

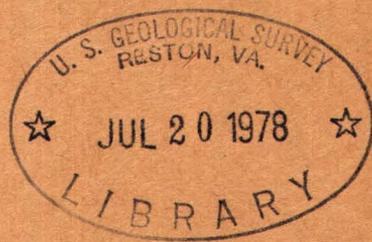
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OCCURRENCE OF SELENIUM IN SULFIDES
FROM SOME SEDIMENTARY ROCKS OF THE
WESTERN UNITED STATES

By R. G. Coleman and Maryse Delevaux



Trace Elements Investigations Report 632
UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

Geology and Mineralogy

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R. G. Coleman and Maryse Delevaux

November 1956

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OCCURRENCE OF SELENIUM IN SULFIDES FROM SOME SEDIMENTARY
ROCKS OF THE WESTERN UNITED STATES

By R. G. Coleman and Maryse Delevaux

ABSTRACT

Investigations of the minor- and trace-element content of sulfides associated with uranium ore deposits from sandstone-type deposits have shown that selenium commonly substitutes for sulfur. The Morrison formation and Entrada sandstone of Jurassic age and the Wind River formation of Eocene age seem to be seleniferous stratigraphic zones; sulfides deposited within these formations generally contain abnormal amounts of selenium. The selenium content of the pyrite, marcasite, and chalcocite is much greater than that reported in previously published data.

Under the prevailing temperatures and pressures of formation of the Colorado Plateau uranium deposits the maximum amount of Se substituting for S in the pyrite structure was found to be 3 percent by weight. Ferroselite, the iron selenide (FeSe_2), was found in two deposits on the Colorado Plateau, and it was also established that galena (PbS) forms an isomorphous series with clausthalite (PbSe) in nature.

During oxidation of the selenium-bearing sulfides and selenides in the Colorado Plateau and Wyoming, the selenium forms pinkish crusts of either monoclinic or hexagonal native selenium intergrown with soluble sulfates, suggesting that under "normal" oxidizing conditions native selenium is more stable than selenites or selenates.

The above-normal selenium content of these sulfides from sedimentary rocks of Mesozoic and Tertiary age is significant. The high selenium in

these sulfides is related to periods of volcanic and intrusive activity penecontemporaneous with the formation of the containing sediments.

INTRODUCTION

Mineralogic studies of the Colorado Plateau uranium deposits, conducted by the U. S. Geological Survey on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission, reveal a rather persistent association of selenium with these uranium deposits. The unique geochemical character and restricted occurrence of selenium make it an indicator element that can be used as a tool for interpretation of the processes that have given rise to these ore deposits. The first mention of the association of selenium with these ore deposits was given by Beath (2), who has shown that selenium-bearing plants are consistently present where the Morrison formation of Jurassic age crops out. Cannon (8,9,10) in more recent studies has used selenium-bearing plants as prospecting guides in the location of uranium deposits on the Colorado Plateau. Shoemaker and others (written communication), in their minor-element study of several hundred mill pulps from producing uranium mines, show that selenium has been concentrated in the ores from sandstone-type uranium deposits.

The purpose of this investigation was to determine the nature and amount of selenium within the ore deposits and to establish its distribution with respect to the ore bodies and their host stratigraphic units. To do this the sulfide minerals were chosen as the best possible means of detecting selenium present in the ores. Goldschmidt and Hefter (19) have shown that sulfur and selenium are very closely related in ionic size and that very frequently selenium substitutes for sulfur in sulfide minerals.

Pyrite is almost universally associated with the unoxidized ore bodies on the Colorado Plateau and was chosen as the best mineral to test the distribution of selenium. Where pyrite was not found, galena, chalcocite, and chalcopyrite were tested. The sulfur/selenium ratio of sulfides has been used by several workers to distinguish between ore deposits of sedimentary or hydrothermal origin. Goldschmidt and Strock (20) have shown that pyrite formed during diagenesis of sedimentary rocks has a S/Se ratio of 200,000 or more, and pyrite of hydrothermal origin has a S/Se ratio of 10,000 to 20,000. Carstens (7) found that sedimentary pyrite from Norway contained less than 1 ppm Se as compared to 20 to 30 ppm in pyrite from hydrothermal deposits. A more recent comprehensive study by Edwards and Carlos (15) on the selenium content of Australian sulfides shows a similar genetic relationship. They restrict the use of the S/Se ratio to those provinces that generally have a low selenium background and have picked pyrite or marcasite or both as the most satisfactory index sulfides. Edwards and Carlos assume that when the S/Se ratio is equal to or less than 10,000 the deposit containing pyrite and/or marcasite may be of hydrothermal origin. Applying this concept to certain ore deposits associated with particularly persistent stratigraphic horizons, Edwards and Carlos infer that these deposits are hydrothermal and not of sedimentary origin on the basis of the S/Se ratio of the sulfides from these deposits.

This interesting relationship may be valid for the Australian deposits if it can be shown that all of the selenium was derived from mineralizing solutions originating at depth, but Edwards and Carlos do not indicate what the S/Se ratio may have been in pre-ore (diagenetic) sulfides from the host stratigraphic units. These inferences regarding origin based on S/Se ratios must be used with great care unless one knows the selenium

content of the host rock before mineralization. For instance, the uranium deposits of the Colorado Plateau region of the western United States occur in persistent sandstone units that are known to have an exceptionally high background in selenium as pointed out by Beath (2) and Trelease and Beath (32); therefore, one would expect sulfides forming during diagenesis or later in such a host rock to contain Se indigenous to the rock and here it would be difficult to determine the source of the selenium--that is, sedimentary or hydrothermal.

METHODS OF MINERAL SEPARATION

To insure pure samples for selenium determinations, special precautions were taken using several unusual separatory techniques. The samples containing sulfide were crushed fine enough to release the sulfide from the gangue material and then elutriated to remove the clay-size fraction (little or no sulfide was lost in the elutriate). The sulfide was then separated from the gangue by flotation using a Mayeda cell (22). The advantage of the Mayeda cell is the small quantity of material that can be used. Satisfactory separations were obtained on 10-gram samples containing less than 1 gram of sulfide. The sulfide concentrates obtained from flotation were then centrifuged in bromoform to remove the lighter gangue. For pyrite and marcasite further purification of the concentrate was effected by treatment with warm concentrated hydrochloric acid to remove oxidation products and carbonates; when silicates remained, the concentrate was further treated with warm hydrofluoric acid. Tests have shown that pyrite and marcasite are unharmed by warm hydrochloric and hydrofluoric acid (1, 21); however, the other sulfides analyzed, such as galena, chalcocite, and

chalcopyrite were not acid treated. The superpanner was used to effect further purification with these sulfides. Almost all of the samples analyzed were at least 95 percent pure. X-ray and spectrographic determinations on each sample were made to determine what impurities remained, if any. Quartz and barite were the most common impurities, and it was felt that these minerals would not alter the ultimate selenium determinations.

PROCEDURE FOR THE DETERMINATION OF SELENIUM IN SULFIDES

The method for the determination of selenium is based on the widely used distillation of selenium tetrabromide, particularly as described by Robinson and others (27). A 1-gram sample of the sulfide is transferred to the distillation flask and is decomposed with nitric acid. The selenium is distilled with a solution of hydrobromic acid and bromine. The distillate is treated with a slow stream of sulfur dioxide to reduce the free bromine to hydrogen bromide, and hydroxylamine hydrochloride is added to precipitate the selenium in its elemental form. The selenium is then determined colorimetrically or gravimetrically.

For the colorimetric estimation, an aliquot of the distillate containing 3 to 100 micrograms of selenium is used, and estimation is made visually against a series of standards containing 5, 10, 20, 30, 40, 50, 75, and 100 micrograms of selenium. For samples containing more than 0.2 mg of selenium, the precipitated selenium is filtered, dried, and then weighed on a semi-micro balance. The chemical analyses were made by the junior author.

GEOLOGIC AND GEOGRAPHIC DISTRIBUTION OF THE ANALYZED SULFIDES

Most of the sulfide samples studied were taken from uranium and uranium-vanadium ore deposits in sedimentary rocks. The Colorado Plateau region was sampled extensively and here most of the uranium deposits are within several persistent stratigraphic units; the Morrison formation of Jurassic age, Entrada sandstone of Jurassic age, Todilto limestone of Jurassic age, and Chinle formation of Triassic age. Outside the Colorado Plateau, samples were tested from uranium ore deposits and associated sediments within the Tertiary sedimentary rocks of Wyoming, particularly the Wasatch and Wind River formations of Eocene age. In the Black Hills area of South Dakota and Wyoming, sulfides were analyzed from the Fall River sandstone, Fuson shale, Minnewaste limestone, and Lakota sandstone, all of Cretaceous age. Other samples from nonuranium-bearing sediments and igneous rocks from the western United States were also tested to establish the general selenium background. The location of these samples is shown in figure 1.

FORM AND OCCURRENCE OF THE SULFIDES

Pyrite and marcasite are the most abundant sulfides associated with the uranium deposits and commonly form fine disseminations or nodular concretions. In most of the deposits pyrite was found to be more abundant than marcasite. Where sulfides have been precipitated within carbonaceous material, they assume the structure of the woody material which they replace (fig. 2).

The sulfides have been divided into two types according to their position with respect to the unoxidized uranium-vanadium ore deposits. The relatively

abundant sulfides taken from within the ore or following the outline of the ore bodies are considered as ore sulfides (rock containing > 0.01 percent U_3O_8). There is no evidence to suggest that the uranium deposits in sandstone-type deposits are accompanied by a surrounding zone of sulfides away from the ore, as is commonly found in hydrothermal vein-type deposits. The ubiquitous and scattered sulfides in the unmineralized rock show no relationship with the ore bodies and are considered barren sulfides. It is assumed that most of the sulfides in the barren rock formed independent of and prior to the deposition of the uranium-vanadium ores either during diagenesis or later from nonuraniferous circulating intrastratal solutions. The sulfides within the ore are considered to have formed from the fluids transporting the metals for the uranium deposits or by reconstitution of the pre-ore sulfides by these fluids or by both (figs. 3 and 4). This division is arbitrary as there is difficulty in establishing criteria to distinguish early sulfides from those sulfides produced by the later ore-bearing fluids.

The presence of iron sulfides has been recorded in many drill cores of unoxidized barren rocks from the Morrison and Chinle formations on the Colorado Plateau and from the Wind River formation in Wyoming. Shawe (29) has shown that two types of diagenetic changes have taken place in the sedimentary rocks of the Colorado Plateau prior to uranium mineralization:

1. oxidation, producing hematite and the characteristic red coloration,
2. reduction, producing iron sulfides and the characteristic green coloration.

Thus it seems likely that iron sulfides must have formed in these sediments where reducing conditions existed before ore deposition. Another line of evidence suggesting two distinct periods of iron sulfide

deposition has been found in the Ni:Co ratio of these sulfides. Hegemann (21) and Talluri (30) have shown that pyrites formed by sedimentary processes generally have $Ni > Co$ and those pyrites formed by hydrothermal processes generally have $Co > Ni$. Exceptions to this general rule are common, but the senior author has found that the barren iron sulfides used in this study usually show $Ni > Co$ and those from the ore have $Ni < Co$. This illustrates that the division of the sulfides into barren and ore groups reflects a change in composition of the sulfides which probably results from different environments of deposition. Undoubtedly some of the sulfides are placed in the wrong group because the collection of these samples was based primarily on their position as related to the ore bodies described above; however, this classification is convenient to illustrate the partition of the selenium in sulfides with respect to the uranium deposits.

The chalcopyrite, chalcocite, and galena deposited in the uranium ores are probably formed by the ore fluids, as there is no geologic evidence to prove that they are pre-ore. Pyrite and marcasite seem to be the only early sulfides.

The most unusual characteristic of the sulfide deposition with respect to the ore is the thin sulfide bands that follow the outline of the roll ore bodies. These roll ore bodies, described by Fischer (16), are layered deposits that cut across the sandstone bedding in sharply curving forms (figs. 5 and 6). The sulfides within the band have been deposited interstitial to the sand grains (fig. 7) and the band is usually characterized by a monomineralic sulfide--either pyrite, chalcocite, or galena-clausthalite. The sulfides within the bands usually have extremely high selenium contents, as much as 18 percent. Shawe (28) believes that these

sharp depositional features were formed at a static interface between fluids of different composition and density.

The coalified wood within the deposits seems to have controlled to a large extent the precipitation of the ore and also the sulfides. Larger coalified wood fragments and logs contain abundant sulfide that may completely replace parts of the wood preserving the cell structure (figs. 8 and 9). The pyrite also commonly forms an aureole around the log as fine disseminations in the containing sandstone (fig. 2). The more prevalent tabular ore bodies contain sulfides disseminated throughout with marked concentrations at the boundaries of the bodies, and within the bodies small carbonaceous fragments show strong localization of sulfide.

