ALUNITIC ALTERATION AT MARYSVALE, UTAH

by

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This report is preliminary and has not
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ABSTRACT

Deposits of alunite in the Marysvale region, Utah, are nearly all confined to the Bullion Canyon Volcanics of Tertiary age. The deposits consist of two types, alunite veins and irregular alunite replacement bodies. The vein deposits are restricted to the vicinity of Alunite Ridge southwest of Marysvale in the Tushar Mountains, and the replacement bodies are distributed circumferentially about a quartz monzonite stock in the Antelope Range northeast of the village.

The wall rock alteration that borders the alunite veins has been divided into three phases. In order of their zonal distribution toward the vein, the phases are the feeble phase, the moderate phase, and the intense phase. Feeble phase alteration is characterized by illite-montmorillonite mixed lattice clay, kaolinite and minor quartz which were formed at the expense of carbonate, seritized plagioclase and some of the chlorite of the regionally altered Bullion Canyon volcanics. Alteration of the moderate phase is represented by the assemblage, alunite, kaolinite and quartz which were produced in part from the mixed lattice clay and chlorite of the feeble phase. Strongly alunitized and silicified rock adjacent to the vein represents the intense phase of alteration.

Alteration in the replacement deposits is represented by the feeble and moderate phases. The alunite bodies represent the moderate phase of alteration, and those bodies that are sharply defined are surrounded by an envelope of feeble phase alteration. The mineralogy of the corresponding alteration phases of the vein and replacement deposits is the same.

Laboratory data on the environmental conditions of formation of the minerals, symmetrical zoning of the minerals and chemical analyses of the veins and altered rocks of the alunite deposits lead to the following conclusions:

1. Alteration and alunite deposition resulted from the same solutions and were contemperaneous processes.
2. Solutions transported K_2O, Al_2O_3, SO_3, H_2S and probably SiO_2 to the vein deposits.
3. Solutions transported at least SO_3 to the replacement deposits.
4. The alunite depositing solutions were acid at the level of deposition.
5. The solutions became progressively less acid with increasing distance from the channelway, a fact which largely accounts for the zonal distribution of wall rock alteration.
6. The temperature of the solution at the time and level of alunite deposition was below 350° C.

Sharply defined veins with banded and comb structure suggest that the vein deposits are fissure fillings and are due to ascending hydrothermal solutions which were confined largely to nearly vertical fracture zones. The replacement bodies are also believed to be due to ascending hydrothermal solutions. The bodies are distributed around a quartz monzonite intrusive, and some deposits are aligned along what is considered to have been a vertical channelway. The irregular and diffuse nature of the replacement deposits is explained by the lateral spreading or directed lateral flow of the hydrothermal solutions which entered porous horizons in the volcanics.

Isomorphous substitution of sodium for potassium has been studied in both natural and synthetic alunite samples. Unit cell dimensions distinguish two naturally occurring mineral types of the composition $(K,Na)Al_3(SO_4)_2(OH)_6$, a high potassium alunite termed alunite, and a high sodium alunite termed natroalunite. The c lattice constant for alunite ranges from 17.28 to 17.31 Å; whereas the constant for natroalunite is 16.71-16.72 Å. The relation between the c lattice constant and the sodium-potassium composition suggests that isomorphism exists over a restricted range for alunite, though insufficient samples were obtainable to determine the nature of isomorphism for natroalunite. In the range of composition between alunite and natroalunite only samples which are mixtures of alunite and natroalunite have been found, and the possibility is suggested that natural homogeneous alunite does not occur in this range of composition.

Synthetic alunite samples with a range of sodium-potassium contents were synthesized at atmospheric pressure in boiling solutions of sodium, potassium and aluminum sulfates. Most synthetic alunite samples had a higher K:Na ratio than the solutions from which they were produced. Although the synthetic alunites crystallized with the alunite structure, their unit cell dimensions differ slightly from natural alunites of corresponding composition. Also chemical analyses reveal that the synthetics deviate from the theoretical alunite composition, the greatest deviation being the excess of water. The partial substitution of oxonium ions (H_3O^+) for sodium and potassium ions is proposed as the explanation for these anomalies. Complete isomorphism from the sodium to the potassium end of the synthetic alunite series is evidenced by the linear shrinkage relations of the unit cell dimensions. This relation is in strong contrast to that shown by natural alunite samples.

The thermal behavior of alunite and the practicability of semi-quantitative differential thermal analysis of alunite ores has been studied from artificial mixtures of alunite, quartz and kaolinite and from chemically-analyzed alunite ores. The chemistry of thermal reactions of alunite are summarized in the following equations:

$$6\ \mathrm{KAl_3(SO_4)_2(OH)_6} \xrightarrow{590} 6\mathrm{Kal(SO_4)_2} + 6\ \mathrm{Al_2O_3} + 18\mathrm{H_2O}$$

$$6\mathrm{Al_2O_3}\ \text{(Amorphous)} \xrightarrow{780} \mathrm{Al_2O_3}\ (\gamma\ \text{alumina})$$

$$6\mathrm{Kal(SO_4)_2} \xrightarrow{800} 2\mathrm{K_3Al(SO_4)_3} + 2\mathrm{Al_2O_3} + 6\mathrm{SO_3}$$

$$2\mathrm{K_3Al(SO_4)_3} \xrightarrow{800-870} 3\mathrm{K_2SO_4} + \mathrm{Al_2O_3} + 3\mathrm{SO_3}$$

Differential thermal curves of alunite samples of coarse grain size are characterized by a double endothermic peak in the temperature range 570 -640° C. Fine-grained alunite samples, however, produce a single endothermic peak at 590° C. The doublet condition of this thermal peak is due to two stages of alunite decomposition in the coarse-grained samples.

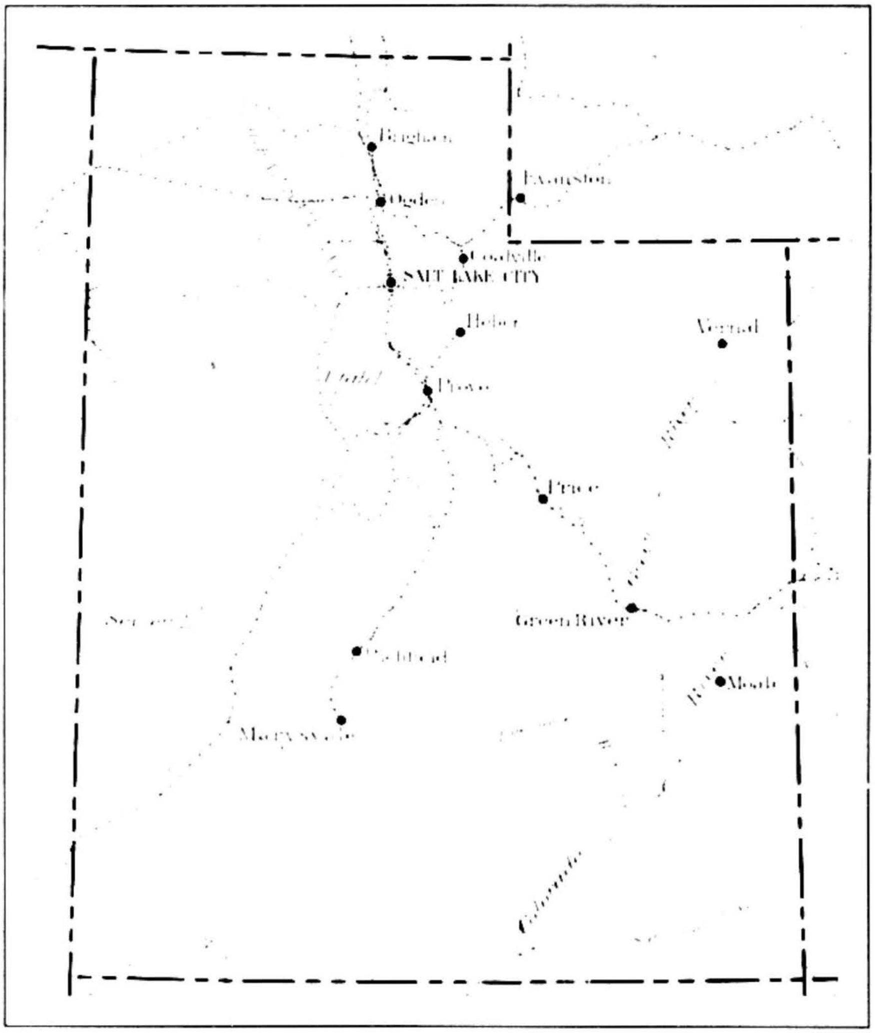
Careful control and standardization of variable procedures and factors inherent in the differential thermal analysis technique and apparatus has permitted accurate semi-quantitative analysis of alunite mixtures. Graphs which relate the alunite percentage in mineral aggregate to the area and amplitude of the 590° C. endothermic peak of alunite have been established for both artificial mixtures and analyzed alunite ores. Differences between the graphs for the artificial mixtures and the corresponding graphs for the alunite ores are attributed contributed to the variation of grain size in the alunite ores. The area enclosed by the thermal peaks is the most reliable measure of the composition of samples in which the grain size is variable. If the grain size is consistent among the samples, the peak amplitude can also be used.

INTRODUCTION

Deposits of alunite, $(K,Na)Al_3(SO_4)_2(OH)_6$ were discovered in 1910 in the vicinity of Marysvale, Utah, in the southwest-central part of the state (see Fig. 1). Large quantities of alunite exist in the region, but only during the two world wars was mining on a large scale attempted. At the present time cheaper sources of potash and alumina render exploitation not economically feasible; nevertheless, the alunite deposits remain a potential resource of these materials.

In the Marysvale region the large deposits of alunite and their associated alteration haloes are free from metallic-ore minerals (pyrite excepted) and therefore afford an opportunity to study alunitization without the complicating effects of other types of mineralization. With the aid of x-ray, differential thermal analysis, staining and optical techniques, the nature of the alunitic alteration has been accurately determined. Interpretation of the origin and chemistry of formation of the deposits, based on the minerals in the alteration zones, represents a major part of this study. The availability of alunite ore samples, which have been analyzed chemically, has made it possible also to study the nature of the isomorphic substitution of sodium for potassium in alunite as well as to test the thermal behavior of known alunite mixtures.

This study has been made under the auspices of the United States Geological Survey as a part of a comprehensive geologic report on the Marysvale region.



INDEX MAP

Figure 1.--Index map of Utah

Columbia University and the New Mexico Bureau of Mines and Mineral Resources generously furnished the writer with research facilities.

GENERAL GEOLOGY

The geology of the Marysvale, Utah region has been described by Butler and Gale (1912), Eugene Callaghan (1938, 1939), Callaghan and Willard, and Callaghan and Parker (U.S.G.S. Map Series reports in press). Callaghan (1939) distinguished the major stratigraphic and structural elements of the region and described in detail the petrologic and petrographic character of the Tertiary volcanics.

Pre-Volcanic Sedimentary Rocks

Paleozoic, Mesozoic and early Tertiary sedimentary strata are exposed along the Tushar fault scarp and in the canyons west and southwest of Marysvale. (See Fig. 2). The aggregate thickness of these rocks is in excess of 6,000 feet. The oldest exposed rocks are gray and tan quartzites, limestones and shales of the Permiam Kaibab formation. The overlying Triassic Moenkopi formation, Shinarump conglomerate, and Chinle formation comprise a conspicuous group of tan sandstones, red, green, and purple shales and thin gray limestone beds. Above the Triassic strata the Jurassic Navajo sandstone and Carmel formation consist of yellowish gray cross-bedded quartzitic sandstone and light colored limestones and shales respectively.

Overlying the pre-tertiary formations but separated from them by an angular unconformity is about a 50-foot thickness of conglomerate and sandstone. The fragments in the conglomerate are composed of limestone and quartzite boulders. In most exposures the overlying Tertiary volcanics conform to the bedding of these strata, but in some places the conglomerates are entirely absent and the volcanics rest on the older rocks.

Tertiary Igneous Rocks

On the basis of a marked unconformity Callaghan (1939) has separated the igneous rocks in the region into the earlier and later Tertiary groups. Paleontological evidence in the underlying and overlying sedimentary rocks suggests that both the earlier and later Tertiary groups are most likely Miocene and possibly in part Pliocene in age. The youngest formation overlain by the Bullion Canyon volcanics is the Wasatch formation. Fresh water fossils from the formation have been determined by Mr. T. C. Yen of the United States Geological Survey as late Eocene or early Oligocene in age. The age of the Sevier River formation which overlies the volcanic section is regarded by Mr. K. E. Lohman of the United States Geological Survey as late Pliocene or early Pleistocene (Callaghan, 1938).

Earlier Tertiary igneous rocks

The oldest and most widespread volcanic rocks in the region are the Bullion Canyon volcanics. All granular intrusives as well as nearly all of the mineral deposits are confined to them. These volcanics are composed of both pyroclastics and flows. In general the pyroclastics form great thicknesses in the lower part of the sequence whereas the upper part consists principally of flows. However, the proportion of flows to pyroclastics varies greatly from place to place. In the general vicinity of the alunite deposits in the Tushar Mountains nearly 2500 feet of latitic and andesitic tuffs and breccias occur with only a minor number of flows. In the Antelope Range, the site of most of the replacement alunite deposits, latitic flows, tuffs and breccias are abundant. Details of lithology in parts of these volcanics associated with the alunite deposits are discussed in later appropriate sections of the text.

Bodies of quartz monzonite have intruded the Bullion Canyon volcanics in several places in the region. The largest of these intrusives is exposed over an area of about four square miles in the Antelope Range. The eroded surface of this intrusion is overlain by rocks of the Later Tertiary volcanic sequence, clearly establishing the relationship between the two major volcanic series. The monzonite is nearly equigranular in texture. The grain size is mostly from 1 to 4 mm. for the major minerals. The rock consists of calcic oligoclase, orthoclase, quartz, augite, and biotite with accessory magnitite apatite sphene. Deuteric (?) tourmaline epidote chlorite and sericite are developed. Orthoclase replaces plagioclase to a certain extent and is also intergrown with quartz. In places the proportion of orthoclase is sufficient to give the rock the aspect of granite. Although the content of quartz is less than 10 percent the rock is closer to the composition of quartz monzonite than monzonite.

Sills of latite intrude the conglomerate at the base of the Tertiary section southwest of the mouth of Cottonwood Canyon. The intrusive latite is dark gray and porphyritic and contains small cavities filled with quartz and carbonate. The phenocrysts are augite and hornblende 0.3 to 1 mm. in length and the ground mass is oligoclase and quartz averaging 0.1 mm. (Callaghan, 1939).

Later Tertiary igneous rocks

The Later Tertiary volcanic rocks consist of the Dry Hollow volcanics, the Mount Belknap rhyolite, and the Joe Lott tuff in order of decreasing age.

The Dry Hollow volcanics are composed of tuff, latite and basalt members. The tuff is pink to light brownish gray and contains abundant crystal fragments of oligoclase, quartz and biotite. The latite ranges from pink to gray and is strongly porphyritic. Some varieties have sanidine crystals as much as 10 mm. across. Quartz is more abundant in some varieties than others. Chemical analyses (Callaghan, 1939) show that both the latite and tuff are simular in composition. The basalt member is dark gray and locally is extremely vesicular. Some flows are strongly porphyritic whereas others are fine grained or glassy. Labradorite, augite, pigeonite, hypersthene and olivine may all appear as phenocryts. The groundmass is glass with tiny embedded plagioclase laths. Only the Dry Hollow latite is exposed in the region of the alunite mineralization.

The Mt. Belknap rhyolite is present as three distinct members in the Antelope Range. The members are the red, gray and porphyritic facies and although they are all rhyolitic in composition, their lithologic aspects are quite different. The red facies is reddish to salmon colored and is aphanitic. Both the tuffaceous matrix material and the enclosed rhyolite fragments are devitrification aggregates, and the entire mass may be regarded as a welded tuff. Phenocrysts of orthoclase up to 0.8 mm. and rare quartz crystals are set in a matrix of minute feldspar crystals. The gray facies is characterized by prominent light gray and darker gray laminae which are complexly contorted. The difference in color is due to the degree of devitrification of the bands, the darker gray layers being only slightly devitrified whereas the lighter bands are more completely crystalline. Thin lenses parallel to the banding contain tiny orthoclase and quartz crystals. The porphyritic facies, exposed in a group of eroded domes at the foot of the Sevier Plateau escarpment, is light gray and strongly porphyritic. Large phenocrysts of quartz and orthoclase (?) are contained in a devitrified base.

The youngest of the Later Tertiary volcanics, the Joe Lott tuff, is a welded tuff. Its color ranges from white to pale brownish gray. Fragments of latite, probably derived from the Bullion Canyon volcanics, and gray banded rhyolite of the Mt. Belknap gray facies, are enclosed in an ashy matrix that is rhyolitic in composition.

Late Tertiary or Early Quaternary Rocks

Partly consolidated fanglomerate, conglomerate, sand and silt, which for the most part have been derived from the highlands in the vicinity of these deposits are called the Sevier River formation (Callaghan 1939). The composition varies from place to place depending upon the nature of the source materials. The fact that the Sevier River formation is tilted and faulted serves to distinguish it from similar deposits younger in age. In some places thin basalt flows are interbedded with the formation.

Quaternary Deposits

Glacial debris in the Tushar Mountains, terrace gravels, land slides and alluvium are youngest deposits found in the region.

Structure

The gross structural features of the region are broad monoclinal flexures at the fronts of the ranges and great range front fault systems. These were recognized by Dutton (1880) during his reconnaissance of the High Plateaus of Utah.

Two major fault systems outline the Sevier Valley, the Sevier fault on the east and the Tushar fault on the west. Along the strike, the displacement on these systems ranges between zero and a few thousands of feet. In places where the displacement is at a minimum along the fault trend, anticlinal cross structures occur with their axes running normal to the trend of the valley (Callaghan and Willard, manuscript in press). The Antelope Range is such a cross structure. Others are found along the course of the Sevier Valley outside of the area under consideration.

The alunite veins in the Tushar Mountains outline a system of northwest and northeast trending fracture or fissure zones. Many normal faults are parallel to the trend of the great Tushar fault. Other normal faults strike northeast and east-west.

Detailed mapping in and about the alunite deposits in the Antelope Range has also shown a complex pattern of closely spaced normal faults. At the Yellow Jacket deposit the faults strike northeast and northwest and offset gouge zones and mineralized zones which trend approximately east-west. The normal faults at the White Hills deposit have north-northwest and west-northwest trends.

Tectonic folding is not characteristic in the volcanic rocks of the Marysvale region. Flowage folds related to the extrusion of the lava were observed in some of the latite flows. A broad, shallow, north plunging anticline in the tuff at the Mary's Lamb deposit, however, may be of tectonic origin, possibly related to the anticlinal warping that produced the Antelope Range.

ALUNITE MINERALIZATION

Two types of alunite deposits described in the Marysvale region by Callaghan (1938) are the vein and the replacement deposits. Compositional and structural differences are generally sufficient to distinguish the two types. As the name implies, the vein deposits are formed by one or more distinct fillings of open fractures and are of high purity. The replacement deposits on the other hand are irregularly shaped bodies of altered volcanic rock in which alunite, quarts and clay minerals are the dominant constituents. The alunitized and silicified wall rock of the vein deposits has many aspects in common with the altered volcanic rock of the replacement bodies.

The vein type and the replacement type alunite deposits are mutually exclusive in their distribution. All of the vein deposits are located in the Tushar Mountains on Alunite Ridge in the upper reaches of Cottonwood Creek. The replacement deposits are more widespread. Most of them are found in the Antelope Range in the Bullion Canyon volcanics surrounding the quartz monzonite intrusive. Alunitized rock is also found atop Marysvale Peak on the Sevier Plateau and on the western slope of the Tushar Mountains north of Beaver.

The most extensively explored vein deposits are the Mineral Products, Bradburn, Sunshine and L and N. The J and L, White Horse, White Hills, Al Kee Mee, Marys Lamb, Yellow Jacket, Hindenburg, Krotki, Big Star and Winkleman deposits are the most important replacement bodies. Figure 2 shows the distribution of the deposits as well as their geologic setting. Analyses of the ore and descriptions of the deposits are given by Callaghan (1938).

Vein Deposits

Structure

The vein system along Alunite Ridge has two distinct trends. The main vein system strikes N. 35° W. and is nearly vertical with dips recorded to the northeast and southwest in different places. The West vein system strikes N. 60-80° E. and dips 30-85° northwest, branching almost perpendicularly from the main vein. The vein system is complex and is composed of veins that pinch, swell, curve, branch and fork in a complicated manner. Lenses and horses of silicified rock occur in the veins and in places appreciably lower the grade of the ore. At the portal of the Mineral Products upper tunnel, the lens of alunite is 65 feet in width but pinches out 180 feet to the northwest. The main productive lens at the Mineral Products deposit is over 1,000 feet in length and extends downward from the surface below the lower level which in places is over 400 feet from the surface. (See Fig. 3).

Mineral relations in the veins

The veins are composed of both coarsely crystalline and finely crystalline alunite. The coarsely crystalline variety is commonly banded and the tabular alunite crystals, which are aggregated to form parallel or slightly diverging crystal groups, are normal to the banding. Under the microscope what appear to be single crystals are seen to be groups of smaller alunite crystals which are arranged in plumose aggregates. The alunite crystals are anhedral except in vugs or open spaces between bands or in the cavities lined with coarsely crystalline alunite in finely crystalline alunite masses. (See Plate 1). Here rhombohedral faces are the terminations on the elongate crystals surrounding the openings. In many of the cavities the crystal faces have been etched by solution and are coated by iron oxides. Curved surfaces formed at the ends of compound crystal groups resemble curved dolomite crystals. These forms are the result of the combination of numerous rhombohedral faces terminating the crystals of the plumose aggregate.

The bands, which separate the coarsely crystalline parts of the veins, consist of finely crystalline, diversely oriented alunite cyrstals. These bands range in width from a fraction of an inch to one inch and are commonly pigmented with iron oxides (See Plate 2). Some banding is due merely to color changes without a change in crystal character and probably is a result of slight variations in the iron oxide content of the depositing solutions (Loughlin, 1915). Across some bands the optical continuity of alunite crystals and crystal groups is maintained suggesting that the bands are fillings of fractures that broke across the crystals. Another interpretation suggested by Butler and Gale (1912) is that a slight change in conditions interrupted deposition or altered the rate of deposition and caused the formation of diversely oriented fine-grained alunite instead of the large crystals. A return to the original condition permitted the largest crystals to continue their growth, while crystallization in part began at new centers.

The coarsely crystalline alunite is pink and translucent, although in places shades of red and yellow result from iron oxide staining. It is nearly pure except for some yellowish isotropic material, probably limonite, that fills fractures and openings between grains, and except for minor microscopic inclusions in the grains. Although Loughlin (1915) reported pyrite as a constituent of the vein alunite, none was seen in the our samples studied. Table 1 gives the chemical analysis of a selected sample of the vein type alunite together with the theoretical composition of the mineral.

A massive, pink-to-white, fine-grained variety of alunite occurs in the veins closely associated with the coarsely crystalline type. The crystals are mostly less than 0.1 mm. in length and are diversely oriented. This fine-grained variety is cut by intersecting veins of coarsely crystalline alunite, and vugs and cavities in the fine-grained alunite are lined with coarse alunite crystals. Large alunite crystals enclose fine-grained alunite within their borders and appear to have grown at the expense of the smaller crystals, suggesting that the coarsely crystalline alunite has resulted from recrystallization of the finely crystalline variety (See Plate 3).

