skins generally are well developed as cementing material in alluvial deposits (figs. 22 and 23). Clay skin is defined as optically oriented clay formed on the walls of interstices in the soil (Buol and Hole, 1961, p. 378). Optically, the clay skins are either uniaxial negative or biaxial negative having an extremely small axial angle; the index of refraction in clay skins is greater than that in balsam. A fragment of clay skin showed a few weak X-ray diffraction lines that may be those of illite, which is in good agreement with the optical properties exhibited in clay skins. In the soil zone illite weathers further to form vermiculite; this relation is discussed in the section entitled "Clay Minerals in the Residual Constituents."

Potassium feldspar is the second most stable major mineral in the rock. In the transition from grus to soil, potassium feldspar, although somewhat fractured, remains chemically unaltered, which is in contrast to the associated highly fractured and kaolinized plagioclase feldspar (figs. 20B and 24).

Quartz is the most stable major mineral, and there is no optical evidence that it dissolves in the weathering environment. Essentially, it is an inert component in the rock.

The stability of the heavy minerals in grus is similar to the stability of the heavy minerals in soil and alluvial deposits and can be generalized as follows.

0 0.5 mm

Figure 23. -- Well-developed clay skins as cementing material in alluvial gravel.

Polarized light.

0 0.5 mm

Figure 24. --Fractured but chemically unaltered potassium feldspar surrounded by strongly altered plagioclase feldspar in the grus beneath soil profile P-1.

Polarized light.

Stable: Garnet and zircon.

Unstable: Biotite, apatite, pyrite, magnetite, and
clinozoisite.

New stable minerals formed: Hematite, epidote, and
rarely chlorite.

Garnet and magnetite are ubiquitous in the heavy-mineral fractions of fresh rock, grus, and soil, although there is less garnet in the muscovite-biotite gneiss than in the muscovite-garnet gneiss. A comparison of the relative amounts of garnet in the upper and lower parts of soil profiles indicates that garnet may be slightly unstable (table 5). Most garnet in the soil profiles, however, showed no optical evidence of alteration that would distinguish it from the garnet in fresh rock. Magnetite is a deuteric type alteration product of biotite and did not form as a result of weathering; in fact, magnetite is unstable under weathering conditions because many grains in the grus, soil, and alluvial deposits are coated with hematite. The percentage of zircon increases in the heavy fraction of weathered material, which was expected. Apatite, which was present in all thin sections of the fresh rock, was not present in significant amounts in the weathered material, and pyrite was not identified in any weathered material. Generally, epidote is a product of the deuteric alteration of plagioclase feldspar. Some epidote may form from clinozoisite, which decreases in abundance in the upper parts of the soil profiles. The

TABLE 5

HEAVY MINERALS IN FRESH AND WEATHERED ROCK MATERIALS

(Expressed in percent of total grains counted)

Sample number	Sample description	Garnet	Magnetite	Hematite	Epidote	Zircon	Chlorite	Biotite	Clinozoisite	Pyrite	Remarks
MUSCOVITE-BIOTITE GNEISS											
R-54	Fresh rock	12	31	5.6	6.0	--	--	17	1.9	26	
R-55	Fresh rock	9.0	23	2.2	3.4	0.8	1.1	42	4.9	13	
R-56	Fresh rock	6.5	6.5	22	1.9	--	2.8	56	4.7	--	
P-6b	Soil, 0-2 inches below surface	17	51	1.6	15	1.6	2.8	1.2	9.4	--	Garnet is as much as 10 times larger than other grains. Some magnetite has partial to complete coatings of hematite.

TABLE 5—HEAVY MINERALS IN FRESH AND WEATHERED ROCK MATERIALS—Continued

Sample number	Sample description	Garnet	Magnetite	Hematite	Epidote	Zircon	Chlorite	Biotite	Clinozoisite	Pyrite	Remarks
P-6d	Soil, 5-13 inches below surface	42	42	0.8	11	1.1	--	--	3.8	--	Some hematite-coated magnetite.
P-7a	Soil, 1-2 inches below surface	9.2	63	6.9	9.7	2.8	1.8	3.2	1.4	--	Some hematite-coated magnetite.
P-7c	Grus, 11-26 inches below surface	26	35	10	18	3.4	.3	.3	6.1	0.3	Part of grains identified as hematite may be hematite-coated magnetite.
P-8a	Soil, 1-inch surface layer	43	42	1.0	8.1	2.5	2.0	--	1.5	--	Some magnetite is hematite coated.

TABLE 5—HEAVY MINERALS IN FRESH AND WEATHERED ROCK MATERIALS—Continued

Sample number	Sample description	Garnet	Magnetite	Hematite	Epidote	Zircon	Chlorite	Biotite	Clinozoisite	Pyrite	Remarks
P-8c	Grus, 4 inches below surface	60	12	5.8	12	1.2	2.9	--	5.8	--	Some garnet is coated with a limonitic stain.
G-17	Grus, about 3 feet below surface	.3	.3	16	83	.2	--	0.2	.2	--	Trace of anatase present.
G-4a	Grus, about 10 feet below top of roadcut	50	31	2.6	8.6	--	--	7.7	--	--	Some garnet grains have ragged edges.

MUSCOVITE-GARNET GNEISS

R-53	Fresh rock	70	12	--	.4	--	--	--	17	--	
R-57	Fresh rock	70	7.3	1.5	.7	--	--	.7	12	7.3	

TABLE 5—HEAVY MINERALS IN FRESH AND WEATHERED ROCK MATERIALS—Continued

Sample number	Sample description	Garnet	Magnetite	Hematite	Epidote	Zircon	Chlorite	Biotite	Clinozoisite	Pyrite	Remarks
P-2c	Soil, 2-4 inches below surface	60	23	0.9	7.5	0.9	5.6	--	1.9	--	
P-2f	Grus, 32 inches below surface	75	13	--	--	--	--	--	12	--	
G-4b	Grus, about 10 feet below top of roadcut	98	.3	1.3	--	.3	.3	--	--	--	Nearly all garnet grains have ragged edges.
ALLUVIAL DEPOSITS ^{1/}											
G-14a	Soil, composite of 6-inch bleicherde horizon	20	42	2.6	13	1.9	.8	0.8	19	--	

See footnote at end of table.

TABLE 5—HEAVY MINERALS IN FRESH AND WEATHERED ROCK MATERIALS—Continued

Sample number	Sample description	Garnet	Magnetite	Hematite	Epidote	Zircon	Chlorite	Biotite	Clinozoisite	Pyrite	Remarks
G-14b	Soil, 6-24 inches below surface	23	15	20	32	5.2	4.4	--	0.9	--	

^{1/} Alluvial deposits contain fragments of both muscovite-biotite gneiss and muscovite-garnet gneiss.

crystal structure and chemical composition of epidote and clinozoisite are very similar.

Chemical Composition: The chemical composition of grus differs from that of unweathered rock in varying degrees, depending on the amount of weathering. Comparisons of chemical analyses of weathered material and fresh rock show obvious changes, such as losses of SiO_2 and gains of H_2O and Al_2O_3 (appendix A).

The concentrations of the chemical constituents in a rock or soil sample are analyzed and reported in weight-percent of their oxides, the sum of which should equal 100 percent; therefore, the analytical results are ratios or relative amounts. For example, a chemical analysis of a weathered rock that has been leached of sodium and calcium with little loss of aluminum would indicate a substantial increase in aluminum, although the absolute concentration of aluminum remained constant. The same would be true for any constituent that undergoes little or no loss during the weathering process.

A determination of the gains and losses of chemical constituents during the weathering process is more meaningful if it is assumed that aluminum is immobile during weathering and then correcting the amounts of all the other constituents by the ratio of the percent alumina in the fresh rock to the percent alumina in the weathered rock (Krauskopf, 1967, p. 103). (See table 6.) Although the assumption is

TABLE 6
METHOD OF CALCULATING GAINS AND LOSSES OF
CHEMICAL CONSTITUENTS IN WEATHERED MATERIAL

[Method from Krauskopf, 1967]

Chemical constituents	1 Gneiss, recalculated to 100 percent ^{1/}	2 Weathered material, recalculated to 100 percent	3 $\frac{14.8}{15.7} \times \text{column 2}$	4 Column 3 minus column 1 Increase or decrease in each constituent	5 $\frac{\text{Column 4}}{\text{Column 1}} \times 100$ Gains or losses in percentage of original amounts
SiO ₂	73.8	72.3	68.2	-5.6	-7.6
Al ₂ O ₃	14.8	15.7	14.8	0	0
Fe ₂ O ₃	.64	.57	.54	-.10	-16
FeO	.31	.48	.45	+.14	+45
MgO	.19	.18	.17	-.02	-10
CaO	1.3	.77	.73	-.57	-44
Na ₂ O	4.3	4.2	4.0	-.30	-7.0
K ₂ O	3.8	3.6	3.4	-.40	-11

See footnote at end of table.

TABLE 6—Continued

Chemical constituents	1 Gneiss, recalculated to 100 percent ^{1/}	2 Weathered material, recalculated to 100 percent	3 $\frac{14.8}{15.7} \times \text{column 2}$	4 Column 3 minus column 1 Increase or decrease in each constituent	5 $\frac{\text{Column 4}}{\text{Column 1}} \times 100$ Gains or losses in percentage of original amounts
H ₂ O ⁻	0.08	0.28	0.26	+0.18	+225
H ₂ O ⁺	.48	1.6	1.5	+1.02	+212
TiO ₂	.09	.10	.09	0	0
P ₂ O ₅	.04	.03	.03	-.01	-25
MnO	.07	.18	.17	+.10	+143
CO ₂	<.05	<.05	--	--	--
Total	100	100	94.3		

^{1/} Average of four samples of unweathered muscovite-biotite gneiss or average of three samples of unweathered muscovite-garnet gneiss are used in column for basis of comparison.

not entirely correct—Roberson and Hem (1969) show that aluminum readily reacts with certain anions found in natural water to form complex ions—the amounts of aluminum in the ground water and surface water in the study area are less than 0.10 mg/l and generally range from 0.01 to 0.03 mg/l (appendix C). In addition, analyses of weathered material show the greatest increase in aluminum of that of all the common constituents. Therefore, the assumption that aluminum is immobile during weathering probably does not create a large error in gain and loss calculations in the study area. Minor errors in the gains and losses may be caused by the fact that the composition of the rock from which the weathered material was derived may not have been exactly the same as the average composition of the unweathered rock; analyses of seven samples of unweathered rock, however, are very similar (appendix A). Therefore, the method probably is sufficiently reliable to obtain a generalization of the gains and losses in chemical constituents in weathered material.

The percentage gains and losses in chemical constituents as a result of weathering were calculated and plotted for four soil profiles that include grus (fig. 25). The gains and losses, which are by no means completely uniform among the four profiles, are generalized as follows.

Figure 25. --Percentage gains and losses in chemical constituents as a result of weathering. soil profiles P-2, P-5, P-6, and P-8.

Samples are listed in order of increasing depth below land surface in each profile. Soil profiles are described in appendix D.

<u>Gains</u>	<u>Losses</u>
Fe ₂ O ₃ (in the most strongly weathered material [fig. 25A and B])	SiO ₂
MgO	FeO
H ₂ O ⁻ and H ₂ O ⁺	CaO > Na ₂ O > K ₂ O
TiO ₂	
MnO	P ₂ O ₅

Oxidation of iron (FeO to Fe₂O₃) is one of the common chemical changes that takes place as a result of increased weathering. The change, however, is well shown only in soil profile P-2 (fig. 25A), which is the most weathered of the four profiles. The less weathered profiles obviously contain oxidized iron, as evinced by their brownish hue, but the actual changes in the amounts of the FeO and Fe₂O₃ may be very small and may be masked by analytical errors.

The plots of gains and losses indicate that magnesium (expressed as MgO) is concentrated by weathering (fig. 25). Vermiculite forms from illite in the soil zone, and magnesium probably is retained in the structure of the vermiculite crystals.

The increase of water (H₂O⁺ and H₂O⁻) is greater than the increase of any constituent and is one of the best indicators of the degree of chemical weathering. The largest gains in water generally occur in the soil that contains the most clay; this is especially true of uncombined (H₂O⁻) water.

Titanium (expressed as TiO_2) is concentrated by weathering in all the soil profiles (fig. 25). Common titanium minerals, such as ilmenite or sphene, were not identified in thin sections or in heavy-mineral fractions; however, ilmenite is difficult to distinguish from magnetite, and small amounts may be present. Titanium can substitute for aluminum in biotite (Mason, 1958, p. 134) and less commonly for iron in magnetite (Berry and Mason, 1959, p. 354).

Manganese (expressed as MnO) is concentrated by weathering in the upper parts of the soil profiles. In general, manganese is not present in sufficient quantities to form independent minerals in igneous rocks but may substitute for other metallic ions (Rankama and Sahama, 1950, p. 643). Manganese may substitute for iron in magnetite and garnet. Garnets collected near the Palisade Ranger Station have a composition intermediate between four end members—almandite $[\text{Fe}_3\text{Al}_2(\text{SiO}_4)_3]$, andradite $[\text{Ca}_3\text{Fe}_2(\text{SiO}_4)_3]$, pyrope $[\text{Mg}_3\text{Al}_2(\text{SiO}_4)_3]$, and spessartite $[\text{Mn}_3\text{Al}_2(\text{SiO}_4)_3]$ (Pilkington, 1961, p. 119). Magnetite and garnet are resistant minerals and are concentrated in the soil by weathering. The presence of these minerals may account for the gains in manganese.

Silica (SiO_2) decreases in all weathered material, and the greatest decrease is in the most weathered material. Losses in silica and gains in uncombined water are directly related and are a relative

measure of the amount of weathering. Weathering of the plagioclase feldspar is responsible for most of the silica losses.

During the weathering process, the three major cations are removed in the general order $\text{Ca}^{+2} > \text{Na}^{+} > \text{K}^{+}$; however, variations do occur in the order of removal (fig. 25B). Plagioclase feldspar is unstable during weathering and accounts for the losses in calcium and sodium. Potassium feldspar is stable in the weathered material, and the potassium probably is derived from the leaching of muscovite in the formation of illite.

Phosphorous (expressed as P_2O_5) has the greatest percentage of loss of any chemical constituent for which an analysis was made. Phosphorous, although present only in small amounts in igneous rocks, forms the independent mineral apatite $[\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{Cl}, \text{OH})]$. As much as 95 percent of the phosphorous in igneous rocks is contained in apatite (Rankama and Sahama, 1950, p. 585). Because apatite is unstable in the weathering environment, the solution of this mineral accounts for the losses in P_2O_5 .

In the interpretation of the chemical data for the study area, it should be remembered that weathered material originally may not have had exactly the same composition as the average composition of unweathered rock and that constituents present in very minor amounts may show large percentage gains or losses as a result of analytical errors.

Particle Size: The salient textural characteristics of grus and soil are the large amounts of sand-size particles—between 0.0625 and 2.00 mm in diameter—and the small amounts of clay—less than 0.0039 mm in diameter. Grus generally contains from 30 to 40 percent gravel, 50 to 60 percent sand, less than 10 percent silt, and less than 2 percent clay (samples G-4a, G-4b, G-5, G-16f, P-1f, P-1g, P-2f, P-3f, fig. 26). In the transition from grus to soil, the histograms in figure 26 show that the particle-size mode shifts from gravel to medium sand to fine sand (samples P-1, P-2, P-3, P-6, P-7). The more intense the weathering, the poorer the sorting, as may be seen by the general flattening of the histograms (fig. 26).

The texture of the grus is classified as gravelly sand, based on a soil classification (U.S. Department of Agriculture, 1951, p. 209), or sandy gravel, based on sediment classification (Folk, 1961). The texture of slightly weathered grus (samples G-4a, G-4b, G-5, fig. 26) approximates the texture of unweathered gneiss. All the grus samples for which particle-size determinations were made contained less than 3 percent clay.

Sample G-17 is unique in the sense that it is the most strongly altered grus found in the study area; it is devoid of gravel-size material, is extremely friable, and retains the texture and structure of the original rock. Parts of the grus exhibit intense shearing and may have formed in a fault zone. Kaolinite is the only clay mineral present, and

Figure 26. --Particle size of selected samples of weathered material.

crystals of epidote, some of which have well-developed prismatic forms, make up more than 80 percent of the heavy-mineral fraction of the sample. The outcrop is north of Girl Scout Spring near the foot of a steep slope (fig. 1), which receives more water than would be expected from the 25 to 30 inches of mean annual precipitation. The outcrop is near the bottom of a canyon but is high enough to provide considerable gradient for the water moving through the soil and grus, which favors increased leaching. The soil developed on the grus outcrop is a podzol that contains a well-developed ashen layer in the A horizon underlain by the brown slightly clay-rich B horizon.

