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Toni: File under Missouri Copper Proposal

May 25, 1971

Mr. Donald M. Mann
Apt. 4 A
909 Logan Street
Denver, Colorado 80203

Dear Don,

On a recent trip I finally had time to read your proposal on Missouri Copper in depth. I am impressed with your ideas and the proposal you have prepared. As you may know, I developed the exploration program for ASARCO in the West Fork area, did the geology, optioned the property and drilled the discovery holes that led to the West Fork ASARCO orebody. Your copper proposal was therefore of special interest to me.

Unfortunately, Essex is now committed to several projects that do not give us room for your proposal at this time. In addition, the pressure of Essex's copper demand of almost one million pounds of copper per day makes me consider at this time projects that would lead to more immediate copper production than your proposal suggests.

Thank you for sending the proposal for review. I hope you will continue to consider Essex as a potential joint partner for projects you want to develop. At your request I am returning your proposal but keeping your resume.

Best regards,

Paul I. Eimon
Manager of Exploration

ESSEX INTERNATIONAL, INC.

PIE:td
enclosure

MISSOURI COPPER

BY

DONALD M. MANN

March 1971

TABLE OF CONTENTS

	Page
Summary and Recommendations	1
Introduction	2
Geology	2
Discussion	4
Land	5
Drilling	6
Conclusions and Recommendations	6
Bibliography	7

LIST OF ILLUSTRATIONS

Figure 1 Location Map
Figure 2 Generalized Geologic Map of Missouri
Figure 3 Cambrian System
Figure 4 Major Mineralized Districts In the Ozark Region
Figure 5 Major Geologic Features and Lead Districts of Southeast Missouri
Figure 6 Copper Occurences on Missouri
Figure 7 Generalized Geologic Section, Madison Mine
Figure 8 Distribution of Precambrain Prophyry Outcrops In Shannon County Missouri
Figure 9 Map of Underground Workings, Cornwall Copper Mine
Figure 10 Approximate Solubilities of Some Base-Metal Sulfides
Figure 11 Distribution of Mississippi Valley-Type Deposits

Plate 1 Map of the Fredericktown Area, Missouri (in pocket)

Appendix A Alley Spring, Eminence Powder Mill Ferry, Bartlett, Winnona, Stegall Mountain Quadrangles (in pocket)
Appendix B Fredericktown, Higdon, Perryville quandrangles (in pocket)
Appendix C Federal Prospecting Permit and Lease (in pocket)
Appendix D State Prospecting Permit and Lease (in pocket)

SUMMARY AND RECOMMENDATIONS

SUMMARY

Copper deposits occur in at least five localities in southeast Missouri (Figure 6). The possibility of discovering copper or copper-nickle-cobalt deposits such as those at Mine LaMotte and the Madison Mine at Fredericktown is good. The problem will be to find a deposit large enough and rich enough to satisfy a major mining group. Based solely on past production, exploration priorities should be: Fredericktown - Emenence - Ste. Genevieve.

RECOMMENDATIONS

I should spend one or two more months searching the literature and compiling. Specifically, the Leadwood-Flat River-Bonne Terre and Annapolis areas (Figure 5) should be studied. The Bunker Hill Company should be contacted as regards the status of the Higdon Mine. A review of the recent literature of the geochemistry of lead, zinc, and copper would be helpful.

INTRODUCTION

LOCATION

The project area lies in southeast Missouri (Figure 1) being bounded by the towns of Sullivan, Bonne Terre, Fredericktown, and Winona. Access from St. Louis by rail and highway is excellent. The Missouri Geological Survey along with a branch of the University of Missouri is located at Rolla. Field work can be done all year.

GEOLOGY

GENERAL

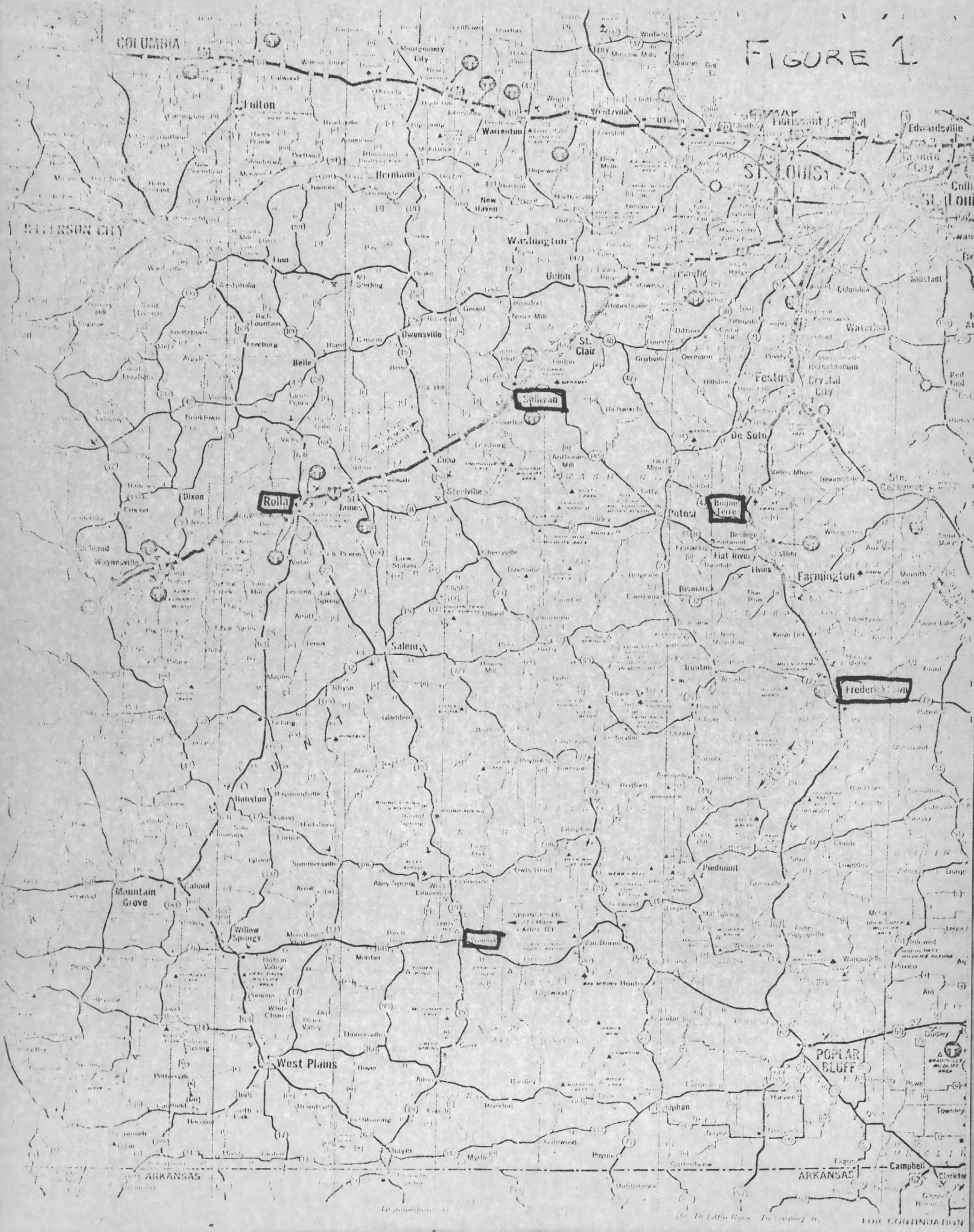
Precambrian rhyolites, granites, and basic rocks outcrop in the St. Francis Mountains. These older rocks are overlain by sediments, the most important economically being the Upper Cambrian Lamotte sandstone and Bonneterre dolomite (Figures 2 and 3, from Howe and Koenig, 1961, p. 13, 17). Paleozoic cryptoexplosion structures and igneous rocks occur in Missouri, but their relationship to the mineral deposits is, at best, obscure.