Veinlets of bluish white clay, which are massive and nearly isotropic in thin section, cut the alunite veins as well as the enclosing wall rock and are therefore later than the vein alunite. This clay was (has been) reported by C. S. Ross (Callaghan, 1938) as dickite. X-ray diffraction patterns of blue clay samples from the Land N deposit, collected during this study, [illegible] indicate that the mineral is kaolinite.

Wall rock alteration

The latite breccia in the vicinity of the alunite veins is altered to aggregates of secondary minerals that are not present in the country rock remote from the veins. The texture of the original unaltered rock is, however, preserved in some of the most intensely altered phases. Symmetrically bordering the alunite veins, three phases of wall rock alteration have been recognized. In order of their zonal disposition outward from the vein, they are the intense, moderate and feeble phases. Rocks of the intense phase are strongly silicified and extend from a few feet to tens of feet normal to the vein forming a siliceous selvage at its borders. The moderate and feeble phases represent the zone of argillic alteration which separates the silicified rock from the country rock.

Most of the numerous exploratory trenches and workings do not continue far enough normal to the trend of the veins to expose the argillic zone or show its actual contact with the country rock. However, at places in the Mineral Products mine where the alunite veins are thin and sparse, the argillic altered rock is exposed in the walls of the tunnel. At the L and N deposit a bulldozer cut crosses the vein and exposes the entire argillic zone and its contact with the country rock. Here the spacial relation in the zone of alteration about the alunite veins is clearly shown.

Detailed petrographic and mineralogic studies on the samples from these deposits show that the zones are mutually gradational and the phases of alteration are defined on the basis of the predominance, presence or absence of certain characteristic minerals. Detailed descriptions of the alteration phases are given in the following paragraphs.

Country Rock

The host rock for the alunite veins is a latite breccia which occupies a position in the lower part of the Bullion Canyon volcanics (Callaghan 1938, 1939). The rock, which is sufficiently remote from the alunite veins to have escaped mineralization and alteration related to the deposition of the alunite, shows the effect of an earlier and very widespread alteration. This earlier alteration, characterized by the formation of chlorite, sericite, carbonate epidote and quartz, is believed to be a regional alteration because of its wide areal extent. A sample of the latite breccia taken near the Mineral Products Mine is typical of the host rock free from the effects of alteration clearly related to the alunite veins. The rock is dark purplish gray with porphyritic texture in both fragments and matrix.

The plagioclase phenocrysts are as large as 2 mm. and are oligoclase. Small plagioclase laths in the groundmass average 0.03 mm. Former mafic minerals, showing amphibole and possibly a few pyroxene cross sections, are now an aggregate of carbonate, chlorite, magnetite and hematite. Quartz is abundant and forms nests in the groundmass and phenocryts. Sericite is found as fibrous grains in the plagioclase as well as in radiating clusters in the groundmass. The country rock at the L and N deposit is similar in these respects although a few grains of epidote (?) are present. (See Plate 5, A and B).

Feeble Phase

The feeble phase of alteration associated with the alunite veins is characterized by the presence of mixed lattice illite-montmorillonite type clay, minor kaolinite and quartz, and the absence of alunite. This phase grades into the moderate phase toward the alunite vein and into the country rock in the opposite direction.

The feeble phase is well illustrated at the L and N deposit and in places in the Mineral Products mine (See Plate 7, A, B and D). The texture of the latite breccia is well preserved although the minerals have been changed. The groundmass is a highly birefringent fibrous aggregate of mixed lattice illite-montmorillonite clay (See Appendix II). Clay pseudomorps after plagioclase feldspars are composed of mixed lattice montmorillonite-illite clay and a clay mineral of low birefringence, probably kaolinite. The mixed lattice clay mineral fringes the outlines of the original feldspar as well as occurring as single fibres and radiating groups of fibres dispersed in the kaolinite. Secondary quartz is not abundant, but numerous relict quartz phenocrysts are found in the rock. The original brown biotite has been bleached and tiny grains of sphene (or rutile) which have separated from it are aligned in the direction of the cleavage. In some samples the biotite is mainly chlorite fringed with mixed lattice clay. Sericite laths and pyrite are sparsely distributed in some thin sections.

Moderate Phase

The moderate phase of alteration is characterized by the presence of kaolinite, alunite, secondary quartz and pyrite. The secondary quartz is not so abundant as in the intense phase of alteration. The moderate phase is gradational into the intense phase and is spearated on the basis of the presence of kaolinite. It grades into the intense phase on the side toward the alunite vein and into the feeble phase in the opposite direction.

Samples from the L and N deposit well illustrate the features of the moderate phase of alteration (See Plate 8, D). The original rock texture is strikingly preserved. The groundmass, composed largely of finely crystalline quartz, outlines the shapes of the original plagioclase crystals which are now composed of kaolinite, quartz and minute fibrous skeletal alunite crystals. A few fibrous alunite crystals are scattered also in the siliceous groundmass. Relict quartz phenocrysts and apatite crystals are sparsely distributed and show no effect of the alteration. In some secondary quartz grains, clusters of a high birefringent fibrous mineral, presumably mixed lattice illite-montmorillonite clay, are present as inclusions. The clay mineral clusters were probably isolated by the enveloping quartz and are believed to represent relicts of the feeble phase of alteration. Small irregular grains of sphene or rutile (?) commonly occur in the feldspar pseudomorphs. A golden brown material, abundantly dispersed in the rock, is a mixture of supergene limonite and jarosite(?) produced by the oxidation of pyrite once sparsely disseminated in the rock.

In the Mineral Products upper tunnel on the west wall 1,220 feet from the portal, the wall rock is strongly argillized, purplish gray to pale green, coarse volcanic breccia which is so friable and soft that thin sections could not be made. X-ray and DTA (differential thermal analysis) results indicate that it is composed of kaolinite, montmorillonite-illite mixed lattice clay and quartz. Kaolinite is the most abundant constituent, so this material probably represents the transition between the moderate and the feeble phases. At this place the alunite vein is only about one foot in width and sheathed in a thin silicified envelope. The appearance of the moderate, feeble phase rock within ten feet of the vein indicates that the width of the zone of alteration is related incidentally to the thickness of the vein.

Intense Phase

Adjacent to the alunite veins and as horses within the veins, the volcanic rock is strongly silcified, alunitized and pyritized. Mosiac nests of quartz make up most of the groundmass. Quartz and alunite in the original phenocrysts preserve the once porphyritic texture. In the most intensely silcified rock the texture is destroyed or barely preserved by the difference in grain size of the quartz in the groundmass and in the ghost phenocrysts (Plate 9). Alunite is commonly present as radiating groups of plumose crystals or as reticulated network of long alunite laths. Some large quartz grains are rounded and embayed by the groundmass material in both the unaltered and silicified latite breccia and are therefore most likely relicts of the original rock. Tiny residual grains of apatite and zircon have also escaped alteration. Pyrite, mostly cubic in habit, forms as much as five percent of the rock. In some thin sections tiny, irregular grains of sphene or rutile (?) are abundant. Abundant silica, together with the absence of replacement clay minerals, characterize this phase.

Larger scale features seen in the wall rock are quartz and alunite veinlets. The quartz veinlets cut the silicified rock and are in turn cut by the alunite veinlets (Plate 4).

Veinlets and blebs of kaolinite, previously described, cut across the alunite veinlets and are therefore later.

Replacement Alunite Deposits

Many features are common among the replacement alunite deposits. The deposits are extremely irregular in size, shape and grade, but their mineralogy is similar. They are all (with the possible exception of the Sheep Rock deposit)[1] found in the upper part of the Bullion Canyon volcanics. In certain respects they differ. Some deposits are characterized by the dominant presence of the sodic variety of alunite, natroalunite. Some deposits are replacements of volcanic flows, whereas others are replacements of pyroclastics.

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[1] It is believed by Callaghan (personal communication) that the Sheep Rock alunite deposit is a result of the replacement of the Mt. Belknap rhyolite.

Localization in volcanics

At the White Horse alunite deposit, described in detail by Willard and Proctor (1946), the alunite bodies are located in biotite quartz latite in the cores of flow-folds. According to these authors the alunitized cores represent infolds of the porous vesicular part of the flow, which furnished troughs of high porosity for the circulation of the mineralizing solutions, resulting in more complete alunite replacement in these places.

The White Hills deposit, which lies 1-3/4 miles to the northeast and is up-dip from the White Horse deposit, appears to be the result of alunite replacement of the same biotite latite as well as the overlying tuffs. The presence of flow folds as a localizing influence is not clearly indicated. The Outcrop pattern of the more strongly altered rock in the deposit suggests either irregular alunite replacement or some haphazard contortion of the layers that were replaced. Numerous post-mineral faults have offset the alunite bodies.

The alunite deposits on the northern flank of the Antelope Range are located both in a series of tuff beds and in underlying calcic latite flows. The tuff series is either weakly alunitized or altered to a suite of minerals related to the alunitization over most of the area of the outcrop. The calcic latite, on the other hand, is fresh in most of the exposures remote from the alunite deposits, but is alunitized and characteristically altered near many of the alunite deposits.

The Al Kee Mee alunite deposit is restricted to the calcic latite. An irregular vein or lens that is roughly flat-lying grades into the alunitized and kaolinized latite. The ratio of natroalunite to kaolinite is variable from place to place in the "vein". The flat-lying character of the "vein" suggests that it may be a result of the alunitization of a more porous layer in the latite such as a vesicular zone.

The Mary's Lamb, Yellow Jacket, Hindenburg and Krotki deposits are located primarily in the tuff series although the latite is also mineralized or altered. The alunitization is evidently localized at the Marys Lamb deposit in the tuff along the crest of a broad north plunging anticline. The latite beneath the tuff is strongly altered to mixed lattice illite-montmorillonite clay and chlorite.

The Krotki, Hindenburg and Yellow Jacket deposits are roughly aligned in an east-west direction. Along this trend gypsiferous alteration, which is later than the alunite, occurs sporadically. At both the Yellow Jacket and Hindenburg deposits the tuff and underlying calcic latite are more strongly alunitized near this zone suggesting that the deposits are aligned along fissure zones or solution channels.

Alteration

Alteration zones about the replacement alunite bodies are less clearly defined than the zones about the alunite veins. The irregular nature of the replacement zones caused by the apparently preferential replacement in certain porous horizons and in different lithologies, requires that the alteration of the different rock types at the replacement deposits be studied individually. Although the susceptibility to alteration differs among these rock types, similar mineralogic changes are found between alunitized and unalunitized equivalents.

Two phases of alteration are apparent in the alunitized rocks. They are the moderate phase, which is characterized by the formation of abundant alunite, kaolinite and quartz, and the feeble phase, which is characterized by the formation of illite-montmorillonite mixed lattice clay.

Country Rock

The Bullion Canyon volcanics, that are sufficiently remote from the replacement alunite bodies to have escaped mineralization by the alunite-bearing solutions, are characterized by the same type of regional alteration that is found in the country rock of the vein alunite deposits. As stated previously, this alteration is believed to be earlier and unrelated to the alunitic mineralization. The development of carbonate, chlorite, sericite and quartz are characteristic.

The biotite quartz latite at the White Horse deposit has been described by Willard and Proctor (1946). The latite is strongly porphritic with closely spaced phenocrysts of andesine and biotite ranging from 1 to 5 mm. long. The groundmass is largely crystalline but individual crystals are too small to be accurately identified in thin section. Probably the groundmass is composed mostly of orthoclase and quartz. Grains of ilmenite, magnetite and apatite are also present. The effects of the regional alteration are noticed in the formation of sericite in the plagioclase, chlorite in the biotite, and the formation of carbonate in irregular-shaped grains and lath-like pseudomorphs in the groundmass (See Plate 5, D). The chemical analysis is given in Table 2.

Owing to the widespread alunitization and related alteration in the tuff series along the northern flank of the Antelope Range, unaltered samples were not obtained. The least altered samples of these rocks reveal that the tuff is thinly bedded to massive. The grain size is very fine, though some crystal fragments are as much as 3 mm. in width, suggesting that the original material was ash.

The unaltered calcic latite which lies below the tuff series along the northern flank of the Antelope Range is orphrytic with phenocryts of andesine, and enhedral to subhedral augite (See Plate 5, C). The andesine crystals are as much as 4 mm. and the largest augite are 2 mm. in length. Magnetite and a few grains of apatite are dispersed in the groundmass. Most of the microcrystalline groundmass has a low index of refraction and is doubtless rich in orthoclase. A few cuneiform-shaped grains of quarts are intergrown with the groundmass material. The only expression of the regional alteration is the incipient sericitization of the plagioclase and the formation of highly birefringent fibrous material along cracks in the augite. In some places the calcic latite is notably vesicular, and radially arranged fibrous growths of low index of refraction, presumably zeolite, are in some of the vesicles.

Feeble Phase

Grading outward from the alunite bodies into the country rock at the White Horse and White Hills deposits is a less intense zone of alteration characterized by the presence of mixed lattice illite-montmorillonite clay and the absence of alunite. The mixed lattice clay is present in place of the original plagioclase phenocrysts as well as in the groundmass. Kaolinite and quartz also are found in the feldspar pseudomorphs in various proportions, depending upon the intensity of alteration. Secondary quarts also occurs in nests and mosaic-like aggregates in the groundmass. Biotite may be fresh or may be represented only by concentrations of leucoxene and rutile, which in some grains are arranged along crystallographic directions of the biotite forming a sagenitic structure. Intermediate stages of biotite alteration are bleaching and hydration. In the less intensely altered rock of this phase, the magnetite and ilmenite are rimmed by hematite, but with increasing intensity and closer proximity to the alunite bodies only hematite and leucoxene are found. In the zone of gradation between rocks of the moderate and the feeble phases of alteration alunite is incipiently developed in the feldspar pseudomorphs which are mainly kaolinite with variable amounts of quartz (See Plate 7, C).

Feeble phase of alteration of the calcic latite at the Yellow Jacket deposits is similar in most respects to the feeble phase at the White Horse and White Hills deposits. Specimens were taken in sequence across the east quarry face from the unaltered calcic latite to its highly alunitized equivalent. The least altered rock of the feeble phase still contains in the replaced phenocrysts minor amounts of the original plagioclase. Most of the plagioclase has altered to the fibrous, highly birefringent, mixed lattice illite-montmorillonite clay. Some large fibres may be sericite. Low birefringent kaolinite (?) is also found in minor amounts in the phenocrysts. The mafic minerals have been changed to a highly birefringent fibrous mass that is light brown in plane light, probably nontronite or an iron rich mixed lattice clay. Nests of quartz and clusters of mixed lattice clay are scattered in the groundmass most of which is relatively unaltered.

A sample, thought to represent the feeble phase alteration in the tuff series, was taken near the Marys Lamb deposit. The rock is light purplish gray due to disseminated hematite dust. Original laminations are still preserved. The rock is microcrystalline but the crystals are too small to identify accurately (presumably they are quartz and feldspar). Tiny acicular crystals of a mica-like or fibrous clay mineral are arranged in a reticulated network in the groundmass. Some larger grains ranging up to 3 mm. in diameter, probably originally feldspar, are now kaolinite. No transitions between this type of rock and either the alunitized or unaltered equivalents have been established because of the widespread alteration.

Moderate Phase

Regardless of the type of rock replaced, either latite flows or tuffs, the most intense alunitic alteration produces an aggregate of alunite kaolinite and quartz with minor hematite and leucoxene. In some deposits halloysite occurs with the kaolinite. Variations in the proportion of these constituents exists from deposit to deposit as well as from place to place in the same alunite body. The sodium and potassium contents of the alunite are also variable, the sodium predominating in some places giving natroalunite.

In the more highly alunitized parts of the alunite bodies, the texture of the replaced country rock is destroyed. This strongly alunitized rock is seen under the microscope to be an aggregate of acicular, bladed or flat plates of alunite, equant grains of quartz, and interstitial and irregular masses of kaolinite. Minor constituents are irregularly dispersed. The grain size is barely discern~~a~~ible with the highest power microscope objective. Some residual quartz grains and zircon crystals are the only recognizable remnants of the original rock.

In the less strongly alunitized parts of the alunite bodies in which kaolinite becomes more abundant, the original rock texture is strikingly preserved. The geometrical outlines of the original phenocrysts are vis~~a~~ible from textural or color contrasts between the groundmass minerals and the minerals occupying the position of the phenocrysts. At the edge of some phenocryst outlines alunite crystals can be seen projecting into the kaolinite which is pseudomorphous after the original feldspar. Other shapes are preserved by contrasts in grain size between the groundmass aggregate and the mineral or minerals occupying the site of the original phenocrysts (See Plate 8, A, B and C). In other specimens the opaque minerals, leucoxene and hematite are found only in the groundmass and set off the feldspar outlines which are free from these constituents. Concentrations of leucoxene and hematite in places outline original biotite crystals.

Other Mineral Bodies Associated with Alunite Deposits

A conspicuous feature at the Yellow Jacket deposit is a zone characterized by gypsum which cuts the alunitized tuff and latite. The gypsum crops out discontinuously along an east-west direction in the saddle in which the alunite deposit is located. In the bulldozer cuts at the eastern extremity of the saddle massive pod-like masses of gypsum occur surrounded by porous, friable, cellulor quartz. The siliceous zone fans outward and upward in the highest exposure of the gypsum zone. In depth the gypsum pods pinch out, but the porous siliceous zone continues downward as can be seen in the tunnel that has been driven beneath this part of the alunite deposit.

Thin sections from the cellular quartz zone reveal that the cell walls are formed by large patchy quartz grains with interstitial, finely granular quartz. The large grains have the appearance of growing at the expense of the smaller ones. One section shows tiny alunite laths dispersed in the finely granular quartz and many of the larger quartz patches containing within their borders small areas composed of alunite needles and finely granular quartz. Alunite needles alone are contained in some of the larger grains, presumably the result of the associated finer-grained quartz having been incorporated into the larger. Another section shows high concentrations of very finely granular alunite in the pores of the siliceous rock, although the rock is still porous. Pods and veinlets of porcellaneous, extremely fine granular alunite are common at the borders of the siliceous sinter zone and perhaps represent regions of alunite solution and reprecipitation.

At the Hindenburg Big Chief deposit, a short distance west of the Yellow Jacket, gypsum mineralization also occurs and is believed to be part of the zone represented at the Yellow Jacket. Here the gypsum appears occurs as anastomosing veinlets and as a replacement of the alunite in the alunitized tuff.

Strongly silicified tuff and breccia form resistant cappings for the knobs and hills surrounding the Yellow Jacket deposit. Iron Peak to the west and Chalcedony Peak to the east are two of the most prominent occurrences. The texture of the original rock is commonly preserved by the finely granular quartz. Porosity is low and the rock is hard and resistant to weathering.

On the slopes below Iron Peak are the Hindenburg alunite deposit on the east and the Krotki mines on the west. Both of these deposits, as well as the Yellow Jacket, show the common features of the occurrence of iron oxide between the alunitized tuff and the silicified capping. Iron oxide is so concentrated beneath the capping at Iron Peak that it has been mined as iron ore in the past. This iron oxide body has been explored by underground workings, but those bodies present beneath other silicified cappings are indicated by the color of the soil.

Chemistry of Alteration

Mineralogic changes

The concentric arrangement of the alteration zones about the principal channelways of the mineralizing solutions can be explained in either of two ways: (1) the alteration zones represent separate periods of mineralization with the alteration of each later period (being) superimposed on the more widespread alteration of the next earlier; or (2) the alteration zones represent one continuous period of mineralization during which all the zones were formed contemporaneously as a result of the gradual change in the nature of the solution outward from the source. The first method is unduly complicated and depends on a series of events that fortuitously produces the regularity of the zonal pattern and alteration chemistry. On the other hand, the second process is simpler and more reasonable than the first and seems to be the best explanation for the alteration at Marysvale. Only a single event is necessary, and the resulting zonal configuration of the wall rock alteration is that expected on a physical and chemical basis.

This concentric zonal pattern of alteration, produced by a continuously flowing hydrothermal solution, has been described recently in great detail by Sales and Meyer (1950). According to their concept, at a specific point of reference located in the wall rock near the vein, successive waves or fronts corresponding to the alteration phases are developed and recorded with the passage of time during the mineralization. The different phases of alteration are thus contemporaneous, and the frontal attacks of each alteration zone on its next outermost neighbor are being made at the same time though at successively greater distances from the channel. So long as active upward circulation takes place within the channel and the composition of the solutions at their source does not greatly change, each zone migrates away from the fissure by growing at the outer edge and simultaneously receding at the innermost edge because of encroachment by the next innermost zone.

Thus to trace the mineral changes from the unaltered rock through the increasingly intense phases of alteration about the alunite bodies and veins is in effect to determine the paragensis of the minerals. Assuming that the veins and the intensely alunitized replacement bodies were channelways from which the altering solutions spread laterally, the wall rock at any fixed position near the original channelway has previously gone through the mineralogic changes characteristic of alteration phases of less intensity. A study of the mineral changes across the zone of alteration should therefore furnish valuable information on its history and chemistry of formation.

In the original regionally altered latitic wall rock, upon which alteration of the feeble phase has been imposed, the carbonate, epidote and some of the chlorite have been destroyed. The plagioclase (somewhat seritized) has been replaced by illite-montmorillonite mixed layer lattice clay and kaolinite. The biotite has become bleached and has lost its pleochroism, probably a progression toward illite.

In the zone of moderate phase alteration the rocks of the feeble phase have been changed to an aggregate of kaolinite, alunite and quartz. The mixed-layer lattice illite-montmorillonite clay in the original feldspars phenocrysts has been replaced by kaolinite, alunite and quartz. Only streaks of leucoxene and rutile mark the site of the once present biotite. Chlorite has been destroyed.

The more intense alteration produces a highly silicified and alunitized rock at the expense of the kaolinite.

Gains and losses of constituents

Unfortunately at the time of this writing complete analytical data and bulk and powder densities are not available for precise quantitative treatment of the gains and losses of constituents in the alteration zones. However, with the few analyses on hand and with a knowledge of the mineralogy of the altered rock, a qualitative interpretation can be made. Table 1 gives the analyses of the vein alunite, the silicified and alunitized rock next to the vein (intense phase), and the country rock sufficiently remote from the vein to be free from the effects of the alteration associated with the alunite.

Similarly, Table 2 shows the analyses of alunitized and argillized latite and latite country rock at the White Horse replacement alunite deposit.

Differences in porosity among analyzed rocks reduce the preciseness with which the oxide percentages can be compared. The following generalizations are made with this reservation in mind. A comparision of the SiO_2 and Al_2O_3 in Table 1 shows that these percentages have not appreciably changed between intensely altered and the original regionally altered latite breccia at the vein deposits. MgO, CaO, Na_2O, CO_2 have been nearly completely eliminated from the intensely altered rock, and K_2O, H_2O and SO_3 have been added. Some Fe is fixed as FeS_2 though certainly a large decrease in iron is shown. Because of the small percentage of the other oxides, comparisons cannot be safely made.

Although no analyses are available for the feeble and intermediate phases of altered rock for the vein type deposits, the minerals provide an indication of the chemical composition.

