THE LOCALIZATION OF COPPER AND SILVER SULFIDE MINERALS IN POLISHED SECTIONS BY THE POTASSIUM CYANIDE ETCH PATTERN

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ABSTRACT

Copper and silver sulfide minerals that are etched by potassium cyanide can be localized in polished sections by contact printing on a lead cyanide emulsion moistened with potassium cyanide. The specificity of the method is studied and conditions formulated for the differentiation of the copper sulfides from other metallic sulfide minerals.

INTRODUCTION

The positive identification of copper sulfide minerals in rock drillings is of importance in economic geology, as these minerals may serve as an index in furthering the exploration of deep seated copper ore bodies. The traces of copper sulfides often occur as minute grains which renders their identification difficult by the standard techniques of ore microscopy.

The methods of contact printing are particularly adapted to the study of minute grains as the mechanical removal of individual micro samples from the surface is avoided. This insures freedom from contamination by particles of non-cupriferous sulfides surrounding or located beneath the polished grain. Also, once a selective printing pattern for a given constituent is devised, the method localizes all identical particles in the polished section. The application of these novel methods of surface analysis in mineralogy have been reviewed by Gutzeit (6) and the diverse printing procedures applicable to the analysis of mineral and biological materials have been classified by Yagoda (12).

Briefly, the printing procedure consists in the dissolution of a thin film from the polished section and its simultaneous transfer to a nondiffusing medium such as gelatin. The ions brought into solution can then be developed for one or more chemical constituents by treating the medium with suitable selective reagents. When the film is stripped with the aid of solvents the developed image is known as a contact print. A large number of the opaque sulfide minerals are good conductors of the electric current. Massive conducting specimens can be stripped electrolytically. This electrographic technique is advantageous in that the flow of positively and negatively charged ions migrating into the gelatin film can be altered by varying the polarity of the specimen. Electrographic methods of analysis are not applicable to minute conducting grains embedded in in-

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sulating mounting media or when surrounded by non-conducting gangue minerals.

The copper sulfide minerals most commonly encountered are chalcocite, covellite, bornite and chalcopyrite. Grains of these tracer minerals may be accompanied by other non-sulfide copper minerals such as cuprite, malachite, azurite, chrysocolla, turquoise and native copper. The problem of the identification of the copper sulfide minerals is further complicated by the presence of sulfide minerals of other heavy metals, such as pyrite, sphalerite and galena. In order to identify any given particle as a copper sulfide mineral, there must be a point to point correlation between the copper and sulfide patterns of the polished section.

Satisfactory printing methods are available for demonstrating the presence of copper minerals (5). Difficulties were encountered in obtaining sulfide patterns of the more common opaque minerals utilizing the contact printing methods described in the literature. The method of Baumann (2) utilizing a silver bromide emulsion moistened with 10 per cent hydrochloric acid does not yield a brown silver sulfide print when applied to the common copper sulfide minerals. Likewise, the method of Gutzeit (6) employing 40 per cent hydrochloric acid as the etching agent and antimony trichloride as the indicator failed to yield the characteristic orange colored antimony sulfides when the test was applied as a contact print. In the course of these investigations it was observed that potassium cyanide exhibited a selective solvent action on several members of the copper and silver sulfide groups of minerals and that the sulfide ion liberated by the reaction could be readily fixed in the emulsion by simultaneous precipitation as dark brown lead sulfide.

MECHANISM OF THE POTASSIUM CYANIDE ETCH

Potassium cyanide dissolves freshly precipitated copper or silver sulfide with the formation of complex salts. The basic reaction is expressed by the following equations:

(1) $Cu_2S + 2KCN \rightarrow 2CuCN + K_2S$

(2) $CuCN + KCN \rightarrow KCu(CN)_2$
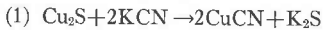
This type of complex formation with metallic sulfides is known only for the metals of the first sub-group of the periodic system (Ag, Cu and Au). According to Ephraim (3) thallium and mercury also form complex cyanides which are less stable than those of silver and copper. The stability of the cuprocyanide complex has been utilized as the basis for delicate tests for cyanides by Barnebey (1) and Feigl (4), using freshly precipitated copper sulfide as the reagent. Hiller has described a printing method for the detection of silver sulfide minerals utilizing a mixture of potassium cyanide and the specific silver reagent, p-dimethylaminobenzylidene

rhodanine as the etching medium (8). The solvent action of potassium cyanide has also been employed by Hermance (7) in the stripping of sulfide tarnish films from copper and silver alloys.

