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LABORATORY NOTES - 13  
SOME EXPERIMENTS IN THE GEOCHEMISTRY  
OF COPPER AND ZINC

By

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## A METHOD OF DETERMINING EPIGENETIC (AMMONIUM CITRATE SOLUBLE) Cu AND Zn BY AAS

Experimental work has found that the ammonium citrate soluble zinc and copper extracted into dithizone can be read directly by the AAS unit. The zinc levels on 40 samples ranged from 0.6 to 3 ppm and the copper levels ranged from 0.1 to 1.7 ppm. Lead was not detected in any sample. Replicate analyses show good precision. However, these are preliminary results.

The analysis consisted of adding 15 ml ammonium citrate to 0.75 g of sample, letting the sample and solution react overnight, adding 5 ml of dithizone-extract (regular dye solution), shaking for 75 strokes and reading AAS absorbance on the organic portion. The absorbances are compared to those of prepared standard solutions.

The original test was to compare the field results (in ml of dye solution) on these samples to the AA quantitative values for Zn and Cu. There should be a correspondence between AA ammonium citrate soluble Zn and Cu and ml of dye. The comparison however, was very poor. We therefore reran the samples in the lab. on the dried and screened samples by the field test and compared those values (ml of dye) to both the previous field test and the AA analysis. The correspondence between AA and the new field test analysis was better but still not good. I would expect no correspondence between epigenetic and syngenetic values for the obvious reason that different variables are being measured. Table 1 shows these comparisons.

By inspection of Table 1 it is seen that the correlations between lab vs. field colorimetric and colorimetric vs. AA analyses for ammonium citrate soluble metal is not good. In order to get a numerical evaluation of the correspondence the correlation coefficients ( $r$ ) between the various methods were calculated. The coefficient of correlation is a numerical value between 0.0 for no correlation and  $\pm 1.0$  for perfect correlation. The correlation coefficient squared ( $r^2$ ) times 100 results in a percentage value which describes the percentage of the variation that is explained by the correlation between the two variables. Table II lists the correlations examined, the correlation coefficients obtained, and the percentage of explained and unexplained variations.

## SOME EXPERIMENTS IN THE GEOCHEMISTRY OF COPPER AND ZINC

### INTRODUCTION

The technique of geochemical exploration for subsurface ore bodies using stream sediment samples is primarily based on the theory that: 1) ground water samples the subsurface rock units by dissolving heavy metals in some reasonable proportion to their concentration in the rocks, 2) those waters with their dissolved metals eventually reach the surface and contribute to stream flow, 3) ion exchange forces of clay-sized particles in the stream beds extract from the water a portion of the dissolved metal, 4) analytical techniques are available which determine the metal level in the stream sediments, and 5) the consequence is that rather large subsurface rock units are sampled and their heavy metal content is indicated from an analysis of the stream sediment. The presence of hidden ore bodies can then be inferred by interpretation techniques. Obviously, there are a large number of uncontrolled variables such as rock unit permeability, the proportion of the ground water that reaches the surface, stream characteristics such as gradient, water characteristics such as pH and Eh, sediment characteristics such as fineness and mineral content, sampling variation, choice of the analytical method and its precision all of which contribute to smearing the resulting data and making data interpretation less reliable.

In my conversations with the field geologists and engineers I can only conclude that the confidence in the field geochem test is accompanied with many reservations. The present AA analysis for "total" Cu, Pb, and Zn is both accurate and precise for the purpose of geochem interpretations. But a question arises about the usefulness of "total" metal obtained from a hot acid leach of the sample. The reason for questioning the usefulness of total metal relates to geochem theory. Considering the theory of stream sediment sampling, should we be more interested in only that portion of the total metal that is adsorbed metal. If our purpose is to be able to infer the presence of subsurface ore bodies sampled by water then maybe we should be more interested in the epigenetic metal (ionic metal attached to clay particles by ion exchange forces) content rather than total metal content. With the above in mind I have performed a number of experiments which have some bearing on the question of the analytical values and use of 1) total metal (syngenetic) by hot acid digestion, 2) epigenetic metal determined by the ammonium citrate-dithizone xylene field test, 3) epigenetic metal determined by the field test as run in the lab on dried and screened samples, 4) a method of determining epigenetic metal by AA, and 5) epigenetic/syngenetic ratios.

### TOTAL METAL BY HOT ACID EXTRACTION

A method of total heavy metal (Cu, Pb, and Zn) by hot acid dissolution and reading by AA had been developed. The procedure is fast and accurate. Comparisons have been made to the analyses done by the U.S.G.S. on last seasons samples. The comparisons are good and I believe the A. analyses from last season are perfectly acceptable and amenable to the normal "total" metal geochem interpretation methods. We will try to provide similar analyses on this year's samples.

