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By Edward C. Walker, Frank Cuttitta, and Frank E. Senftle

Trace Elements Investigations Report 696

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SOME NATURAL VARIATIONS IN THE RELATIVE ABUNDANCE OF COPPER ISOTOPES

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ABSTRACT

The relative isotopic abundance of copper has been measured in a number of minerals. Suites of samples from Michigan and the Colorado Plateau have been examined to determine if local variations due to isotopic exchange or diffusion could be found. The relative isotopic abundance of copper in specimens from a number of other places was also determined. The variations noted were small but in most cases were felt to be significant because they were larger than the experimental error (0.1 percent in the ratio). A total spread of +3 to -8 parts per mil compared to the standard was found in the specimens tested.

INTRODUCTION

As Rankama (1954) has pointed out, little attention has been paid to the possibility of terrestial fractionation of copper isotopes. The mass difference of the copper isotopes is small and no large variations can be expected. Brown and Inghram (1947) have compared the isotopic composition of copper from Cañón Diablo meteorite with two terrestial copper samples and obtained 2.244, 2.236, and 2.234 for the Cu^{63}/Cu^{65} ratio, respectively. They felt that this difference of a little less than 0.5 percent was within their experimental error and hence was not significant.

Regardless of the small fractionation anticipated it would be of interest if a real variation of this order of magnitude could be established with improved accuracy of the measurements. Copper is relatively easily dissolved by slightly acidic aqueous solutions. Therefore, one would expect a greater possibility of isotopic fractionation of copper by such processes as diffusion (Senftle and Bracken, 1955) or exchange reactions when the copper is in an ionic state. Klemm (1943) obtained a 5.5 percent increase in the Cu^{63}/Cu^{65} ratio in the laboratory by controlled high-temperature diffusion of copper through AgS. Hence, it is reasonable to assume that a small but measurable variation may occur in nature. Further, if these small variations in isotopic abundance are due to diffusion processes, they will probably be evident only if the element in question is a minor constituent of the host rock. Effects of such local fractionation processes are likely to be masked in a bulk deposit or specimen of such an element. For instance, in a similar investigation of the variation of the zinc isotopes in nature by Blix, v. Ubisch, and Wickman (1957) no variations were noted. However, only bulk zinc-bearing minerals were investigated, and small variations may have been masked.

The present investigation was undertaken to determine whether significant variations of the Cu^{63}/Cu^{65} ratio occur in nature, particularly in specimens where these fractionation processes are suspected to have taken place, that is, where the abundance of copper was relatively low. Special efforts have been made to keep the experimental error less than 0.1 percent at the 95 percent confidence level.

METHOD OF ANALYSIS

The mass spectrometer used was a 60°, 6-inch radius instrument of the Nier type. The ion current was measured by a vibrating reed electrometer and recorded by an automatic recorder. Manual magnetic scanning was used for peak selection and the null point method was used to determine the ratios. The buck-out potential was obtained by placing two Dekapot potentiometers alternately across a 1.2-volt mercury cell. These potentiometers have an accuracy of better than ± 0.05 percent of their nominal value, a linearity of ± 0.01 percent and a resolution of better than 0.0002 percent. The potentials obtained in this way were used to buck-out the two peaks. The ratio of the resistance of the potentiometers, which is inversely proportional to the ratio of the ion currents, is used as the ratio of the peak heights. Using this system at least fifty ratios were taken for each measurement completed.

Although the $[Cu^{63}]^+$, $[Cu^{65}]^+$ and $[Cu^{63}I]^+$, $[Cu^{65}I]^+$ peaks were well resolved and gave good intensity they were not as reliable as the $[Cu_2I_2]^+$ peaks. It was found difficult to remove completely the background contamination peaks from the $[Cu]^+$ and $[CuI]^+$ peaks, and at times an unexplained instability was observed. More stable operation and negligible background effects were observed in the higher mass region of $[Cu_2I_2]^+$ peaks. Another feature in favor of the $[Cu_2I_2]^+$ peaks is the formation of a $[Cu^{63}Cu^{65}I_2]^+$ peak. This peak is about the same size as the $[Cu^{63}{}_2I_2]^+$ peak, whereas the $[Cu^{63}I]^+$ peak is about twice that of the $[Cu^{65}I]^+$ peak. The errors incurred in measuring two peaks of the same relative magnitude are about the same.

It was further noted that the ratio of Cu^{63}/Cu^{65} varied with time as shown in figure 1. When the ion source is first turned on, the light isotope is preferentially removed probably due to diffusion processes at the surface of the sample itself. After a short while equilibrium is approached resulting in the much lower slope observed in the figure. When smaller samples are used, equilibrium is reached in a somewhat shorter time (fig. 1). To obtain a greater reproducibility, the mass spectrometer was always run during the same interval of time for all samples of approximately the same weight. For instance, with a full sample charge the instrument was allowed to run for four hours before any data were collected, and then all of the data were collected during the three and one-half hours that followed. For samples of less than a full furnace charge, only weighted amounts were used, which yielded curves similar to curves such as shown in figure 1. Although analysis would start at a somewhat earlier period for the smaller samples, the samples reported here were all done after four hours. In this way values were obtained from that section of the curve with a fairly constant and nearly zero slope. This waiting period also allowed sufficient time for the magnet to stabilize thus minimizing any drift error from this source.