Potassium cyanide is readily hydrolyzed in aqueous solution with the formation of a high concentration of hydroxide ion. This alkalinity may give rise to side reactions which interfere with the specificity of equations (1) and (2). As a preliminary survey, droplets of solutions of the more common metallic ions were allowed to evaporate on gelatin paper. The sheet was exposed to hydrogen sulfide gas, causing the precipitation of the metallic sulfides. Droplets of 5 per cent potassium cyanide were then placed on the colored sulfides and the solvent action noted: The freshly precipitated sulfides of copper, silver and arsenic dissolved rapidly and completely. Thallium, iron, nickel and cobalt sulfides showed evidence of partial decomposition. The sulfide stains of lead, bismuth, cadmium and antimony remained completely unaltered during a three minute period of contact with the potassium cyanide. These etch reactions on freshly precipitated sulfides indicated that interfering reactions may be anticipated from pulverulent metallic sulfide minerals that are attacked by alkalies.

Method of Obtaining the Potassium Cyanide Etch Pattern

The etching action of potassium cyanide on the copper and silver sulfides is rendered visible as an analytical pattern through the interaction of the potassium sulfide, liberated during the solution process, with a sparingly soluble lead compound incorporated in a gelatin emulsion. The test papers are made by dipping pure gelatin coated paper* for one minute in a 2 per cent solution of lead nitrate. Excess solution is removed by blotting between lintless absorbent paper, and the moist sheets are allowed to dry gelatin face up on a layer of cheese cloth. The supply of lead nitrate paper is then cut into small strips somewhat larger than the size of the polished section. The paper keeps well if stored in an atmosphere free from hydrogen sulfide.

When ready to make a print, a piece of the dry lead nitrate paper is immersed in a 5 per cent solution of potassium cyanide for about 10 seconds, and is moved about in the dish so as to dislodge any adhering air bubbles from the gelatin surface. The paper is drained and all excess fluid removed by blotting between filter paper with the aid of a rubber

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* Pure gelatin coated paper free from silver halides can be secured from the Eastman Kodak Co. under the name "Imbibition Paper" or from the Defender Photo Supply Co., Rochester, N. Y., under the designation "Backing S, non-sensitized." A suitable medium can also be made by extracting the silver halide salts from a glossy photographic paper with hypo, washing thoroughly and drying.

roller. This process results in the formation of finely divided insoluble lead cyanide dispersed in a gelatin film wetted by excess potassium cyanide.

The damp freshly prepared emulsion is placed on a soft rubber mat** and the polished section is inclined onto the gelatin surface, so as to avoid the inclusion of air bubbles. The section is pressed against the emulsion and subjected to a pressure of 1 kg. for a period of 1 minute. Those copper or silver sulfide minerals, which are etched by cyanide, are revealed in the print, as mirror images, by the formation of dark brown lead sulfide.
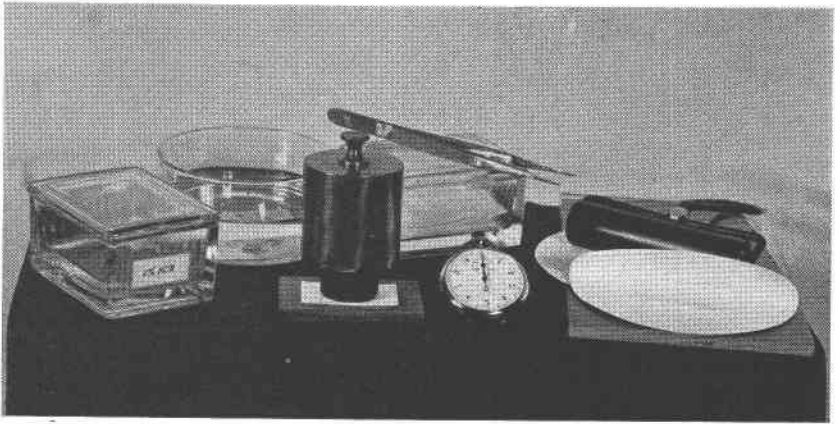

FIG. 1. Apparatus for contact printing.