TABLE I  
ANALYTICAL COMPARISONS

SAMPLE NO.	ML DYE FIELD NOTES	ML DYE LAB RUN	EPIGENETIC METAL ANMONIUM CITRATE SOLUBLE READ BY AA		TOTAL METAL HOT ACID SOLUBLE BY AA	
			ZINC PPM	COPPER PPM	ZINC PPM	COPPER PPM
8L 96	-	2	2.4	0.2	44	10
8L 102	2	4	2.4	0.3	30	10
103	2	2	0.9	0.1	78	10
104	2	3	0.6	1.7	60	10
105	2	4	1.7	0.7	38	10
112	2	-	0.9	0.1	86	10
113	3	3	3.6	1.8	84	25
114	8	-	2.1	0.3	78	26
116	13	2	0.7	0.3	66	14
121	8	3	1.3	0.4	110	22
123	5	5	2.3	1.1	76	16
SP 45	3	4	2.2	0.4	120	29
46	3	3	2.5	0.4	120	34
47	2	4	1.6	1.1	86	23
48	2	4	1.4	0.6	110	22
50	1	4	0.8	0.6	66	11
51	12	3	—	0.1	80	39
52	18	3	2.8	0.7	140	30
53	2	5	2.6	0.3	92	17
54	1	4	1.2	0.2	88	20
55	2	3	1.8	0.3	110	20
56	3	4	1.2	0.6	130	35
57	1	2	2.3	0.2	150	25
60A	1	2	1.1	0.6	94	16
61	2	2	0.9	1.3	94	22
62	4	4	2.7	0.9	68	20
429	2	2	1.1	0.8	80	37
BH 66	1	5	3.1	0.4	80	21
95	2	3	1.6	0.2	70	36
102	4	4	1.8	0.3	100	42
104	2	2	1.4	0.4	70	45
105	2	4	3.0	0.7	100	27
106	8	2	0.7	0.6	80	26
112	1	3	1.0	1.1	50	5

**TABLE II**  
**CORRELATION COEFFICIENT DATA**

VARIABLES	CORRELATION COEFFICIENT	EXPLAINED VARIATION $r^2 \times 100$	UNEXPLAINED VARIATION $100 - r^2 \times 100$
ml dye, field vs. ml dye, lab.	-0.10	1%	99%
ml dye, field vs. ppm Zn + Cu by AAS	0.001	0.1%	99.9%
ml dye, lab vs. ppm Zn + Cu by AAS	0.44	19%	81%
ml dye, lab vs. ppm Zn by AAS	0.44	19%	81%
ml dye, lab vs. ppm Cu by AAS	0.35	12%	88%

The correlations are shockingly poor. There is essentially zero correlation between the field test (run in the field) and the AA analysis for ammonium citrate soluble metal. Of course, the samples had been dried and screened between the time they were run in the field and when the AA analysis was made. To eliminate that variable, the correlation was found between the AA values and new colorimetric analyses on the dried - screened samples. There was a significantly better correlation (19% explained) but still not good. At this point I have no hint about the nature of the poor correlation. Replicate analyses by both the AA and the colorimetric show fairly good reproducibility, at least much better than the correlation coefficient for "between samples".

Some other observations about the ammonium citrate - colorimetric AAS analysis were made. After extracting the metal and lining up the containers according to intensity of color there was a fairly good "eyeball" match between intensity of the color and the total metal determined by AAS. However, when the extract had stood overnight most of the dye solutions had bleached out and were colorless. Some solutions had retained their color. Repeat AA analyses showed the solutions that had retained their color had retained their metals. The metal had returned to the aqueous phase of the bleached solutions. However, the retained color was mostly due to copper, not zinc. The zinc relatively quickly (several hours) returned to the aqueous phase; the copper returned more slowly. Color from zinc alone yields a red - purple color; color from copper alone yields an orange - brown dye solution.

Obviously a good deal more needs to be known about the field test.

## SOME EXPERIMENTS IN USING THE DATA

Twenty-three of the samples were collected by R. Asher in the area about the Big Hurrah Mine on the Seward Peninsula during last field season. The results were plotted on maps using total metal, epigenetic metal, syngenetic metal, and epigenetic/syngenetic ratios. Those values were compared to known geological features of the area. Some statistical features of the geochemical data are: 1) There was no sample with an epigenetic metal value higher than 3σ above the mean. 2) There was one sample with more than 2σ above the mean in Cu, and two samples with more than 2σ above the mean in Zn values. These did not occur in the same sample. 3) There were no samples as high as 2σ above the mean in Zn and Cu from the syngenetic values. Plots of syngenetic zinc and copper are shown in Figs. 1 and 2. The area consists of the Big Hurrah Creek with several tributaries. The grain of the tributary drainage is roughly north-south joining the east-west trending Big Hurrah Creek. The orange line is the approximate zone of contact between black slate on the west and schist on the east. The Big Hurrah Mine occurs near the junction of Big Hurrah Creek and Little Hurrah Creek. According to Mr. Asher minor mineralization was observed on the north side of Big Hurrah Creek just west of the Big Hurrah Mine. There were many prospect pits on quartz veins in the slate north of the Big Hurrah Mine.