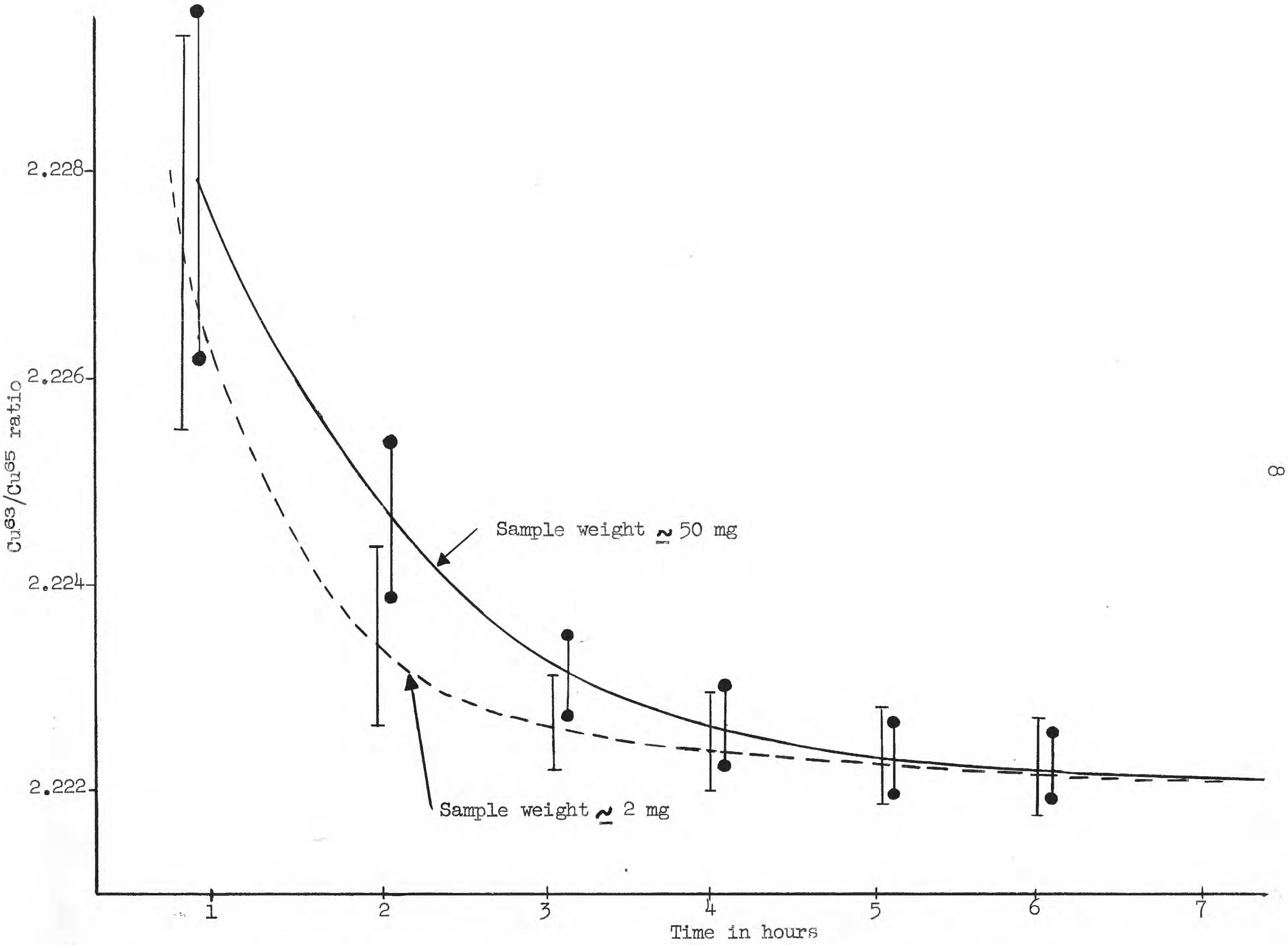

Figure 1.4-Variation of Cu^{63}/Cu^{65} ratio with time and sample weight.

Reagent grade, copper (I) iodide was used as a working standard, and the National Bureau of Standards copper (II) oxide sample no. 29 was used as a primary reference. Table 1 indicates the reproducibility of the results on the working standard sample. The average Cu^{63}/Cu^{65} ratio obtained on this standard, 2.223, is smaller than the value of 2.236 obtained by Brown and Inghram (1947), but is reasonably close to 2.220 obtained by White and Cameron (1948). As all results were taken in the equilibrium portion of the curve (fig. 1) the copper isotope ratios are low compared to data taken within an hour or so after the instrument was turned on. This may help to explain the higher value of the ratio found by Brown and Inghram. All analyses are referred to the National Bureau of Standards reference sample no. 29 on which was obtained a Cu^{63}/Cu^{65} abundance ratio of 2.223, the same as on the working standard. As far as possible either the working standard or the National Bureau of Standards reference sample was run before and after each unknown sample.

Table 1.--Cu^{63}/Cu^{65} ratios for the working standard.

Date run	Cu^{63}/Cu^{65} ratio	Date run	Cu^{63}/Cu^{65} ratio
8/11/55	2.223	2/1/56	2.222
10/25/55	2.223	2/16/56	2.223
11/1/55	2.224	3/28/56	2.222
12/13/55	2.223	4/18/56	2.223
1/17/56	2.223	4/27/56	2.222
1/19/56	2.223	12/7/56	2.223

To avoid contamination, the samples were prepared as suggested by Myers and Barnett (1953) and Barnett and others (1955). The ground samples were freed of carbonates and organic matter by ignition at 900° to 950° C. The ignited samples were then brought into solution by means of aqua regia and converted to chlorides. The metals of the hydrogen sulfide group were precipitated with H_2S at a pH 0.5 using as a carrier lead in which copper could not be detected spectrographically. Separation of the copper from most of the sulfide metals was accomplished by the precipitation of copper (II) cupferrate (Furman, Mason, and Pekola, 1949) in ice-cold dilute HNO_3 using electrolytic iron as a carrier followed by an extraction of the copper by 6N NH_4OH (Baudisch, 1938). Copper was not detected spectrographically in the insoluble cupferrates. The copper was further purified by precipitation as copper (I) thiocyanate. All processes were made as quantitative as possible and at least 10 milligrams of copper were prepared from each unknown sample.

