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Hydrothermal Alteration and Weathering

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ABSTRACT

A considerable group of minerals, including the clay minerals, zeolites, pyrophyllite, chlorite, alunite, vermiculite, certain carbonates, sulfates, and other minerals under special circumstances, may originate through the interaction of thermal fluids with rock masses. The fluids consisting of heated waters, water vapor under pressure, and frequently metallic ions originate well within the earth's crust as an aftermath of volcanism. The reaction halos, aureoles, disseminations, and bleached zones in which the products of hydrothermal alteration are found represent the locale of alteration. In the interpretation of the origin of mineral deposits alteration areas are frequently as significant as associated intrusives.

Alteration minerals form a group with unusual stability which exhibits a remarkable tendency toward convergence.

The effects of weathering and the minerals produced are often similar to the products of hydrothermal alteration insofar as the hydrous silicates are concerned. Temperature and chemical environment are equally important as controlling factors in supragenetic processes as under hypogene conditions.

The alteration effects may represent a single progressive epoch in a single rock type or may be due to different epochs embracing several types of wall rock. Alteration of younger igneous rocks may have a high argillic content, as in the Tertiary sequences of the western United States. On the other hand, alteration of old rock masses where regional metamorphism has been prevalent may yield a large content of chlorite of different types, hydromica, pyrophyllite, or serpentine. Both are more or less widespread hydrothermal effects in contrast to more local alteration such as zeolitization.

The fluids responsible for aggregates of hydrothermal minerals have long since vanished. However, through a gradual accumulation of evidence on mineral synthesis, microscopic study of sequence, observations on thermal springs and fumaroles, a much improved picture of the conditions prevalent during hydrothermal alteration is emerging.

The accumulation of field relationships becoming known through the studies of various observers places emphasis upon the relative role of wall rock in determining the nature and magnitude of alteration halos. Such factors as permeability, porosity, and conduits for fluid penetration assume an importance parallel to rock type. Essentially similar alteration aggregates may result from rocks as dissimilar as diorite and alaskite, while tremendous differences in the magnitude of the alteration halo may be noted between a porous tuff and a compact quartz monzonite even in the same district.

Halos of hydrothermal alteration are frequently a prelude to metallic mineralization. This has been particularly noted in connection with certain tungsten-bearing veins, disseminated porphyry copper deposits, certain lead-zinc deposits, some gold-bearing veins, and some uranium-bearing veins. In such deposits the metallic epoch is ordinarily closely associated with the culmination of hydrothermal activity.

The source solutions with H₂S, HCl, HF, steam, and other reagents may be neutralized or even rendered slightly alkaline by reaction with wall rock and release of alkali or alkaline earth elements. The temperatures under which the alteration takes place as interpreted from the minerals formed appear to lie in the range 100°-400° C with emphasis on the middle temperature zone.

Through the utilization of improved techniques in identification the fine mineral

aggregates of alteration halos are becoming better understood. The evidence of this study is contributing to a better understanding of the origin of associated minerals.

INTRODUCTION

The products of hydrothermal alteration as emplaced in the outer portions of the earth's crust are formed by a process which follows crystallization of igneous rocks or regional metamorphism. The resultant minerals are distinct from the early products of magmatic crystallization and are largely due to crystallization brought about by reactions between the final magmatic fluids and the enclosing rocks. In contrast to the total precipitation, the addition of elements from below is quantitatively important. Minerals which may originate during alteration include: clay minerals, zeolites, pyrophyllite, chlorite, alunite, sericite, vermiculite, certain carbonates, and sulfates. Deposits of these minerals may range from small scattered pockets to wide areas covering mountain slopes.

Alteration minerals may form under widely varying conditions; some are produced by the action of compressed water vapor at several hundred degrees of pressure and grade, whereas others occur during soil formation, weathering, or diagenesis. The transition from one extreme to the other is gradual, and the proper location of a given mineral on the geologic temperature scale is often difficult. Furthermore, the gradation is at times confusing since supergene clay aggregates formed under atmospheric conditions may grade into hypogene masses.

Gases, vapors, or solutions from below often force their way upward through the rocks of the earth's crust to produce deposits of clay minerals. These in turn are a part of the form halos associated with metallic mineralization. In this process the elements found in clay minerals themselves are derived largely from the invaded rocks, and little aside from water comes from below. Metallic mineralization is frequently localized, but it is also more dependent upon addition from below.

The temperatures prevailing at the time of hypogene clay crystallization probably range from less than 100°C to somewhat above 400°C. Since the solutions are influenced by acid vapors from the magma, the pH is frequently low. However, an increase in pH often results from reactions with invaded rocks, and neutral or alkaline conditions may develop.

Fumaroles, geysers, and volcanic vents may provide centers for the formation of clay and other forms of alteration in wall rock. The most active agents are gas emanations, compressed vapors, and thermal waters. The most abundant deposits of clay, tufa, or siliceous sinter are attributed to thermal waters either at depth or near the surface. Nevertheless, at times compressed vapors or mixed fluids and vapors may bring about argillic alteration of rock-forming minerals buried in cavities of pegmatite dikes or igneous masses.

Rock decomposition is not restricted to hydrothermal processes, but particularly at the surface or near the surface of the earth's crust it is often accomplished by weathering. Even here, temperature and pH as well as the abundance and composition of solutions become all-important factors.

Temperature and chemical conditions appear to be the most significant factors in

hydrothermal processes. Pressure is believed to be of minor importance near surface conditions. For example, the pressure gradient is surprisingly small in Miocene rocks at depths in excess of 15,000 feet. Like hydrothermal curves are comparatively shallow, but at much greater depths are employed to study alteration whether supergene or hypogene and are studied with difficulty by techniques as x-ray diffraction, differential thermal analysis, infrared absorption, in addition to mineralogical methods. Substantial progress has been made in the study of alteration minerals.

In the studies in which techniques are outlined in this paper the reader is referred to such works as those of Fenner (1953), and the reports of Research Committee on Hydrothermal Alteration (Fenner *et al.*, 1951).

DIRECT MEASUREMENT OF HYDROTHERMAL TEMPERATURES

Three types of data may be utilized to determine the formation of hydrothermal mineralization: (1) direct measurements of active hydrothermal areas; (2) indirect measurements of temperatures observed during mineralization; (3) thermometry of drill holes in the ground. The thermometry of drill holes in the ground was first reported by Fenner (1934) in his studies of the geothermal system of the Geysers Basin the temperature was 180°C at a depth of 100 feet and the temperature was 205°C at a depth of 200 feet.

At Larderello, in Italy, a major power plant is operated from steam derived from holes drilled in the ground. Fenner and Valduga (1946) report at a depth of 100 feet the pressure of 63.5 pounds per square inch. The temperature was 180°C (Mazzoni, 1948), and the distribution of the geothermal system.

Fenner *et al.* (1948) report that the temperature of the geothermal system at Geysers, Nevada, was 138°C.

Direct measurements at Kilauea Volcano, Hawaii, have been reported. Fenner (1953) reports that the temperature of boiling water at the surface was 100°C. Fenner (1953) in a study of hydrothermal alteration at Wairakei, New Zealand, reports temperatures of 100°C at 100 feet where adularia occurs. The solution is saturated with calcium and lime.

It would appear that the temperatures are generally lower than those which may prevail in fumaroles near the surface. The minerals found in localities of hydrothermal alteration of former hot-spring areas as at Mariposa, California, are of interest for observation. It seems likely that the temperatures

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DUCTION

ion as emplaced in the outer portions which follows crystallization of igneous minerals are distinct from the early stages largely due to crystallization brought about by fluids and the enclosing rocks. In the case of elements from below is quantitatively altered include: clay minerals, zeolites, vermiculite, certain carbonates, and sulfates from small scattered pockets to wide

widely varying conditions; some are formed by vapor at several hundred degrees, and the formation, weathering, or diagenesis of minerals is gradual, and the proper location on the scale is often difficult. Furthermore, the formation of supergene clay aggregates formed under conditions of bog masses.