The major structural element of this area is the Ozark Dome, with Precambrian rocks exposed along its axis (Figure 4, from Brown, ed, 1967, p. 35). These older rocks were eroded into numerous knobs and basins prior to the deposition of the Lamotte sandstone. Local relief is as much as 1500 feet. Faults ring the area of exposed Precambrain rocks; the major trend is northwest (Figure 5, from Ridge, 1968, p. 329).

Southeast Missouri is a lead district. Most of the production has come from pinchout, reef, and bar reef ore bodies in the Bonneterre dolomite. Production through 1968 was (Wharton, et al, 1969, p. 63):

METAL	RECOVERABLE SHORT TONS	VALUE
Lead	10,179,997	$ 1,615,070,607
Zinc	125,954	24,994,057
Copper	73,263	38,022,073
Silver (Troy Oz.)	9.325,177	8,350,104
Cobalt, Nickel, Cadmium	N.A.	N.A.
		$ 1,686,436,841

FIGURE 1


COLUMBIA
Fulton
Montgomery City
Warrenton
Wentzville
Hermann
New Haven
Washington
Union
St. Clair
Owensville
Belle
Freeburg
Rich Fountain
Westphalia
Linn
St. Aubert
Brinkton
Vienna
Dixon
Crocker
Waynesville
Rolla
St. James
Cuba
Steelville
Sullivan
Potosi
Bonne Terre
Flat River
Bismarck
Farmington
De Soto
Festus
Crystal City
Ste. Genevieve
Salem
Ironton
Fredericktown
Houston
Summersville
Mountain Grove
Cabool
Willow Springs
West Plains
Piedmont
POPLAR BLUFF
Dudley
Campbell
Clarkton
ARKANSAS
ST. LOUIS
Edwardsville
Waterloo
Columbia
Pacific
Grubville
Oermann
Hillsboro
Leadwood
Bonne Terre
Bismarck
Fredericktown
Van Buren
Eglantine
Doniphan
Mountain View
Thomasville
Alton
Shayer
Myrtle
Peyton
Carondelet
Fagus
Hornersville
Malden
Gideon
Holcomb
Qulin
Gatewood
Bardley
Birdton
Lochwood
Lesterville
Ellington
Ironton
Arcadia
Leadwood
Bismarck
Flat River
Elvins
Farmington
Piedmont
Poplar Bluff
Dudley
Campbell
Clarkton
Gideon
Holcomb
Qulin
Malden
Hornersville
Fagus
Carondelet
Peyton
Myrtle
Shayer
Alton
Thomasville
Mountain View
Doniphan
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Van Buren
Leadwood
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Birdton

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posits occur near the
depths of from 1,400
. Ridge mine locality
n replaced by copper-,
of the eposits is of
-bearing veins occur
dison County there are
Neither of these is of

upper Cambrian sedi-
ite was very rugged,
eal relief of as much
places. This rugged
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ore than 6,000 feet of
and the surface of the
n corner of Missouri
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had been formerly es-
surface. Many small
n outcrop area. The
outh-central Camden
their present position,
high altitude in this

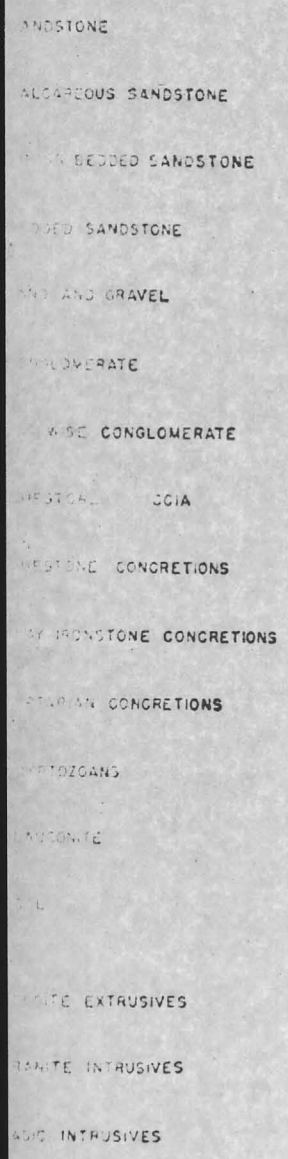
PALEOZOIC ERA

Bedrock through most of Missouri is Paleozoic in age. Of all the Systems represented, the Cambrian, Ordovician, Mississippian, and Pennsylvanian are the most prominent from the standpoint of total thickness and areal distribution (Fig. 2). Rocks of the Cambrian and Ordovician Systems are present over most of the southern half of the state. Mississippian rocks are extensively exposed in the northeastern and southwestern parts of the state, and Pennsylvanian rocks make up the balance of the state's bedrock. Relatively limited exposures of Silurian and Devonian rocks are present in eastern Missouri.

Fig. 2. Generalized geologic map of Missouri.

