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SELECTIVE CHEMICAL DISSOLUTION OF SULFIDE MINERALS: A METHOD OF MINERAL SEPARATION[1]

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ABSTRACT

Many potentially informative studies of sulfides are handicapped by a lack of methods that readily separate sulfide minerals from one another and from coexisting silicate minerals. Simple chemical procedures were developed that: 1) selectively dissolve the sulfide fraction of comminuted silicate rocks; 2) selectively dissolve galena from ground ores; and 3) selectively dissolve sphalerite from ground sphalerite-pyrite mixtures and inter-growths. The second procedure, in particular, has proven useful in sulfur isotope studies.

INTRODUCTION

Sulfides are generally susceptible to attack by oxidizing agents in aqueous or organic solution. A broad spectrum of mild oxidants is widely employed in metallographic practice to aid in identification of inclusions on the basis of etch reactions. Careful selection among these has allowed us to dissolve sulfides selectively. Aqueous solutions of bromine, ferric chloride, and alkaline permanganate have been used successfully.

Prior to selective chemical attack, an examination of a polished section of the material is necessary to determine how finely it should be ground to ensure exposure of the phases to be dissolved.

DISSOLUTION OF SULFIDES FROM SILICATE ROCKS

Chemical analysis of sulfide-bound metals in rocks requires a solution procedure that will attack the sulfides and not the silicate matrix. In the course of an investigation of sulfide inclusions in eclogite (Desborough and Czamanske, in press), the following technique was developed to determine sulfide-bound metals and their respective proportions.

Procedure. To several grams of rock powder in a 400 ml beaker, add 200 ml of water and sufficient acid to prevent precipitation of metal hydroxides. Add 3–5 ml of bromine, cover, and stir gently for 12 hours or more. The acid to be used depends on the metals sought. Usually 0.5–1.0 ml of hydrochloric acid will be adequate. Perchloric acid may be preferable if lead or silver are of interest. Uncover the beaker and warm gently until excess bromine is removed. Decant or filter the solution

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and determine its metal content by any means available. In our practice, stirring is done on an oscillating hot plate, and the solution is analyzed by atomic absorption.

Much of the sulfur may remain in the liquid bromine (as sulfur bromides). Remove the bromine phase by means of a separatory funnel, or, more conveniently, a separatory flask (Ingamells, 1964). If free sulfur remains, repeat the treatment with bromine. Remove bromine dissolved in the aqueous solution by repeated extraction with carbon tetrachloride. The metals remain in the aqueous solution. Removal of the bromine by warming may cause precipitation of the sulfur and/or reformation of metallic sulfides. Determination of sulfur in the rock, if required, can be quickly accomplished by X-ray spectrography (Fabbi and Moore, 1970). Chemical determination of total sulfur requires that any sulfate formed be removed from the aqueous solution and combined with the sulfur in the bromine phase.

Bromine oxidation is effective with all sulfides we have treated, including chalcopyrite, galena, pyrite, pyrrhotite, sphalerite, and even cinnabar. Cinnabar is unattacked by most other reagents at room temperature; in fact, bromine extraction is the only simple procedure we know that will permit separation of mercury from sulfur while retaining each quantitatively. Magnetite is not attacked to any appreciable extent, nor are the following silicate rocks and minerals: peridotite, serpentine, eclogite, garnet, biotite, and hornblende. However, a second leaching process may be advisable to check for slow extraction of iron and other metals from silicates in the sample. In experiments with eclogite, the metal content of the second leach solution was only 2 percent of that of the initial leach. If attack of nonsulfides is excessive, the acid addition may be omitted, and hydrolysed metal compounds dissolved by brief treatment with dilute acid at the end of the procedure.

PREFERENTIAL DISSOLUTION OF GALENA

Galena may be preferentially removed from mixtures with most sulfides by treatment with $FeCl_3$ at room temperature. In our particular application, we have been concerned with separating galena from intimate galena-sphalerite mixtures and intergrowths to allow sulfur isotope analysis of each coexisting phase. An advantage of the technique described is that the galena-associated sulfur can be recovered and analysed isotopically.

Procedure. A sample containing approximately 200 mg of galena is added to 300 ml of aqueous 10 percent $FeCl_3$ in a 600 ml beaker. (In this and other procedures, addition of a few drops of a wetting agent may be helpful.) Cover the beaker to prevent splashing and stir for about 24 hours with an intensity sufficient to gently move the grains around the perimeter of the beaker. Agitation of the grains is necessary to permit contunuid attack of refreshed galena surfaces. Iron oxide films formed during this procedure may be removed by washing with diluted HCl.