Podzolic Soil. The degree of development of the soil in the study area is extremely variable, but nearly all the soil profiles show some podzolic characteristics. Podzolic soil forms in a subhumid to humid cool to cold climate under a deciduous and (or) coniferous forest.

Description, Classification, and Distribution: The great soil groups were established by the U.S. Department of Agriculture (1938, p. 993) in 1938, and the groups are divided into zonal, intrazonal, and azonal soils. Although a new soil classification was adopted by the U.S. Department of Agriculture in 1965, the well-known 1938 classification is used in this report. Most of the soil in the study area is classified as zonal soil. The morphology of zonal soil is controlled by broad zonal climatic, topographic, and vegetation factors. The

development of intrazonal soil is controlled by local relief and (or) changes in the parent material, which override the effects of climate and vegetation. Azonal soil lacks well-developed characteristics, either because of active erosion or sedimentation or because of the young age of the parent material.

The soil in the study area is typified by the B2 horizon—a zone of maximum soil accumulation that is richer in clay and metallic oxides than the overlying A horizon. The podzolic soil may or may not have a prominent ashen or bleicherde A2 horizon in which leaching of chemical constituents is at a maximum. Where the A2 horizon is well developed, it usually is lighter in color than the B2 horizon. A near-surface accumulation of decayed organic matter commonly occurs above the A2 horizon and imparts an acidic nature to the soil. In the study area the C horizon, which is below the B horizon, consists of weathered muscovite-biotite gneiss or muscovite-garnet gneiss in which the original rock structures are visible.

The soils in the upper parts of the Santa Catalina Mountains are classed as Western Brown Forest, Gray Wooded, and Lithosols on a regional basis (Agricultural Experiment Stations of the Western States Land-Grant Universities and Colleges, 1964). Lithosols are rocky azonal soils that lack definite profile development. In the Pinaleno Mountains, which are about 60 miles northeast of the Santa Catalina Mountains, the soil at about the same altitude as that in the

study area is classified as Gray Brown Podzolic (Martin and Fletcher, 1943). The soil in the study area exhibits characteristics of all four great soil groups.

Most of the soil in the study area is classified as Western Brown Forest, which is characterized by a lack of strong differentiation between the A, B, and C horizons (Agricultural Experiment Stations of the Western States Land-Grant Universities and Colleges, 1964, p. 34). Surface organic horizons usually are thin and are dark gray or dark grayish brown (Munsell Color Co., 1954). Although a bleicherde A2 horizon is absent, eluviation is indicated by the bleached silt and sand in the lower part of the A horizon and some clay films in the B horizon. The A horizon grades into the B horizon, which may have only a slightly greater clay content than the A horizon, but soil structures are not strongly developed. The B horizon occasionally is browner than the A horizon and grades into the lighter colored C horizon. The entire profile usually is less than a foot thick. (See appendix D, soil profiles P-5, P-6, and P-8.) When viewed in the field, the outstanding characteristics of the soil are the thin nature and lack of development of the profile, the general grayish-brown to brown color, and the absence of yellowish-brown or strong-brown colors in the B horizon (figs. 14B and 27A). The soil is present on rock where the weathered material is protected from erosion and may grade laterally into Lithosols on more exposed surfaces.

Figure 27. --Soils developed on rock and alluvium.

A

Soil developed on muscovite-garnet gneiss. The soil is characteristic of Western Brown Forest soils. Relatively fresh rock is at the bottom of the 6-inch rule, and grus extends to the top of the rule. A and B horizons are weakly developed. The principal color is grayish brown; yellowish-brown or strong-brown colors are not present. The exposure is along a secondary road 0.3 mile northeast of Girl Scout Camp.

B

Soil developed on alluvium. The soil is a well-developed podzol that is classed as Gray Wooded soil because of the thick bleicherde A2 horizon and the brown to strong-brown B2 horizon. Other similarly developed soils on the alluvium and in places on rock have thinner A2 horizons and are more characteristic of Gray Brown Podzolic soils. The exposure is on the Mount Lemmon Highway near the entrance to Rose Canyon Campground.

A

B

Figure 27. --Soils developed on rock and alluvium.

A better developed but less widely distributed soil occurs on the alluvium and in places on rock (fig. 27B). The soil probably is older than the Western Brown Forest soil and has characteristics typical of the Gray Brown Podzolic and Gray Wooded soils. The principal differences between these soils and the Western Brown Forest soil are in thickness, the development of an identifiable A2 horizon, and a heavier B horizon that commonly contains clay films and is noticeably yellowish in the lower part. (See fig. 27B; appendix D, soil profiles P-1, P-2, P-3, and P-7.) Some of the better developed soil cannot be placed in a single great soil group. Gray Brown Podzolic soil has a moderately thick dark-colored surface A1 horizon; a thin bleicherde A2 horizon; and a B horizon that contains more clay, has stronger structure, and is darker than the A horizon. Gray Wooded soil has a thin A1 horizon, a thick A2 horizon, and a B horizon that contains more clay than the A2 horizon and that has moderate to strong structure. The A2 and B2 horizons dominate the Gray Wooded soil (Agricultural Experiment Stations of the Western States Land-Grant Universities and Colleges, 1964, p. 34). The A horizons in most of the better developed soil contain significant amounts of organic matter and a rather thin bleicherde horizon; therefore, the soil is classified as Gray Brown Podzolic. The topographic position of the soil may be the main cause of its being more fully developed than the Western Brown Forest soil. The alluvium is on the upper parts of the benches near the base of the

steep slope that extends to the crest of the mountains (fig. 1). The slope break receives more water than areas farther from the slope; the increase in leaching caused by the greater amounts of moisture may be as responsible for the soil development as is time.

Mineralogical and Chemical Composition: The mineralogical composition of the soil is similar to that of the grus except for the presence of vermiculite (tables 4 and 5). All soil contains vermiculite, which is derived from illite; however, not all grus contains vermiculite. The chemical composition of soil and grus are similar (appendix A). Soil, however, usually has larger losses of calcium, sodium, and silica and larger gains of water than grus (fig. 25).

Particle Size: In the study area the soil is coarse grained and generally ranges from gravelly sandy loam to gravelly loamy sand (appendix D). The better developed soil on alluvium contains a lower percentage of gravel and a higher percentage of silt than the less-developed soil on rock (fig. 26; appendix D, soil profile P-3); however, the clay content in nearly all the soil profiles is less than 4 percent. The greatest amount of clay occurs in the B horizon. In the transition from grus to soil, the histograms in figure 26 show that the particle-size mode shifts from gravel to medium sand to fine sand in the upper parts of the soil profiles. Soil is more poorly sorted than grus, as may be seen by the general flattening of the histograms (fig. 26).

Alluvium. The alluvium is present in scattered deposits on the erosional benches near the break in slope. The alluvium is composed of boulder- to silt-size material and has undergone the greatest chemical alteration of any material in the study area; the soil on the alluvium is better developed than the soil on rock. The alluvium has been transported short distances, and it may be argued that it should be considered a mobile constituent. The distance of transport is very short, however, and may be only a few tens of feet in places. The alluvium on the benches is residual.

Description: The alluvium is very poorly sorted owing to the small amount of fluviation in the deposit; however, some degree of bedding is evident in most exposures. The bedding ranges from semi-aligned boulders in a silt to gravel matrix to well-defined alternating beds of silty sand and sandy gravel (fig. 28A and B). Where exposed, alluvium generally is yellowish brown to brown, and in places where the bedding is fairly well developed the silty sand is lighter and ranges from brown to pale brown. The gravel beds are dark yellowish brown and yellowish brown to brown and strong brown. In places the alluvium is reddish yellow. The dark alluvium is in striking contrast to the light-grayish-brown grus (fig. 28A).

Gray Brown Podzolic soil is well developed on some of the alluvial deposits; the soil consists of a light-colored A2 horizon

Figure 28.--Alluvium near Rose and Willow Canyons.

A

Poorly sorted weakly bedded alluvium on the Mount Lemmon Highway at the entrance to the Rose Canyon Campground. The white material is muscovite-biotite grus. The maximum thickness of the deposit is about 10 feet (left side of photograph).

B

Relatively well-bedded silty sand and sandy gravel on muscovite-biotite grus. The contact of the alluvium and the grus is at the upper end of the hammer handle (a foot long). The beds dip about 6° W. The exposure is on a fire road near the Mount Lemmon Highway just northeast of Lizard Rock.

A

B

Figure 28. --Alluvium near Rose and Willow Canyons.

overlying a heavier darker B2 horizon (fig. 27). The podzols on other alluvial deposits are less developed, and in some of the podzols the A and B horizons or bedding(?) seem to be disturbed or mixed (fig. 29A). Disturbance of the material may have been caused by slumping or by churning by the roots of fallen trees.

The alternating light and dark beds (fig. 28B) and the mixed horizon (fig. 29A) may be buried soil or they may be zones of contrasting permeability, which cause differences in oxidation and alteration of materials. Some of the gravel is better sorted than the finer material and is more permeable (samples G-14b, G-15c, fig. 26). Where bedding is distinct, the fine-grained beds are light in color, lack clay skins, and contain noticeable amounts of muscovite. The coarse-grained beds generally are dark in color, contain well-developed clay skins, and muscovite is not as noticeable as in the fine-grained beds. The fine-grained beds probably restrict the movement of ground water and, therefore, are less oxidized and altered than the coarse-grained beds.

Brown to strong-brown grus that contains silt and a small amount of clay immediately underlies the alluvium. Some of the clay may have migrated from the overlying alluvium, which contains well-developed clay skins. Although most of the grus is a medium sand to gravel, it is tacky and is quite distinguishable from the friable grus that has not been covered by alluvium.

Figure 29. --Alluvium in the Willow Canyon area.

A

Disturbed or mixed podzolic soil or bedding(?) on alluvium exposed 100 yards east of the exposure shown in figure 28B. The material may represent more than one soil profile or may be bedding. Hammer handle is a foot long.

B

Alluvium in an exposure at the east end of the south loop of the secondary road in the Willow Canyon area. The maximum thickness of the alluvium is about 12 feet. The top of the grus is at road level. The exposure generally is poorly bedded and contains silt- to boulder-size material; some well-sorted gravel beds are present.

A

B

Figure 29. --Alluvium in the Willow Canyon area.

Distribution and Thickness: Most of the alluvial deposits occur on the upper parts of the erosional benches near the base of the slope that extends to the crest of the Santa Catalina Mountains (fig. 1); the grus also is thickest along the break in slope. In places, such as in the Boy Scout Camp area, only the tacky grus is present, and the alluvium has either been removed by erosion or was never present. The tacky grus probably is the upper C horizon of an old weathering profile. The alluvium is from less than 2 feet to as much as 12 feet thick (fig. 29B; appendix D, soil profile P-3). The thickness of the alluvium decreases rapidly with increasing distance from the slope break.

Mineralogical Composition: The common rock-forming minerals are the same in the alluvium as those in the grus and soil. Weathering of muscovite is evident, and well-developed clay skins serve as the cementing material in the gravel beds (figs. 22 and 23). Although the alteration of minerals is as severe in the alluvium as it is in the grus and soil, some plagioclase feldspar is surprisingly fresh (fig. 23). The plagioclase in figure 23 is albite and is more resistant to weathering than the more calcium-rich plagioclase feldspar in the original rock. Kaolinite and vermiculite are the most abundant clay minerals; the suite of heavy minerals in the alluvium is similar to that in grus and soil (table 5).

Particle Size: Most of the alluvium, including the B soil horizon, is sandy gravel or muddy sandy gravel (samples G-14b, G-15c, G-16b, G-16d, fig. 26). The light-colored sedimentary beds, including the A2 soil horizon, are fine grained—usually gravelly muddy sand—and make up a small percentage of the alluvial deposits (samples P-3b, P-3c, P-3d, P-3e, G-14a, G-16a, fig. 26). The histograms in figure 26 show that the particle-size mode for the coarse-grained beds is coarse sand and gravel and that the mode for the fine-grained beds is silt. Some of the histograms for the fine-grained beds show a minor mode in the coarse sand or gravel sizes, and some of the histograms are relatively flat for the sand and gravel sizes. The alluvium contains from about 2 to 5 percent clay, and the coarse-grained beds are better sorted than the fine-grained beds.

Origin and Age: The alluvium shows some degree of bedding and sorting, and, therefore, it is obvious that it is a streambed deposit rather than colluvium or landslide debris. The writer considered postulating a different climatic environment than that of the present to explain the deposition and former areal extent of the alluvium; however, significant amounts of younger alluvium are present beneath the modern streams in the same general area as the exposures of older alluvium. At the head of Palisade Canyon upstream from Girl Scout Spring and west of the Boy Scout Camp (fig. 1) for example, the

younger alluvium is as much as 8 feet thick; therefore, drastic climatic changes are not necessary to explain the deposition of the older alluvium. Uplift of the mountains and canyon cutting took place after the older materials were deposited; some of the older alluvial deposits are now as much as 50 feet above the adjacent modern canyon bottoms.

The elongated outcrop of older alluvium northeast of Lizard Rock (fig. 1) has been breached by a stream, and bedrock has been removed to a depth of about 8 feet below the base of the alluvium. The alluvium is at least Wisconsin in age, based on degree of alteration, color, soil development, and elevation with respect to the canyon bottoms.

Clay Minerals in the Residual Constituents

In this report, clay minerals are identified according to the scheme of Warshaw and Roy (1961) supplemented by data from Grim (1953), Brown (1961), and Molloy and Kerr (1961). The reports contain descriptions of the well-known techniques used to determine the reaction of clay minerals to thermal and polar-liquid treatments.

Kaolinite is present in all the samples of weathered material and is the first clay mineral to form in grus. Illite probably forms later than kaolinite, but illite is present in slightly weathered grus. The amount of illite decreases as vermiculite increases in the B and A soil horizons; in some soil, illite is absent, and kaolinite and vermiculite are the only clay minerals present.

Kaolinite. The crystallization of kaolinite is poor in the weathered material, as indicated by the strong 001 reflections at about 7.2 Å (angstrom unit) and the 002 reflections at about 3.6 Å, the lack of strong reflections in the 4.5 Å to 3.5 Å range, and the lack of usable clay-mineral reflections greater than about $30^\circ 2\theta$ on X-ray diffractograms. Halloysite has a crystal structure similar to that of kaolinite, and X-ray diffractograms of the two minerals overlap. An important diagnostic feature in identifying halloysite mixed with kaolinite is the relation of the relative intensity of the 001 reflection and the combined 020 and 111 reflections at about 4.4 Å (Brown, 1961, p. 88). Kaolinite has a 001:020+111 reflection ratio of at least 2, and where the ratio is nearer unity, halloysite may be present; however, in the samples examined the ratio is always more than 2 and commonly is more than 4, which indicates that halloysite is not present (figs. 30 and 31).

The grus samples from which the diffractograms shown in figures 30 and 31 were obtained are moderately weathered. The approximate degree of weathering of the samples is shown in figure 20B and corresponds to weathering stages 3 or 4 shown in table 4.

Illite. The crystallization of illite is poor compared to that of muscovite; only illite 001, 002, and 003 reflections at 10.0 Å, 4.95 Å, and 3.33 Å, respectively, are present in diffractograms of the weathered material, and only a weak broad 001 reflection is present in some soil diffractograms. The strongest and most symmetrical illite

Figure 30. --X-ray diffractograms of miscellaneous grus samples (< 2-micron fraction).

⚙ Unidentified peak that disappears upon mild heating; not present in all samples.

Figure 31. --X-ray diffractograms of grus sample G-5 (< 2-micron fraction).

reflections are in the <2 -micron fraction of grus in which kaolinite and illite are the principal clay minerals (figs. 30 and 31). With increased weathering, particularly in the A and B soil horizons, the illite reflections become weaker and asymmetrical in the direction of the larger basal spacings (fig. 32). In the diffractograms for some soil the 10 A reflection is broad and does not have a well-defined peak (fig. 33). The development of asymmetry on the 10 A reflection is caused by the weathering of illite to vermiculite. The alteration forms mixed layers of illite and vermiculite, minor mixed layers of illite and montmorillonite, and subsequent diffraction peaks between 10 A and 14 A. If the 10 A illite basal peak is present in soil, it is always significantly weaker and more rounded than the same peak in the <2 -micron fraction of grus.

The illite is dioctahedral in the weathered material. Powder X-ray photographs of samples in which illite is the principal mica-type clay mineral show an 060 reflection between 1.50 A and 1.51 A. Trioctahedral mica-type clay minerals show a reflection between 1.53 A and 1.54 A.

