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A METHOD OF MINERAL SEPARATION USING HYDROFLUORIC ACID*

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The major minerals and many minor minerals of most rocks are readily decomposed by hydrofluoric acid. Some of the minor minerals, however, which generally must be isolated for positive identification and study, are decomposed extremely slowly or not at all by hydrofluoric acid. These include most sulfides and sulfosalts, many beryllium minerals, anatase, barite, bastnaesite, carbon, graphite, rutile, topaz, zircon, and doubtless others not yet investigated. This fortuitous contrast in solubility is the basis for a separation method that offers some useful advantages over physical methods of mineral separation.

Briefly, the method consists of decomposition of a rock fragment, weighing about 200 grams, by repeated application of hydrofluoric acid over a period of several weeks. Water-insoluble reaction products are removed by boiling in a solution of aluminum chloride. The method is slow and somewhat hazardous, but requires little attention. Only a few minutes work with a sample is required each day the process is in operation, and the operator is free for other less routine work.

For those minerals to which it is applicable, this method is advantageous in several respects. Separated mineral grains are exceptionally clean and pure, and crystal breakage is held to a minimum, which facilitates and enlarges possibilities for studies of crystal morphology. The true size distribution and abundance in a rock can be determined for those minerals that do not react at all with hydrofluoric acid. Easy separation can be made of at least three mineral groups that are normally very difficult to separate: (1) minerals of such fine grain as to be almost inseparable physically, as pigmenting carbon in slates; (2) minerals present in extremely minute proportions in a rock; and (3) minerals whose densities do not differ appreciably from the common rock minerals, beryl for example. The suitability for chemical studies of minerals separated by this method has not been investigated.

The following minerals, apparently unchanged in form, have been recovered by this method from a limited variety of ordinary crystalline rocks: anatase, arsenopyrite, barite, bastnaesite, bertrandite, beryl, bornite, carbon, chalcocite, chalcopyrite, chrysoberyl, covellite, euclase, graphite, molybdenite, pyrite, rutile, silver, sphalerite (Fe-poor), topaz, and zircon. *X*-ray patterns made of most of these minerals showed

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no evidence of their having reacted with hydrofluoric acid or aluminum chloride. I am indebted for contributions to this list to Theodore Botinelly, Keith Ketner, and W. N. Sharp, who have found this method useful.

Finely ground samples of a few additional minerals were tested by digesting them in cold 48 per cent hydrofluoric acid for two days, decanting, washing, and drying before bringing to a 1-minute boil in aluminum chloride solution. Apatite, cinnabar, cuprite, monazite, uraninite, and xenotime were partly or completely decomposed in this test. The minerals that survived are boulangerite, cassiterite, digenite, enargite, gold, loellingite, melonite, pyrargyrite, stibnite, tetrahedrite, tourmaline, and zinckenite. Some in the latter group, however, might not last through the full decomposition of a rock, as this involves much more intense and prolonged treatment with hydrofluoric acid. Also, some rocks might react with hydrofluoric acid to produce compounds that would in turn decompose some of these minerals.

The effect of hydrofluoric acid on some sulfides was tested quantitatively by treating finely ground samples of pure minerals in parallel with a group of rocks being separated by the procedure given at the end of this note. The results are shown in Table 1. No changes were visible in the appearance of chalcopyrite, molybdenite, and pyrite; the losses for these minerals could be mainly from repeated handling of such small quantities of finely divided material. Galena was etched and coated with a thin iridescent film. Pyrrhotite was largely dissolved, the residue being partly coated with a brown film. The grain form and crystal structure of sphalerite persist, but the mineral is partly dissolved and is heavily filmed by a black substance.

The sulfide mineralogy of 37 samples of quartz monzonite and granodiorite from the Boulder batholith, Montana, was studied by means of polished sections, heavy media separation, and hydrofluoric acid separa-

TABLE 1. SOLUBILITY OF SULFIDES IN HF

	Sample weight	Recovered weight	Weight loss
Chalcopyrite	0.0497 g (0.0518 g)*	0.0473 g (0.0508 g)*	4.8% (1.9%)*
Galena	0.0986 g (0.0591 g)*	0.0705 g (0.0508 g)*	28.5% (14.0%)*
Molybdenite	0.0245 g	0.0244 g	0.4%
Pyrite	0.0431 g (0.0278 g)*	0.0410 g (0.0260 g)*	4.9% (6.5%)*
Pyrrhotite	0.0881 g	0.0056 g	93.6%
Sphalerite (Fe-rich)	0.0549 g	0.0450 g	20.0%

* Treated with technical instead of analytical grade HF.

tion. The results of the three methods of study are in substantial agreement, except that the relative abundance and variety of sulfides found with hydrofluoric acid are greater. The amount of total sufide separated with hydrofluoric acid indicates a sulfide abundance in the rock of 2 to 3 times that indicated by the results of heavy media separation.

Further study of the method, particularly of its quantitative effect in partly dissolving some minerals, is obviously needed. However, sufficient experience has been had with the method to demonstrate its usefulness in solving some difficult problems in mineral separation. I am particularly indebted to Professor Paul Ramdohr for his spoken suggestion (1960) that I try to isolate sulfides from the Boulder batholith rocks with hydrofluoric acid.