Center: Polished specimen in bakelite mount in contact with moist emulsion.

Right: Excess cyanide solution removed by blotting between filter paper with aid of rubber roller.

Rear: Staining dishes make convenient receptacles for etching solutions. Test papers are handled with platinum tipped forceps.

The print is washed in water for about 10 minutes to remove soluble cyanides. It is dried by placing the gelatin face down on a glass plate and blotting dry with the aid of a rubber roller. When the paper is thoroughly dry the print springs away from the glass imparting a glossy finish to the gelatin surface. The glass plate should be surfaced occasionally by rubbing with a cloth moistened with a few drops of a 0.1 per cent solution of paraffin in carbon tetrachloride. The paraffin film prevents sticking of the gelatin to the glass.

** This slightly resilient support facilitates perfect contact between the test paper and the polished surface. It is made by cementing a sheet of rubber about 1 mm. thick to a slab of bakelite measuring about $7 \times 5 \times 0.5$ cm.

To facilitate subsequent comparison of the print with the polished surface, it is convenient to make an indicating mark on the cylindrical wall of the mounted section and to orient this mark with the central axis of the paper, as shown in Fig. 1. The dry prints have a tendency to curl. Distortion of the image is avoided by mounting the gelatin paper on a stiff cardboard by means of rubber cement. Typical cyanide etch patterns of massive copper sulfide minerals are reproduced in Fig. 2.
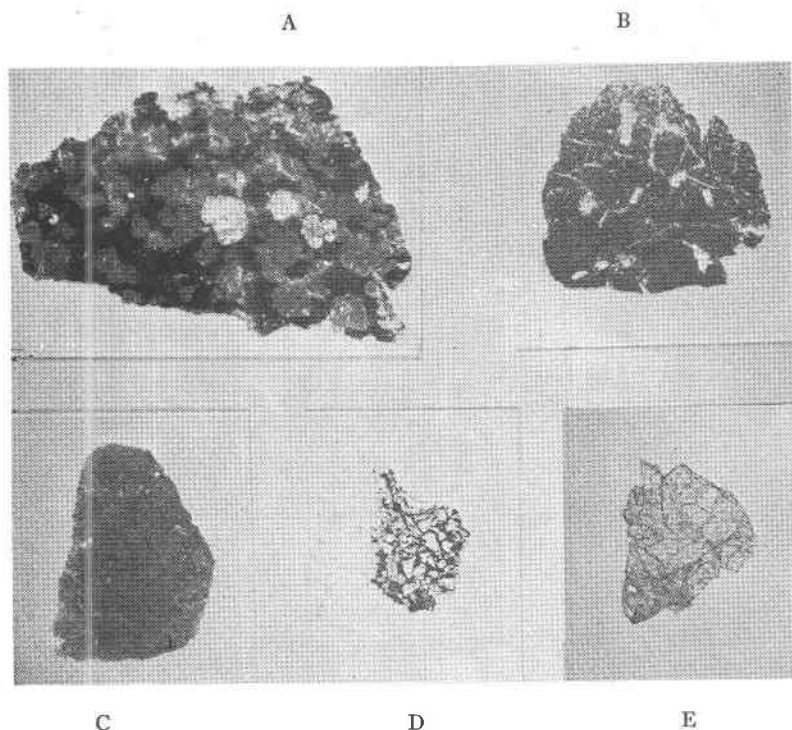

FIG. 2. Sulfide prints of typical copper sulfide minerals.
A: Bornite and chalcocite, Butte, Montana.
B: Enargite, Cerro de Pasco, Peru.
C: Bornite, Bisbee, Arizona.
D: Stromeyerite, Mt. Lyell, Tasmania.
E: Enargite, California (specimen, highly polished).

