Copper Sulfides in the Lower Permian Redbeds of South-Central Kansas

Ore Mineralogy

Kansas Geological Survey
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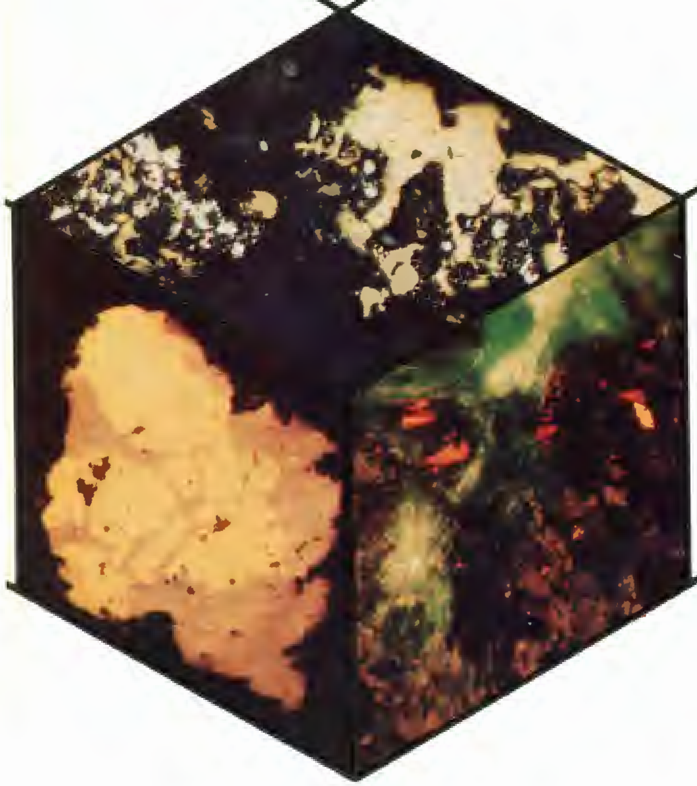

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Part 2: Ore Mineralogy

ABSTRACT

Subeconomic concentrations of copper sulfide minerals are irregularly distributed throughout the Lower Permian Wellington Formation and the Ninnescah Shale of south-central Kansas. The host rocks consist principally of gray shales and siltstones with lesser argillaceous dolomites and limestones in which the sulfides occur principally as replacements of earlier diagenetic pyrite or as irregular stringers.

Although two spatially distinct and separate sulfide assemblages are identified on the basis of drill hole information, the sequence of ore minerals indicates that a descending copper-rich solution percolating downward was slowly depleted of its copper content.

In the northern portion of the area, pyrite is replaced by chalcopyrite and bornite at shallower depths, while in the southern part of the area pyrite is replaced by "chalcocite-like" minerals. It is suggested that pH and oxygen fugacity are controlling factors responsible for the different assemblages.

Electron microprobe studies indicate that no true chalcocite (Cu_2S) is present; instead two phases having the compositions $Cu_{1.75\pm0.01}S$ (similar to anilite) and $Cu_{1.91\pm0.03}S$ (similar to djurleite) were identified. The mineral anilite has not been reported before associated with the Midcontinent copper occurrences.

We propose that the mafic rocks associated with the Central North American Rift System were the source rocks of the copper that was subsequently introduced into the Permian basin and adsorbed onto the sediments. Oxidizing groundwaters were responsible for redissolving the copper and secondarily concentrating it in a reduced environment.

INTRODUCTION

Redbed-associated copper deposits are stratibound copper sulfide occurrences that exist as layers or disseminations in organic-rich shales and carbonate beds and as replacements of organic material in continental sandstones. Although the ore occurs in dark-colored, reduced sediments, the host sequence is generally characterized by substantial amounts of red, oxidized clastics. In Kansas, Oklahoma, and Texas, copper sulfide mineralization associated with shale rather than sandstone is of greater economic significance (Johnson, 1976).

Ore-grade material was mined from the Creta copper-bearing shale in southwestern Oklahoma from October 1965 to February 1975, when a drop in the price of copper forced the mine to close. The Creta copper shale has an average copper content of 2.3 volume percent, and chalcocite (Cu_2S) is the mineral that was mined. At the nearby Magnum copper prospect, malachite [$CuCO_3Cu(OH)_2$] is the most abundant copper mineral that has been identified, although chalcocite may be the dominant ore mineral in the subsurface. The Magnum site averages one percent copper by volume.