PROCEDURE

The detailed procedure developed for use on the Boulder batholith rocks serves to illustrate the method. It should be considered only as a guide. Modifications may be necessary in treating rocks of different compositions and in separating minerals that react with difficulty but that do react finally with hydrofluoric acid or with aluminum chloride. For example, most of the magnetite of a rock can be preserved by removing it physically just before the final residue of rock is treated with hydrofluoric acid in step 3, below.

The initial, preferred sample is a single piece of rock, weighing about 200 grams. Crushed or ground samples pose the danger of violent reaction with hydrofluoric acid; addition of hydrofluoric acid to rock powders as coarse as 10 mesh can result in as much effervescence as that produced by the addition of concentrated hydrochloric acid to powdered chalk. Fragmentation of the sample unneccessarily breaks desired grains, especially of the brittle sufides, and introduces possibilities of inter-sample contamination and selective loss of some components. Apart from finely ground samples, the rate of decomposition of a rock by hydrofluoric acid appears to be slow and not materially affected by grain size; no more than one-third saving in time is had by fragmenting to a pea-sized product.

All work with hydrofluoric acid must be done in a well-ventilated hood, and the operator must take every caution to avoid contact with the acid or its fumes. An ordinary laboratory hood may be used and will apparently suffer no damage from long contact with hydrofluoric acid fumes. Analytical grade reagents are not required in the following procedure.

STEP 1. Add about 70 ml. of approximately 52% hydrofluoric acid to the sample in a polyethylene beaker, which is conveniently cut from emptied hydrofluoric acid bottles of the size used for 1-lb quantities of the acid and of the type not requiring cardboard reinforcement. The reaction is allowed to proceed at room temperature for 24 hours, after which the liquid phase is evaporated overnight to moist dryness on a steam bath. The beaker now contains unreacted rock, water-soluble reaction products, and water-insoluble reaction products. These reaction products are removed in the next step before further addition of acid, lest they interfere with the efficiency of the further acid treatment of the unreacted rock.

STEP 2. The residue from step 1 is digested in 150 ml. of water for one hour on the steambath, with occasional stirring. The reaction products are washed into another polyethylene beaker; 70 ml. more of hydrofluoric acid is added to the remaining undecomposed rock and step 1 is repeated. The separated material is filtered and washed to remove most of the water-soluble reaction products. The undissolved material, consisting of HF-insoluble minerals, loose fragments of reaction products, and small rock particles, some of which are armor-plated with reaction products, is dried and set aside. Filtering rather than decanting is necessary because some of the sulfides float on the surface of the liquid. If loss of materials less than 200 mesh in size can be tolerated, appreciable time, bother, and reagent are saved by wet-sieving through 200-mesh silk bolting cloth instead of filtering through paper.

The first and second steps are repeated until no more rock is visible in the first beaker. This point is reached in 4 to 6 weeks, apparently varying with mineralogy and with texture; each 70 ml. of hydrofluoric acid decomposes from 10 to 30 grams of the sample.

STEP 3. The residues from step 2 are combined and gently pulverized by grinding with a rubber-tipped (soil) pestle. These residues still contain some water-soluble reaction products, which are removed by heating to boiling with 1 to 1½ liters of water and filtering or sieving. The residue remaining at this point is dried and then treated once more—or oftener if necessary—with hydrofluoric acid to dissolve any included rock particles. Some minerals such as magnetite and pyrrhotite may be quite resistant up to this step, then dissolve with considerable rapidity.

STEP 4. The material from step 3 is brought to a 1-minute boil in 200 ml. of a solution of aluminum chloride (227 grams of $AlCl_3 \cdot 6H_2O$ in 1 liter of water) in pyrexware, allowed to settle for 1 minute and filtered. Again it is preferable to wet-sieve through 200-mesh silk bolting cloth, here for the additional reason that the liquid phase may gelatinize on cooling. Gelatinization has been uncommon in practice and it can be avoided by diluting with hot water. The residue on the screen or filter is washed back into the beaker, 200 ml. of aluminum chloride solution is added to it, and the mixture is allowed to stand overnight before boiling and filtering once again.

STEP 5. The residue from step 4 is again treated with hydrofluoric acid, to remove HF-soluble minerals that were armor-plated with water-insoluble reaction products in earlier steps. The addition of hydrofluoric acid at this point *must* be made with extreme caution, because the first increment of acid usually reacts violently and may cause dangerous spattering.

Steps 4 and 5 can be repeated as often as necessary to clean the minerals concentrated by the first application of step 5. Attempts to shortcut the method by heavy media separations were unsatisfactory owing to very inefficient recoveries, presumably because of a tendency for adhesion of some insoluble reaction products to the HF-insoluble minerals.

Besides a mixture of minerals, the final product contains organic material, principally filter paper fibers. Lichens, or some modification thereof, are obtained from samples taken from the surfaces of natural outcrops. Paint or paper labels, if left on the sample, may also contaminate the product.