Copper (I) iodide was prepared from a solution of the isolated copper (as the sulfate). In the present method, SO_2 was used as the reducing agent and a solution of reagent grade KI as the source of iodide ions. Special precautions (Lean and Whatmough, 1898; Fernelius, 1946) were taken to remove all traces of moisture from the copper (I) iodide. The prepared iodide varied from a gray-white to a tan-white crystalline powder that remained practically unchanged for indefinite periods of time if kept dry. Spectrographic analyses affirmed the purity of the prepared copper (I) iodides. Copper (I) iodide was used in all the mass spectrometric analyses.

To check the reproducibility of the chemistry, the National Bureau of Standards reference sample copper oxide no. 29 was processed a number of times. The standard preparation of the copper (I) iodide as described above was generally followed, but in several cases drastic chemical procedures were used to see if any fractionation occurred. As is shown in table 2 no fractionation was evident in any of these trials.

Because of the good reproducibility of the combined chemical procedures and the mass spectrometric measurement, the error in the ratios is considered to be less than 0.1 percent in the mean at the 95 percent confidence level. For example, the sample with the widest range of ratios had a probable error of ± 0.6 part per mil at the 95 percent confidence level or an error of 0.06 percent.

The results are quoted as the deviation, Δ, from the standard ratio (Cu^{63}/Cu^{65} = 2.223) in parts per mil (o/oo), where

$$Cu^{63}/Cu^{65}\ (\text{sample}) = \frac{2.223\ (\text{standard})}{1 + \frac{\Delta}{1{,}000}}.$$

An enrichment of the heavy isotope or the light isotope is indicated by a positive or negative number, respectively.

Table 2.--Tests of chemical fractionation using National Bureau of Standards reference sample CuO no. 29.

Date prepared	Type of preparation	Cu^{63}/Cu^{65} ratio
12/17/56	Standard preparation*	2.223
4/10/57	Standard preparation* but only 2 mg processed for isotopic analysis.	2.223
4/10/57	Standard preparation*	2.223
4/12/57	Electroplating plus standard preparation*	2.223
4/15/57	Electroplating, precipitation, chemical displacement with Al followed by standard preparation*	2.223

*See text for details of standard preparation.

ANALYTICAL RESULTS

Samples from White Pine mine, Ontonagon County, Michigan

The rocks of the White Pine copper mine, described in detail by White and Wright (1954), represent a geologic environment in which isotopic fractionation of copper may have taken place. Copper, in the form of both chalcocite and the native metal, is finely disseminated in several layers in the lowermost 25 feet of the Nonesuch shale. The stratigraphic distribution of copper and grades typical of the various layers in the mine area are shown diagrammatically in figure 2. The beds dip 5°-10°E and are cut, in places, by steeply dipping to vertical joints and small faults, along some of which calcite and other vein minerals have been deposited.

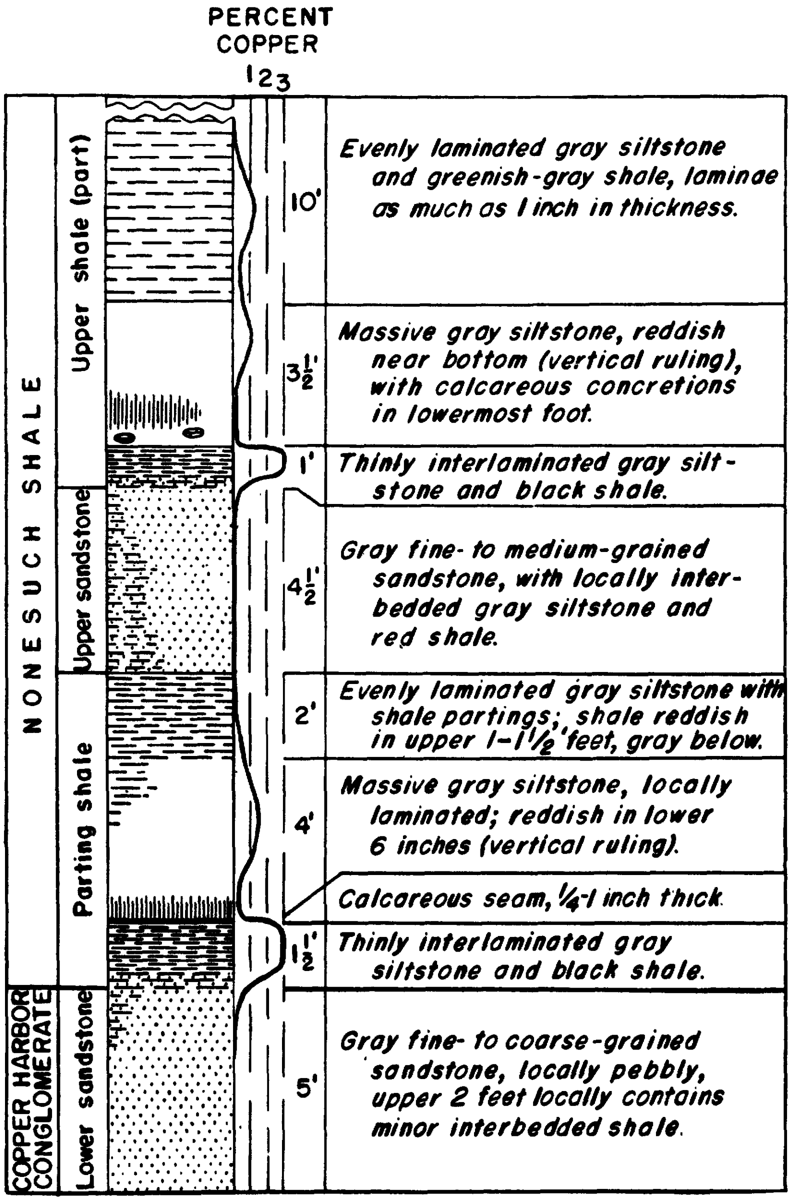

Figure 2.--Typical stratigraphic section of cupriferous zone, White Pine area, Michigan (White and Wright, 1954, fig. 3).

Some of the joints contain films of chalcocite or native copper, particularly where they cut the more highly cupriferous layers.