Vermiculite. The strongest vermiculite 001 reflections at about 14 A are in the <2 -micron fraction of soil (figs. 32, 33, and 34). If the 002 reflection is present, it is covered by the strong 001 reflection of kaolinite at about 7.2 A. Vermiculite is more common in the upper parts of soil profiles than in the lower parts, and it may be

Figure 32. --X-ray diffractograms of grus and soil near soil profile P-5 (< 2-micron fraction).

Figure 33. --X-ray diffractograms of bleicherde A2 soil horizon, sample G-16a (< 2-micron fraction).

Figure 34. --X-ray diffractograms of soil profile P-4 (< 2-micron fraction).

related to the presence of organic matter. The degree of crystallization in illite decreases in the transition from grus to the A and B soil horizons; concomitantly, the degree of crystallization in vermiculite increases (fig. 32).

The transition of illite to vermiculite in the weathered material may involve only a slight substitution of cations and additions of interlayered water because vermiculite is dioctahedral as is illite. Vermiculite is classed as dioctahedral on the basis of the following criteria: (1) the 001 reflection of dioctahedral vermiculite decreases to about 11 Å after heating to 500°C (fig. 33), and the 001 reflection of trioctahedral vermiculite decreases to about 10 Å after heating to only 400°C (Warshaw and Roy, 1961, p. 1491); and (2) weak 060 reflections of between 1.50 Å and 1.51 Å are obtained from powder X-ray photographs of samples of soil in which vermiculite is the principal mica-type clay mineral. A lack of reflections in the 1.53 Å to 1.54 Å range indicates the absence of trioctahedral minerals.

Vermiculite has a strong 001 reflection at about 14 Å. Although chlorite and montmorillonite also may have 001 reflections of about 14 Å, vermiculite may be distinguished from them on the basis of the effects of thermal and ethylene glycol treatments.

Theoretically, montmorillonite and vermiculite form a continuous series, and either mineral may have properties common to both. When treated with ethylene glycol, magnesium vermiculite will not

expand to more than 14.5 Å, but magnesium montmorillonite will expand to about 18 Å (Brown, 1961, p. 315). Slurries of the < 2-micron fraction of weathered material were saturated with magnesium ions by adding a few drops of 1 normal MgCl_2 solution, and the mixture was sedimented onto glass petrographic slides. X-ray diffractograms were made of the slide after air drying and treatment with ethylene glycol. The diffractograms were compared to those made using parts of the sample that were not saturated with MgCl_2 (fig. 35). Diffractograms of the unsaturated material show reflections at 14.4 Å. The sample treated with MgCl_2 had a 14.4 Å reflection before and after treatment with ethylene glycol, which verifies the presence of vermiculite.

Montmorillonite. When present, montmorillonite is only a minor constituent in the weathered material; upon treatment of the montmorillonite with ethylene glycol, a weak reflection occurs in about the 15 Å to 17 Å range. Although montmorillonite is the dominant clay mineral in soil profile 2, the situation is anomalous and may have been caused by the weathering of a mafic dike that occurs near the soil profile.

Randomly Mixed-Layer Minerals. Diffractograms of soil containing illite and vermiculite show reflections in the 10 Å to 14 Å range, which indicates mixed-layer illite and vermiculite (fig. 34). Mixed-layer clay minerals generally are not present in grus (figs. 30 and 31) but increase upward in the soil profiles (figs. 32 and 34). The

Figure 35. --X-ray diffractograms of weathered material before and after saturation with magnesium ions (< 2-micron fraction).

increase in mixed-layer illite and vermiculite probably represents the intermediate stages in the alteration of illite to vermiculite.

Mobile Constituents

The term "mobile constituents" may be expressed as the dissolved-solids content of the water. The mobile constituents are the soluble materials that have been derived from the weathering of the gneiss and that have been dissolved and transported by surface water and ground water. Aluminum hydroxide, however, may be transported as polymers or as complexes by natural water, but the amount of aluminum in these forms generally is small.

In the study area the average amounts of dissolved solids in surface water and ground water are small and range from about 20 to 70 mg/l. In the transition from precipitation to ground water, the water becomes increasingly mineralized because of the addition of all the common chemical constituents. Silica, sodium, and bicarbonate show the greatest increases. In order to assess the chemical changes that take place during the progressive mineralization of the water, the surface water and ground water in the study area have been divided into four classes—direct runoff, base runoff, ephemeral springs, and perennial springs.

Direct Runoff. Direct runoff is the surface water that flows in the canyons in immediate response to precipitation. Direct runoff is

the least mineralized water because of the short time of water-rock contact, which may range from several minutes to a few hours. Flood peaks that result from heavy rains in the high drainages of Sabino Creek reach the basin in 4 to 6 hours. Direct runoff contains from 10 to 30 mg/l of dissolved solids and averages 18 mg/l (table 7; appendix C). Silica, bicarbonate, sulfate, and calcium are the dominant constituents and make up about 75 percent of the dissolved solids. Direct runoff is moderately acid, and pH values range from about 5.0 to 7.5 and average 6.1.

Base Runoff. Base runoff is the surface water that flows in the major canyons following storm events and after tributary canyons no longer contain runoff. Base runoff is essentially the same as ephemeral spring flow, the difference being that the ephemeral spring flow is localized. Base runoff drains from the soil, alluvium, and colluvium that absorb moisture during wet periods. The length of time of water-rock contact for base runoff ranges from hours to weeks. Base runoff contains from about 30 to 70 mg/l of dissolved solids and averages 43 mg/l (table 7; appendix C). Silica, bicarbonate, and sodium are the principal constituents and make up about 75 percent of the dissolved solids. The water is slightly acid to slightly basic and has a mean pH value of 6.83, which is nearly neutral.

Ephemeral Springs. Ephemeral spring flow is essentially the same as base runoff, the difference being that the ephemeral spring

TABLE 7

MEAN CONCENTRATIONS OF PRINCIPAL DISSOLVED CONSTITUENTS AND MEAN VALUES OF SPECIFIC CONDUCTANCE, pH, AND BICARBONATE-SULFATE RATIOS FOR PRECIPITATION, DIRECT RUNOFF, BASE RUNOFF, AND WATER FROM SPRINGS

[Values of dissolved constituents in milligrams per liter, except where indicated]

Constituent	Precipitation (9 samples)	Direct runoff (9 samples)	Base runoff (10 samples)	Ephemeral springs (4 samples)	Perennial springs (5 samples)
Silica (SiO ₂)	0.1	5.4	16	18	32
Iron (Fe)	---	---	.15	--	.21
Calcium (Ca)	.5	2.0	3.4	3.0	4.5
Magnesium (Mg)	.1	.7	.8	1.3	1.5
Sodium (Na)	.5	1.4	5.2	4.1	9.2
Potassium (K)	.3	.9	1.2	.6	.9
Bicarbonate (HCO ₃)	1.2	6	17	11	32
Sulfate (SO ₄)	1.3	3.8	4.9	7.0	4.4
Chloride (Cl)	1.2	.9	2.8	2.6	3.7
Fluoride (F)	---	.1	.2	.1	.1

TABLE 7—Continued

Constituent	Precipitation (9 samples)	Direct runoff (9 samples)	Base runoff (10 samples)	Ephemeral springs (4 samples)	Perennial springs (5 samples)
Dissolved solids	5.2	18	43	43	73
Specific conductance (micromhos at 25°C)	14	24	52	54	73
pH	5.4	6.08	6.83	5.95	6.05
$\frac{\text{HCO}_3}{\text{SO}_4}$	.84	1.28	2.84	1.51	6.65
Calculated carbon dioxide (CO ₂) ^{1/}	9.2 (21 x 10 ⁻⁵ moles)	7.6 (17 x 10 ⁻⁵ moles)	4.2 (9 x 10 ⁻⁵ moles)	17 (40 x 10 ⁻⁵ moles)	51 (120 x 10 ⁻⁵ moles)

^{1/} Water in equilibrium with CO₂ in air contains 0.44 mg/l CO₂ (10⁻⁵ moles).

flow is localized. The ephemeral springs drain from the soil, alluvium, and colluvium that absorb moisture during wet periods. The spring orifices are in alluvium or in the fractures in the bedrock in the small canyons. The catchment areas of the springs are small, and flow is sustained for only short periods. The chemical composition of the ephemeral spring flow is similar to that of base runoff (table 7; appendix C), and the length of time of water-rock contact probably is about the same. Ephemeral spring flow contains less bicarbonate, more sulfate, and is more acid than base runoff; the mean pH value is 5.95.

Perennial Springs. Perennial springs differ from ephemeral springs mainly in that the size of catchment area and the storage capacity of the material are greater. Some perennial springs issue from the alluvium upstream from bedrock exposures in canyon bottoms. The storage capacity of the alluvium may be sufficient to sustain flow between wet periods or the flow may be supplemented by seepage from fractures. A few springs are fed through a system of fractures, and the orifices are in the sides of the canyons well above the alluvial material in the canyon bottoms. The length of time of water-rock contact for perennial springs may be as much as 4 months. This estimate is based on the approximate length of the longest dry period, which occurs between March and July. The estimate may be high because some precipitation falls during the dry period—at the Palisade Ranger

Station, about 6 percent of the annual precipitation falls in April, May, and June. On the other hand, the length of time required for water to move through a fracture system may be much longer than 4 months. The perennial spring flow contains the largest amount of dissolved solids of all the sources; the mean dissolved-solids concentration is 73 mg/l, which is a little less than twice the concentration in ephemeral spring flow and base runoff (table 7). Silica, bicarbonate, and sodium are the main constituents and make up more than 80 percent of the dissolved solids. The water is slightly acidic and has a mean pH of 6.05.

Chemical Transition from Precipitation to Surface Water and Ground Water. Precipitation has a diverse chemical composition (fig. 36; appendix B). All the common constituents in surface water and ground water are found in precipitation. Sodium and calcium usually are the dominant cations, but analyses indicate that any one of the three major anions—bicarbonate, sulfate, or chloride—may dominate. Large amounts of ammonia and nitrate also may be present.

As soon as precipitation comes in contact with the ground it becomes direct runoff, and the chemical composition of the water changes from a diverse chemical type to a calcium sodium sulfate bicarbonate type (fig. 36). In the transition from precipitation to direct runoff the dissolved solids increase more than three times (table 8). Analyses of direct-runoff samples collected minutes after the rain began indicate that the change in chemical composition takes place very

Figure 36. --Chemical composition of precipitation, surface water, and ground water.

TABLE 8

CHANGES IN MEAN CONCENTRATIONS OF CHEMICAL CONSTITUENTS IN THE TRANSITION
FROM PRECIPITATION TO SURFACE WATER AND GROUND WATER

[Values used in determining ratios were milligrams per liter]

Constituent	Ratios of mean concentrations					
	<u>Direct runoff</u> <u>Precipitation</u>	<u>Base runoff</u> <u>Direct runoff</u>	<u>Ephemeral</u> <u>springs</u> <u>Direct</u> <u>runoff</u>	<u>Perennial</u> <u>springs</u> <u>Base</u> <u>runoff</u>	<u>Perennial</u> <u>springs</u> <u>Ephemeral</u> <u>springs</u>	<u>Perennial</u> <u>springs</u> <u>Precipi-</u> <u>tation</u>
Silica (SiO ₂)	54	3.0	3.3	2.0	1.8	320
Calcium (Ca)	4.0	1.7	1.5	1.3	1.5	9.0
Magnesium (Mg)	7.0	1.1	1.9	1.9	1.2	15
Sodium (Na)	2.8	3.7	2.9	1.8	2.2	18
Potassium (K)	3.0	1.3	.67	.75	1.5	3
Bicarbonate (HCO ₃)	5.0	2.8	1.8	1.9	2.9	27
Sulfate (SO ₄)	2.9	1.3	1.8	.90	.63	3.4
Chloride (Cl)	.8	3.1	2.9	1.3	1.4	3.1
Dissolved solids	3.3	2.4	2.4	1.7	1.7	14

rapidly. Feth and others (1964, p. 35) and Hembree and Rainwater (1961, p. 6) reported a similar rapid chemical change when snowmelt comes in contact with the lithosphere. All the common constituents, except chloride, increase in concentration in the transition from precipitation to direct runoff. The most striking example is silica, which increases 54 times (table 8). The second largest percentage increase is in magnesium, which increases seven times, followed by bicarbonate, calcium, potassium, and sulfate. Silica and magnesium show large percentage increases because they were the least abundant constituents in precipitation.

As water-rock contact time increases, the mineralization rate of the water decreases. The dissolved-solids content in base runoff and ephemeral springs is 2.4 times greater than that in direct runoff, and the dissolved-solids content in perennial springs is less than twice that in base runoff and ephemeral springs (table 8). Silica increases 320 times in the transition from precipitation to perennial spring flow and has the largest percentage increase of all the dissolved constituents.

The increase in dissolved solids during mineralization of the water is in direct relation to the increases in silica and bicarbonate (fig. 37), which make up more than 50 percent of the dissolved solids. Although the rate of mineralization decreases with time and is an exponential function, the relation of the two principal constituents to the dissolved solids remains a linear function.

Figure 37. --Silica and bicarbonate versus dissolved solids in surface water and ground water.

In the transition from direct runoff to perennial spring flow the chemical composition of the water changes from a calcium sodium sulfate bicarbonate type to a sodium bicarbonate type. On a trilinear plot, the trend of the ionic chemical constituents is toward the sodium bicarbonate apex, which indicates that sodium and bicarbonate are the major ions being added to the water (fig. 36). As discussed in the section entitled "Estimated Chemical Denudation Rates," silica and sodium are the main chemical constituents being derived from the gneiss. The other constituents are contributed wholly or in part by precipitation or by the interaction of gases in the atmosphere and soil.

Estimated Rate of Mineralization of Water. The mean concentrations of dissolved solids were plotted versus time in an attempt to obtain a semiquantitative measure of the rate of mineralization of water (fig. 38). Although the length of time of water-rock contact for direct runoff was plotted as 1 day, it equally could be 0.1 or 0.01 day owing to the almost instantaneous acquisition of dissolved solids in the transition from precipitation to direct runoff. The length of time of water-rock contact for perennial springs was plotted at about 100 days, which is about the amount of time between wet seasons. The length of time of water-rock contact for base runoff and ephemeral springs is estimated to be from 10 to 14 days.

The estimated rates of mineralization determined in the laboratory are similar to those determined under natural conditions. For

Figure 38. --Estimated changes in mean dissolved-solids concentrations with time in surface water and ground water.

the laboratory tests, 11 samples of soil, grus, and crushed fresh rock were mixed with rainwater, and the specific conductance and pH were monitored periodically for about a year. The specific conductance-time plot for the laboratory data (fig. 39) is similar to the dissolved solids-time plot for the surface-water and ground-water data (fig. 38). The specific conductance of the rainwater immediately increases 2.5 to 3.5 times upon contact with rock or soil; the rate of mineralization was greatest in the first 2 weeks of water-rock contact, but the mineralization changed very little after about 2 weeks in most of the samples. Under natural conditions, the mineralization does not stop after 2 weeks but proceeds at a much slower rate. The similarity between the specific conductance- and the dissolved solids-time plots (figs. 38 and 39) illustrates that rainwater has a great potential for reacting with the rock minerals and that the estimate of about 10 days for the length of time of water-rock contact for base runoff and ephemeral springs probably is in the correct order of magnitude.

Specific conductance generally is higher in the rainwater and soil mixtures than in the rainwater and fresh rock or grus mixtures. The soil contains greater amounts of altered minerals and salts from precipitation and atmospheric dust than does the fresh rock and grus; therefore, the soil contains a greater amount of soluble material. An exception is sample R-54—a mixture of rainwater and fresh rock that contains the greatest amount of dissolved material of any of the

samples. At the end of 2 weeks, the mineralization of the water had not leveled off in sample R-54 as it had in the other rainwater-fresh rock samples; instead, the leveling-off period was about 100 days. Sample R-54 contains pyrite, whereas the other samples of fresh rock do not. The alteration of sulfide to sulfate produces hydrogen ions, which in turn react with other minerals and probably cause the anomalously high specific-conductance values.

The pH values were less than 6.2 for the rainwater and soil mixtures and were more than 6.2 for the rainwater and fresh-rock or grus mixtures at the end of 100 days (fig. 40). The pH is lowest in the part of the soil profile that contains the most organic matter (fig. 13). The pH of soil is influenced more by the presence of organic matter than by the hydrolysis of silicate minerals. In fresh rock and grus, which contain little or no organic matter, the opposite is true; the smaller amounts of hydrogen ions are consumed by hydrolysis of silicate minerals, which causes the higher pH values.