RESPONSE OF SULFIDE MINERALS TO CYANIDE ETCH PATTERN

This particular sulfide printing procedure is highly selective. Positive reactions are secured only with those species that are decomposed by potassium cyanide with the liberation of sulfide ion. Table 1 describes the behavior of the common, and several of the available rare members,

of the copper and silver sulfide groups. Of the collection of sulfide speci-
mens studied, only chalcocite, covellite, bornite, argentite and stromeyer-
ite give dark brown positive prints. The more complex copper and silver
sulfides which contain the As_2S_3 grouping in their structure, as enargite,
tennantite and proustite also give positive reactions. The patterns fur-
nished by these minerals, for the identical period of contact, are not quite

TABLE 1. COMPARATIVE BEHAVIOR OF MINERALS TO CYANIDE ETCH REACTIONS

Mineral	Composition	Staining with 20% KCN	Sulfide Pattern with 5% KCN
Chalcocite	Cu_2S	quickly stains black	dark brown (3)*
Covellite	CuS	stains black	dark brown (1)
Stromeyerite	$(Cu, Ag)_2S$	quickly stains black	dark brown (2)
Argentite	Ag_2S	stains brown to black	dark brown (3)
Bornite	Cu_5FeS_4	stains brown	brown (2)
Enargite	$Cu_2S \cdot 4CuS \cdot As_2S_3$	stains black	light brown (4)
Proustite	$3Ag_2S \cdot As_2S_3$	stains black	light brown (3)
Argyrodite	$4Ag_2S \cdot GeS_2$	stains light brown	light brown (1)
Tennantite	$5Cu_2S \cdot 2(Cu, Fe)S \cdot 2As_2S_3$	weak or negative	light brown (1)
Tetrahedrite	$5Cu_2S \cdot 2(Cu, Fe)S \cdot 2Sb_2S_3$	weak or negative	negative (2)
Chalcopyrite	$CuFeS_2$	negative	negative (5)
Stannite	$Cu_2S \cdot FeS \cdot SnS_2$	negative	negative (2)

* Number of specimens tested from different localities.

as intense as in the case of the simple sulfides. When occurring in the
same section the two types of minerals can be differentiated by the rela-
tive intensity of their prints. A study of Table 1 reveals that in general a
good correlation exists between the character of the cyanide etch pattern
and the nature of the stain imparted to the polished surface of the mineral
when acted on by 20 per cent potassium cyanide. The description of the
stains listed in Table 1 are those recorded by Short (11). Minerals which
do not stain with 20 per cent potassium cyanide, as chalcopyrite, in-
variably yield negative sulfide patterns under the conditions of the test.

A representative collection of the more common opaque ore minerals
was printed by the cyanide etch procedure for possible interfering reac-
tions. The following species gave unambiguous negative tests, the figure
in parenthesis showing the number of specimens tested from different
localities:

Native Elements: copper (2), silver (2), gold (1), tellurium (2).
Sulfides: stibnite (1), molybdenite (1), galena (3), sphalerite (3), cinnabar (1), pyr-
                  rhotite (2), pyrite (3), marcasite (2), realgar (2), millerite (1), ullmanite (2),
                  zinkenite (1), bismutoplagionite (1), jamesonite (1), stannite (2), bravoite (1),
                  tetrahedrite (2), livingstonite (1), chalcopyrite (5), pyrargyrite (1), bournonite
                  (1), cubanite (1).

Arsenides: smaltite (1), niccolite (2), algodonite (1).
Tellurides: rickardite (1), calaverite (1), tetradymite (1), petzite (1).
Selenides: tiemannite (1).

One sample of black sphalerite from Tsumeb, S. W. Africa, gave a strong positive cyanide etch pattern. A confirmatory copper pattern revealed the presence of considerable copper. Schneiderhöhn (10) who has made an extensive study of the sphalerite from this locality concludes that the ore consists of a fine intergrowth of copper sulfides and zinc sulfide.

Polished sections of native copper which had been exposed to laboratory fumes gave a faint stain indicative of a superficial sulfide coating. The freshly polished sections yielded a negative cyanide etch pattern.

Orpiment-As_2S_3 gives an interfering pattern identical in color with those produced by copper and silver sulfides. This reaction is caused by the hydrolysis of the potassium cyanide and the consequent solvent action of the alkali on arsenious sulfide. The more compact realgar-AsS is not etched by cyanide solutions and does not yield an interfering pattern. Orpiment is readily recognized by its characteristic yellow color. The mineral can also be differentiated by the following modification of the contact print procedure. The lead nitrate gelatin paper is moistened with 10 per cent sodium carbonate solution and contacted with the specimen for 1 minute. Orpiment is attacked by the sodium carbonate and yields a brown print of lead sulfide fixed in the lead carbonate emulsion. Sodium carbonate has no solvent action on the copper and silver sulfides, hence they do not print, and the resultant pattern is selective for orpiment.

