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A PROCEDURE FOR THE IDENTIFICATION OF SMALL CRYSTALS BY X-RAY DIFFRACTION ANALYSIS[1]

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INTRODUCTION

In the analysis of rock and mineral fragments, especially from soils and sediments, it is often necessary to identify small single grains. Normally, mineralogical analysis of single grains is done with the petrographic microscope, but in many instances a much more satisfactory analysis would result if both X-ray and petrographic information were available. The objective of this investigation was to create a general procedure whereby X-ray diffraction data could be obtained on the same grain used for petrography. The techniques described herein were developed for use with Norelco Debye-Scherrer type powder cameras.

MOUNTING THE GRAIN

The grain should be mounted as securely as possible, since very small grains, when accidentally detached, are usually irretrievably lost. Several cements were tried,[2] but by far the best found for this purpose is Shell

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[1] Scientific Paper No. 2815, College of Agriculture, Washington State University, Pullman, Project 3489.

[2] General Cement Mfg. Co. label, vinyl, general, and service cements; Dupont Duco cement; U. S. Plywood Corp. Weldwood white glue; Vaseline petroleum jelly; gelatin.

Epon 828 epoxy resin, recommended by Toman (1962). It was found to be practically insoluble in various immersion oils, common solvents such as water, acetone, and xylene; and it does not give an objectional amount of X-ray scatter. Very few Epon 828-mounted specimens have been lost during routine procedure.

To prepare a specimen mount, 1 cm of 1 mil tungsten wire[1] is inserted about 4 mm into slightly tacky Duco cement in the end of a powder camera specimen holder. The specimen holder is conveniently manipulated by slipping it onto the blunted tapered end of a common laboratory needle probe. The tip of the tungsten wire is then dipped into the tacky epoxy resin and the excess wiped off on a clean glass slide near the specimen, leaving a thin film of epoxy resin on the wire tip.[2] Under the microscope the wire tip is then brought into contact with the mineral grain (20–2000 μ), which will adhere. For best results in optical work, excess epoxy resin should not cover more of the grain than is absolutely necessary. The mounted grain is left in a 60°C oven overnight, allowing the epoxy resin to harden completely.

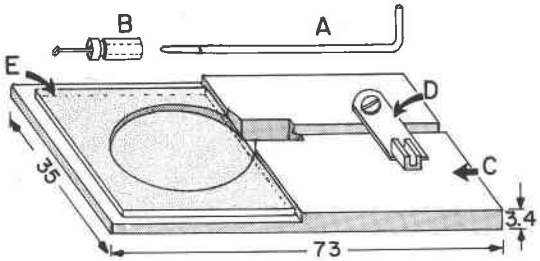

FIG. 1. Modified spindle stage: blunted steel needle probe bent as shown (A), powder camera brass specimen holder with mounted grain (B), aluminum base (C), spring brass clip (D), petrographic microscope glass slide (E) cut to fit and cemented to the base with Duco cement. Dimensions are in millimeters.

SPINDLE STAGE

The spindle stage of Wilcox (1959) was adapted to accommodate a grain mounted in the powder camera specimen holder (Fig. 1). The tapered end of the spindle (A) is inserted into the center hole of the specimen holder (B) which is then locked in the V-shaped slot on the base (C) by the spring clip (D) with the wire-mounted specimen protruding about 3 mm toward the center of the glass slide (E). Immersion oil can then be

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[1] Obtained from Mr. S. R. Blumberg, General Electric Co.

[2] The Epon 828 and approximately 20% by volume of Epon curing agent T-1 must be thoroughly mixed. They are conveniently measured and dispensed with droppers.

dropped onto the slide, embedding the specimen. The specimen can be washed with xylene to remove immersion oil. If lack of working distance between the sample and specimen holder prevents using high-power objectives, the Dupont cement can be softened with acetone and the wire-mounted specimen pulled out from the holder several millimeters. Although the epoxy resin is a strong cementing agent, there is always some danger of specimen loss with manipulation, so, if only one grain is available, optical examination may best follow X-ray examination.

X-RAY TECHNIQUE

Sorem (1961) has pointed out that small powder cameras are not only advantageous compared to large ones with respect to exposure time, but with small powder samples they are often necessary to obtain a usable diffraction pattern. For small single-crystal samples, these advantages are even more pronounced. Small powder cameras have the additional advantage of recording a greater portion of each diffraction cone, increasing the chances of intercepting diffraction spots from single crystals. The two major deficiencies of small powder cameras are that low angle diffraction cones near the exit beam-catcher are deleted, and there is relatively small separation of diffraction cones with attendant low accuracy in determining line spacings. These deficiencies can be compensated for sufficiently to permit satisfactory mineral identification, the former by using a narrower exit beam-catcher, and the latter by photographically enlarging the X-ray pattern.