The gentle attack provided by this procedure oxidizes the galena-associated sulfur only to the native sulfur state. Quantitative recovery of this sulfur has been accomplished as follows. Vacuum filter the solution through a suitable fine filter (we use Gelman Type E glass filter pads). Dry the filter pad with carried material at <60°C. Dissolve the free S from the filter in boiling benzene by use of a 50 or 100 ml boiling flask equipped with a refluxing column. Filter the sulfur-pregnant benzene solution into an appropriate vessel and evaporate at <60°C.

Crystallized sulfur is collected, then ground and heated at <60°C. for several hours to drive off occluded benzene. The sulfur is combined with a slight excess of zinc or silver filings, sealed in an evacuated silica tube, and reacted to form a sulfide suitable for routine isotopic analysis. This final procedure, the quantitative reaction of native sulfur with Zn or Ag at elevated temperature in evacuated tubes, is considered superior to most previously employed means of preparing free sulfur samples for precise isotopic analysis. (Reaction with Pb to reform galena is not favored due to slightly greater difficulty in reacting galena quantitatively with the CuO technique.)

Our control showed that we dissolved 1–2 mg of Zn with the $FeCl_3$ treatment. The associated 0.3–0.7 mg of S would, of course, be incorporated in the analyzed sulfur. In isotopic analysis this level of contamination would generally be insignificant; if necessary, Zn analysis of the filtered $FeCl_3$ solution, combined with sulfur isotopic analysis of the sphalerite, would allow correction of the isotopic data. In other applications, for example, trace-element analysis of coexisting galena and sphalerite, the contamination resulting from minor sphalerite dissolution could be a much more serious problem.

Preferential Solution of Sphalerite from Pyrite

Sphalerite is dissolved preferentially from pyrite by a solution of 1 percent $KMnO_4$ and 15 percent NaOH. This procedure has been applied most extensively by our colleague C. A. Anderson in a study of trace elements in pyrite. We are grateful for the details of his auxiliary techniques. The samples treated were from fine-grained, massive pyritic deposits in central Arizona. Samples were crushed and sieved; material ranging from -100 or -120 to $+170$ mesh was used for the chemical treatment.

The Franz magnetic separator was used to remove much of the sphalerite present in the ore samples, but it was impossible to remove aggregate grains of sphalerite and pyrite. This nonmagnetic fraction was treated with HCl to remove carbonate gangue, then with HF to remove quartz gangue. If any Ca remains when HF is added, CaF_2 is formed, which can be removed by boiling with a 50 percent aluminum chloride solution ($AlCl_3 \cdot 6H_2O$).

Procedure. Add sphalerite-pyrite sample containing about 40 mg of sphalerite to 250 cc of solution in a 600 ml geaker. Heat at 80°C on a hot plate, cover with Saran wrap to retain splashed solution, and stir with a glass rod attached to an electric stirrer. The fastest stirring speed possible without considerable splashing is preferable. When the solution turns green, oxidizing action has stopped. Decant the solution, wash the sample with water, and check under the microscope to determine if any sphalerite remains. If sphalerite is present, the process is repeated until all sphalerite has been removed.

Pyrite is gradually attacked by this treatment. Insoluble ferric compounds formed by the oxidation of this pyrite and iron-bearing sphalerite are removed by heating the sample briefly in diluted HCl.

ACKNOWLEDGMENTS

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REFERENCES

FABBI, B. P., AND MOORE, W. G. (1970) Rapid X-ray fluorescence determination of sulfur in mineralized rocks from the Bingham mining district, Utah. *Appl. Spectrosc.* **24**,

INGAMELLS, C. O. (1964) Devices for liquid-liquid extraction. *Chemist-Analyst*, **53**, 55.

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AN IRON-SENSITIVE STAIN FOR IRON-RICH SPHALERITE: ERRATUM

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Page 1051, Figure 2 is reversed relative to Figure 1; the broad band of 25 mole percent FeS on the right (between 150 and 300 microns) in Figure 2 corresponds to the broad band of dark colored sphalerite on the left in Figure 1.

REFERENCE

EINAUDI, M. T. (1970) *Amer. Mineral.* **55**, 1048–1051.