Violarite-$(Ni, Fe)_3S_4$ is also attacked by alkali and yields a faint greenish brown pattern when contacted against a lead cyanide emulsion moistened with 5 per cent potassium cyanide. Here too the etching is caused by the hydrolysis of the cyanide, as a similar print is obtained when the lead nitrate paper is moistened with sodium carbonate. Short (11, 1st ed., p. 77) describes violarite as unstable and usually crumbly

In the systematic examination of available polished sections for interferences with the copper and silver sulfide pattern, a very unusual color reaction was obtained with an old, surface weathered, specimen from Joachimsthal, Bohemia, labelled "Argentopyrite." Inclusions within the hard massive material yielded a pale blue print. The identical coloration is obtained when pure gelatin paper moistened with 5 per cent potassium cyanide is pressed against the polished surface, indicating that the blue print is formed by the action of the cyanide on a soluble iron mineral. The formation of complex ferro- or ferricyanides is further demonstrated by dipping the pale blue print into dilute hydrochloric acid which causes

a marked intensification of the blue color—identical in appearance with Prussian blue. When the specimen is contacted with gelatin paper moistened with *neutral* 10 per cent potassium thiocyanate the inclusions yield a deep red print of ferric thiocyanate. The blue color reaction with potassium cyanide and the red print with potassium thiocyanate has also been observed on some unidentified grains embedded in a massive section of pyrrhotite from Ontario, Canada. These observations are recorded as potential interferences in the detection of copper sulfides, but they also suggest a novel approach in the localization of the native ferric sulphate and ferric chloride minerals.

The native copper and silver selenides are a potential source of interference with the specificity of the sulfide pattern. Short (11) describes the following cyanide etch reactions for the selenide minerals: Aguilarite, $Ag_2(S,Se)$—stains weak brown. Eucairite, $Cu_2Se \cdot Ag_2Se$—instantly stained black. Klockmannite, $CuSe$—quickly stains black. Umangite, Cu_3Se_2—tarnishes blue. The solvent action of potassium cyanide causes the liberation of potassium selenide, which reacts with the lead cyanide and forms a brown image of lead selenide. The extreme rarity of these species and the difficulty of securing specimens free from accompanying copper and silver sulfides renders their experimental investigation difficult. An ore specimen from Sierra de Umango, Argentina, reported to contain admixed eucairite, klockmannite and umangite furnished a positive brown colored pattern on a lead cyanide-potassium cyanide emulsion.*

The mineral sections employed in these investigations were not polished to a mirror finish. They were simply ground plane on a glass plate with FFF grade carborundum powder. Subsequent comparison of the sulfide prints of ground and highly polished sections showed that for an equal period of contact the polished sections yielded positive prints of lower intensity. Mirror finished mineral surfaces are in general resistant to etching agents. While yielding contact prints exhibiting fine detail in the case of the more readily soluble species, a finely polished specimen may give only a faint or a negative reaction in the case of minerals not readily etched by potassium cyanide as, enargite, tennantite and proustite. These minerals can be printed from highly polished specimens by prolonging the period of contact, or preferably, by dulling the surface on very fine emery paper (grit 4/0) prior to making the print.

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* Preliminary work indicates that the selenides of copper and silver can be differentiated from the more common sulfides by contacting the freshly polished surface against a cadmium ferrocyanide emulsion moistened with potassium cyanide. The selenides yield an orange colored print of cadmium selenide. Sulfides do not react with the insoluble cadmium ferrocyanide.

Differentiation of Copper and Silver Sulfides

The cyanide etch pattern gives positive reactions with chalcocite, bornite, covellite and enargite which are indistinguishable from silver sulfide minerals such as argentite or proustite. In view of the comparative rarity of the silver sulfide minerals, a positive pattern is usually indicative of the more common copper sulfides. However, the members of the two groups can be differentiated by making further contact prints of the polished section and developing these for copper and silver by appropriate selective reagents.