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may provide centers for the formation of minerals in rock. The most active agents are geothermal waters. The most abundant deposits are related to thermal waters either at depth or at the surface. Vapors or mixed fluids and vapors are responsible for the formation of mineralizing minerals buried in cavities

hydrothermal processes, but particularly in the earth's crust it is often accomplished by the action of pH as well as the abundance and

appear to be the most significant factors

hydrothermal processes. Pressure is believed to be much less effective, particularly at near-surface conditions. For example, the amount of mineral change due to pressure is surprisingly small in Miocene clays from oil wells in southern Louisiana at depths in excess of 15,000 feet. Likewise, changes in x-ray-diffraction measurements or thermal curves are comparatively slight when artificial pressures corresponding to much greater depths are employed.

The products of alteration whether supergene or hypogene are for the most part finely crystalline and are studied with difficulty. However, through the application of such techniques as x-ray diffraction, differential-thermal analysis, electron microscopy, infrared absorption, in addition to more conventional microscopic and chemical methods, substantial progress has been made in recent years in the study of these materials.

For studies in which techniques are outlined in addition to much general information, the reader is referred to such works as those by Brindley (1951), Eitel (1952), and Kerr (1953), and the reports of Research Project 49, American Petroleum Institute (Kerr *et al.*, 1951).

DIRECT MEASUREMENT OF HYDROTHERMAL TEMPERATURES

Three types of data may be utilized to ascertain the temperatures prevailing during the formation of hydrothermal minerals: (1) thermometry of drill holes which penetrate active hydrothermal areas; (2) thermometry of surface emanations; and (3) temperatures observed during mineral synthesis.

The thermometry of drill holes in the geyser basins of Yellowstone Park was described by Fenner (1934) in his studies of hydrothermal metamorphism. At 265 feet in Norris Basin the temperature was 180°C, and in Upper Geyser Basin at 406 feet the temperature was 205°C.

At Larderello, in Italy, a major power development is maintained, and borax is produced from steam derived from holes drilled in a fumarole area (Ippolito, 1947). Fenner and Valduga (1946) report at a depth of 876 feet a temperature of 205°C and a pressure of 63.5 pounds per square inch. The general range in temperature is 140–200°C (Mazzoni, 1948), and the distribution is irregular, depending largely on the nature of the geothermal system.

Brannock *et al.* (1948) report that the temperature at 156 feet in a well at Steamboat Springs, Nevada, was 138°C.

In measurements at Kilauea Volcano, Hawaii, Macdonald (1944) reports that the fumarole had the temperature of boiling water (95.5°C) at that altitude.

Steiner (1953) in a study of hydrothermal alteration in the hot-spring and fumarole area at Wairakei, New Zealand, reports temperatures of 198°C to 213°C at a depth of 295 feet where adularia occurs. The solutions that leave this zone are enriched in silica and lime.

It would appear that the temperatures as measured in drill holes are considerably lower than those which may prevail in fumarole areas several thousand feet below the surface. The minerals found in localities where erosion has exposed deeper portions of former hot-spring areas as at Marysvale, Utah (Kerr *et al.*, 1952), confirm this observation. It seems likely that the temperatures in such hydrothermal areas

are considerably higher than those required to satisfy the thermal gradient. They may be properly attributed to remote magmatic activity.

The temperatures of hot springs or fumaroles cover a wider range than are recorded for drill holes. Zies and his associates (1924) carried on an elaborate program of such measurement in the Valley of Ten Thousand Smokes, Alaska, following the Katmai eruption in 1912. Gases escaping from fumaroles were found to range from less than 100°C to 650°C.

Temperature measurements were also made at Parícutin Volcano in Mexico (Zies (1946); values up to 640°C were observed for fumaroles in the older Zies flow.

The springs, geysers, and fumaroles of Iceland have been investigated by Zies (1950). Here superheated steam is rare, but it is found occasionally in hot lavas and around active craters. It has been reported from two hot springs with recorded temperatures of 118°C and 120°C. Other steam vents exhibit temperatures above the boiling point of water with slight but inconspicuous superheating.

Cone A in Okmok Caldera, on northeastern Sumnak Island, was examined by Byers and Brannock (1949). The temperatures dropped from 320°C on July 19 to 90°C on September 5 in 1946. More information on such geologically rapid changes is to be desired.

TEMPERATURES OF MINERAL SYNTHESIS

Direct measurement of temperature is inapplicable to the many areas of hydrothermal alteration which are of geologic interest and no longer thermally active. It is here that minerals such as kaolinite, dickite, nacrite, montmorillonite, halloysite, nontronite, illite, sericite, adularia, alunite, etc., become valuable indicators. In order to understand their genesis much work on mineral synthesis has been undertaken in a number of laboratories. While the extent to which these temperatures apply to field interpretation is often uncertain, in lieu of more direct data such temperatures cannot be ignored.

An alteration mineral frequently referred to is kaolinite. Noll (1934) reported that kaolinite was formed at 320°C in N/2 HCl. He also found (1936) that kaolinite forms in neutral alkali-free solutions or in acidic alkali-bearing solutions below 400°C. He concludes that under acid conditions kaolinite would form even below 200°C if given sufficient time.

Through the use of diluted hydrofluoric acid acting on orthoclase, Collins (1934) claimed that kaolinite formed in 96 hours at 16°C. While identification of the product should probably be verified by more recently developed techniques, the possibility of alteration at room temperature by strong acid is of interest.

Schwarz and Walcher (1925) stated that kaolinite must form between pH 4.5 and 5.2, with best results from a pH of 4.8 to 5.2. Schwarz (1933) produced kaolinite from feldspar by treating with 0.5N to 1.0N NH_4Cl or H_2SO_4 at 300°C for 250 hours.

The alteration of feldspars under laboratory conditions has been studied by Zies (1947). He found that kaolinite forms in acid solutions up to about 350°C when K is rather high and Al low. Muscovite forms as low as 200°C through 525°C in acid

solutions and, if K and Al are high, in neutral solutions at about 300°C and 550°C when Al and K are low. Zies and Insley (1935) synthesized kaolinite from albite. The temperature of direct synthesis was 300°C. The liberation of feldspar was observed.

Inference from experimental evidence, kaolinite may also form under supergene conditions given sufficient time. It may also form under pressure and temperature conditions in fumaroles. The hydration curve for kaolinite is above 400°C.

Montmorillonite, the clay mineral most representative of hydrothermal alteration (Zies, 1930), has been synthesized by E. J. Mott (1930) from silica gels at 350°C and 365°C. The presence of dickite is stable at higher temperatures. Dickite has been recognized by many as a hydrothermal mineral. The lowest temperature of formation to be 225°C (Gruner (1944), on the basis of numerical experiments. sericite) forms above 350°C, and nacrite was altered with HCl solutions at 300°C.

He found that pyrophyllite would form from albite in experiments. Norton (1937) demonstrated that kaolinite forms at 280°C and 1800 pounds per square inch. He also found that kaolinite forms at 100 pounds per square inch.

Adularia is a significant vein feldspar which has been synthesized by Morey and Ingerson (1937) synthesized from albite. Morey (1936) has formed adularia (or orthoclase) from albite in bombs in aqueous solutions of KHC_2O_4 and H_2SO_4 produced in 7 days at 300°C. After 10 days the albite and the feldspar became distinct. The strong acid solution was at 245°C. No change was detected in 4 days at 245°C.

Montmorillonite group is common in alteration zones. Montmorillonite using ratios of alkali:alumina:silica as 1:1:1 and $\text{Ca}(\text{OH})_2$ at 87 atmospheres and 300°C. He found that kaolinite forms from mixtures with alkali or alkaline earths. Montmorillonite is present in excess, magnesium is present in excess, magnesium is present in excess.