The aggregate thickness of the Paleozoic rocks within the state is approximately 10,000 feet with less than half of this thickness being present in any one locality. The thickest and most systemically complete section of rocks in the state is present within the confines of the Forest City basin in northwestern Missouri. Here the section is approximately 3,700 feet thick and is composed of rocks representing all

Figure 3



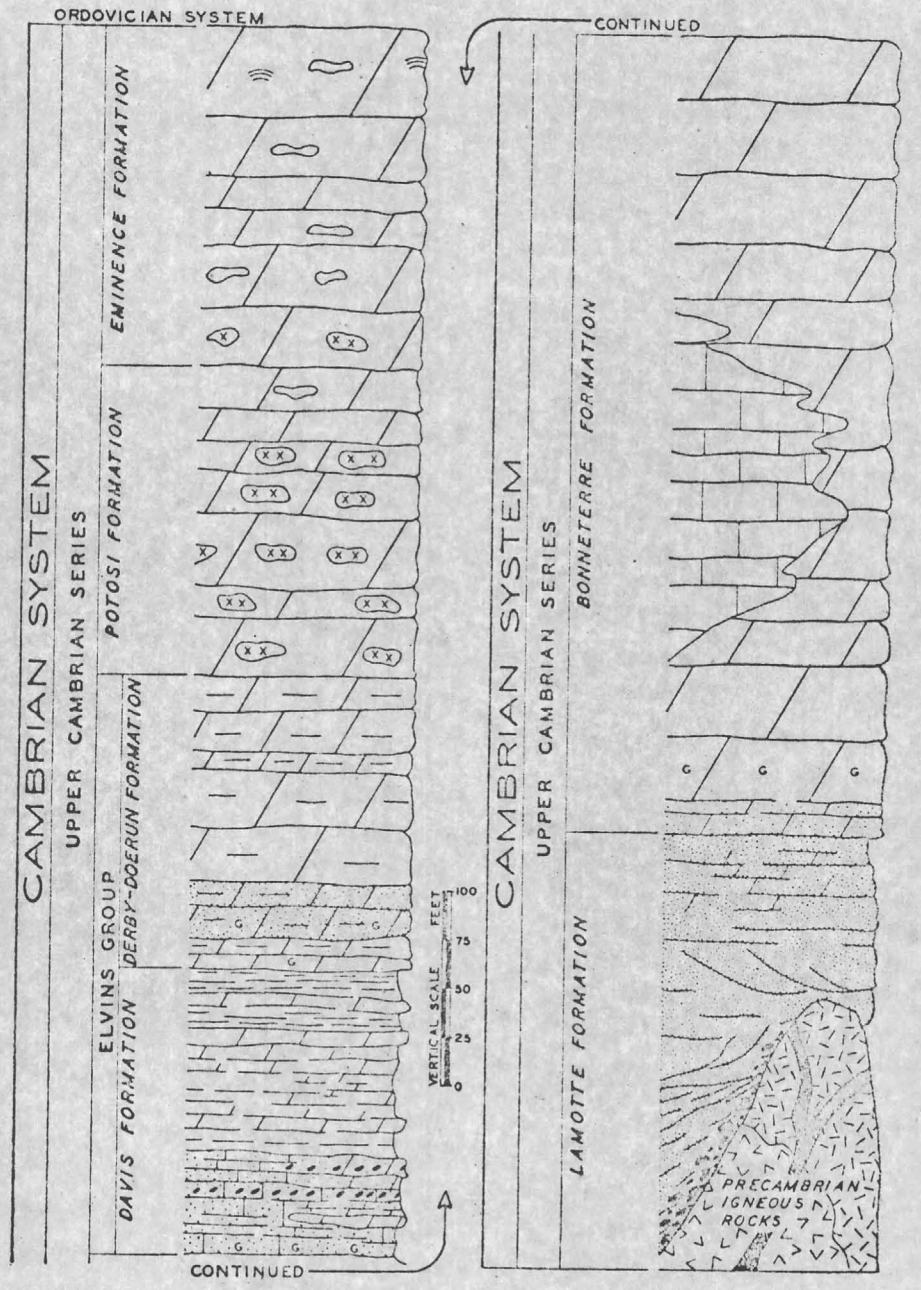


Fig. 3. Cambrian System; Upper Cambrian Series.

Figure 4

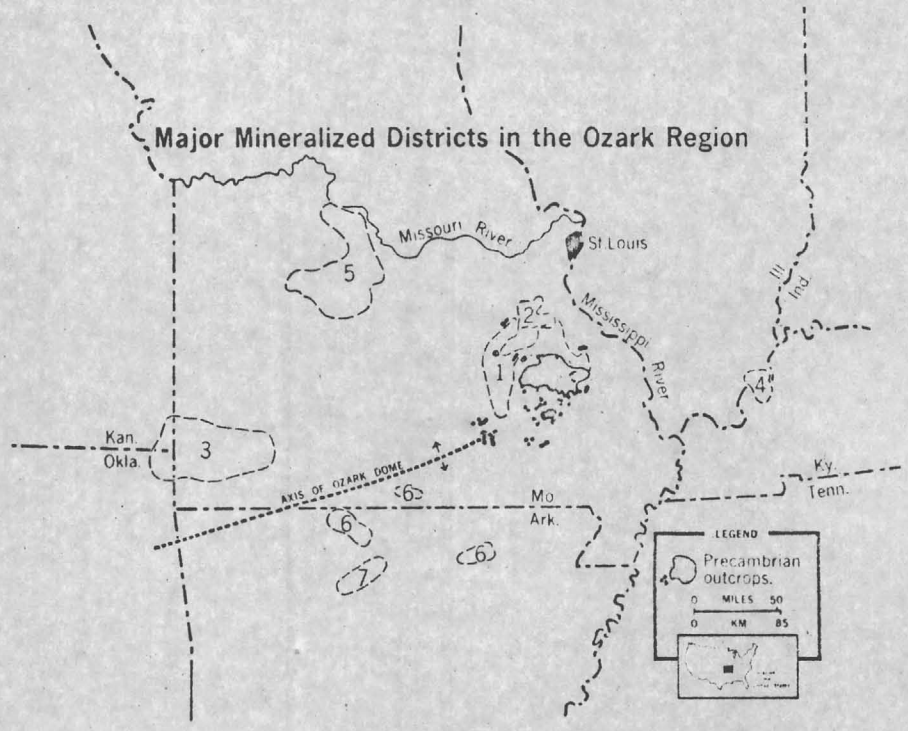


FIG. 1. Distribution of major ore types in the Ozark Region of Central United States. Indicated areas are: 1, Southeast Missouri lead district; 2, Southeast Missouri barite district; 3, Tri-State zinc-lead district; 4, Illinois-Kentucky fluorspar district; 5, Central Missouri barite district; 6, Arkansas-Missouri zinc district (Ordovician); 7, Arkansas zinc-lead district (Mississippian).

Either the proposed hydrothermal source must have been large or there was an almost inconceivable plumbing system to effect the distribution of ore fluid over tens, even hundreds of square miles. The former seems the more likely alternative of the two—that there was a large, and possibly deep-seated, igneous mass which gave off the mineralizing emanations over a broad area. These emanations then rose into the overlying sedimentary column and deposited their load.

The great size of the mineralized areas over which uniform ore types were deposited represents one of the most difficult problems for explanation by the hydrothermal method.

