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Alunite-Natroalunite Identification Using Field Tests and a Computer-Plotted Overlay for X-ray Diffraction Charts

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ALUNITE-NATROALUNITE IDENTIFICATION USING FIELD TESTS AND A COMPUTER-PLOTTED OVERLAY FOR X-RAY DIFFRACTION CHARTS

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INTRODUCTION

The mineral alunite is a potentially important source of aluminum, potassium sulfate fertilizer, and sulfuric acid in the United States. Alunite, and its sodium-bearing analog natroalunite, also are important prospecting guides because of their common associations with base- and precious-metal deposits.

Alunite and natroalunite occur as hydrothermal minerals in strongly solfatarically (acid-sulfate) altered volcanic rocks of andesitic to rhyolitic composition, where they form both veins and replacement bodies of hypogene origin. Alunite also occurs as a supergene, low-temperature mineral. Commonly associated alteration minerals are quartz, sericite, kaolinite, pyrophyllite, diaspore, and hematite. Many alunite-bearing altered volcanic rocks are similar in appearance to other fine-grained, light-colored rocks, which may contain little or no alunite but contain considerable kaolinite, sericite, gypsum, anhydrite, barite, brucite, and certain clays and carbonates.

Alunite and natroalunite can be recognized in the field by using a simple test requiring a portable propane torch, test tube, and pH-sensitive paper. The potassium:sodium ratio and the relative proportions of various contaminant minerals can be determined by X-ray diffraction. A quick, simple method to determine potassium content should be an important aid in evaluating grade during exploration, development and production in alunite deposits.

FIELD TEST PROCEDURE

One of the first field tests for alunite was developed by Schaller and described in Butler and Gale (1912, p. 63): "...boil the powdered sample with water or with hydrochloric acid for several minutes; after allowing the powder to settle, pour off the liquid and repeat the operation to insure the removal of all soluble sulphates. Dry the powder and heat to a dull red. Again boil in water and, after settling, pour off some of the clear liquid. To this add a small fragment or a solution of barium chloride. If the mineral is alunite a heavy white precipitate will form." This test is for sulfate in solution, and the precipitate formed is barium sulfate.

Another test for hydrous potassium/sodium aluminum sulfates which is simple, quick, involves no chemicals and is easily used in the field, is herein described (fig. 1). The test involves crushing a small amount of sample, heating it in a test tube, and measuring the pH of the water that condenses on the side of the tube. Pulverize a small amount of sample at the outcrop using a hammer or small mortar and pestle. Place about 1 g of the sample in a pyrex test tube, filling it to a depth of about 0.5 cm. Insert a strip of pH-sensitive test paper into the test tube so that the end of the paper is about 2 cm above the sample. Fold the paper strip so that it will hook over the top of the test tube. Hold the test tube about 30 degrees from horizontal, and heat the sample using a portable propane torch. The open end of the test tube can be held by hand, and the sample end should be placed at the tip of the blue flame. The test tube need not be rotated. Water in the sample is driven off by the heat and condenses about half-way up the test tube. Remove the test tube from the heat, insert the eraser end of a pencil, and press the pH-sensitive paper against the condensed water so as to absorb it. The paper will change color to indicate the pH of the water.

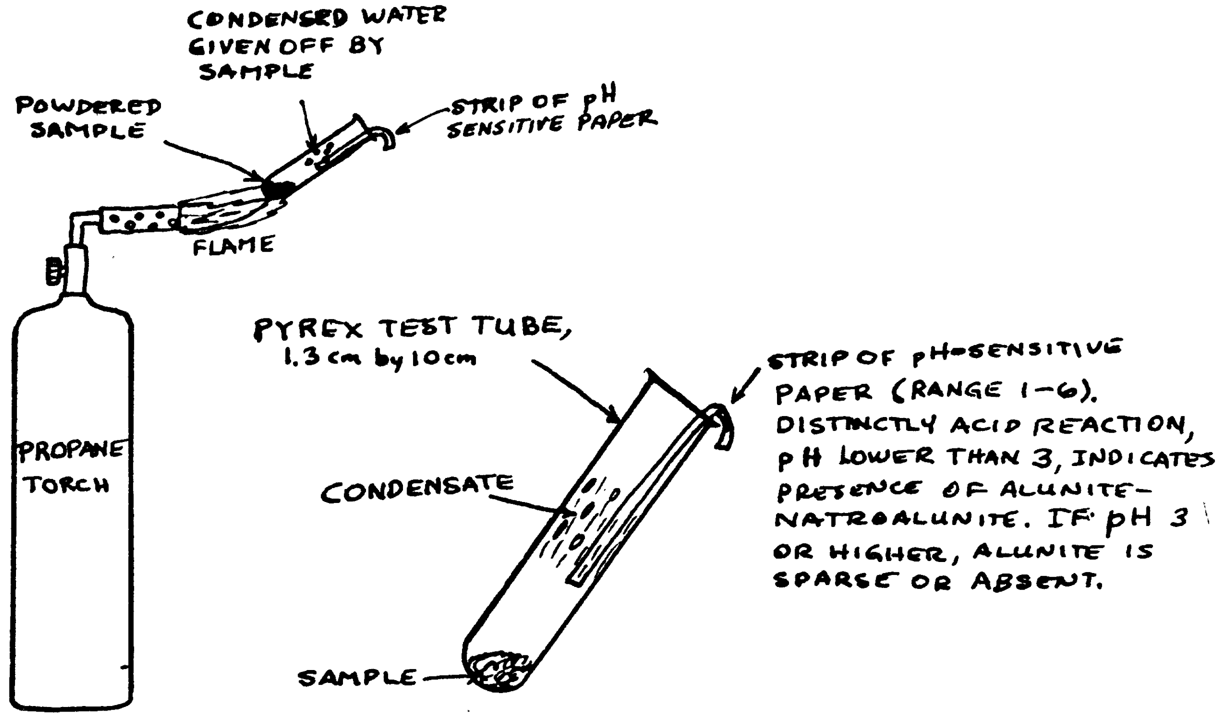

FIGURE 1

Simple field test for identifying alunite-natroalunite in hydrothermally altered rocks.