In the feeble phase the large amount of illite-montmorillonite mixed lattice clay suggests an increase in K_2O and H_2O. Small amounts of MgO,

TABLE I

Vein Alunite and Wall Rock Analyses

	(a) Host Rock	(b) Intense Phase	(c) Vein Alunite	Theoretical Alunite
SiO_2	57.83	60.15	.22	-
Al_2O_3	13.34	12.82	37.18	36.92
Fe_2O_3	7.21	.07	trace	
FeO	.87	.43		
MgO	1.10	trace		
CaO	5.60	.13		
Na_2O	5.76	.50	.33	
K_2O	1.08	3.75	10.45	11.37
H_2O-	.24	.14	.09	
H_2O+	.95	4.93	12.90	13.05
TiO_2	.96	.62		
ZrO_2	.01	trace		
CO_2	4.73	trace		
P_2O_5	.38	.19	.58	
SO_3		12.75	38.34	38.66
S	.07			
Cr_2O_3	none	none		
MnO	.06	none		
BaO	.10	.03		
FeS_2		3.19		
	100.29	99.70	100.10	100.00

(a) Latite (?) breccia on trail 1,200 feet west of Mineral Products mine. R. E. Stevens, Analyst.

(b) Silicified, alunitized and pyritized latite breccia from Mineral Products main tunnel. R. E. Stevens, Analyst.

(c) Vein alunite from Mineral Products property. W. T. Shaller, Analyst.

CaO, FeO-Fe_2O_3 and Na_2O undoubtedly are contained in the mixed lattice clay, chlorite and bleached biotite, but the quantity of the oxides should be greatly reduced from that of the original latite. SiO_2 released in the replacement of the feldspar by the mixed lattice clay and kaolinite is thought to be represented by some of the secondary quartz in the groundmass and replaced phenocrysts, and may maintain a silica-content close to that in unreplaced rock. The clays have a greater Al_2O_3 content than has the plagioclase, so this percentage is expected to remain at a high level. Sulfur has been added to form pyrite.

The nearly complete loss of CaO and MgO is to be expected in the moderate phase rocks. Iron is fixed as hematite and pyrite, and a little Na_2O may be present in the alunite. The Al_2O_3 content may remain at about the same level as in the feeble phase; that released by the destruction of the mixed lattice clay being taken up by kaolinite and alunite. The presence of the alunite necessarily indicates an increase in SO_3. Some SiO_2 released in the destruction of the mixed lattice clay may be expressed by the increase in groundmass quartz.

The alunite veins, because of their banded and vuggy nature, their purity, their coarse crystallinity and their clearly defined walls are considered to be fissure fillings. The solutions that ascended along these fissures necessarily were rich in SO_3, Al_2O_3 and K_2O, the constituents of alunite. The solutions which migrated laterally from the fissures were capable of adding these constituents to the wall rock, and deficiencies in K_2O and Al_2O_3 and possibly SiO_2 in the alteration zones could have been made up from the solutions. Whether or not oxides, that are common among the alteration minerals, were added, subtracted or recombined can only be determined by precise sampling and calculating of analytical data.

At the White Horse replacement deposit (Table 2) Al_2O_3 and K_2O remain roughly constant in the unaltered biotite latite and feeble and moderate phase altered latite. SiO_2 is reduced in the moderate phase because it is displaced by the large quantity of alunite. MgO and CaO have been subtracted from the altered rock and Na_2O and iron oxide markedly reduced. Only SO_3 and H_2O have been added to the altered rock in appreciable quantities.

Nature of Solutions

Perhaps knowledge of the nature of the mineralizing solutions that formed the Marysvale alunite deposits and the associated rock alteration can be gained from the examination of synthesis and experimental data on minerals which occur in the alteration zones. Minerals of particular interest in this regard are illite, montmorillonite, kaolinite, alunite, chlorite and carbonate.

The work of Noll (Grim, 1953) has shown that kaolinite can form in both acid and alkaline solutions. At temperatures below 300°C. in alkaline solutions in which all of the constituents of montmorillonite were present but in which the proportions of the alkalies and alkaline earths were less than the stoichiometric values, both montmorillonite and kaolinite were formed. In acid solutions at 300°C. only kaolinite was formed regardless of moderate variations in the proportions of K_2O, Al_2O_3 and SiO_2.

Gruner (1939, 1944) has shown that muscovite (sericite) can form in acid solutions from feldspars above 350°C. provided that K and Al are in sufficient concentration. Below 350°C. kaolinite forms if Si:Al is about 1:1. Pyrophyllite is the stable form in acid solutions above 350°C. if the K ion concentration is low. In the presence of excess K ions kaolinite is

TABLE 2

Analyses from the White Horse Replacement Alunite Deposit (a)

	(b) Unaltered Latite	(c) Feeble Phase	(d) Moderate Phase
SiO_2	60.47	64.72	47.88
Al_2O_3	19.29	17.59	20.33
Fe_2O_3	1.27	1.70	.97
FeO	3.93		
MgO	1.54		
CaO	2.28		
Na_2O	3.24	3.43	.10
K_2O	5.11	5.89	4.59
H_2O-	.44	.94	.10
H_2O+	.61	4.67	6.82
TiO_2	.56	1.34	.62
CO_2	.49		
P_2O_5	.02		
SO_3	none	.37	19.60
MnO	.38		
	99.63	100.65	101.01

(a) Willard and Proctor (1946).

(b) Fresh latite on "old road" at south end of White Horse deposit. Cyrus Feldman, Analyst.

(c) Altered latite between alunite lenses on east side of north ore body. Cyrus Feldman, Analyst.

(d) Alunitized latite near south end of north ore body. Cyrus Feldman, Analyst.

converted to muscovite in acid solutions above 350°C. Muscovite can also form in slightly basic solutions at lower temperatures.

Laboratory experiments on the synthesis of alunite (Leonard 1927) show that alunite can be produced in acid solutions. In the writer's experiments with synthetic alunite the pH of the alunite forming solution ranged from 3.5 to 1.5 during the course of alunite precipitation.

Carbonates and chlorites are decomposed by acids, although resistance to slightly acid solutions is conceivable. The reaction, $CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2CO_3$ can proceed to the left if the pressure of CO_2 is sufficiently high (Gruner 1944). Chlorite resists decomposition in cold, weak acids but readily decomposes in warm, strong acids.

The environmental conditions favoring the formation of illite and illite-montmorillonite mixed layer clays are little known at the present time. Barshad (1950) has shown that an illite-like mineral is formed from montmorillonite by the substitution of K ions for all exchangeable cations. The same author suggests that expanding lattice clay reported to be associated with the "hydrous mica" is not necessarily montmorillonite as such, but is probably the result of alteration of mica by replacement of K with Ca, Mg and H ions. Inasmuch as the basic crystal structure is similar for micas, hydrous micas and montmorillonoids, the availability of exchangeable cations and the little known chemical nature of the cation containing solution appear to be the sensitive factors that determine which mice-like mineral is formed.

A reasonable conception of the nature of the hydrothermal solutions can be gained by the application of the above experimental data to the alteration minerals associated with the alunite deposits. In the feeble phase of alteration the formation of kaolinite together with the destruction of the carbonate of the original wall rock suggest that the responsible solutions were acid and that the resultant minerals formed below 350°C. The survival of some of the chlorite suggests that the solutions were not strongly acid.

The presence of illite and illite-montmorillonite mixed layer clays provide little conclusive information on the nature of the environmental conditions. It is even possible that the layers of montmorillonite randomly stratified with illite have been produced by the leaching of illite layers and the exchange of cations through the agency of later ground water circulation.

The solutions forming the moderate and intense phase minerals are interpreted to have been more strongly acid than those responsible for the feeble phase alteration. The formation of alunite and the increased proportion of kaolinite at the expense of the illite-montmorillonite mixed lattice clay and chlorite are the bases for this deduction.

The minerals of the alteration phases indicate the progressive increase in acidity of the solutions towards the channelway. The same conclusion is reached if the reaction between the volcanic rock and acid solutions is considered. Inasmuch as feldspathic rocks are alkaline in reaction, acid solutions should be neutralized at some distance from the channelway of the solutions. Conceivably, a pH gradient would then be established from the fringe of solution penetration to the channelway, the pH decreasing in this direction. Of course the nature of the solutions flowing in the channelway is assumed to have remained consistently acid.

Sales and Meyer (1950) report a suite of minerals of alkaline affinities in the fringe zone of alteration, and they suggest that the advancing front of the altering solution was alkaline. The assemblage of chlorite, epidote, sericite and carbonate developed in the Bullion Canyon volcanics is similar to the alkaline suites of these authors, so that if a later alkaline suite of minerals were present they could not be distinguished. In the alunitized and silicified wall rock of the veins (intense phase) shattered quartz veinlets are cross-cut by alunite veinlets and are clearly the oldest structures in the altered rock (See Plate 4). The possibility exists that these quartz veinlets represent relicts of an earlier alkaline phase of alteration although all traces of minerals which may have been associated with the quartz have been obliterated by the superimposed alunitic mineralization.

In summary, the foregoing data on the synthesis and stability relations of the alteration minerals suggest that the solution in the region of the feeble phase alteration was weakly acid, and its acidity increased progressively through the moderate and intense phases. In the fissure in which the vein alunite was deposited the solution is considered to have been the most acid, and in addition to silica, the solution was rich in all of the constituents of alunite. The temperature was probably below 350°C.

Origin of Alunite

Vein deposits

The vein deposits are pictured as having been formed from hydrothermal solutions that ascended along fissure zones. The sharply-defined walls, the banded and comb structure and vuggy nature of the alunite indicate that the veins are fissure fillings.

A possibility exists that the ground was prepared for later alunite deposition by the earliest solutions that ascended along fractures at the site of the present alunite veins. These solutions deposited quartz and doubtless silicified the volcanic country rock to some degree. All evidence of this earlier mineralization is obliterated by the later alunitic alteration, except for dismembered cherty quartz veinlets which are displaced by alunite veinlets in the silicified and alunitized wall rock. The early silicification may have rendered the tuff sufficiently brittle along the fracture zones to promote the formation of open fissures. Periodic opening and fracturing of the rock in the fissure zone is evidenced by the complex cross-cutting nature of the alunite veinlets and the stockwork-like structure of the vein system.

The symmetrical zoning of alteration minerals is interpreted as representing one continuous period of mineralization during which all zones were formed contemporaneously as a result of the gradual change in the chemical and physical nature of the solution outward from the channelway. As long as the solution continued to flow in the channelway, the fringe of solution penetration continued to advance outward, and consequently so did each reacting front of the alteration phases.

Stability relations and environmental conditions of formation of the alteration minerals afford information on the nature of the mineralizing solution. At the outer edge of the alteration halo (feeble phase) the solution was only slightly acid, a fact evidenced by the destruction of carbonate and by the preservation of some of the chlorite. The increased abundance of kaolinite and alunite and the destruction of chlorite and mixed lattice clay indicate that toward the vein the solution was progressively more strongly acid. The temperature of formation is inferred to have been was below 350°C. because kaolinite instead of muscovite or pyrophyllite was formed in the acid solution.

The mineralizing solution was rich in K_2O, Al_2O_3 and SO_3, and probably contained H_2S and SiO_2. Other constituents in the solution are not clearly recorded. SO_3 and K_2O of the altered wall rock are in excess of the proportions originally present in the unaltered rock and therefore were derived in part from the solution. The amount of vein alunite requires that large quantities of Al_2O_3, SO_3 and K_2O were introduced by the solution at the level of deposition. The presence of H_2S is suggested by the formation of minor amounts of pyrite presumably produced by the reaction between iron oxide released from mafic silicates and H_2S. Whether or not the constituents in the solution were derived in part from the underlying shale of pre-Tertiary formations is not known.

After the deposition of alunite minor fracturing occurred in the veins and wall rock. These fractures were filled with kaolinite, the final phase of the acid mineralization.

Replacement deposits

The replacement alunite deposits are also believed to have been formed by hydrothermal solutions. The circumferential distribution of the deposits about the quartz monzonite intrusion suggests a genetic relation with the intrusive. However, the size, shape and grade of the deposits, the general restriction of the deposits to originally porous horizons and the structures that control the sites of replacement suggest that the details of origin are different from those of the vein deposits.

The hydrothermal solutions are believed to have either ascended along fractures from the magmatic source to the tuffs or to vesicular zones, where they spread laterally and caused the widespread alunitization, or migrated directly into the porous horizons at their contact with the intrusion. Evidence that fissure zones intersected the tuff and furnished channelways for solutions is found in the calcic latite flow at the Yellow Jacket deposit. This flow is characteristically altered along an east-west zone in which gypsum and siliceous sinter also are found. The overlying tuff is most strongly alunitized near the zone which suggests that the solutions entered the tuff at this place.

The lateral flow of solutions in the porous horizons may have been effectively directed by such structures as flowage folds or zones of high permeability. More intense mineralization was caused in these places.

The feeble and moderate phases of alteration of the replacement deposits are similar in most respects to the corresponding phases of alteration in the vein deposits, and consequently the chemistry of the solutions is also similar. Chemical analyses indicate, however, that SO_3 and H_2O are the only constituents that were necessarily added to the unaltered rock to form the deposits.

The mineralization of the replacement deposits is believed to have taken place closer to the surface than the mineralization of the alunite veins. The much finer grained nature of the alunite in the replacement deposits suggests lower temperature and pressure during formation, a condition attainable nearer the surface.

Discussion of previous hypotheses

A review of the hypotheses for the origin of alunite as well as alunite occurrences are given by Ransome (1909), Butler and Gale (1912) and Knizek and Fetter (1950). Ransome, who has discussed the origin in greatest detail, considers three possible modes of formation: (1) the direct volcanic hypotheses, (2) the hypotheses of formation resulting from oxidation of pyrite and (3) the hypotheses of simultaneous solfatarism and oxidation. These hypotheses are mainly concerned with the origin of the sulfate in the solution, and are so broad in their coverage of origin that their application is apt to be misleading. It therefore seems advisable to define these hypotheses and discuss their application to the Marysvale deposits in light of the data that has been produced in this study.

The direct volcanic hypothesis admits the formation of alunite from solutions of volcanic origin which are charged with sulfuric acid and are directly evolved from the magma chamber. This hypothesis of origin is applied to the alunite veins at Marysvale, Utah, by Butler and Gale (1912) who make the reservation that the Al_2O_3 and K_2O may have been in part derived from the walls of the fissure at greater depth. A later report by Loughlin (1915) is in agreement with these conclusions. Callaghan (1938) suggests that the constituents of alunite were entirely derived from a magmatic source.

The oxidation of pyrite or the supergene hypothesis for the formation of alunite is maintained for the origin at the type locality, Mount Tolfa, Italy, by Delaunay (in Ransome 1909) and for the deposits of alunite in the oxidized zone at Cripple Creek, Colorado (Ransome, 1909). The oxidation of pyrite produces sulfuric acid solutions which percolate downward and react with the feldspathic rock constituents to form alunite.

Many workers do not believe that acid sulfate solutions directly evolve from the magma source; therefore, mechanisms have been conceived for the production of such solutions at the site of alunite deposition. The hypotheses of simultaneous solfatarism and oxidation was proposed to explain the origin of the alunite and associated metallic ores at Goldfield, Nevada. Conserning this hypotheses, Ransome postulates,

> "....that the ore constituents were brought up in hot solutions charged with hydrogen sulfide, a little carbon dioxide, and probably some alkali sulfides; that the hydrogen sulfide was oxidized at or near the surface to sulfuric acid, which percolated down through the warm rocks to mingle with uprising currents carrying sulphydric acid; and that the precipitation of the richest ores took place in the zone where two kinds of solutions mingled and as a consequence of such mingling."

A means of producing sulfuric acid in the absence of atmospheric oxygen from alkaline solutions bearing sulfur or sulfur compounds was proposed by Butler (1919). The process requires the attac~~h~~k of sulfur on ferric compounds oxidizing the sulfur to form sulfuric acid with water of the solution and reducing the iron to the ferrous state.

Graton (1936) proposed another process whereby the originally alkaline hydrothermal solutions can be converted later to a sulfuric acid solution. This hypothesis is based on the reaction

$$4H_2O + 4S = 3H_2S + H_2SO_4$$

which proceeds to the right under suitable pressure-temperature relationships. The oxygen for such a reaction is furnished by the hydrothermal water, presumably oxidizing the sulfur to SO_3 which forms sulfuric acid. According to Graton this reaction would operate effectively to produce a H_2S bearing sulfuric acid solution if the normal pressure-temperature relationships in the hydrothermal system were altered by the reduction of pressure or the increase in temperature. He maintains that these conditions were obtained in the veins at Cerro de Pasco by the preheating of the country rock and by the abrupt reopening of fissures.

The hypothesis of origin from oxidation of pyrite in both vein and replacement deposits can be eliminated from consideration. As previously pointed out by Butler and Gale (1912) and confirmed in the present study, no evidence is found to indicate the former presence of pyrite in sufficient quantities to account for the great volumes of alunite and alunitized wall rock. Furthermore, fresh pyrite is found in the alunitized rock.

The simultaneous solfatarism and oxidation hypothesis is not applicable to the vein deposits. Diffusion of the sulfate solutions in the groundwater and precipitation of alunite in the zone of mixing between oxygenated groundwater and rising H_2S bearing solutions cannot be pictured as forming the features characteristic of the alunite veins. The veins are sharply defined with banded and comb structure and crop out over a vertical range of 2,000 feet.

The replacement bodies, however, are irregular in shape and are confined to originally porous horizons in the volcanics. If the now alunitized horizons were at the level of active meteoric water circulation at the time of mineralization, oxidation of sulfur compounds introduced at this level would likely result in an acid sulfate solution. On the other hand, if the ascending solutions were in an acid sulfate condition prior to their arrival at the groundwater level, their mixing with oxygenated water would probably produce an acid solution little different from the one derived from oxidation.

In a recent report, Steiner (1953) shows that tuffaceous and arenaceous rocks at Wairakei, New Zealand, are characterized by four alteration zones which decrease in alteration intensity from the surface downward. The uppermost zone contains alunite, kaolinite and opal which are believed to have been formed by sulfuric acid generated by the oxidation of rising H_2S vapors by the descending oxygenated meteoric waters. H_2S is presently escaping from the ground and sulfur is being deposited at the surface. This present day occurrence indicates that oxidation of H_2S bearing solutions by groundwater is a valid process in alunite formation. Although the method is feasible for the formation of the Marysvale replacement deposits, no proof exists that it was the responsible process.

Whether the solutions which formed the vein deposits were acid or alkaline at their inception cannot directly be proved. The information at hand suggests that the solutions were acid at least at the level of observation during the course of wall rock alteration and alunite deposition.

If the theory that the solutions were originally alkaline is entertained, a mechanism, such as that proposed by Butler or Graton, must have been effective to produce sulfuric acid solutions in the hydrothermal system of the veins at the level of alunite deposition. Minerals containing ferrous iron have not been observed in sufficient quantities to produce the required amount of sulfuric acid by the Butler method. However, inasmuch as the reaction proposed by Graton derives all of its constituents from within the hydrothermal fluid, it could have conceivably been effective in producing the acid solutions.

If the solutions which ascended along the alunite-bearing part of the fissures had been originally alkaline and then later changed to acid, a record of this change should be recorded in the wall rock alteration bordering the veins. It is possible that the dismembered quartz veinlets in the alunitized and silicified wall rock of the alunite veins is a relict of an earlier alkaline phase of alteration. The superimposed alunitic alteration, however, masks any evidence of the co-existence of other minerals with the quartz, so that no proof of alkaline alteration exists.

In conclusion, it may be stated that data gathered in this study indicate~~s~~ that acid sulfate-bearing solutions were effective in producing both the vein and replacement alunite deposits. The data do not justify conclusions as to the nature of the solutions beyond the level of observation and alunite deposition. However, for the sake of simplicity and in the absence of any proof to indicate otherwise, sulfate-bearing mineralizing solutions are considered in this study to have ascended from a magmatic source in an acid condition.

Plate 1. -- VEIN ALUNITE

Block from open cut on ridge above Mineral Products mine. Mottled pinkish very fine-grained alunite with vuggy veinlets of coarsely crystalline alunite (dark). Natural size.

PLATE 1

Plate 2. -- VEIN ALUNITE

Typical band of crystalline alunite from vein on main working level of Mineral Products mine. The banding is parallel to the walls of the vein, but the plumose crystals are normal to the banding. Small spots of very fine-grained pinkish alunite appear at the margins of the band. A single vein may be composed of one or a great many of such bands. Natural size.

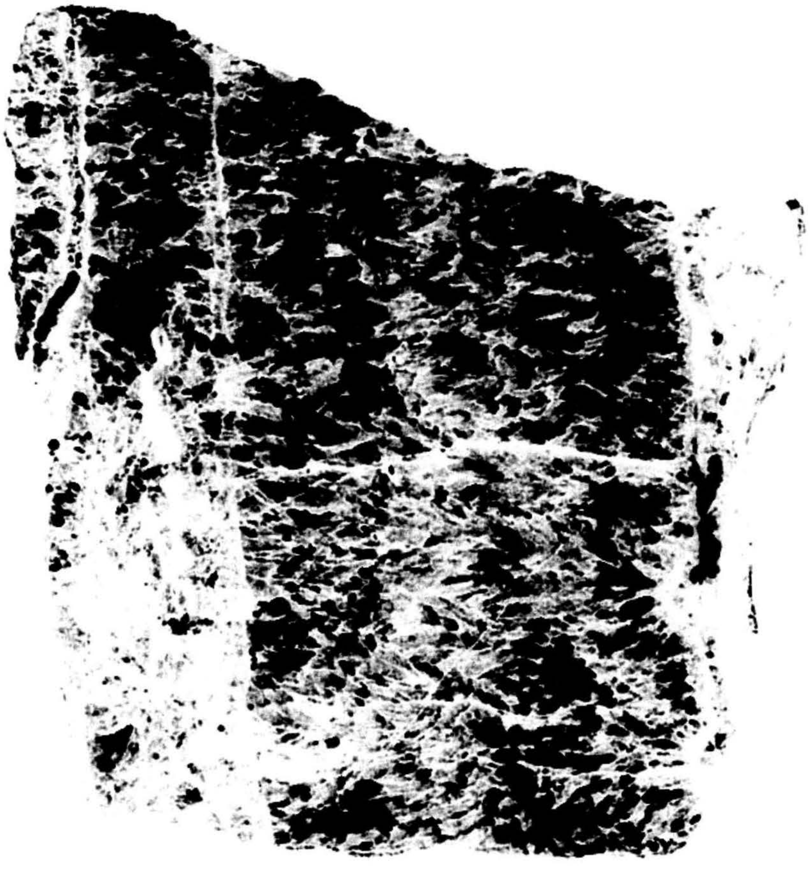


PLATE 2

Plate 3. -- VEIN ALUNITE

Block from vein in Mineral Products mine showing mottled very fine-grained alunite veined by coarse crystalline alunite. Natural size.

PLATE 3

Plate 4. — SILICIFIED AND ALUNITIZED VOLCANIC ROCK VEINED BY QUARTZ AND ALUNITE

Block from upper tunnel of Mineral Products mine. Silicified and alunitized volcanic rock (dark) with quartz veins (slightly lighter) are shattered and invaded by crystalline alunite (light). Alunite veins (banded) have been further fractured and healed by still later alunite which tends to be more vuggy. Natural size.