In Texas, three prospects have been identified in the San Angelo Formation. In each case the ore mineral is chalcocite, which weathers to malachite and azurite [$Cu_3(CO_3)_2(OH)_2$] near the surface (Johnson,

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ECONOMIC GEOLOGY

COPPER SULFIDES IN KANSAS

The host rocks for the copper sulfide mineralization in Kansas are the shale, siltstone, and carbonate of the Wellington Formation and the Ninnescah Shale, which are discussed in some detail in Part 1 of this bulletin. The copper-bearing minerals occur principally as the result of solution (in vugs) and replacement processes. The most common replacement process is that of the megaspore *Triletes* by sulfides. Mineralization also occurs in vertical stringers that may be related to the activity of burrowing organisms, or dessication features.

Veinlets are commonly associated with copper sulfide mineralization in the thin carbonate units. Large euhedral carbonate grains rim the veinlets and these in turn are surrounded and partially replaced by younger, large euhedral quartz crystals. A second generation of very fine grained quartz is the most abundant mineral phase in the veinlets, and this phase corrodes the surface of the older, larger grains of euhedral quartz. Figure 2 illustrates copper sulfide grains in micritic dolomite, and Figure 3 shows large euhedral quartz grains and younger, finer grained quartz in a veinlet.

Because redbeds in the upper part of the Wellington Formation are discontinuous, the entire formation can be considered as one thick greenish-gray shale as far as the migration of any ore-forming fluid is concerned. According to Swineford (1955), fully 80 percent of the Wellington is shale and silty shale, but only 15 percent is red shale.

Ripple marks and mud cracks visible in surface outcrop and core in the study area suggest a shallow marine (lagoonal) environment of deposition. Both mechanical and biological agents have extensively reworked many of the beds that contain copper sulfides and are responsible for creating the veinlets that have since been filled with the carbonate so often associated with copper sulfide grains.

ORE MINERALOGY

Covellite (CuS) occurs as a near-surface alteration product of primary copper sulfides in drill hole 7. Within 7 m of the surface, azurite [$Cu_3(CO_3)_2(OH)_2$] surrounds and has replaced grains of "chalcocite" (a chalcocite-like phase described below), which have partially altered to covellite (Fig. 4). The azurite is in turn rimmed by malachite [$CuCO_3Cu(OH)_2$], which penetrates the azurite along cracks (Fig. 5).

The chalcocite-like phase is present in the southern part of the study area where it replaces pyritized spores (Fig. 6). A mineral identified as chalcocite is reported to replace pyritized spores in the redbed copper ore deposit at Creta in southwestern Oklahoma (Hagni and Gann, 1976). In Kansas the chalcocite-like phase also occurs as vertical stringers in greenish-gray shale, in structures that may have been formed by burrowing organisms (Fig. 7).

At drill location 15 the chalcocite-like phase is clearly related to the replacement of spores. Core from drill holes 10 and 11 contain the chalcocite-like phase in vertical stringers, and in drill hole 13 the sulfide grains have characteristics of both spore-related and vertical stringer mineralization. The depth at which the chalcocite-like phase first appears increased from 26.52 m at drill location 13 to 32.67 m at drill location 15.

A transition between ore mineralogies at the southern and northern parts of the study area occurs at drill location 7. Grains of the chalcocite-like phase are found 6 m below the surface; and grains of chalcopyrite ($CuFeS_2$), partially replaced by bornite (Cu_5FeS_4), occur 16.95 m beneath the surface in the same core.

The chalcocite-like phase replaces bornite at a depth of 22.86 m in drill hole 2, and bornite is clearly a replacement of chalcopyrite in drill holes 2 and 3 (Fig. 8). Root-like patches of bornite intrude into the chalcopyrite and progressively replace more and more chalcopyrite in grains nearer the surface. Bornite is first identified at a depth of 15.91 m in drill hole 3, and at 22.81 m in drill hole 2 farther to the south. The chalcopyrite occurs as an irregular growth without clear replacement texture around pyrite framboids (Fig. 9), and as replacement of pyrite. The depth at which chalcopyrite is first identified increases from 18.41 m in drill hole 3 to 25.45 m in drill hole 2.