Selenides are common in the ores from the Morrison formation and Entrada sandstone and extremely rare in the ores from uranium deposits in rocks of Triassic age. Clausthalite ($PbSe$) is the typical selenide found, and in the vanadium deposits from the Rifle and Garfield mine, Garfield County, Colo., a persistent sulfide band contains clausthalite-galena in variable amounts; the band can be traced for several thousand feet along the strike of the ore deposit. An exceptional concentration of clausthalite was found (Lee Eicher, U. S. Geological Survey, personal communication) in the Corvusite mine, Montrose County, Colo. Here a band of clausthalite a quarter of an inch wide formed a semicircular band around a large log (18 in. in diameter and about 10 ft. long) representing the largest concentration of selenide yet found on the Colorado Plateau. An unusual occurrence of clausthalite is found in chalcocite nodules from the Cougar mine, San Miguel County, Colo. Clausthalite is intergrown with chalcocite (Cu_2S) and digenite ($Cu_{2-x}S$) (figs. 10 and 11), and in some nodules the rare selenide, eucairite ($CuAgSe$) (fig. 12) is associated with the chalcocite

and clausthalite. Ferroselite (5), the iron selenide FeSe_2 , is the only selenide so far identified in Triassic deposits. In the Triassic it has been found only in the Chinle formation in the Temple Mountain area, where it occurs in the AEC No. 8 mine, Emery County, Utah, associated with pyrite and coalified wood. In the Morrison formation of Jurassic age ferroselite has been found at the Virgin No. 3 mine, Montrose County, Colo., by D. R. Shawe of the U. S. Geological Survey.

The sulfides in barren rock from the Colorado Plateau are present within mudstones and sandstones, usually as nodular masses, small euhedral crystals (fig. 13), or as concretions. In mudstones the pyrite and marcasite usually form larger crystals and tend to be more euhedral, whereas in sandstone these sulfides are anhedral to subhedral filling the interstitial areas. Marcasite and pyrite seem to be of equal abundance in these rocks. Barren coalified wood contains abundant sulfide and some of the sulfide in mineralized coalified wood fragments within the ore has formed before the deposition of the uranium ore; some of it may have been reconstituted by the ore fluids or may have been unchanged by these processes of ore deposition (fig. 14).

Sulfides from the Tertiary uranium deposits in Wyoming do not exhibit the unusual distribution found in the sulfides from the Colorado Plateau. The sulfides from these Tertiary deposits are present as extremely fine disseminations in sandstone and in some areas are concentrated along bands formed by secondary enrichment. The sulfides in barren rock form small concretions within mudstones and irregular nodular masses in the sandstone. Marcasite and pyrite are the only sulfides yet found associated with these Tertiary deposits; selenides have not been reported.

DISTRIBUTION OF SELENIUM IN THE SULFIDES

In the early stages of this investigation it became apparent that the sulfides deposited in the sedimentary rocks of the Colorado Plateau and Wyoming were exceedingly high in selenium. The recent survey of trace elements in sulfides by Fleischer (17) shows that the highest selenium recorded in 112 pyrites and/or marcasites from all types of deposits was 300 ppm. Bergenfelt (4) provides an example of a selenium-rich province in the Skellefte district, Sweden; however, even the maximum contents he records for the sulfides from this district are not comparable to those determined in the present investigation. Sulfides from the Boliden mine, Skellefte district, show the following maximum selenium contents: lead-bismuth-antimony sulfides, 6.4 percent Se; galena, 1.4 percent; chalcopyrite, 0.14 percent; arsenopyrite, 0.16 percent; and pyrite 0.03 percent. Derriks and Vaes (13) have found 19 percent Se in vaesite (NiS_2) and 11 percent Se in siegenite from unoxidized uranium ores at Shinkolobwe, but they have not analyzed the associated pyrite for selenium.

In contrast to these published data, the sulfides analyzed for this investigation from the sedimentary rocks of the western United States show the following maximum selenium values: "pyrite," 5 percent; marcasite, 0.65 percent; galena-clausthalite, 18 percent; and chalcocite, 5 percent.

The control on the selenium content of the sulfides from this province seems to be stratigraphic rather than a function of the type of ore deposit--that is, hydrothermal versus sedimentary origin, as suggested by Edwards and Carlos (15) for the Australian deposits. The sulfides from the Morrison formation consistently contain more selenium than those from the Chinle formation, with the exception of the Temple Mountain deposits,

Emery County, Utah. The pyrite and/or marcasite from both the barren and mineralized rock from the Morrison contain much more selenium than the average shown by Fleischer (17), whereas these two types of sulfides from the Chinle deposits have much less selenium.

Sulfides from the Morrison formation, Entrada sandstone,
and Catskill formation

Thirty-nine samples of marcasite or pyrite or both were analyzed from the Morrison formation (table 1). The average selenium content of the iron sulfides both from barren and mineralized rock is 0.17 percent. The averages discussed are arithmetical and those samples containing Se below the sensitivity of the chemical method (3 ppm for a 1-gram sample) are averaged in as zero. The average selenium content of 20 iron sulfides from mineralized rocks is 0.20 percent and for 18 sulfides from barren rock the average selenium content is 0.14 percent. One pyrite-marcasite sample contained 5 percent Se, but this sample was found to contain clausthalite (PbSe) as an impurity. The selenium content of sulfides from mineralized rock is not significantly higher than that of sulfides from barren rock. It would seem that if most of the barren pyrite is pre-ore, selenium was apparently available in the same relative amounts in sediments of the Morrison formation during pre-ore sulfide formation as during the period of uranium mineralization. Therefore, where reducing conditions existed and iron sulfides have been formed in the Morrison formation, either before ore deposition or in the period of uranium ore deposition, selenium has been concentrated in these sulfides, although the ore fluids may have been enriched in selenium as they apparently have traveled laterally through the Morrison for great distances.

The chalcocite bands and nodules characteristic of the Slick Rock district, San Miguel County, Colo., are restricted to the ore bodies and seem to have formed during the uranium mineralization. Some of these sulfide concentrations have extremely high selenium content for copper sulfides, averaging 1.22 percent Se for 11 samples, with a high of 4.93 percent Se. Study of polished sections of these copper sulfides reveals small inclusions of clausthalite and intergrowths of clausthalite and chalcocite-digenite (figs. 10 and 11). Rarely small concentrations of eucairite (fig. 12) are present in these copper sulfides. These inclusions of selenides account, in part, for the exceptionally high selenium content of the chalcocite, but much of the selenium is probably substituting for sulfur in the chalcocite structure.

The persistent "galena" band developed in the vanadium deposits within the Entrada sandstone is composed of galena-clausthalite in solid solution (fig. 6). This band is fairly uniform in composition but progressive variations in selenium along the strike of the band were found. The average selenium content of nine samples of galena-clausthalite from these bands is 12.2 percent with a high of 18 percent (table 1). In contrast, pyrite and marcasite deposited in late fractures spatially associated with these vanadium deposits contain only 0.02 percent Se.

Sandstone collected by Harry Klemic, U. S. Geological Survey, from the upper part of the Catskill formation, of Devonian age, Carbon County, Pennsylvania, also contains a thin clausthalite band (about a quarter of an inch thick) in juxtaposition with uranium minerals. Further work is needed to determine the relationship of these unique bands to the uranium.

Sulfides from the Chinle formation

The distribution of selenium in sulfides from sedimentary rocks of Jurassic age is not reflected by the sulfides from sedimentary rocks of Triassic age. These sulfides, exclusive of the Temple Mountain uranium deposits, show a much lower selenium content than those from the Jurassic (table 2). Fifty-five samples of pyrite or marcasite or both from sediments of the Chinle formation of Triassic age have an average selenium content of 0.0015 percent. The average selenium content of 27 iron sulfides from mineralized rocks is 0.0019 percent and of 28 iron sulfides from barren rock 0.0012 percent. These averages do not include samples from the Temple Mountain deposits. Again, as with the sulfides from rocks of Jurassic age, there is no apparent difference in the selenium content of the barren sulfides as compared to the ore sulfides. This supports the premise that the same relative amount of selenium was available for pre-ore and ore periods of sulfide deposition. The uranium ore deposits in rocks of Triassic age usually contain more sulfide than do the deposits in rocks of Jurassic age, but the former sulfides have not mobilized to form continuous bands but have been more thoroughly disseminated throughout the deposits. The associated copper sulfides (bornite, chalcopyrite, and chalcocite) analyzed for selenium show the same relative amounts of selenium as the iron sulfides (table 2).

In contrast to the other deposits in rocks of Triassic age, the Temple Mountain deposits have an unusual partition of selenium. The sulfide concentrates from ore in this area contain the highest concentration of selenium yet found in the Colorado Plateau, although the sulfides from barren rock contain the same relative amounts of selenium as the average

found in other sulfides from rocks of Triassic age. Eight sulfide concentrates from ore containing ferroselite (FeSe_2) from the Temple Mountain deposits average 12 percent Se, whereas four sulfide concentrates from barren rock average only 0.004 percent selenium. Thus at Temple Mountain the sulfide minerals in uranium ore are strongly enriched in selenium when compared to the pre-ore sulfides, suggesting that the ore-forming fluids contained abundant selenium.

Sulfides from sedimentary rocks of Tertiary age

Sulfides associated with the uranium deposits in Wyoming sedimentary rocks of Tertiary age have also been tested for comparison with the Colorado Plateau uranium deposits. The Wind River and Wasatch formations of Eocene age contain the important uranium deposits of this region. The Gas Hills area in the Wind River Basin, the Pumpkin Buttes area, and Crooks Gap area, all in Wyoming, are the three districts sampled. Fifty samples of pyrite or marcasite or both from these three areas have an average selenium content of 0.04 percent (table 3).

The iron sulfides from mineralized rock have an average selenium content of 0.087 percent, a marked enrichment over the iron sulfides from barren rock which average 0.0015 percent selenium. Secondary enrichment of uranium has occurred near the ground-water table in the Gas Hills area, and the pyrite from this zone contains as much as 1.5 percent Se. The solutions forming the uranium ore deposits in these sediments were considerably enriched in selenium as compared to the solutions responsible for the formation of sulfides before ore deposition. Marcasite and pyrite are the only sulfides observed in the samples collected from the sedimentary rocks of Tertiary age from Wyoming.

One sample from the Maybell district, Colo. (table 3, no. 203) also contains significant Se as does a sample from Karnes County, Tex. (table 3, no. 202).

Sulfides from rocks of Cretaceous age

Sulfides from various sedimentary rocks of Cretaceous age in the western United States have been tested for selenium, but only a few samples from any one formation were analyzed (table 4). The average selenium content of 19 samples of pyrite or marcasite or both from these rocks is 0.0058 percent Se. Six sulfides from uranium ore average 0.005 percent Se, and 13 sulfides from barren rock average 0.006 percent Se. As these samples are so widely spaced and from several different formations, it is not possible to evaluate the relationship of the selenium content in the sulfides from barren rock as compared with the sulfides from ore-bearing rock.

The five samples of pyrite and marcasite from the Mancos shale of Cretaceous age were taken from a drill core located in the Slick Rock district, Colo., and these average 0.014 percent selenium. Trelease and Beath (32) have shown that the Mancos shale supports a variety of selenium-bearing plants (and it may be that the Se is derived from the oxidized iron sulfides). The sulfides in the Mancos occurred in a black shale containing no uranium minerals.

Sulfides from hydrothermal and igneous rocks

Various sulfide samples from hydrothermal deposits and intrusive rocks from the Colorado Plateau have also been tested for selenium to determine

its spatial distribution with respect to the host rock and its mode of formation (table 5).

Seven copper and iron sulfides from the laccolithic intrusions within the Colorado Plateau (including the La Sal, Utes, and Carrizo intrusives) average 0.008 percent selenium. Chalcopyrite from a diorite porphyry located in the La Sal Mountains, Utah, shows the maximum concentration of 0.016 percent Se. These contents, although much lower than many of those found in sulfides from sedimentary rocks, indicate the presence of selenium in the magmas giving rise to the intrusive rocks.

Four samples of pyrite from hydrothermal base-metal vein deposits of this region contain as much as 0.017 percent selenium, suggesting that selenium was present in the base-metal ore-forming fluids. Further testing is necessary to establish the regional and local trends in the sulfides from the hydrothermal deposits and the igneous rocks, but it seems that the Colorado Plateau area is a selenium-rich province.

MECHANISM OF SUBSTITUTION, SELENIUM FOR SULFUR

The mineragraphic study on these selenium-bearing sulfides has shown that inclusions of selenides within the sulfides are generally lacking, except for the clausthalite found in the chalcocites from Slick Rock district (figs. 10 and 11). Therefore, it is assumed that fluids from which these sulfides were deposited contained selenium, and that this selenium has entered the sulfur positions in the sulfide structure during crystallization.

The bonding in sulfides is generally considered to be a combination of covalent, metallic, and ionic. Both the atomic and ionic radii of sulfur and selenium are similar.

| | Ionic radius (A) | | Covalent radius (A) |
|----------|------------------|---------------|---------------------|
| | <u>Valence</u> | <u>Radius</u> | |
| Selenium | -2 | 1.98 | 1.17 |
| Sulfur | -2 | 1.84 | 1.04 |

Goldschmidt's generalization (18) on isomorphous substitution shows that where ionic radii of two elements are within 15 percent of each other the possibility of substitution is good. Both the ionic and covalent radii of S and Se fall well within the limit suggested by Goldschmidt. Other factors that may influence the isomorphous substitution, such as coordination number, polarization, and ionic potential are also similar in sulfur and selenium. Therefore, one may conclude, on the basis of crystal chemistry, that diadochic substitution of sulfur by selenium may be accomplished with comparative ease.