Alunite up to 15.3 per cent MgO . Norton (1937) charged water on albite at 275°C-325°C. He found that kaolinite from coprecipitated $\text{Fe}_2\text{O}_3 \cdot 2\text{SiO}_2$ gels. He found that kaolinite is at times associated with clay minerals.

Leonard (1927) formed 60-90 per cent alunite from albite which were heated for 7 days with 0.1 M solution of ammonium sulfate. Alunite (50-90 per cent) was formed for 100 days in 0.05 M solutions with ammonium sulfate. Alunite (50-90 per cent) was formed in 60 days.

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Studies cover a wider range than those of Noll (1924) carried on an elaborate apparatus at Thousand Smokes, Alaska, following which fumaroles were found to react with feldspar.

At Parícutin Volcano in Mexico, the alteration of feldspar for fumaroles in the older zone has been investigated by Noll (1934). It is found occasionally in hot lava flows and is derived from two hot springs with temperatures of 200°C. In fumaroles vents exhibit temperatures of 200°C and conspicuous superheating.

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GENERAL SYNTHESIS

Applied to the many areas of interest and no longer thermally active, such as nacrite, montmorillonite, kaolinite, etc., become valuable indicators of the extent to which these temperatures have been reached. In lieu of more direct data such as that of Noll (1934) on kaolinite.

Noll (1934) reported that kaolinite is also found (1936) that kaolinite would form even below 200°C in solutions of alkali-bearing solutions below 400°C.

Acting on orthoclase, Collins (1936) found that kaolinite is formed at 200°C. While identification of the mineral is of interest.

Kaolinite must form between pH 10 and 12. Schwarz (1933) produced kaolinite from orthoclase with H₂SO₄ at 300°C for 250 hours. The conditions has been studied by Noll (1934) in solutions up to about 350°C. At 200°C through 525°C in solutions of alkali-bearing solutions below 400°C.

Aluminous solutions and, if K and Al are high, in acid solutions. Pyrophyllite forms between about 300°C and 550°C when Al and K are both low.

Ewell and Insley (1935) synthesized kaolinite from alumina-silica gels in a bomb at 350°C. The temperature of direct synthesis thus falls within the range observed in the alteration of feldspar.

Inference from experimental evidence, kaolinite could form from the alteration of feldspar under supergene conditions given adequate time with acid conditions. The mineral may also form under pressure and at the lower temperatures which prevail in fumaroles. The hydration curve for kaolinite indicates that it is not likely to form above 400°C.

Dickite, the clay mineral most representative of hydrothermal conditions (Ross and Kerr, 1930), has been synthesized by Ewell and Insley (1935) from hydrous alumina-silica gels at 350°C and 365°C. The peaks on differential-thermal curves also indicate that dickite is stable at higher temperatures than kaolinite.

Sericite has been recognized by many as a hydrothermal mineral. Noll (1932) found the lowest temperature of formation to be 225°C, but the greatest amount formed at 300°C. Gruner (1944), on the basis of numerous experiments, concludes that muscovite (var. sericite) forms above 350°C, and kaolinite below. In his experiments feldspars were altered with HCl solutions at 300°C to 400°C and in one instance at 500°C. He found that pyrophyllite would form throughout the temperature range of his experiments. Norton (1937) demonstrated the formation of sericite by CO₂ in 180 days at 280°C and 1800 pounds per square inch, as well as in 150 days at 320°C and 2950 pounds per square inch.

Adularia is a significant vein feldspar which may form under hydrothermal conditions. Morey and Ingerson (1937) synthesized adularia between 245°C and 300°C. Gruner (1936) has formed adularia (or orthoclase) by heating montmorillonite in sealed bombs in aqueous solutions of KHCO₃ (10%). Well-crystallized adularia was produced in 7 days at 300°C. After 10 days at 272°C the x-ray-diffraction pattern of the feldspar became distinct. The stronger lines of orthoclase appeared after 7 days at 245°C. No change was detected in 4 weeks at 200°C.

The montmorillonite group is common in alteration halos. Noll (1936) synthesized montmorillonite using ratios of alkali:alumina:silica of 0.02:1:4 to 1:1:4 and NaOH, KOH, and Ca(OH)₂ at 87 atmospheres and 300°C. He concluded that montmorillonite forms from mixtures with alkali or alkaline earth metals when solutions are alkaline. When Mg(OH)₂ is present in excess, magnesium enters into the composition of montmorillonite up to 15.3 per cent MgO. Norton (1939) produced beidellite by the use of CO₂-charged water on albite at 275°C-325°C. Ewell and Insley (1935) produced kaolinite from coprecipitated Fe₂O₃·2SiO₂ gels in a bomb at 350°C.

Alunite is at times associated with clay minerals and forms under hydrothermal conditions. Leonard (1927) formed 60-90 per cent alunite at 200°C in sealed pyrex bombs which were heated for 7 days with 0.1 M solutions of H₂SO₄, K₂SO₄, and Na₂SO₄ together with ammonium sulfate. Alunite (50-99 per cent) was also formed at 100°C by heating for 100 days in 0.05 M solutions with 50 gm of aluminum sulfate. Similar solutions gave 40-60 per cent alunite in 60 days at 22°C.

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 lar solutions gave 40-60 per cent alunite in 60 days at 22°C.

Noll (1936) reports that the same type of experiment in which montmorillonite was synthesized also produced analcite with an excess of NaOH, Ca(OH)₂, and Mg. Noll believes that zeolites will form under more alkaline conditions than montmorillonite or sericite.

Stringham (1952) has furnished a tabulation which outlines the generally accepted temperature ranges of formation of the more common hydrothermal minerals. To a large degree these represent a summary of observations on synthesis by various authors.

GASEOUS EMANATIONS CAUSING ALTERATION

Steam and minor amounts of acid are the vapors from fumaroles, fissure eruptions, or hot springs. Zies (1929) found that the vapors of the Valley of Ten Thousand Smokes contain the acid constituents HCl—0.117%; H₂S—0.029%; and SO₂—0.032%. The fumarole gases on northeastern Umnak Island were identified by Brannock and Brannock (1949) as water vapor, carbon dioxide, and sulfur dioxide. The same authors found that the springs on Umnak Island contain as high as 159 ppm boron expressed as B₂O₃ with a few parts per million of arsenic and antimony. Shepherd and Merwin (1927) studied the residual gases in the freshly erupted lavas of Mt. Pelee. The samples were heated *in vacuo*, the chief volatiles being H₂O—90%; CO₂—9%; with Cl, S, and F in smaller amounts.

Mazzoni (1948) in his account of steam vents of Tuscany and the Larderello region furnishes the average composition (in gm) of 1 kg of natural steam as follows:

Steam, H ₂ O	955.29
Carbon dioxide, CO ₂	41.88
Combustible gas, (CH ₄ , H ₂)	1.10
Hydrogen sulfide, H ₂ S	0.92
Nitrogen, N ₂	0.30
Boric acid, H ₃ BO ₃	0.35
Ammonia, NH ₃	0.19
Rare gases, (He, Ar, Ne)	1.00

He also gives the average speed of flowing steam as 410 ft/sec.

Many cavities in pegmatite dikes or within intrusive masses contain alteration minerals. The fluids present are presumed to have formed under considerable pressure. Silva and Neiva (1948) attribute montmorillonite in granite pegmatites to hydrothermal conditions. Cymatolite at Branchville, Connecticut, first recognized by Brush and Dana (1880), is a pink claylike alteration closely related to montmorillonite. Apparently it resulted from an early stage of alteration when high pressure prevailed. Clay minerals that coat crystals in pegmatitic cavities are fairly common.