Figure 1 shows contour lines on the syngenetic zinc values. Figure 2 shows contour lines on the copper values. Similar trends are noted for the zinc and copper values. Highs occur near, and parallel to, Big Hurrah Creek, with a broad low between.

Figures 3 and 4 show similar maps of the epigenetic zinc and copper as determined by AAS. A striking difference between the contours of the epigenetic versus syngenetic is apparent. The epigenetic metal values contour with trends at right angles to the syngenetic contours. Figure 5 shows the epigenetic values contoured on Zn plus Cu. In this case a closure forms which centers just west of Hutt Creek approximately parallel to the schist-slate contact.

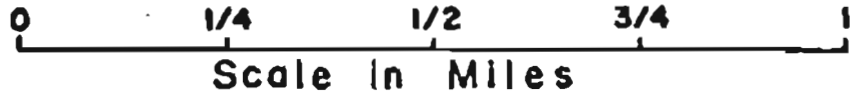
The ratios of epigenetic/syngenetic values were formed for Zn plus Cu as determined by AA. This manipulation in effect superimposes the epigenetic Zn plus Cu on a zero syngenetic base and therefore emphasizes the metal content that has come from ground waters. The ratio value is multiplied by 100 and so the value plotted is the percentage of total metal that is epigenetic. Figure 6 shows this plot which indicates the highest epigenetic Zn plus Cu is roughly along the slate-schist contact with a closure.

Whether this latter figure is the best picture of the geochemical profile is, of course, conjectural.

## SUMMARY

These experiments have shown that there is reason for having doubts about the significance of the field test, or at least confidence in the method was not established. The experiments have also shown that different interpretations of the geochemical profile can be made depending on the "type" of metal determined analytically. Possibly a simple analysis of total, or syngenetic, metal is not the most important value for establishing the geochemical profile. A good deal of work in areas of known significant mineralization needs to be done in order to establish the most useful geochemical parameters. Effort needs to be expended on establishing a reliable field method, in terms of both the type and quality of the analysis, as well as interpretation procedures.

Approximate Zone  
of Contact



Zinc

Ore Vein at  
Big Hurrah Mine

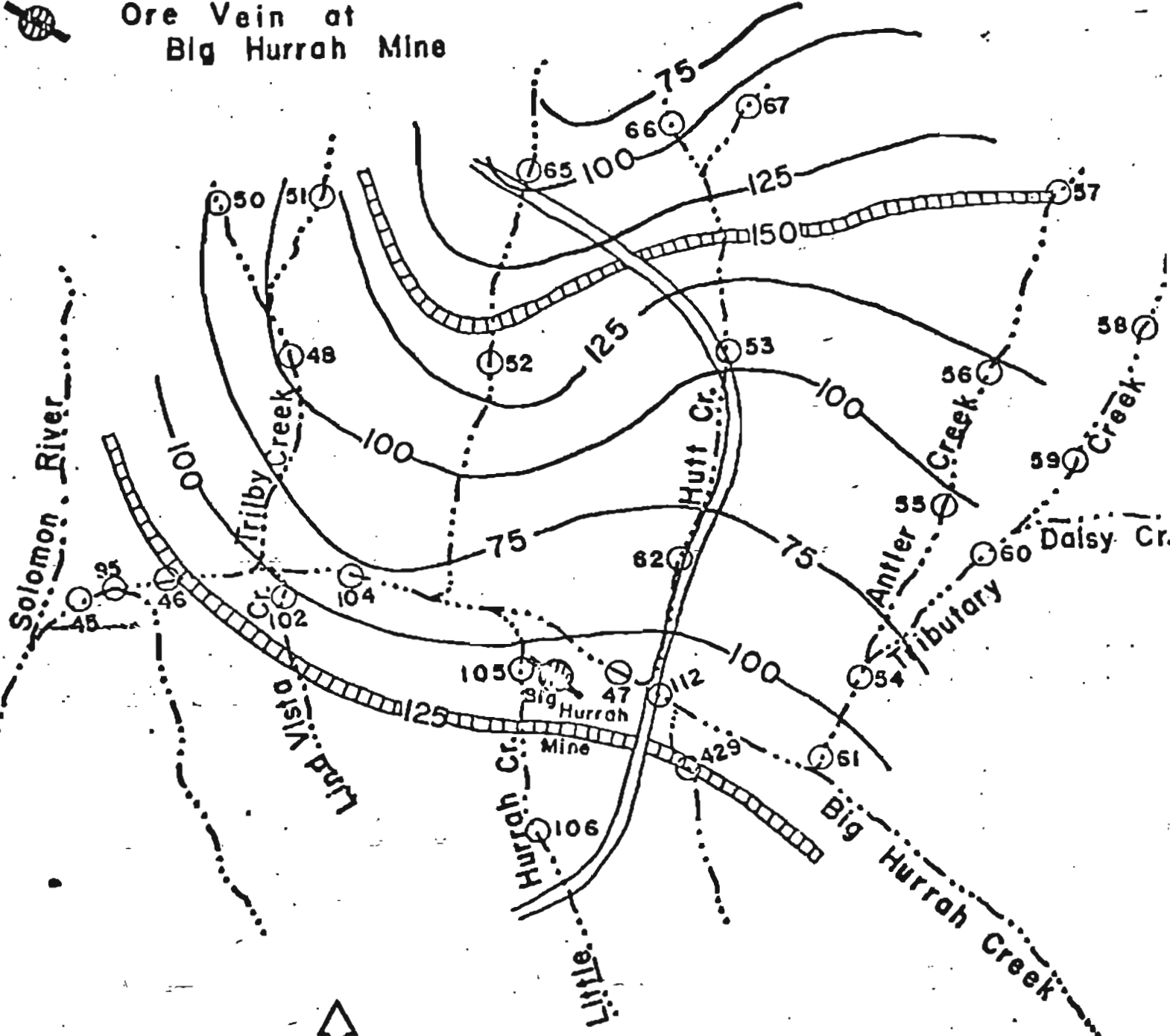
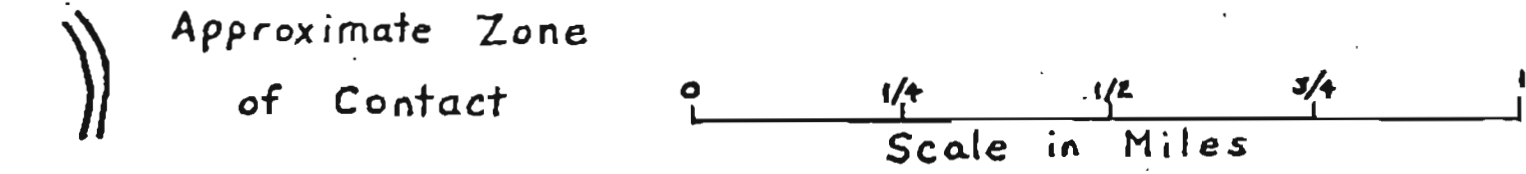