The pyrite containing large amounts of selenium (greater than 1 percent) shows some expansion of the lattice as might be expected, as selenium is somewhat larger than sulfur. Synthetic FeSe_2 has a structure similar to that of rammelsbergite (Gunnar Kullerud, personal communication) and it would seem that a complete solid solution between FeS_2 - FeSe_2 is not possible on the basis of crystal chemistry. The temperatures and pressures of formation of the uranium ore deposits from the Colorado Plateau have been estimated to be less than 138°C and 800 atmospheres (11) and from this present study it appears that 3 percent by weight of selenium is the maximum amount that may enter the pyrite structure at these P-T conditions where excess Se is available. Ferroselite (FeSe_2) has been found associated with selenian pyrite; therefore where the sulfur and selenium are present in a reducing environment with Fe, about 4 percent (molecular) FeSe_2 can enter the pyrite (FeS_2) structure; and if excess iron and selenium are

present, ferroselite (FeSe_2) is formed. This relationship seems to hold for the sulfide-selenide formation in the low temperature and pressure environment of the western uranium deposits, but at higher temperatures and pressures a complete FeS_2 - FeSe_2 series with the pyrite structure might be possible.

The ferroselite (FeSe_2) from the AEC No. 8 mine, Temple Mountain, Utah, has a ratio of $\text{Fe}:\text{Co} = 4:1$ and here the structure is identical with that of FeSe_2 and also hastite (CoSe_2) described by Ramdohr and Schmitt (26). Thus a complete isomorphous series between FeSe_2 - CoSe_2 seems to be possible.

Galena forms a complete isomorphous series between clausthalite as shown by Earley's work (14) on synthesis of this series. Most of the series was found to form under natural conditions at the Rifle mine, Colorado, where the galena-clausthalite band contains various proportions of Se in solid solution with S. These varying ratios of S and Se were reflected by an increase in the unit-cell size with an increase of Se as pointed out by Earley.

Bergenfelt (4) has shown that selenium apparently is enriched preferentially in different sulfides from the same mines. He has listed the sulfides in decreasing amounts of contained selenium: galena, chalcopyrite, arsenopyrite, sphalerite, pyrite, and pyrrhotite. Edwards and Carlos (15) show that the Australian sulfides have a completely different sequence, listed here in decreasing amounts of contained selenium: chalcopyrite, arsenopyrite, pyrite (hydrothermal), pyrrhotite, sphalerite, and galena.

As shown earlier, the S and Se atomic and ionic radii are similar and variations in size are probably slight from one sulfide structure to the

next. It would seem that the amount of selenium available, crystal structure, and P-T conditions all control the amount of selenium found in any particular sulfide from any one mine or district. This is verified in this investigation where the main controls on the amount of selenium found in sulfides are crystal structure and selenium supply.

OXIDATION OF SELENIFEROUS SULFIDES AND SELENIDES

The fate of the selenium during oxidation of the seleniferous sulfides and selenides is incompletely known. Selenites and selenates have not been found near oxidized selenium-bearing sulfides or selenides, but native selenium has been identified from many localities by Thompson and coworkers (31). These observations agree with the physical-chemical differences between Se and S in the geochemical weathering cycle, as pointed out by Goldschmidt and Hefter (19), who have shown that selenates and selenites are stable only under extremely high oxidizing conditions. Sulfates on the other hand are stable under the normal Eh-pH conditions found in oxidizing sulfide ore deposits.

The pH and Eh equilibrium diagram as presented by Delahay and others (12) (fig. 15) illustrates the possible forms of selenium that might be expected under normal surface conditions. Krauskopf (24) has shown the limits of Eh and pH that are found at the surface under normal conditions and this field has been superimposed on the diagram. The diagram shows that metallic selenium is stable over a large area of this field both in acid and alkaline solutions. Selenites may form at high oxidation potentials, particularly in alkaline solutions, whereas selenates might be expected only in extremely high oxidizing conditions as suggested by Goldschmidt.

The field observations support these assumptions which are based on thermodynamic calculations. Two forms of native selenium have been observed: the stable hexagonal form, and an unstable monoclinic form. The native selenium commonly crystallizes near or implanted on the oxidized sulfide grains. Pinkish crusts composed mostly of soluble sulfates contain intergrowths of native selenium and these crusts form near mine portals or where mine waters have evaporated. Selenium has been detected in mine and ground waters, although the form of the selenium in these waters has not been established, that is, SeO_3^{--} , HSeO_3^- , or SeO_4^{--} .

Limonitic concretions formed during oxidation of seleniferous sulfides contain selenium, and Byers and coworkers (6) believe that the selenium may be present in the limonite as a basic ferric selenite $\text{Fe}_2(\text{OH})_4\text{SeO}_3$; this selenite has not been isolated from the seleniferous limonite.

DISCUSSION

Some of the rocks of Mesozoic and Tertiary age of the Colorado Plateau and Wyoming are rich in selenium, which is strongly concentrated in the sulfides formed before or during ore deposition. The presence of significant quantities of selenium in hydrothermal sulfides and in sulfides formed in the intrusive rocks of the region shows that this area is a selenium-rich province.

An adequate hypothesis regarding the sources of selenium concentrated in the sulfides should explain the differences in selenium content of the various geologic formations, variations within a single formation, and the availability of selenium during deposition of the sulfides.

The average selenium content of igneous rocks as given by Goldschmidt (18) is 0.000009 percent Se; sedimentary rocks exclusive of the western United States generally contain less than 0.0001 percent Se. Selenium is concentrated in sulfides of magmatic and volcanic origin and in native sulfur of volcanic origin. Also, selenium can be concentrated in sediments derived from seleniferous source rock, such as that recorded in Recent sediments in the Gulf of California (25). Therefore, three possible sources of selenium should be considered: selenium derived from volcanic activity, selenium from magmatic fluids, and selenium from pre-existing seleniferous terrains.

The selenium in the Morrison formation seems to have been derived from both volcanic emanations and reworked volcanic debris. Waters and Granger (33) have shown that volcanic materials are common in the Morrison, and, as the sulfides from barren and mineralized rock in the Morrison contain the same relative amounts of selenium, it seems likely that the selenium was introduced into the Morrison during its deposition by attendant volcanism. No evidence was found to support the idea that the source material for the Morrison, other than the volcanics, was seleniferous.

The Chinle formation of Triassic age also contains volcanic debris (33), and this seems to be the source of the Se in these rocks, but either the primary volcanic source for this material must have contained less selenium than the primary volcanic source of the Morrison debris or the over-all volume of volcanic material was much less. The Temple Mountain deposits present a different picture as there is a strong enrichment of selenium in the sulfides from ore when compared to the barren sulfides. The source of the selenium here seems to be hydrothermal fluids (23) whose magmatic source may have been rich in selenium, or these hydrothermal

fluids may have abstracted the selenium from seleniferous beds through which they passed.

The source of the selenium within the sulfides from the sediments of Tertiary age in Wyoming is apparently tuff beds. Selenium-bearing tuffs in the Wind River Basin, Wyoming, have been described by Beath and others (3) and they report a maximum of 187 ppm Se. These tuffs are either incorporated in or overlie the Wind River formation. The enrichment of Se in the sulfides from coarse arkosic uraniferous sandstone when compared to the sulfides in nonuraniferous mudstones illustrates the fact that the selenium has been introduced into the Wind River formation by downward or laterally percolating ground water charged with selenium derived from these tuffs. The seleniferous sulfides were concentrated at or near the top of the ground-water table, whereas the sulfides in barren rock below the ground-water table were protected by impervious mudstones and show negligible selenium. The uranium follows the same depositional pattern as the selenium, and it would seem to have an origin related to that of the selenium; hence, the uranium and selenium are geochemically coherent in the Wind River formation.

The presence of selenium in the base-metal hydrothermal ores from the Colorado Plateau region indicates that deposits produced by hydrothermal fluids may have derived their selenium from igneous intrusions enriched in selenium; or these fluids may have abstracted selenium from seleniferous beds through which they passed.

The ultimate source of the selenium in the sulfides from the Colorado Plateau and Wyoming can be related to a magmatic province that has contained exceptionally high selenium during periods of volcanic and intrusive activity in Mesozoic and Tertiary times.

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Table 1.--Selenium content of sulfides from sedimentary rocks of Jurassic age.

| Location <u>1/</u> | Mineral <u>2/</u> | Type <u>3/</u> | Percent Se <u>4/</u> |
|---|-------------------|----------------|----------------------|
| MORRISON FORMATION | | | |
| Uravan district, Montrose County, Colorado | | | |
| 1. North Star mine | pyrite | O | 0.014 |
| 2. Virgin No. 3 mine | pyrite | O | 0.009 |
| 3. Long Park No. 1 mine | pyrite | B | 0.039 |
| 4. do. | pyrite | B | 0.001 |
| Gypsum Valley district, San Miguel County, Colorado | | | |
| 5. Pitchfork mine | pyrite | B | 0.019 |
| Monticello district, San Juan County, Utah | | | |
| 6. Basin No. 1 mine | pyrite | O | 0.19 |
| 7. Cottonwood No. 3 mine | pyrite | O | 0.065 |
| 8. Found claim | pyrite | B | 0.025 |
| Thompsons district, Grand County, Utah | | | |
| 9. Little Eva mine | pyrite-marcasite | O | 0.0003 |
| 10. Blackstone No. 6 mine | pyrite | O | 0.081 |
| Bull Canyon district, Montrose County, Colorado | | | |
| 11. Mineral Joe mine | pyrite-marcasite | B | 0.074 |
| 12. do. | pyrite-marcasite | B | 0.39 |
| 13. do. | pyrite-marcasite | O | 0.10 |
| 14. Mineral Joe No. 2 mine | pyrite | B | 0.004 |
| 15. J. J. mine | marcasite-pyrite | O | 0.58 |
| 16. do. | pyrite-marcasite | B | 0.20 |
| 17. do. | pyrite-marcasite | O | 0.55 |
| 18. do. | marcasite-pyrite | B | 0.51 |
| 19. do. | marcasite | O | 0.65 |
| 20. do. | marcasite-pyrite | B | 0.39 |
| 21. do. | marcasite-pyrite | O | 0.13 |
| 22. do. | marcasite(pyrite) | O | 0.087 |
| 23. do. | marcasite-pyrite | B | 0.21 |
| 24. do. | marcasite(pyrite) | B | 0.003 |
| 25. do. | marcasite(pyrite) | B | 0.58 |

Table 1.--Selenium content of sulfides from sedimentary rocks of Jurassic age--Continued.

| Location <u>1/</u> | Mineral <u>2/</u> | Type <u>3/</u> | Percent Se <u>4/</u> |
|--|-----------------------|----------------|----------------------|
| MORRISON FORMATION (cont.) | | | |
| Slick Rock district, San Miguel County, Colorado | | | |
| 26. Grant claim | pyrite | O | 0.66 |
| 27. King No. 4 mine | pyrite | O | 0.25 |
| 28. Tailholt mine | pyrite(marcasite) | O | 0.015 |
| 29. do. | "chalcocite" | O | 0.066 |
| 30. do. | pyrite | B | 0.018 |
| 31. Drill core 700 ft depth, U.S.V., Burro Canyon | "pyrite-marcasite" | O | 5.00 |
| 32. Mucho Grande mine | "chalcocite" | O | 1.2 |
| 33. Cougar mine | chalcocite | O | 1.9 |
| 34. do. | "chalcocite-digenite" | O | 1.7 |
| 35. do. | "chalcocite" | O | 0.2 |
| 36. do. | "chalcocite" | O | 0.13 |
| 37. do. | "chalcocite" | O | 4.1 |
| 38. do. | chalcocite | O | 4.93 |
| 39. do. | "chalcocite" | O | 0.42 |
| 40. do. | "chalcocite" | O | 0.18 |
| 41. do. | chalcocite | O | 0.45 |
| Grants district, Valencia County, New Mexico | | | |
| 42. Woodrow Pipe mine | pyrite | O | 0.001 |
| 43. do. | marcasite-pyrite | O | < 0.0003 |
| 44. do. | pyrite | B | < 0.0003 |
| 45. Poison Canyon mine | "pyrite" | O | 1.00 |
| Henry Mountains district, Garfield County, Utah | | | |
| 46. Walter's claim | pyrite | B | < 0.0003 |
| 47. Ellen No. 2 mine, North Wash | pyrite(marcasite) | O | 0.10 |
| 48. do. | pyrite-marcasite | O | 0.35 |
| Cortez district, Montezuma County, Colorado | | | |
| 49. Drill core, McElmo Creek | pyrite-marcasite | O | < 0.0008 |
| Crook County area, Wyoming | | | |
| 50. Shannon Oil Company claims | pyrite | B | < 0.0003 |

Table 1.--Selenium content of sulfides from sedimentary rocks of Jurassic age--Continued.

| Location <u>1/</u> | Mineral <u>2/</u> | Type <u>3/</u> | Percent Se <u>4/</u> |
|---|---------------------|----------------|----------------------|
| ENTRADA SANDSTONE | | | |
| Rifle district, Garfield County, Colorado | | | |
| 51. Garfield mine | marcasite | 0 | 0.021 |
| 52. do. | galena-clausthalite | 0 | 8.66 |
| 53. do. | galena-clausthalite | 0 | 8.1 |
| 54. do. | galena-clausthalite | 0 | 7.09 |
| 55. Rifle mine | clausthalite-galena | 0 | 14.2 |
| 56. do. | pyrite | 0 | 0.14 |
| 57. do. | galena-clausthalite | 0 | 11.8 |
| 58. do. | clausthalite-galena | 0 | 18.0 |
| 59. do. | marcasite | 0 | 0.014 |
| 60. do. | clausthalite-galena | 0 | 17.0 |
| 61. do. | clausthalite-galena | 0 | 15.1 |
| Placerville district, Montrose County, Colorado | | | |
| 62. Bear Creek mine | galena-clausthalite | 0 | 10.0 |
| 63. Fall Creek mine | pyrite | 0 | 0.41 |
| TODILITO LIMESTONE | | | |
| Grants district, Valencia County, New Mexico | | | |
| 64. F. O. Manol mine | pyrite | B | 0.014 |
| 65. Crackpot mine | pyrite | B | 0.026 |

1/ General geographic location of samples shown in figure 1.