In almost all the samples, the pH increased during the period of water-rock contact. At the end of 1 week, the pH of the rainwater and grus and rainwater and fresh-rock mixtures increased more than that of the rainwater and soil mixtures. After 2 weeks, the pH values of the rainwater and grus and rainwater and fresh-rock mixtures were only slightly higher than the initial values. Although the reason for the fluctuation of the pH is not known, the increase occurred during the

Figure 40. --pH of rock material-rainwater mixtures versus time.

period of rapid mineralization of the water. Samples G-4a and G-4b, in which the pH values rose sharply by the end of 1 week, showed very little change in specific conductance during the same period. After 100 days, organic growth and a light-brown gelatinous material developed in some of the samples, which may account for the erratic pH in the later part of the period (fig. 40).

Dissolved Solids from Precipitation. Precipitation contributes a large part of the dissolved-solids content in surface water. A simple comparison of the mean dissolved-solids values in precipitation to those in base runoff indicates that precipitation contributes about 12 percent of the dissolved solids (table 7). If the amount of dissolved constituents in precipitation and base runoff is weighted for the amount of water involved, however, precipitation contributes 40 or 53 percent of the dissolved solids to base runoff, depending on whether the mean concentration of each dissolved constituent or the mean value of dissolved solids is used in the calculation.

The first step in the calculation is to determine the total load of dissolved material contributed by precipitation and the percent contributed by each major constituent. The mean dissolved-solids value of 5.2 mg/l (table 7) for nine precipitation samples (appendix B) and the mean annual precipitation of 30 inches for the Palisade Ranger Station were used in the calculation. The mean annual volume of precipitation per square mile is:

$$6.98 \times 10^7 \text{ ft}^3 \text{ per year} = 1.98 \times 10^9 \text{ liters per year,}$$

and the mean annual weight of dissolved solids in precipitation per square mile is

$$\begin{aligned} & (5.2 \times 10^{-3} \text{ grams per liter})(1.98 \times 10^9 \text{ liters per year}) \\ & = 1.03 \times 10^7 \text{ grams per year.} \end{aligned}$$

The mean annual runoff per square mile was estimated from records from the U.S. Geological Survey streamflow-gaging station on Sabino Creek near Mount Lemmon (Wells, 1959, p. 423). The runoff measured at the station is from a 3.19-square-mile area on the east slope of Mount Lemmon. Although the station is northwest of the study area (fig. 1), the location and altitude (7,250 feet above mean sea level) are about the same, and the unit discharge at the station is assumed to be the same as that in the study area. Based on 7 years of record, the mean annual discharge is 1,180 acre-feet, and the mean annual discharge per square mile is

$$\begin{aligned} & 370 \text{ acre-feet per square mile per year} \\ & = 4.56 \times 10^8 \text{ liters per square mile per year.} \end{aligned}$$

In order to determine the weight of dissolved material in the unit discharge, the mean value of 43 mg/l dissolved solids in base

runoff was used (table 7). The mean annual weight of dissolved solids in base runoff per square mile is

$$\begin{aligned} & (43 \times 10^{-3} \text{ grams per liter}) \\ & (4.56 \times 10^8 \text{ liters per square mile per year}) \\ & = 1.96 \times 10^7 \text{ grams per square mile per year.} \end{aligned}$$

Therefore, the percentage contribution of precipitation to the dissolved-solids content of base runoff is

$$\frac{1.03 \times 10^7 \text{ grams}}{1.96 \times 10^7 \text{ grams}} = 52.6 \text{ percent.}$$

Using the preceding calculations, the percentage contribution of the individual dissolved constituents may be obtained by substituting the weight of each constituent in precipitation and in base runoff using the mean concentrations given in table 7. The results of the calculations are given in table 9.

The calculations show that larger amounts of potassium, sulfate, and chloride are present in precipitation than are present in runoff. If the calculations are reasonably correct, the constituents are being selectively removed in the transition from precipitation to runoff. The selective removal of ions that have been added by precipitation is not uncommon. In a study in eastern North Carolina and southeastern Virginia Gambell and Fisher (1966) showed that the amounts of sulfate

TABLE 9

SOURCES OF DISSOLVED SOLIDS IN BASE RUNOFF

Constituent	Dissolved solids from precipitation (percent)	Mean concentrations of dissolved solids in base runoff (milligrams per liter)	Dissolved solids in base runoff corrected for contributions from precipitation		Dissolved solids from weathering of rock (milligrams per liter)
			(milligrams per liter)	(moles per liter $\times 10^{-4}$)	
Calcium (Ca)	63.8	3.4	1.2	0.30	1.2
Magnesium (Mg)	54.3	.8	.4	.16	.4
Sodium (Na)	41.8	5.2	3.0	1.30	3.0
Potassium (K)	109	1.2	.0	.0	.0
Bicarbonate (HCO ₃)	30.7	17	11.8	1.94	<u>1</u> /.0
Sulfate (SO ₄)	115	4.9	.0	.0	.0
Chloride (Cl)	186	2.8	.0	.0	.0
Silica (SiO ₂)	2.7	16	15.6	2.60	15.6

See footnotes at end of table.

TABLE 9—Continued

Constituent	Dissolved solids from precipitation (percent)	Mean concentrations of dissolved solids in base runoff (milligrams per liter)	Dissolved solids in base runoff corrected for contributions from precipitation		Dissolved solids from weathering of rock (milligrams per liter)
			(milligrams per liter)	(moles per liter x 10 ⁻⁴)	
Dissolved solids	--	<u>2</u> / ₄₃	<u>2</u> / ₂₆	--	20

Contribution of dissolved solids from precipitation = $\frac{43-26}{43} = 40$ percent.

Contribution of dissolved solids from weathering of the rock = $\frac{20}{43} = 46$ percent.

Contribution of dissolved solids from atmospheric-biospheric reactions = $100 - (40 + 46) = 14$ percent.

1/ The bicarbonate is assumed to be from atmospheric-biospheric reactions and not from the weathering of the rock.

2/ Dissolved solids are computed by adding 0.49 x bicarbonate + other constituents. The correction converts bicarbonate to carbonate, which is the form of carbonate in anhydrous residues of evaporated water (Rainwater and Thatcher, 1960, p. 272).

and nitrate contributed by rainfall to drainage basins exceed the amounts carried in the streams. Feth and others (1964) suggested that sulfate and chloride are removed in the transition from snowmelt to perennial springs in the Sierra Nevada. In a study in the Blue Ridge physiographic province of North Carolina Laney (1965) showed that selective removal of sulfate occurs in the transition from rainwater to ground water.

The removal of the dissolved constituents in the transition from precipitation to runoff may be caused by consumptive use by vegetation or anion exchange with clay minerals and organic matter. Based on laboratory studies of soil from four areas in Australia, Barrow, Spencer, and McArthur (1969) stated that soil has a marked affinity for adsorbing sulfate and that the amount of adsorption increases directly with increasing amounts of precipitation. Sulfate may be reduced and subsequently removed from the A horizon of the podzolic soil. The near-surface part of the podzolic soil has a lower redox potential than the underlying B horizon (McKenzie, Whiteside, and Erickson, 1960). Bear (1955, p. 140) illustrated that kaolinitic clay has an affinity for adsorbing chloride and sulfate in the 5.8 to 6.9 pH range and that the capacity for adsorption is greatest at the lower pH values.

The precipitation samples were collected from a clean surface that was covered between samplings, and the samples do not contain dry fallout. If dry fallout had been collected in addition to the rain and

snow—the bulk precipitation of Whitehead and Feth (1964)—the actual contribution of dissolved solids from precipitation probably would be greater.

Based on the sum of the individual constituents (table 9), the calculated contribution of dissolved solids from precipitation is 40 percent; whereas, based on the mean values of dissolved solids, the contribution is about 53 percent. In the 53 percent value, it is assumed that all the soluble constituents contributed to base runoff by precipitation are concentrated by evaporation. However, some constituents are removed, and, therefore, the calculation based on the summation of individual constituents is a more realistic evaluation of the contribution of dissolved material by precipitation.

Ratios of Mobile Constituents. A comparison of the relative amounts of the principal constituents in surface water and ground water gives an insight into the gross chemical reactions involved in weathering. If several minerals are altered significantly by weathering, the relation between the minerals and the soluble constituents removed from the rock by water is complex. Chemical weathering of the granodioritic rocks in the Santa Catalina Mountains, however, involves mainly plagioclase feldspar (table 4), and most of the chemical constituents contributed to the water by the rock are derived from this mineral.

Five minerals—quartz, potassium feldspar, muscovite, biotite, and plagioclase feldspar—comprise more than 99 percent of the granodioritic rocks. For all practical purposes, quartz is an inert substance in water at low temperatures (Hess, 1966, p. 292), and its solubility does not vary significantly in water having a pH of less than 9 (Krauskopf, 1967, p. 167). Potassium feldspar does not undergo much alteration in grus. Muscovite alters to illite in grus, and vermiculite forms from illite in the A and B soil horizons. The alteration of muscovite to vermiculite is a solid-state change and requires only slight losses of potassium (muscovite to illite) and gains in magnesium (illite to vermiculite). The biotite in the muscovite-biotite gneiss is altered mainly to magnetite and hematite; the alteration is of a deuteric or hydrothermal type and occurred before the rocks were exposed to weathering. Hematite is stable in the weathering environment, and magnetite alters to hematite in the soil horizons. The alteration of magnetite involves a change in the oxidation state of the iron and does not add significantly to the dissolved constituents in the water. Plagioclase feldspar is the only major mineral that alters to a mineral of a different structural class.

The change from the tectosilicate structure (framework structure) of plagioclase to the phyllosilicate structure (sheet structure) of kaolinite is an incongruent reaction that results in a surplus of silica, sodium, and calcium; the surplus constituents are removed by water.

If the alteration of plagioclase is the principal chemical change in the weathering of the rock, the theoretical mole ratios of silica, calcium, sodium, and bicarbonate—the latter from the disassociation of carbonic acid—that are derived from a balanced weathering equation should be similar to the mole ratios that are calculated from analyses of surface water and ground water. The balanced weathering equation for the alteration of plagioclase (oligoclase, An_{20}) to kaolinite is

The calculated mole ratios determined from the graphs showing bicarbonate, sodium, and calcium versus silica and sodium versus calcium (fig. 41) are less than the theoretical ratios derived from the weathering equation. (See table 10.) If the weighted mean of the chemical constituents contributed by the precipitation is subtracted from the weighted mean of the dissolved constituents in the base runoff, however, the calculated mole ratios for the remaining constituents are much closer to the theoretical ratios (tables 9 and 10). The close agreement of the theoretical and corrected calculated mole ratios substantiates the hypothesis that the alteration of plagioclase to kaolinite is the principal chemical reaction in the weathering of the granodioritic

Figure 41. --Bicarbonate, sodium, and calcium versus silica and sodium versus calcium in ground water and surface water.

TABLE 10

COMPARISON OF THEORETICAL AND CALCULATED MEAN MOLE RATIOS FOR SILICA, SODIUM, CALCIUM, AND BICARBONATE IN BASE RUNOFF

Chemical constituent	Theoretical mole ratio ^{1/}	Calculated mean mole ratio	
		From plots of constituents ^{2/}	Corrected for contributions from precipitation ^{3/}
<u>Silica</u> Bicarbonate	1.33	0.96	1.26
<u>Silica</u> Sodium	2.00	1.17	1.76
<u>Silica</u> Calcium	8.00	3.18	7.23
<u>Sodium</u> Calcium	4.00	2.70	4.12

^{1/} From the weathering equation.

^{2/} From figure 41.

^{3/} Calculated using data in table 9.

rocks and is the major source of the dissolved constituents in the surface water and ground water.

Reconstruction of Original Minerals

A method of calculating back to the original minerals in the rock from the chemical composition of the base runoff may be used to identify the source of the dissolved constituents in the water and to verify the weathering of plagioclase to kaolinite, calcium, sodium, and silica. The procedure used by Garrels and Mackenzie (1967, p. 226) involves the conversion of the constituents in the water from milligrams per liter to moles per liter, the subtraction of constituents contributed by precipitation, reversing the form of the weathering equation, and the subtraction of the appropriate amounts of dissolved constituents until all are accounted for. The procedure was slightly modified for this report. Garrels and Mackenzie (1967) used chemical analyses of ephemeral spring flow in the Sierra Nevada and corrected for the contribution of dissolved constituents from precipitation by subtracting the mean values of the constituents in precipitation from the mean values of the constituents in ephemeral spring flow. In the Santa Catalina Mountains the contribution of dissolved solids from precipitation is determined on a weighted-mean basis rather than by subtracting mean values of dissolved constituents in precipitation from those in base runoff (table 9).

After correcting for the contribution of constituents by precipitation, the calculations show that nearly all the dissolved constituents in base runoff are contributed by the weathering of plagioclase feldspar (table 11). The calculations indicate an excess in magnesium of 0.16 mole per liter and slight deficiencies in calcium and bicarbonate. Potassium, silica, and bicarbonate should be present to balance a back reaction of kaolinite to biotite or possibly garnet in order to account for the excess magnesium. The imbalances may be caused by averaging of the data, by assuming that the nine precipitation samples are completely representative of the chemical quality of all the precipitation, or by analytical errors in the chemical analyses of the water.

The equations and calculations presented in the section of the report entitled "Ratios of Mobile Constituents" and in this section indicate that the weathering of the granodioritic rock can be represented by a simple weathering model—the alteration of plagioclase to kaolinite by water charged with carbon dioxide. The validity of the model is strengthened further by use of stability diagrams.

Stability Relations among Selected Minerals

Stability diagrams, which are graphical representations of the chemical equilibrium among selected minerals, can be used to relate water chemistry to the minerals in the rock. Equilibrium among minerals can be described as any set of variables that can be

TABLE 11

SOURCE MINERALS FOR DISSOLVED CONSTITUENTS IN BASE RUNOFF

Item	(Concentrations in moles per liter $\times 10^{-4}$)							
	SiO ₂	Ca	Mg	Na	K	HCO ₃	SO ₄	Cl
Initial concentrations in base runoff	2.7	0.85	0.33	2.3	0.31	2.8	0.51	0.79
Corrected for contribution by precipitation (table 9)	2.6	.30	.16	1.3	.00	1.9	.00	.00
Back reaction of kaolinite to plagioclase (An ₂₀): $0.97\text{H}_4\text{Al}_2\text{Si}_2\text{O}_9 + 1.30\text{Na}^+ + 0.32\text{Ca}^{+2}$ $+ 2.60\text{H}_4\text{SiO}_4 + 1.94\text{HCO}_3^- \longrightarrow$ $1.62\text{Na}_{.80}\text{Ca}_{.20}\text{Al}_{1.20}\text{Si}_{2.80}\text{O}_8$ $+ 8.10\text{H}_2\text{O} + 1.94\text{CO}_2$	.00	-.02	.16	.00	.00	-.04	.00	.00

interconnected by balanced chemical equations (Garrels and Christ, 1965, p. 352). Feth and others (1964) and Garrels and Christ (1965) constructed stability diagrams for the systems $\text{Na}_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ and $\text{K}_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ at 25°C and 1 atmosphere. Hess (1966) presented stability diagrams for the combined system $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$. These investigators enumerate the assumptions and limitations involved in the construction of stability diagrams. The stability diagrams in this report (figs. 42 and 43) represent planes through a three-dimensional phase diagram (Hess, 1966), which has axes of $\log [\text{K}^+]/[\text{H}^+]$, $\log [\text{Na}^+]/[\text{H}^+]$, and $-\log \text{SiO}_2$.

The chemical analyses of the water are in the stability field of kaolinite in the $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ and $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ stability diagrams (figs. 42 and 43), which is the expected stability because kaolinite is the principal mineral in these systems in weathered material. Although kaolinite is the stable mineral expected as a result of weathering, chemical data for fresh water from a variety of rock types also are in the stability field of kaolinite (Garrels and Christ, 1965, p. 361; Bricker and Garrels, 1967, p. 464), which raises a question as to the meaningfulness of the data in figures 42 and 43. Garrels and Mackenzie (1967, p. 225) and Bricker and Garrels (1967, p. 461), however, support the validity of the chemical data for water in the kaolinite stability field and show evidence that by its presence, kaolinite controls the composition of the water that is in contact with it.

Figure 42. --Stability relations of some phases in the system $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ at 25°C and 1 atmosphere.

Figure 43. --Stability relations of some phases in the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ at 25°C and 1 atmosphere.

They conclude that kaolinite is the initial expected clay mineral in the weathering of silicate minerals by "aggressive" CO_2 -charged surface water and ground water.