DEEP-SEATED VEINS

Field relationships suggest that among the clay minerals dickite is usually formed under deeper-seated conditions. It is usually, if not always, hydrothermal in origin. At Cerro de Pasco, Peru, coarse crystals of enargite formed in vugs are associated with granular dickite. The veins at Ouray, Colorado, contain dickite associated with primary sulfides. The original dickite of Anglesey (Ross and Kerr, 1930) is considered to be hydrothermal. Sales and Meyer (1949), in describing the hydrothermal alteration along the veins at Butte, Montana, place dickite in the higher-temperature

HYDROTHERMAL ALTERATION

attention to the occurrence of the mineral. It has been reported by Frankel (1949) that dickite is found associated with pyrrhotite, gray clay, and lustrous organic material of hydrothermal origin on the basis of association studies of the volcanic region at Matanzas, Cuba. The earlier phases of hydrothermal alteration are well above the ore bodies at Gilman, Colorado, a temperature clay-mineral phase. Dickite, as a mineral, yields the most precise x-ray diffraction pattern of mineral structure.

It has been reported from too few localities to be a good indicator mineral. However, the mineral has been reported from George, Utah (Kerr *et al.*, 1951), and from the well-known occurrence at Brand, S. D.

HYDROTHERMAL MINERALIZATION

In recent years great emphasis has been placed on the economic mineralization. Considerable work has been done at Tintic, Utah, by Lovering (1949); at Castle Dome, Arizona, by Peterson, and at Bingham, Utah, by O'Neill; Bingham, Utah, by Sales and Williams (1952). These studies as well as others in various regions of late Mesozoic or Tertiary volcanic areas of the United States. They are based to a considerable extent on field relationships. More recently, close studies of the District by Price (1953) has shown the importance of deep-seated mineralization. It is now recognized that zinc, lead, copper, gold, and uranium mineralization is commonly associated with hydrothermally altered, which in turn is related to the presence of the most common features observed in the field. These are associated with mineral deposits are the alteration of and dolomitization of carbonate rocks. This is well illustrated by Lovering *et al.*, 1949). At Silver Bell, Arizona, and at Cerro de Pasco (Kerr *et al.*, 1950), chlorite marks the transition from

to dickite (Kerr, 1954) in a study of the relationship between hydrothermal alteration at Santa Rita, New Mexico. The mineralization is directly related to an end stage of alteration of the altered intrusive associated with the mineralization. The content increases considerably at this stage. Sales and Meyer (1949) found montmorillonite associated with hydrothermal alteration at Butte, Montana. The mineralization of solutions and vapors from the hydrothermal system reviewed through the courtesy of the New

of experiment in which montmorillonite was formed in the presence of an excess of NaOH, Ca(OH)₂, and Mg(OH)₂. Under more alkaline conditions than those used in the experiment, a clay mineral was formed which outlines the generally accepted composition of the more common hydrothermal mineral. The observations on synthesis by various authors are summarized in Table 1.

FACTORS CAUSING ALTERATION

The vapors from fumaroles, fissure vents, and geysers at the Valley of Ten Thousand Smokes, Utah, and at Umnak Island were identified by Davidson and Bowie (1951) as carbon dioxide, and sulfur dioxide. The vapors from Umnak Island contain as high as 159 parts per million of arsenic and antimony. The residual gases in the freshly erupted fumaroles at Vulcano, the chief volatiles being H₂O, CO₂, and H₂S.

The vapors from the vents of Tuscany and the Larderello, Italy, contain 1 kg of natural steam as follows:

.....	955.29
.....	41.85
.....	1.10
.....	0.92
.....	0.30
.....	0.35
.....	0.19
.....	1.00

... steam as 410 ft/sec. Within intrusive masses contain alteration zones which are thought to have formed under considerable pressure. Montmorillonite in granite pegmatites at Danbury, Connecticut, first recognized by Davidson and Bowie (1951), is an alteration closely related to montmorillonite. The early stage of alteration when high pressure is present in pegmatitic cavities are fairly common.

ALTERED VEINS

The clay mineral dickite is usually found in veins, if not always, hydrothermal veins. Enargite formed in vugs are common in veins at Leadville, Colorado, contain dickite associated with enargite. The study by Ross and Kerr (1930) is cited by Davidson and Bowie (1951), in describing the hydrothermal alteration of veins. The dickite in the higher-temperature veins is associated with enargite.

... all attention to the occurrence of the mineral in the lowest levels of the mines. The mineral has been reported by Frankel (1949) in the gold-bearing rocks of the Witwatersrand. It is found associated with pyrrhotite, gersdorffite, chloritic material, a black-gray clay, and lustrous organic material. Davidson and Bowie (1951) favor a hydrothermal origin on the basis of association with the organic material thucholite. Recent studies of the volcanic region at Marysvale, Utah, dickite has been identified with the earlier phases of hydrothermal alteration. In the alteration of the dioritic sill above the ore bodies at Gilman, Colorado, dickite appears to represent a higher-temperature clay-mineral phase. Dickite forms the best crystals of all the clay minerals, yields the most precise x-ray reflections, and appears to have the most regular internal structure.

Dickite has been reported from too few localities to compare with dickite as a hydrothermal indicator mineral. However, the mineral occurs intergrown with dickite at St. George, Utah (Kerr *et al.*, 1951), and is presumably of similar hydrothermal origin. The well-known occurrence at Brand, Saxony, is also hydrothermal.

HYDROTHERMAL DEPOSITS

In recent years great emphasis has been placed on the relationship of alteration to economic mineralization. Considerable data have accumulated through studies at Tintic, Utah, by Lovering (1949); Butte, Montana, by Sales and Meyer (1949); Castle Dome, Arizona, by Peterson, Gilbert, and Quick (1946); Gilman, Colorado, by O'Neill; Bingham, Utah, by Stringham (1953); and at Park City, Utah, by Williams (1952). These studies as well as similar others are largely confined to regions of late Mesozoic or Tertiary volcanism in the western Cordillera of the United States. They are based to a considerable degree upon the observation of mineral relationships. More recently, close attention to chloritic zones in the Grand District by Price (1953) has shown the applicability of alteration studies to Cambrian mineralization. It is now recognized that deposits of tungsten, molybdenum, zinc, lead, copper, gold, and uranium may occur where the wall rock has been hydrothermally altered, which in turn is related to mineralization.

Two of the most common features observed in the early stages of hydrothermal alteration associated with mineral deposits are the development of chloritization in intrusives and dolomitization of carbonate rocks. Both have been described at Tintic, Utah (Lovering *et al.*, 1949). At Silver Bell, Arizona (Kerr, 1951), and at Santa Rita, New Mexico (Kerr *et al.*, 1950), chlorite marks the earliest phase of alteration of the intrusive.

Le Roy (1954) in a study of the relationship between copper mineralization and hydrothermal alteration at Santa Rita, New Mexico, concludes that the hypogene copper mineralization is directly related to an end stage of argillic alteration. Chemical analyses of the altered intrusive associated with the mineralization show that the sulfur content increases considerably at this stage.

Sales and Meyer (1949) found montmorillonite as one of the earliest indications of hydrothermal alteration at Butte, Montana. The margin of alteration outlines the latest penetration of solutions and vapors from fissures into the wall rock. At this

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point the alkali and alkali-earth ingredients of the wall rock react more strongly with acidic fluids from the magma, and there is a tendency to produce neutral or slightly alkaline conditions.

Sales and Meyer (1949) have carefully sampled and reported analyses for the alteration sequence along the Butte veins. An outer montmorillonite zone is bordered within by a hydromica (illite) zone of slightly lower pH. On the vein side of this zone kaolinite becomes the dominant mineral. The zone closest to the vein is predominantly sericite.

In the zones of alteration which border veins the mineral constituents observed indicate an increase in temperature toward the center. There is also a variation of pH from slightly alkaline along the periphery to neutral, slightly acid, or slightly alkaline toward the center. The processes of metallic mineralization are influenced by the chemical and physical conditions which also control the zones of alteration.

Stringham (1953) has carried on an extended study of the hydrothermal alteration at Bingham, Utah. Here the alteration halo and the ore zone are closely similar. The suite of alteration minerals is essentially the same as may be observed in other porphyry copper deposits of the region.