Figure 1 Zn Syngenetic (total)



Copper

Ore Vein at Big Hurrah Mine

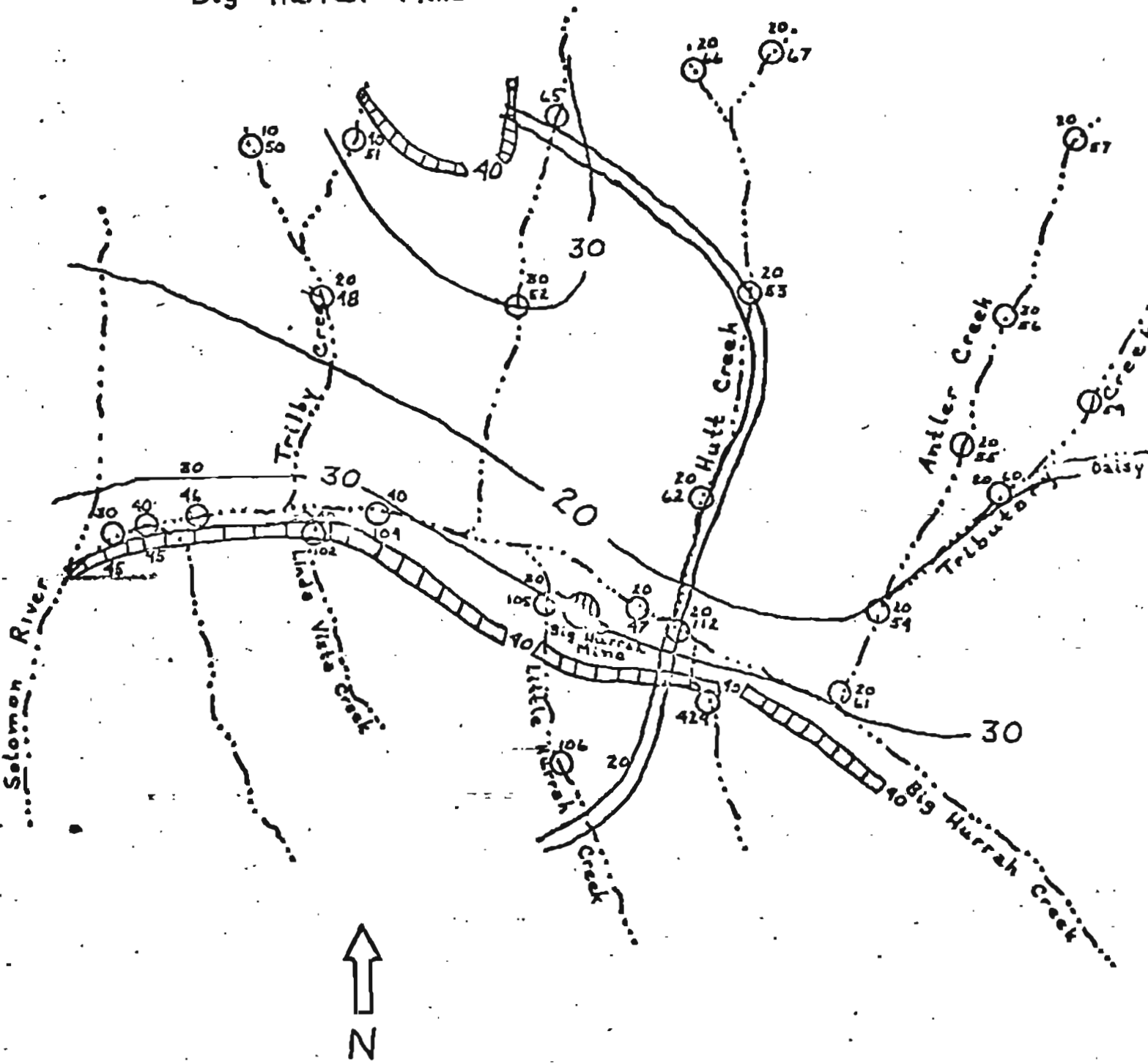
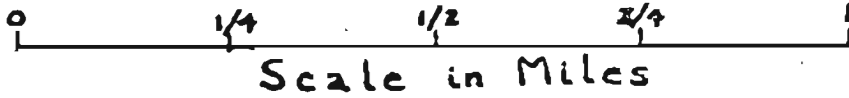