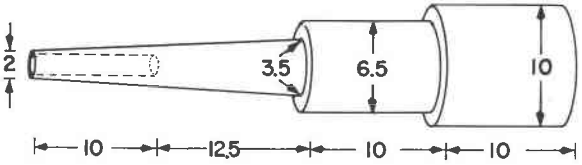

FIG. 2. Brass beam-catcher for a 57.3 mm dia. Norelco powder camera. Dimensions are in millimeters. Use a No. 53 wire drill for end hole.

Several modifications of the exit beam-catcher of the standard Norelco 57.3 mm powder camera that permit recording low angle lines have been proposed. They include an auxiliary beam catcher, or an extension for the present exit collimator (Martin Vivaldi *et al*, 1959), or a smaller beam-catcher (Aruja, 1961; Cole, 1961).

The exit-collimator extension was found to be an improvement, but frequently also resulted in an excessive amount of scattered radiation around the exit collimator. The simple exit beam-catcher plug in Figure 2 was found to be satisfactory. The sample is first carefully centered by conventional alignment procedures. To utilize this beam-catcher fully, the film exit hole should just permit the plug to pass through without contact.

MEASUREMENT OF X-RAY SPACINGS AND INTENSITIES

Since a given diffraction cone from a small single crystal is sometimes represented on the powder camera film by as little as a single spot near one edge, conventional line spacing measurements along the center of the film are not possible. Spot positions can be measured, however, with a suitable Ångstrom gridscale, where each grid-arc spans the width of the film. Such a grid-scale, shown in Figure 3, was constructed using an enlarged mock-up of a portion of the powder camera. From a pivot at the simulated sample position, arcs (at computed angstrom distances) were struck about a shaft passing through zero degrees θ. Error in arc placement was smaller than the thickness of the tungsten standard lines.

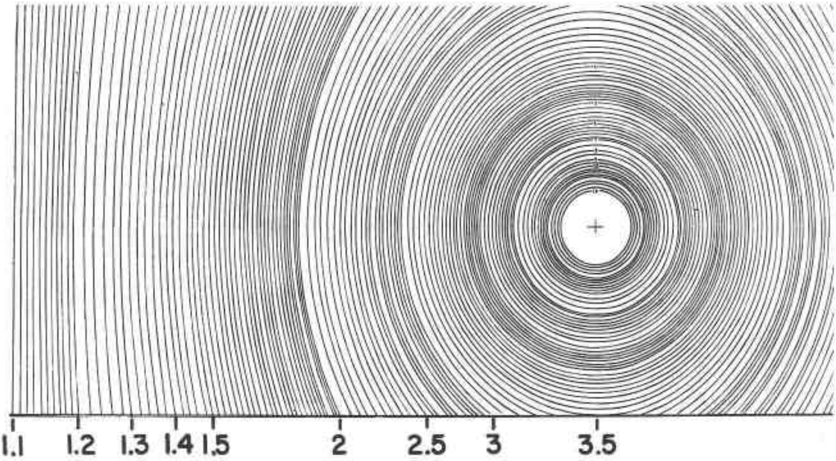

FIG. 3. Grid-scale in Ångstroms (CuKα) for measuring spot patterns. This grid is enlarged to approximately 20 in. in length and the spot pattern is projected upon it.

Measurement of spot positions is best accomplished by enlarging the grid-scale about 8 times the X-ray film size and then projecting the spot-pattern upon it. Using a light box and a binocular headband magnifier, each spot is pricked at its center with a needle to ensure that all spots are seen. The film is projected with a $3\frac{1}{4}\times 4\frac{1}{4}$ slide projector using a cooling cell to prevent excessive film heating.

The tungsten wire on which the specimen is mounted serves as an internal standard, with three lines (2.24, 1.58, and 1.29 Å) usable for exact film-grid alignment. The film is enlarged until the tungsten lines on the film coincide with their positions previously marked on the grid-scale. The process also compensates for film shrinkage.

Equivalent line spacings from the projected spot-pattern can be read directly from the grid-scale in a darkened room, or preferably photographed (in our laboratory, a 35 mm camera with a good 135-mm telephoto lens was used). Prints of convenient size show black spots on the grid-scale with a white background. Kodabromide, single weight paper 20×24 in., with a semi-matte surface is cut to give two photographs 10×24 in., which are dry-mounted on cardboard to give a permanent record.