Under reflected light, a dark-blue isotropic material is observed as a replacement of bornite grains in the cored material (Fig. 10). Digenite ($Cu_{1.8}S$), a copper sulfide that has these optical properties, is reported from the Prewitt copper shale of Oklahoma as an intergrowth with chalcocite (Cu_2S) (Hagni and Gann, 1976). Morimoto and Gyobu (1971) have determined that digenite is stable in the copper-iron-sulfur field and contains about one percent iron. Electron microprobe analysis showed the mineral to be digenite (Table 1).

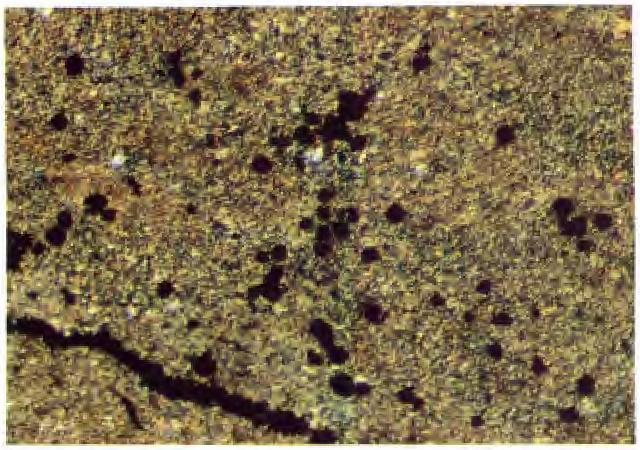

FIGURE 2.—Copper sulfide grains (black) in micritic dolomite. Drill hole 10, 44.0 m deep, polarized transmitted light. The field width is 1.8 mm.

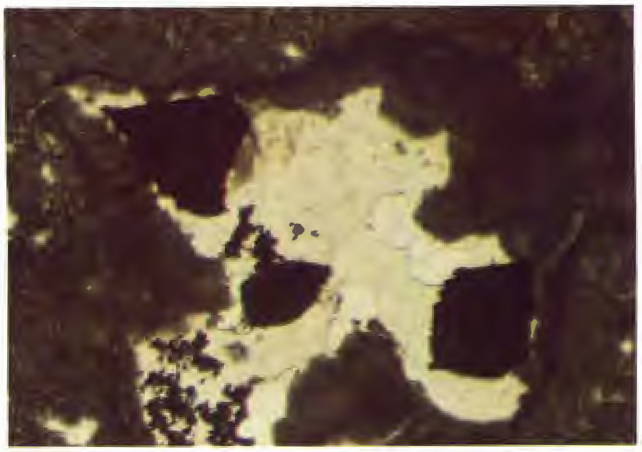

FIGURE 3.—Copper sulfide grains (black), large euhedral quartz grains (light gray), and younger fine-grained quartz in a veinlet. Drill hole 7, 16.3 m deep, plain transmitted light. The field width is 1.8 mm.

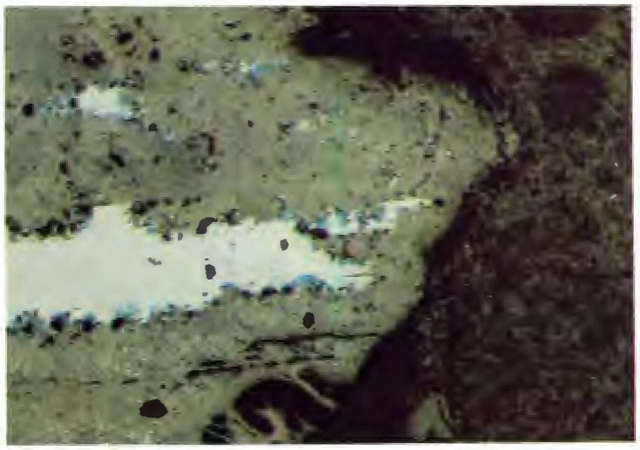

FIGURE 4.—Chalcocite-like phase (light blue) partially replaced by covellite (dark blue) and surrounded by azurite (light gray). Drill hole 7, 6.0 m deep, plain reflected light. The field width is 3.6 mm.