2/ X-ray identification on analyzed material. Quotation marks indicate impure sample; mixtures are hyphenated with dominant phase listed first, i.e., marcasite-pyrite; (parentheses) indicate trace amounts.

3/ Sulfides divided into two types: 0 = sulfides taken from mineralized rock (usually showing greater than 0.01 percent U_3O_8), and B = sulfides taken from barren rock.

4/ Lower limit of detection is 0.0003 percent Se for a 1-gram sample; when less sample is available the lower limit of detection is correspondingly higher.

Table 2.--Selenium content of sulfides from the Chinle formation of Triassic age.

| Location <u>1/</u> | Mineral <u>2/</u> | Type <u>3/</u> | Percent Se <u>4/</u> |
|--|--------------------|----------------|----------------------|
| San Rafael district, Emery County, Utah | | | |
| 66. Lucky Strike mine | marcasite | O | 0.001 |
| 67. do. | marcasite-pyrite | O | 0.03 |
| 68. do. | pyrite(marcasite) | O | 0.002 |
| 69. do. | pyrite | B | 0.013 |
| 70. Adams Uranium Company mine | pyrite | B | 0.0006 |
| 71. do. | galena | O | < 0.0007 |
| 72. do. | pyrite(marcasite) | B | < 0.0003 |
| 73. do. | pyrite | B | < 0.0003 |
| 74. Hidden Splendor mine | pyrite | B | 0.0003 |
| 75. do. | pyrite | B | 0.0005 |
| 76. do. | pyrite | O | 0.003 |
| 77. do. | marcasite(pyrite) | B | 0.003 |
| 78. do. | pyrite | B | < 0.001 |
| 79. do. | digenite | O | 0.0004 |
| 80. do. | pyrite | O | 0.006 |
| 81. do. | pyrite | O | < 0.0003 |
| 82. do. | pyrite | O | < 0.0003 |
| 83. do. | pyrite | O | 0.003 |
| 84. Donna B. claims | pyrite | O | 0.0003 |
| 85. Flop Over mine, Temple Mountain | pyrite | B | 0.0005 |
| 86. AEC No. 8 mine, Temple Mountain | pyrite | O | 0.003 |
| 87. do. | pyrite(marcasite) | B | 0.006 |
| 88. do. | pyrite | B | 0.006 |
| 89. do. | pyrite-ferroselite | O | 23.9 |
| 90. do. | pyrite | O | 0.50 |
| 100. do. | pyrite-ferroselite | O | 13.6 |
| 101. do. | pyrite-ferroselite | O | 40.2 |
| 102. do. | pyrite-ferroselite | O | 18.0 |
| 103. do. | pyrite | B | 0.002 |
| 104. North Mesa No. 9 mine, Temple Mountain | pyrite | O | 0.030 |
| 105. do. | pyrite(marcasite) | O | 0.012 |
| White Canyon district, San Juan County, Utah | | | |
| 106. Happy Jack mine | pyrite | O | < 0.0003 |
| 107. do. | pyrite-marcasite | B | 0.0006 |
| 108. do. | pyrite | O | < 0.0003 |
| 109. do. | "chalcopyrite" | O | < 0.0003 |
| 110. do. | chalcopyrite | O | < 0.0003 |

Table 2.--Selenium content of sulfides from the Chinle formation of Triassic age--Continued.

| Location <u>1/</u> | Mineral <u>2/</u> | Type <u>3/</u> | Percent Se <u>4/</u> |
|--|-----------------------|----------------|----------------------|
| 111. Happy Jack mine | chalcopyrite | 0 | < 0.0003 |
| 112. do. | covellite-bornite | 0 | < 0.0004 |
| 113. Blue Lizard mine | pyrite | B | < 0.0005 |
| 114. do. | pyrite | 0 | < 0.0003 |
| 115. do. | bornite(chalcopyrite) | 0 | < 0.0004 |
| 116. do. | chalcopyrite | 0 | < 0.0003 |
| 117. do. | chalcopyrite | 0 | < 0.0004 |
| 118. McCarthy-Coleman claim | pyrite | B | < 0.0003 |
| 119. Foley Uranium Company mine | pyrite | B | < 0.0004 |
| 120. Maybe mine | pyrite-marcasite | 0 | < 0.0003 |
| 121. do. | pyrite | B | < 0.0003 |
| 122. do. | pyrite(marcasite) | B | 0.0006 |
| 123. Gismo mine | bornite(chalcopyrite) | 0 | 0.001 |
| 124. do. | pyrite | 0 | < 0.0005 |
| 125. do. | pyrite | B | 0.0003 |
| 126. do. | pyrite | 0 | < 0.0004 |
| 127. Okie mine | pyrite | 0 | 0.003 |
| 128. do. | pyrite | 0 | 0.002 |
| 129. Hideout mine | pyrite | B | 0.0015 |
| 130. Sandy claim | pyrite | B | < 0.0003 |
| 131. Notch No. 1 mine | pyrite | B | 0.0003 |
| 132. Happy Surprise claim | pyrite-marcasite | B | 0.0003 |
| Monticello district, San Juan County, Utah | | | |
| 133. Mi Vida mine | pyrite | B | 0.0003 |
| 134. do. | pyrite | 0 | < 0.0003 |
| 135. do. | pyrite | 0 | < 0.0008 |
| 136. do. | pyrite | B | < 0.0003 |
| 137. do. | pyrite | 0 | < 0.0003 |
| 138. do. | pyrite | B | < 0.001 |
| 139. do. | pyrite | 0 | < 0.001 |
| 140. do. | pyrite | 0 | < 0.0005 |
| 141. do. | pyrite | B | 0.0008 |
| 142. do. | greenockite | 0 | 0.002 |
| 143. La Sal No. 2 mine | pyrite | 0 | 0.0004 |
| Monument Valley district, Apache County, Arizona | | | |
| 144. Monument No. 2 mine | pyrite | B | 0.0005 |
| 145. do. | pyrite | 0 | < 0.0003 |
| 146. do. | pyrite | B | 0.0005 |

Table 2.--Selenium content of sulfides from the Chinle formation of Triassic age--Continued.

| Location <u>1/</u> | Mineral <u>2/</u> | Type <u>3/</u> | Percent Se <u>4/</u> |
|--|-------------------|----------------|----------------------|
| Green River district, Grand County, Utah | | | |
| 147. Shinarump No. 3 mine | pyrite | 0 | < 0.0003 |
| Slick Rock district, San Miguel County, Colorado | | | |
| 148. Unknown mine, Dolores Canyon | pyrite | 0 | 0.0009 |
| 149. do. | pyrite | B | 0.0007 |
| 150. Hunt No. 2 claim | pyrite | B | 0.009 |

1/ General geographic location of samples shown in figure 1.

2/ X-ray identification on analyzed material. Quotation marks indicate impure sample; mixtures are hyphenated with dominant phase listed first, i.e., marcasite-pyrite; (parentheses) indicate trace amounts.

3/ Sulfides divided into two types: 0 = sulfides taken from mineralized rock (usually showing greater than 0.01 percent U_3O_8), and B = sulfides taken from barren rock.

4/ Lower limit of detection is 0.0003 percent Se for a 1-gram sample; when less sample is available the lower limit of detection is correspondingly higher.

Table 3.--Selenium content of sulfides from sedimentary rocks of Tertiary age.

| Location <u>1/</u> | | Mineral <u>2/</u> | Type <u>3/</u> | Percent Se <u>4/</u> |
|---|-----------------------|-------------------|----------------|----------------------|
| WIND RIVER FORMATION (EOCENE) | | | | |
| Gas Hills district, Fremont County, Wyoming | | | | |
| 151. | Vitro mine | pyrite | B | 0.0008 |
| 152. | do. | pyrite(marcasite) | O | 0.018 |
| 153. | do. | marcasite | B | 0.0005 |
| 155. | do. | marcasite(pyrite) | B | < 0.0003 |
| 156. | do. | pyrite(marcasite) | O | 0.006 |
| 157. | do. | pyrite(marcasite) | B | < 0.0003 |
| 158. | do. | marcasite-pyrite | B | < 0.0003 |
| 159. | do. | pyrite(marcasite) | O | 0.0009 |
| 160. | do. | pyrite | B | 0.003 |
| 161. | do. | pyrite | O | 0.013 |
| 162. | do. | pyrite | B | < 0.0003 |
| 163. | do. | pyrite(marcasite) | O | 0.051 |
| 164. | do. | pyrite(marcasite) | O | 0.0009 |
| 165. | do. | pyrite | B | < 0.0003 |
| 166. | do. | pyrite | B | < 0.0003 |
| 167. | do. | pyrite | B | < 0.0003 |
| 168. | do. | pyrite(marcasite) | B | 0.0003 |
| 169. | do. | pyrite(marcasite) | O | 0.005 |
| 170. | do. | pyrite | B | < 0.0003 |
| 171. | do. | marcasite-pyrite | B | < 0.0003 |
| 172. | do. | pyrite(marcasite) | B | < 0.0003 |
| 173. | do. | marcasite-pyrite | B | < 0.002 |
| 174. | do. | pyrite(marcasite) | B | < 0.0003 |
| 175. | do. | pyrite-marcasite | B | 0.0005 |
| 176. | do. | pyrite(marcasite) | O | 1.5 |
| 177. | do. | pyrite | O | 0.67 |
| 178. | Lucky Mc mine | pyrite | O | 0.003 |
| 179. | do. | pyrite-marcasite | B | 0.002 |
| 180. | do. | pyrite-marcasite | B | 0.004 |
| 181. | do. | pyrite | O | 0.12 |
| 182. | do. | marcasite(pyrite) | B | < 0.0003 |
| 183. | do. | marcasite-pyrite | B | < 0.0003 |
| 184. | do. | pyrite | O | 0.41 |
| 185. | do. | pyrite-marcasite | O | 0.10 |
| 186. | Sarcophagus Butte | pyrite | B | 0.002 |
| 187. | Ridge No. 1 mine | marcasite(pyrite) | O | 0.011 |
| 188. | do. | pyrite-marcasite | B | 0.0008 |
| 189. | Big Horn No. 18 claim | pyrite | B | 0.003 |

Table 3.--Selenium content of sulfides from sedimentary rocks of Tertiary age--Continued.

| Location <u>1/</u> | Mineral <u>2/</u> | Type <u>3/</u> | Percent Se <u>4/</u> |
|---|-------------------|----------------|----------------------|
| WASATCH FORMATION (EOCENE) | | | |
| Pumpkin Buttes district, Campbell County, Wyoming | | | |
| 190. Channel claim | pyrite | 0 | 0.01 |
| 191. Van No. 1 claim | pyrite | 0 | 0.17 |
| 192. Craney Draw | pyrite(marcasite) | B | 0.008 |
| 193. do. | pyrite(marcasite) | B | 0.003 |
| 194. Jeanette mine | pyrite(marcasite) | 0 | 0.03 |
| 195. Willow Creek | pyrite | B | 0.004 |
| 196. Blowout mine | pyrite | 0 | 3.00 |
| Converse County district, Wyoming | | | |
| 197. Dead Cow area | pyrite | B | 0.003 |
| 198. Fetterman Creek | pyrite | B | 0.001 |
| 199. Dry Fork | pyrite | B | 0.0003 |
| Crooks Gap district, Fremont County, Wyoming | | | |
| 200. Helen May claim | pyrite | 0 | 0.019 |
| 201. Sno Ball No. 1 mine | pyrite | 0 | 0.005 |
| JACKSON FORMATION (EOCENE) | | | |
| Karnes County district, Texas | | | |
| 202. Pete Lyssy claim | pyrite-marcasite | B | 0.024 |
| BROWNS PARK FORMATION (MIOCENE ?) | | | |
| Maybell district, Moffat County, Colorado | | | |
| 203. Sugarloaf Mining property | pyrite-marcasite | 0 | 0.006 |

1/ General geographic location of samples shown in figure 1.