Figure 2 Cu Syngenetic (total)



Approximate Zone of Contact



Zinc

Ore Vein at Big Hurrah Mine

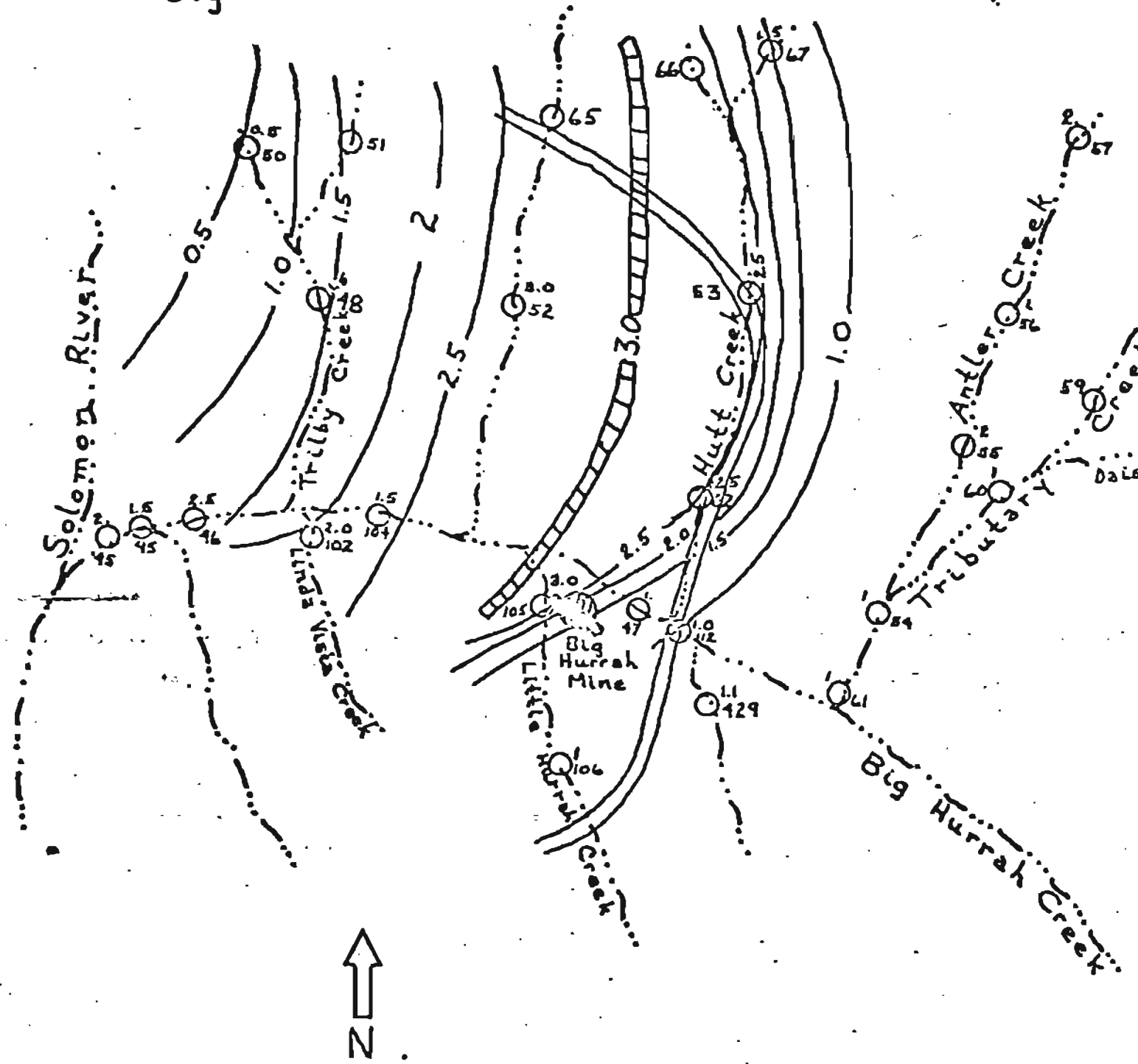
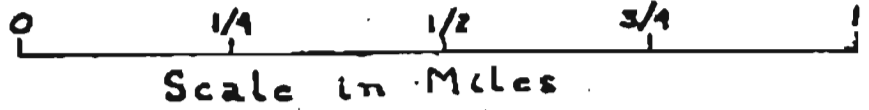