PLATE 4

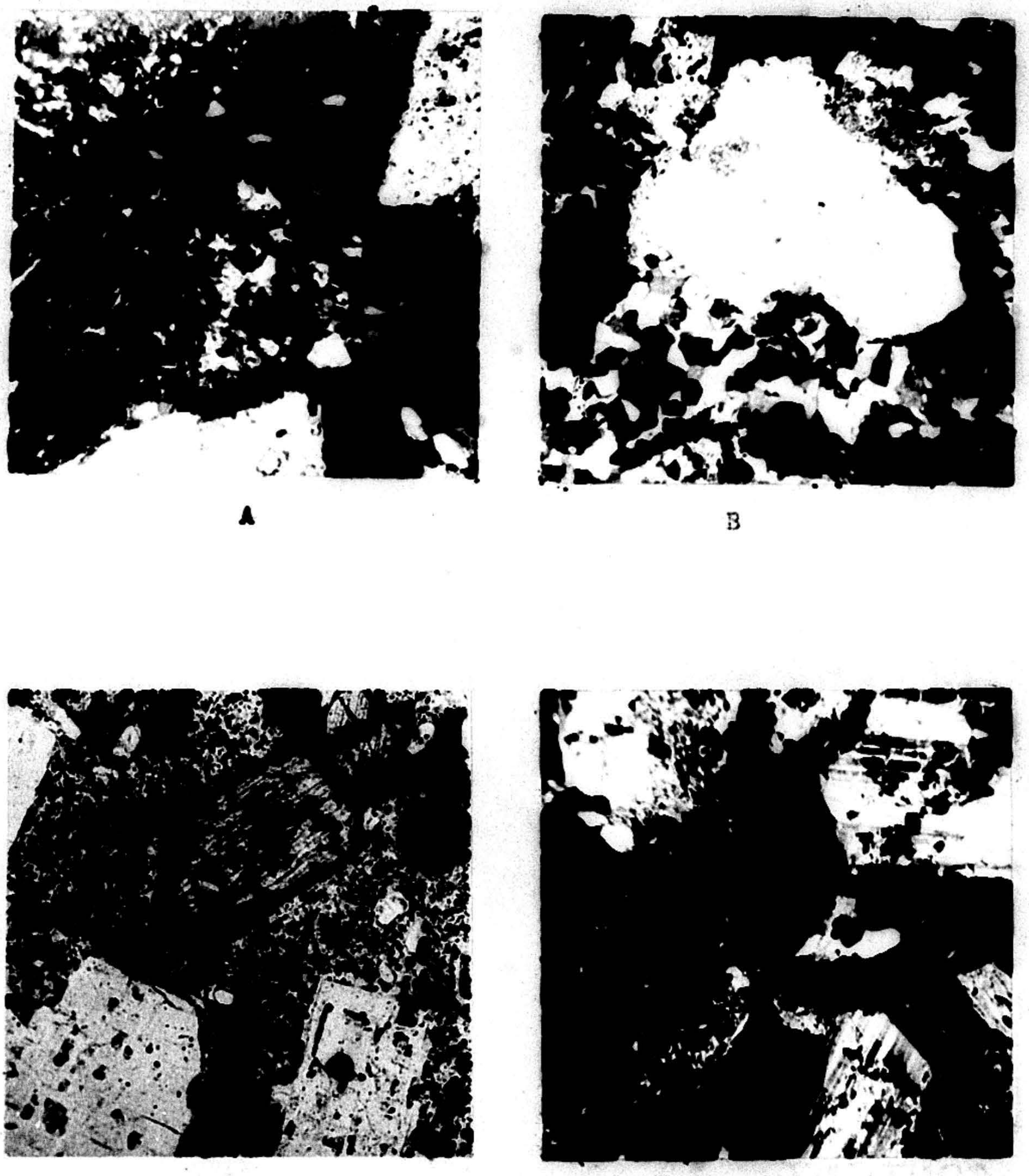
Plate 5. -- HOST ROCKS OF THE ALUNITE DEPOSITS

A. Latite breccia at the L and N deposit. Oligoclase crystal in the upper left-hand corner contains abundant sericite (white). Aggregate in center consists of chlorite (gray) and carbonate (white) which border altered biotite lath. Crossed nicols, X 80.

B. Latite breccis from near the Mineral Products mine. Sericitized oligoclase crystal in center is bordered and replaced in part by carbonate (light gray mottled). Note quartz mosaic left of center. Crossed nicols, X 80.

C. Fresh calcic latite from the Yellow Jacket deposit. Crystals of high relief are augite, and large white crystals are andesine. Chlorite (?) borders large augite grain in center of photograph. Plane polarized light, X 70.

D. Least altered porphyritic latite from the White Horse deposit. Large phenocrysts are sericitized oligoclase. In center of photograph magnetite grain is surrounded by carbonate (light). Some rather large areas of groundmass quartz are in optical continuity. Crossed nicols, X 15.



A

B

C

D

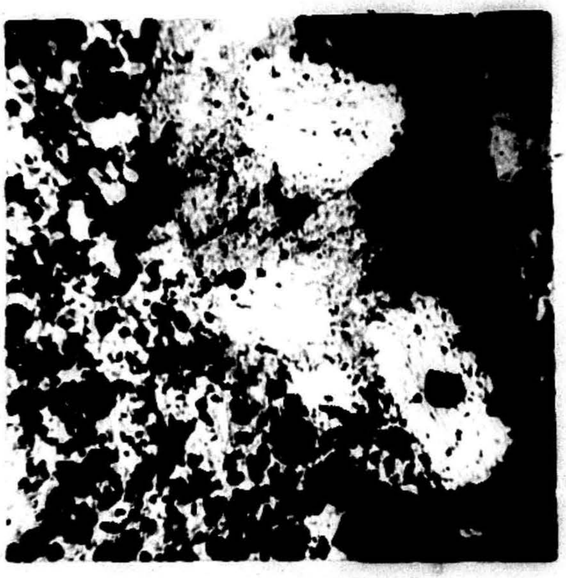
PLATE 5

Plate 6. -- HOST ROCKS OF THE ALUNITE DEPOSITS

A. Fresh porphyritic latite from near the White Hills deposit. Pleochroic brown biotite is surrounded by weakly sericitized plagioclase. Aggregate in center of photograph is carbonate encircled by laths of epidote. Groundmass is microcrystalline aggregate of quartz and orthoclase. Plane polarized light, X 25.

B. Same as A with crossed nicols. Note the large areas of groundmass quartz in optical continuity.

A



B

PLATE 6

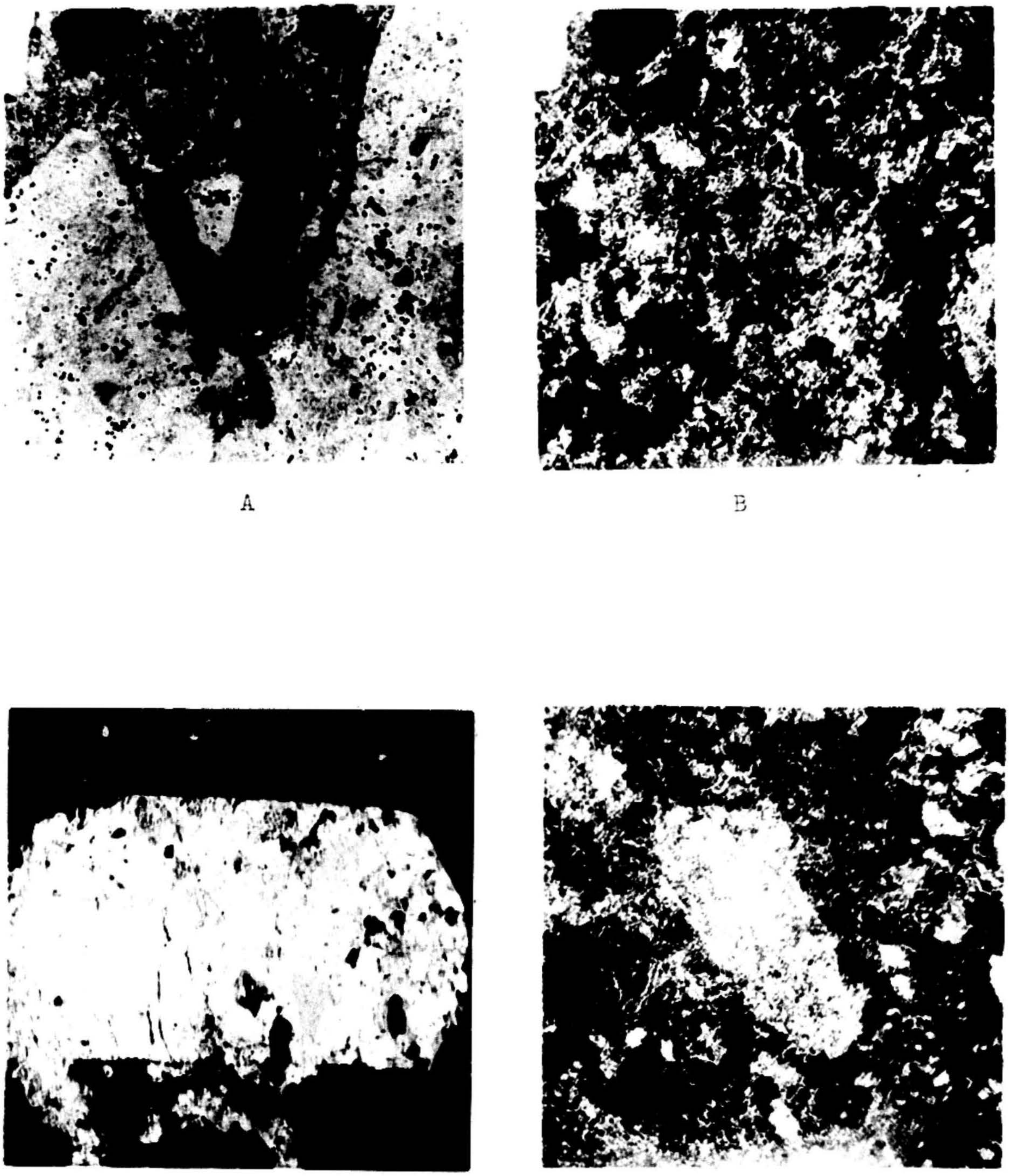
Plate 7. -- FEEBLE PHASE ALTERATION

A. Altered latite breccia from the L and N deposit. Light areas are original plagioclase crystals now replaced by kaolinite (light) and illite-montmorillonite mixed lattice clay (slightly darker). Lath-shaped crystal in upper center is altered biotite, and opaque areas are leucoxene. Plane polarized light, X 70.

B. Same as A with crossed nicols. Fibrous highly birefringent material (white) is illite-montmorillonite mixed lattice clay.

C. Altered phenocryst in porphyritic latite from the White Horse deposit. Left-hand quarter of crystal (light gray) is illite-montmorillonite mixed lattice clay. Kaolinite (irregular patches of darker gray) and quartz (white and gray) comprise the remainder. Crossed nicols, X 30.

D. Altered latite breccia from Mineral Products mine. Relict phenocryst in center of photograph is composed of quartz (light gray) and veinlets and patches of illite-montmorillonite mixed lattice clay (white mottling). The groundmass consists of kaolinite (dark gray) and illite-montmorillonite mixed lattice clay (white mottling) with disseminated quartz. Crossed nicols, X 70.



A

B

C

D

PLATE 7

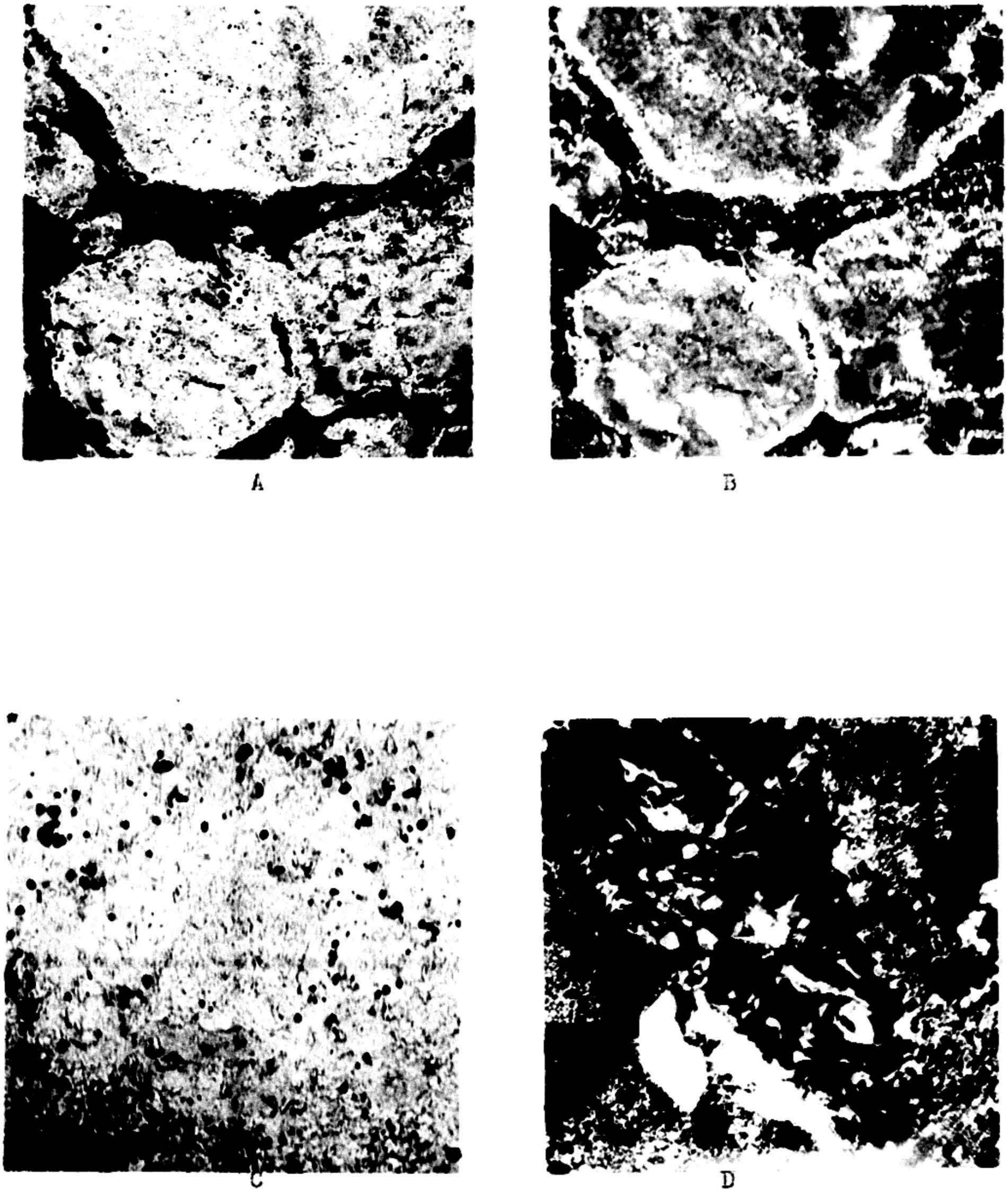
Plate 8. -- MODERATE PHASE ALTERATION

A. Alunitized and kaolinized calcic latite from the Yellow Jacket deposit. Original plagioclase (?) phenocrysts now replaced by kaolinite (gray) and alunite (white). Plane polarized light, X 80.

B. Same as A with crossed nicols. Note the distribution of the alunite (white) within and bordering the relict crystals.

C. Altered latite from the White Horse deposit. Grains of high relief are alunite. Groundmass is composed of microcrystalline kaolinite and quartz. Plane polarized light, X 80.

D. Alunitized, kaolinized and silicified latite breccia from the L and N deposit. Altered phenocryst or breccia fragment in center of photograph is composed of kaolinite (dark) with scattered irregular and acicular crystals of alunite (white). Note that many of the alunite crystals have hollow centers (now filled with kaolinite). Large white grains at bottom are quartz. The groundmass (mottled) is mostly fine-grained quartz with a little kaolinite. Crossed nicols, X 80.



A

B

C

D

PLATE 8

Plate 9. -- INTENSE PHASE ALTERATION

A. Silicified and alunitized latite breccia from the mineral products mine. Light polygonal areas were originally plagioclase crystals which are now completely replaced by alunite. Groundmass (darker) is fine-grained quartz. Black crystal at left is pyrite. Plane polarized light, X 80.

B. Same as A with crossed nicols. Note plagioclase crystal forms preserved by aggregates of bladed alunite crystals.

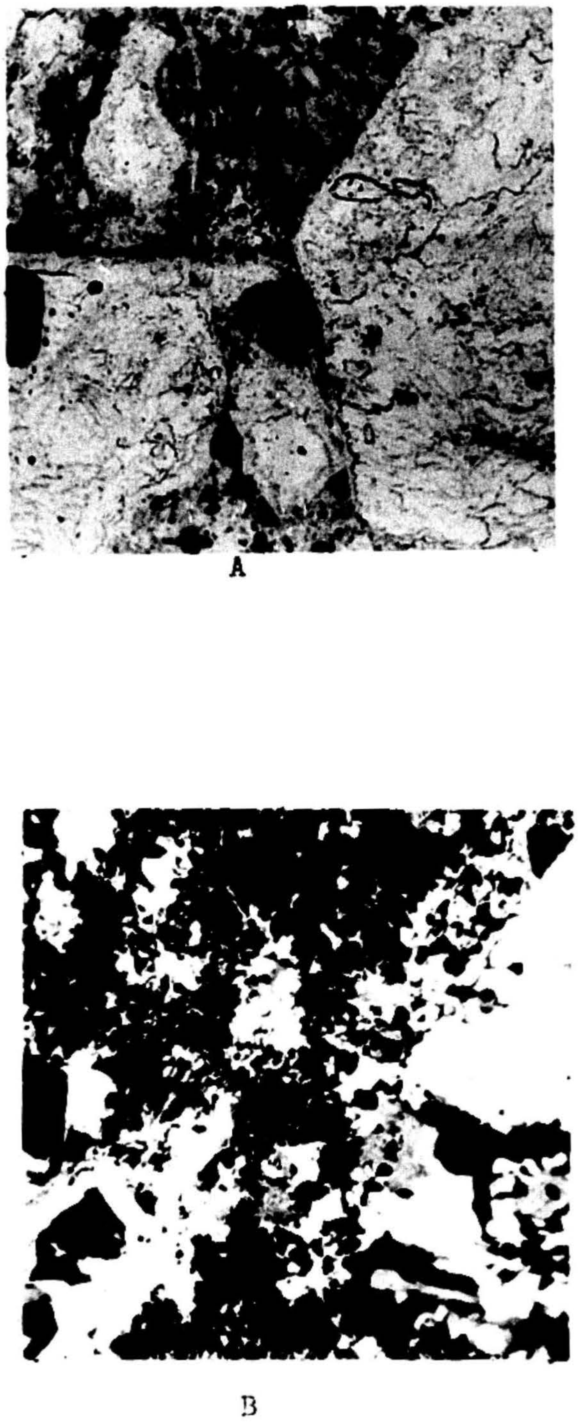


PLATE 9

NATURE OF ALUNITE

Physical Properties and Crystal Structure

The physical properties of alunite, $(K,Na)Al_3(SO_4)_2(OH)_6$, summarized from Palache et. al. (1951) are given in Table 3.

The crystal structure of alunite has been determined by Hendricks (1937) who assigned the mineral to the space group C_{3v}^{5}-R3m. Pabst (1947) however says that alunite may be considered to be in the space group D_{3d}^{5}-R$\bar{3}$m because a center of symmetry is evidenced by the centrosymmetrical disposition of the atoms in the structure about the potassium.

Concerning the distribution of the ions and atoms, Hendricks (1937, p. 780) states,

> "...electrostatic requirements are well satisfied. An Al^{+3} ion is at the maximum possible distance, permitted by the crystal symmetry, from other Al^{+3} ions and near the maximum possible distance from S^{+6} that still permits an Al^{+3} to oxygen of SO_4^{--} distance of ca. 2.0 Å. Aluminum has the expected coordination number, six, being surrounded at the corners of an approximately regular octahedron by four OH groups and two oxygen atoms of SO_4-- ions. The coordination number of potassium is twelve there being six oxygen atoms at 2.80 Å and six hydroxyl groups at 2.85 Å.
>
> Sulfate oxygen atoms on trigonal axes are surrounded by three OH- groups at 2.52 Å, the error being possibly as great as 0.15 Å. It would seem that the hydrogen atoms must be so placed as to give hydroxyl binding to these oxygen atoms since no other ions, other than S^{6}, approach them closely. Hydroxyl groups are near: 2 Al at 2.04 Å. 1 K at 2.58 Å, 1 oxygen at 2.52 Å, 2 oxygen at 2.65 Å, two other hydroxyl groups at 2.65 Å and two other hydroxl groups at 2.68 Å. These distances are near the expected values."

Figure 4 is a perspective drawing of the atoms immediately surrounding the potassium ion.

TABLE 3

Physical Properties of Alunite and Natroalunite

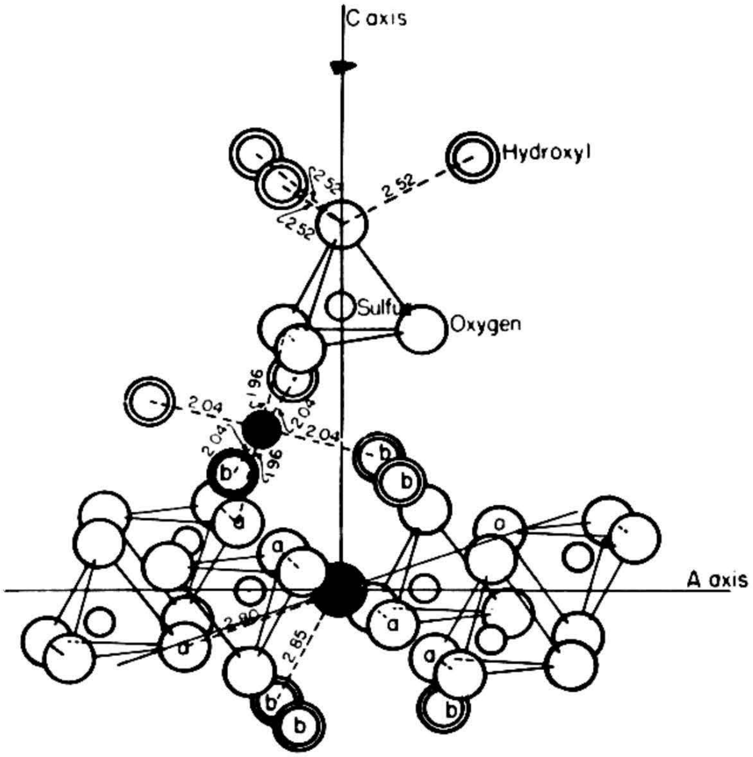
Cleavage ..... (0001) distinct, $(01\bar{1}2)$ in traces
Fracture ..... crystal -- conchoidal, dense masses -- splintery uneven to conchoidol
Hardness ..... 3½ - 4
Specific Gravity ..... 2.6 - 2.9
Lustre ..... vitreous, somewhat pearly on (0001)
Color ..... white, grayish, yellowish, reddish and reddish brown; transparent to semi-translucent
Streak ..... white
Other ..... Strongly pyroelectric
Optical Properties ..... colorless in transmitted light, uniaxial positive; $n_\epsilon = 1.592$, $n_\omega = 1.572$, $n_\epsilon - n_\omega = 0.02$ (alunite); $n_\epsilon - n_\omega = 0.01$, $n_\omega = 1.585$ (natroalunite) (Larson and Berman); Bladed and acicular cyrstals are length fast.