A relative measure of diffraction intensities is essential for X-ray identification of minerals. Since most data for standard minerals are derived from powder samples, some procedure must be used to convert information from single crystal spot-patterns into values comparable to powder-pattern line intensities. Such a procedure has been empirically devised, taking into account the number of spots on a line as well as their intensity. The grid-scale in Figure 3 is divided into 4 intensity zones corresponding to the areas between the standard tungsten lines indicated in Table 1. In each zone individual spot intensities are interpreted as strong, medium, weak and very weak. Numerical values are then assigned to each spot according to its intensity and the zone in which it lies. Corresponding powder-pattern line intensities are estimated by multiplying this value by the number of spots on the line. Intensities are then scaled relative to the strongest line. The width of a line is considered to be the distance between the outer edges of the spots comprising it.

TABLE 1. EMPIRICAL VALUES USED IN CALCULATING LINE INTENSITIES

Spot intensity	Zone No. 1 16-2.24 Å	Zone No. 2 2.24-1.58 Å	Zone No. 3 1.58-1.29 Å	Zone No. 4 1.29-1.1 Å
Strong (very black)	20	15	10	4
Medium (less black)	15	10	5	3
Weak (gray)	10	5	3	2
Very Weak (only prick mark seen)	5	3	2	1

Example: Five strong spots on a line in zone No. 2, corresponding to an intensity value of 5×15 or 75. Each value can then be expressed relative to the strongest intensity value.

Since the grain cannot assume all possible orientations when attached to the wire mount, commonly a line will not be represented, or it may be represented by only one or two spots. To aid evaluation of line position and intensity, the wire mount can be bent, giving the grain a different orientation, and the grain re-X-rayed. Usually this will result in spots that fall at different positions on the same hypothetical line. The film from the second orientation can then be projected over the enlargement of the first orientation and the composite pattern interpreted as one. Provided that the crystal is properly centered within the x-ray beam, the tungsten wire gives the same spacings regardless of how mis-shapen it may become.

Interpretation of X-Ray Spot-Patterns

In order to determine the correlation among data from x-ray diffraction traces (Norelco diffractometer), spot-patterns, small powder cameras, and ASTM diffraction files,[1] a comparison was made of x-ray data obtained from eight phosphate minerals: ellestadite, wilkeite, apatite, triphylite, brazilianite, montebrasite, amblygonite, and brushite.[2]

For these eight minerals, the five strongest lines derived from the spot patterns included the three strongest lines given in published powder data. Typical results for two of the eight phosphates are shown in Fig. 4. *Diffractometer* peaks shown correspond, as closely as possible, to the shape, position and relative intensity of those found in the recorder trace. The bargraph for the *spot-pattern* data derives from spot intensities (by the method discussed previously) and the measured width of the spot-clusters making up the line. *Powder* lines on a photographic enlargement of the film were measured for position and width, assigned relative intensity values and graphed as solid bars. The width of *ASTM* lines is arbitrary.

In general, the spot-pattern data are in much better agreement with the powder-pattern and diffractometer-trace data (which were obtained from the same mineral sample) than with the ASTM data. This illustrates a major problem in identification, for phosphates at least, i.e., the degree of variation in the x-ray patterns of different samples of the "same" mineral, probably due to variations in isomorphous substitution.

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[1] X-ray Powder Diffraction File, published by American Society for Testing Materials, Philadelphia 3, Pennsylvania.

[2] Amblygonite and montebrasite are thought to be triclinic members of the same series differing only in the OH to F ratio (Palache, Berman, and Frondel, 1951).

Amblygonite and triphylite, S. Dakota, and apatite, Quebec were purchased from Wards Natural Science Establishment, Rochester, N.Y.; montebrasite from W. L. Roberts, Rapid City, South Dakota. Brushite (synthetic) was obtained from E. C. Moreno, TVA, Alabama; brazilianite, Brazil, from Miss Barbara Lowe, Washington State University; wilkeite and ellestadite, California, from A. W. Woodford, Pomona College.