Figure 3 Epigenetic Zn by AAS

Approximate Zone of Contact



Copper

Ore Vein at Big Hurrah Mine

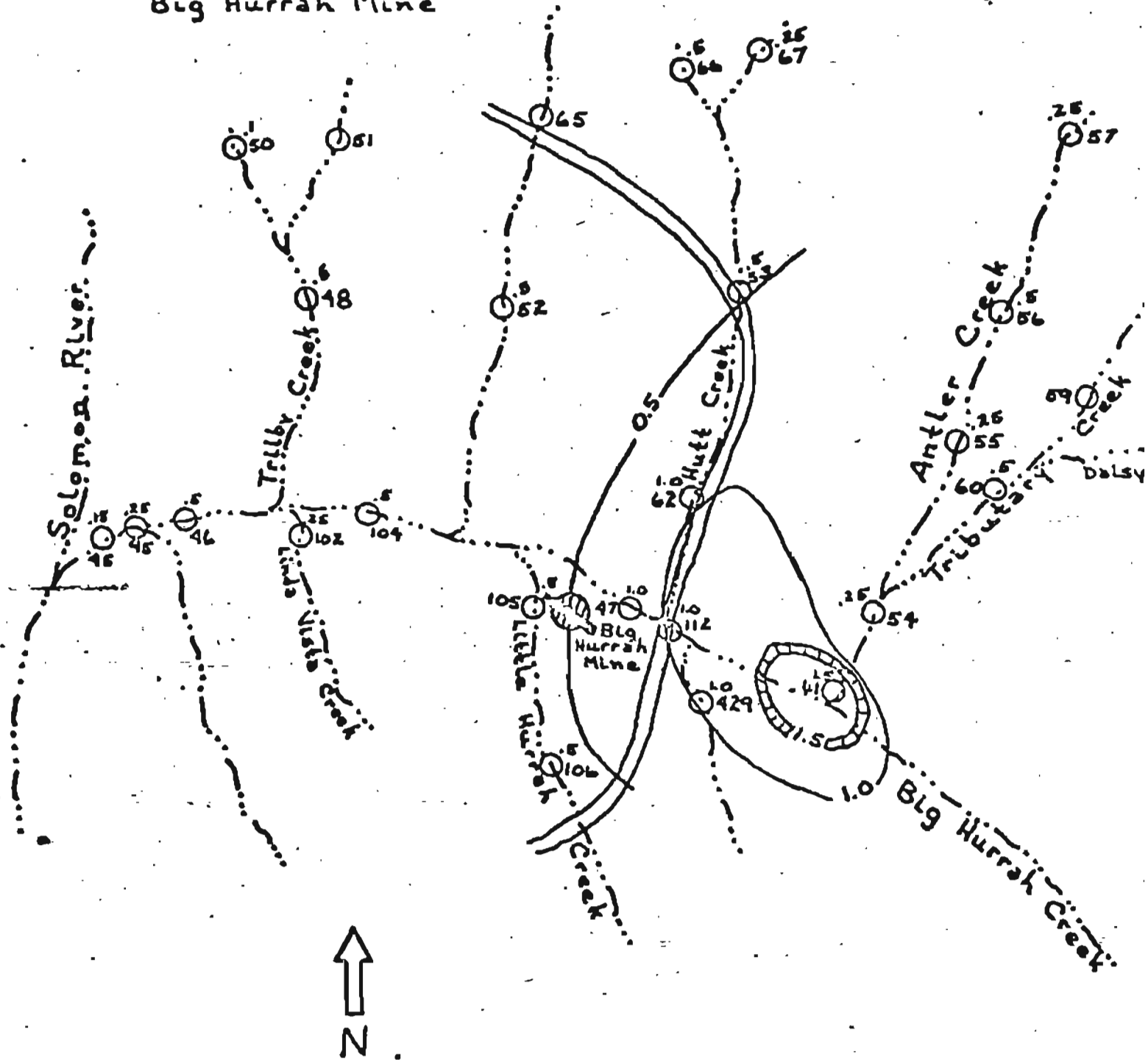
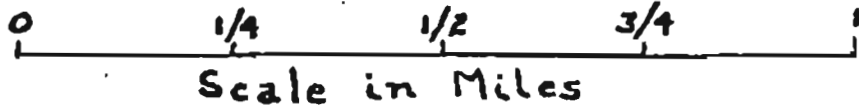