In the Coeur d'Alene district, however, Mitcham (1952) reports that hydrothermal bleaching of large areas of country rock is largely the destruction of rock pigments, and no strong sericitization is involved.

Field studies in the Marysvale district, Utah, have demonstrated that montmorillonite and hydromica (illite) may be formed by hydrothermal alteration of glass in volcanic dikes. The transition from glass to clay may be quite sharp. In the vicinity of Lovelock, Nevada, masses of volcanic glass may be observed altered by hydrothermal solutions to montmorillonite.

The susceptibility of various rock types to hydrothermal alteration and the resultant products constitute a feature of considerable complexity. At Marysvale, Utah, recent studies have shown that of the rock types observed volcanic ash and tuff are the most susceptible to alteration. In the same area a fine-textured aplitic granite is the least altered of the igneous rock types. Quartz monzonite is not highly altered in contrast to the tuff or even granular flow rocks, but the emplacement of uranium mineralization has been heaviest in this rock. Sediments found in the district consist of limestones, shales, conglomerate, and quartzitic sandstone, chiefly upper Paleozoic and Mesozoic. Aside from the limestones these show comparatively little hydrothermal alteration in contrast to the igneous rocks. The latter show alteration along fractures to light-gray chlorite (Kerr *et al.*, 1953).

Burbank (1950) in a study of alteration in Colorado mining districts concludes that clay alteration and silicification are characteristic of a comparatively shallow environment in volcanic rocks extending to somewhat more than a mile below the original surface. In the zone of alteration the altering solutions are dominated by leaching agents. Voids occur at higher levels but diminish abruptly with depth. In the tighter zone below, sericite and quartz predominate as alteration products. Above hydrothermal clays and voids are a characteristic feature.

Schwartz (1950), in studying alteration of limestone bordering ore bodies at Silver Lake, Arizona, found that a large amount of manganese as well as lesser amounts of

and probably magnesia had been present. The histories are available generally for hydrothermal solutions in contact with limestone. One of the most significant features observed is the sequence of clay mineralization which through such a sequence as montmorillonite is now looked upon as a characteristic feature. An occurrence of palygorskite, believed to be a granite owing to the action of hydrothermal solutions (Stephen (1954). This high-magnesian alteration under supergene conditions may also

HYDROTHERMAL

Although the magmatic source material, HF, and H₂S, contact with granite under alkaline conditions. The character of the wall rock penetrated and the alteration sequence. Acceleration of alteration due to hydrothermal solutions (1946) in volcanic regions. Two examples are given in Hawaii. At steam vents where the pH is slightly acidic, and alkali and alkaline-earth elements are present. At vents where sulfur dioxide is present, leaving hydrated oxides of aluminum and iron. Macdonald (1944) has described a sequence of carbonic, sulfurous, and sulfuric acid alteration. Also cavities may be lined with opsum, alum, mirabilite, kieserite, and other minerals. In studying the geyser basins and fields (1955) felt that the bicarbonates of sodium and potassium upon the wall rocks at depth. In the study of (1936) found two processes causing alteration: (1) leaching of the feldspars, and kaolin was formed. Steiner (1953) reports that hydrothermal alteration in New Zealand, have altered and are characterized by (1) not the interbedded argillaceous rocks, (2) hydrothermal alteration observed in the study of (1955) (1) silicification, (2) zeolitization, and (3) (4) alteration near the surface, in the zone of alteration. Adularia and pyrite are characteristic hydrothermal alteration products. Zeolites present. Adularia forms in the study of (1949) has pointed out that the alteration zone may yield a quartz-alunite zone. In the study of (1949) near the surface alunite would give rise to the study of (1949) at Tintic, Utah, Lovering (1949)

the wall rock react more strongly
tendency to produce neutral or slightly

and reported analyses for the
montmorillonite zone is bordered
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zone closest to the vein is predom-

the mineral constituents observed
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hydrothermal alteration and the result
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area a fine-textured aplitic granite
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rocks, but the emplacement of uranium
Sediments found in the district of
quartzitic sandstone, chiefly of
zones these show comparatively
ous rocks. The latter show alteration
Z., 1953).

Colorado mining districts conclude
characteristic of a comparatively shallow
somewhat more than a mile below
the altering solutions are dominated
that diminish abruptly with depth
dominate as alteration products. A
characteristic feature.

granite bordering ore bodies at
manganese as well as lesser amounts

and probably magnesia had been added from invading solutions. Until more
histories are available general conclusions concerning the additive effect of
hydrothermal solutions in contact with wall rock will be open to question.

One of the most significant features of hydrothermal veins now coming to be recog-
nized is the sequence of clay minerals. The progressive alteration from fresh wall
rock through such a sequence as montmorillonite, illite, kaolinite, sericite, and dickite
is now looked upon as a characteristic feature of many hydrothermal veins.

An occurrence of palygorskite, believed to have formed along a zone of shearing in
granite owing to the action of hydrothermal solutions, has recently been described
by Stephen (1954). This high-magnesia clay mineral formerly recognized to form
under supergene conditions may also originate because of hydrothermal action.

HYDROTHERMAL SOLUTIONS

Although the magmatic source may consist of vapors rich in acid vapors such as
HCl, HF, and H₂S, contact with ground water and wall rocks may produce neutral
or alkaline conditions. The character of the solutions may be inferred at times from
the wall rock penetrated and the alteration minerals produced.

Acceleration of alteration due to acid solutions has been noted by Payne and
Mau (1946) in volcanic regions. Two types were observed in basalt around Kilauea
water in Hawaii. At steam vents where sulfur dioxide is present, alteration proceeds
rapidly, and alkali and alkaline-earth elements are removed, leaving a siliceous yellow
residue. At vents where sulfur dioxide is absent silica and soluble bases are leached
away, leaving hydrated oxides of aluminum and iron.

Macdonald (1944) has described the action of solutions believed to be weak in
carbonic, sulfurous, and sulfuric acids. Opal and a smaller amount of kaolinite are
developed. Also cavities may be lined with sulfur crystals, and minerals such as
gypsum, alum, mirabilite, kieserite, apthitalite, and epsomite may be deposited.

In studying the geyser basins and igneous emanations of Yellowstone Park, Allen
(1935) felt that the bicarbonates of alkalis in the thermal waters indicated attack by
CO₂ upon the wall rocks at depth. In other studies at Yellowstone Park, Fenner
(1936) found two processes causing alteration to clay. Near the surface acid sulfate
attacked the feldspars, and kaolin was formed. At depth, beidellite was produced.

Steiner (1953) reports that hydrothermal agents in the thermal area at Wairakei,
New Zealand, have altered and are still altering tuffaceous and arenaceous rocks,
but not the interbedded argillaceous rocks, which are impervious. Four main zones
of hydrothermal alteration observed downward are: (1) sulfuric acid leaching, (2)
zeolitization, (3) zeolitization, and (4) feldspathization. Kaolinite, alunite, and opal
occur near the surface, in the zone of sulfuric acid leaching. Montmorillonitelike
clay and pyrite are characteristic hydrothermal minerals. Ptilolite and analcite are
the zeolites present. Adularia forms in the zone of feldspathization.

Lovering (1949) has pointed out that sulfur acids on the outlet side of an altera-
tion zone may yield a quartz-alunite rock, while at greater distance from the outlet
the nearer the surface alunite would give way to diaspore. This feature was observed
by Whitman Cross (1896) in the alteration of rhyolite on Mount Robinson, Colorado.
At East Tintic, Utah, Lovering (1949) concludes that alunite is formed in a less acid

environment than the kaolin minerals, because of an increase in pH through wall-rock influence.

Lovering (1950) has also pointed out that the solubility of silica in pure water increases from about 275 ppm at 50°C to some 2400 ppm at 350°C. The solubility in NaOH and Na₂CO₃, however, is much greater, although the increase in solubility due to acids depends on prevailing conditions. He concludes that the great change in solubility with temperature probably accounts for much of the precipitation of hydrothermal silica.