If the joints have acted as channelways for the introduction of the copper, movement of copper was from the joint into the rock; conversely, if the copper in joints is a product of lateral secretion of copper that was already in the rock before the joint formed, movement was from the rock into the joint. To the extent that diffusion played a part in the migration of the copper, there might be enough isotopic fractionation to give evidence for one or the other direction of migration. Convincing evidence for the direction of migration would greatly reduce the present range of speculation on the possible origins of the deposit.

As an exploratory test, three sets of samples (Sets A-C, table 3) were picked, each set consisting of a specimen of chalcocite or copper coating a joint face, and a specimen of the cupriferous wallrock 1/2 to 1 1/2 feet from the joint, at the same stratigraphic position as the specimen from the joint. Sample no. 2 contains visible specks of native copper, but the other specimens of wallrock contain only chalcocite. These specimens were isotopically analyzed, and the results are given in table 3. In Sets B and C, the lighter isotope is slightly more abundant in the specimens from the joints than in the associated host rock. If this were generally true throughout the deposit, it would suggest that a fractionation process may have been operative in transporting the copper, and that the direction of diffusion was from wallrock to joint. In Set A, on the other hand, in which both specimens contain native copper, the suggested direction of diffusion is from joint to wallrock. This difference in behavior could be most simply interpreted as follows: chalcocite was present in the beds

Table 3.--Isotopic abundance of copper from White Pine mine, Ontonagon County, Michigan.

Set	Sample no.	Sample description	Δ Cu^{63}/Cu^{65} (o/oo)
A	1	Native copper in joint	+3.0
	2	Host rock 20 inches from joint	+0.3
B	3	Chalcocite in joint	-1.1
	4	Host rock 6 inches from joint	+0.1
C	5	Chalcocite in joint	-0.4
	6	Host rock 8 inches from joint	+1.3
D	10	Chalcocite from calcite veinlet	0.0
	11a	Host rock next to veinlet	+1.5
	11b	Host rock 3/4 inch from veinlet	+2.9
	11c	Host rock 1 1/2 inches from veinlet	-1.2
	11d	Host rock 2 1/4 inches from veinlet	0.0
	11e	Host rock 3 inches from veinlet	+1.1
	12	Chalcocite from another veinlet	0.0

Set A. From massive, very finely laminated dark-gray siltstone, about 3 1/2 feet above base of parting shale. Drift W-19, 25 feet west of Drift A.

Set B. From thinly laminated dark-gray shale about 1 foot above base of parting shale. Drift N5, 70 feet north of Drift E1.

Set C. From same layer as Set A. Drift N5, 50 feet north of Drift E1.

Set D. From interlaminated gray siltstone and shale about 4 1/2 feet above base of parting shale. Between Drifts N24 and N26 on W27. Specimen 12 is from another veinlet at the same locality, about 4 feet above base of parting shale in massive dark-gray siltstone.

before the joints were formed, and some of it migrated into the joints during or after their formation. Native copper was introduced into the rocks after the formation of the joints, and these joints acted as channelways. This later stage of mineralization might be connected with the introduction of native copper and chalcocite into the sandstone beds above and below the parting shale; White and Wright (1954, p. 706-708) present evidence that much of the copper in the sandstone beds was introduced after the rocks were deformed. The present data are insufficient, however, to make these interpretations at all conclusive, and serve mainly to show the kind of interpretation that can be made should the results be confirmed by a larger number of samples.

Because of the inconclusive results obtained with a larger distance between samples from joint and host rock, respectively, the extent of isotopic variation in the wallrock within three inches of a vein was tested by a suite of more closely spaced samples (Set D, table 3). The individual samples (nos. 11a-11e) were sawed from a block, one face of which bordered the calcite-chalcocite veinlet represented by sample no. 10; each sample was a slice parallel to the vein. It was hoped that there would be a systematic variation in isotopic composition with distance from the vein that would permit a conclusion about geologic processes involved. As shown in table 3, the differences in isotopic composition are small and show no systematic variation.

Samples from Cougar mine, Montrose County, Colorado

Uranium and vanadium in ores on the Colorado Plateau generally occur in flat-lying tabular bodies parallel to the bedding of the sandstone. Occasionally these bodies are undulating and cut across the bedding planes. Where the ore body crosses the bedding plane and exhibits a sharp interface between the ore and barren sandstone, the term "roll" has been applied to the ore body. These "rolls" have been the subject of investigation for many years, and, although there have been a number of theories as to their formation, no one theory will completely explain all the features embodied in this type of deposit (Shawe, 1956). Some isotopic measurements were made to determine if fractionation occurred in the roll.

A suite of nine samples was taken in and adjacent to a uranium-rich roll in the Cougar mine, Montrose County, Colo. The position of the samples is shown in figure 3. The ore cuts across the bedding planes in a brown sandstone. It is highly oxidized, and the minerals present are secondary. The copper-rich zones are associated with the uranium ore and occur along the edges of the roll. The central portion of the roll contains more Fe_2O_3 than the edges. The main copper-bearing mineral is volborthite, a hydrous vanadate of copper, barium, and calcium; minor amounts of malachite and azurite are present. It may be significant that in the brown sandstone about 7 or 8 feet above the roll there is a bed with abundant carbonate and some copper minerals. This bed may originally have been the source of the copper in the roll below. Unfortunately no specimens containing copper were available from this zone.