Figure 4 Epigenetic Cu by AAS

Approximate Zone of Contact



Zinc and Copper

Ore Vein at Big Hurrah Mine

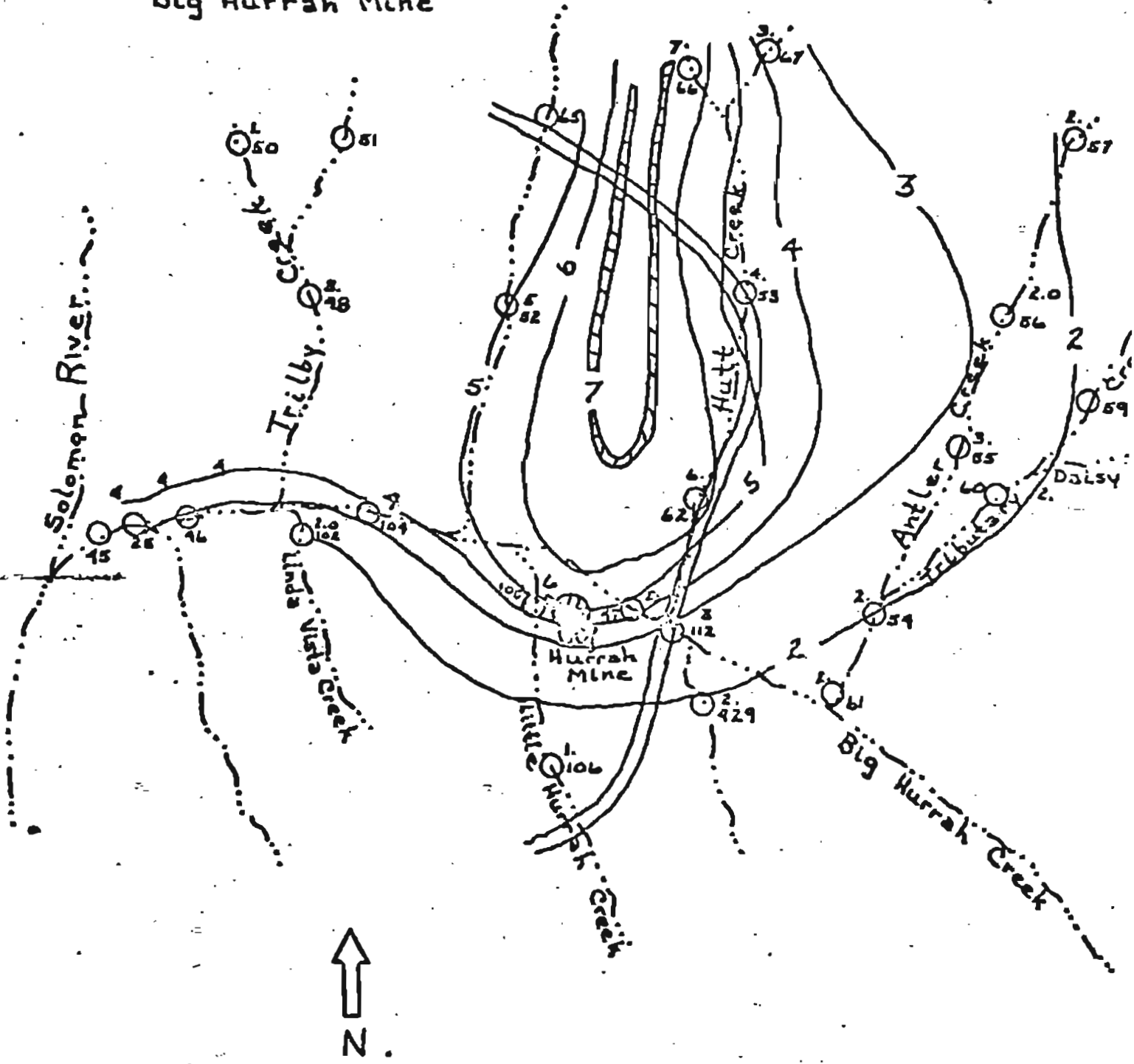
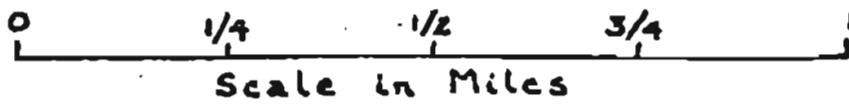