The formation of halloysite by sulfate-bearing solutions acting on kaolinitic clay has been postulated by Ross and Kerr (1934). Vapors containing SO₂, S vapor, and a trace of HCl in solfataric action have formed kaolinite (Macdonald, 1944).

At Park City, Utah, Williams (1952) points out that kaolinite results from acid solutions in siliceous or argillaceous-siliceous wall rocks, while in the overlying carbonate rocks halloysite is formed.

Localities such as Liège, Belgium, Tintic, Utah, and Park City, Utah, may represent the precipitation of halloysite due to acid solutions acting on carbonate rock.

It was pointed out by Nutting (1945) that minerals of the montmorillonite group as found in soils will dissolve or disperse in water solutions containing 0.01 to 0.04 per cent acid.

SUPERGENE PROCESSES

In the absence of special conditions which may accelerate the process of weathering, normal surficial clay-mineral development or the development of related mineral aggregates may require a long time. The chemistry involved is complex and not too well understood, but it is generally believed that if given sufficient time even weak concentrations of acid or alkali solutions in the presence of small amounts of alkali or alkaline-earth elements, alumina, silica, and other chemical constituents may weather to large masses of clay and other deposits.

Special climatic conditions may yield increases in temperature which combined with the introduction of solutions giving a more concentrated chemical action may decrease the time factor.

Diagenesis may be a factor in surficial mineral changes where saline conditions prevail in bodies of water where sediments are accumulating. Organic acids may play an important role in hot humid regions. Even organic concentrations in bogs are active in clay formation although temperatures are not extreme.

The transportation and redeposition of the clay minerals in a new site may be considered a simple process. On the other hand, considerable alteration of the minerals involved is apt to occur during the process.

NORMAL SURFACE ACTION

In normal surface action leaching and deposition may be distinguished from weathering and soil formation.

The formation of bentonite illustrates a process in which supergene leaching and deposition are involved. Bentonite as defined by Ross and Shannon (1926) is formed by the alteration of glassy igneous material, usually tuff or volcanic ash. The bentonite deposits of the lower Mississippian occur in a stratigraphic sequence altered under other than supergene conditions by montmorillonite at Pontotoc, Mississippi. It indicates that alumino-silicate sols may remove the original bases in the areas in which volcanic materials are present in clays derived directly from volcanic clays are low in available aluminum. Bentonite clays derived from leaching aluminous clays.

Foster (1953) has studied the swelling of bentonite with octahedral substitution. A montmorillonite substitution has a lower swelling volume. The greater swelling of Na-montmorillonite is explained by the greater dissociation of the number of structural units are left over.

Weaver (1953) in a study of bentonite formed originally as an expanded lattice of montmorillonite but later adsorbed water to form a nonexpanded lattice corresponding to place under supergene conditions in a transformation *in situ*.

Attapulgite (polygorskite) is the most abundant in large quantities in the Georgia-Florida region. Accumulations are believed to have been formed in the highlands. It may be suggested that it represents more than simple transport of clays that waters containing magnesium and magnesia-rich clay.

Foshag and Woodford (1936) have reported bentonite formed by the alteration of Tertiary igneous rocks in Georgia. Presumably the alteration is supergene.

Tarr and Keller (1936) report kaolinite in Missouri.

Kaolinite occurs in quartz geodes at Keokuk, Iowa.

A clay mineral from Ballater, Aberdeen, Scotland, described by MacKenzie (1949) as formed in a altered vein in granite. Since the extent of alteration determined the distinction between supergene and hydrothermal.

Stringham and Taylor (1950) have reported a product of diopside, tremolite, and pyroxene inclusions. The mineral occurs in a contact zone. Halloysite (4H₂O) from Bedford, Massachusetts.

ate deposits of the lower Mississippi Valley and Gulf Coast region (Hagner, 1939) occur in a stratigraphic sequence in which it seems unlikely that ash would have formed under other than supergene conditions. The complete replacement of shells by montmorillonite at Pontotoc, Mississippi, as pointed out by Nutting (1945) indicates that aluminosilicate sols may be deposited under conditions that suffice to remove the original bases in the shell-forming material. In certain Pacific Coast areas in which volcanic materials predominate, Allen (1944) emphasizes the importance of sedimentary processes in the formation of clay minerals. Montmorillonite is present in clays derived directly from volcanic materials. For the most part these clays are low in available alumina. However, kaolinite is a dominant mineral in clays derived from leaching aluminous rocks under conditions of thorough drainage.

Foster (1953) has studied the swelling of montmorillonite and finds that it correlates with octahedral substitution. A montmorillonite with a high degree of octahedral substitution has a lower swelling volume than one with a low degree of substitution. The greater swelling of Na-montmorillonite in contrast to Ca-montmorillonite is explained by the greater dissociation of Na-montmorillonite by which a greater number of structural units are left with a negative charge.

Weaver (1953) in a study of Ordovician K-bentonites concludes that the clay formed originally as an expanded 2:1 layered mineral probably corresponding to montmorillonite but later adsorbed potassium which caused 80 per cent of the layers to form a nonexpanded lattice corresponding to illite. Such changes shown to take place under supergene conditions indicate the susceptibility of montmorillonite to transformation *in situ*.

Attapulgite (polygorskite) is the chief mineral constituent of fuller's earth found in large quantities in the Georgia-Florida area (Kerr, 1937). The sedimentary accumulations are believed to have been transported from areas of crystalline rocks in the highlands. It may be suggested, however, that the accumulation of attapulgite represents more than simple transport and deposition. It is reasonable to believe that waters containing magnesium contributed to the formation of this unusual magnesia-rich clay.

Foshag and Woodford (1936) have described the magnesian clay mineral hectorite formed by the alteration of Tertiary volcanic rocks in the Mojave Desert of California. Presumably the alteration is supergene.

Tarr and Keller (1936) report kaolinite deposited from solution in several localities in Missouri.

Kaolinite occurs in quartz geodes and in small solution cavities in limestone near Keokuk, Iowa.

A clay mineral from Ballater, Aberdeenshire, somewhat related to illite has been described by MacKenzie (1949) as formed by supergene action. The clay occurs in an altered vein in granite. Since the extent of the alteration in depth has not been determined the distinction between supergene and hypogene origin is uncertain.

Stringham and Taylor (1950) have described nontronite formed as a weathering product of diopside, tremolite, and pyrophyllite owing to the action of slightly acid solutions. The mineral occurs in a contact zone at Bingham, Utah.

Halloysite ($4H_2O$) from Bedford, Indiana, is believed by Callaghan (1948) to

represent a supergene reorganization. A former residual soil is represented by other clay types.

Kaolinite derived from limestone by supergene processes has been described by Allen (1937). An earthy limestone subjected to the action of carbonic acid waters is considered to have given rise to the Cheltenham clay of Missouri. The sedimentary clay deposit has been formed by erosion into a closed basin or choked sink hole.

Presumably nontronite found in cracks or fissures and in spaces between polygonal joints in basalt near Garfield and Manito, Washington (Kerr *et al.*, 1951), has been formed by the action of solutions of a neutral or slightly alkaline character, at normal temperature and under supergene conditions.

Hole (1951) has described the surface decomposition of limestone with the formation of residual clays in the Austinville area, Virginia. Owing to the erosional remnants remaining *in situ* in the sedimentary series and the surficial character of the clay deposits the accumulation is believed to be essentially supergene.

An unusual deposit of kaolinite was encountered during the construction of a subway tunnel beneath Newtown Creek, Brooklyn (Kerr, 1930). The clay mineral, along with vermiculite as an intermediate stage, has been derived from the decomposition of Ravenswood granodiorite. Apparently the occurrence represents an old bog deposit in which organic acids played an important role.

WEATHERING

Surface temperatures, rainfall, and drainage as well as rock type are important factors in weathering and soil formation. Probably surface temperature is highly significant.