Copper Pattern: Moisten pure gelatin paper with $(1+1)NH_4OH$, blot off excess fluid and contact with polished surface for a period of one minute. Develop paper by immersion in a freshly prepared solution of dithiooxamide of the following composition: Dissolve 100 mg. dithiooxamide in 10 ml. acetone, dilute with 40 ml. methanol and add 1 ml. of glacial acetic acid. Wash print in distilled water and dry. Copper minerals etched by ammonia yield dark olive green prints.

This procedure is a modification of the method described by Niessner (9) for the localization of copper inclusions in alloys, and its application to polished sections of minerals has been described by Gutzeit, Gysin and Galopin (5). Certain nickel bearing minerals which etch with ammonia yield blue prints with dithiooxamide. Likewise, cobalt minerals may yield an interfering brown pattern. Silver minerals soluble in ammonia, as cerargyrite, also yield a brown print on development with dithiooxamide. In general, the olive green markings characteristic of the copper derivative are very distinctive and are readily differentiated from the colors imparted by ammonia soluble nickel, cobalt or silver minerals.

Of the copper sulfide minerals yielding positive cyanide etch patterns, chalcocite, covellite, stromeyerite and bornite yield intense copper prints when etched by ammonia. Enargite and tennantite furnish green prints of lesser intensity. The silver sulfide minerals, argentite, proustite and argyrodite do not print. Chalcopyrite may yield a faint print, but in general, most specimens react negative. Tetrahedrite does not etch with ammonia and therefore yields a negative copper pattern. Certain non-sulphide copper minerals as malachite, azurite, native copper and to a lesser extent cuprite, furnish positive copper prints. The cyanide and copper patterns must therefore be closely examined for proper correlation of points or areas in order to identify a particular grain as a copper sulfide mineral. The high selectivity of the cyanide etch pattern greatly simplifies the examination as only copper or silver sulfides register on the emulsion.

When a given area of the polished section gives a positive cyanide etch pattern for sulfides and the corresponding copper pattern is negative, the mineral may be either orpiment or a member of the silver sulfide group. Orpiment can be identified by inspection and confirmed by etching with sodium carbonate, as previously described. The presence of silver
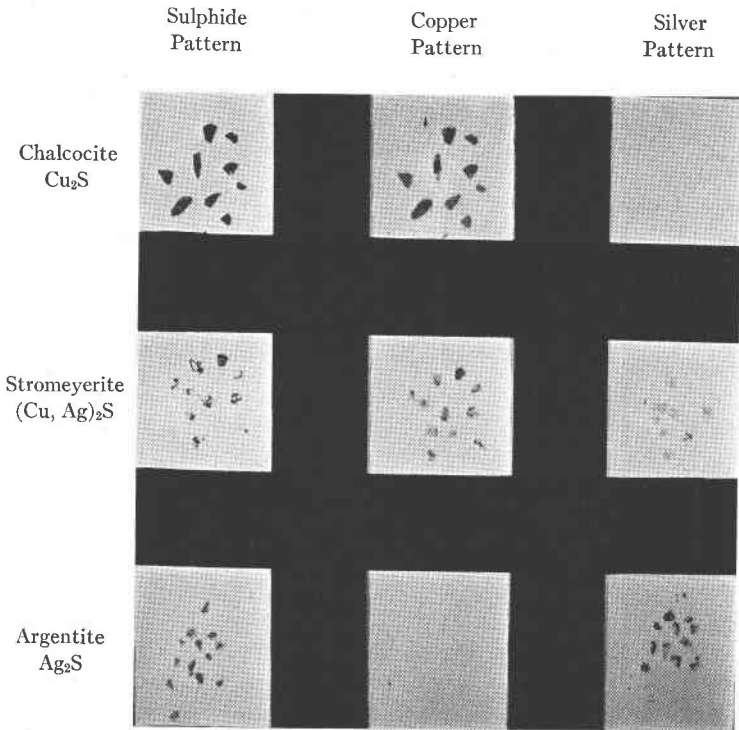

Fig. 3. Differentiation of chalcocite, stromeyerite and argentite by successive analytical patterns.

in argentite and stromeyerite can be confirmed by means of the following simplification of the silver pattern originally described by Hiller (8) as an electrographic method.