2/ X-ray identification on analyzed material. Quotation marks indicate impure sample; mixtures are hyphenated with dominant phase listed first, i.e., marcasite-pyrite; (parentheses) indicate trace amounts.

3/ Sulfides divided into two types: 0 = sulfides taken from mineralized rock (usually showing greater than 0.01 percent U_3O_8), and B = sulfides taken from barren rock.

4/ Lower limit of detection is 0.0003 percent Se for a 1-gram sample; when less sample is available the lower limit of detection is correspondingly higher.

Table 4.--Selenium content of sulfides from sedimentary rocks of Cretaceous age.

| Location <u>1</u> / | Mineral <u>2</u> / | Type <u>3</u> / | Percent Se <u>4</u> |
|--|--------------------|-----------------|---------------------|
| FALL RIVER SANDSTONE | | | |
| Edgemont district, Fall River County, South Dakota | | | |
| 204. Flint Hill Quadrangle, sec. 23, T. 8 S., R. 3 E. | pyrite | B | 0.0007 |
| 205. No. 4 mine | pyrite | O | 0.006 |
| 206. Trail Fraction claim | pyrite | O | 0.004 |
| 207. Flint Hill Quadrangle, sec. 15, T. 9 S., R. 4 E. | pyrite | B | 0.0008 |
| Crook County district, Wyoming | | | |
| 208. Busfield mine | pyrite | O | 0.0006 |
| 209. do. | "pyrite" | B | < 0.0003 |
| 210. Homestake mine | "pyrite" | O | 0.017 |
| FUSON SHALE | | | |
| Edgemont district, Fall River County, South Dakota | | | |
| 211. Edgemont N. E. quadrangle, sec. 35, T. 7 S., R. 2 E. | pyrite | B | 0.001 |
| 212. Disney uranium mine | pyrite | B | 0.008 |
| MINNEWASTE LIMESTONE | | | |
| Edgemont district, Fall River County, South Dakota | | | |
| 213. Burdock Quadrangle, sec. 8, T. 7 S., R. 22 E. | pyrite(marcasite) | B | 0.002 |
| LAKOTA SANDSTONE | | | |
| Crook County district, Wyoming | | | |
| 214. Shannon Oil Company claims | pyrite | O | 0.0006 |
| 215. do. | pyrite | B | 0.0006 |
| 216. do. | pyrite | O | < 0.0003 |
| TIMPAS FORMATION | | | |
| El Paso County, Colorado | | | |
| 217. Sec. 12, R. 66 E., T. 16 S. | marcasite | B | 0.0007 |

Table 4.--Selenium content of sulfides from sedimentary rocks of Cretaceous age--Continued.

| Location <u>1/</u> | Mineral <u>2/</u> | Type <u>3/</u> | Percent Se <u>4/</u> |
|---|-------------------|----------------|----------------------|
| MANCOS SHALE | | | |
| Slick Rock district, San Miguel County, Colorado | | | |
| 218. Drill core, Disappointment Valley (depth 219.3 ft) | pyrite | B | 0.023 |
| 219. do. (depth 240.2 ft) | pyrite(marcasite) | B | 0.028 |
| 220. do. (depth 274 ft) | pyrite | B | 0.003 |
| 221. do. (depth 330.6 ft) | pyrite | B | 0.008 |
| 222. do. (depth 415.8 ft) | pyrite(marcasite) | B | 0.007 |

1/ General geographic location of samples shown in figure 1.

2/ X-ray identification on analyzed material. Quotation marks indicate impure sample; mixtures are hyphenated with dominant phase listed first, i.e., marcasite-pyrite; (parentheses) indicate trace amounts.

3/ Sulfides divided into two types: O = sulfides taken from mineralized rock (usually showing greater than 0.01 percent U_3O_8), and B = sulfides taken from barren rock.

4/ Lower limit of detection is 0.0003 percent Se for a 1-gram sample; when less sample is available the lower limit of detection is correspondingly higher.

Table 5.--Selenium content of sulfides from hydrothermal vein deposits and intrusive rocks.

| Location <u>1/</u> | Mineral <u>2/</u> | Percent Se <u>3/</u> |
|---|-------------------|----------------------|
| INTRUSIVE ROCKS | | |
| La Sal Mountains, Grand County, Utah | | |
| 223. Diorite porphyry | chalcopyrite | 0.016 |
| 224. Contact zone in Paradox formation | pyrite | 0.008 |
| 225. Diorite porphyry | pyrite | 0.006 |
| 226. Diorite porphyry | bornite | 0.015 |
| Ute Mountains, Montezuma County, Colorado | | |
| 227. Hornfels (Mancos shale) contact zone | pyrite | 0.004 |
| 228. Diorite porphyry | pyrite | 0.004 |
| Carrizo Mountains, Apache County, Arizona | | |
| 229. Diorite porphyry | pyrite | < 0.001 |
| HYDROTHERMAL VEIN DEPOSITS | | |
| Placerville district, Montrose County, Colorado | | |
| 230. Black King mine | pyrite | 0.017 |
| Rico district, Montezuma County, Colorado | | |
| 231. St. Louis Tunnel | pyrite | 0.006 |
| La Plata Mountains, La Plata County, Colorado | | |
| 232. Bessie G. mine | pyrite | 0.002 |
| Monticello district, Abajo Mountains, San Juan County, Utah | | |
| 233. Blanding Water Tunnel | pyrite | 0.010 |

1/ General geographic location of samples shown in figure 1.

2/ X-ray identification on analyzed material; all samples taken from nonuraniferous rocks.

3/ Lower limit of detection is 0.0003 percent Se for a 1-gram sample; when less sample is available the lower limit of detection is correspondingly higher.

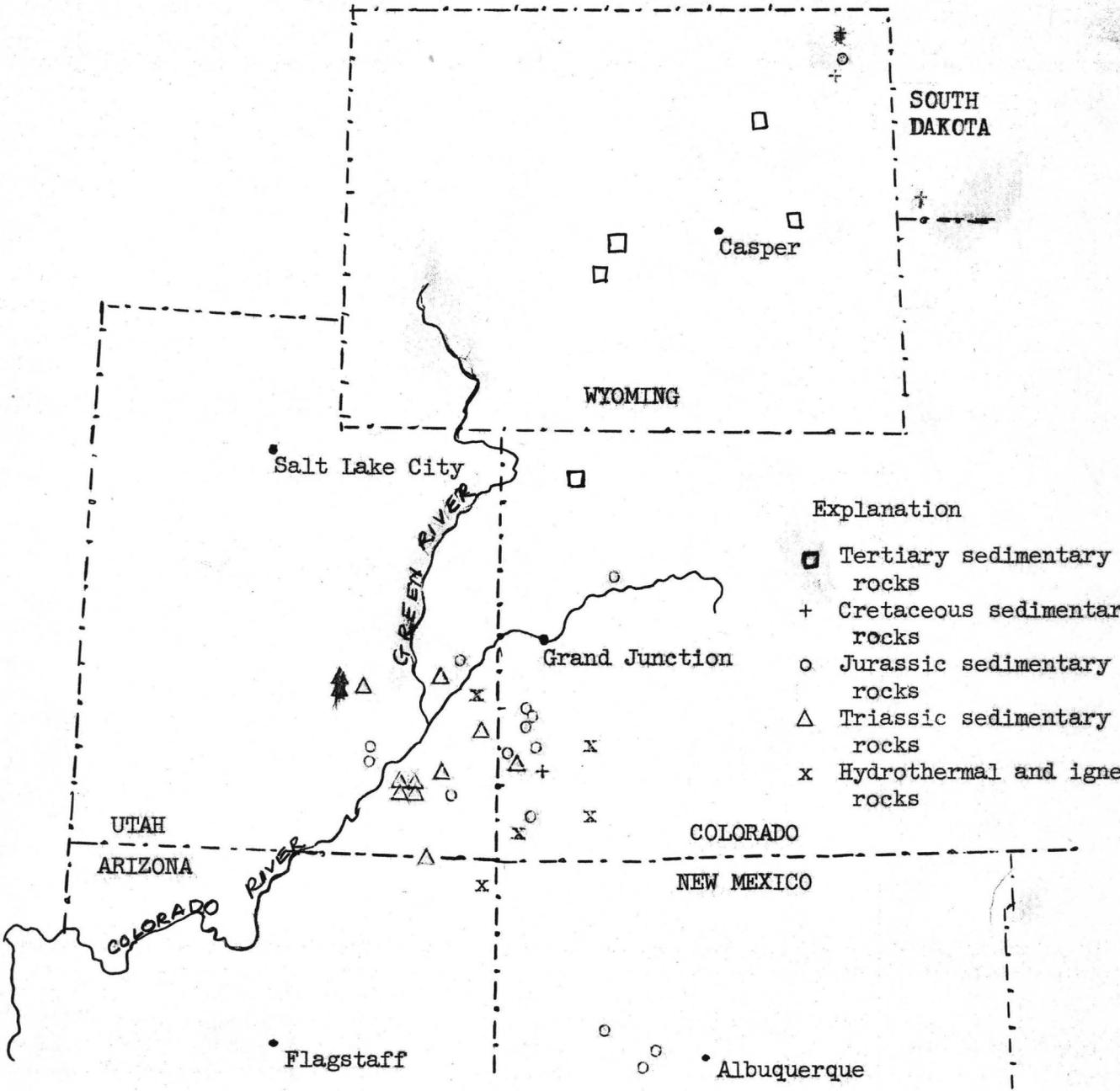


Figure 1.--Locations of samples.

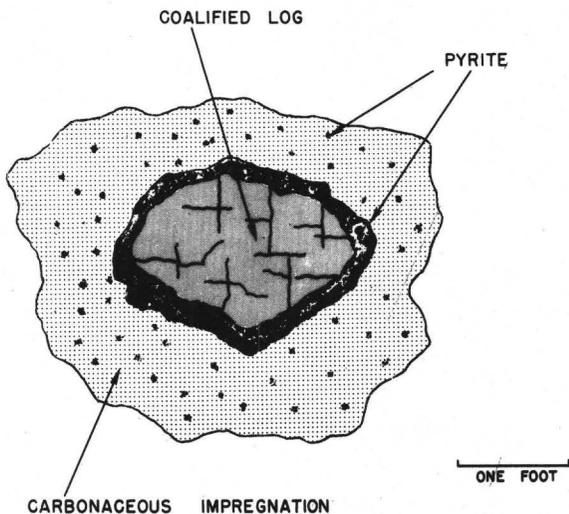


Figure 2.--Coalified log showing typical sulfide concentration.

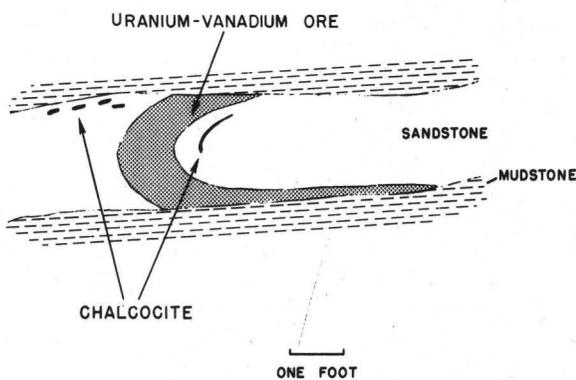


Figure 5.--Roll ore body and associated sulfides, Morrison formation.