In cold zones or areas of glacial action clay minerals commonly formed elsewhere by weathering are sparsely produced. Allen (1947) in studying varved clays deposited under conditions of Pleistocene glaciation along the Hudson Valley at Newburgh, New York, found a relatively small clay-mineral content; the varves were composed largely of rock flour. The same feature has been reported elsewhere by various investigators.

Under tropical or semitropical conditions, as at Fazenda Pacu, Brazil, Kerr (1942) has called attention to deep weathering *in situ* in the wall rock of quartz-crystal deposits. Such weathering may produce kaolinitic masses which extend for hundreds of feet in depth. At Fazenda Pacu the original texture of the granite is preserved in the clay.

The weathered products of granites and pegmatites in the southern Appalachian region have been studied by Sand and Bates (1952). Halloysite is formed only from the weathering of feldspars under conditions of intense leaching. Original mica alters to vermicular kaolinite. Where leaching is less intense, potash feldspars may yield vermicular kaolinite with an intermediate stage of secondary mica. Halloysite, however, appears to form directly from plagioclase.

It seems to be generally agreed that, given abundant time, decomposition of rocks by the action of normal surface waters results. Water in soil may occur in cavities and capillaries, as hygroscopically combined water, as adhering water, as chemically combined water, and as water vapor. Constant additions and subtractions change

the total water content of a soil. The soils Mohr (1944) reports a range from even quartz, which is resistant in acid than 7.5. In the tropics acid water is Mohr concludes that pure water, or water would cause the weathering of feldspar conditions where alkali or OH ions pre

Correns and Engelhardt (1938) have of potash feldspar. With an abundance clay may occur in soil in the case of not ordinarily considered particularly

The ion-exchange characteristics of extensively studied by Kelley (1939) permeability; calcium-saturated clays while sodium clays are highly dispersed may be influenced in a significant manner free from calcium carbonate, are approximately sodium clays may be highly alk

Kelley points out that, although sodium abundance than magnesium, the magnesium sediments with which it comes in contact marine origin contain substantial amounts

Kelley also notes that ordinary water ions, while rain water is commonly acidic clays the hydrogen ions that have strong with the consequent formation of dilute carbonate, or sodium hydroxide. Thus the

The clay minerals in Illinois sediments in an attempt to interpret climatic conditions both kaolinite and illite has been interpreted had a warm climate and in other parts

Hosking (1940) has compared Australian parent material. In several soils of granitic In soils of basaltic origin, however, the types tions during weathering. Kaolinitic type morillonitic types prevail in the red-brown of the black earths.

MECHANICAL

A number of sedimentary basins on v remarkably similar clay-mineral assembla climate products exists which is in some stages observed in hydrothermal alteration the two cases differ.

Recent studies of clays in the Mississipi

residual soil is represented by

These processes have been described by the action of carbonic acid water on the kaolinite clay of Missouri. The sedimentary clays in a closed basin or choked sink hole are found in fissures and in spaces between rocks in Washington (Kerr *et al.*, 1951). The soil is neutral or slightly alkaline character under these conditions.

The decomposition of limestone with the formation of kaolinite in Virginia. Owing to the erosional features and the surficial character of the soil, it is essentially supergene.

Formed during the construction of a soil in the Hudson Valley (Kerr, 1930). The clay mineral, kaolinite, has been derived from the decomposition of primary minerals. The occurrence represents an important role.

ING

As well as rock type are important factors, probably surface temperature is high.

Minerals commonly formed elsewhere (Kerr, 1947) in studying varved clays deposited along the Hudson Valley at Newburgh. The clay mineral content; the varves were compared with those reported elsewhere by various authors.

at Fazenda Pacu, Brazil, Kerr (1947). The kaolinite in the wall rock of quartz-crystaline masses which extend for hundreds of feet. The texture of the granite is preserved.

kaolinites in the southern Appalachians (Kerr, 1952). Halloysite is formed only from primary minerals of intense leaching. Original mica and chlorite, potash feldspars may yield secondary mica. Halloysite, kaolinite, and chlorite.

At abundant time, decomposition of rocks in soil. Water in soil may occur in cavities, as adhering water, as chemical additions and subtractions char-

acteristic of total water content of a soil. The pH ranges widely. In a discussion of tropical soils, Mohr (1944) reports a range from below 3 to more than 9. He points out that quartz, which is resistant in acidic conditions, dissolves in time at a pH greater than 7.5. In the tropics acid water is effective in the formation of kaolinite deposits. Mohr concludes that pure water, or water containing carbonic, sulfuric, or humic acids, would cause the weathering of feldspar to kaolinite. However, under similar tropical conditions where alkali or OH ions prevail montmorillonite is apt to form.

Correns and Engelhardt (1938) have investigated the mechanism of weathering of potash feldspar. With an abundance of time and suitable pH, decomposition to kaolinite may occur in soil in the case of a number of rock-forming silicates, which are ordinarily considered particularly soluble.

The ion-exchange characteristics of clays and argillaceous sediments have been extensively studied by Kelley (1939). The most conspicuous effect is reflected in permeability; calcium-saturated clays tend to be granular and comparatively porous, while sodium clays are highly dispersed and relatively impervious. The pH of a clay may be influenced in a significant manner by ion exchange. Calcium clays, where derived from calcium carbonate, are approximately neutral, but under certain circumstances sodium clays may be highly alkaline.

Kelley points out that, although sodium is present in sea water in greater abundance than magnesium, the magnesium takes a more active part in ion exchange in sediments with which it comes in contact. This may explain why many clays of marine origin contain substantial amounts of magnesium.

Kelley also notes that ordinary water contains a low concentration of hydrogen ions, while rain water is commonly acidic because of dissolved carbon dioxide. In clays the hydrogen ions that have strong replacing power tend to replace sodium, with the consequent formation of dilute solutions of sodium bicarbonate, sodium carbonate, or sodium hydroxide. Thus the sodium clays tend to become alkaline.

The clay minerals in Illinois sediments have been utilized by Grim *et al.* (1939) in an attempt to interpret climatic conditions of the source areas. The presence of both kaolinite and illite has been interpreted to indicate that some parts of the source had a warm climate and in other parts the climate was cool.

Hosking (1940) has compared Australian soils derived from granitic and basaltic parent material. In several soils of granitic origin kaolinitic clay has been identified. In soils of basaltic origin, however, the type of clay reflects the soil-moisture conditions during weathering. Kaolinitic types characterize the red loams, while montmorillonitic types prevail in the red-brown earth. Montmorillonite alone is typical of the black earths.

MECHANICAL ACCUMULATION

A number of sedimentary basins on various parts of the earth's surface yield remarkably similar clay-mineral assemblages. Apparently a convergence in the ultimate products exists which is in some respects similar to the convergence of end stages observed in hydrothermal alteration, although the mineral suites formed in the two cases differ.

Recent studies of clays in the Mississippi delta region of Southern Louisiana un-

dertaken at Columbia University show a remarkable uniformity of illite-montmorillonite-kaolinite mixtures throughout some 15,000 feet vertically and over a considerable area laterally. Studies of a large number of samples show only minor variation from a fairly uniform aggregate.

Bates (1947) has shown that illite (hydromica) forms the bulk of the fine micaceous material in slates from the Lehigh-Northampton district of northeastern Pennsylvania. In this case, however, some alignment by metamorphic processes following transportation and deposition is believed to have taken place. However, the illite of the underclays of Illinois described by Grim and Bradley (1939) is believed to have been both transported and deposited as illite. The so-called fuller's earth from the Porter's Creek formation of the Eocene near Olmstead, Illinois (Grim, 1933), contains montmorillonite as the most abundant mineral constituent and the only clay mineral.

Henry and Vaughan (1937) have described the sedimentary kaolinite of Georgia. Prior to the Cretaceous feldspathic rocks of the Piedmont Plateau were deeply weathered. Clays derived from the erosion of the plateau were carried to the coast and accumulated in fanlike fresh-water deltas.