INTERPRETATION OF RESULTS

When both sulfur and water are driven off from the heated sample and combine in the condensed water, they form sulfurous and sulfuric acid. If alunite [$KAl_3(SO_4)_2(OH)_6$] or natroalunite [$NaAl_3(SO_4)_2(OH)_6$] is present in the powdered rock sample in amounts greater than 12 percent, the condensed water will give an acid reaction. The pH of condensed water from alunite is one, and pH-sensitive papers are available that turn a bright, diagnostic red at this pH. Gypsum evolves much water but no sulfuric acid when heated to the minimum temperature necessary to drive off water of crystallization, and the pH of its water is near neutral. Barite and other anhydrous sulfates release no water except adsorbed hygroscopic water (H_2O^-), which gives a much less acid reaction than water evolved from alunite.

This field test has greater reliability when used in conjunction with other basic geologic information. Obviously, heating a sample containing both pyrite and sericite can produce water with a low pH, so the test cannot be used on a sulfide-bearing sample. Hydrothermal alunite is formed in an oxidizing, sulfate environment in which sulfides commonly are not stable; consequently, sulfides would rarely be a problem and their presence can often be recognized. Other hydrous sulfates of the alunite and jarosite groups would be expected to react in a manner similar to alunite. They can be identified to some extent using additional criteria such as color, morphology, and mineralogical association, but further identification requires X-ray or chemical data (Botinelly, 1976).

X-RAY DIFFRACTION METHOD OF DETERMINING POTASSIUM CONTENT

Alunite and natroalunite form an isomorphous series (Parker, 1962); but alunite, the potassium-rich member, is more abundant in nature than natroalunite, the soda-rich member. (By convention, the name "natroalunite" is applied to material in which the Na:K ratio exceeds 1:1). The pure end-members are practically nonexistent in nature, although many alunites have a K:Na ratio greater than 9:1. By contrast, natural natroalunites nearly always contain appreciable potassium, with a K:Na ratio rarely lower than 3:7. Parker found it difficult to synthesize pure natroalunite, even with potassium-free reagents; evidently the small amount of potassium dissolved out of his laboratory glassware was able to enter his synthetically produced natroalunite (Parker, 1962, p. 128). Natroalunite seemingly is less stable than alunite and requires a very high Na:K ratio in aqueous solution in order to form (Hemley and others, 1969).

Alunite is considered to have greater potential commercial value than natroalunite. Although both minerals contain virtually the same amount of alumina, alunite contains much more potassium sulfate, which is a valuable fertilizer coproduct extracted with the alumina from alunite (Walker and Stevens, 1974). Accordingly, a quick and easy method of estimating the K:Na ratio in alunite ore would be an aid to any organization engaged in exploration for or mining of alunite. Whereas K and Na are readily determined by various modern analytical techniques, these can be tedious and time-consuming; in contrast, powder X-ray diffraction patterns can be quickly obtained. The technique described below can be used to estimate the K:Na ratio of alunite ore samples; and, although it lacks high precision, it may save time and money by reducing the number of conventional chemical determinations that might otherwise be necessary.

COMPUTER-PLOTTED OVERLAY

Alunite and natroalunite can be easily identified and the atomic percent potassium can be determined using X-ray diffraction techniques. Place the computer-plotted mylar sheet (plate 1) over an X-ray diffraction chart that has the same scale (four degrees-two theta per inch) and match the patterns. Align the chart by matching the quartz (101) peaks at 26.665° 2 theta. The height of the lines match the relative peak intensities. The atomic percent potassium (alunite:K=100) (natroalunite:K=0) is read from the right-hand scale. The d-spacing using CuKα1 (1.54051) is read from the upper or lower scale. It should be noted that the alunite-natroalunite rhombohedral 102 peak varies systematically as a function of composition. The two theta position of the 102 peak is given on the mylar sheet.

The data base consists of 18 analyzed samples of alunite and natroalunite containing 20 to 96 atomic percent potassium. The samples were prepared using a standard powder-pack method, and X-rayed at one half degree-two theta per minute using a Picker diffractometer. Alpha quartz was used as an internal standard. The peak positions and intensities were measured and several major peaks indexed.

The X-ray diffraction data plots were created using the DEC System 10 computer program, XRDPLT, (VanTrump and Hauff, 1976) and a special-purpose application of this program (VanTrump and Hauff, written communication). In addition to speed and convenience, this method directly determines the K:Na atomic proportion in alunite, even though the sample may contain other potassium-bearing minerals. Standard chemical analyses do not distinguish between the potassium in alunite and that in other minerals which may be present in the sample.

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