The reaction of CO_2 -charged water with silicate minerals can be evaluated by the behavior of silica. One of the obvious features of the stability diagrams is the limited concentration range of SiO_2 , which varies from 10^{-4} to 10^{-3} moles per liter—6 to 60 mg/l SiO_2 . Most of the values fall between those for the solubility of quartz and amorphous silica—6-14 mg/l for quartz and about 120-140 mg/l for amorphous silica. Krauskopf (1959) and Siever (1962) note the sluggishness of the dissolution and precipitation of quartz and amorphous silica at about 25°C ; as a result, natural water usually is supersaturated with respect to quartz and undersaturated with respect to amorphous silica. Although it may seem logical to relate the lower and upper limits of SiO_2 on the stability diagrams to the solubilities of quartz and amorphous silica, Bricker and Garrels (1967, p. 461) showed that the minimum silica concentrations are about 3 mg/l based on analyses of water from a variety of felsic rock types. The value is below that for the solubility of quartz and close to the theoretical 1 to 2 mg/l value calculated from free-energy data for the equilibrium between kaolinite and gibbsite. Water from Jamaican bauxitic soil—the soil contains a mixture of gibbsite and kaolinite—contains from 3 to 6 mg/l of silica, which is close to the 1 to 2 mg/l theoretical value. The upper limit for silica

of about 60 mg/l (10^{-3} moles per liter) is well below the limit for the solubility of amorphous silica. Bricker and Garrels (1967) concluded that neither quartz nor amorphous silica exert control on the silica content of surface water and shallow ground water but that the silica concentrations are controlled by the weathering of silicate minerals, mostly plagioclase feldspar.

The upper limit of the concentration of silica may be governed by the equilibrium between kaolinite and montmorillonite. Garrels (1967, p. 414) derived an expression involving Ca^{+2} , SiO_2 , and pH from an equation for the formation of montmorillonite—an assumed composition for calcium montmorillonite—from kaolinite and plotted this value versus the HCO_3^- content for several water samples. As the HCO_3^- content of the water increases, the value of the expression increases; at an HCO_3^- concentration of about 100 mg/l, the expression becomes constant. Although Garrels (1967) acknowledged several approximations in the derivations, he interpreted the expression as equilibrium of montmorillonite and kaolinite. Garrels (1967) further concluded that water that contains less than 100 mg/l HCO_3^- contains large amounts of CO_2 and is actively kaolinizing rocks; however, in water having more than 100 mg/l HCO_3^- the CO_2 is used up, which results in higher pH values, and the amounts of HCO_3^- , SiO_2 , and cations increase when montmorillonite begins to form.

Nearly all the direct runoff is undersaturated with respect to quartz, and the base runoff and spring flow are supersaturated with respect to quartz (figs. 42 and 43). The highest values for $[K^+]/[H^+]$ and $[Na^+]/[H^+]$ are those for base runoff. Ephemeral spring flow contains about the same amounts of cations as base runoff, but, because the pH of ephemeral spring flow is about one unit lower, the ratios are lower. Perennial spring flow has a pH value in about the same range as that for ephemeral spring flow, and cation to hydrogen ratios also are lower than those for base runoff.

The values of $[K^+]/[H^+]$ and $[Na^+]/[H^+]$ versus SiO_2 in direct runoff and base runoff seem to follow the expected path of compositional change for a CO_2 -charged water that weathers silicate minerals (fig. 43). The theoretical changes in water composition in terms of $[Na^+]/[H^+]$ versus SiO_2 in a closed system of an initially pure water charged with CO_2 are shown in figure 43. Theoretically, the first reaction would be the formation of gibbsite, which immediately would be silicated to form kaolinite. As the mineralization of the water increases, the montmorillonite-kaolinite equilibrium boundary will be reached, beyond which the compositional changes in the water will parallel the boundary. However, the water is not in contact with the rock for a sufficient length of time to come into equilibrium with montmorillonite. Most of the values for $[Na^+]/[H^+]$ versus SiO_2 in direct and base runoff are within the theoretical limits and may represent

closed-system conditions, but most of the values for ephemeral and perennial spring flow are outside the limits. Most of the springs issue from the alluvium, which contains large amounts of organic matter. Sustained contact of the spring flow with the organic matter maintains a high CO_2 pressure (table 7) and accounts for the low pH and log $[\text{Na}^+]/[\text{H}^+]$ values as compared to those in base runoff.

The data given in figure 44 further substantiate the theory that direct and base runoff follow a closed-system path. The bicarbonate and pH values for precipitation, direct runoff, and base runoff show an inverse straight-line relation to dissolved carbon dioxide, which indicates that precipitation receives an initial charge of carbon dioxide and that the carbon dioxide is used up gradually as the resultant carbonic acid ($\text{CO}_2 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{CO}_3$) attacks the silicate minerals. The hydrogen ions in the acid displace the cations from the silicate structures resulting in a higher pH of the water, and the HCO_3^- increases in concentration. The data also indicate that ephemeral and perennial springs depart from a closed-system relation and contain as much as 2 to 13 times more dissolved carbon dioxide than the runoff. These results differ slightly from those of Bricker and Garrels (1967, p. 465), who used the ephemeral-spring data of Feth and others (1964) from the Sierra Nevada; Bricker and Garrels showed that these ephemeral springs have a closed CO_2 system. Garrels (1967, p. 416) showed that the compositional changes in the ground water from a variety of

Figure 44. --Mean calculated dissolved carbon dioxide versus mean bicarbonate and pH in water.

igneous rocks in different areas also follow the trend for a closed system.

The stability of the minerals for the $K_2O-Al_2O_3-SiO_2-H_2O$ system can be evaluated from the phase diagram (fig. 42), although calculations indicate that precipitation contributes all the potassium to the water (table 9). The calculations probably are not completely accurate, and a small amount of potassium probably is contributed by potassium-bearing minerals; chemical analyses of weathered rock show losses in K_2O when compared to those for fresh rock (fig. 25). Although the alteration of muscovite to vermiculite removes potassium, the stability of the minerals in the phase diagram can be evaluated without regard for the source of potassium.

All the $[K^+]/[H^+]$ versus SiO_2 values are in the stability field of kaolinite; theoretically, gibbsite, muscovite, and potassium feldspar are unstable. The water contains too much silica for gibbsite to be stable. In some grus samples muscovite is altered visibly by weathering (figs. 20A and 22), but in other samples muscovite seems to be unaffected. Illite, which probably is derived from fine-grained muscovite, is present in all the samples of grus. Theoretically potassium feldspar is unstable in this weathering environment; however, the potassium feldspar is metastable in the weathered material in the study area.

Gibbsite, montmorillonite, and plagioclase are the unstable minerals in the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ system (fig. 43). Plagioclase, which is represented in figure 43 by the end member albite, is the most reactive major mineral in the rock and contributes most of the dissolved constituents that result from weathering to the surface water and ground water. Gibbsite is unstable owing to the silica concentrations in the water. Montmorillonite is not a common clay mineral in the weathered material, but it is present in trace amounts in some samples of grus and soil. Montmorillonite is the dominant clay mineral in soil profile P-2, but, because of the acid soil conditions, the montmorillonite probably is very unstable.

Vermiculite is the only principal mineral not included in the stability diagrams. Free-energy data are not available for mineral phases in the systems containing MgO at 25°C and 1 atmosphere; however, Garrels and Christ (1965, p. 364) prepared a preliminary three-dimensional stability diagram based on high-temperature data in the system involving kaolinite, potassium mica, potassium feldspar, chlorite, and phlogopite. The chemical data for ground water and surface water obtained during this study are well within the stability field of kaolinite.

In summary, diagrams representing fields of stability for silicate minerals can be prepared by using certain simplifying assumptions that only approximate natural conditions. The diagrams are

useful as a model for the comparison of the behavior of silicate minerals under actual weathering conditions and to give insight into the geochemical controls on the composition of surface water and ground water. Theoretically, kaolinite is the only stable mineral in the $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ system in the study area. Most of the dissolved constituents in the ground water and surface water, with the exception of those contributed by precipitation, are derived from the alteration of plagioclase (oligoclase) to kaolinite. The other minerals in the diagrams are gibbsite, muscovite, potassium feldspar, plagioclase (albite), and montmorillonite, all of which theoretically are unstable (figs. 42 and 43). With the exception of potassium feldspar, the minerals show alteration, are present only in trace amounts, or are absent; potassium feldspar is metastable and shows very little alteration from weathering.

ENERGY OF THE WEATHERING ENVIRONMENT

The type and the extent of completion of the chemical reactions in the weathering environment are governed by the energy impressed upon the rock minerals. Sources of energy include thermodynamic energy, which is caused by the instability of rock minerals in relation to temperatures and pressures at the earth's surface (free energy of reaction), and less definable and measurable sources of energy, such as climate and biota.

Weathering equations for the formation of clay minerals from the minerals in granodioritic rocks indicate that only small changes in the free energy of reaction (ΔF_r°) are involved (table 12). The equation for the alteration of albite to kaolinite is an exception because the large negative value for ΔF_r° indicates that the reaction is spontaneous. The other possible reactions for which free-energy data are available have low negative values or even positive values, which indicate that little or no potential exists for spontaneous reaction. The values for ΔF_r° indicate the relative stability of two or more minerals or compounds under given physical conditions. Theoretically, the negative values for the albite-kaolinite reaction show that the product (kaolinite) is more stable than the reactant (albite) at the earth's surface and that the same

TABLE 12

CALCULATED VALUES FOR THE FREE ENERGY OF
REACTION (ΔF_r°) FROM SELECTED WEATHERING EQUATIONS

Reaction ^{1/}	(ΔF_r° , in kilogram calories) ^{2/}		
	Values of ΔF_r° and source of data on ΔF_f° of phases		
	Robie and Waldbaum (1968)	Krauskopf (1967)	Garrels and Christ (1965)
Albite $\longrightarrow$ Kaolinite	-396	-377	--
Muscovite $\longrightarrow$ Kaolinite	-74	--	-20
Orthoclase $\longrightarrow$ Kaolinite	+29	+29	+1.3
Orthoclase $\longrightarrow$ Muscovite	+122	+52	+13

^{1/} Reactions are written and balanced conserving aluminum and have the general form:

^{2/} Free energy of reaction is calculated from the free energy of formation of the compound or ion:

$$\Delta F_r^\circ = \sum \Delta F_f^\circ \text{ of the products of the reaction} \\ - \sum \Delta F_f^\circ \text{ of the reactant of the reaction.}$$

relation exists between the muscovite-kaolinite pair. The positive values for the orthoclase-kaolinite and orthoclase-muscovite reactions indicate that orthoclase is the most stable mineral in each reaction and does not tend to alter to either kaolinite or orthoclase. The calculations of ΔF_r° substantiate the stability of these minerals in the weathering environment in the study area (table 12). Other possible reactions for which no free-energy data are available for the transformation of one clay mineral to another—i.e., illite to vermiculite—probably have small values of ΔF_r° and can react in either direction depending on the energy variations in the environment. Energy variations may be caused by differences in the amount, type, and composition of parent minerals, differences in climate, differences in vegetation, or other factors. A comparison of the data from the study area with data from the Sierra Nevada and New Zealand illustrates this point.

Feth and others (1964) reported on the mineral-water relations in the granitic terrane of the Sierra Nevada, where rock composition and amounts of dissolved constituents in the surface water and ground water are comparable to those in the study area. The calcium to sodium ratios are slightly higher in the rock and water in the Sierra Nevada than in the rock and water in the study area. Andesine is the most common plagioclase in the Sierra Nevada, whereas oligoclase is the principal feldspar in the Santa Catalina Mountains. The mean annual precipitation and temperatures are similar in the areas, although

precipitation in parts of the Sierra Nevada may be as much as 50 inches annually. In the Sierra Nevada most of the precipitation falls in the winter as snow, and the area has only one wet season per year as compared to two wet seasons in the Santa Catalina Mountains. The major differences between the two areas are the clay mineral assemblages. Feth and others (1964) showed that most of the material in the <2-micron fractions of samples collected near spring orifices is either amorphous or is so poorly crystalline that no X-ray diffraction peak is readable. In places, well-crystallized montmorillonite, kaolinite, and micaceous clay minerals [illite(?)] are present. Montmorillonite is as abundant as kaolinite and the micaceous clay minerals. In the study area the clay mineral assemblage is kaolinite and illite in grus, kaolinite and vermiculite in soil, and trace amounts of montmorillonite. Why are the clay mineral assemblages and their degree of development different in the two areas? The differences in the calcium-sodium ratios in the rock or the differences in distribution of annual precipitation may exert significant controls on the weathering. The slightly higher calcium content and the long dry period in the Sierra Nevada may be more favorable for the formation of montmorillonite than the lower calcium content and different precipitation pattern in the higher parts of the Santa Catalina Mountains. Both areas are covered by coniferous forests, but the species are different. It may be possible that the different decay products—organic acids, chelating compounds, etc.—from

the various species of trees have an effect on the type and degree of clay mineral formation.

Fieldes and Swindale (1954) reported a clay mineral assemblage in New Zealand soils similar to that in the weathered material in the higher parts of the Santa Catalina Mountains. The New Zealand clay mineral assemblage weathers from mica in yellow-gray earth—a moderately developed Podzol formed under a mean annual temperature and precipitation of 52°F and 20 to 40 inches, respectively—and is mica → illite → vermiculite → montmorillonite. The parent material is different in the New Zealand soils and consists of sediment and shale that have a composition similar to that of intermediate felsic igneous rocks. The major difference between the two areas is the location of the development of the illite, vermiculite, and montmorillonite in the soil profile. In the Santa Catalina Mountains illite develops in the grus, and in passing upward from grus to soil vermiculite increases and illite decreases. The near-surface soil contains vermiculite and very little illite. Weathering is more intense near the surface, which results in the further degradation of the mica structure to an expandable-layered structure. Fieldes and Swindale (1954) expected an increase in expanded mica from the subsoil to the topsoil, but this situation does not occur in the New Zealand soils. The amount of expanded mica is greatest in the subsoil and decreases toward the surface to a 10 Å nonexpanded structure. Fieldes and Swindale (1954)

explained this phenomenon as possibly being caused by the fixation of potassium ions from the "organic cycle" in the topsoil. The "organic cycle" was not defined.

The conclusion drawn from the comparisons of these studies is that although the general weathering mechanism is known, weathering and alteration of clay minerals do not conform to strict rules and boundaries. Subtle differences in the environmental energies in different areas may be sufficient to control or affect the formation of alteration products; this is especially true of weathering reactions of layered silicates that involve small values of ΔF_r° . The energy applied by the weathering environment may be of opposite sign and greater magnitude than the potential for spontaneous reaction on the basis of free-energy calculations.

ESTIMATED CHEMICAL DENUDATION RATES

Denudation is defined as the stripping loose of weathered material from the landscape by different processes of erosion and mass wasting (Fairbridge, 1968, p. 261); this common definition of the term applies only to mechanical or physical denudation. A complete definition should include chemical denudation, which is the removal of soluble material by runoff. Although the amount of chemical denudation is less than that of physical denudation, chemical denudation often has been neglected in estimating erosion rates.

The determination of chemical denudation rates is based on the amount of chemical constituents derived from rock weathering. In most instances, the calculation of chemical denudation rates includes the total dissolved-solids load in a stream, which is all the ions contributed from all the sources. Bicarbonate, sulfate, chloride, and nitrate make up from 60 to 80 percent of the dissolved-solids load in streams that drain crystalline silicate rocks (Janda, 1969; written commun., 1970). These anionic constituents are derived either directly from the atmosphere or from atmospheric-biospheric reactions and are not present in the underlying rock. The major cations in streamflow are contributed either by the atmosphere or by rock

weathering; a large part of the cations are contributed by the atmosphere. Janda (1969) estimated that, in the past, computations of chemical denudation rates have been exaggerated 2.5 to 5 times by the use of the total dissolved load in streams.

Method of Calculation

In this study the amounts of the chemical denudation constituents were estimated by determining the amount of dissolved solids contributed by precipitation and atmospheric-biospheric reactions and subtracting this amount from the dissolved solids in base runoff. The calculations indicate that only about half the dissolved solids in base runoff are the result of rock weathering. Of the 43 mg/l of dissolved solids in base runoff, 17 mg/l or 40 percent is contributed by precipitation (table 9). The remaining 26 mg/l of dissolved solids is derived from atmospheric-biospheric reactions and the weathering of the rock. All the bicarbonate in the 26 mg/l of dissolved solids is assumed to be from atmospheric-biospheric reactions, and, when the 6 mg/l of bicarbonate (see footnote 2, table 9) is subtracted, the remaining 20 mg/l of dissolved solids is the contribution from weathering of the rock.