Silver Pattern: Moisten pure gelatin paper with (1+1) nitric acid, blot off excess fluid and contact polished specimen for one minute. Immerse paper in 2 per cent potassium bromide for about 5 minutes and wash under running tap water for about 10 minutes until the emulsion is substantially free from excess acid and soluble metallic salts. The silver

remains fixed in the gelatin as insoluble siver bromide which can be rendered visible by reduction to black metallic silver with the aid of a photographic developing solution.† The print is develped for 3 minutes in full strength *D61a* developer, rinsed with water, immersed in 5 per cent acetic acid for 2 minutes and washed in water for about 15 minutes. Jet black or gray markings on the print serve to localize the silver minerals in the polished section. Native silver and argentiferous alloys such as electrum also yield positive silver patterns.

The application of these contact printing methods in the localization and differentiation of copper and silver sulfide grains is exhibited in Fig. 3. Chalcocite—Cu_2S, stromeyerite—$(Cu, Ag)_2S$ and argentite—Ag_2S yield positive cyanide etch patterns. The chalcocite furnishes a positive copper pattern and a negative silver pattern. Stromeyerite gives positive prints for both copper and silver. The grains of argentite yield a negative copper pattern and a positive silver pattern.

APPLICATIONS OF THE CYANIDE ETCH SULFIDE PATTERN

The selective sulfide pattern secured by means of potassium cyanide etching is of particular interest in conjunction with the determination and localization of chalcocite, covellite, bornite and enargite in copper ore sections. These particular species are frequently of secondary origin and the occurrence of grains of these copper sulfides in upper rock drillings may indicate the presence of deep seated copper ore bodies. Preliminary analyses of heavy mineral concentrates from rock drillings have demonstrated the applicability of the method in detecting copper sulfide minerals with grains only 0.1 mm. diameter. Details of the mounting of fine grains for contact printing and their identification by successive analytical patterns will be published subsequently.

Copper sulfide minerals occurring in the same section can often be differentiated by noting the relative intensity of the areas on the sulfide pattern. Print *A* of Fig. 2 is a reproduction of the sulfide pattern of a massive copper ore composed of an intergrowth of chalcocite and bornite. The two species are readily differentiated by the dark brown and light brown markings on the pattern. The enclosed crystals of pyrite do not print, but the fine intergrowths of copper sulfide veins within the pyrite are clearly evident in an enlargement print, Fig. 4, of the original pat-

† Eastman developer *D61a* yields deep black images It is prepared by dissolving 3.1 grams of elon, 90 grams of anhydrous sodium sulphite, 2.1 grams of sodium bisulphite, 5.9 grams hydroquinone, 11.5 grams anhydrous sodium carbonate and 1.7 grams potassium bromide in about 500 ml. of water warmed to 52°C. This is filtered into a stock bottle and diluted with water to 1 liter.
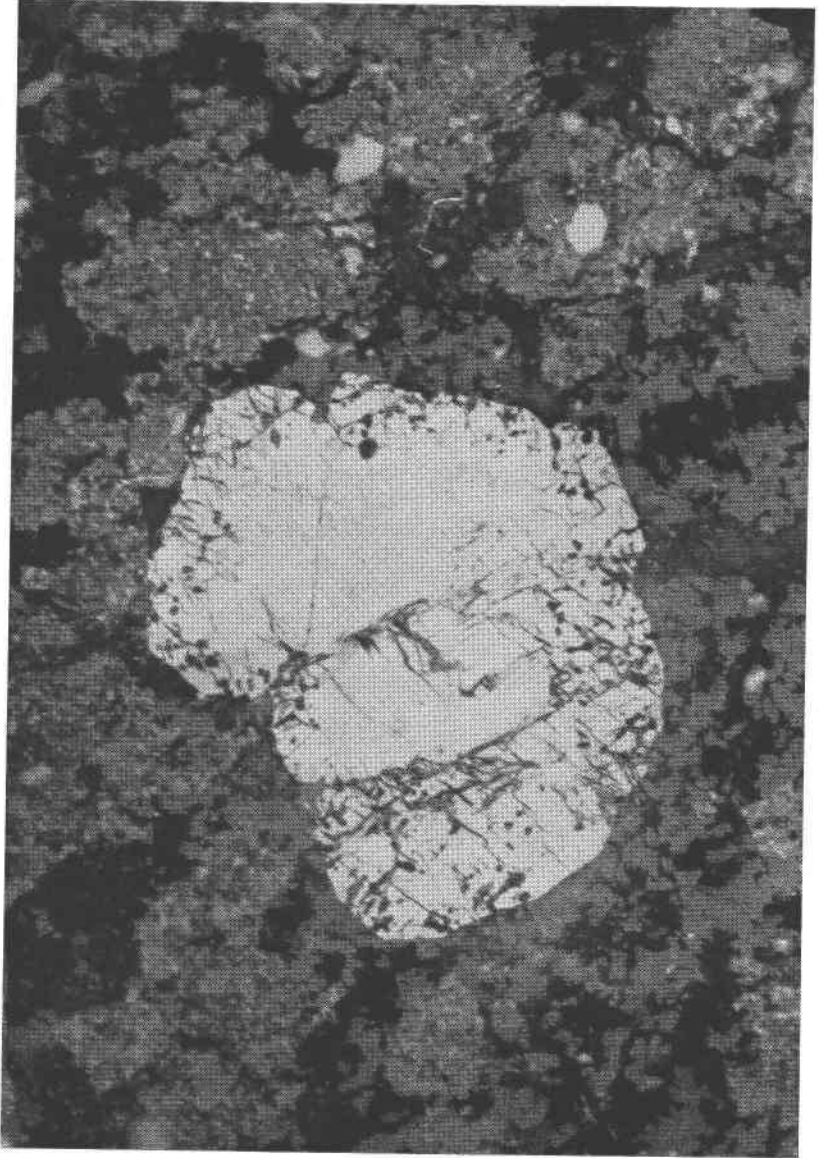
FIG. 4. Fine veins of copper sulfides in pyrite crystal. Pattern enlarged 12 X.