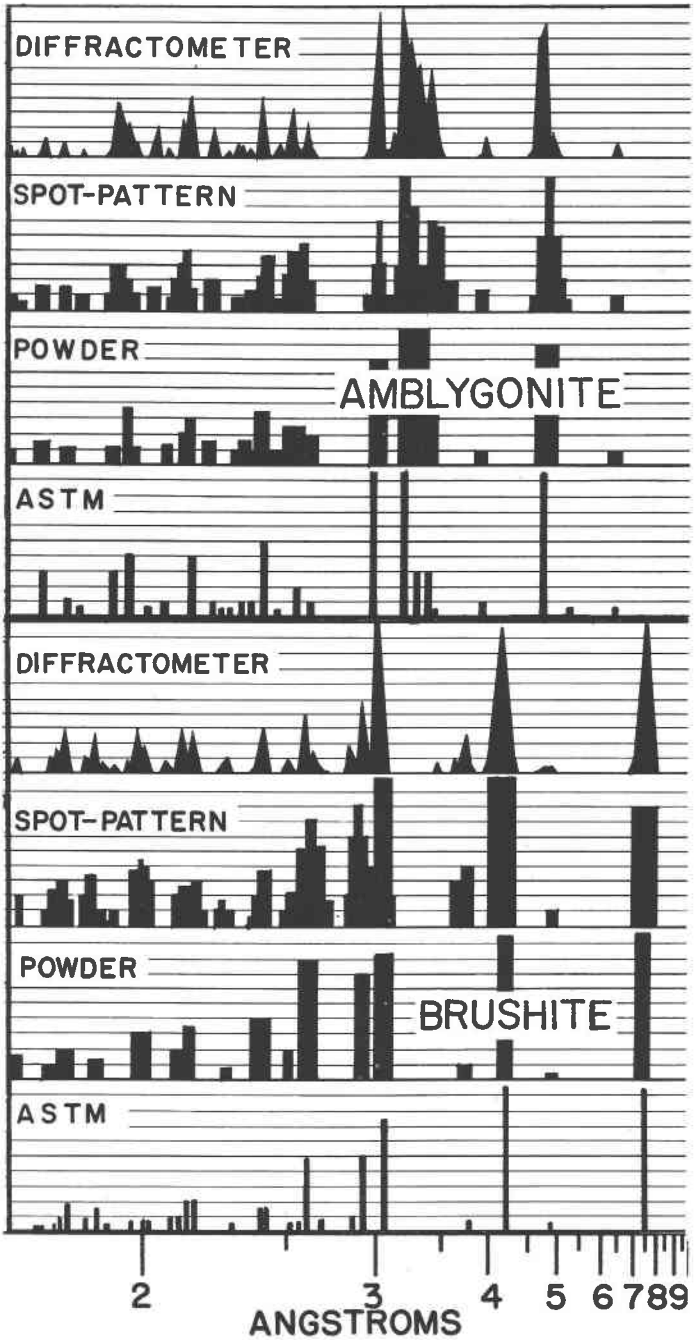

FIG. 4. ASTM x-ray data compared with three diffraction methods for two phosphates. Intensities on the ordinate are relative to the strongest line in each pattern.

This identification problem is not, of course, peculiar to the single crystal spot-pattern method. For reasonably certain identifications, the spot-pattern should be compared with the powder-pattern or diffractometer data from a suitable standard mineral.

MINERALS IDENTIFIED

In an investigation of a relatively unweathered soil from southeastern Idaho, reasonably certain identification of six phosphate minerals in the 50–100 μ size range was possible where petrographic methods alone would have, at best, allowed only tentative identification. Grains of amblygonite, montebrasite, herederite, and isokite were isolated with a staining procedure (Kittrick and Hope, 1967). X-ray spot-pattern data confirm the optical identification of these four phosphates. A species of monazite was isolated with the petrographic microscope; its spot-pattern also confirmed the optical identification.

Apatite grains were isolated using 10.7 $N H_2SO_4$ (Shipp and Matelski, 1960). Single grains showing the radiated acicular calcium sulfate crystals were picked out, washed, and X-rayed. A spot-pattern not only confirmed the presence of apatite, but also gave the pattern for calcium sulfate. Eleven opaque mineral grains were also X-rayed. Spot-patterns showed four of them to be magnetite, three to be hematite, and four contained a mineral for which no published data were found; the latter remain unidentified.

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DIFFERENTIAL THERMAL ANALYSIS OF BIOTITIC VERMICULITE TO DETERMINE VERMICULITE CONTENT

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INTRODUCTION

Differential thermal analysis was used to determine the vermiculite component of biotitic vermiculite by G. F. Walker in 1951. This was accomplished by measuring the area associated with the endotherms below 350°C and then comparing this area to that of a high purity vermiculite. Essentially identical thermograms were obtained by Walker from a biotitic vermiculite (or hydrobiotite: Gruner, 1934) sample and from a mixture of vermiculite with a suitable amount of inert material.

A rapid method of ascertaining the approximate vermiculite content of biotitic vermiculite is presented here. The methods avoids some of the difficulties of determining a true base-line and of attaining equilibrium at constant humidity. The data show that in at least one instance by any reasonable criterion a mechanical mixture of minerals is an inadequate substitute for a natural mixed-layer sample. Some observations on the structure of the low temperature peaks are also presented.

METHOD

Table 1 lists the samples used. These samples, obtained as large flakes up to 5 g, were vigorously washed and prepared for DTA by slicing them (with a razor) into pieces that passed through a 250 μ sieve but not through a 150 μ sieve. Slicing rather than grinding was used to preserve the layered nature of the samples. The samples were stored at constant humidity. Where ion exchange was used, the methods of Barshad (1948) were employed.

The vermiculite contents of the samples were gratefully received from

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[1] Present address: U. S. Naval Research Laboratory, Wash., D. C.