CROSS-CUTTING RELATIONSHIPS

Cross-cutting mineralized structures are found in virtually every district of the Mississippi Valley type. These range from simple veins (Southern Illinois-Kentucky, Central Kentucky-Tennessee, Wisconsin-Illinois, Northern

Figure 5

t 12,000 tons of ore
pper are recovered.
mines, mills, mines
ve mines are shown

Production

Francois County
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36,301 tons
its leadership
first time since
production for
pany and years

ORY AND
RAPHY

the northeastern
neous core of the
is some-

duced by Fifteen Mining
–1865 through 1965[1]

Period of Operation (Incl.)	Total Tons of Pig Lead Produced
1865–1965	5,889,529
1877–1886	28,916
1887–1914	337,601
1893–1894	329
1893–1928	400,812
1894–1904	51,404
1894	499
1897–1933	716,278
1900	22
1900–1904	11,713
1902	336
1902	498
1902–1923	721,303
1913–1918	36,921
1924	2,000
	8,198,161

n Mine L , Indian
outlying are ... Produc-
mpany records.

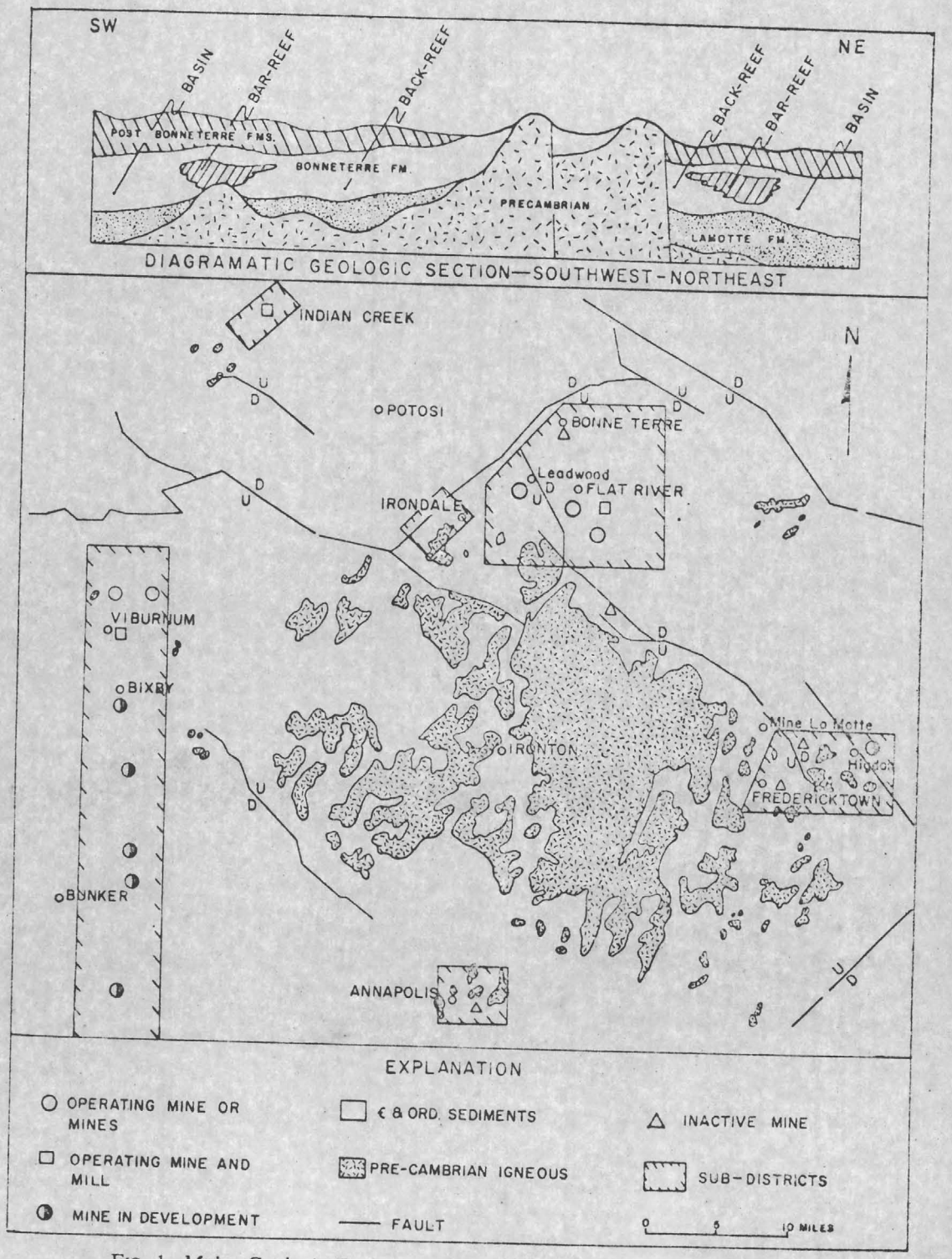


FIG. 1. *Major Geologic Features and Lead Districts of Southeast Missouri.*

Source of the metals is thought to be brines from deep sedimentary basins: the Forest City to the Northwest and the Illinois to the Northeast (Synder and Gerdeman, 1968, in Ridge, 1968, p. 357) If, as Helgeson (in Brown, ed, 1967, p. 339) suggests, the lead and copper are derived in a 10:1 ratio from the metamorphism of arkosic sediments, in excess of 900 thousand tons of copper remain unaccounted for.

COPPER DEPOSITS

Copper is an important metal in five areas (Figure 6, from Wharton, et al, 1969, p. 46):

1. FREDERICKTOWN

Chalcopyrite-siegenite-galena ores were developed in the Mine La Motte Copper Mine and the Missouri Cobalt Mine (now National Lead's Madison Mine) Plate 1 (from James, 1949, Plate II). The ore occurred at Precambrian-Lamotte-Bonneterre contacts and on local highs and lows in the Lamotte sandstone in inter-knob basins (Figure 7, from Kline, et al, 1961. p. 5).

Mine La Motte Copper Mine was discovered in the 1830's and shipped a matte containing Cu, Ni, and Co in 1840-48, 1857-64, and 1870-1904. I have no production figures. Copper-nickle-cobalt ore was apparently spatially separate from lead ore as St. Joe Minerals removed a lead ore body from this mine several years ago.

The Madison Mine, in 1906, had blocked out an ore body 600' x 500' x 12' (288,000 tons) which ran 6.91% Pb, 3.5% Ni, 4.0% Cu and 2% Co. (Grawe, 1945, p. 357). The ore zone occurred at 250 feet. This material was difficult and expensive to treat, and the company failed. The mine was re-opened in World War II; in 1943, developed reserves were 1.77 million tons averaging 2.29% Pb., 1.43% Cu, 0.46% Ni, and 0.28% Co. The Madison is estimated to have produced 25,00 tons of copper.