The mean annual weight of dissolved solids contributed to base runoff per unit area by the weathering of the rock is:

$$\begin{aligned}
 & (20 \times 10^{-3} \text{ grams per liter}) \\
 & (4.56 \times 10^8 \text{ liters per square mile per year}) \\
 & = 10 \text{ tons per square mile per year} \\
 & = 3.52 \times 10^{-4} \text{ grams per square centimeter per year.}
 \end{aligned}$$

In order to calculate the chemical denudation rate from 1 square centimeter of land surface, a rock density of 2.70 g/cm^3 is used.

$$\begin{aligned}
 \text{Chemical denudation rate} &= \frac{3.52 \times 10^{-4} \text{ grams per square centimeter per year}}{2.70 \text{ grams per cubic centimeter}} \\
 &= 1.30 \times 10^{-4} \text{ centimeters per year} \\
 &= 0.13 \text{ centimeter per 1,000 years.}
 \end{aligned}$$

Chemical denudation rates expressed as the amount of vertical lowering of the land surface in a given length of time are not completely realistic and imply that the removal of soluble material is followed by topographic lowering of the land surface. This assumption probably is not valid. The transition from fresh rock to grus involves very little volume change, as indicated by the preservation of rock textures and structures in the grus; however, the bulk density of the grus decreases with increased weathering because of the formation of less dense clay minerals and the removal of soluble constituents. Ollier (1969, p. 180-181) stated that, except for limestone and other relatively soluble rock, no general lowering of the land surface results from weathering;

most of the lowering of the land surface in the Santa Catalina Mountains probably is accomplished by erosion following weathering and not by weathering. Although chemical denudation rates expressed as weight per unit area per unit time probably are more valid, vertical rates of surface lowering per unit time also are given in this report for comparison with those reported in the literature for other areas.

Table 13 gives comparisons among the vertical chemical denudation rates in the Sangre de Cristo Range, New Mexico (Miller, 1961), the Wind River Range, Wyoming (Hembree and Rainwater, 1961), and the Santa Catalina Mountains, Arizona—all of which have similar granitic terranes. In order to correct for the contribution of dissolved solids from precipitation, Miller (1961) and Hembree and Rainwater (1961) used total dissolved solids in the runoff and subtracted the contribution of dissolved solids by precipitation, which was determined by the ratio of precipitation to runoff. Constituents are removed from precipitation when it comes in contact with the ground, however, and the amount of dissolved solids contributed to runoff by precipitation is not simply concentrated by evaporation. When the denudation rates are corrected by subtracting the anions from the dissolved solids in runoff in the Sangre de Cristo and Wind River Ranges, the rates are about the same as those in the Santa Catalina Mountains, which supports Janda's (1969) statement that as little as 30 percent of the

TABLE 13

COMPARISON OF VERTICAL CHEMICAL DENUDATION RATES IN THE SANTA CATALINA MOUNTAINS WITH THOSE IN OTHER GRANITIC AREAS

Area	Mean annual precipitation (inches)	Chemical denudation rate (feet per 10^6 years)	
		Based on total dissolved solids in surface water (uncorrected for contributions from nonrock sources)	Based on dissolved solids contributed by rock weathering
Sangre de Cristo Range, New Mexico			
8,000 feet in altitude	17	12	$\frac{1}{4.8}$
7,000 feet in altitude	13	8	$\frac{1}{3.2}$
Wind River Range, Wyoming	25	19	$\frac{1}{3.8}$
Drainage basin of 900 square miles, most of which is between 7,000 and 9,000 feet in altitude			
Santa Catalina Mountains, Arizona	25-30	9	4.2
From about 7,000 to 8,000 feet in altitude			

$\frac{1}{}$ Value was derived by subtracting HCO_3^- , SO_4^{-2} , Cl^- , and NO_3^- from the dissolved solids; significant amounts of these constituents are not derived from weathering of granitic rocks. No correction was made for cations contributed by precipitation.

dissolved load of streams that drain granitic rocks is derived from chemical weathering of the underlying rock.

Qualitative Analyses of Errors

Three major sources of error may be involved in the calculation of denudation rates in the study area. First, the value of 30 inches of precipitation per year may be slightly high. The value is the mean for 4 years of record, 1965-68, at the Palisade Ranger Station; 1966 was a year of abnormally large amounts of precipitation in southern Arizona. The normal annual precipitation in 1931-60 was more than 25 but less than 30 inches in the study area (University of Arizona, 1965a; 1965b). If the amount of annual precipitation is overestimated in the calculation, the contribution of constituents by precipitation will be overestimated, which will result in too low a denudation rate.

Secondly, the collection of representative samples of precipitation presents a problem in regard to chemical composition. The chemical composition of precipitation may vary with the season, the type of precipitation (rainfall or snow), the time of collection during the precipitation event, and the amount of dry fallout in the precipitation. During a study in eastern North Carolina and southeastern Virginia, Gambell and Fisher (1966) obtained composite monthly precipitation samples from a collecting surface that remained exposed at all times. As a result of the exposed collecting surface, bulk

precipitation—dry fallout and water—was sampled. The results of the study by Gambell and Fisher (1966) are compatible with those of large regional studies by Junge and Werby (1958), in which the collecting surfaces were covered between precipitation events to eliminate inclusion of dry fallout in the samples. In contrast, Whitehead and Feth (1964) reported that bulk precipitation at Menlo Park, Calif., contains from 4 to 10 times more mineral matter than rainwater. The nine precipitation samples analyzed for this study had the same mean dissolved-solids concentrations as the bulk precipitation in eastern North Carolina and southeastern Virginia (Gambell and Fisher, 1966) and as the snow in the Sierra Nevada (Feth and others, 1964)—5 mg/l dissolved solids. Although only nine precipitation samples were analyzed from the study area, the dissolved-solids content of 5 mg/l is near the average concentration of dissolved solids (less bicarbonate and nitrate) in precipitation sampled at Tucson from July 1955 to June 1956 (table 3).

Third, the estimated mean annual runoff per unit area may be slightly large for the study area. The unit runoff of 370 acre-feet per square mile per year is for the gaged part of Sabino Creek above an altitude of 7,200 feet. Although most of Sabino Creek is at an altitude similar to that in the study area, a number of tributary canyons drain areas at higher altitudes. As a result, the unit runoff of Sabino Creek above the gage probably is slightly greater than that near the Palisade

Ranger Station. An overestimation of runoff in the calculation will cause the chemical denudation rates to be too large.

Relation of Chemical Denudation to Physical Denudation

In temperate regions streams that drain granitic terranes generally have suspended sediment loads of more than twice their annual dissolved loads (Janda, 1969). If the dissolved load is calculated using the constituents that are derived only from the underlying rock and if it is realized that calculated rates of chemical denudation are not completely realistic (table 9), chemical denudation seems to be ineffective in the evolution of landscapes. As reported by Janda (1969), however, the apparent ineffectiveness of chemical weathering is misleading in the overall denudation of granitic rocks. The small amounts of chemical weathering mainly are restricted to boundaries, fractures, and cleavage planes of plagioclase crystals, and, although the overall chemical changes in the rock are small, the end result is a thoroughly weakened rock and an abundant supply of relatively unweathered detritus.

SUMMARY

The weathering of the granodioritic rocks near Rose Canyon Lake was considered in terms of reactants and products of the chemical equation:

The granodioritic rocks have an almost uniform mineral and chemical composition. For purposes of this study, the rocks were divided into three lithologic units—muscovite-biotite gneiss, muscovite-garnet gneiss, and a transitional unit, which is a mixture of the muscovite-biotite gneiss and the muscovite-garnet gneiss. Physically, the muscovite-garnet gneiss is weaker than the muscovite-biotite gneiss, but the major weathering products developed on both units are identical. Cataclastic metamorphism has affected nearly all the rock. The resultant shearing and jointing have placed the rock minerals in a reactive state by reducing grain size and forming openings through which water may enter the rock.

The precipitation in the Santa Catalina Mountains is an acid carbon dioxide-charged solution that contains about 5 mg/l of dissolved

solids. The principal constituents in the precipitation are calcium, sodium, sulfate, chloride, and nitrate, but the chemical composition varies greatly. The chemical composition of the precipitation has little effect upon the weathering of minerals in the study area, but the dissolved carbon dioxide in the precipitation has a significant effect on weathering.

The hydrogen ions initiate the chemical weathering of silicate minerals. These small cations penetrate the crystal structures and replace other cations, which causes an electrical imbalance and subsequent alteration of the crystal. The hydrogen ions are derived mainly from carbonic acid formed from the solution of carbon dioxide in precipitation and soil water. Carbon-dioxide concentrations in the soil atmosphere caused by organic material may be 10 times those in the air. Spring water that has been in contact with decaying organic matter in soil and sediment contains as much as 13 times more dissolved carbon dioxide than runoff. Some hydrogen ions are contributed directly by organic acids.

The products of weathering consist of residual and mobile constituents. The residual constituents are grus, podzolic soil, and alluvium and their contained clay minerals. The mobile constituents are the soluble materials that have been derived from the weathering of the gneiss and that have been dissolved and transported by surface water and ground water.

The grus is a weak slightly chemically weathered rock composed of angular and gritty material that has resulted from in situ weathering. Original rock textures and structures usually are preserved in the grus. Commonly, the grus is from 2 inches to as much as a foot thick and is at least 15 feet thick in places where conditions are more favorable for its formation. In the transition from rock to soil plagioclase alters to kaolinite along fractures and in the cores of crystals, and clay skins develop with increased weathering. Because the plagioclase makes up about one-third of the rock, the rock loses its cohesive strength and changes into friable grus. The principal chemical changes in the grus as a result of weathering are gains in water and slight losses in silica, calcium, and sodium. Most of the grus contains less than 2 percent clay.

The degree of development of the podzolic soil in the study area is extremely variable, but nearly all the soil profiles show some podzolic characteristics. Most of the soil is classified as Western Brown Forest, which is characterized by a lack of strong differentiation between the A, B, and C horizons. The soil is less than a foot thick and is typically grayish brown to brown. A better developed but less widely distributed soil occurs on the alluvium and, in places, on rock. The soil probably is older than the Western Brown Forest soil and has characteristics of the Gray Brown Podzolic and Gray Wooded soils. The principal differences between these soils and the Western

Brown Forest soil are in thickness, the development of an identifiable A2 horizon, and a heavier B horizon that commonly contains clay films and is noticeably yellowish in the lower part. The mineralogical composition of the soil is similar to that of the grus except for the presence of dioctahedral vermiculite, which forms at the expense of illite. The chemical composition of soil and grus is similar. The soil ranges from gravelly sandy loam to gravelly loamy sand and generally contains less than 4 percent clay. In the transition from grus to soil the particle-size mode shifts from gravel to medium sand to fine sand in the upper parts of soil profiles.

The alluvium is very poorly sorted, although some degree of bedding is evident in most exposures. The alluvium is made up of boulder- to silt-size material and is as much as 12 feet thick near the base of the slope that extends to the crest of the Santa Catalina Mountains; the grus also is thickest along the break in slope. The deposits are yellowish brown to strong brown. The alluvium has undergone the greatest amount of weathering and soil development of any material in the study area. The mineralogical composition of the alluvium is similar to that of soil developed on rock. Some of the fine-grained beds in the alluvium contain nearly 5 percent clay.

Kaolinite, illite, and dioctahedral vermiculite are the principal clay minerals in the grus, soil, and alluvium. Kaolinite is present in all the weathered material; illite is present in grus but decreases as

vermiculite increases in the B and A soil horizons. Montmorillonite is present in minor amounts in some weathered material.

The mobile constituents may be expressed as the dissolved-solids content of the water. Based on the length of time of water-rock contact, the occurrence of water is classed as direct runoff, base runoff, ephemeral springs, and perennial springs. The average amounts of dissolved solids in water range from about 20 to 70 mg/l. The approximate length of time of water-rock contact in relation to mean dissolved-solids concentrations is several minutes to a few hours for 18 mg/l in direct runoff, several hours to a few weeks for 43 mg/l in base runoff and ephemeral springs, and a few weeks to a few months for 73 mg/l in perennial springs.

As soon as precipitation comes in contact with the ground it becomes direct runoff, and the chemical composition of the water changes from a diverse chemical type to a calcium sodium sulfate bicarbonate type. In the transition from precipitation to direct runoff the dissolved solids increase more than three times. As water-rock contact time increases, the mineralization rate of the water decreases. The dissolved-solids content in base runoff and ephemeral springs is 2.4 times greater than that in direct runoff, and the dissolved-solids content in perennial springs is less than twice that in base runoff and ephemeral springs. Silica increases 320 times in the transition from precipitation to perennial spring flow and has the largest percentage

increase of all the dissolved constituents. In the transition from direct runoff to perennial spring flow the chemical composition of the water changes from a calcium sodium sulfate bicarbonate type to a sodium bicarbonate type.

Precipitation contributes about 40 percent of the dissolved solids to base runoff. In the transition from precipitation to runoff potassium, sulfate, and chloride are removed selectively; therefore, the constituents are not concentrated simply by evaporation of precipitation. About 30, 40, 50, and 60 percent of the bicarbonate, sodium, magnesium, and calcium, respectively, are contributed to base runoff from precipitation.

Chemical weathering of the granodioritic rocks involves mainly plagioclase feldspar, and most of the chemical constituents contributed to the water are derived from this mineral. The theoretical mole ratios of silica, calcium, sodium, and bicarbonate that are derived from a balanced weathering equation are similar to the mole ratios calculated from analyses of surface and ground water after subtraction of the dissolved solids contributed by precipitation. The balanced weathering equation for the alteration of plagioclase (oligoclase, An_{20}) to kaolinite is:

The close agreement of the theoretical and corrected calculated mole ratios substantiates the hypothesis that the alteration of plagioclase to kaolinite is the principal chemical reaction in the weathering of the granodioritic rocks and is the major source of the dissolved constituents in the surface water and ground water. Theoretically kaolinite is the only stable mineral in the $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ system in the study area.

Precipitation and direct and base runoff follow a closed-system path. The bicarbonate and pH values for precipitation, direct runoff, and base runoff show an inverse straight-line relation to dissolved carbon dioxide, which indicates that precipitation receives an initial charge of carbon dioxide and that the carbon dioxide is used up gradually as the resultant carbonic acid attacks the silicate minerals. Ephemeral and perennial springs depart from the closed-system relation because of their contact with decaying organic matter.

The rate of chemical denudation based only on the amount of dissolved constituents from weathering of the rock is 4.2 feet per 10^6 years (10 tons per square mile per year), which compares favorably with rates similarly calculated for other granitic terranes; this rate is

about half that calculated using total dissolved solids uncorrected for contributions from precipitation. If the dissolved load in runoff is calculated using the constituents that are derived only from the underlying rock and if it is realized that calculated rates of chemical denudation are not completely realistic, chemical denudation seems to be ineffective in the evolution of landscapes. The small amounts of chemical weathering mainly are restricted to boundaries, fractures, and cleavage planes of plagioclase crystals, and although the overall chemical changes in the rock are small, the end result is a thoroughly weakened rock and an abundant supply of relatively unweathered detritus.

