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ALUNITE: A NEW OCCURRENCE NEAR WICKENBURG, ARIZONA

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ABSTRACT

A new occurrence of alunite is located about 3 miles west of Morristown and 10 miles south of Wickenburg, Maricopa County, Arizona. It is associated with clay deposits and constitutes the major mineral of several outcrops within a one half mile area. The host rock containing the alunite is a rhyolite which has undergone hydrothermal alteration. In hand specimen, pink patches of alunite up to 5 mm in diameter are surrounded by a matrix of clay and quartz. The unit cell content calculated from chemical analysis is: $(K_{2.54}Na_{0.46})(Al_{10.21}Fe_{0.01})[SO_4]_{5.52}(OH)_{17.22}$ The refractive indices ($\omega = 1.577 \pm .002$, $\epsilon = 1.593 \pm .002$) and unit cell dimensions ($a = 6.986 \pm .002$, $c = 17.332 \pm .005$) are compatible for alunite with 15 atomic percent Na substituted for *K*.

INTRODUCTION

A significant amount of alunite was detected in several samples taken near Wickenburg, Arizona during routine investigation of a clay deposit. Subsequent study revealed that alunite constitutes a major phase within an area of about one-half square mile of hydrothermally altered rhyolite. This report is based upon samples obtained from four patented claims located on the west side of the Hassayampa River about 3 miles west of Morristown and 10 miles south of Wickenburg, Arizona (Fig. 1).

This occurrence is in the eastern part of the Vulture mining district near the northern boundary of the Basin and Range physiographic province of central Arizona. The geologic history of this district is complex and the ages of most rock units are uncertain. The basement is composed of highly-deformed Precambrian gneiss, schist, greenstone and metasediment. Overlying Cenozoic lavas, tuffs, and breccias of intermediate to silicic composition have gentle to moderate dips.

The Wickenburg alunite is found within a grayish-pink rhyolite. Hydrothermal alteration of the host rock and concealment of contacts by alluvium obscure the field relations, but relic textures showing primary flow banding and brecciation are apparent at several localities. The rhyolite texture varies from uniform felsite to coarse breccia with fragments of lava and a few clasts of Yavapai Schist. Irregular jointing is well developed throughout the area. A red rhyolite that surrounds the kaolinite-alunite deposit appears to be an older sequence of flows into which the altered rock has been down-faulted. Kaolinite is presently mined at this location, but no alunite is being produced.

Two other sizeable deposits of subcommercial-grade alunite are known in Arizona.

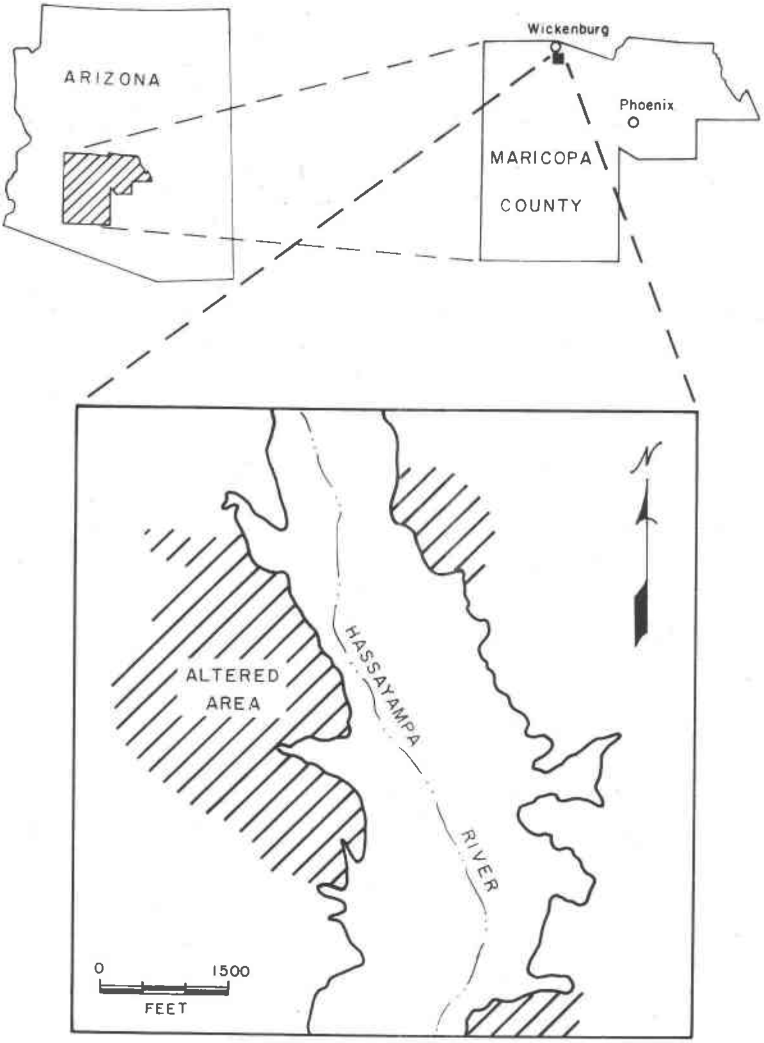

FIG. 1. Index to study area.