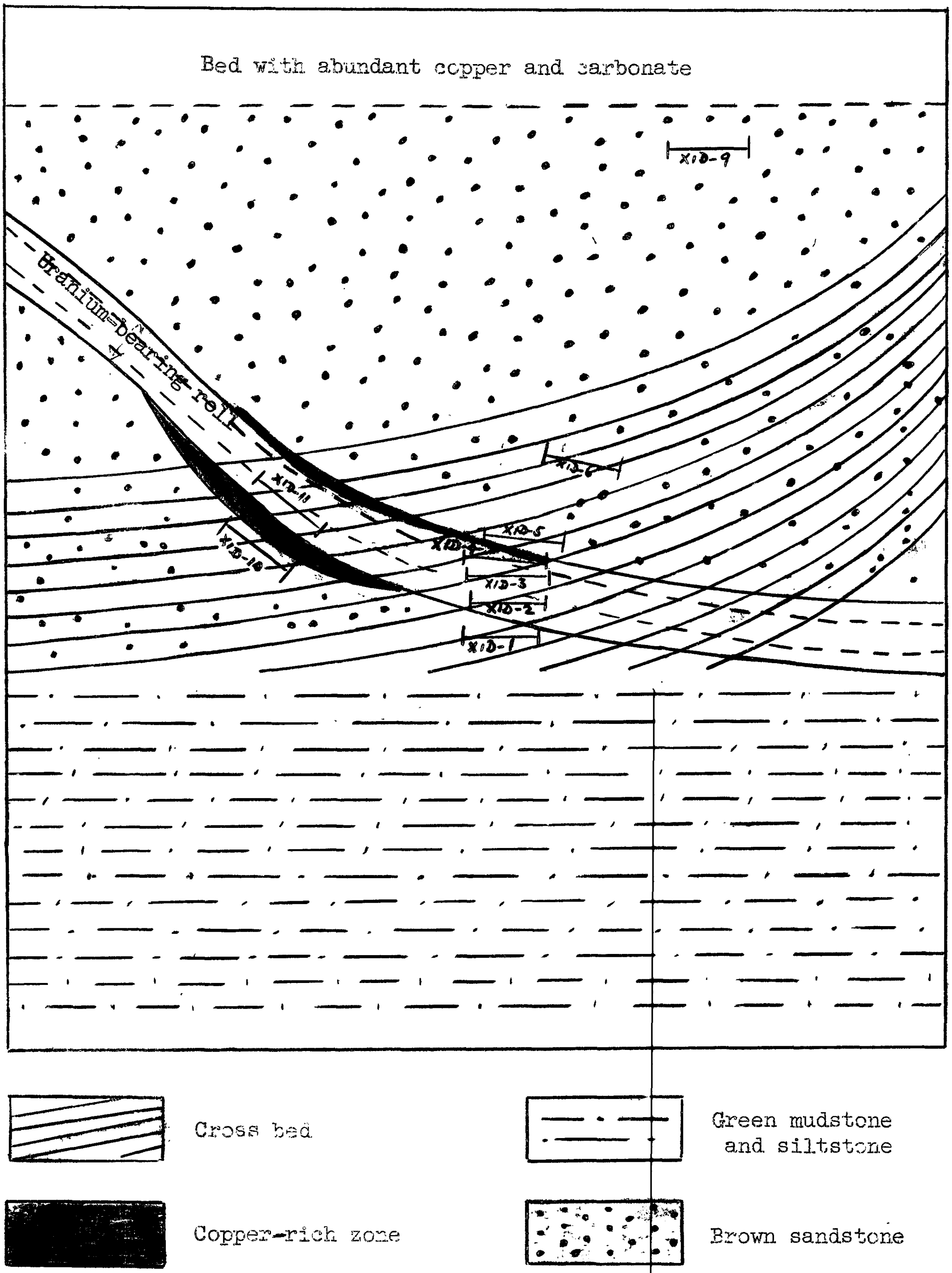

Figure 3.--Sketch of roll surface showing position of samples taken for isotopic analyses, Cougar mine, Montrose County, Colorado. (See table 4.)

The results for these samples (plotted in figure 4 and tabulated in table 4) show an enrichment of Cu^{65} of about 2.5 o/oo within the roll. Sample XID-6 which lies just outside the roll surface is 0.7 o/oo lighter than the standard. The enrichment of Cu^{65} within the roll is a little better than twice the experimental error. Although this is not a large enrichment, it is believed to be significant. Two possible explanations of such a pattern can be given. The copper may have migrated along the roll and undergone an exchange reaction with some copper mineral originally within the roll, or a normal copper may have been laid down within the roll and subsequently redissolved, diffusing into the host rock. If the latter is the case, one would expect the copper just outside the roll to be enriched with Cu^{63} which preferentially diffused out of the roll structure. The data indicate this latter hypothesis, but the enrichment of the light isotope is not large enough nor are there enough determinations to support such a mechanism.

Miscellaneous samples

As little is known about the necessarily small variations in the isotopic abundance of copper in nature, a variety of samples from different geologic environments was chosen for isotopic analysis. The localities, copper content, and change in isotopic ratio for several such samples are shown in table 5 and are described in more detail below.