APPENDIX A
CHEMICAL ANALYSES OF UNWEATHERED AND WEATHERED MATERIAL

[Analyses in percent]

Sample number	Material	Sampling interval from surface of soil profile, in inches	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MgO	CaO	Na ₂ O	K ₂ O	H ₂ O ⁻	H ₂ O ⁺	TiO ₂	P ₂ O ₅	MnO	CO ₂	Sulfur as SO ₃	Sum
UNWEATHERED MATERIAL																		
R-54	Muscovite-biotite gneiss	---	73.6	14.7	0.62	0.44	0.33	2.0	4.2	3.6	0.07	0.46	0.10	0.04	0.10	< 0.05	0.00	100
R-55	Muscovite-biotite gneiss	---	73.4	14.7	1.0	.24	.19	.86	4.2	3.8	.12	.56	.13	.05	.08	.05	.00	99.4
R-56	Muscovite-biotite gneiss	---	73.7	14.9	.42	.28	.08	.93	4.4	3.9	.07	.37	.05	.04	.04	< .05	.00	99.2
R-59	Muscovite-biotite gneiss	---	73.8	14.7	.51	.28	.17	1.5	4.3	3.9	.06	.54	.07	.03	.05	.05	.00	100
R-53	Muscovite-garnet gneiss	---	74.4	14.8	.33	.36	.14	.67	4.6	3.5	.07	.68	.06	.13	.12	< .05	.00	99.9
R-57	Muscovite-garnet gneiss	---	73.6	14.6	.22	.32	.08	.65	4.2	4.6	.03	.60	.04	.05	.16	< .05	.00	99.2
R-58	Muscovite-garnet gneiss	---	74.7	14.7	.31	.24	.10	.82	4.2	3.9	.00	.71	.04	.05	.08	< .05	.00	99.8

Sample number	Material	Sampling interval from surface of soil profile, in inches	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MgO	CaO	Na ₂ O	K ₂ O	H ₂ O ⁻	H ₂ O ⁺	TiO ₂	P ₂ O ₅	MnO	CO ₂	Sulfur as SO ₃	Sum
WEATHERED MATERIAL																		
P-2b	Soil	0- 2	61.6	21.0	1.1	0.24	0.45	0.62	5.9	5.6	0.82	1.3	0.10	0.09	0.18	< 0.05	0.00	99.0
P-2c	Soil	2- 4	62.5	21.4	.84	.24	.43	.43	5.9	5.5	.84	1.7	.10	.04	.08	< .05	.00	100
P-2d	Soil	4-13	62.3	21.1	.95	.32	.49	.40	5.9	4.8	1.3	1.8	.13	.03	.11	< .05	.00	99.6
P-2e	Soil	13-32	66.5	18.3	.90	.36	.35	.49	5.1	4.1	.80	1.8	.18	.03	.21	< .05	.00	99.1
P-2f	Grus	32+	70.0	16.4	.72	.44	.31	.79	4.8	3.9	.57	1.3	.21	.04	.32	< .05	.00	99.8
P-5b	Soil	1- 2	74.6	14.3	.34	.44	.09	.46	3.5	4.2	.17	1.2	.07	.02	.14	< .05	.00	99.5
P-5c	Soil	2- 4	71.8	15.6	.74	.24	.15	.69	4.2	3.3	.35	2.6	.13	.02	.08	.08	.00	100
P-5d	Slightly weathered gneiss	24+	73.9	14.6	.35	.20	.13	1.1	4.3	3.5	.20	1.2	.10	.02	.02	.05	.00	99.7
P-6c	Soil	2- 5	72.2	15.5	.26	.76	.19	.88	3.9	3.4	.43	1.6	.13	.02	.13	< .05	.00	99.4
P-6d	Soil	5-13	72.0	15.3	.56	.40	.22	.82	3.3	3.8	.42	2.1	.10	.02	.08	< .05	.00	99.1
P-6e	Grus	13+	73.3	14.9	.51	.36	.28	1.4	3.5	3.9	.17	1.5	.07	.02	.06	< .05	.00	100

Sample number	Material	Sampling interval from surface of soil profile, in inches	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MgO	CaO	Na ₂ O	K ₂ O	H ₂ O ⁻	H ₂ O ⁺	TiO ₂	P ₂ O ₅	MnO	CO ₂	Sulfur as SO ₃	Sum
P-8a	Soil	0- 1	71.9	15.6	0.57	0.48	0.18	0.77	4.2	3.6	0.28	1.6	0.10	0.03	0.18	< 0.05	0.00	99.5
P-8b	Soil	1- 4	72.4	15.2	.60	.36	.28	1.2	3.7	3.9	.23	1.7	.11	.03	.13	< .05	.00	99.8
P-8c	Grus	4+	73.6	15.0	.56	.24	.09	.50	3.2	4.1	.20	1.5	.07	.02	.11	.05	.00	99.2
P-8d	Slightly weathered gneiss	48+	73.9	15.0	.38	.24	.09	.82	4.1	3.9	.11	1.0	.05	.03	.05	< .05	.00	99.7

APPENDIX B

CHEMICAL ANALYSES OF PRECIPITATION, PALISADE RANGER STATION

[Analyses in milligrams per liter, except as indicated]

Date of collection	Silica (SiO ₂)	Aluminum (Al)	Iron (Fe) (in solution at time of analysis)	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Potassium (K)	Ammonia (NH ₄)	Bicarbonate (HCO ₃)	Sulfate (SO ₄)	Chloride (Cl)	Fluoride (F)	Nitrate (NO ₃)	Dissolved solids (sum)	Specific conductance (micro-mhos at 25°C)	pH	Remarks
8-10-66	0.0	---	0.00	0.4	0.0	0.2	0.2	---	0	2.7	0.5	0.0	---	4.0	13	5.0	Thunderstorm.
9-15-66	.0	---	.02	.8	.0	.2	.2	---	0	.4	3.0	.1	---	4.7	12	4.8	Tropical storm "Helga." Composite of 4 days of rainfall.
9-15-66	.0	---	.02	.0	.2	.2	.2	---	1	.3	2.0	.0	---	3.4	9	6.2	Thunderstorm.
10-10-66	.0	---	.04	.8	.5	.4	1.8	---	0	.4	3.0	.0	---	6.9	18	5.0	Rain shower. Field pH=4.45.
11- 8-66	.3	---	.01	1.6	.0	.8	.2	---	6	.0	1.0	.0	---	6.9	13	6.5	Rain shower. Field pH=6.3.
7- 8-67	.22	0.04	---	.22	.03	.92	.09	0.24	0	4.50	.24	---	0.75	7.2	25	4.46	Thunderstorm.
7- 9-67	.37	.01	---	.42	.05	.47	.07	.36	0	2.45	.49	---	1.41	6.1	17	4.76	Thunderstorm.
10- 3-67	.00	.00	---	.18	.02	.65	.09	.40	1.9	.78	.40	---	.25	3.6	7.9	5.92	Thunderstorm.
7-67 to 10-67	.00	.00	---	.38	.03	.69	.08	.10	1.7	.50	.35	---	.87	3.8	7.3	6.06	Two-gallon composite of rainwater collected from July to October 1967. Seven samples total.
12- 8-69	---	---	---	---	---	---	---	---	4	.0	1.5	---	---	---	10	7.32	Snow.

APPENDIX C

CHEMICAL ANALYSES OF DIRECT RUNOFF, BASE RUNOFF, AND EPHEMERAL AND PERENNIAL SPRINGS

[Analyses in milligrams per liter, except where indicated]

Map num- ber (see fig. 1)	Location	Date of collec- tion	Tem- pera- ture (°C)	Silica (SiO ₂)	Iron (Fe)		Cal- cium (Ca)	Mag- ne- sium (Mg)	So- dium (Na)	Po- tas- sium (K)	Bicar- bonate (HCO ₃)		Sulfate (SO ₄)	Chlo- ride (Cl)	Fluo- ride (F)	Ni- trate (NO ₃)	Dis- solved solids (sum)	Specific conduct- ance (micro- mhos at 25°C)	pH		Remarks
					Total dis- solved	In solu- tion at time of analysis					Field	Lab							Field	Lab	
DIRECT RUNOFF																					
4	Head of Palisade Canyon	8-10-66	11.0	5	--	--	0.7	0.2	0.5	1.7	--	3	2.0	1.3	--	0.5	13	8	--	5.8	Collected during thunder- storm.
5	Northeast of Girl Scout Camp	8-10-66	11.0	3	--	--	.8	.3	.4	1.6	--	2	3.0	.0	--	2.0	12	14	--	6.0	Do.
6	Canyon north of Lizard Rock	8-10-66	11.5	6	--	--	1.0	.6	2.2	1.1	--	6	4.0	1.0	--	.7	20	33	--	6.8	Do.
26	Rose Canyon near Mount Lemmon Highway	7-28-67	17.0	3.5	--	0.10	2.4	1.0	1.2	.9	9	8	4.0	1.0	0.1	--	18	27	7.50	6.6	Collected during thunder- storm. Aluminum= 0.022 mg/l ₁ .
36	South of Boy Scout Camp	10- 3-67	13.5	5.4	--	.01	2.0	.7	.8	.3	3	5	3.0	1.0	.2	--	15	22	5.07	5.3	Collected about 12 hours after end of thunder- storm.
38	Head of Syc- amore Canyon and Mount Lemmon Highway	10- 3-67	9.5	5.4	--	.02	2.8	.2	2.0	.5	7	6	3.0	1.0	.1	--	18	26	6.58	6.1	Collected during thunder- storm.

See footnotes at end of table.

Map num- ber (see fig. 1)	Location	Date of collec- tion	Tem- pera- ture (°C)	Silica (SiO ₂)	Iron (Fe)		Cal- cium (Ca)	Mag- ne- sium (Mg)	So- dium (Na)	Po- tas- sium (K)	Bicar- bonate (HCO ₃)		Sulfate (SO ₄)	Chlo- ride (Cl)	Fluo- ride (F)	Ni- trate (NO ₃)	Dis- solved solids (sum)	Specific conduct- ance (micro- mhos at 25°C)	pH		Remarks
					Total dis- solved	In solu- tion at time of analysis					Field	Lab							Field	Lab	
39	Head of Willow Canyon	10- 3-67	13.5	5.9	--	0.01	2.4	0.7	1.5	0.6	5	6	4.0	1.0	0.1	--	19	26	5.75	5.8	Collected during thunder- storm.
40	Northeast of Lizard Rock	10- 3-67	14.5	4.6	--	.02	2.4	1.0	.8	.7	2	8	4.0	.5	.1	--	18	21	5.26	5.4	Do.
41	Rose Canyon near Mount Lemmon Highway	10- 3 67	14.0	8.9	--	.04	3.2	1.4	3.4	.9	9	10	7.0	1.0	.2	--	31	42	6.35	6.3	Collected shortly after end of thunderstorm.
52	Head of Palisade Canyon	12- 8-69	5.0	--	--	--	--	--	--	--	--	24	--	--	--	--	--	80	--	6.1	Snowmelt.
53	Head of Sycamore Canyon and Mount Lemmon Highway	12- 8-69	4.0	--	--	--	--	--	--	--	--	8	--	--	--	--	--	38	--	6.4	Do.
54	Head of Willow Canyon	12- 8-69	5.0	--	--	--	--	--	--	--	--	8	--	--	--	--	--	44	--	6.1	Do.

Map num- ber (see fig. 1)	Location	Date of collec- tion	Tem- pera- ture (°C)	Silica (SiO ₂)	Iron (Fe)		Cal- cium (Ca)	Mag- ne- sium (Mg)	So- dium (Na)	Po- tas- sium (K)	Bicar- bonate (HCO ₃)		Sulfate (SO ₄)	Chlo- ride (Cl)	Fluo- ride (F)	Ni- trate (NO ₃)	Dis- solved solids (sum)	Specific conduct- ance (micro- mhos at 25°C)	pH		Remarks
					Total dis- solved	In solu- tion at time of analysis					Field	Lab							Field	Lab	
BASE RUNOFF																					
2	Southeast of Spencer Peak	8-10-66	--	13	--	--	4.4	0.1	4.4	1.3	--	19	4.0	1.6	--	0.6	38	43	--	7.4	No rainfall 2 days prior to sampling; 0.72 inches total for 10 days prior to sampling.
7	Southeast of Spencer Peak	8-12-66	10.0	11	--	--	3.0	.8	3.0	1.0	--	9	4.0	1.7	0.4	.9	30	36	6.29	6.9	Collected 2 days after rainfall of 1.81 inches.
11	Near head of Palisade Canyon	8-12-66	10.5	13	--	--	3.5	1.1	4.0	2.9	15	--	4.0	3.0	--	.9	39	53	6.32	6.6	Collected at Girl Scout Spring, which was flooded by runoff. No rainfall for previous 4 days.
12	Head of Willow Canyon	8-25-66	18.0	19	--	--	2.0	.8	5.0	1.1	14	--	3.0	2.9	--	.8	42	42	6.51	7.2	No rainfall for 4 days prior to sampling.
13	Rose Canyon above Rose Canyon Lake	9- 2-66	10.0	13	--	--	3.5	1.0	4.4	1.5	18	--	4.0	3.8	--	.5	41	43	6.79	7.9	0.26 inches rainfall day before sample was collected.
14	Sycamore Canyon above Rose Canyon	9- 2-66	16.0	13	--	--	2.1	.8	1.4	.3	11	--	3.0	1.9	--	.7	28	58	7.02	7.4	Do.
19	South of Boy Scout Camp	9-19-66	--	14	--	--	1.6	.6	3.4	1.1	6	--	2.0	2.2	--	1.0	29	29	6.46	7.4	No rainfall for 4 days prior to sampling.

Map number (see fig. 1)	Location	Date of collection	Temperature (°C)	Silica (SiO ₂)	Iron (Fe)		Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Potassium (K)	Bicarbonate (HCO ₃)		Sulfate (SO ₄)	Chloride (Cl)	Fluoride (F)	Nitrate (NO ₃)	Dissolved solids (sum)	Specific conductance (micro-mhos at 25°C)	pH		Remarks
					Total dissolved	In solution at time of analysis					Field	Lab							Field	Lab	
28	Bear Canyon about 2 miles southwest of Windy Point	8- 2-67	23.5	26	0.25	--	5.6	1.7	12	0.8	33	34	8.0	3.5	0.1	--	75	86	7.12	7.3	0.58 inches of rainfall 2 days prior to sampling. Total for 14 days prior to sampling is 1.17 inches.
29	Sycamore Canyon about 2½ miles west-southwest of Windy Point	8- 2-67	22.0	16	.12	--	3.2	.7	5.4	.8	15	16	7.0	3.0	.0	--	44	51	7.38	7.2	Do.
30	Palisade Canyon about 3 miles west of Windy Point	8- 2-67	--	20	.08	--	5.2	1.4	8.7	.7	21	23	12	4.5	.1	--	64	79	7.06	7.2	Do.

EPHEMERAL SPRINGS

1	Canyon north of Lizard Rock	8- 8-66	22.0	20	--	--	3.2	1.3	2.1	.4	6	--	11	3.2	--	0.4	45	65	5.83	7.3	Seep from alluvial material in bottom of canyon. Discharge estimated < 1 gpm.
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Map number (see fig. 1)	Location	Date of collection	Temperature (°C)	Silica (SiO ₂)	Iron (Fe)		Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Potassium (K)	Bicarbonate (HCO ₃)		Sulfate (SO ₄)	Chloride (Cl)	Fluoride (F)	Nitrate (NO ₃)	Dissolved solids (sum)	Specific conductance (micro-mhos at 25°C)	pH		Remarks
					Total dissolved	In solution at time of analysis					Field	Lab							Field	Lab	
16	Northeast of Girl Scout Camp	9-15-66	15.0	12	--	--	1.5	1.7	2.6	0.4	--	9	5.0	3.0	--	0.8	31	48	--	6.4	Seep from base of soil profile P-2. Soil saturated by 6.5 inches of rainfall during 4 days prior to sampling.
32	South of Spencer Peak	8-29-67	13.0	17	0.19	--	4.8	1.0	5.1	.8	17	16	7.0	2.0	0.2	--	46	52	5.58	6.8	Water issued from alluvial material in bottom of canyon. Discharge estimated < 0.5 gpm.
35	Northeast of Girl Scout Camp	10- 3-67	12.5	22	--	0.05	2.4	1.2	6.6	.9	18	20	5.0	2.0	.1	--	50	50	5.93	6.8	Water issued from thin alluvial material in canyon bottom. Discharge estimated < 0.5 gpm.

PERENNIAL SPRINGS

22	Rose Canyon upstream from Rose Canyon Lake	5-10-67	14.0	15	.61	--	3.6	1.7	4.8	.7	14	15	6.0	3.0	.0	--	42	48	6.00	6.6	Developed spring. Spring box is sealed and is on first terrace 1-2 feet above canyon bottom. Discharge could not be determined. Sufficient to supply Forest Service picnic area. Aluminum= 0.022 mg/l ₁ .
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See footnotes at end of table.

Map number (see fig. 1)	Location	Date of collection	Temperature (°C)	Silica (SiO ₂)	Iron (Fe)		Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Potassium (K)	Bicarbonate (HCO ₃)		Sulfate (SO ₄)	Chloride (Cl)	Fluoride (F)	Nitrate (NO ₃)	Dissolved solids (sum)	Specific conductance (micro-mhos at 25°C)	pH		Remarks
					Total dissolved	In solution at time of analysis					Field	Lab							Field	Lab	
31	Near head of Palisade Canyon, Girl Scout Spring	8-23-67	14.0	16	0.16	--	4.8	1.9	5.5	1.8	26	25	6.0	5.0	0.1	--	53	67	6.10	6.8	Water issued from alluvial deposits on upstream side of rock exposure in canyon bottom. On 8-23-67 discharge estimated 2-3 gpm. On 6-1-66 discharge measured 6 gpm. No continuous streamflow in canyon on either day. Aluminum=0.033 mg/l ¹ .
43	Southeast of Boy Scout Camp	11- 1-67	10.5	43	.02	--	4.4	.7	11	.6	34	36	2.0	3.5	.1	--	83	76	5.61	5.9	Orifice near the lip of canyon. Water may discharge from a set of prominent nearly vertical joints that strike N.10° W. Water piped from spring box to storage tank; discharge could not be measured. Estimated to be <1 gpm.
46	East of Boy Scout Camp	12-11-67	3.0	32	.22	--	2.8	.7	7.0	.5	20	20	3.0	2.5	.3	--	59	49	6.35	6.6	Seep is near lip of canyon at prominent slope break. Water issues from beneath massive pegmatite ledge; discharge < 1 gpm. Well-developed joints at seep strike N. 25° W. and dip 75° SW.