Natroalunite from Sugarloaf Butte, 5 miles west of Quartzite in Yuma County, occurs in a complex of veins cutting schist and prophyritic dacite (Heineman, 1935; Thoenen, 1941). Most veins are small and contaminated by quartz and minor gypsum, but several attain widths of a foot or more and appear to be relatively pure alunite. Schrader (1914, 1915) reports alunite in the wall rock of the Evening Star prospect (Three R mining group) 5 miles south of Patagonia in Santa Cruz County. This occurrence is the result of feldspar alteration adjacent to a sulfide vein in pegmatitic granite. The altered zone is several feet wide and may contain as much as 30 percent alunite.

Elsewhere in Arizona alunite occurs as a minor accessory of noneconomic importance. It has been reported in association with jarosite in veinlets in altered rocks at the Silver Bell mine (Kerr, 1951). A similar occurrence is reported from the Santa Rita district of New Mexico (Kerr and others, 1950) where alunite, kaolinite, pyrite, and quartz veinlets occur in ore-bearing rocks. The few economic alunite deposits in the United States include Goldfield, Nevada; Rosita Hills, Colorado; and the Marysvale district of Utah (Kerr and others, 1957). The latter deposit is of particular interest because the details of alteration bear a striking resemblance to those of the occurrence near Wickenburg.

ANALYTICAL PROCEDURES AND RESULTS

Concentration. Alunite was concentrated for chemical analysis by crushing bulk samples to pass a 125 micron screen. This fraction was washed and centrifuged in a mixture of bromoform and neothene adjusted to a specific gravity of 2.705 to remove light grains. The heavy fraction was again centrifuged in pure bromoform with a specific gravity of 2.85 to remove the denser contaminant. Optical examination of the concentrate indicates 95 percent alunite; composite grains carrying quartz are the chief impurity. A semiquantitative spectrographic analysis of the concentrate yielded, in weight percent, Si 2.0, Mg 0.04, Ga 0.006, Cu 0.002, Ca 0.6, V 0.005, Ti 0.010 (analyst: C. E. McLean, Jr.). This analysis indicates an approximate quartz content of 5 percent.

Optical Properties. The refractive indices of alunite in the concentrate were determined by immersing grains in oils (calibrated at increments of .002) and observing the Becke fringe with sodium-lamp illumination. The values of the oils were checked with an Abbe 3L refractometer and measurements were corrected to 25°C. The alunite is optically homogeneous with $\omega = 1.577 \pm .002$ and $\epsilon = 1.593 \pm .002$. These values are nearly identical to those (1.574 and 1.590) given by Kerr and others (1957, p. 79) for alunite with a similar composition from Marysvale, Utah.

Chemical Analysis. Chemical analysis of the concentrate gave, in weight percent, SiO_2 4.96, Al_2O_3 39.20, Fe_2O_3 0.05, CaO 0.43, K_2O 9.00, Na_2O 1.08, H_2O 11.67, CO_2 0.34, SO_3 33.27 (analyst: C. F. Royse, Jr.).

Sodium, potassium and iron were determined for replicate samples by wet chemical analysis. One half gram of sample was digested on a steam bath in a hydrofluoric-sulfuric-nitric acid solution. Sodium and potassium contents were determined photometrically on an NIL Automated Flame Photometer using lithium as an internal standard. Calibration curves for the optimum operation range were made using Atomic Absorption Standards. Samples were decomposed for aluminum analysis by fusion with sodium hydroxide in nickel crucibles and put into solution with dilute hydrochloric acid (Shapiro and Brannock, 1962, p. 21–22). Aluminum was determined by measuring the absorption of the calcium-aluminum alizarin red S complex at 745 nm. Total iron was measured after reduction with hydroxylamine hydrochloride and buffering with sodium citrate. After one hour, the orange orthophenanthroline color was measured at 555 mμ; the method parallels that of Shapiro and Brannock (1962). Total reactive carbon was determined by combustion at about 1600°C in a LECO Model 589-400 low carbon analyser (Moore and Lewis, 1967). Alunite values were determined by comparison to a standard curve established with NBS-101E (low carbon steel). Sulfur was measured by combustion in the same furnace and at the same temperatures as the carbon. The sulfur dioxide liberated was passed into an acidified potassium iodate solution with a starch indicator. The iodide formed by reaction with the sulfur dioxide was automatically back titrated to maintain a fixed endpoint. The accuracy of all analyses was checked with one or more of the reference samples NBS-1b, NBS-99a, and the CAAS Syenites 2 and 3 (Sine and others, 1969) and were found to agree well within the limits of analytical precision. Water was analysed in quadruplicate with a C.E.C. moisture analyzer by Everett Gibson. The method is specific for water and other volatile oxides will not interfere. Nearly all water was released in a single stop between 520–560°C, only 0.1–0.2 percent was released below 150 C. CaO was calculated as weight needed to form $CaCO_3$ and SiO_2 was calculated by difference.