TABLE 4

Data on the Synthesis of Alunite

Sample	K_2SO_4	Na_2SO_4	$Al_2(SO_4)_3 \cdot 18\ H_2O$	H_2O	Time	Calculated (a) K	Na
S-1	1.000g	0.000g	4.000g	150 ml	2 days	100%	0%
S-2	.700	.400	4.000	150	2	58	42
S-3	.600	.490	4.000	150	2	50	50
S-4	.500	.700	4.000	150	2	37	63
S-5	.200	1.000	4.000	150	2 3/4	14	86
S-6	.150	1.500	6.000	200	4	7	93
S-7	0.000	1.500	6.000	200	4	0	100

(a) Computed relative atomic percentages of potassium and sodium in solution.



The surroundings of potassium (large black circles), aluminum (small black circles), and oxygen at 00z. Potassium is at the indicated distances from six oxygen atoms of SO_4 groups (marked *a*) and six hydroxyl groups (marked *b*).

Figure 4.--Perspective drawing of alunite crystal structure from Hendricks (1937, p. 782)

Isomorphous Substitution

Many ionic substitutions are theoretically possible in the alunite series.[1] The substitution of sodium for potassium is commonly recognised and it is likely that phospherous substitutes for sulfur. As much as 0.58 percent P_2O_5 is found in the purest alunite from the Marysvale region (Callaghan 1938, p. 120), but neither its presence as a phosphate mineral impurity nor its presence as a constituent in the alunite structure has been definitely established. According to Hendricks (1937) it may be possible for silicon to replace some of the aluminum atoms if at the same time the electrostatic balance is maintained by the substitution of calcium for potassium. Another possible substitution is suggested by the similarity in ionic radius and charge between trivalent iron and aluminum which would form a transition between the alunite and jarosite series. Such a mineral intermediate in composition between alunite and jarosite is described by Palache et. al. (1951, p. 561).

Here the principal interest is focused upon the alunite-natroalunite relationship because of the significant quantities of both in the Marysvale region. The relation between the crystal structure and the chemical composition and the completeness of ionic substitution of sodium for potassium are problems which have been investigated by the x-ray study of both mineral and synthetic alunites.

---

[1] The alunite series includes alunite in which the content of potassium exceeds sodium, and natroalunite in which the quantity of sodium is greater than potassium (Palache et. al. 1951). /

Synthetic alunite series

Synthetic alunite and natroalunite were prepared in the laboratory to permit a wide range in composition in samples for study and to allow the chemical reactions involved in their precipitation to be applied to the interpretation of the formation of the naturally occurring minerals.

The technique of alunite synthesis used in this study was patterned with certain modifications after that of Leonard (1927). Reagent grade K_2SO_4 and Na_2SO_4 were combined so that the ratio of K to Na was the same as that desired in the alunite product. The potassium and sodium sulfates were added to three times as much as $Al_2(SO_4)_3 \cdot 18\ H_2O$ with an additional 20-30% excess of $Al_2(SO_4)_3 \cdot 18H_2O$ added to promote complete reaction of the sodium and potassium ions. The salts were then dissolved in 150 to 200 ml. of distilled water and allowed to boil 2 to 4 days at atmospheric pressure. A reflux condenser was connected to the flask in order to maintain the boiling solution at a constant level. Data on the particular samples synthesized in the study are given in Table 4. The precipitate was washed, and separated by decanting and centrifuging.

The sulfates which were dissolved in 200 ml. of distilled water registered a pH of 3.0-3.5, but after the precipitation of alunite the pH of the solution was lowered to 1.5-2.0.

Chemical analyses of the synthetic alunite samples are given in Table 5. A comparison of the relative potassium-sodium atomic percentages, calculated from the stoichiometric proportions of the ingredients in the original solution (Table 4), and these percentages, computed from the chemical analyses of the alunite precipitates (Table 5), shows that the final alunite product does not have the same composition as the solution from which it crystallized. All of the samples intermediate in

TABLE 5

Chemical Analyses of the Synthetic Alunite Samples

	S-1	S-2	S-3	S-4	S-5	S-6	S-7
K_2O	9.79	9.31	9.00	8.78	7.33	5.70	.11
Na_2O	.12	.47	.58	.75	1.64	2.74	6.03
Al_2O_3	32.1	32.8	32.6	33.7	34.0	34.7	36.6
SO_3	39.2	38.9	38.6	38.6	38.3	39.2	40.0
Rem(a)	18.79	18.52	19.22	18.17	18.73	17.66	17.26
	100.00	100.00	100.00	100.00	100.00	100.00	100.00
K (b)	98	93	91	89	75	58	1
Na(b)	2	7	9	11	25	42	99

(a) Rem. includes H_2O-, H_2O+ and impurities, computed by difference.
(b) Relative percentages of alkali in the alunite formula computed from chemical analyses, the total alkalies having been summed to 100 percent.

Samples are the same as in Table 4.

TABLE 6

Theoretical Composition of Alunite, Natroalunite, and $(H_3O)Al_3(SO_4)_2(OH)_6$

	Alunite	Natroalunite	$(H_3O)Al_3(SO_4)_2(OH)_6$
K_2O	11.35	-	-
Na_2O	-	7.79	-
Al_2O_3	36.96	38.44	38.83
SO_3	38.65	40.20	40.61
H_2O	13.04	13.56	20.56

composition between the potassic and sodic end members crystallized richer in potassium, and both potassic and sodic end members crystallized with minor amounts of sodium and potassium, respectively. Presumably the source of the sodium and potassium contaminants in the end members was the glass vessel, because only one alkali was introduced into the solution in either synthesis.

The chemical analyses also show that the synthetic samples deviate somewhat from the theoretical composition of alunite. The total alkalies and alumina are deficient and sulfur trioxide and water are in excess of the theoretical values. Because the analyses were made on extremely small samples, slight errors in oxide percentages are to be expected. The excess water, however, is believed to be too great to be ascriped (contributed) to analytical errors and minor compositional irregularities. Part of the excess is probably due to the fact that combined water, absorbed water and impurities are totaled together in computing this constituent by difference from the chemical analyses. Some of the excess water is probably also present as oxonium ions (H_3O^+) which may occupy some of the potassium positions in the crystal lattice. Isomorphous substitution of H_3O^+ for K^+ and NH_4^+ in jarosite and ammoniojarosite (iron-bearing analogues of alunite) has been demonstrated by Shishkin (1950, 1951). The effective ionic radius of H_3O^+ is given in the same reports as 1.32-1.35 Å, a value nearly identical with radius of K^+. Inasmuch as very few studies have been made on the oxonium ion in crystalline compounds, its ionic radius may not be precise. The theoretical compositions of alunite, natroalunite and the H_3O^+ bearing analogue of alunite are given in Table 6 for comparison with the analyzed compositions.

The x-ray patterns of the synthetic samples, discussed in a later section of this report, are so similar to those of natural alunite that little doubt exists that the synthetic specimens have the alunite structure.

Natural alunite samples

Chemically analyzed alunite and natroalunite ore samples were selected on the basis of their relative potassium-sodium atomic percentages to represent the range of composition of potassium and sodium bearing alunites (Table 7). The samples commonly contain admixtures of other minerals which have been identified by optical, x-ray and differential thermal analysis methods. Kaolinite (and halloysite), quartz (and opal), and alunite (or natroalunite) are the principal constituents with minor amounts of hematite, leucoxene (and rutile) and gibbsite. The chemical analyses were recomputed in terms of these minerals, and the relative atomic percentages of potassium and sodium in the alunite and natroalunite are used as a basis for comparing the lattice constants. Table 7 also gives the recomputed percentages of the constituents in the samples. Small deficiencies and excesses of certain oxides occur in the recomputation of some of the analyses. These irregularities may be due in part to the presence of small amounts of amorphous material such as allophane or other undetected substances or they may be due to slight errors in quantitative analysis.

TABLE 7

Chemical Analyses and Computed Constituents of some Marysvale Alunite Ores

Sample No.	1	2	3	4	5
SiO_2	31.72	.22	10.85	30.04	27.10
Al_2O_3	25.14	37.18	38.50	23.98	28.70
Fe_2O_3	.57	tr.	-	4.32	-
Na_2O	.14	.33	.26	.25	.38
K_2O	7.15	10.46	7.90	6.90	6.75
TiO_2	.86	-	-	.78	-
P_2O_5	-	.58	-	-	-
SO_3	24.62	38.34	29.30	23.67	23.41
H_2O+	9.81	12.90	13.33	9.11	9.50
H_2O-	.06	.09	.10	.22	.10
	100.07	100.10	100.24	99.27	98.73
$(K,Na)_2O.3Al_2O_3\cdot 4SO_3\cdot 6H_2O$	63.7	100.2	75.4	61.2	67.5
$Al_2O_3\cdot 2SiO_2\cdot 2H_2O$	3.9	-	26.3	3.4	6.5
SiO_2	30.0	.2	-	28.5	24.1
Impurities (a)	+2.47	+ .6	- 1.56	+6.17	+ .63
K (b)	97.5	96.0	96.0	95.0	92.0
Na (b)	2.5	4.0	4.0	5.0	8.0
Excess (K,Na) (c)	2.5	- -	-	3.9	-
Deficiency(K,Na) (c)	-	3.4	3.7	-	4.9

(a) The impurities consist of hematite, leucoxene, gibbsite. Negative values indicate quantitative deficiencies in some oxides in the calculation of the indicated minerals.

(b) Represents the relative percentages K and Na indicated in the alunite formula, Na+K= 100%.

(c) The percentage of total K and Na (summed to 100%) that is greater or less than the amount required to combine with the SO_3.

TABLE 7 continued

Sample No.	6	7	8	9	10	11
SiO_2................	34.80	4.65	42.56	38.14	4.38	43.78
Al_2O_3...............	24.40	37.70	22.67	23.32	37.32	24.80
Fe_2O_3...............	.24	-	.16	7.32	.36	.81
Na_2O................	.67	1.12	1.18	1.30	3.77	3.11
K_2O.................	6.49	8.25	5.26	2.54	4.46	1.04
TiO_2................	.35	-	.69	1.60	.10	.62
P_2O_5................	-	-	-	-	-	-
SO_3.................	23.41	34.00	20.50	15.40	34.95	16.86
H_2O+................	8.28	13.00	7.30	8.76	13.77	8.61
H_2O-................	.16	.10	.08	.92	.56	.34
	98.80	98.82	100.40	99.30	99.67	59.97
$(K,Na)_2O.3Al_2O_3.4SO_3.6H_2O$......	50.2	88.1	52.4	39.1	88.3	43.7
$Al_2O_3.2SiO_2.2H_2O$....	4.4	13.0	8.0	21.4	9.8	21.9
SiO_2................	42.4	-	38.8	28.2	-	33.6
Impurities (a)......	+1.80	-2.28	+1.2	+10.6	+1.57	+ .77
K (b)...............	86.0	83.0	74.6	56.2	44.0	18.
Na (b)..............	14.0	17.0	25.4	43.8	56.0	82.
Excess (K,Na) (c)...	8.4	-	14.7	0	0	13.1
Deficiency(K,Na)(c).	-	.6	-	0	0	-

1. Sample from Yellow-Jacket deposit at northeast corner of lower excavation in quarry. J. G. Fairchild, Analyst.

2. Sample of purest alunite from Mineral Products mine believed to be representative of the material analyzed by W. T. Schaller.

3. Sample from L and N deposit taken across 4.3 feet on face of west drift in tunnel on south slope. R. K. Bailey, Analyst.

4. Sample from Yellow Jacket deposit taken across 4.8 feet as same location as #1. J. C. Fairchild, Analyst.

5. Sample from L and N deposit taken across 9.4 feet crystal vein in T-shaped cut above big tunnel cut. R. K. Bailey, Analyst.

6. Sample from White Horse deposit taken as channel sample horizontally across 11.5 feet in upper cut of main quarry. R. E. Stevens, Analyst.

7. Sample from Sunshine deposit taken at south side of rise from tunnel at northwest end of glory hole. R. K. Bailey, Analyst.

8. Sample from Aluminum Bar deposit in pit at elevation 9,860 feet. J. J. Fahey, Analyst.

9. Sample from Al Kee Mee deposit taken across 6.5 feet on south wall of short tunnel, 33 feet from portal. J. G. Fairchild, Analyst.

10. Sample from Al Kee Mee deposit taken vertically across 1.1 feet of alunite vein at portal of tunnel. J. G. Fairchild, Analyst.

11. Sample from Big Star deposit taken through 9.2 feet on south side of main quarry. R. E. Stevens, Analyst.

X-ray study of synthetic and natural alunite

In order to obtain a more satisfactory resolution of lattice spacings, the samples were examined with the Norelco x-ray diffractometer set to traverse at the rate of one-fourth degree (2θ) per minute. A chart speed of 15 inches per hour and copper radiation were used exclusively.

The instrument was standardized using silcon powder furnished by the manufacturer, and the observed interplanar spacings agreed within 0.01° (2θ) of the standard values. This value is the same ar the error of measurement and the deviation from standard values may be due mostly to the measuring error.

The reproducibility of peak measurements was determined to be ±0.0015 Å (±0.015° 2θ) for 0006 in natural alunite and synthetic samples. In natroalunite the reproducibility was ±0.003 Å (±.03° 2θ) for this reflection because of poorer definition of the peak. The error in computing the c lattice constant, c_o, is therefore 6 times as great, or ± 0.0009 Å for natural and synthetic alunite and ±0.018 Å for natroalunite. The reproducibility of 2240 in all of the samples was ± 0.00045 Å (±0.015° 2θ), an error of ± 0.0018 Å in determining a_o, the a lattice constant. The Bragg angle for 0006 is about 15.5°, and that for 2240 about 26.2°. It is realized that greater accuracy in the determination of lattice constants could be obtained from reflections of higher Bragg angle, however the reflections in the high angle region for many of the alunite samples examined were weak and poorly resolved, and thus were unsuitable for lattice computations. The value of the c and the a lattice constants respectively for alunite are given by Hendricks as 17.385 Å (17.35 KX) and 6.974 Å (6.96 KX) in contrast to 17.310 Å and 6.977 Å determined in the present study.

The previous study of Pabst (1947) gives indices for the reflections in the alunite pattern so that it is possible to correlate many of the diffraction lines with those of the synthetic mineral. By using the 0006 and 22$\bar{4}$0 reflections the unit cell dimensions, a_0 and c_0 were calculated.[1] The cell dimensions were checked and the validity of the indexing for each synthetic alunite was established by comparing the calculated $\sin^2\theta$ with the observed $\sin^2\theta$ value for each line of the diffraction patterns using the formula:

$$\mathrm{SIN}^2\theta_{hkl} = \frac{\lambda^2}{3a^2}(h^2+hk+k^2)+\frac{\lambda^2}{4c^2}l^2$$

Natural alunite and natroalunite were also indexed in this manner to confirm the assignment of indices to diffraction lines which were present in the diffractometer patterns but not observed in the powder diffraction films of Pabst. Fig. 5 shows the diffractometer patterns of natural and synthetic alunite in diagrammatic form in order that diffraction line shifts, indices and intensities can be compared. Table 8 shows the same data in tabular form, together with the observed and calculated values of Pabst.

The unit cell dimensions, a_0 and c_0, clearly show the effect of compositional differences in alunites. Table 9 gives the lattice constants for alunite and natroalunite along with the constants for several synthetic specimens. The same data ~~is~~ are plotted in Figs. 6 and 7 as curves showing the relation between the unit cell dimensions and the relative sodium-potassium atomic percentages of the samples.

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[1] Although alunite is rhombohedral, it is here referred to hexagonal axes to simplify calculations.

TABLE 8

X-ray Diffraction Data for Natural and Synthetic Alunite and Natroalunite Samples

Sample #2[(a)] Mineral Products Alunite

hkil	Observed $\sin^2\theta$	Calculated $\sin^2\theta$	Observed d	I
$00\bar{0}3$	.0179	.0178	5.757	28
$10\bar{1}1$	.0182	.0182	5.702	15
$01\bar{1}2$	.0242	.0242	4.948	53
$11\bar{2}0$	.0488	.0487	3.486	21
$11\bar{2}3$	.0665	.0666	2.984	100
0006	.0714	.0713	2.884	106
$02\bar{2}4$	.0969	.0967	2.473	6
$10\bar{1}7$	.1131	.1133	2.291	81
$12\bar{3}2$	.1216	.1217	2.208	6
$11\bar{2}6$		.1200		
$01\bar{1}8$	.1432	.1430	2.040	2
$21\bar{3}4$	.1453	.1454	2.021	1.5
$30\bar{3}0$		.1462		
$00\bar{0}9$	.1603	.1604	1.923	
$30\bar{3}3$	.1640	.1641	1.902	
$20\bar{2}8$	.1924	.1917	1.761	2.3
$22\bar{4}0$	.1949	.1950	1.744	16
$21\bar{3}7$	.2095	.2108	1.683	2
$11\bar{2}9$		.2081		
$13\bar{4}1$	.2138	.2132	1.665	1.5
$30\bar{3}6$		.2175		
$31\bar{4}2$	.2189	.2192	1.646	2
$12\bar{3}8$	.2404	.2405	1.570	2
$31\bar{4}5$	.2607	.2608	1.508	4
$02\bar{2}10$	.2628	.2630	1.502	36
$22\bar{4}6$	.2660	.2663	1.492	9

(a) Sample number is the same as in Table 7.

TABLE 8 continued

Tolfa, Italy Alunite[(b)]

hkil	Calculated		Observed	
	d	I	d	I
$00\bar{0}3$	5.795	1		
$10\bar{1}1$	5.70	38	5.76	.30
$01\bar{1}2$	4.956	59	4.99	.65
$10\bar{1}4$	3.53	3		
$11\bar{2}0$	3.488	62	3.51	1.05
$01\bar{1}5$	3.02	16		
$11\bar{2}3$	2.991	424	3.01	2.80
$02\bar{2}1$	2.98	138		
0006	2.898	23	2.90	.55
$20\bar{2}2$	2.854	0		
$02\bar{2}4$	2.479	54	2.49	.65
$10\bar{1}7$	2.297	148	2.29	2.40
$20\bar{2}5$	2.281	28	2.26	.95
$21\bar{3}1$	2.264	14		
$11\bar{2}6$	2.231	5	2.21	.25
$12\bar{3}2$	2.208	35		
$01\bar{1}8$	2.046	12	2.04	.20
$21\bar{3}4$	2.022	0		
$30\bar{3}0$	2.014	2		
$00\bar{0}9$	1.932	9		
$02\bar{2}7$	1.918	18		
$12\bar{3}5$	1.908	0	1.90	3.30
$03\bar{3}3$	1.901	133		
$30\bar{3}3$		4		
$22\bar{4}0$	1.744	145	1.75	2.90
$20\bar{2}8$	1.702	1		

(b) Data from Pabst (1947) converted from KX to Å.

TABLE 8 continued

Sample # S-5(c) Synthetic Alunite

hkil	Observed $\text{Sin}^2\theta$	Calculated $\text{Sin}^2\theta$	Observed d	I
$10\bar{1}0$	.0182	.0182	5.706	9
$01\bar{1}2$	.0244	.0244	4.929	56
$11\bar{2}0$	.0485	.0484	3.500	32
$11\bar{2}3$	.0669	.0669	2.978	100
0006	.0739	.0740	2.833	5
$02\bar{2}4$	.0976	.0975	2.467	25
$10\bar{1}7$	.1169	.1168	2.251	23
$12\bar{3}2$	.1211	.1212	2.213	6
0009	.1662	.1665	1.889	4
$30\bar{3}3$	.1637	.1638	1.903	29
$22\bar{4}0$	.1935	.1937	1.750	19
$31\bar{4}3$	.2181	.2181	1.649	2.5
$12\bar{3}8$	.2440	.2445	1.558	2.5
$31\bar{4}5$	.2610	.2613	1.507	2.5
$02\bar{2}10$	.2696	.2701	1.483	9
$22\bar{4}6$	.2674	.2677	1.488	6

(c) Sample number is the same as in Tables 4 and 5.

TABLE 8 continued

Sample # S-7(c) Synthetic Natroalunite

hkil	Observed Sin²θ	Calculated Sin²θ	Observed d	I
$10\bar{1}1$	.0184	.0183	5.706	4
0003	.0193	.0192	5.552	4
$01\bar{1}2$	.0247	.0247	4.902	93
$11\bar{2}0$	.0486	.0486	3.494	30
$10\bar{1}4$	.0504	.0503	3.433	3
$02\bar{2}1$	.0670	.0669	2.977	60
$11\bar{2}3$	.0677	.0677	2.971	100
$01\bar{1}5$	.0694	.0694	2.922	15
$20\bar{2}2$	.0736	.0733		
0006	.0767	.0767	2.782	10
$02\bar{2}4$	.0989	.0988	2.449	3
$20\bar{2}5$	.1183	.1180	2.238	3
$10\bar{1}7$	.1206	.1206	2.218	38
$12\bar{3}2$		.1218		
$30\bar{3}3$	.1646	.1649	1.897	35
$02\bar{2}7$	.1690	.1692	1.873	4
0009	.1725	.1725	1.854	70
$22\bar{4}0$	.1941	.1943	1.748	22
$31\bar{4}2$	.2189	.2190	1.646	6
$13\bar{4}4$	.2443	.2446	1.557	3
$12\bar{3}8$	.2496	.2496	1.541	6
$40\bar{4}1$	.2610	.2611	1.507	3
$22\bar{4}6$	.2712	.2710	1.479	6
$02\bar{2}10$	.2777	.2777	1.461	15

(c) Sample number is the same as in Tables 4 and 5.

TABLE 8 continued

Sample #10(a) Al Kee Mee Natroalunite

hkil	Observed Sin²θ	Calculated Sin²θ	Observed d	I
$10\bar{1}1$	.0184	.0184	5.683	17
0003	.0192	.0191	5.572	11
$01\bar{1}2$	.0248	.0248	4.897	64
$11\bar{2}0$	.0489	.0489	3.482	32
$10\bar{1}4$				
$02\bar{2}1$	.0674	.0673	2.969	100
$11\bar{2}3$		.0680		
$01\bar{1}5$				
$20\bar{2}2$				
0006	.0765	.0764	2.787	21
$02\bar{2}4$				
$20\bar{2}5$				
$10\bar{1}7$	.1203	.1203	2.221	38
$12\bar{3}2$				
$30\bar{3}3$	.1655	.1656	1.893	32
$02\bar{2}7$	.1689	.1691	1.874	6
0009	.1723	.1719	1.856	7.5
$22\bar{4}0$	.1953	.1954	1.742	25
$31\bar{4}2$	.2200	.2202	1.642	4
$11\bar{2}9$		.2208		
$13\bar{4}4$				
$12\bar{3}8$	.2499	.2497	1.540	4
$40\bar{4}1$				
$31\bar{4}5$	.2639	.2648	1.501	11
$22\bar{4}6$				
$02\bar{2}10$	.2774	.2773	1.462	13

(a) Sample number is the same as in Table 7.

TABLE 9

Lattice Constants of Natural and Synthetic Alunite and Natroalunite

Sample # [(a)]	a_o	c_o
1	6.977	17.310
2	6.977	17.310
3	6.974	17.283
4	6.977	17.315
5	6.977	17.294
6	6.977	17.294
7	6.976	17.304
8	6.975	17.288
9	6.972	16.715
10	6.971	16.721
11	6.975	16.711
S-1	7.010	17.105
S-2	7.010	17.068
S-3	7.002	17.063
S-4	7.008	17.052
S-5	7.004	16.989
S-6	7.003	16.926
S-7	6.993	16.685

(a) Samples numbers correspond to those described in Table 4, 5 and 7; Numbers prefixed by S represent synthetic samples.