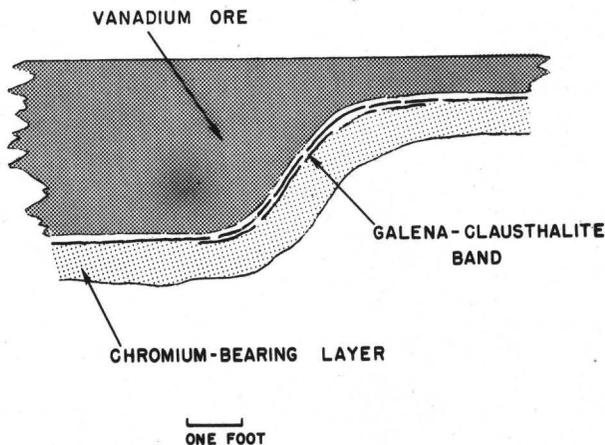


Figure 6.--Galena-clausthalite band and its relationship to vanadium deposit in Entrada sandstone

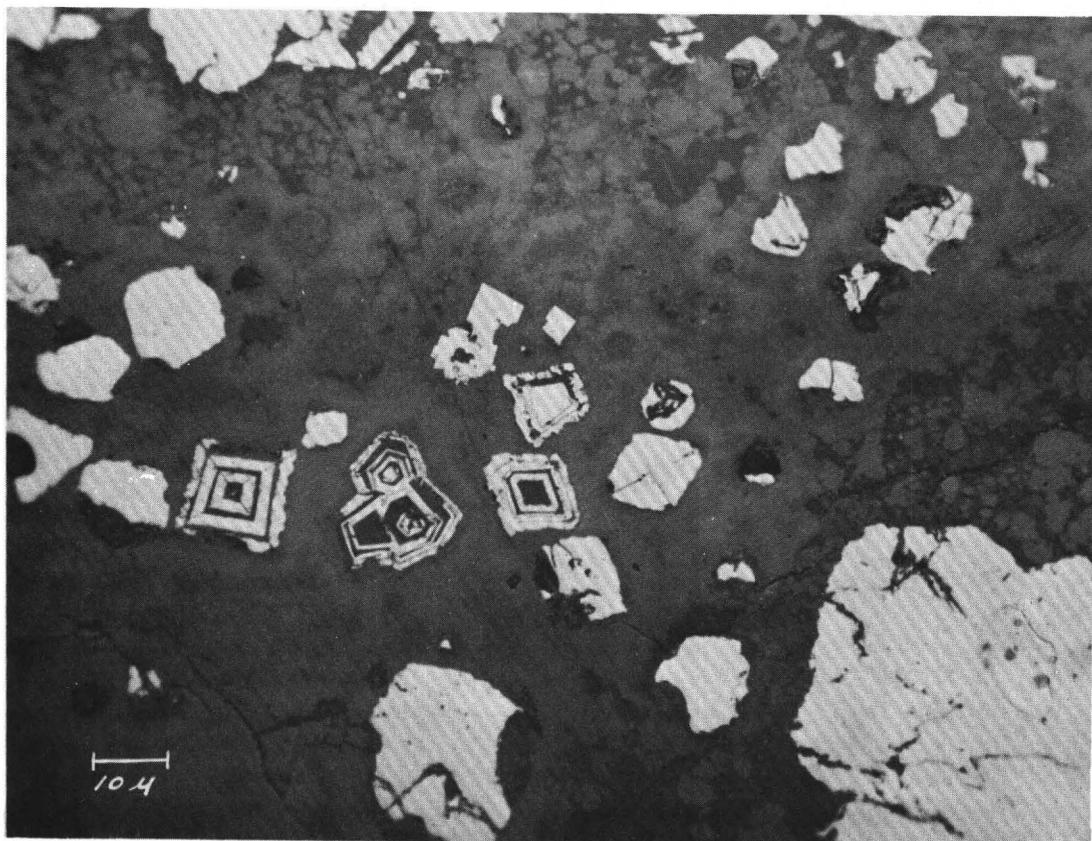


Figure 3.--Pyrite associated with uraninite and coffinite. The mottled dark-gray groundmass is an intimate mixture of uraninite and coffinite. Zoned crystals of pyrite show selective replacement by galena, uraninite, and coffinite. The light irregular patches are also pyrite and they show strong corrosion by the uranium minerals. Mi Vida mine, Monticello district, San Juan County, Utah. Polished section, plain light.

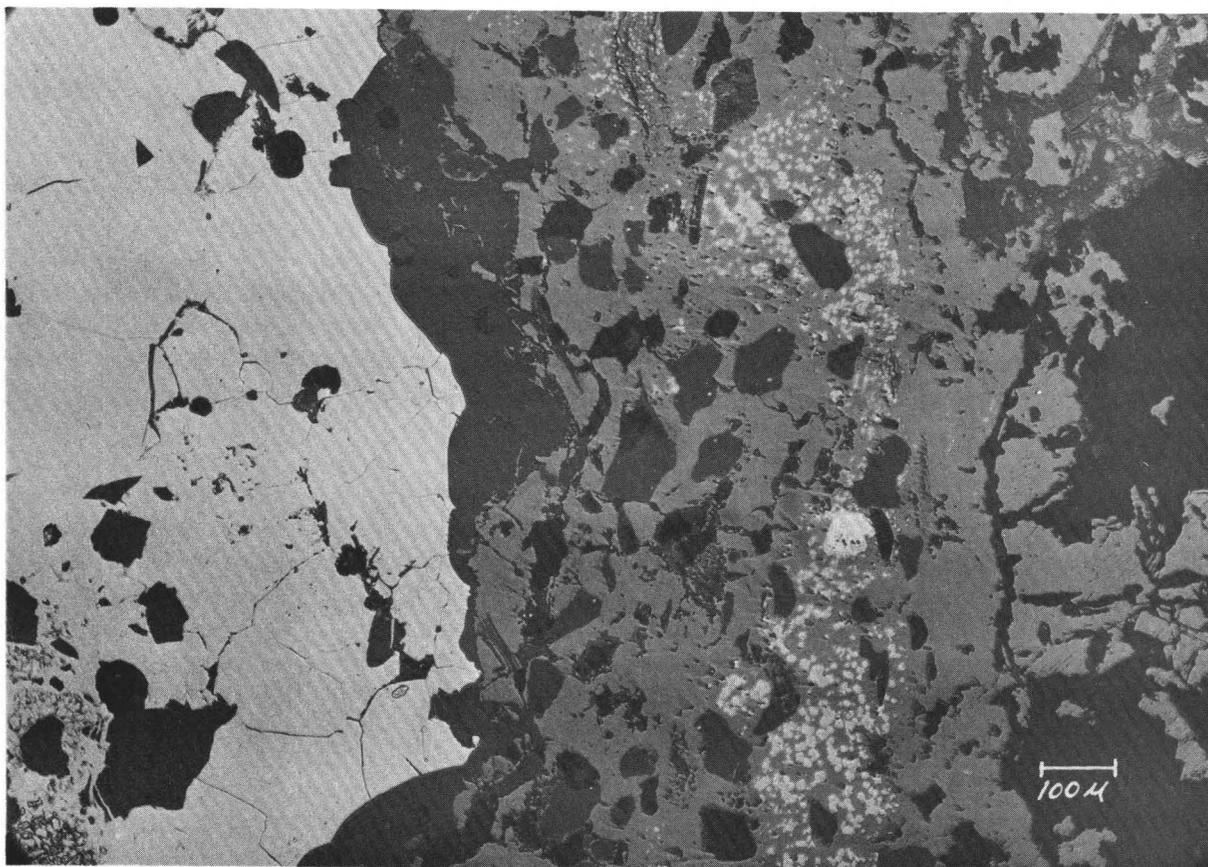


Figure 4.--Pyrite associated with uraninite. Massive pyrite on the left is replaced by calcite. Light-colored zoned crystals in the uraninite (medium gray) are second-generation cobalt-rich pyrite. A band of sphalerite is along the right-hand border of the picture. Hidden Splendor mine, San Rafael district, Utah. Polished section, plain light.

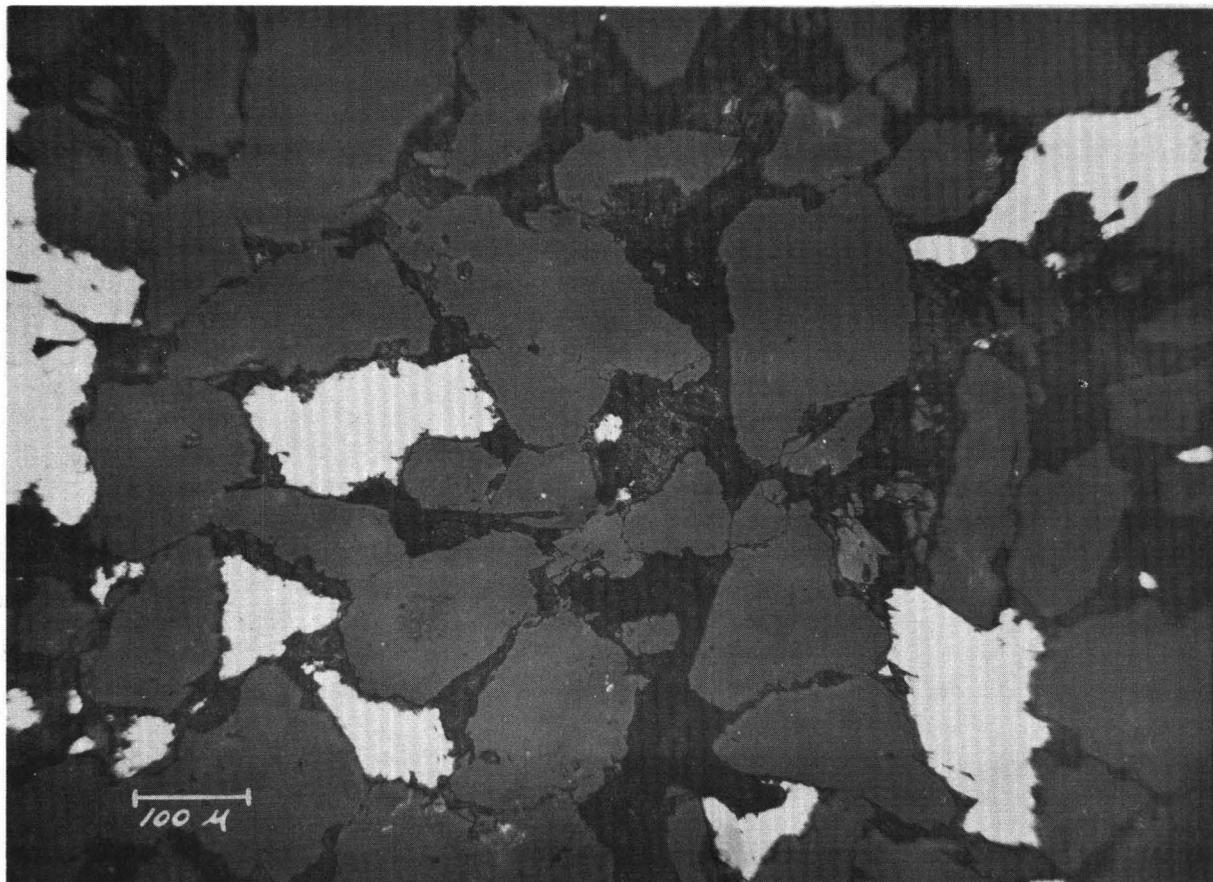


Figure 7.--Galena-clausthalite band. Galena-clausthalite (white) interstitial to detrital quartz grains; other intergranular areas between the quartz are filled with clay minerals. Rifle mine, Rifle district, Garfield County, Colo. Polished section, plain light.

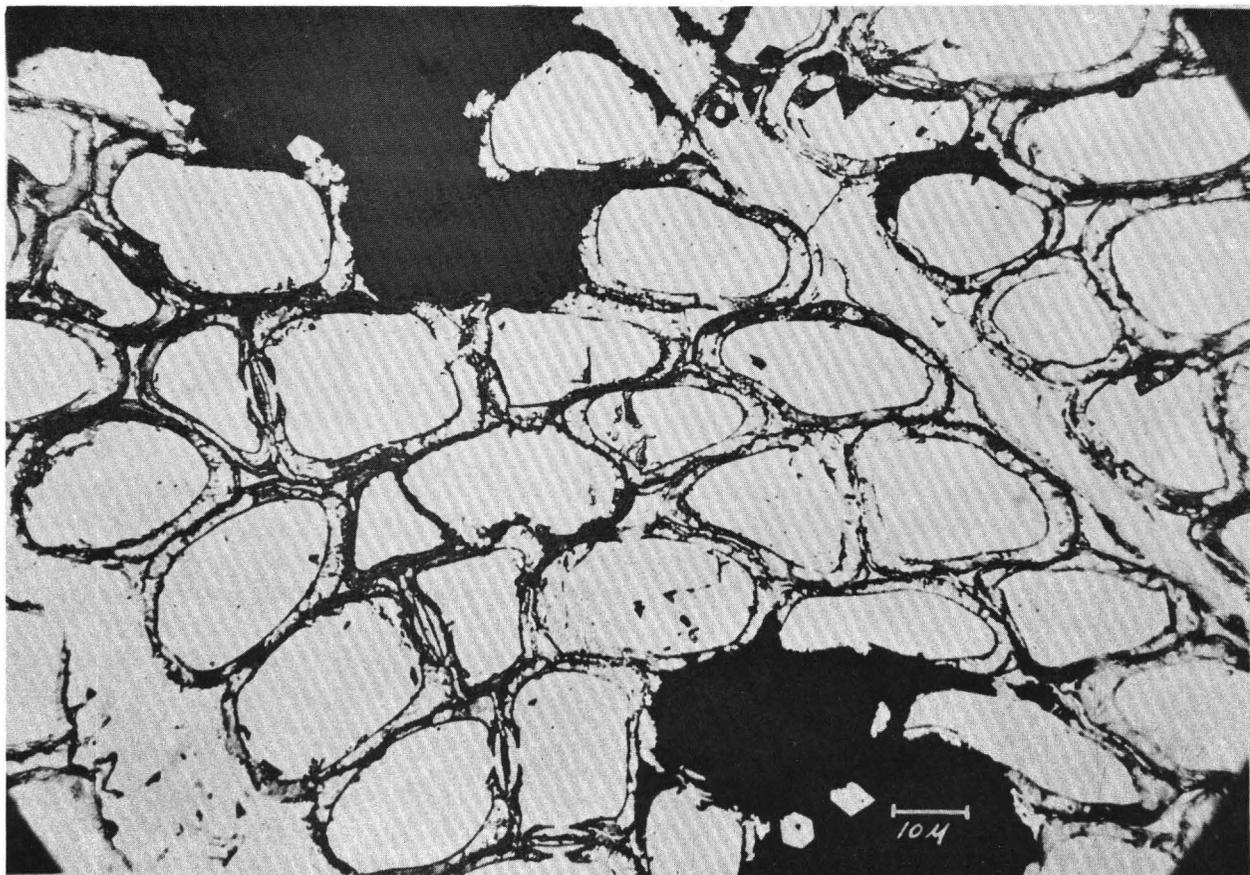


Figure 8.--Pyrite (white) impregnating and replacing wood structure. Black interstitial areas consist of quartz and relict carbonaceous material. Marshbank Canyon claim, San Rafael district, Emery County, Utah. Longitudinal polished section, plain light.