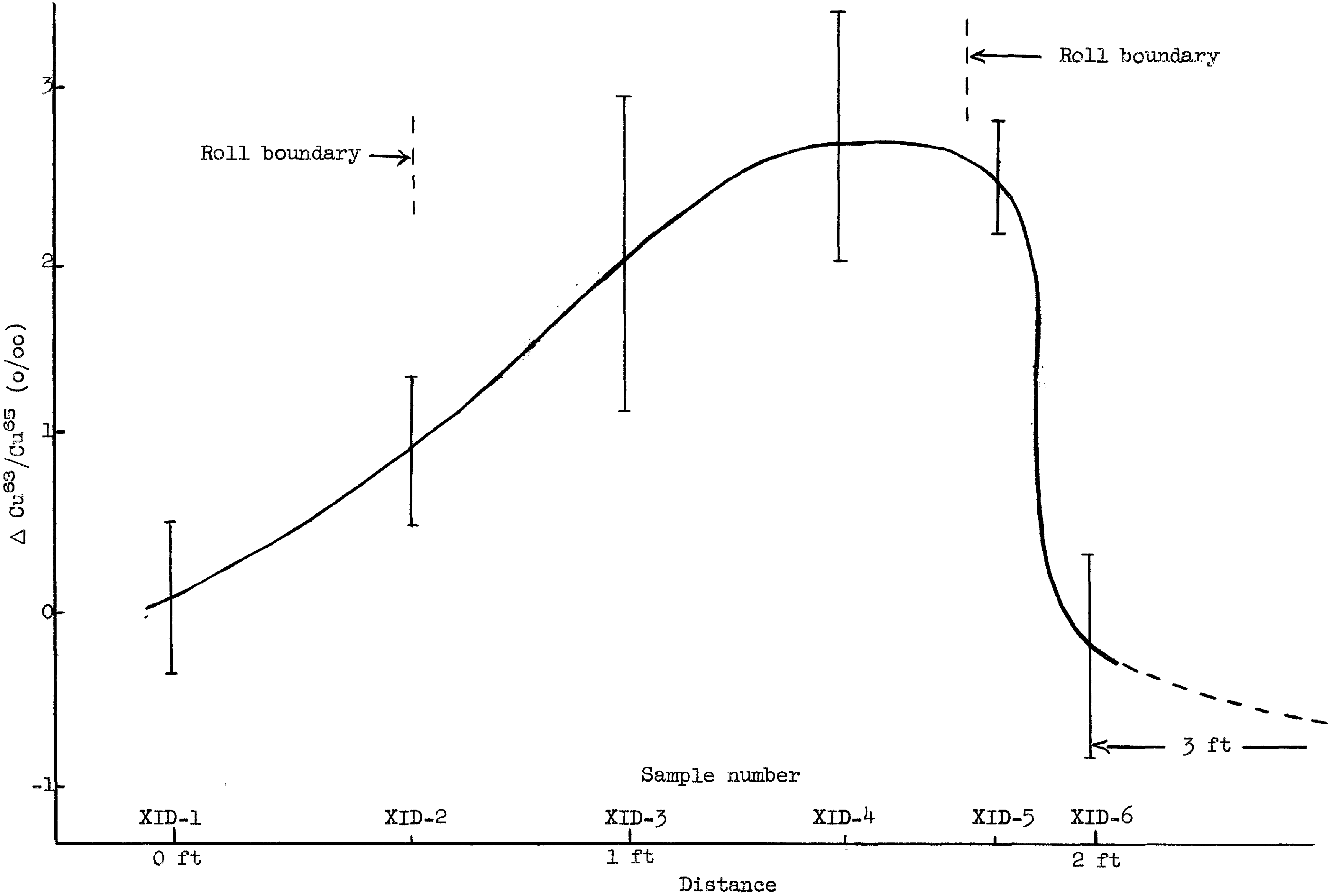

Figure 4.--Change in Cu^{63}/Cu^{65} ratio (Δ in o/oo) of copper in roll structure, Cougar mine, Montrose County, Colorado.

Table 4.--Δ Cu^{63}/Cu^{65}, o/oo, and analytical data, in percent, for samples from a roll, Cougar mine, Montrose County, Colorado.

Constituent	Sample								
	XID-1	XID-2	XID-3	XID-4	XID-5	XID-6	XID-9	XID-10	XID-11
Δ Cu^{63}/Cu^{65} (o/oo)	0.02	0.9	2.0	2.6	2.5	-0.7	-0.5	-0.2	0.2
Percent U	0.51	0.25	0.29	0.86	0.29	0.002	0.002	0.042	0.35
Percent CuO	0.63	0.71	0.76	0.94	3.4	0.18	0.35	0.45	1.5
Percent Fe_2O_3	*	0.007	0.03	0.007	< 0.001	0.04	*	*	*
Percent V_2O_3	*	3.65	5.19	3.85	8.77	0.61	*	*	*
Percent $CaCO_3$	*	3.09	2.25	6.50	1.70	6.39	*	*	*

---

*Not determined.

Table 5.--Comparison of the Δ Cu^{63}/Cu^{65}, o/oo, in various specimens with the National Bureau of Standards reference sample.

Sample no.	Description and location	Cu (ppm)	Δ Cu^{63}/Cu^{65}, (o/oo)
HT-3	Brochantite-stained celestite, Klondike area, San Miguel County, Colorado	*	0.80
GC-2	Brochantite-stained sandstone, near base of Bright Angel Trail, Grand Canyon, Colorado	*	-0.27
M-1	Chalcanthite-stain in ore-bearing sandstone, Monument No. 1 mine, Arizona	*	-0.51
GBL-1	Pitchblende, Great Bear Lake, Northwest Territories	100	0.13
TL-3	Dolomite, Chief mine, Tintic district, Utah	14	-0.27
BM-1	Marine sediment, East Sound, Orcas Island, Washington; depth 30 meters, collected April 16, 1955	~3.5	-8.1
BM-2	Marine sediment, East Sound, Washington; depth 30 meters, collected June 1955	~3.5	0.00
SP-104	Niccolite and gangue minerals, Teheran, Iran	*	-0.27
SP-104a	Pure niccolite separated from SP-104	130	0.17
SP-104b	Gangue minerals from SP-104	20	-1.20
SP-256	Nickel ore (primarily niccolite), Cuzco, Peru	300	0.13

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*Not determined.

Although brochantite is a relatively rich copper mineral, the first two samples shown in table 5, HT-3 and GC-2, occurred as slight green stains on the host material. HT-3 was a brochantite-stained celestite sample from San Miguel County, Colorado, and GC-2 was a brochantite-stained sandstone from near the bottom of Grand Canyon. In both cases the copper appeared as a slight green stain and was apparently brought in by ground-water solutions. Similarly, sample M-1 was a slight chalcanthite stain found in the ore-bearing sandstone of the Monument No. 1 uranium mine, Montrose County, Colo. These copper mineral stains are considered essentially normal as the enrichments obtained are somewhat less than 0.1 percent, the approximate experimental error.