Unit Cell Content. Unit cell content calculated from the chemical analysis is compared below with the theoretical cell based on 84 cation charges (Hendricks, 1937).

Calculated Unit Cell Content: $K_{2.54}Na_{0.46}Al_{10.21}Fe_{0.01}[SO_4]_{5.52}(OH)_{17.22}$

Theoretical Unit Cell Content: $K_3Al\text{-}[SO_4]\text{-}(OH)_{18}$

It can be seen that K plus Na sum to 3.0. However, Al is high and SO^4 and (OH) are low. The excess Al is probably derived from amorphous allophane (see Keller *et al.*, 1967) which is not detected by X-ray analysis. The SiO_2 of the analysis is attributed to intergrown quartz impurity because quartz lines are present on all X-ray patterns. Calcite lines are also present in several powder photographs. Thus the detected carbon is stoichiometrically combined with calcium and oxygen and reported as calcite. The deficiency in SO_4 is unexplained although Malcolm Ross (personal comm., 1970) suggests that perhaps some P_2O_5 substitution for SO_4 may be the cause. The low (OH) content suggests no hydronium substitution for alkalies in the Wickenburg alunite.

X-Ray Crystallography. X-ray powder data from several alunite specimens are reported in order to demonstrate the similarity in composition of alunite throughout the deposit. Peaks for the chemically analysed specimen (sample 1000) were measured by diffraction at 1° two-theta per minute using copper radiation and a nickel filter. All other data are from samples exposed to nickel-filtered copper radiation recorded on powder films using a camera of 114.59 mm diameter. The two-theta values were corrected for a quartz internal standard and substituted in the U. S. Geological Survey least-squares unit cell refinement program 9214 (Evans and others, 1963). As is evident in Table 1, the unit cell values

TABLE 1. X-RAY DATA
Standard deviations in parentheses

Sample	Degrees Freedom	a (Å)	c (Å)	V (Å^3)
1000	11	6.986(2)	17.332(5)	732.5(4)
300	15	6.986(1)	17.317(9)	731.9(4)
301	7	6.985(8)	17.346(43)	732.9(0)
302	5	6.980(4)	17.363(15)	732.6(8)
308	10	6.976(2)	17.293(6)	728.8(5)

for several samples are nearly identical to those of the analysed specimen which has $a=6.986\pm.002$ Å, $c=17.332\pm.005$ Å and $V=732.5\pm0.4$ Å^3.

Parker (1962) has shown that a remains fairly constant throughout the alunite-natroalunite series, but c systematically decreases with increasing substitution of Na for K. The c value for the Wickenburg alunite is compatible with Parker's (1962, p. 134, Fig. 2) for a composition of 85 atomic percent K as given by the chemical analysis of this material.

DISCUSSION

Although hydronium (H_3O^+) may replace alkalies to a large degree in the jarosite-natrojarosite series (Kubisz and Michalek, 1959; Brophy and Sheridan, 1965), no hydronium replacement occurs in the Wickenburg alunite. Hydronium replacement is reported for natural natroalunite (Ross and others, 1968) and synthetic alunite (Parker, 1962). Published D.T.A. curves (Kulp and Adler, 1950; Kerr and others, 1957) show no hydronium substitution in certain other samples. D.T.A. and T.G.A. records are useful in detecting hydronium substitution for alkalies because water held as hydronium ion in the alkali cation position is released during an endothermic reaction in the range of 250° to 350°C (Brophy and Sheridan, 1965); whereas water held as hydroxyl is given off during an endothermic reaction in the range of 520° to 570°C (Kulp and Adler, 1950). Alunites from Marysvale (Kerr and others, 1957) as well as the Wickenburg alunite show no water given off below 530°C, but these alunites do show either strong endothermic peaks or total water release in the range 530° to 570°C. Further study of the conditions under which hydronium substitution occurs in synthetic members of the alunite-natroalunite series may provide a means of distinguishing alunite of diagenetic origin (Ross and others; 1968) and alunite of hydrothermal origin (Kerr and others, 1957). The diagenetic or low temperature alunites appear to have hydronium substituted for alkalies whereas the hydrothermal alunites do not.

The Wickenburg alunite locality is the first massive replacement body of the Marysvale type reported in Arizona. Although this deposit is small, others of the same character may have gone undetected or unreported. The association of alunite with sulfide mineralization at Santa Rita (Kerr and others, 1950) and at Silver Bell (Kerr, 1951) suggest that in the proper volcanic-tectonic situation alunite might be used as an indicator of copper mineralization at depth. The possibility of alunite as a high-level hydrothermal alteration associated with ore bodies is a concept worthy of further investigation.

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