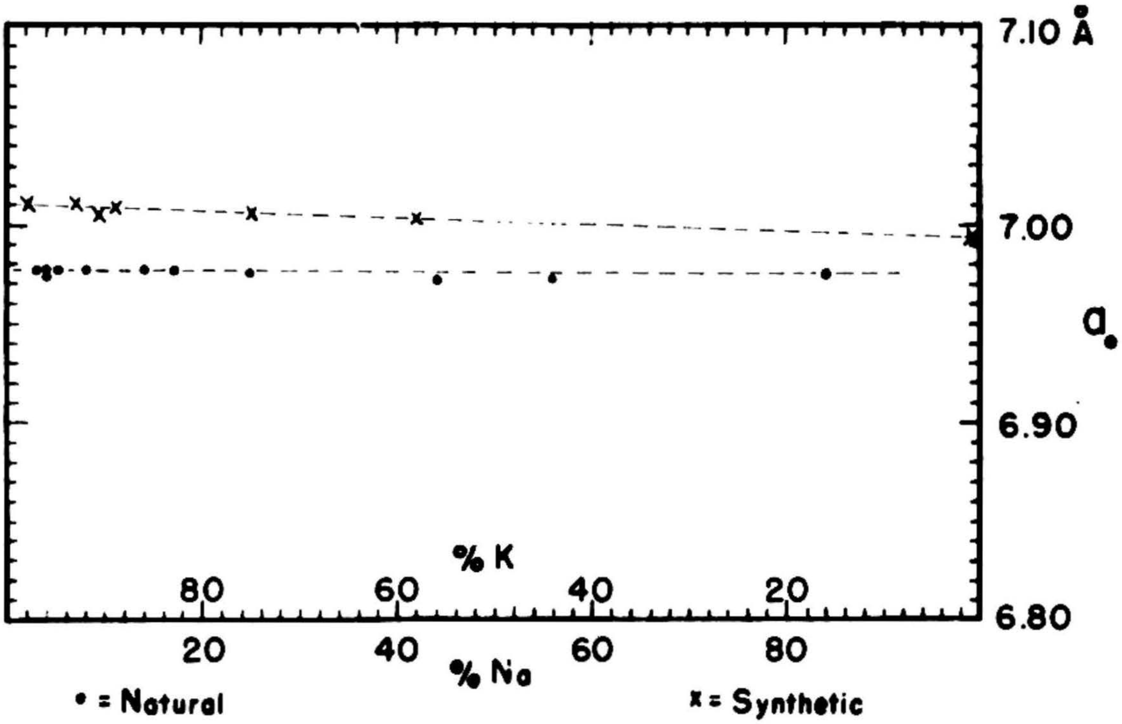

Figure 6.—Variation of the a lattice constant with changes in the relative atomic percentages of potassium and sodium in synthetic and natural alunite and natroalunite.

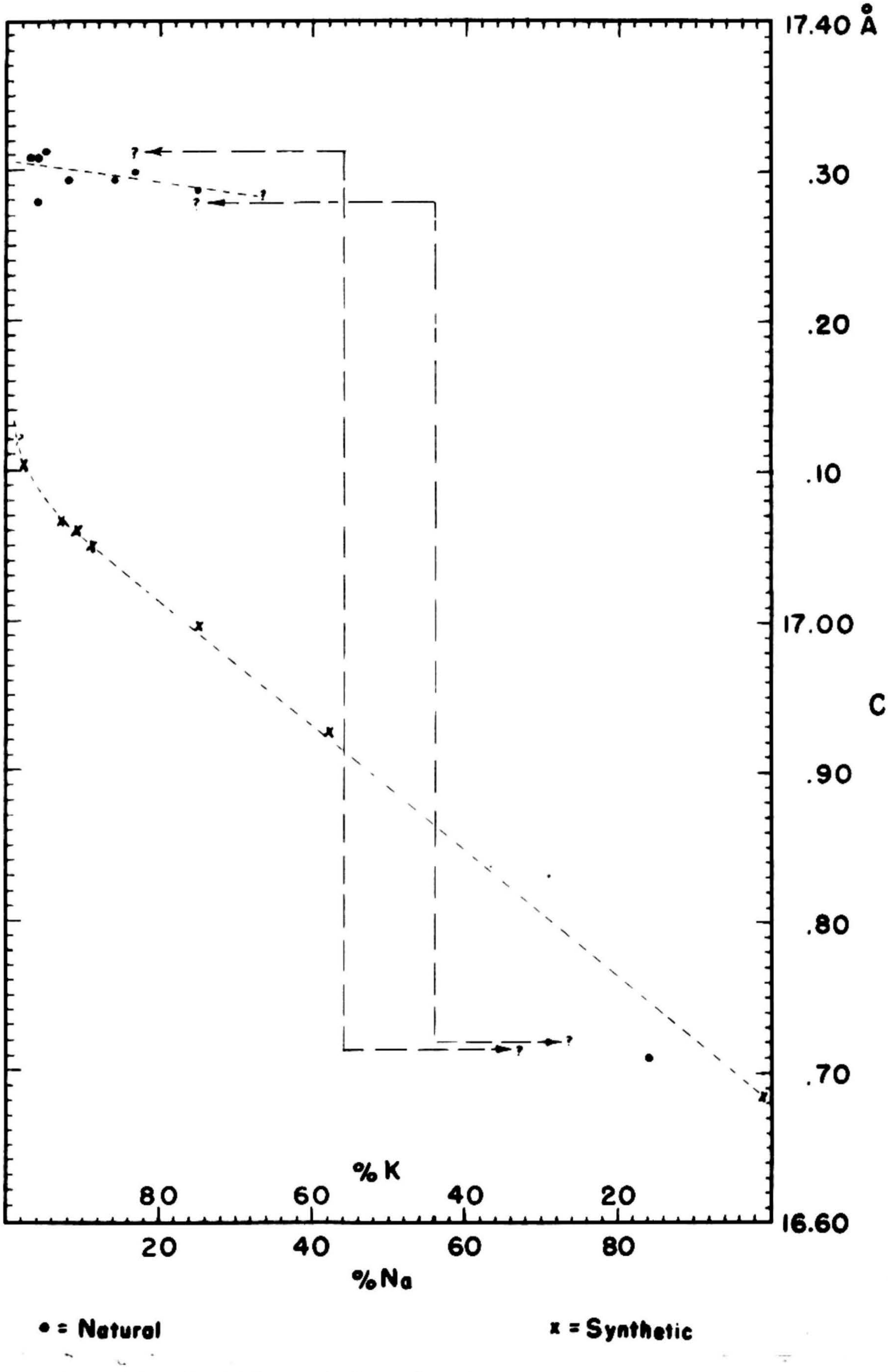

Figure 7.—Variation of the c lattice constant with changes in the relative atomic percentages of potassium and sodium in synthetic and natural alunite and natroalunite.

The naturally occurring samples comprise two groups, one with c_o ranging between 17.31 Å and 17.28 Å, and the other with c_o between 16.71 Å and 16.72 Å. The group of samples characterized by the larger c_o are confined to the potassium side of the diagram between K_{100} and $K_{70}Na_{30}$ and represent the mineral alunite in the true sense. It is noteworthy that nearly all chemical analyses of the Marysvale alunites fall in this region. The plot of the composition vs. c_o defines a line which slopes slightly toward the sodium side of the diagram, suggesting that an isomorphous series exists in this restricted area. Samples characterized by the smaller c_o represent natroalunite and are restricted to compositions near the sodium side of the diagram. However, the limits of the region are not well defined. The two samples in the center of the diagram, upon careful identification of all diffraction peaks proved to be a mixture of alunite and natroalunite. Thus the composition as derived from the analyses is the sum of both types so that the composition of neither can be accurately established. It is certain, however, that the composition characterizing the larger c_o value should be shifted toward the potassium side of the diagram and the smaller toward the sodium side. An attempt has been made to show this relation on the composition diagram by a vertical line representing the analyzed composition of the sample with horizontal arrows projecting oppositely at either end of the line. The position of the horizontal lines denotes the value of c_o, and the arrow indicates the region of composition to which either phase of the mixture belongs.

No distinction between natroalunite and alunite has been possible by optical means in the two samples of intermediate composition that give x-ray patterns of both alunite and natroalunite. The mixture is believed to be of such small scale that it is below the resolution of the microscope. Such an intimate mixture is more likely to be a product of unmixing rather than a result of metasomatic replacement of one alunite for another.

It is apparent from the figures that a_o of the synthetic samples is slightly larger than that of natural alunite (.02 Å larger), and c_o of the end member synthetics is smaller than that of the corresponding natural alunite (.20 Å smaller) and natroalunite (.03 Å smaller) specimens. The explanation for these irregularities is believed to be the partial substitution of H_3O^+ for K^+ and Na^+ as discussed in a previous section of this report. Although the ionic radius of H_3O^+ is given as 1.32-1.35 Å, substitution H_3O^+ for K^+ in the jarosite-carphosiderite series (iron bearing analoques of alunite) suggests that it may be smaller. Jarosite, $(KFe_3(SO_4)_2(OH)_6)$, has the cell dimensions, $a_o = 7.20$ Å and $c_o = 17.00$ Å, whereas carphosiderite, $(H_3O)Fe_3(SO_4)_2(OH)_6$, has the dimensions, $a_o = 7.16$ Å and $c_o = 16.70$ Å (Palache, et. al., 1951). Hence a_o and c_o for carphosiderite are .04 Å and .30 Å smaller respectively than those for jarosite. Inasmuch as the only difference between these two minerals is the ionic substitution of H_3O^+ in the potassium position, it is logical to assume that the smaller unit cell of carphosiderite is due to the smaller effective ionic radius of the H_3O^+. Thus the differences in c_o between the synthetic and natural alunite and natroalunite can be explained by the substitution of H_3O^+ in the alunite lattice if H_3O^+ is considered to be smaller than K^+. It should also be noticed that the difference in c_o between synthetic and natural natroalunite is much less than that between synthetic and natural alunite, suggesting that the effective radius of H_3O^+ is closer to that of Na^+ than K^+.

The plot of a_o and c_o against the relative atomic percentages of potassium and sodium suggests that an isomorphic series exists between potassic and sodic synthetic alunite. Both a_o and c_o show linear shrinkage relationships with increasing sodium content of the samples, although the curve for c_o is the more striking. Such a linear relationship satisfied Vegard's law which requires that unit cell dimensions vary linearly with the change in composition for true isomorphic series.

The most reasonable interpretation of the contrasting relations between the synthetic and natural alunites is that the synthetic alunite series represents a disordered and metastable state. The sodium and potassium (and H_3O^+) are considered to be randomly distributed, and any slight change in the proportion of one ion to the other consequently causes a corresponding change in the lattice constants over the entire range of isomorphism. Whatever physical or chemical factors that are required to produce a more ordered state are not known.

On the other hand the naturally occurring alunite and natroalunite are believed to represent the state of greater order and stability. A limited range of isomorphism apparently exists in nature at the potassic end of the system and possibly at the sodic end, although the paucity of data for the sodic end of the system leaves a great deal of uncertainty. The only naturally occurring samples of intermediate composition obtained in this study are mixtures of the two alunite end members, and if the interpretation is correct, that these samples represent unmixed phases from an original homogenous alunite, the intermediate range of composition is one of instability. Furthermore, naturally occurring alunites of intermediate composition should not exist. None occur in the ores from Marysvale that have been examined in the study.

Summary

Unit cell dimensions distinguish two naturally occurring mineral types of the composition (K, Na) $Al_3(SO_4)_2(OH)_6$, a high potassium alunite, termed alunite, and a high sodium alunite termed natroalunite. The c lattice constant for alunite ranges from 17.28 to 17.31 Å; whereas the constant for natroalunite is 16.71-16.72 Å. Data suggest that isomorphism exists over a restricted range at the potassium end of the series, though insufficient samples were obtainable to determine the nature of isomorphism at the sodium end. In the range of composition between alunite and natroalunite no isomorphic relationship appears to exist in nature, and in this range it is likely that natural minerals do not occur.

Synthetic alunite samples with a range of sodium-potassium contents were synthesized at atmospheric pressure in boiling solutions of sodium, potassium and aluminum sulfates. Solutions in which both sodium and potassium sulfates were introduced produced alunite which was richer in potassium than the stoichimetric proportions of these sulfates in the solutions. Although the synthetic alunites crystallized with the alunite structure, their unit cell dimensions differed slightly from natural alunites. Also, chemical analyses reveal that the synthetics deviate from the theoretical alunite composition, the greatest deviation being the excess of water. The partial substitution of oxonium ions (H_3O^+) for sodium and potassium ions is proposed as an explanation for these anomalies. The synthetic alunites represent a low-temperature, low-pressure, acid, disordered and unstable phase of alunite. A complete isomorphic series is evidenced by the linear shrinkage relations of the unit cell dimensions with the progressive relative changes in the atomic percentages of sodium and potassium. This relation is in strong contrast to that shown by natural alunite samples of similar composition.

Thermal Behavior

Alunite and the kaolin group of minerals are ideal substances for examination by methods of thermal analysis because of the magnitude of the heat exchanges produced by their thermal reactions. These minerals, as well as the associated quartz and small amounts of other minerals, are usually found as microcrystalline aggregates in the Marysvale alunite deposits, so that techniques such as differential thermal analysis should be a great aid in qualitative and semi-quanitative study. In order to appreciate fully the usefulness, limitations and the significance of the results obtained by this method, it seems justifiable to discuss in some detail factors which influence variations in the thermal curves, to examine the chemistry of the thermal reactions and to appraise the application of this method to the semi-quantitative analysis of alunitized rocks.

The differential thermal apparatus used in this study was the multiple type, modifications of which have been described by Kerr and Kulp (1948), Kerr et. al. (1949) and Kulp and Kerr (1949). The equipment consists of a resistance type furnace, a six-sample stainless-steel sample block, a Leeds and Northrup "Micromax" temperature controller and "Speedomax" point recorder. A d.c. pre-amplifier, also manufactured by the Leeds and Northrup Company, can be introduced into the circuit to produce recordings of higher sensitivity. All of the determinations, with the exception of a few qualitative runs on samples that produce very low peaks, were made with the pre-amplifier disconnected. The rate of heating in all of the differential thermal analyses was maintained at 12° C. per minute.

The basic theory of differential analysis is briefly summarized by Kulp et. al. (1951, p. 644) who state, "The ground sample.... is packed into a cylindrical well which contains one terminal of a two-headed thermo-couple. The other terminal is placed in some material, such as alundum, which does not undergo exothermic or endothermic reactions through the heating range. The temperature of the system is then raised at a uniform rate from room temperature to 1050° C. Any thermal changes in the sample well will result in a differential temperature between the two terminals. This is measured by a recording potentiometer in a plot of time or system temperature against differential temperature. The area under a peak on such a curve is proportional to the heat of reaction and concentration of the active ingredients."

Chemistry of thermal reactions

The differential thermal curve of alunite is characterised by strong endothermic peaks at 590° and 870° C. and a weaker exothermic peak at 780° C. The chemical reactions producing these peaks have previously been studied by Fink et. al. (1931), Knisek and Fetter (1950), Kulp and Adler (1949) and Gad (1950). These authors are in general agreement on the chemistry for the two endothermic reactions of alunite, but they differ in their interpretation of the cause of the exothermic reaction at 780° C. Knisek and Fetter attribute (contribute) the reaction to..." the recrystallization of alum which takes place at about this temperature". Gad suggests that the product formed is γ alumina in contrast to α alumina of Kulp and Adler and Fink et. al.

The findings of the previous workers were investigated by the study of alunite samples which were ground to pass 200 mesh and heated to specific temperatures. The compounds that were identified from x-ray diffraction patterns of the samples are listed in Table 10. Products formed at the temperature of the first endothermic peak of alunite gave only diffraction lines of anhydrous alum ($KAl(SO_4)_2$). At the 780° C. exothermic peak temperature, however, strong diffraction lines of tri-potassium aluminum tri-sulfate ($K_3Al(SO_4)_3$), weak lines of potassium sulfate, and faint lines of γ alumina were identified. Tri-potassium

TABLE 10

Compounds present in heated alunite[(a)] samples.

Temperature	Compounds identified by X-ray diffraction.
585° C.	$KAl(SO_4)_2$
620	do
645	do
780	$K_3Al(SO_4)_3$ strong, K_2SO_4 weak, $Al_2O_3\gamma$ weak
870	K_2SO_4 strong, $Al_2O_3\gamma$
950	do do do

(a) Mineral Products alunite, coarsely crystalline variety, ground to pass 200 mesh.

aluminum tri-sulfate has not been mentioned in previous reports as a compound formed in the thermal decomposition of alunite. The compounds present at the temperature of the 870° C. endothermic peak were potassium sulfate and γ alumina, both of which were the only substances found in the 950° C. sample.

The following interpretation of the chemistry of the reactions produced by alunite which is heated up to 1050° C. is based on the author's data summarised in Table 10 and upon the previous work of Kulp and Adler (1949). The first endothermic reaction at 590° C., shown by the thermal curve, indicates the amount of heat absorbed by the complete destruction of the alunite lattice. The combined water in the mineral is liberated, and amorphous alumina and anhydrous alum are formed. The equation is:

$$6KAl_3(SO_4)_2(OH)_6 \xrightarrow{590} 6KAl(SO_4)_2 + 6\,Al_2O_3 + 18H_2O$$

Although the amorphous alumina is not recognized in the x-ray diffraction pattern, its presence is deduced from the fact that the solubility of Al_2O_3 in sulfuric acid is greatest at about this temperature (Fink et. al., 1931).

The exothermic peak which occurs at 780° C. represents the evolution of heat of crystallization of γ alumina from the amorphous alumina formed in the previous reaction. Immediately following the γ alumina crystallization, the anhydrous alum begins to decompose, releasing sulfur tri-oxide and alumina and forming a tri-potassium aluminum tri-sulfate. This reaction is evidently represented on the thermal curve by the slightly flattened slope on the low temperature side of the 870° C. endothermic peak. The heat of crystallization of the alumina that is released is absorbed in the stronger simultaneous endothermic reaction and thus is not expressed on the curve. The equation for the reaction is written:

$$6\,KAl\,(SO_4)_2 \xrightarrow{800} 2K_3Al(SO_4)_3 + 2Al_2O_3 + 6SO_3$$

The culmination of the reaction at 870° C. is a result of the heat absorbed in the decomposition of the tri-potassium aluminum tri-sulfate producing potassium sulfate and alumina, and evolving sulfur tri-oxide. The potassium sulfate and γ alumina remain stable to 1050° C. The equation is:

$$2K_3Al(SO_4)_3 \xrightarrow{870} 3K_2SO_4 + Al_2O_3 + 3SO_3$$

Effect of grain size

The grain size of the alunite affects the peak amplitudes, the peak temperatures and the peak shapes of the thermal curves. The degree to which the grain size is effective has been studied by thermal analyses of the Mineral Products coarsely crystalline vein alunite which was crushed and seived to the following sizes:

-50 mesh
50-80 mesh
80-120 mesh
120-200 mesh
-200 mesh

The most striking feature produced by the variation of grain size in alunite is the shape of the 590° C. endothermic peak (see Fig. 8). A double endothermic peak appears in the temperature range, 570-640° C., in the curves of the coarsest samples, but the doublet condition disappears progressively in the finer-grained samples forming a single endothermic peak at 590° C. in the samples which have been ground fine enough to pass 200 mesh.

X-ray diffraction patterns of the 50-80 mesh and the less than 200 mesh alunite samples, after having been heated to 585° C. and held at this temperature for 30 minutes, reveal diffraction lines of both alunite and anhydrous alum for the coarser sample and diffraction lines of only anhydrous alum for the finer. Therefore, the cause of the

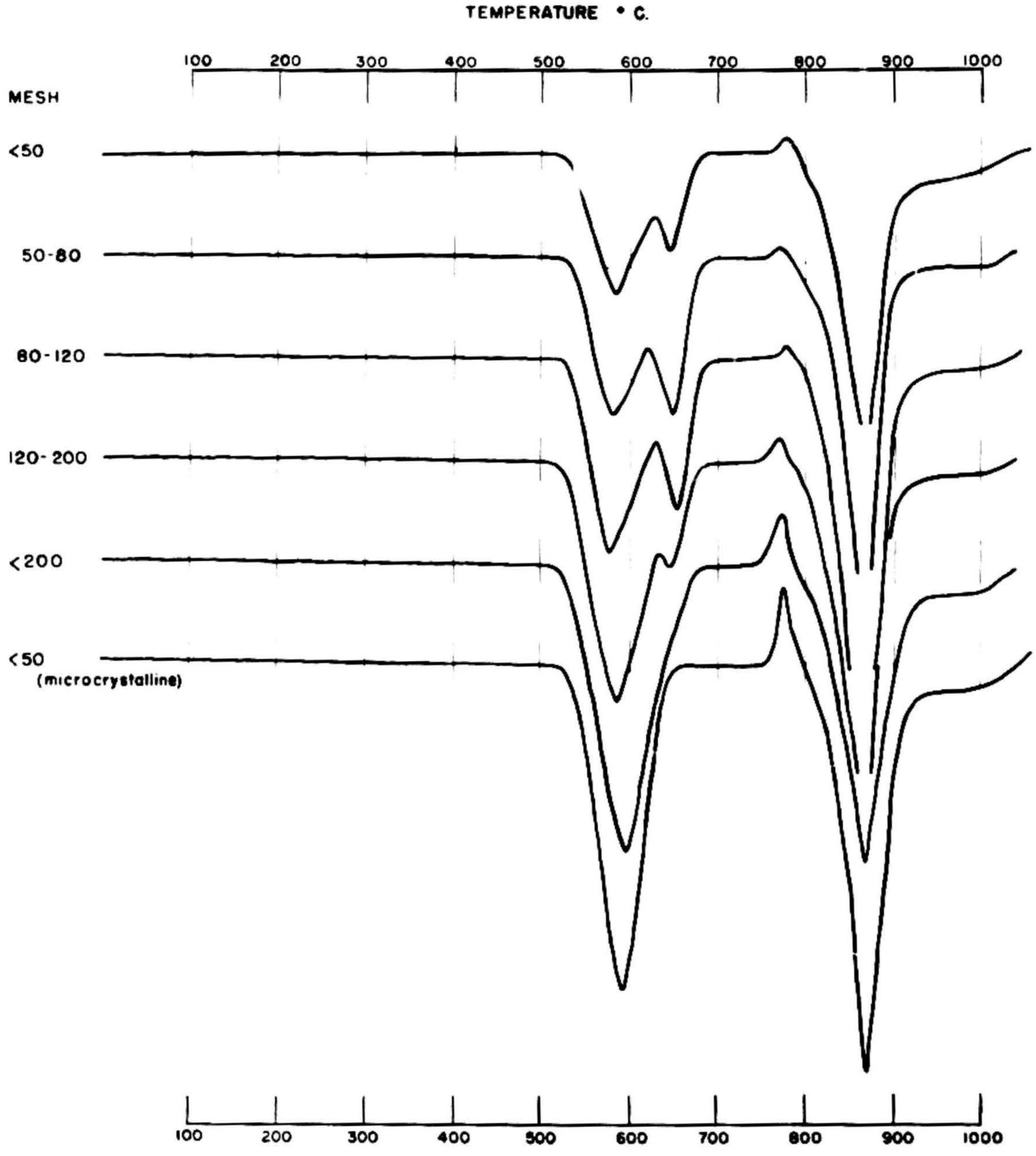

Figure 8.--Differential thermal analysis curves of alunite from the Mineral Products mine. The five uppermost curves are from coarsely crystalline alunite, and the lowermost curve is from the finely crystalline variety.

double endothermic peak is the failure of the larger alunite grains to decompose completely at 590° C. A slightly higher temperature is required to decompose the alunite remaining in the sample, and the second endothermic peak is the expression of this second period of decomposition.