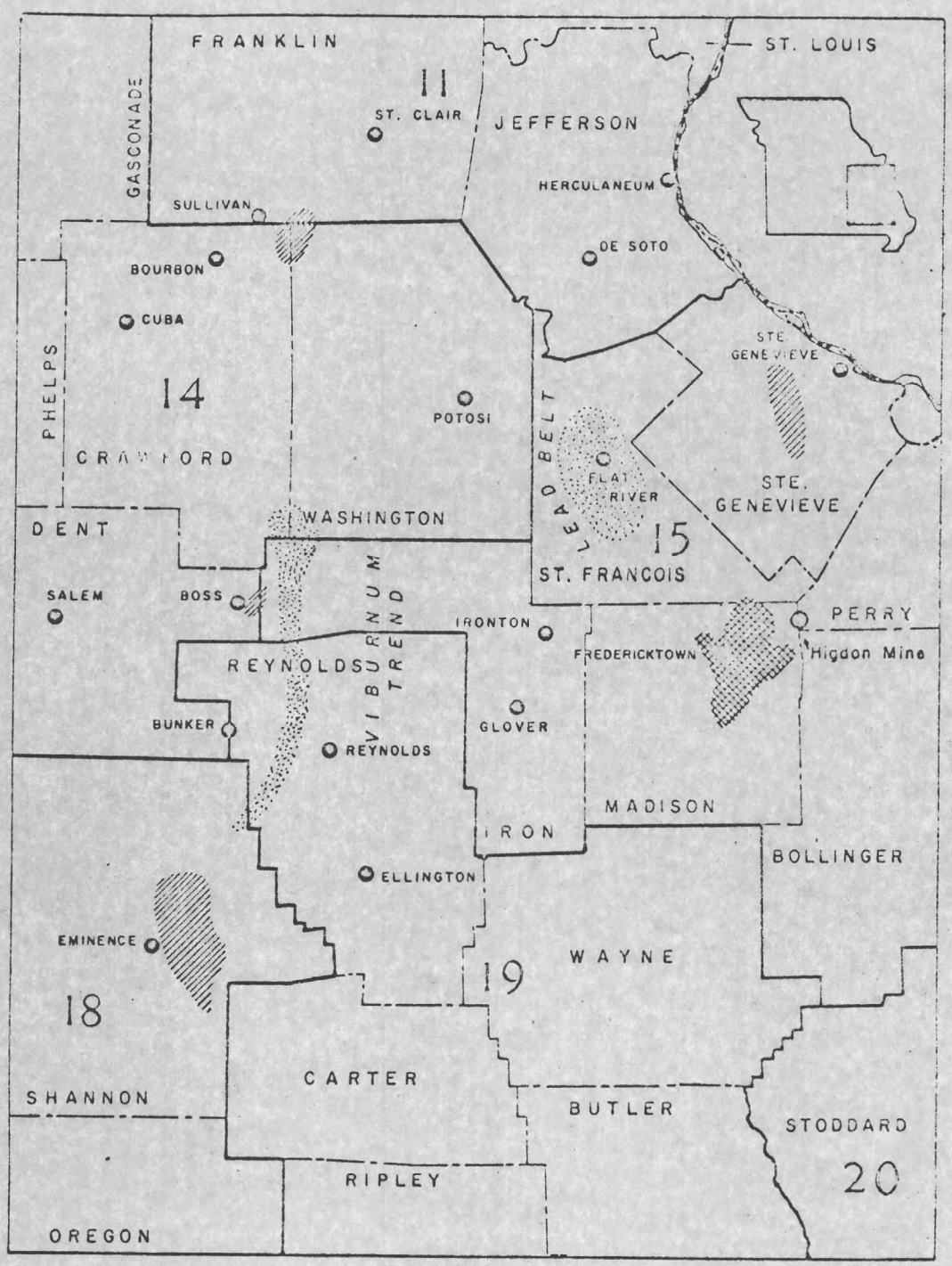
2. EMINENCE

Evans (1959) describes seven copper prospects related to Precambrian knobs (Figure 8). Copper also occurs in a road cut just south of the Casey, and in the vicinity of the knob just to the east of the Casey. The Jerktail, McKinney, Slater, Sutton, and Bolin prospects occur in a basal conglomerate on structural highs at the heads of buried Precambrian valleys (Evans, 1959, p. 57). The Casey and the Jacks Fork are higher in the sedimentary section;

Figure 6

FIGURE 5-1

COPPER OCCURRENCES IN MISSOURI



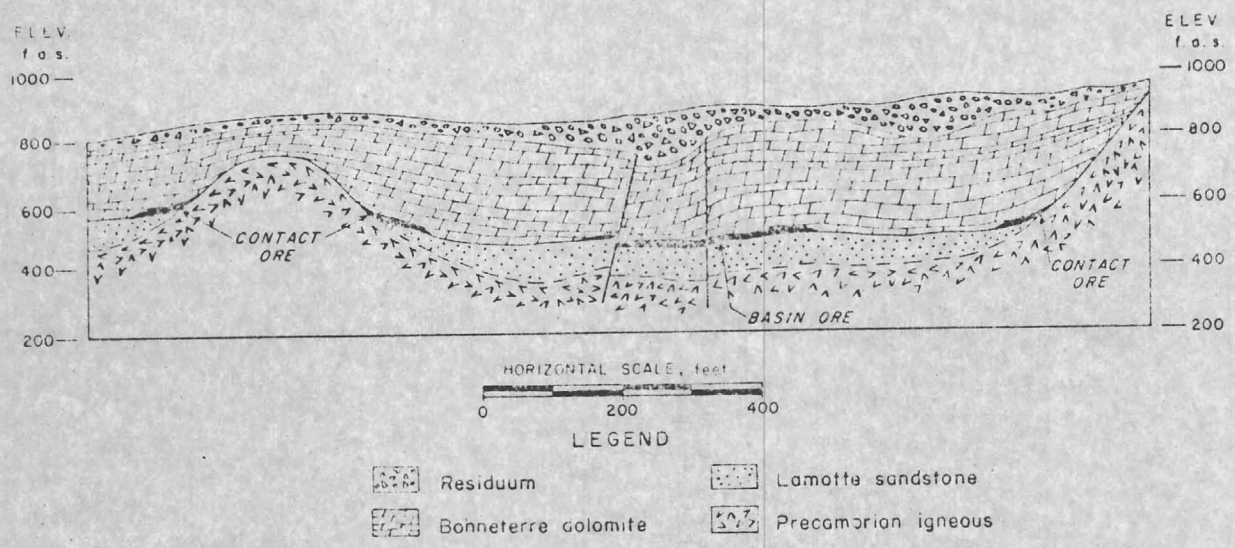


FIGURE 2. - Generalized Geologic Section, Madison Mine.

The LaMotte sandstone is extremely variable in thickness, varying from a trace where it pinches out against the igneous rocks to 250 feet in the deeper basins. In the vicinity of the mines, the Bonne Terre dolomite ranges from a trace to about 400 feet thick.

Ore deposits in the Fredericktown district occur characteristically in the lower 20 to 25 feet of the Bonne Terre dolomite. Average depth from the surface to this zone is 300 to 400 feet. The metallic minerals in the ore are chiefly galena and pyrite with minor quantities of chalcopyrite and siegenite (sulfide of nickel and cobalt) and occur in a disseminated manner throughout the ore zone. Heavy concentrations of pyrite and marcasite are found throughout the Bonne Terre formation but the bodies of iron sulfides lying above the ore zone have little or no apparent association with the ore deposits.