FIGURE 5.—Malachite (green) penetrating and replacing azurite (brown). Covellite (orange) is partially replaced by the azurite. Drill hole 7, 6.0 m deep, polarized reflected light. The field width is 1.8 mm.

The grain that was probed contained digenite as a partial replacement of bornite.

Judging from its optical properties, the chalcocite-like phase that was probed in drill hole 13 was a grain of chalcocite. Table 2 lists the electron microprobe results and reveals that the average composition of the probed grain was $Cu_{1.90}S$. This is close to the composition of djurleite ($Cu_{1.96}S$), a copper sulfide optically identical to chalcocite. Detailed examination of the probed section from drill hole 13 revealed that a light sulfide phase and a dark sulfide phase existed in this possible djurleite phase. Both phases were analyzed and the dark phase was found to be relatively copper-rich with an average composition of $Cu_{1.95}S$. The lighter phase was slightly poorer in copper with an average composition of $Cu_{1.86}S$ (Table 2).

Results of the electron microprobe analysis of chalcocite-like grains in drill hole 7 are listed in Table 3. Not clearly in a grain that was originally a spore, the mineral in this sample has a composition unlike that of djurleite in drill hole 13. The average composition is $Cu_{1.73}S$, similar to the composition of anilite ($Cu_{1.75}S$). Anilite is said to be much like chalcocite in appearance (Morimoto and Koto, 1969).

Recent electrochemical studies of the copper-sulfur system by Potter (1977) have highlighted the phase complexities between $Cu_{1.7}S$ and $Cu_{2.0}S$. The mineral assemblages found in south-central Kansas confirm these complexities in natural samples. The varied stoichiometries of the copper sulfide minerals in Kansas probably resulted from phase transformations after precipitation from fluids with slightly varying copper-sulfur ratios.

The analyses of samples from drill hole 13 (Table 2) fall within a compositional range that, according to Potter's study, should contain a djurleite-anilite mixture. In particular, the $Cu_{1.87}S$ phase probably represents a metastable crystallization product. The analyses of samples from drill hole 7 indicate a copper to sulfur ratio that, according to Potter (1977), should allow both anilite and covellite to form at the low (less than 75°C) temperatures postulated for redbed copper deposits.

The section from drill hole 7 contains covellite as well as anilite. Electron microprobe results indicate that the average composition of the covellite is $Cu_{1.08}S$, quite close to the ideal formula (CuS).

The identification of azurite in the cores was not definitely resolved by optical methods. Comparison of copper content in suspected azurite with that predicted by its ideal formula (shown in Table 4) strongly suggests that the mineral is azurite. A ternary dia-

TABLE 2.—Results of electron microprobe analysis for chalcocite-like phase from drill hole 13 (weight percent).

	Specimen	%Cu	%S	Total %	Formula
Chalcocite-like phase (Cu-rich), 26.12 m depth	6a	78.78	21.46	100.24	$Cu_{1.86}S$
	6b	80.45	21.73	102.18	$Cu_{1.86}S$
	6c	78.79	21.88	100.67	$Cu_{1.81}S$
	6d	79.14	21.53	100.67	$Cu_{1.85}S$
	6e	79.08	21.78	100.86	$Cu_{1.83}S$
	6f	78.33	21.98	100.31	$Cu_{1.80}S$
	6g	78.61	21.76	100.37	$Cu_{1.82}S$
	6h	78.49	20.88	99.37	$Cu_{1.88}S$
	6i	78.49	21.21	99.70	$Cu_{1.87}S$
	6j	78.06	21.25	99.31	$Cu_{1.86}S$
	6k	78.22	20.79	99.01	$Cu_{1.90}S$
	6l	79.13	21.23	100.36	$Cu_{1.88}S$
	6m	78.70	20.94	99.64	$Cu_{1.89}S$
	6n	78.46	20.62	99.08	$Cu_{1.92}S$
	Average	78.77	21.36	100.13	$Cu_{1.86}S$
Chalcocite-like phase (Cu-poor), 26.12 m depth	7a	79.51	20.86	100.37	$Cu_{1.93}S$
	7b	80.38	20.79	101.17	$Cu_{1.95}S$
	7c	79.15	20.63	99.78	$Cu_{1.94}S$
	7d	79.43	20.87	100.30	$Cu_{1.92}S$
	7e	78.73	20.76	99.49	$Cu_{1.91}S$
	7f	79.31	19.98	99.29	$Cu_{2.01}S$
	7g	80.56	20.67	101.23	$Cu_{1.96}S$
	7h	79.31	20.56	99.87	$Cu_{1.95}S$
	7i	79.48	20.61	100.09	$Cu_{1.95}S$
	7j	80.15	20.76	100.90	$Cu_{1.95}S$
	7k	79.75	20.87	100.62	$Cu_{1.94}S$
	7l	80.46	20.88	101.34	$Cu_{1.95}S$
	Average	79.68	20.68	100.37	$Cu_{1.95}S$