Inasmuch as the kaolinite endothermic peak occurs at about the same temperature as the higher temperature member of the alunite doublet, it is important that the doublet condition is recognized for the correct interpretation of the thermal curve.

Effect of admixtures of other minerals

Many workers have shown that the peaks of differential thermal curves of minerals are ~~e~~affected by other minerals in the mixture. The principal constituents of alunitized rocks, alunite, quartz and kaolinite, by their mutual interactions illustrate this principle. Figures 9 and10 show the progressive modification of the thermal peaks of alunite, quartz and kaolinite in artificially prepared mixtures, alunite-quartz and alunite-kaolinite. Except for a small endothermic reaction at about 575°C., which is the inversion point from the alpha to the beta form, quartz is essentially inert. In these mixtures it serves as a diluent reducing the amplitude and area of the alunite peaks. Also peak temperatures of alunite are shifted downward with increasing amounts of quartz. In mixtures in which the content of quartz is less than 70 percent the inversion peak is not expressed.

The mutual modification of the thermal curves of alunite and kaolinite by mixtures of the two minerals is illustrated in Figure 10. The 590°C. peak of alunite and the 620° C. peak of kaolinite form a double peak in this temperature range, the degree of the development of either peak depending on the proportion of the two minerals in the mixture.

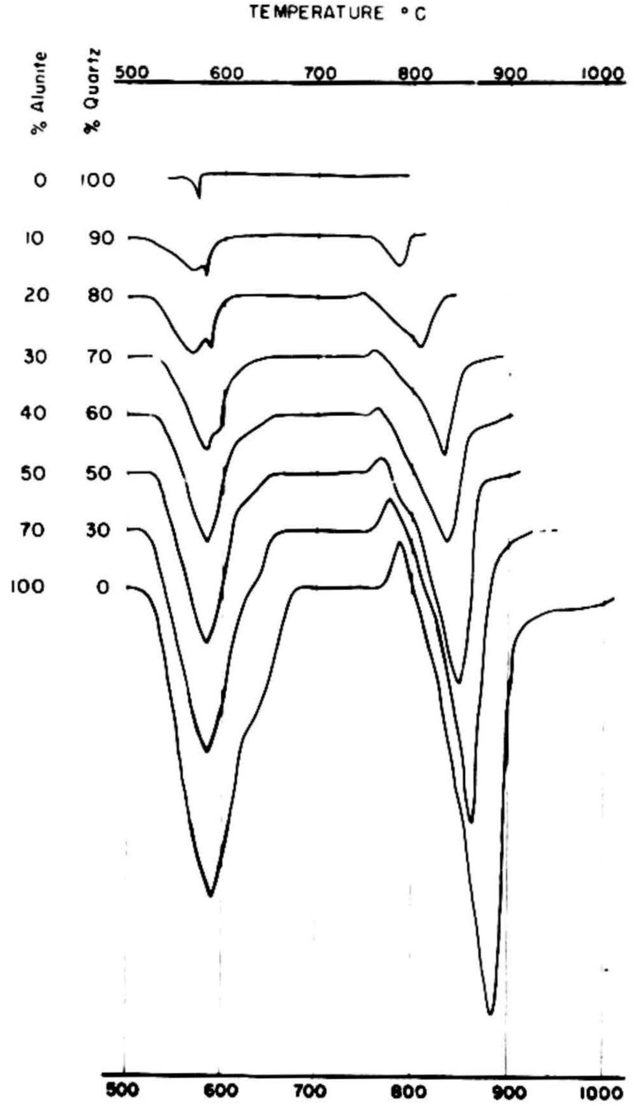

Figure 9.—Differential thermal analysis curves in the temperature range 500-1000° C. of artificial mixtures of alunite and quartz.

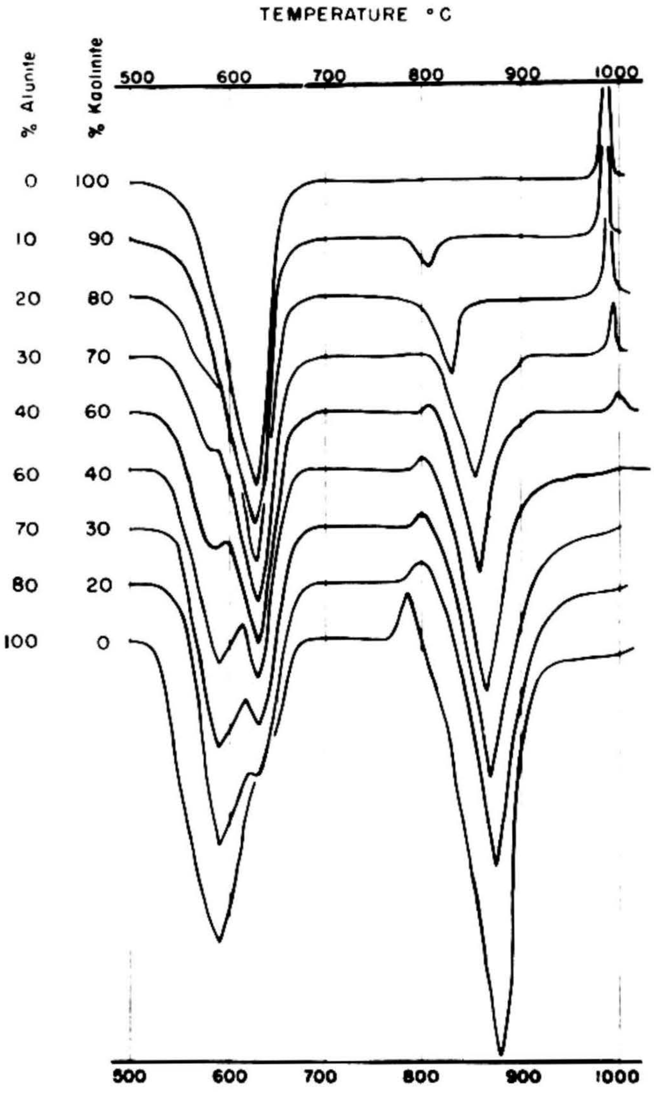

Figure 10.—Differential thermal analysis curves in the temperature range 500-1000° C. of artificial mixtures of alunite and kaolinite.

At temperatures where no thermal reaction occurs in one mineral, that mineral serves as a diluent to the thermal effects of the other. This is true for the 780° C. and 870° C. peaks of alunite that are reduced by the presence of kaolinite, and for the 980° C. peak of kaolinite which is decreased by increasing proportions of alunite. Peak temperatures are also changed. The 780° C. peak of alunite is shifted upward, whereas the 870° C. peak is moved downward with increasing amounts of kaolinite. As the proportion of alunite is increased, the temperature of the 980° C. peak of kaolinite is raised.

It should be mentioned that the chemical and physical condition of the constituents in mineral aggregates can appreciably affect the resulting thermal curves. For example, kaolinite with a wide range of grain size or of poor crystallinity may produce broad peaks of low amplitude (Kerr et. al., 1949, p. 18) which may complicate the identification of the mineral in aggregates. The action of some substances as fluxing agents (Gruver et. al., 1949) or as catalysts is poorly understood but may be effective in producing some differential thermal anomalies.

Semi-quantitative differential thermal analysis

Standardization of Variables

Certain operational procedures and instrumental variations in differential thermal analysis require controlling in order to obtain a high degree of reproducibility necessary for semi-quantitative analysis. Those considered in this study are the alignment of the thermocouples, the centering of the sample block in the furnace, the sensitivity of the thermocouples, the packing of the sample and the establishment of the base line in measuring the thermal peaks.

The centering of the thermocouples in the sample wells and the centering of the sample block in the furnace was carefully established. The thermocouples were aligned by the use of a specially made jig. Duplication of the centering of the sample block was made possible with the aid of a supporting device that imposed the same furnace position each time the furnace was lowered.

The sensitivity of the thermocouples has to be carefully determined because an increase in sensitivity produces an increase in the amplitude and area of the peaks of the thermal curves. In the multiple thermal apparatus the six thermocouple pairs nearly always register different intensities. Also, the sensitivity of the same thermocouple may change with usage. In order to place all thermocouples on a common basis of sensitivity, kaolinite or alunite standards were run alternately with the samples, and a constant, K, for each thermocouple pair was computed from each standardizing run as:

$$K = A/A_s$$

where A is an arbitrarily selected standard amplitude, and A_s is the amplitude of a particular thermal peak that is produced from the standardizing mineral. The amplitude of this peak, that is produced from an unknown sample, is then multifplied by the constant, K, that pertains to the appropriate thermocouple for the particular run, in order to place the value on a common comparison level.

Constants for the thermocouples that are based on the area enclosed by the peaks are derived in the same manner as the amplitude and give almost the same values.

Packing of the sample in the sample well is a critical factor in semi-quantitative determinations because it determines the amount of reacting substance available, as well as the density of the substance around the thermocouple. A standard procedure was adopted in loading the samples in order to produce the same volume and density of packing in all runs. The sample well was successively filled with the powdered sample and compressed under the weight of a steel rod, which was slightly smaller in diameter than the sample well, until the sample bore the weight of the rod and was also flush with the top of the sample block. It may be true, however, that the consistency in results of packing by this method is ~~are~~ affected by variation of the grain size of the sample, but the method is nevertheless a refinement of packing to "finger tightness".

A reproducible base line must be established to close the areas of the thermal peaks for the correct measurement of area and amplitude. For the 590° and 620° C. endothermic peaks of alunite and kaolinite respectively the base line is drawn by extending the straight part of the thermal curve on either side of the peaks. However, for the 870° C. endothermic peak of alunite the position of the base line is uncertain and to produce a consistent line of reference is especially difficult on curves obtained from alunite mixtures. A line drawn between the inflection points of the curve formed at the beginning of the 780° C exothermic peak and formed on the high temperature side of the 870° C. endothermic peak gave only fair results.

Artificial Mixtures

Reference curves for determining the quantity of alunite in alunitized rocks were established from artificial mixtures of alunite from the Mineral Products deposit, Marysvale, Utah; quartz from Minas Geraes, Brazil; and kaolinite from Murfreesboro, Arkansas. The minerals were ground to pass 200 mesh and alunite-quartz and alunite-kaolinite mixtures at 10 percent intervals were prepared. The area and amplitude of the peaks were measured and corrected in the manner explained above, and graphs were constructed for the use of analyzing unknown samples. The graphs are based on the results of three runs for each composition. Because of the limited size of the 780° C. exothermic peak and the difficulty of establishing a baseline for the 870° C. peak of alunite, measurements from them were considered unsatisfactory for semi-quantitative analysis.

Graphs of the variations of the 590° C. alunite peak in alunite-quartz and alunite-kaolinite mixtures are shown in figures 11 and 12. In both graphs the area or amplitude of the peak is the ordinate and the percentage of alunite is the abscissa. In figure 13 the ratio of the amplitude of the 590° C. peak of alunite to the amplitude of the 620° C. peak of kaolinite is plotted against the alunite content in the mixture. This curve gives the actual alunite and kaolinite percentages in mixtures of the two minerals only, although their relative proportions in mixtures with other substances should be determinable from the curve.

The graphs based on the amplitude of the 590° C. peak of alunite in mixtures with quartz and with kaolinite are nearly identical. Thus the graphs should also express the alunite composition in the three component

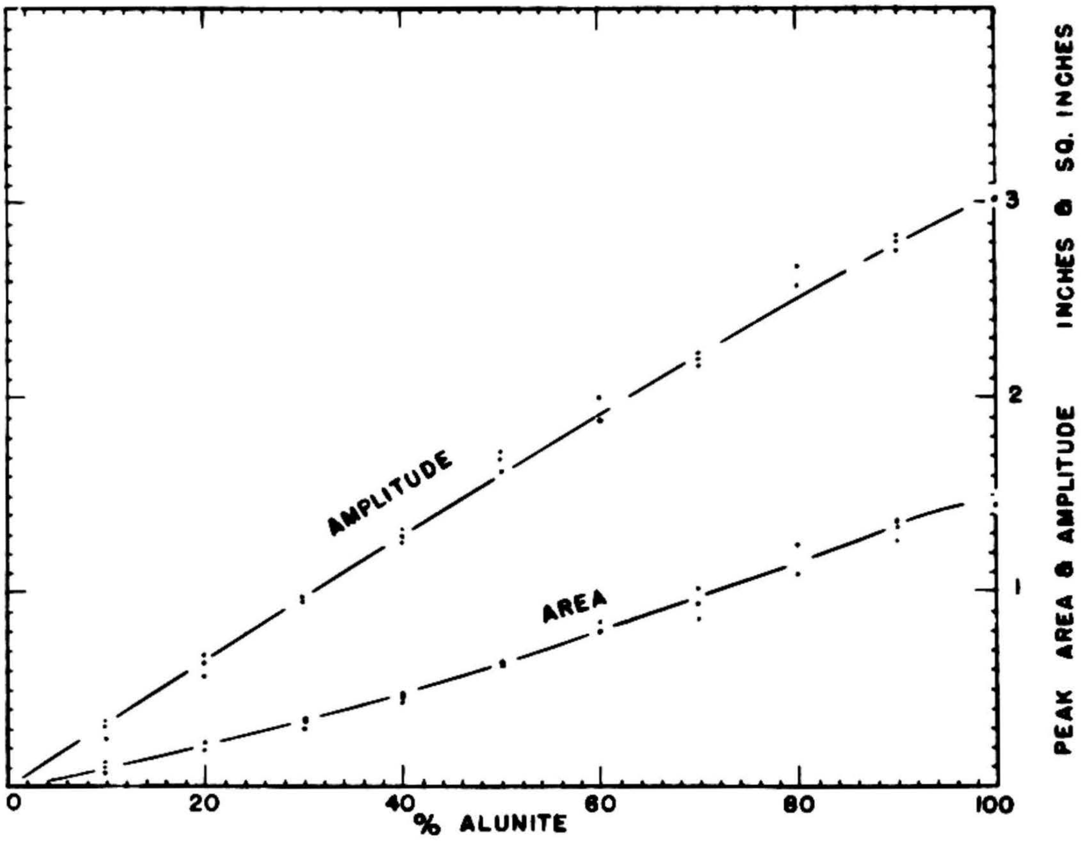

Figure 11.—Amplitude and area of the 590^0 C. thermal peak of alunite in artificial mixtures of alunite and quartz.

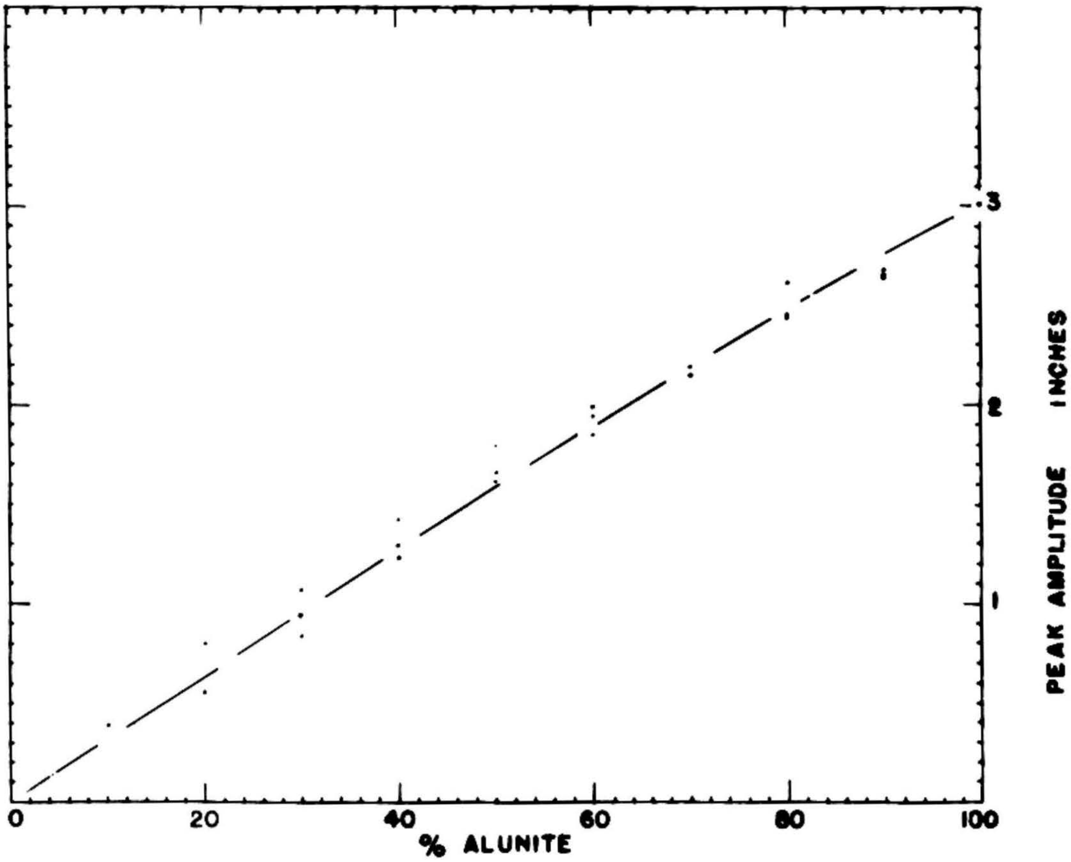

Figure 12.—Amplitude of the 590^0 C. thermal peak of alunite in artificial mixtures of alunite and kaolinite.

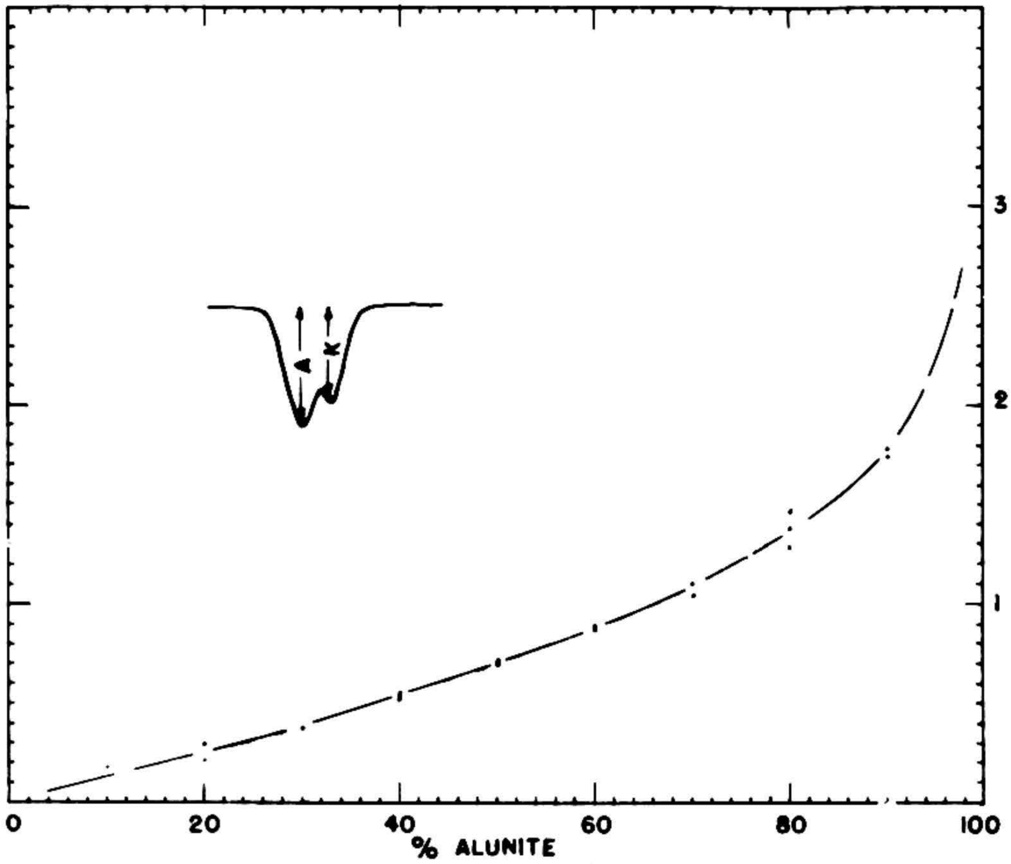

Figure 13.--Ratio of the amplitudes of the 590^0 C. peak of alunite and the 620^0 C. peak of kaolinite in artificial mixtures of alunite and kaolinite.

mixture, alunite-quartz-kaolinite. Figure 14 shows a plot of the experimental points of the amplitude of the 590° C. alunite peak from the alunite-quartz and alunite-kaolinite mixtures. The average error in determining the alunite content from the curve is slightly less than 2 percent; the maximum error is 6 percent.

Naturally-Occurring Mixtures

Ground alunitized rock samples, which were analyzed by the United States Geological Survey, were used as materials for testing the practical application of the analytical data derived from the differential thermal analysis of the artificial mixtures. The major minerals present are alunite, quartz and kaolinite, with minor amounts of hematite, opal, leucoxene and gibbsite (?). In some samples halloysite is present with kaolinite. The analyzed samples contain grain sizes, which range upward to 0.6 mm. The fragments are present either as discrete mineral grains or as microcrystalline aggregates. Many of the larger grains are quartz.

The procedures and techniques were the same in the differential thermal analysis of both the artificial mixtures and in the alunitized rock samples. The mineral composition of the latter, however, was recalculated from chemical analyses.

The results of the thermal analysis of 25 alunitized rock samples are summarized in graphical form on the same basis as the graphs of the artificial mixtures. Figure 15 shows the relation between the alunite content and the amplitude of the 590° C. alunite peak. The lower curve in the figure represents the same relation for the artificial mixtures. Nearly all the plotted points of the analyzed samples fall above the artificial mixture curve. Although the points roughly define a curve of steeper slope, their scattered distribution indicates a low precision

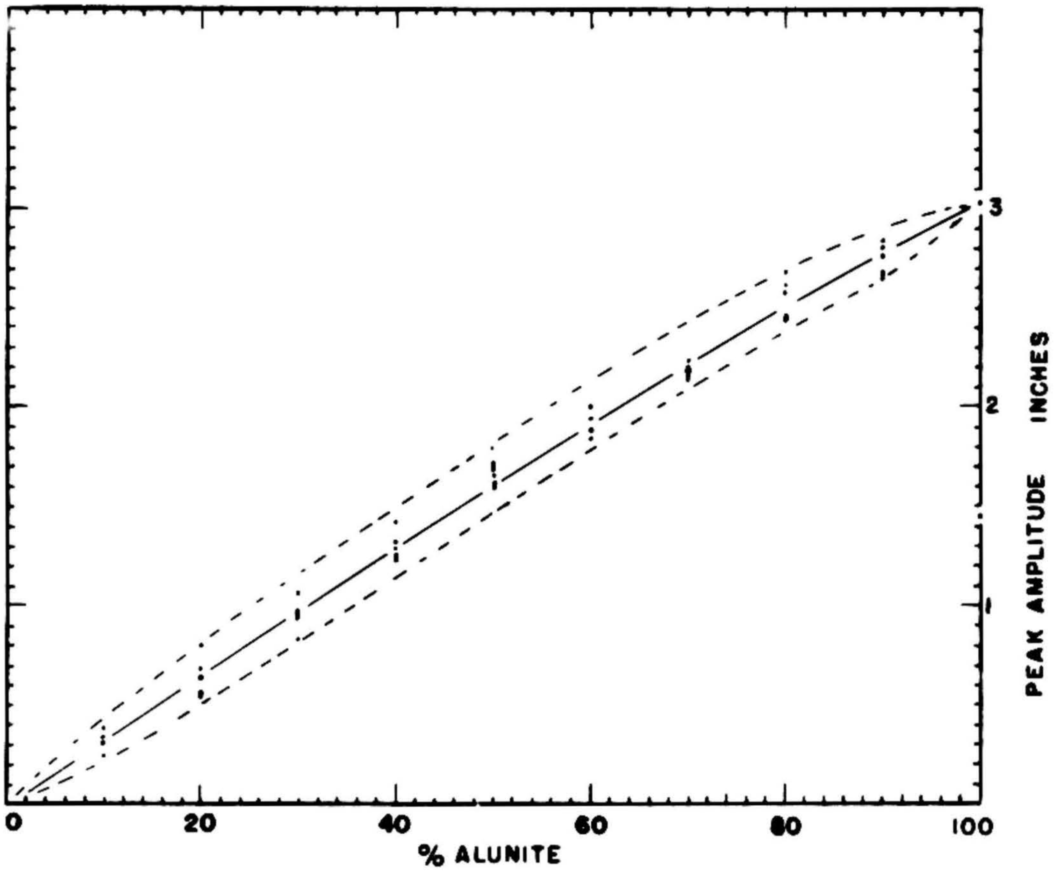

Figure 14.—Amplitude of the 590° C. thermal peak of alunite in artificial mixtures of alunite and kaolinite and alunite and quartz.