Figure 5 Epigenetic Zn & Cu by Al

Approximate Zone of Contact



Zinc and Copper

Ore Vein at Big Hurrah Mine

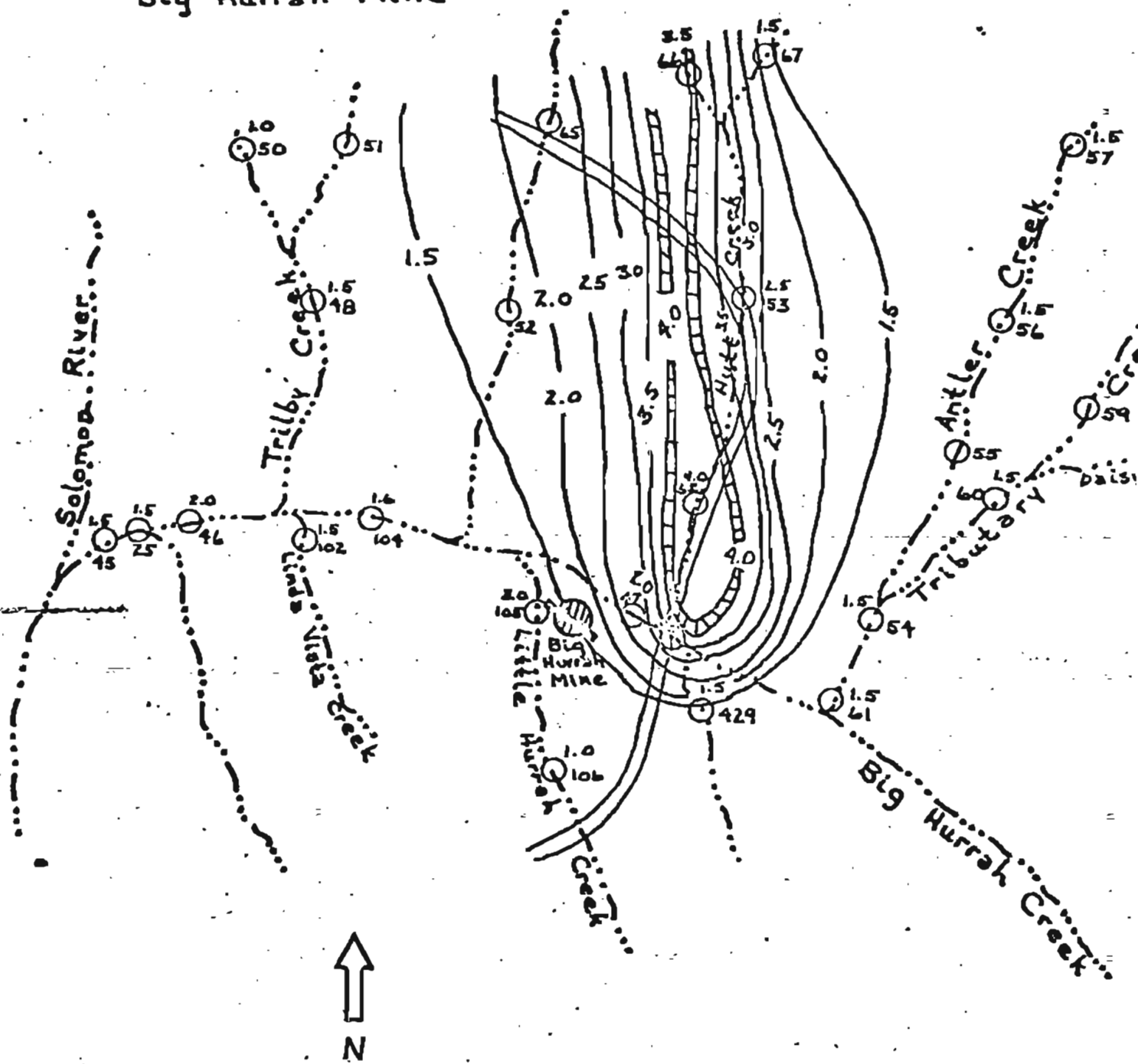


Figure 6

$$\frac{\text{Zn + Cu by AAS, Ammonium Citrate}}{\text{Zn + Cu by AAS, Hot Acid}} = \frac{\text{Epi}}{\text{Syn}}$$