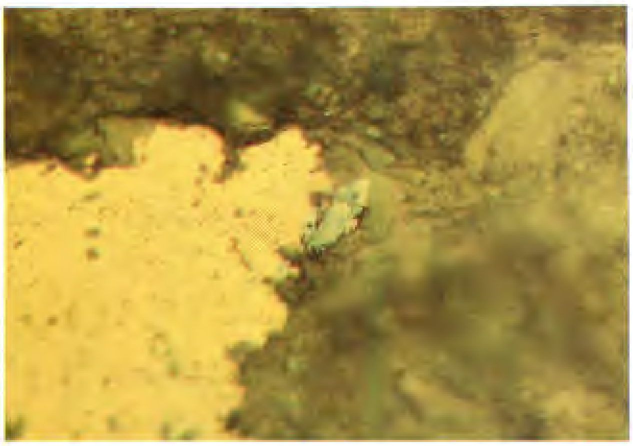

FIGURE 10.—Digenite (blue-green) replacing bornite (light brown). Drill hole 2, 22.9 m deep, plain reflected light. The field width is 0.68 mm.

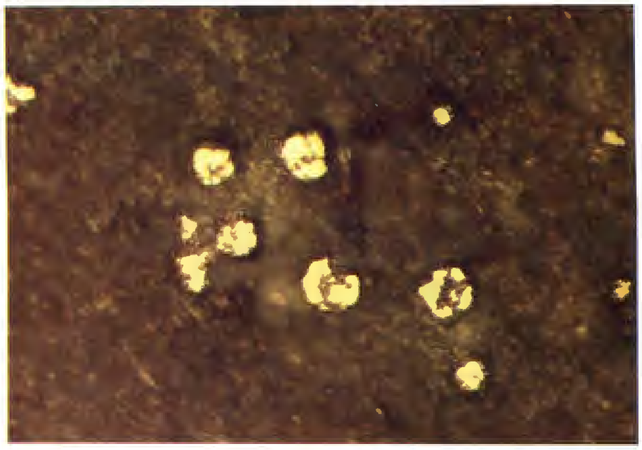

FIGURE 11.—Megaspores replaced by pyrite, from an outcrop in the SE¼, Sec. 20, T.31S, R.2W, plain reflected light. The field width is 1.8 mm.

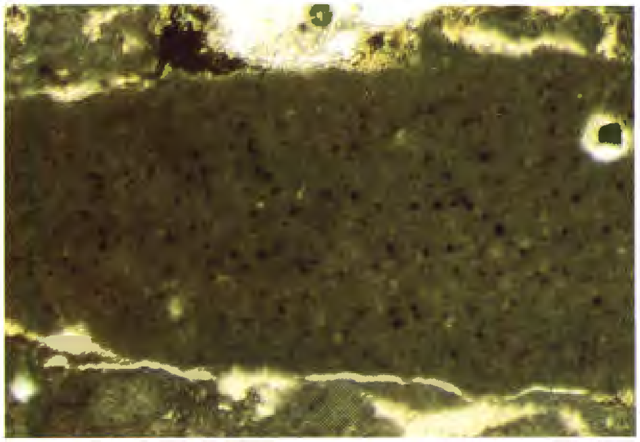

FIGURE 12.—Unreplaced megaspores of the genus *Triletes,* from an outcrop in the SE¼, Sec. 27, T.31S, R.2W, plain transmitted light. The field width is 6.0 mm.