Kerr *et al.* (1951) have studied the textural features of kaolinite from Mesa Alta, New Mexico. Apparently the deposit represents a sedimentary accumulation, but some recrystallization has taken place after deposition.

DIAGENESIS IN SALINE WATERS

It is believed that some minerals, particularly clays or related species, may form under conditions of marine diagenesis. In this process small flakes of mica, kaolinite, or other minerals in position on the floor of the ocean may undergo progressive change to illite and montmorillonite. In some cases research workers have even suggested that the clay-mineral assemblage and the textures of crystallization may indicate depth of deposition. Most clay minerals are found in marine sediments although dickite is either absent or unusual in this occurrence. Halloysite and sepiolite-palygorskite are also missing.

Glass (1951) applied diagenesis in the study of conditions of origin of clay minerals in the Cretaceous and Tertiary sediments of New Jersey. Mineral changes subject to an original marine environment were attributed to a group of minerals which included kaolinite, montmorillonite, hydromuscovite, illite, a chloritic mineral, and glauconite. The crystallinity of kaolinite is said to range from euhedral in fresh-water Triassic shale hollows to irregular in areas of brackish water. Reducing and non-reducing conditions are also said to affect the minerals produced. Dietz (1941) concluded that montmorillonite may be the original clay mineral deposited on the ocean floor at times, but it may be altered to illite.

Grim *et al.* (1949) have attributed the elimination of kaolinite from the sedimentary accumulation along the Pacific Coast to a diagenetic process with increase in depth.

The erosion of illite and chlorite from rock masses may be accompanied by respective losses of potassium and magnesium. The accumulated sedimentary debris con-

taining these "degraded" minerals is believed to be susceptible to the reaccumulation of the original minerals.

LATERITE

Almost a century and a half ago Buchan-
an type of red soil found in southern India.
the nature and mode of origin have long been
have been proposed (Robinson, 1949).

From among many descriptions the status
an ultimate product of the process of laterite.
Weathering is involved. Any one of many
may produce bauxite or laterite. However,
constituents are accelerating circumstances
wet and dry seasons hastens the process.
runoff is considered essential. The original
ore, or manganese results.

The minerals common to laterite are such
boehmite, or diasporite and such ferric
ite. The minerals are usually impure, but
index to the extent of the process of lateritization.

Allen (1948) recognizes three processes
migration, and resilication. The first two
or the union of silica with gibbsite to form
attributes certain cellular kaolin in Georgia.

Lapparent (1936) in describing the bauxite
believes that the laterite began as an aluminous
of silicates under warm humid conditions.
role of carbonated waters in the formation of
ous rocks. Calcareous bauxite in certain
bon dioxide-bearing waters in a warm climate.

According to Goldich (1948) in regions
bauxite the position of the water table
"transitional" clay may form or bauxite
favored as the end product of weathering
end product is bauxite or laterite.

SALINITY

A survey of hydrothermal alteration
most important single factors in the breakdown
either process is temperature. In one case
earth, in the other it is climate.

Of equal importance is chemical activity
reaction in contact with crustal rocks
minerals, due to local decomposition such as

the uniformity of illite-montmorillonite vertically and over a wide area. Most samples show only minor

The bulk of the fine micaaceous material in the northeast of Pennsylvania is the result of diagenetic and metamorphic processes following its deposition. However, the illite of the New York (1939) is believed to have been derived from fuller's earth from the Illinois (Grim, 1933), which is a constituent and the only clay mineral in the

secondary kaolinite of Georgia and the Piedmont Plateau were deeply weathered and were carried to the coast

of kaolinite from Mesa Alta. The kaolinite is a secondary accumulation, but

Other related species, may form small flakes of mica, kaolinite, and chlorite. They undergo progressive changes. Some workers have even suggested that recrystallization may indicate a marine origin although kaolinite, allophane, and sepiolite may

Some of the origin of clay minerals is secondary. Mineral changes subject to a group of minerals which include kaolinite, a chloritic mineral, and illite. They are derived from euhedral in fresh-water and from euhedral in fresh-water. Reducing and non-reducing conditions are produced. Dietz (1941) considered kaolinite as a mineral deposited on the ocean floor

kaolinite from the sedimentary process with increasing

be accompanied by rest of the sedimentary debris

maintaining these "degraded" minerals is believed by Grim (1953) to be especially susceptible to the reaccumulation of the original elements in a new environment.

LATERITE

Almost a century and a half ago Buchanan (1807) proposed the name *laterite* for a type of red soil found in southern India. Notwithstanding the antiquity of the term the nature and mode of origin have long been a problem for which divergent solutions have been proposed (Robinson, 1949).

From among many descriptions the statement of Harder (1949) concerning bauxite, an ultimate product of the process of lateritization, is probably as satisfactory as any. Weathering is involved. Any one of many rock types or their weathered derivatives may produce bauxite or laterite. However, high alumina and the presence of soluble constituents are accelerating circumstances. A warm humid climate with alternating wet and dry seasons hastens the process. A land surface of low relief with sluggish runoff is considered essential. The original rock may determine whether bauxite, iron ore, or manganese results.

The minerals common to laterite are such aluminian minerals as clinochlore, gibbsite, boehmite, or diaspore and such ferrian minerals as limonite, goethite, or lepidocrocite. The minerals are usually impure, but the extent of their development is an index to the extent of the process of lateritization in a given deposit.

Allen (1948) recognizes three processes in the formation of bauxite: desilication, migration, and resilication. The first two have long been recognized, but resilication or the union of silica with gibbsite to form clay is a more recent interpretation. Allen attributes certain cellular kaolin in Georgia to the addition of silica to gibbsite.

Lapparent (1936) in describing the bauxitic clays of Ayrshire, derived from basalt, believes that the laterite began as an alumina-silica gel, resulting from the hydrolysis of silicates under warm humid conditions. Rankama and Sahama (1950) point to the role of carbonated waters in the formation of aluminum hydroxide from mafic igneous rocks. Calcareous bauxite in certain instances is attributed to the action of carbon dioxide-bearing waters in a warm climate.

According to Goldich (1948) in regions favorable for the formation of laterite and bauxite the position of the water table may determine whether an intermediate or "transitional" clay may form or bauxite will be produced directly. Clay minerals are favored as the end product of weathering below the water table, while above, the end product is bauxite or laterite.

SALIENT FACTORS

A survey of hydrothermal alteration and weathering indicates that one of the most important single factors in the breakdown and reorganization of rocks involved in either process is temperature. In one case it is the temperature from within the earth, in the other it is climate.

Of equal importance is chemical activity. Acids derived from within or alkalis due to reaction in contact with crustal rocks produce alteration minerals. At the surface acids, due to local decomposition such as sulfuric acid, organic acids, and carbonic

acid, or alkalis react to form soils or weathered masses. Even in diagenesis environment is an important factor.

Water as steam is often in part the predominant vehicle in hydrothermal alteration. In weathering the most intense effects frequently develop in humid areas of stagnant drainage.

The elements in minerals formed by hydrothermal alteration are largely those derived from the rocks subject to alteration. In weathered areas the predominant constituents come from the rocks near at hand.

Convergence in hydrothermal alteration (Schwartz, 1950) frequently results in a uniform suite of alteration minerals although the originating rocks may be quite different. The great basin of the Mississippi yields clay mineral aggregations over a wide area of considerable similarity. Tendency toward convergence may be a general feature in both hypogene and supergene processes.

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masses. Even in diagenesis environments, hydrothermal alteration is a vehicle in hydrothermal alteration. Alterations frequently develop in humid areas. Hydrothermal alteration are largely those in the altered areas the predominant component. (Dietz, 1950) frequently results in the alteration of originating rocks may be quite different. Clay mineral aggregations over a wide area and convergence may be a general feature.

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the formation of high-alumina clays

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