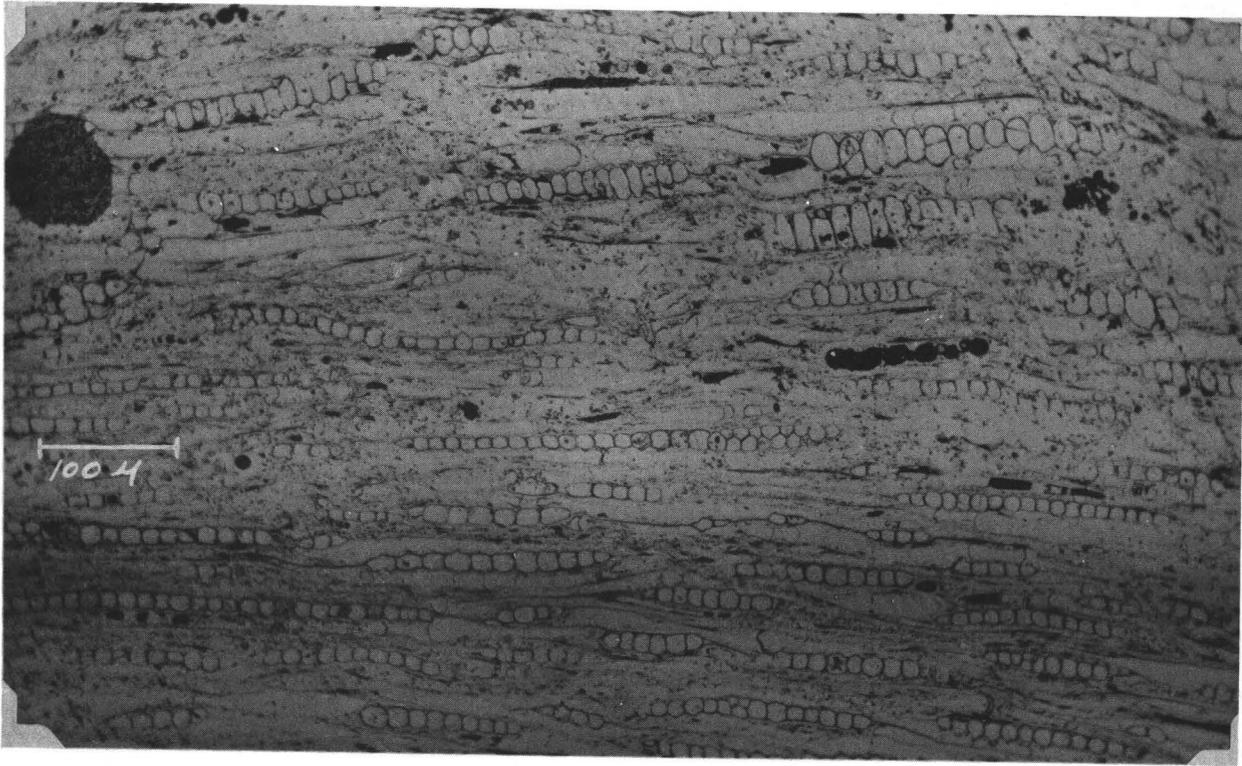


Figure 9.--Pyrite (gray) impregnating and replacing wood structure. Black areas are carbonaceous material. Hideout mine, White Canyon, San Juan County, Utah. Transverse polished section, plain light.

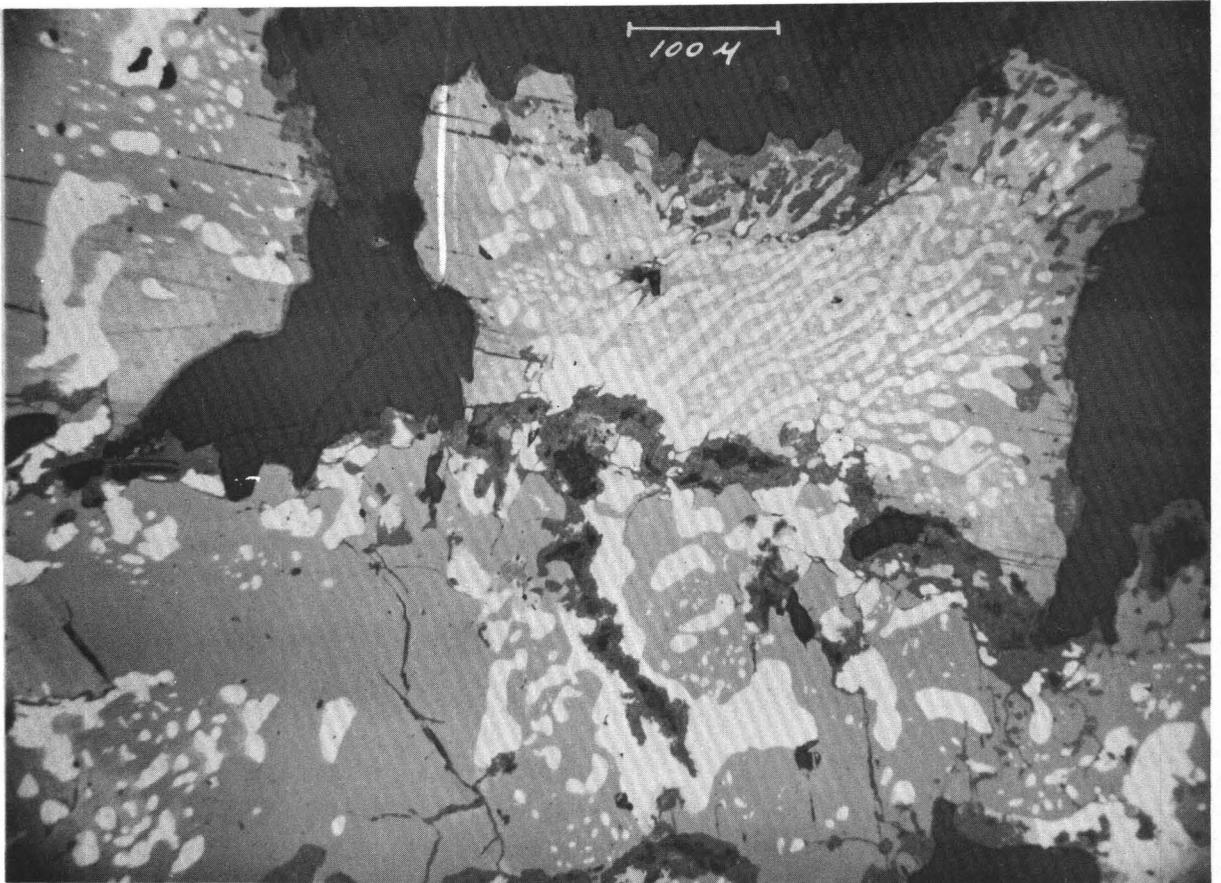


Figure 10.--Chalcocite nodule containing intergrowths of clausthalite (white) and chalcocite (medium gray) surrounded by embayed quartz (dark gray). Cougar mine, Slick Rock district, San Miguel County, Colo. Polished section, plain light.

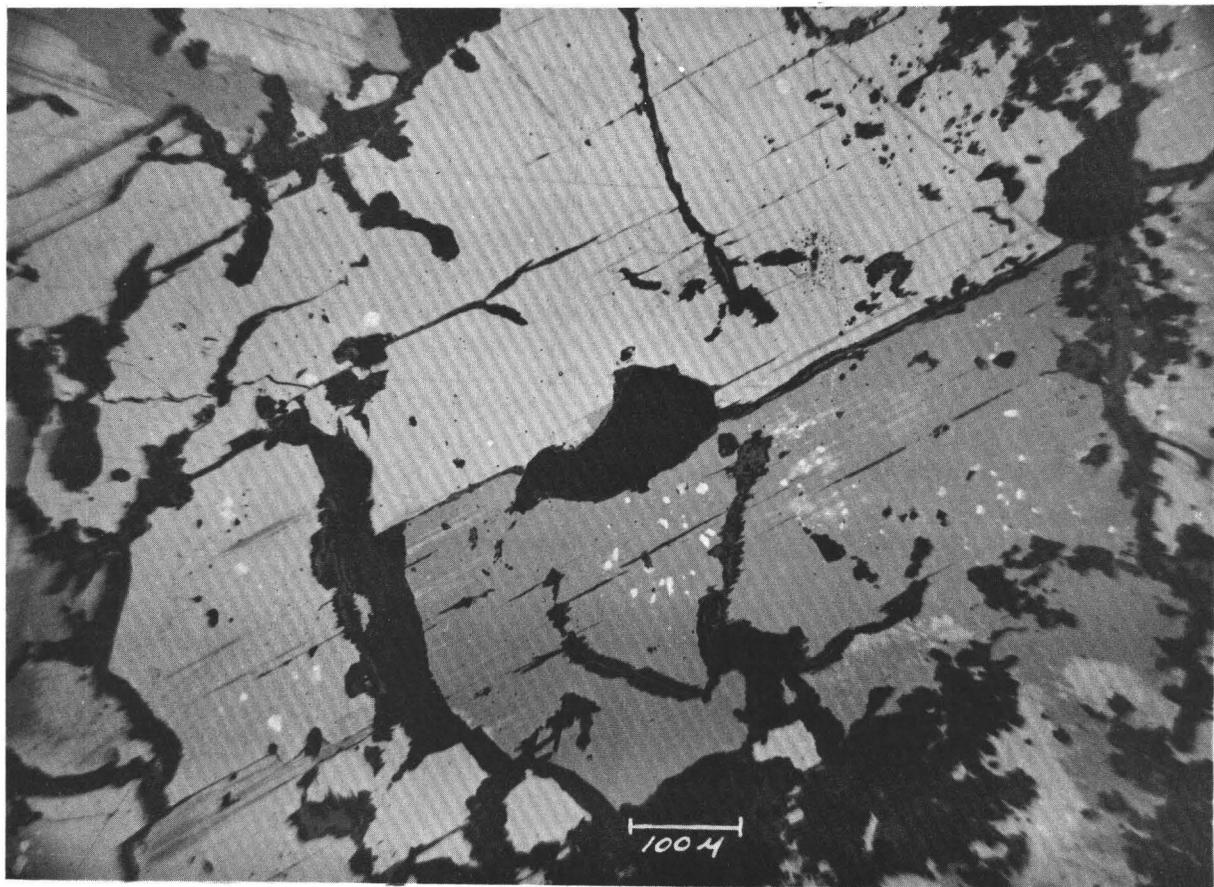


Figure 11.--Chalcocite (light gray) and digenite (medium gray) containing small inclusions of clausenthalite (white). Alteration (oxidation) along irregular veins (black to dark gray) produces secondary copper vanadates and carbonates. Cougar mine, Slick Rock district, San Miguel County, Colo. Polished section, plain light.

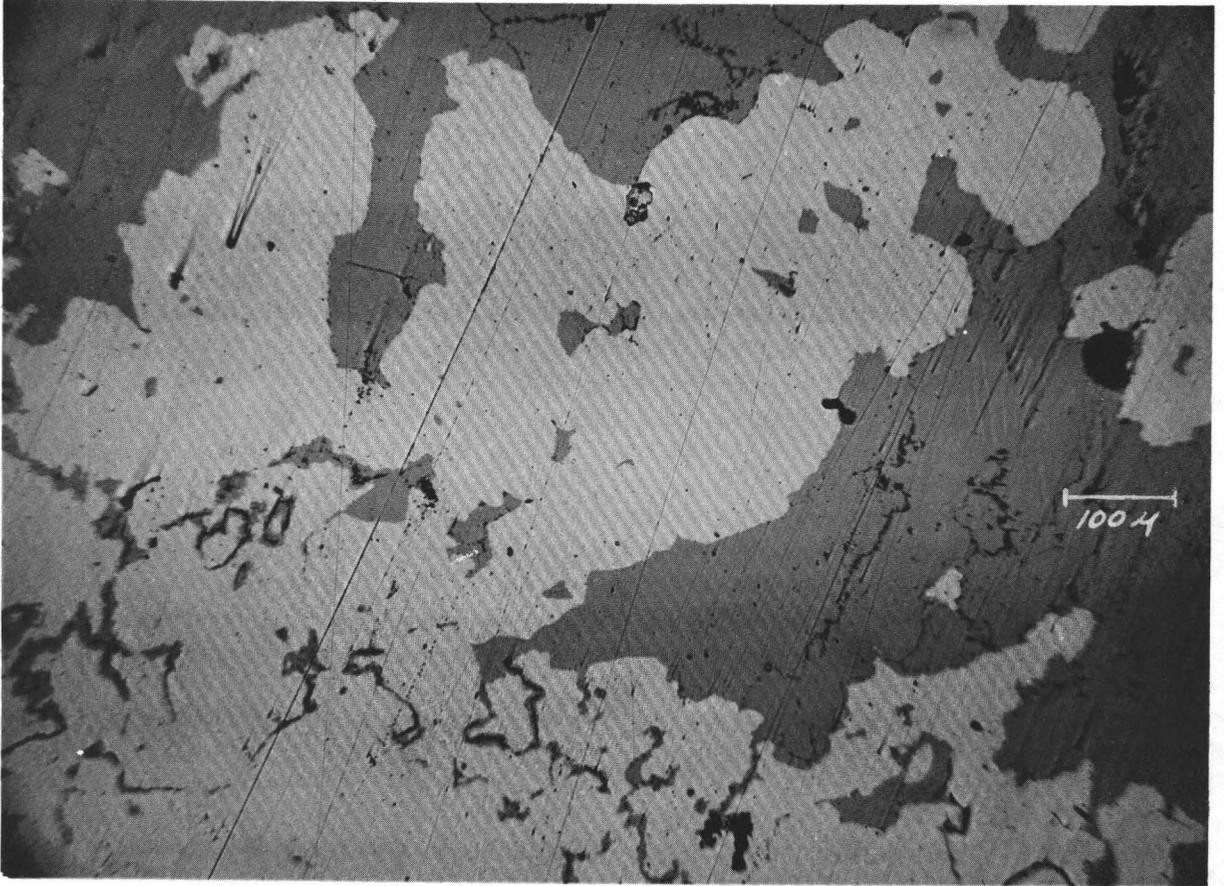


Figure 12.--Clausthalite (light gray) and eucairite (dark gray) in central part of chalcocite nodule. Cougar mine, Slick Rock district, San Miguel County, Colo. Polished section, plain light.