The ore bodies are classified into two types for purposes of prospecting and development. One type, called contact ore, occurs near the pinch-out of the LaMotte sandstone against the sides of Precambrian hills of igneous rock. The other type, called basin ore, occurs in areas of unusual structural highs and lows of the otherwise generally horizontal bedding of the LaMotte. The erratic relief of the LaMotte may have been caused by deposition of the sand on the irregular Precambrian surface, the formation of sand bars at the time of deposition, tectonic disturbances, or a combination of these.

The Bonne Terre host rock near the sandstone pinch-out line was favorably prepared for ore deposition by a series of fractures, including joints and minor faults, which parallel and often coincide with the pinch-out line. The host rock in areas of LaMotte highs and lows was structurally prepared in much the same manner. At least one fault within the district is believed to have displaced the igneous rock.

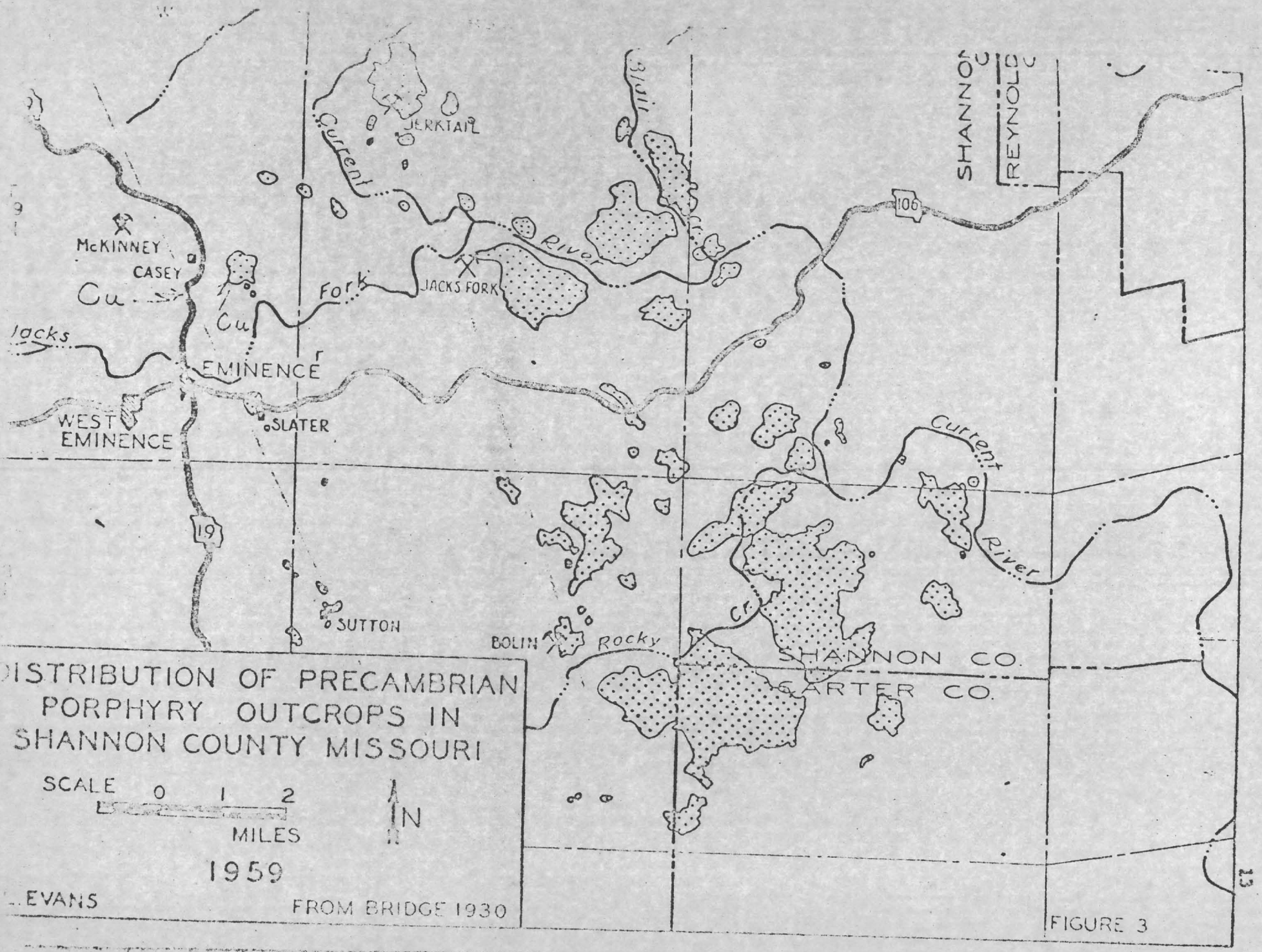

DISTRIBUTION OF PRECAMBRIAN
PORPHYRY OUTCROPS IN
SHANNON COUNTY MISSOURI
SCALE 0 1 2
MILES
N
1959
L. EVANS
FROM BRIDGE 1930
McKINNEY
CASEY
Cu
Jacks
Cu
Fork
EMINENCE
WEST EMINENCE
SLATER
SUTTON
19
JERKTAIL
Current
River
JACKS FORK
Bull
Cr.
106
SHANNON
REYNOLDS
Current
River
BOLIN
Rocky
Cr.
SHANNON CO.
CARTER CO.

FIGURE 3

the deposits parallel the bedding with chimney-like feeders. Chalcopyrite is the dominate copper mineral; chalcocite, malachite, and cuprite are also present.

Production is recorded only from the Sutton. In 1925, 44,390 pounds of ore averaging 27.29% copper was shipped. Another 77,074 pounds averaging 8.365% copper was sold in 1926 (Bridge, p. 178). The ore contains at most 0.1% nickle and a trace cobalt.

3. STE. GENEVIEVE

Chalcopyrite replacing a soft chert bed was discovered at the Cornwall Mine in 1863 (Figures 6 and 9). The mineralization is parallel to the bedding of the Ordovican Powell formation, about 2000 feet above the Precambrian surface. Similar mineralization occurs in the same formation at the Swansea and Herzog Mines four miles to the northwest of the Cornwall (Weller and St. Clair, 1928, pp. 331-336). Production figures are vague; the mines are thought to have produced a few thousand tons of copper. The hand-cobbed ore graded 20% copper or less.

The similarity of the mineralization of the Cornwall, Swansea and Herzog Mines at Ste. Genevieve, and the Casey and Jacks Fork at Eminence suggest that the Ste. Genevieve prospects may overlie other copper bearing zones closer to the Precambrian surface.