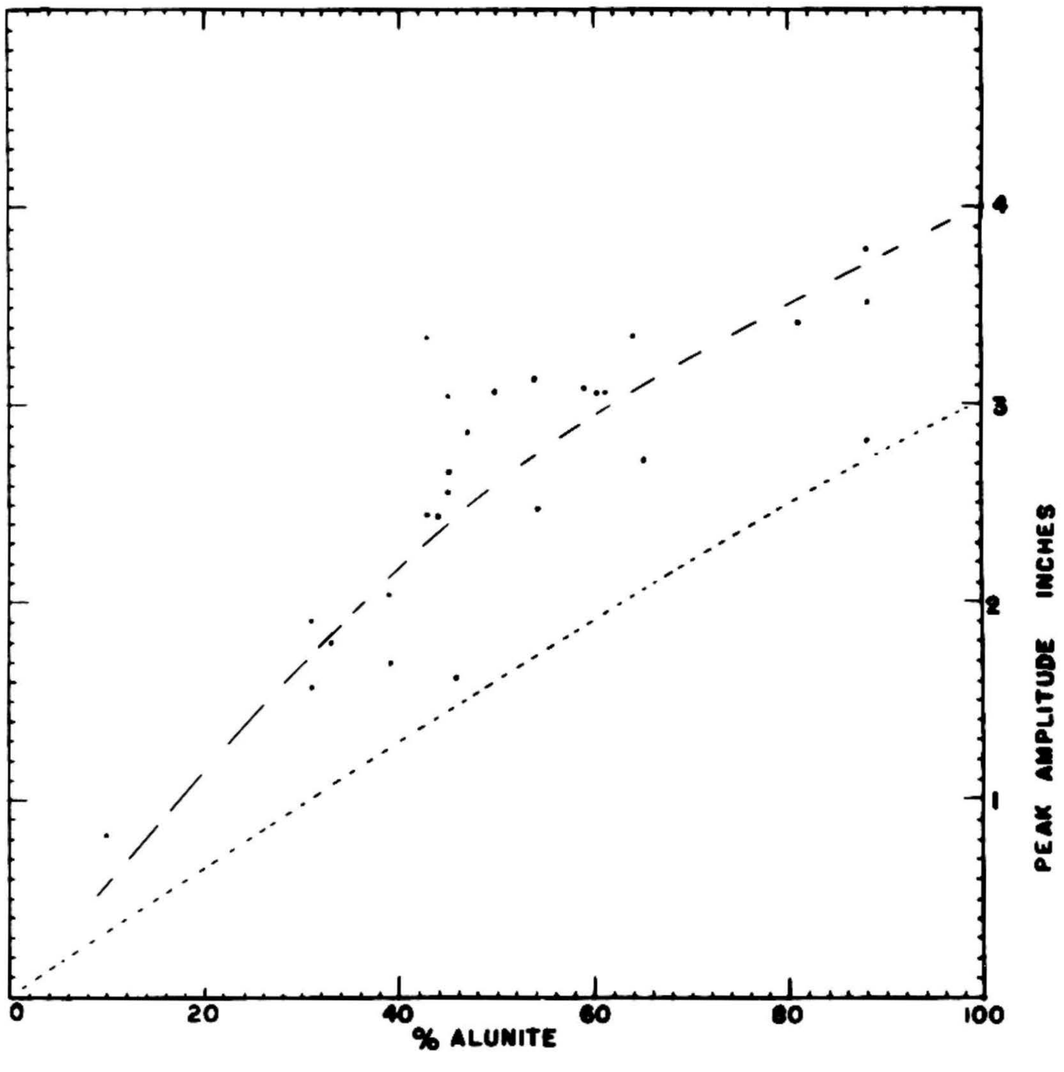

Figure 15.--Amplitude of the 590° C. thermal peak of alunite in chemically analyzed alunite ore samples. Lower curve represents the 590° C. peak amplitude variation in artificial mixtures of alunite and quartz and alunite and kaolinite.

for semi-quantitative analysis based on the peak amplitude from these samples.

The area of the 590° C. peak of alunite, plotted against the alunite content in the analyzed samples, is shown in figure 16. The plotted points define a curve along which the average error in determining the alunite percentage is about 2.5 percent and the maximum error is about 7 percent. This curve corresponds closely to the curve derived from the alunite-quartz artificial mixtures and forms the most reliable basis for semi-quantitative analysis of the naturally occurring samples by the differential thermal analysis technique.

Variation in grain size in the naturally occurring alunite-kaolinite-quartz aggregates is believed to be the factor which causes peak area and amplitude deviations from the values that were predicted from the study of artificial mixtures. Not only are the grain sizes of the particular minerals of the natural aggregates different from sample to sample, but also the mineral components of the same sample are of different sizes. These differences are either inherited from the original size of the grains in the rock or are produced by the grinding of the minerals of different hardness.

Differential thermal analysis is believed to be a practical method for determining the grade of alunite ores if the variable factors mentioned in this study are carefully controlled. The area enclosed by the thermal peaks is the most reliable measurement of composition, although the amplitude of the thermal peaks can also be used if little variation in grain size occurs among the samples. Calibration curves should be made from artificial mixtures which simulate the physical state of the naturally occurring aggregate that is to be studied and the validity of the curves should be checked by quantitative chemical analyses.

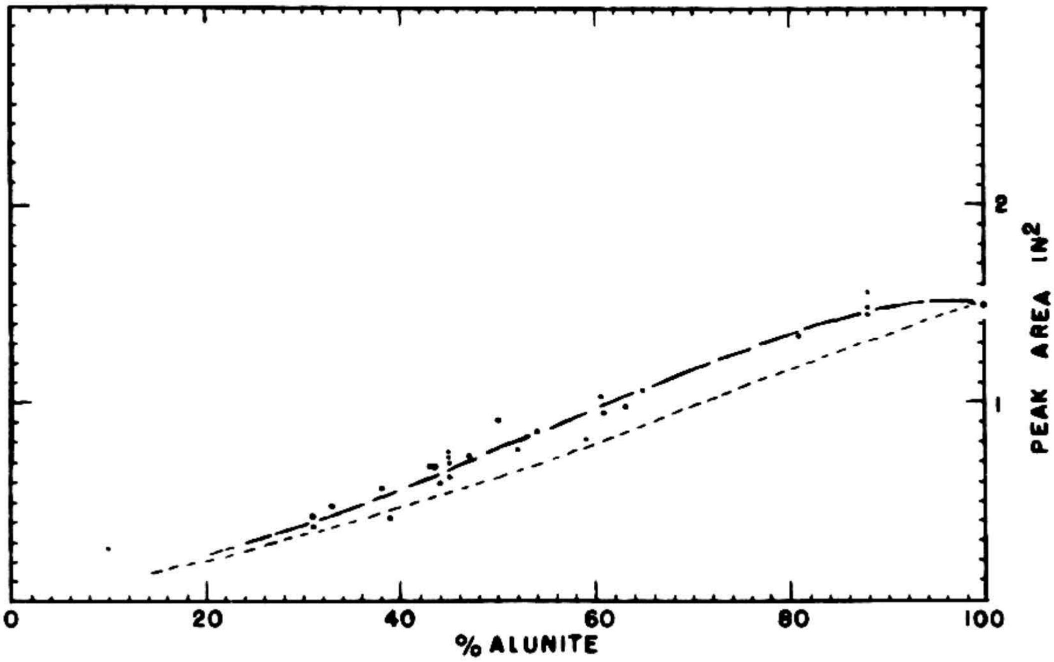

Figure 16.--Area of the 590^0 C. thermal peak of alunite in chemically analyzed alunite ore samples. Lower curve represents the area of the 590^0 C peak of alunite in artificial mixtures of alunite and quartz.

Summary

The chemistry of the thermal reactions of alunite is summarized in the following equations:

$$6\ KAl_3(SO_4)_2(OH)_6 \xrightarrow{590^\circ C} 6KAl(SO_4)_2 + 6Al_2O_3 + 18H_2O$$

$$6\ KAl_2O_3\ (\text{amorphous}) \xrightarrow{780^\circ} 6Al_2O_3(\gamma\,\text{alumina})$$

$$6\ Kal(SO_4)_2 \xrightarrow{800^\circ} 2K_3Al(SO_4)_3 + 2al_2O_3 + 6SO_3$$

$$\underline{2\ K_3Al(SO_4)_3 \xrightarrow{800-870^\circ} 3K_2SO_4 + Al_2O_3 + 3SO_3}$$

$$6\ KAl_3(SO_4)_2(OH)_6 \xrightarrow{590-870^\circ} 3K_2SO_4 + 9Al_2O_3 + 9SO_3 + 18H_2O$$

Differential thermal curves of alunite samples of coarse grain-size are characterized by a double endothermic peak in the temperature range 570-640° C. Fine-grained alunite samples, however, produce a single endothermic peak at about 590° C. X-ray patterns of heated alunite samples indicate that the doublet condition of this thermal peak is due to decomposition of the coarse-grained alunite in two stages. The first stage represents only partial decomposition of alunite at the temperature of the lower temperature-member of the doublet peak; the second stage at the temperature of the higher temperature-member represents the decomposition of the remaining alunite.

Semi-quantitative analysis of alunite ores by the differential thermal analysis technique requires careful control of the following factors and procedures:

1. The alignment of sample holder in the furnace.
2. The alignment of the thermocouples in the sample wells
3. The calibration of thermocouple sensitivity.
4. The packing of the sample in the sample holder.
5. The establishment of the base line in the measurement of peaks.

6. The chemical and physical nature of the samples.

Graphs, which relate the alunite percentage in mineral aggregates to the amplitude and area of the 590° C. thermal peak of alunite, have been established from artificial mixtures of alunite, quartz and kaolinite. Similar graphs have also been produced from thermal curves of chemically analyzed alunite ores. Differences between the graphs for the artificial mixtures and the graphs for the alunite ores are believed to be due to the variable particle size in the ore samples.

The area enclosed by the thermal peaks is the most reliable measurement of the composition of samples in which the grain size is variable. If the grain size is consistent among the samples, the peak amplitude can be used.

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APPENDIX I

Techniques of Alteration Mineral Identification

The samples from the Marysvale, Utah alunite deposits were examined and studied by optical, differential thermal analyses, x-ray and staining techniques in order to establish the most accurate mineral identification and mineral relations possible. The combined results of these techniques furnish the data for the alteration mineralogy of the alunite deposits.

Thin sections of the samples were studied to obtain textural and mineral relationships as well as to identify many of the more coarsely crystalline constituents. Much of the altered alunitic and argillic rock, however, is so extremely fine-grained that optical identification is not wholly satisfactory. The argillic fractions of the rock were viewed in the thin sections, and then these fractions were hand picked from the hand specimens for more positive x-ray identification.

Alunite, quartz and kaolin minerals were easily identified by x-ray powder photographs, however the illite-montmorillonite mixed lattice clays required glycerol treatment and further x-ray diffractometer determinations for their identification. Once the identification for a particular clay mineral was established the optical properties were sufficient to distinguish it from other fine-grained minerals of the thin sections.

Where hand picking of the minerals was not possible, the whole sample was ground and treated by x-ray, thermal and staining tests, and the mineral components of the aggregate were identified. By referring to corresponding thin sections, the minerals were located and their mutual relations determined.

APPENDIX II

Randomly Stratified Mixed Layer Lattice Clay

The mica-like clay mineral, which is characteristic of the feeble phase of alteration in both the replacement and vein alunite deposits, has been identified as a mixed layer lattice illite-montmorillonite clay. X-ray diffraction, differential thermal analysis, staining and optical techniques were used to establish identification.

In thin section the mixed lattice clay is fibrous to scaly, is highly birefringent, and has a high refractive index similar to illite. The clay is found predominately as a replacement of the plagioclase phenocrysts, although in some samples the groundmass is also replaced by this material.

Staining tests using benzidine on the untreated samples as well as the techniques of Mielenz and King (1951) give results which are typical of neither illite nor montmorillonite. The untreated mixed lattice clays give various shades of light blue with a saturated aqueous solution of benzidine. Because of its simplicity the method of applying benzidine directly to the untreated sample proved most satisfactory and was used on all of the samples representing the feeble phase of alteration. In samples in which bluish stains occurred, x-ray diffraction patterns showed the presence of the mixed lattice clay.

The 10.2-10.8 Å x-ray diffraction line of the illite-montmorillonite mixed lattice clay is most significant in identification. This value is larger than is normally characteristic of illite and is the combined result of the x-ray scattering from the 001 planes of illite and montmorillonite. When the mixed lattice clays are solvated in glycerol this diffraction line shifts to 9.8-9.3 Å and is the result of the combined 002/001 planes of montmorillonite and illite respectively.

Table 11 lists the diffraction spacings for two typical Marysvale mixed layer lattice clays, with other specimens for comparison.

By referring the 001/001 and 002/001 diffraction lines of the mixed layer aggregate to the curves published by Brown and MacEwan (1950) a rough estimate of the proportions of the two component minerals in the mixed lattice clay can be obtained. The samples which were x-rayed and measured in this study range from nearly pure illite to 60 percent illite-40 percent montmorillonite. The curves have also been prepared for higher order reflections, 5 Å and 3.3 Å; however, for some unknown reason, the 5 Å line of the untreated mixed lattice clay is absent in the glycerol treated samples. The 3.3 Å line is masked by the strong quartz reflection which occurs in this position. The —/001 diffuse line of montmorillonite is recognized in some of the glycerol solvated samples that contain the most montmorillonite layers and its value is about 11.6 Å (see sample 1, Table 11).

The thermal curves of the Marysvale mixed layer lattice clays are similar to published curves for mixed layer lattice clays. Thermal curves of the Marysvale mixed lattice clays and other clays from the literature are given in Figure 17.

TABLE 11

Lattice Spacings and Intensities of Mixed Layer Clays and Illite

Illite (a)		Sample 1				Sample 2				K-Bentonite (b)	
		untreated		glycerol solvated		untreated		glycerol solvated			
d	I	d	I	d	I	d	I	d	I	d	I
		11.8		11.6	vwb						
10.0	vs	10.8	mb	9.4	m	10.2	m	9.8	m	10.9	m
		8.12	w								
		7.19	m	7.01	m	7.07	m	7.13	m		
5.0	m	5.01	m			4.97	w			4.95	m
4.46	vs	4.50	s	4.46	m	4.45	m	4.45	m	4.47	m
		4.27	m	4.23	w	4.24	s	4.24	s		
		3.57	vw	3.56	w	3.57	m	3.57	m	3.43	m
3.32	vs	3.34	vs	3.33	vs	3.34	vs	3.34	vs	3.35	m
		3.18	vw							3.25	m
		3.10	vw	3.08	vw	3.07	vw			3.11	vw
2.97	vw					2.99	vw				
2.80	vw					2.84	vw			2.83	w
2.55	vs	2.56	m	2.55	m	2.56	m	2.55	m	2.55	m
								2.49	vw	2.495	w
2.44	w	2.45	w	2.45	w	2.45	w	2.45	w	2.45	w
2.37	w	2.38	w	2.37	w	2.37	w	2.37	vw	2.38	w
						2.33	w	2.34	vw		
						2.27	w	2.27	w		
2.23	w			2.23	w	2.23	vw	2.24	vw	2.245	w
2.17	w	2.18	vw	2.18	vw	2.18	vw			2.18	w
2.14	m	2.13	w	2.13	vw	2.12	w	2.12	w	2.13	w
1.98	m	1.975	vw	1.975	w	1.975	w	1.97	w	1.97	m
		1.815	w	1.81	vw	1.815	m	1.82	m		
1.64	m	1.653	wb	1.664	w	1.667	wb	1.658	wb	1.65	w
		1.539	w	1.537	w	1.535	m	1.535	m		
1.49	vs	1.497	m	nm		nm		1.498	w	1.50	m

TABLE 11 continued

(a) Illite described by Nagelschmidt and Hicks (Kerr et. al. 1950).

(b) K-Bentonite mixed layer clay (Weaver, 1953). The sample is reported to contain some chlorite.

Sample 1. Mixed layer clay from the White Horse deposit containing some quartz and kaolinite. About 40 percent montmorillonite layers in mixed lattice clay.

Sample 2. Mixed layer clay from the L and N deposit containing some quartz, kaolinite and possibly chlorite. About 10 percent montmorillonite layers in mixed lattice clay.

vs = very strong; s = strong; m = moderate; w = weak;
vw = very weak; b = broad; nm = not measured

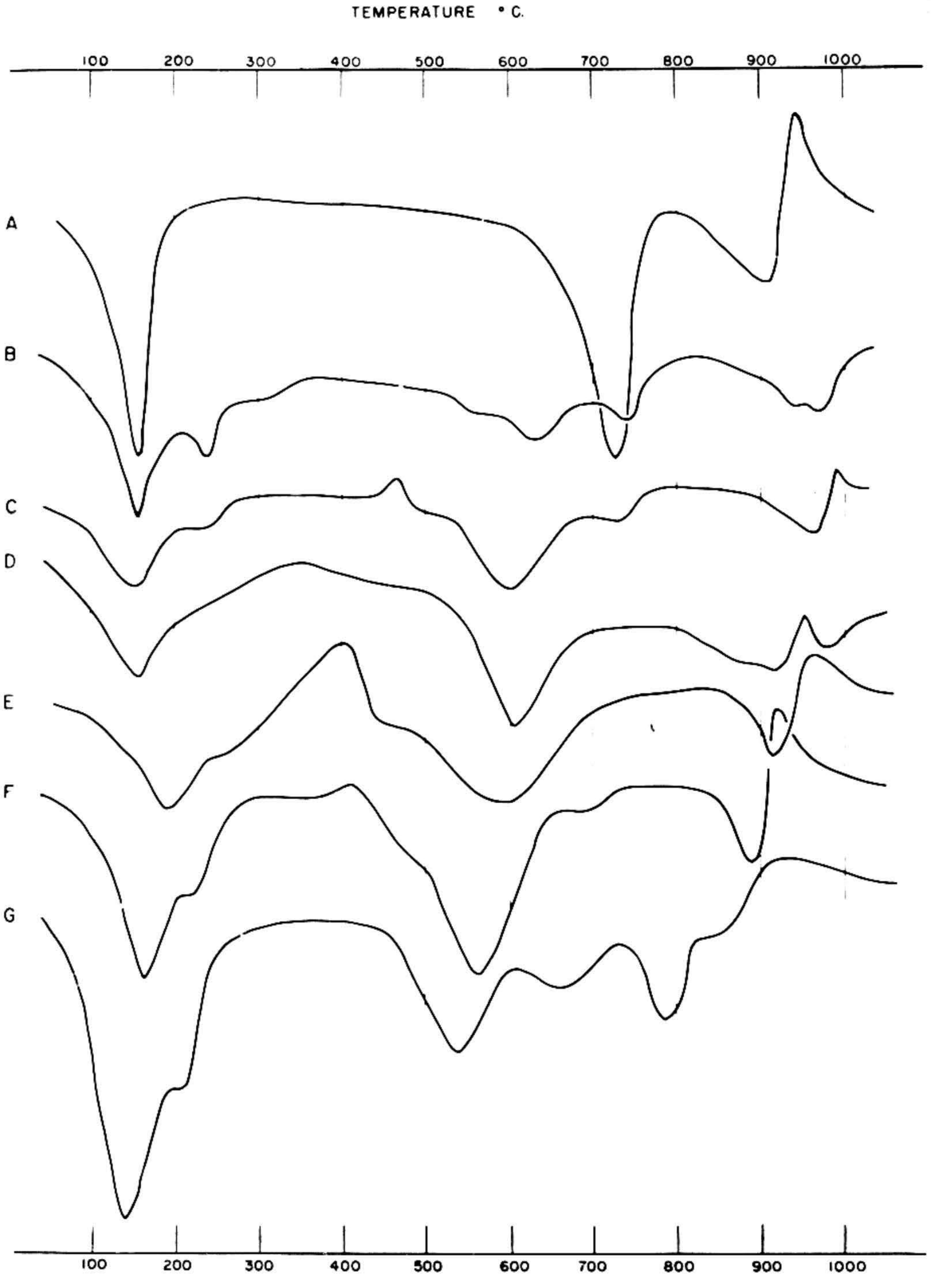

Figure 17.—Differential thermal analysis curves of montmorillonite, illite, and mixed lattice clays. A, montmorillonite, Clay Spur, Wyo.; B, mixed lattice clay from the White Hills alunite deposit, Marysvale, Utah; C, mixed lattice clay from the Marys Lamb alunite deposit, Marysvale, Utah; D, mixed lattice clay from the Yellow Jacket alunite deposit, Marysvale, Utah; E, Illite, Morris, Illinois; F, mixed lattice clay Cameron, Arizona; G, mixed lattice clay, Pioche, Nevada.

The Marysvale region has received the attention of many geologists since the pioneer work of Gilbert[1] and Dutton.[2] The discovery of alunite and its commercial utilization lead to the work of Butler and Gale,[3] Loughlin[4] and Butler.[5] In the years 1936 to 1938 Callaghan and associates mapped all of the area shown in Figure 2, and the geology as interpreted here is only slightly modified from this early work. Since the discovery of uranium in the area, numerous geologists have studied the region. Notable in this regard is the work of Paul F. Kerr and his associates at Columbia University who have mapped the central area of uranium production north of Marysvale in great detail, and whose research work was in part concurrent with that of the writer. In "A Geologic Guide to the Marysvale Area"[6] Kerr and his associates have reviewed the geologic setting of the uranium deposits. They have also produced a large-scale geologic map which differs in certain respects from that of Callaghan.

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[5] Butler, B. S., Ore deposits of Utah: U. S. Geol. Survey Prof. Paper 111, pp. 536-558, 1920.

[6] Kerr, P. F., Brophy, G., Dahl, H. M., Green, J., and Woolard, L. E., A geologic guide to the Marysvale area: A. S. Atomic Energy Commission RMO-924, 1952.