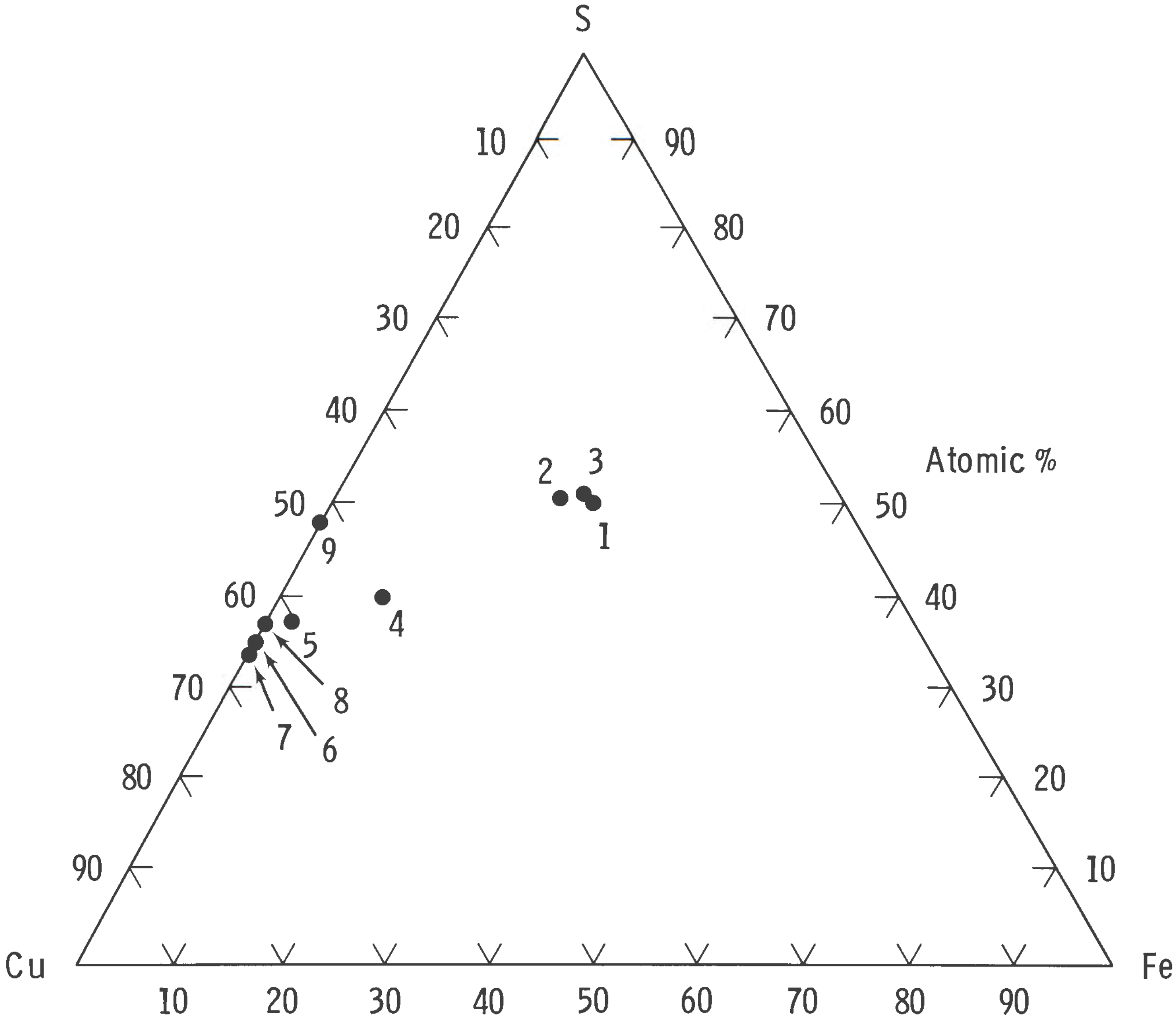

FIGURE 13.—Electron microprobe data for the copper-iron-sulfur system.