The next two samples, GBL-1 and TL-3, contained very little copper and were also found to have a normal abundance. The pitchblende, GBL-1, contained 100 ppm of copper, and the dolomite, TL-3, contained about 14 ppm of copper. It is interesting to note that specimen TL-3 was situated about a foot from a lead-zinc ore body which contained about 0.03 percent copper. There is evidence that the ore body had heated the host rock (Lovering, 1950) and that the copper in TL-3 may have diffused from that ore body. If this were the case, one might expect to find TL-3 enriched in Cu^{63}. The isotopic abundance does not seem to bear out the above mechanism, although one cannot draw a conclusion on the basis of this single sample.

The marine sediment, BM-1, exhibited the largest enrichment of Cu^{63} observed. It contained a relatively large amount of organic matter and was collected in an area where there was a pronounced anaerobic bacterial activity. The concentration of about 500 micrograms-atoms of copper per kilogram of sediment was presumably precipitated from the sea water by the anaerobic action (Chow and Thompson, 1954). A second sample, BM-2, with much less organic matter, taken later at a point further out in East Sound where the anaerobic bacteria were less abundant, showed a normal abundance compared with the standard. As repeat runs on these specimens were made on different days and in one case on different mass spectrometers, it is felt that the results are real. Chow and Thompson have postulated that the hydrogen sulfide produced under anaerobic conditions reacts with soluble copper in the sea water and precipitates copper sulfide in the bottom muds. In addition there is a further concentration of copper contained in dying organisms that are also concentrated in areas of high anaerobic activity. It is well known that biological systems do fractionate isotopes, and it may be that the observed enrichment is due to the copper contained in the dead organisms.

Sample SP-104 was a fairly pure specimen of niccolite from Iran; it had a small amount of gangue. The equivalent uranium analysis of the pure niccolite fraction was 0.12 percent while the gangue fraction ran 0.41 percent. X-ray studies indicated a small amount of a black mineral tentatively identified as uraninite in the gangue fraction. As can be seen in the table, the gangue fraction was slightly enriched in Cu^{63} compared with the pure niccolite fraction. A second niccolite, SP-256, did not show any significant enrichment of either copper isotope. The mineral and gangue fractions were not separated as in the previous sample.

Copper-silver nugget from Michigan

In the Michigan Copper district, native copper and silver occasionally occur intergrown in a single nugget or "half-breed." The copper and silver phases are very pure, each containing only traces of the other, and it was of interest to measure the Cu^{63}/Cu^{65} ratio of the copper in the silver phase at various distances from the copper-silver contact. If a small amount of copper had migrated across the contact by a diffusion process, one would expect some fractionation. A sketch of the nugget is shown in figure 5. Specimen A was native copper adjacent to the interface and was chosen as a reference. Specimen B, native silver, was also adjacent to the interface. This specimen was freed of all attached native copper. Specimens C and D were also from the silver phase but farther removed from the interface, the distance between B and C being about 0.5 inch. The copper extracted from each specimen was mass spectrographically analyzed at the Mass Assay Laboratory of Union Carbide Nuclear Co., Y-12 Plant at Oak Ridge, Tenn., and the results are given in table 6 along with qualitative spectrochemical analyses. The deviations listed are those from the Oak Ridge value of Cu^{63}/Cu^{65} ratio on reagent grade copper (I) chloride and copper (I) iodide ($Cu^{63}/Cu^{65} = 2.210$). This ratio differs from our standard value on copper (I) iodide and these deviations are considered systematic errors in the two instruments or actual differences in the two standards. Further, these samples may not have been prepared by the same chemical technique as the other samples reported here. Thus, while the results are not directly comparable with the data in this paper, they are of sufficient general interest to be reported.