4. SULLIVAN

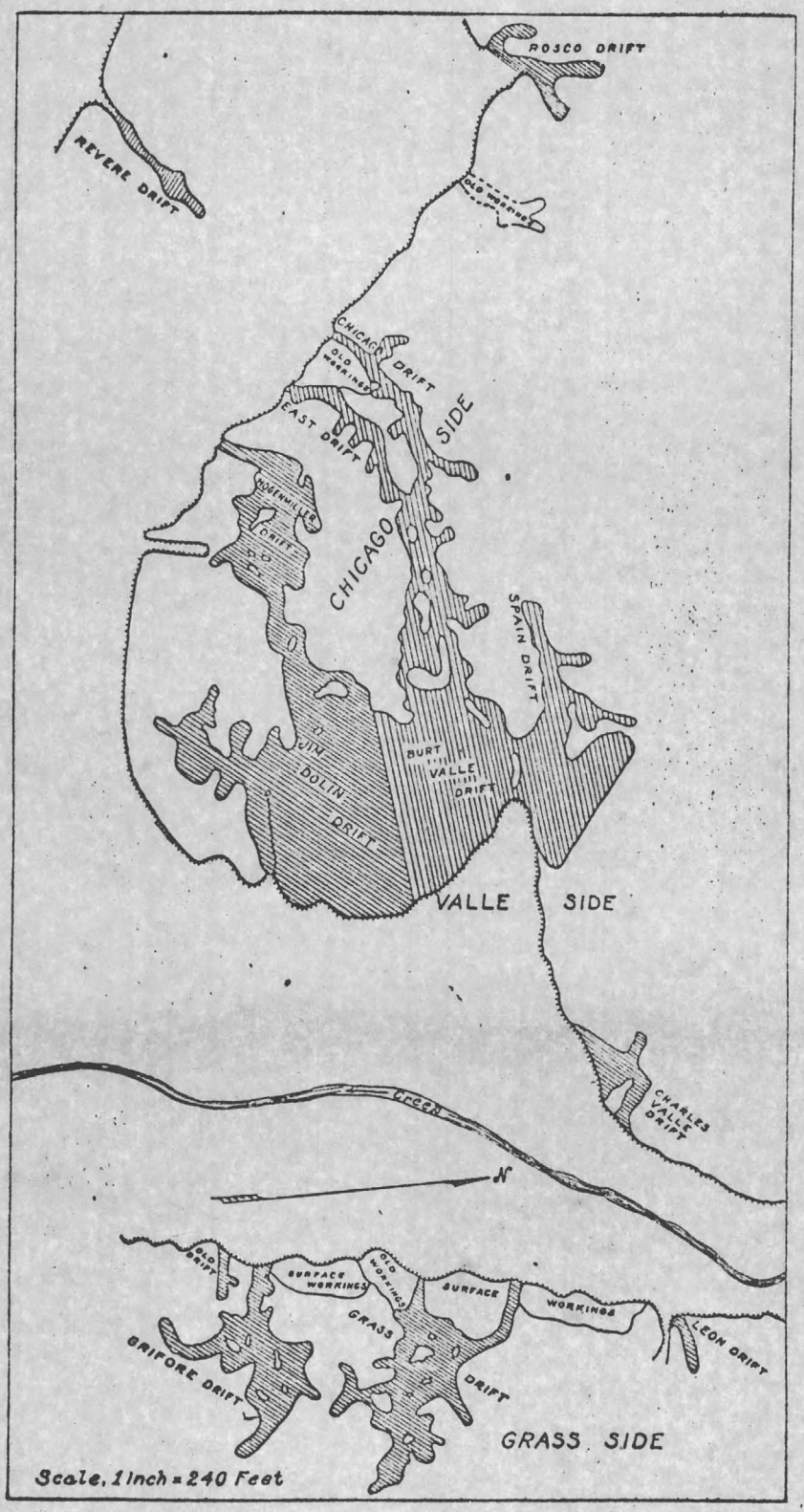
Chalcopyrite occurs in filled sink holes with pyrite, hematite and clay (Figure 6). The deposits are small. Little information is available, but Sullivan too, may overlie other copper occurrences at depth.

5. BOSS

Chalcopyrite, bornite, and magnetite occur in an acid to intermediate rock that intrudes rhyolites in the Precambrian basement (Figure 6). Grade for both copper and iron is reported marginal American Zinc and Getty Oil are drilling Boss now.

DISCUSSION

The case for a copper play in the Paleozoic rocks in Missouri is based on the temperature dependence of copper solubility, and the unimportance of this factor on the solubility of zinc



Map of underground workings, Cornwall Copper mine.

circa 1915

(Figure 10, from Barnes, ed, 1967, p 371). Copper deposits and lead-zinc deposits could be spatially separate (Figure 11, from Barnes, ed, 1967, p. 377). Some such mechanism as this was operant in other types of deposits, such as the zoned porphyry copper-lead-zinc-silver district at Bingham, Utah.

Referring to the Alley Spring, Eminence, Powder Mill Ferry, Bartlett, Winona, and Stegall Mountain quadrangles in the Eminence area (Appendix A) on which land ownership (Kerr-McGee controls Moss Tie), Precambrian knobs, copper prospects, drill holes, etc. are shown, it appears that brines entering the area in the vicinity of the P.D. drill hole in Section. 1, T.27N. on the Winona Sheet and moving North would have risen about 1800 feet by the time they passed just east of the Sutton Mine and moved on towards Ozark Lead's Blair Creek lead-zinc reserves, on the Powder Mill Ferry sheet. This steep slope on the Precambrian surface could provide the temperature gradient sought. Allan Juhas and Paul Trost, T.G.S., pointed out that a rise of this magnitude, assuming a normal temperature gradient, would result in a temperature differential of about 6° C, which might not be sufficient. A steeper than normal temperature gradient might be present here because of the proximity of the ground water table, which may control the elevation of the lead-zinc deposits (Figure 11). The base of the Bonnetene formation, which contains most of the lead-zinc ores is at about -375 feet in the mines immediately to the North. I have no way to project the ground water level into the Eminence area.

Referring to the Fredericktown, Higdon and Perryville quadrangles (Appendix B), the slope of the Precambrian surface steepens markedly between the National Lead drill hole in Sec. 30, T.33N., R.8E., and the National Lead hole in Sec. 11, T.33N., R.8E. Here again, this may indicate a steeper temperature gradient, but it might be necessary to rely on the proximity of the ground water table to attain the required differential.