tern. Some of these lines measure between 0.1 and 0.01 mm. in the enlargement, which proves the registration of fine detail on the pattern corresponding to areas with a minimum width of about 0.001 mm. Print A of Fig. 5, likewise localizes the copper sulfide areas in a banded intergrowth of enargite and pyrite. The adjacent print B is a second pattern of the same section made by contacting the surface for 15 sec. with gelatin paper moistened with $(1+1)$ nitric acid, and developing the print

A   B
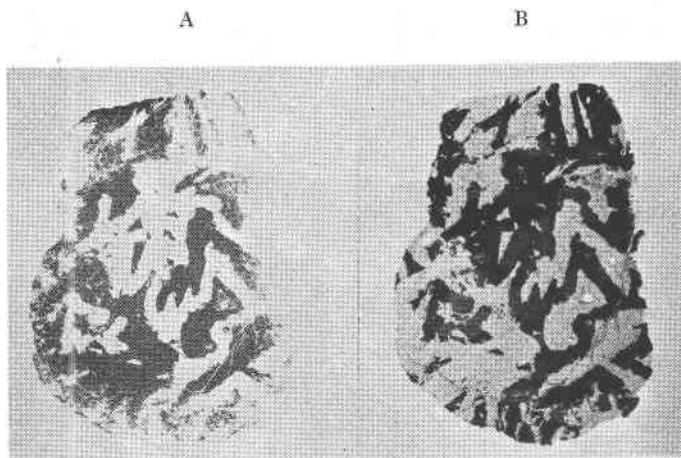
Fig. 5. Banded enargite and pyrite, Cerro de Pasco, Peru

A. Sulfide print of enargite.
B. Combination copper and iron pattern localizing enargite (light) and pyrite (dark).

with 2 per cent potassium ferrocyanide. In the original print the enargite areas reproduce reddish brown and the pyrite dark blue. Comparison of the two prints demonstrates that only the enargite furnishes a sulfide pattern.

The simple sulfides such as chalcocite and argentite yield sulfide prints of greater intensity than the more complex species chemically combined with arsenious sulfide. Combinations of copper or silver sulfides with antimony sulfide are not etched by 5 per cent potassium sulfide and yield negative sulfide prints. These characteristics can be utilized in the differentiation of tennantite, $5Cu_2S \cdot 2(Cu, Fe)S \cdot 2As_2S_3$ from its antimony analogue, tetrahedrite, $5Cu_2S \cdot 2(Cu, Fe)S \cdot 2Sb_2S_3$. Likewise, proustite—$3Ag_2 \cdot As_2S_3$ can be differentiated on the print from pyrargyrite—$3Ag_2S \cdot Sb_2S_3$.

ACKNOWLEDGMENTS

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