See footnotes at end of table.

Map number (see fig. 1)	Location	Date of collection	Temperature (°C)	Silica (SiO ₂)	Iron (Fe)		Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Potassium (K)	Bicarbonate (HCO ₃)		Sulfate (SO ₄)	Chloride (Cl)	Fluoride (F)	Nitrate (NO ₃)	Dissolved solids (sum)	Specific conductance (micro-mhos at 25°C)	pH		Remarks
					Total dissolved	In solution at time of analysis					Field	Lab							Field	Lab	
47	Bear Canyon, General Hitchcock picnic area, Horse Camp Spring	12-11-67	6.5	56	0.04	--	6.8	2.7	18	0.9	65	65	5.0	5.5	0.1	--	127	127	6.17	7.1	Spring box buried in bottom of canyon. Water piped to storage tank. Discharge measured at overflow: 12-11-67, 0.9 gpm; 6-9-69, 1.0 gpm.

^{1/} Sample for aluminum was filtered through 0.1 micron Millipore filter paper and acidified with HCl to dissolve any polymer aluminum. Pontachrome dye was added to form a fluorescing complex for quantitative determination.

APPENDIX D

DESCRIPTIONS OF SOIL PROFILES

Soil Profile P-1

Elevation: 8,055 feet

Exposure: West

Slope: 47 percent

Parent material: Muscovite-biotite gneiss

Great soil group: Zonal, Gray Brown Podzolic

<u>Field sample designa- tion</u>	<u>Soil horizon</u>	<u>Thickness in inches</u>		<u>Description</u>
		<u>From</u>	<u>To</u>	
a	O1-O2	1	0	Dark brown (10YR 3/3, moist) forest litter.
b	A1	0	2	Dark brown (10YR 3/3, moist) gravelly loamy sand; structure- less to weak subangular blocky; friable moist; slightly sticky slightly plastic; clear smooth boundary; thickness fairly uni- form; abundant fine roots, some up to 2 mm hold peds together; some rock fragments up to 20 mm; occasional layers of dark organic material.

Soil Profile P-1—Continued

<u>Field sample designa- tion</u>	<u>Soil horizon</u>	<u>Thickness in inches</u>		<u>Description</u>
		<u>From</u>	<u>To</u>	
c	A2	2	9	Brown (10YR 4/3, moist) gravelly loamy sand, but slightly more silt than above; structureless to weak medium to coarse subangular blocky; friable moist; slightly sticky slightly plastic; clear smooth boundary; fairly uniform thickness; abundant roots somewhat larger than above, some up to 5 mm; rock fragments up to 15 mm.
d	B2	9	17	Dark yellowish brown (10YR 4/4, moist) gravelly loam; weak fine subangular blocky; friable moist; slightly sticky slightly plastic; clear smooth boundary; fairly uniform thickness; fewer roots than above, but some up to 10 mm; rock fragments up to 6 cm, but are heavily weathered and can be broken easily by hand; slight suggestion of gneissic texture locally.
e	B3	17	27	Brownish yellow (10YR 6/6, moist) gravelly loamy sand; structureless medium to coarse subangular blocky; friable moist; slightly sticky slightly plastic; clear smooth boundary; fairly uniform thickness; less roots than above, some up to 3 mm; some rock fragments up to 10 mm; gneissic texture somewhat more evident.

Soil Profile P-1—Continued

<u>Field sample designa- tion</u>	<u>Soil horizon</u>	<u>Thickness in inches</u>		<u>Description</u>
		<u>From</u>	<u>To</u>	
f	C1	27	43	Very pale brown (10YR 7/4, moist) and locally reddish yellow (7.5YR 6/6, moist) gravelly sand; structureless medium to coarse subangular blocky; friable moist; slightly sticky slightly plastic; clear smooth boundary; fairly uniform thickness; a few roots in the upper part of this interval up to 2 mm; gneissic textures evident; reddish yellow segregations appear to be weathering rims that have formed on fragments or along joints and shears, segregations are absent in the interval above.
g	C2	43	67	Yellow (10YR 7/6, moist) muscovite-biotite gneiss grus with reddish yellow (7.5YR 7/8, moist) stains; rock is harder than above, but can be broken by hand.
h	R	--	67+	Light gray (10YR 7/2, moist) gneiss; relatively firm, must be broken with hammer.

Soil Profile P-2

Elevation: 7,770 feet

Exposure: North

Slope: 40 percent

Parent material: Muscovite-garnet gneiss

Great soil group: Zonal, Gray Brown Podzolic

<u>Field sample designa- tion</u>	<u>Soil horizon</u>	<u>Thickness in inches</u>		<u>Description</u>
		<u>From</u>	<u>To</u>	
a	O1-O2	1	0	Forest litter.
b	A1	0	2	Dark grayish brown (10YR 4/2, moist) loamy sand; fine subangular blocky; very friable moist; slightly sticky nonplastic; clear wavy boundary; abundant fine roots up to 1 mm; rock fragments up to 4 cm.
c	A2	2	4	Brown (10YR 5/3, moist) loamy sand; fine to medium subangular blocky; very friable moist; slightly sticky nonplastic; clear wavy boundary; roots less abundant than in horizon above; gneissic rock fragments up to 0.8 cm.
d	B2	4	13	Pale brown (10YR 6/3, moist) sandy loam; fine to medium subangular blocky; very friable moist; slightly sticky slightly plastic; clear wavy boundary; thickness fairly uniform; abundant fine roots from less than 1 mm to as large as 10 mm; no recognizable rock textures; muscovite flakes extremely abundant.

Soil Profile P-2—Continued

<u>Field sample designa- tion</u>	<u>Soil horizon</u>	<u>Thickness in inches</u>		<u>Description</u>
		<u>From</u>	<u>To</u>	
e	B3-C1	13	32	Very pale brown (10YR 7/3, moist) sand; fine to medium subangular blocky; very friable moist; slightly sticky slightly plastic; clear wavy boundary; some slightly less weathered fragments up to 10 cm are rimmed with strong brown iron oxide; textures of gneiss are faint in lower part.
f	R	--	32+	Very pale brown (10YR 8/3, moist) to white (10YR 8/1, moist) muscovite-garnet gneiss grus that crushes easily with fingers; structures and textures of gneiss are evident.

Soil Profile P-3

Elevation: 6,950 feet

Exposure: West

Slope: 5 percent

Parent material: Alluvial material derived from and
deposited on muscovite-biotite gneiss

Great soil group: Zonal, Gray Brown Podzolic

<u>Field sample designa- tion</u>	<u>Soil horizon</u>	<u>Thickness in inches</u>		<u>Description</u>
		<u>From</u>	<u>To</u>	
a	O1-O2	1	0	Forest litter.
b	A1	0	1	Very dark gray (10YR 3/1, moist) to very dark grayish-brown (10YR 3/2, moist) loamy sand; structureless thick platy; very friable moist; slightly sticky slightly plastic; abrupt wavy boundary; abundant fine roots, less than 1 mm diameter; dark coloring of organic matter in this interval is distinctive.
c	A2	1	3	Brown (10YR 5/3, moist) sandy loam; structureless medium sub-angular blocky; very friable moist; slightly sticky nonplastic; clear wavy boundary; abundant roots from less than 1 mm to 3 mm, some more than 15 mm; some rock fragments up to 5 cm.

Soil Profile P-3—Continued

<u>Field sample designa- tion</u>	<u>Soil horizon</u>	<u>Thickness in inches</u>		<u>Description</u>
		<u>From</u>	<u>To</u>	
d	B2	3	9	Pale brown (10YR 6/3, moist) sandy loam; structureless medium sub-angular blocky; friable moist; sticky slightly plastic; abrupt wavy boundary; roots less abundant than above, but generally from 2 to 5 mm; no rock textures evident.
e	B3-C1	9	21	Reddish yellow (7.5YR 6/6, moist) to strong brown (7.5YR 5/6, moist) sandy loam; structureless coarse subangular blocky; firm moist; sticky plastic; clear wavy boundary; decrease in number of roots, most less than 3 mm; quartz grains up to 5 mm are noticeable; rock textures are faint in very lowest part.
f	R	21	26+	White (10YR 8/1, moist) to dark brown (7.5YR 4/4, moist) muscovite-biotite gneiss grus; structures and textures evident; breaks easily by hand.

Soil Profile P-4

Elevation: 7,760 feet

Exposure: South

Slope: 40 percent

Parent material: Muscovite-garnet gneiss

Great soil group: Azonal, Lithosol

Profile about 90-95 percent rubble, of muscovite-garnet gneiss blocks up to 8 inches. Soil fills interstices and only approximate breaks could be made.

<u>Field sample designa- tion</u>	<u>Thickness in inches</u>		<u>Description</u>
	<u>From</u>	<u>To</u>	
a	0	1	Dark grayish brown (10YR 4/2, moist) gravelly loamy sand.
b	1	3	Grayish brown (10YR 5/2, moist) gravelly loamy sand.
c	3	9	Brown (10YR 5/3, moist) gravelly sandy loam.
d	9	14	Light gray (10YR 7/2, moist) gravelly loamy sand.

Soil Profile P-5

Elevation: 6,960 feet

Exposure: North

Slope: 15 percent

Parent material: Muscovite-garnet gneiss and pegmatite

Great soil group: Zonal, Western Brown Forest

<u>Field sample designa- tion</u>	<u>Soil horizon</u>	<u>Thickness in inches</u>		<u>Description</u>
		<u>From</u>	<u>To</u>	
	O1-O2	1	0	Forest litter.
a	A1	0	1	Very dark grayish brown (10YR 3/2, moist) gravelly loamy sand; thick platy; slightly hard dry; nonsticky nonplastic; abrupt smooth boundary; roots not abun- dant, most less than 1 mm.
b	A2-A3	1	2	Dark brown (10YR 3/3, moist) gravelly loamy sand; thick platy; slightly hard dry; nonsticky non- plastic; abrupt smooth boundary; roots not abundant and less than 1 mm; similar to horizon above, except lighter in color.
c	B1-C1	2	4	Brown (10YR 5/3, moist) gravelly loamy sand, but more silt than horizon above; medium subangular blocky; slightly hard dry; non- sticky nonplastic; abrupt smooth boundary; roots fairly abundant, some up to 5 mm.

Soil Profile P-5—Continued

<u>Field sample designa- tion</u>	<u>Soil horizon</u>	<u>Thickness in inches</u>		<u>Description</u>
		<u>From</u>	<u>To</u>	
d	C2-R	--	4+	Fractured muscovite-garnet gneiss and pegmatite; some fine material is in fractures in upper part; distinct sheeting joints, which are parallel to the surface, extend to about 2 feet below surface.

Soil Profile P-6

Elevation: 7,275 feet

Exposure: Northwest

Slope: 34 percent

Parent material: Muscovite-biotite gneiss

Great soil group: Zonal, Western Brown Forest

<u>Field sample designa- tion</u>	<u>Soil horizon</u>	<u>Thickness in inches</u>		<u>Description</u>
		<u>From</u>	<u>To</u>	
a	O1-O2	2	0	Forest litter.
b	A1	0	2	Very dark gray (10YR 3/1, moist) gravelly loamy sand; structureless very fine granular; loose dry; nonsticky nonplastic; abrupt smooth boundary; a few hairlike roots less than 1 mm.
c	A2-A3	2	5	Dark grayish brown (10YR 4/2, moist) gravelly loamy sand; structureless fine subangular blocky; loose dry; slightly sticky slightly plastic; clear smooth boundary; abundant roots 1-5 mm; abundant gravel and pebble fragments; hint of development of gray ashen layer, but not dominant.

Soil Profile P-6—Continued

<u>Field sample designa- tion</u>	<u>Soil horizon</u>	<u>Thickness in inches</u>		<u>Description</u>
		<u>From</u>	<u>To</u>	
d	B1-C1	5	13	Brown (10YR 5/3, moist) gravelly loamy sand; structureless fine granular where rock fragments are abundant to fine subangular blocky in pockets containing fewer rock fragments; loose dry; non-sticky nonplastic in coarser parts to slightly sticky slightly plastic where finer; clear smooth boundary; abundant roots 1-5 mm, some 10-20 mm; abundant iron oxide-coated rock fragments.
e	C2	--	13+	Very pale brown (10YR 8/3, moist) to yellowish brown (10YR 5/8, moist) crumbly muscovite-biotite gneiss grus; iron oxide layer at top.

Soil Profile P-7

Elevation: 7,720 feet

Exposure: South

Slope: 40 percent

Parent material: Muscovite-biotite gneiss

Great soil group: Zonal, Gray Brown Podzolic

<u>Field sample designa- tion</u>	<u>Soil horizon</u>	<u>Thickness in inches</u>		<u>Description</u>
		<u>From</u>	<u>To</u>	
	O1-O2	1	0	Forest litter.
a	A1	0	1	Dark grayish brown (10YR 4/2, moist) gravelly loamy sand; structureless to weak fine subangular blocky; soft dry; nonsticky nonplastic; abrupt smooth boundary; abundant fine roots less than 1 mm.
b	A2	1	2	Light brownish gray (10YR 6/2, moist) gravelly loamy sand; structureless fine subangular blocky; soft dry; nonsticky nonplastic; abrupt smooth boundary; abundant fine roots up to 1 mm.
c	B2	2	11	Pale brown (10YR 6/3, moist) loamy sand; structureless medium subangular blocky; soft dry; slightly sticky nonplastic; clear wavy boundary; abundant roots up to 7 cm; fragments of gneiss up to 8 cm.

Soil Profile P-7—Continued

<u>Field sample designa- tion</u>	<u>Soil horizon</u>	<u>Thickness in inches</u>		<u>Description</u>
		<u>From</u>	<u>To</u>	
d	B1-C1	11	26	Light yellowish brown (10YR 6/4, moist) loamy sand, possibly grus or a weathered boulder; material below more weathered.
e	B1-C1	26	36	Brownish yellow (10YR 6/6, moist) grus; loamy sand texture.
f	C2	--	36+	Light yellowish brown (10YR 6/4, moist) grus; more compact than horizon above; clay films evident.

Soil Profile P-8

Elevation: 7,030 feet

Exposure: South

Slope: 16 percent

Parent material: Muscovite-biotite gneiss

Great soil group: Zonal, Western Brown Forest

<u>Field sample designa- tion</u>	<u>Soil horizon</u>	<u>Thickness in inches</u>		<u>Description</u>
		<u>From</u>	<u>To</u>	
	O1-O2	1	0	Forest litter.
a	A1-A2	0	1	Very dark grayish brown (10YR 3/2, moist) gravelly loamy sand; weak medium to thick platy; soft dry; nonsticky nonplastic; abrupt wavy boundary; a few hair- like roots less than 1 mm.
b	B	1	4	Brown (10YR 4/3, moist) gravelly loamy sand; structureless to weak fine to medium subangular blocky; soft dry; slightly sticky non- plastic; clear smooth boundary; roots abundant, mainly less than 1-3 mm; rock fragments abundant, up to 8 cm.
c	C1	--	4+	Light yellowish brown (10YR 6/4, moist) muscovite-biotite gneiss grus; very crumbly near top; has hint of a strong brown iron oxide accumulation near top.
Most rock fragments in profile and on surface have yellowish brown to strong brown iron oxide coatings.				

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- EXPLANATION
- Muscovite-biotite gneiss
> 75 percent muscovite-biotite gneiss
< 25 percent muscovite-garnet gneiss
 - Transitional unit
75-25 percent muscovite-biotite gneiss
25-75 percent muscovite-garnet gneiss
 - Muscovite-garnet gneiss
< 25 percent muscovite-biotite gneiss
> 75 percent muscovite-garnet gneiss
 - Metasedimentary rocks
Mainly schist and quartzite
 - Alluvial deposits
Clay to boulders
 - Contact
Dashed where approximately located
 - Sampling site
 - W47
Spring
 - W11
Stream
 - P6
Soil profile
 - R53
Fresh rock
 - G14
Miscellaneous sample of soil, grus, or alluvial deposits

Base from U.S. Geological Survey

Geology by R. L. Laney, 1970

Figure 1.--Geology and location of sampling sites.

1 piece
in pocket

Eq. 21

E9791

1971

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