LAND

FEDERAL

Reacquired Federal land is available by obtaining a prospecting permit. The filing fee is $10, and an advance rental of $.25 an acre is necessary. Prospecting permits are issued for a period of two years; they can be renewed. There is an acreage limit. Before going into production, a lease is required. The lessee pays a negotiated royalty on the gross value of the ore. Copies of the prospecting permit and lease form are in Appendix C.

d discrete free particles of solid
formed near 250°C. Enclosed
proportion to the size of the in-
of the inclusion volume, cor-
nearly 60,000 mg/liter.

erals, may not be represen-
are commonly poor in re-
total metal content (see
is difficult to reconcile with a
bisulfide complexes. How-
designed to preserve the
for part of the dilemma.
adients associated with ore
concentrations; neither ap-
ents in veins during ore
ations within ore-
) derived the ther-
such a relation and has
to fix limits to zinc
the Wellington Mine in
studied carefully enough to
perature gradient. A true
use of samples which are
thermal gradients, Chap-
be applied (see Chapter 7).
and Silverman (1965) who
in the wall rocks of ore
gradient on the basis of
concentrations in the
Although these values cor-
1000 mg/liter of ore solu-
for their derivation.

metal concentrations, the activi-
metals at saturation could be
pertinent complexes if ΣS
estimated closely. Recall that
of the aqueous species in-
be H_2S, HS^-, or S^{2-}. Unfor-
only suggestive of the con-
distinct possibilities for the
complexes which deposit
of ΣS have been
activities of metal ions can be

appreciable without exceeding the solubility products and formation of a chloride or other sulfide-free complex is favored. For sphalerite, we have calculated that within our thermodynamically restricted limits, up to 250°C, at neutrality and $a_{Cl^-} \approx 1.0$, the chloride complex provides ΣZn concentrations of 10 mg/liter or larger only if HS^- is about 10^{-9} *m* or less. For a zinc concentration of 10 mg/liter or larger, the ratio of ΣZn/ΣS in solution must be 10^5 or greater and only about 0.0001 mg/liter of the zinc in solution could precipitate as ZnS unless the solution carries a significant concentration of oxidized sulfur species which are reduced during deposition, or unless one could presume an independent source of sulfide ion. The latter two possibilities have already been shown to be unlikely. The obvious conclusion is that high concentrations of Zn^{2+} in natural solutions, such as the Salton Sea brine, are not sufficient for ore formation; the solution must contain at least enough sulfur to precipitate its heavy metal content.

TABLE 8.4. Approximate solubilities in mg/liter of some base-metal sulfides in a solution of 1.0 *m* HS^- and 0.5 *m* H_2S

	25°C 5 atm	200°C 40 atm
[redacted]	[redacted]	[redacted]
CdS	150	?
[redacted]	[redacted]	[redacted]
HgS	120	720
Sb_2S_3	1600	?
$\frac{\Sigma \text{ metals}}{\Sigma S}$	$10^{-2.0}$	$10^{-2.1}$

The second possibility is a comparatively high ΣS, leading to formation of bisulfide or sulfide complexes of the base metals as the mechanism of transport. Solubilities for several base-metal sulfides have been calculated from the constants of Table 8.3 for a bisulfide solution at 25°C, pH 7.3. These results are given in Table 8.4 together with estimated solubility values at 200°C in the same solution, based on the typical temperature dependencies of the solubilities as established by experiment. At fixed composition, the concentrations at 200°C are estimated to be about the same as at 25°C for ZnS, about five times greater for CuS, and about six times greater for HgS. The concentrations of HS^- and H_2S assumed in this calculation are near the upper limits calculated by Holland (1965) from mineral stabilities and may be unusually high, particularly for the 25°C calculations. One can

Figure 11

quantitatively less abundant; the later stage barite has retained fresh crystal forms. Early barite apparently formed during the advance of an ore solution into a somewhat oxidizing environment in a carbonate host-rock saturated with meteoric water; deposition may have taken place under conditions just below the HS^-/SO_4^{2-} boundary of Fig. 8.7. Further advance of the bisulfide ore solution could have readily flushed out most of the oxidizing species and reduced the sulfate content of the environment in which the early barite was deposited. In a bisulfide solution, barite is much more soluble and early barite was at least partially corroded as the ore sulfides were simultaneously being deposited; the conditions would have been more oxidizing than during transport but less so than during early barite deposition. The later barite was primarily deposited vertically above the sulfides but partially with them, perhaps as the oxidation state varied erratically across the barite-insoluble boundary of Fig. 8.7. The end stage of deposition was accompanied by a receding flow of solution and renewed deposition of barite in the area of the main ore body, on top of late sulfides.

The distribution of Mississippi Valley-type deposits in Illinois and Wisconsin suggests that there is a rough parallelism between the ground water table and the elevation of the ore deposits, although there is a regional stratigraphic dip to the south and west. Localization of the ores may well have been at an ore solution-ground water interface where oxidation, acidification, dilution, and decrease in temperature all came about simultaneously. An implication of our model is that drilling under these deposits for extensions of the sphalerite ore in depth would be unlikely to succeed because the solubility of sphalerite does not change sufficiently either with pressure or temperature (to 200°C) to make deposition at depth probable. On the other hand, the solubility of covellite, and perhaps other copper sulfide minerals, does change sufficiently with temperature to suggest that copper deposits could underlie these zinc-lead deposits if these particular ore solutions ever contained copper in significant amounts.

SUMMARY

Transport of base metals in bisulfide or sulfide complexes appears to be both geologically and chemically feasible at temperatures up to 250°C and perhaps higher. These complexes are stable within the limiting conditions of pH, f_{S_2}, f_{O_2}, temperature, and pressure where transport must take place. Calculated solubilities lie within the range of our present best, but poor, estimates of required concentrations. The physical and chemical factors which could cause deposition from these complexes appear to be compatible with the inferred geological environments of deposition. Therefore, at least to 250°C, the evidence supporting sulfide complexing as a mechanism of

STATE

Missouri grants a three year prospecting permit; annual rental is $1.00 per acre. Under a lease, royalty varies from 4-5% of the gross value of the concentrates. A copy of the prospecting permit and lease is in Appendix D.

PRIVATE

In 1959-61, three to four year purchase options were obtained on private land for $1.00 an acre annual rental. Purchase prices were $125-$150 an acre, no royalty. I have no copies of these agreements as Shannon County has no copy machine.

DRILLING

Tenco Drilling Company, Rolla, quoted $2.25 a foot for rotary drilling, with penetration rates of 400 feet a day.

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

Deposits in which copper is an important element do exist in Missouri. The possibility for discovering copper or copper-nickel-cobalt ores similar to those in the Mine La Motte and Madison Mine at Fredericktown is good. The problem will be to find a deposit large enough and rich enough to meet the requirements of a major mining group. Based solely on past production, exploration priorities should be: Fredericktown-Eminence-Ste. Genevieve.

RECOMMENDATIONS

I should spend one or two more months searching the literature and compiling. Specifically, the Leadwood-Flat River-Bonne Terre and Annapolis Areas (Figure 5) should by studied. The Bunker Hill Company should be contacted as regards the status of the Higdon Mine. A review of the recent literature on the geochemistry of lead, zinc and copper would be helpful.

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