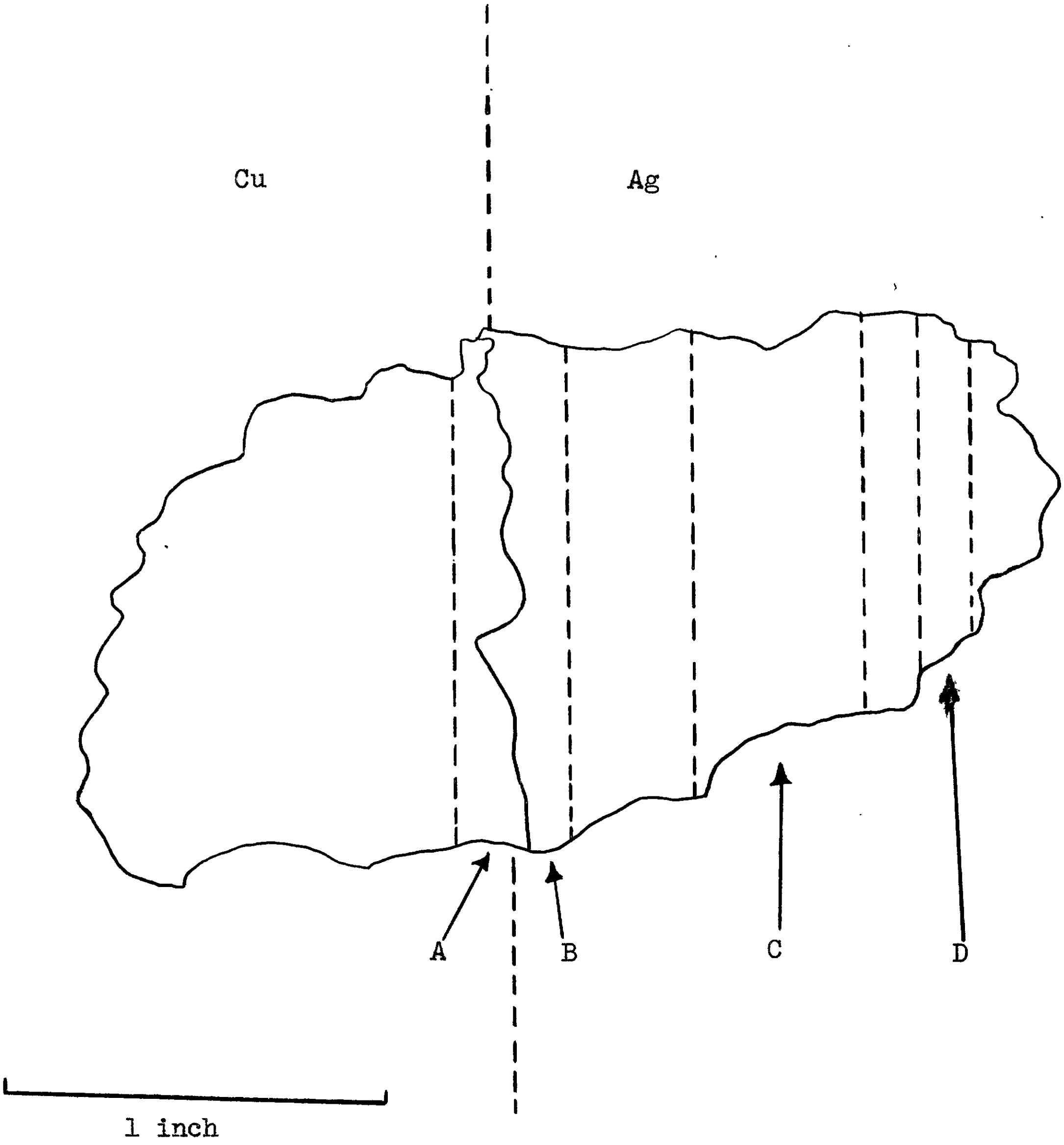

Figure 5.--Section of copper-silver nugget from Michigan.

Table 6.--Isotopic abundance of copper in copper-silver nugget from Michigan.

Sample	Phase	Cu (percent) 1/	Δ Cu^{63}/Cu^{65} (o/oo) 2/
A	Copper	XO.	-1.8
B	Silver	0.0X	-1.8
C	Silver	0.X	-4.9
D	Silver	0.0X	-1.8

1/ Semiquantitative spectrochemical analyses. Katherine V. Hazel, analyst.

2/ Isotopic data from Union Carbide Nuclear Co., Y-12 Plant, Oak Ridge, Tenn. Deviations, o/oo, are referred to the Oak Ridge standard.

As the ratios for specimens A, B, and D are the same, one would suspect that the diffusion of copper into the silver phase produced no significant variation in the Cu^{63}/Cu^{65} ratio. Specimen C showed an enrichment of Cu^{63} and also had a higher concentration of copper than the two specimens in the silver phase on either side of it. This result, however, seems anomalous and cannot be explained.

CONCLUSIONS

Although copper does not undergo severe fractionation in nature, there are slight variations in the abundance of the isotopes that may be significant in unravelling geologic processes. For future investigation of the variations of the isotopic abundance of the mediumto heavy-mass elements, it would seem profitable to study suites of samples from localized areas where there may be some hope of interpreting a specific geologic mechanism, rather than studying widely separated samples.

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BIBLIOGRAPHY

Barnett, P. R., Huleatt, R. P., Rader, L. F., and Myers, A. T., 1955, Spectrographic determination of contamination of rock samples after grinding with alumina ceramic: Am. Jour. Sci., v. 253, p. 121-124.

Baudisch, O., 1938, Uber die verwendung von cupferron in der spektralanalyse: Arch. Kemi Mineral Geol., Band 12B, no. 8, p. 1-6.

Blix, R., v. Ubisch, H., and Wickman, F. E., 1957, A search for variations in the relative abundance of the zinc isotopes in nature: Geochim. et Cosmochim. Acta, v. 11, no. 3, p. 162-164.

Brown, H. A., and Inghram, M. G., 1947, The isotopic composition of meteoritic copper: Phys. Rev., v. 72, p. 347.

Chow, T. J., and Thompson, T. G., 1954, Seasonal variation in the concentration of copper in the surface waters of San Juan Channel, Washington: Jour. of Marine Research, v. 13, no. 3, p. 233-244.

Fernelius, W. C., 1946, Inorganic syntheses, v. II: New York, McGraw-Hill Book Co., Inc., p. 1-4.

Furman, N. H., Mason, W. B., and Pekola, J. S., 1949, Extraction of cupferrates: Anal. Chemistry, v. 21, p. 1325-1330.

Klemm, A., 1943, Isotopenanreicherung durch Diffusion von Kupper in Silbersulfid: Zeitschr. physikal. Chemie, v. 193, p. 29-39.

Lean, Bevan, and Whatmough, W. H., 1898, New method of preparing pure iodine, preparation of cuprous iodide: Chem. Soc. (London) Jour., v. 73, p. 148-157; see p. 149.

Lovering, T. S., 1950, The geochemistry of argillic and related types of rock alterations: Colorado School of Mines Quart., v. 45, no. 1B, p. 231-260.

Myers, A. T., and Barnett, P. R., 1953, Contamination of rock samples during grinding as determined spectrographically: Am. Jour. Sci., v. 251, p. 814-830.

Rankama, K., 1954, Isotope geology: New York, McGraw-Hill Book Co., 535 p.

Senftle, F. E., and Bracken, J. T., 1955, Theoretical effect of diffusion on isotopic abundance ratios in rocks and associated fluids: Geochim. et Cosmochim. Acta, v. 7, nos. 1 & 2, p. 61-76.

Shawe, D. R., 1956, Significance of roll ore bodies in genesis of uranium-vanadium deposits on the Colorado Plateau: Proc. Internat. Conf. on the peaceful uses of atomic energy, Geneva, 1955, v. 6, p. 335-337; U. S. Geol. Survey Prof. Paper 300, p. 239-241.

White, J. R., and Cameron, A. C., 1948, The natural abundance of isotopes of stable elements: Phys. Rev., v. 74, no. 9, p. 991-1000.

White, W. S., and Wright, J. C., 1954, The White Pine copper deposit, Ontonagon County, Michigan: Econ. Geology, v. 49, no. 7, p. 675-716.