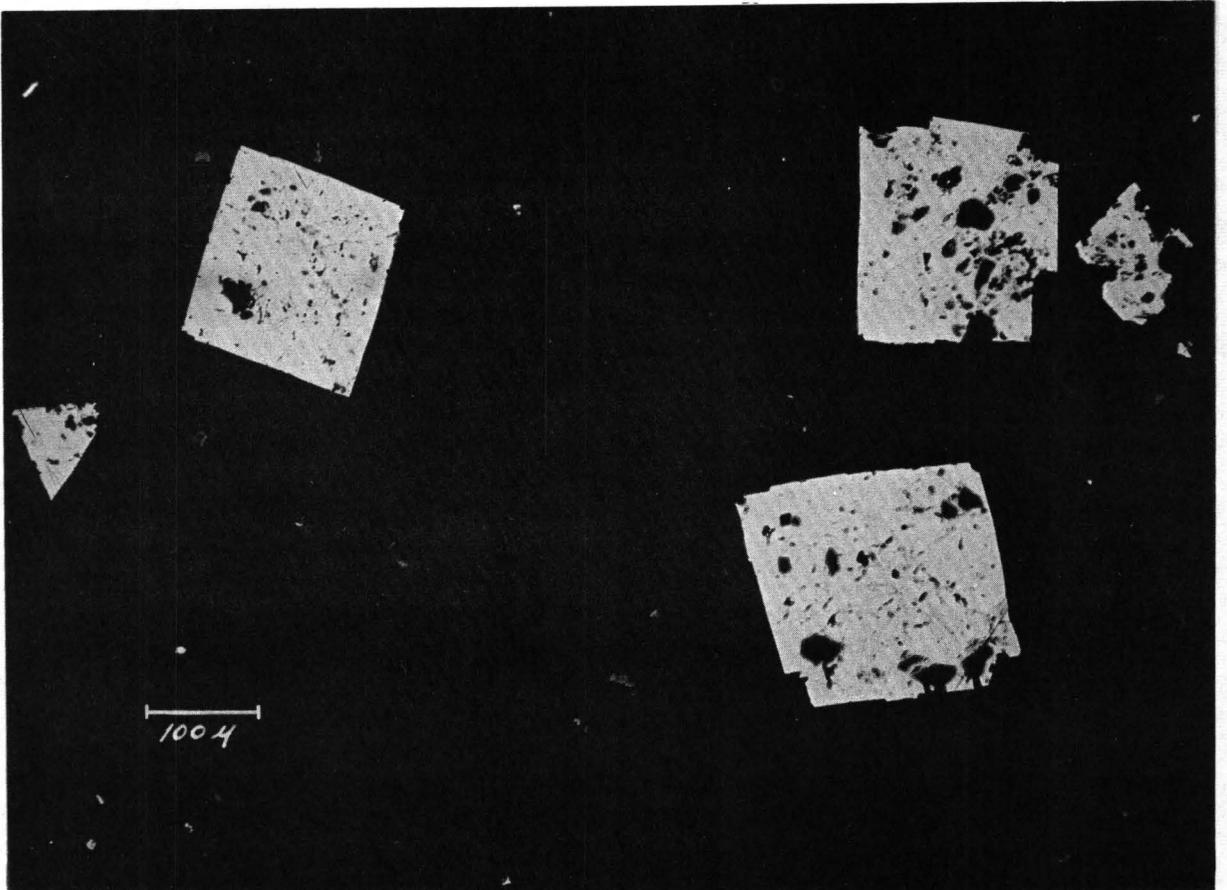


Figure 13.--Euhedral pyrite cubes in barren siltstone underlying mineralized sandstone. Rifle mine, Garfield County, Colo. Polished section, plain light.

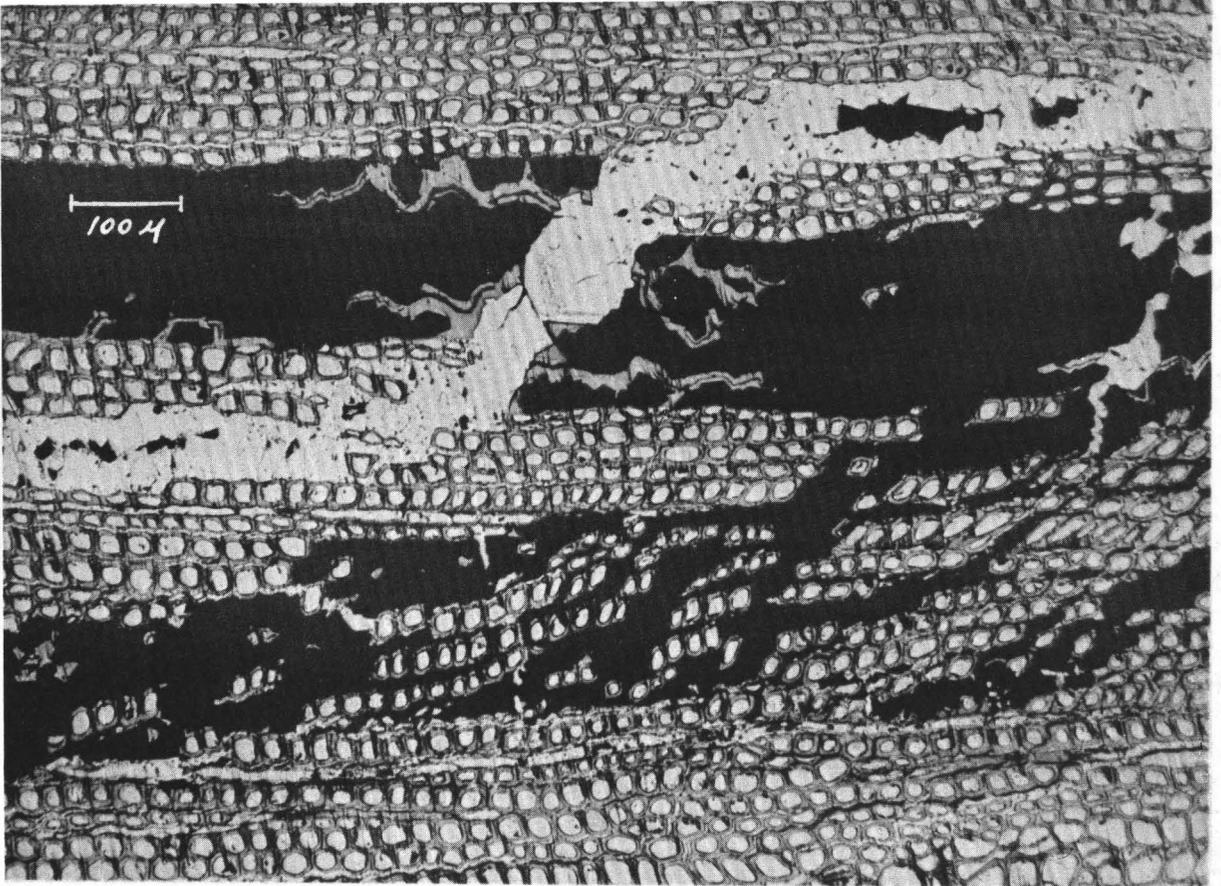


Figure 14.--Mineralized log showing wood structure with the cell walls replaced by marcasite and the lumens (cell cavities) impregnated by pyrite-marcasite. Second generation of pyrite (white vein), calcite (black), and galena (medium gray) cutting and displacing the woody structure. Adams Uranium Co. mine, San Rafael district, Emery County, Utah. Polished section, plain light.

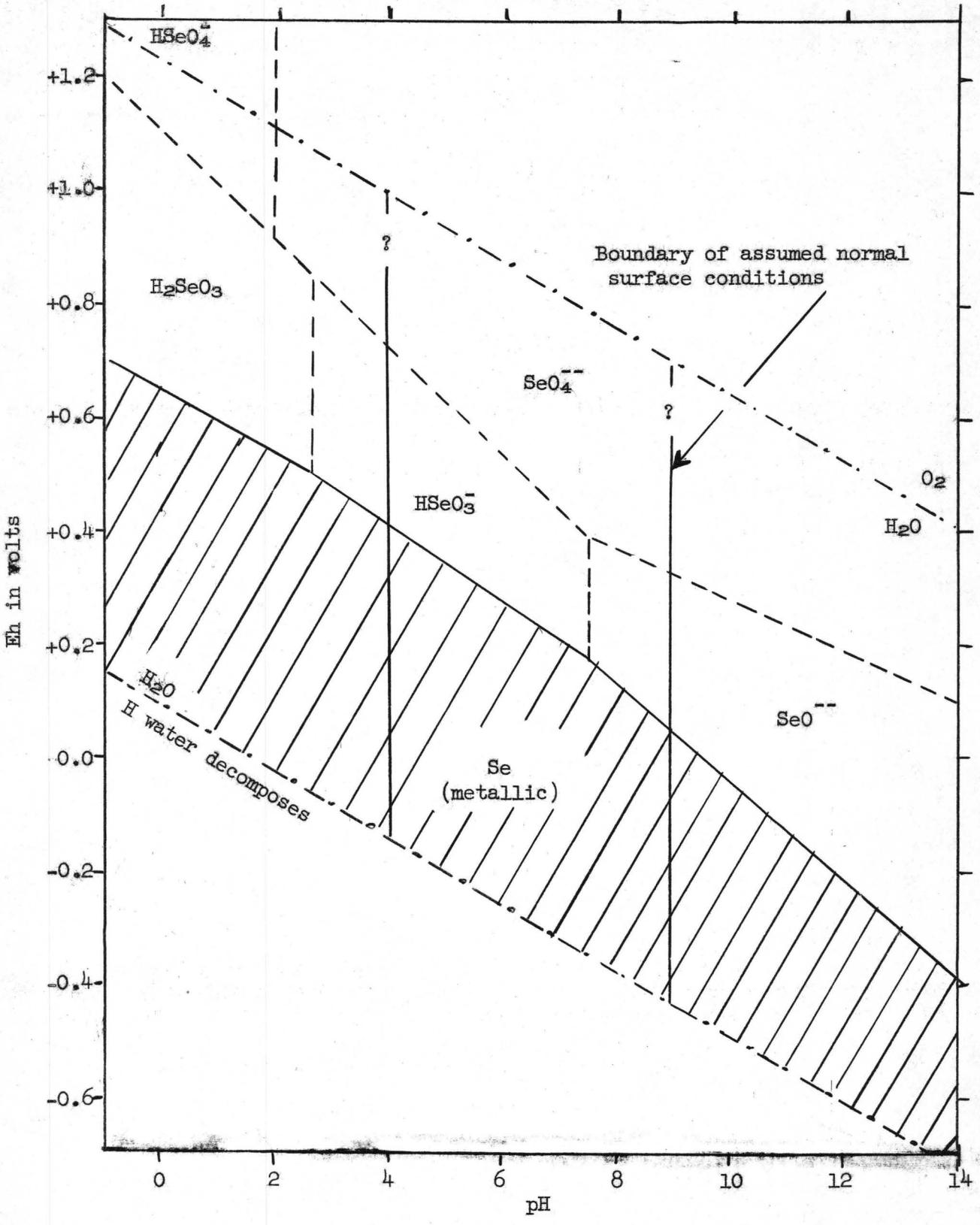


Figure 15.--Stability field of selenium (temperature 25° C, pressure 1 atm, concentration of Se 10⁻⁶ M)--after Delahay, Pourbaix, and Van Rysselberghe (12).