ANALYZED PHASE	AVERAGE FORMULA
1. Chalcopyrite in pure chalcopyrite grains	$Cu_{1.00}Fe_{1.01}S_2$
2. Chalcopyrite in pure chalcopyrite grains	$Cu_{1.01}Fe_{.97}S_2$
3. Chalcopyrite in chalcopyrite-bornite grains	$Cu_{1.01}Fe_{.97}S_2$
4. Bornite in chalcopyrite-bornite grains	$Cu_{1.86}Fe_{.95}S_4$
5. Digenite phase	$Cu_{1.60}Fe_{.059}S$
6. Anilite-djurleite intermediate phase	$Cu_{1.86}S$
7. Djurleite	$Cu_{1.95}S$
8. Anilite	$Cu_{1.73}S$
9. Covellite	$Cu_{1.08}S$

TABLE 6.—Results of atomic absorption spectrophotometry of samples from drill hole 13.

Depth (Meters)	Cu (ppm)	Pb (ppm)	Zn (ppm)	Rock Type
14.17-14.86	7.9 ± 0.9	1.5 ± 0.1	35.3 ± 2.1	gray & red shale
14.86-14.99	202.0 ± 1.7	1.2 ± 0.1	42.7 ± 2.1	gray shale
14.99-15.06	*4490.0 ± 101.0	4.2 ± 0.1	32.6 ± 0.6	limestone
15.06-15.12	427.0 ± 1.7	2.8 ± 0.1	32.8 ± 2.1	limestone
15.12-15.19	266.0 ± 1.7	1.2 ± 0.1	33.9 ± 2.1	gray shale
15.54-15.67	5.8 ± 0.1	2.7 ± 0.1	34.8 ± 2.2	gray & red shale
15.67-15.77	18.2 ± 0.1	5.1 ± 0.1	30.0 ± 0.4	limestone
15.77-15.85	16.1 ± 0.1	5.1 ± 0.1	29.0 ± 2.2	gray shale
15.85-16.15	6.6 ± 0.1	2.2 ± 0.1	44.2 ± 2.1	red shale
25.98-26.00	4.0 ± 0.1	0.1 ± 0.1	4.9 ± 0.4	gypsum
26.00-26.11	*1770.0 ± 10.4	2.1 ± 0.1	51.0 ± 2.1	gray shale
26.11-26.14	*6420.0 ± 98.9	4.7 ± 0.3	35.6 ± 0.5	dolomite
26.14-26.18	*119.0 ± 7.9	3.2 ± 0.1	28.8 ± 0.5	dolomite
26.18-26.24	*1080.0 ± 10.5	2.8 ± 0.1	24.2 ± 0.4	dolomite
26.24-26.29	*1400.0 ± 8.5	3.0 ± 0.1	30.4 ± 0.4	dolomite
26.29-26.31	*99.0 ± 3.5	2.2 ± 0.1	34.3 ± 1.3	dolomite
26.31-26.39	113.0 ± 3.4	4.1 ± 0.1	28.7 ± 1.3	dolomite
26.42-26.49	7.1 ± 0.2	1.0 ± 0.1	67.0 ± 1.3	gray shale
26.54-26.64	*940.0 ± 40.1	2.4 ± 0.1	51.8 ± 0.5	ls. & gray shale
27.74-27.87	3.2 ± 0.1	0.6 ± 0.1	60.2 ± 1.3	gray shale
27.87-27.91	2.5 ± 0.1	0.2 ± 0.1	41.3 ± 1.2	gray & red shale
27.94-28.02	3.4 ± 0.1	0.7 ± 0.1	51.1 ± 1.2	gray shale
28.02-28.17	3.5 ± 0.1	0.5 ± 0.1	71.0 ± 1.3	gray shale
28.17-28.27	4.5 ± .01	0.7 ± 0.1	56.2 ± 1.2	ls. & gray shale
28.65-28.67	3.4 ± 0.1	0.4 ± 0.1	70.4 ± 1.2	ls. & gray shale
28.67-28.80	2.6 ± 0.1	1.2 ± 0.1	41.5 ± 1.2	gray shale
28.89-28.92	*45.8 ± 0.4	1.5 ± 0.1	38.7 ± 1.3	limestone
28.92-28.99	*37.6 ± 0.4	1.7 ± 0.1	34.5 ± 1.3	limestone
	Cu Max = 6420.0	Pb Max = 5.1	Zn Max = 71.0	
	Cu Ave = 625.0	Pb Ave = 2.1	Zn Ave = 40.6	
	Cu Min = 2.5	Pb Min = 0.1	Zn Min = 4.9	

* Sulfide mineralization detected.
Analysis carried out by O. Karmie Galle, Kansas Geological Survey.

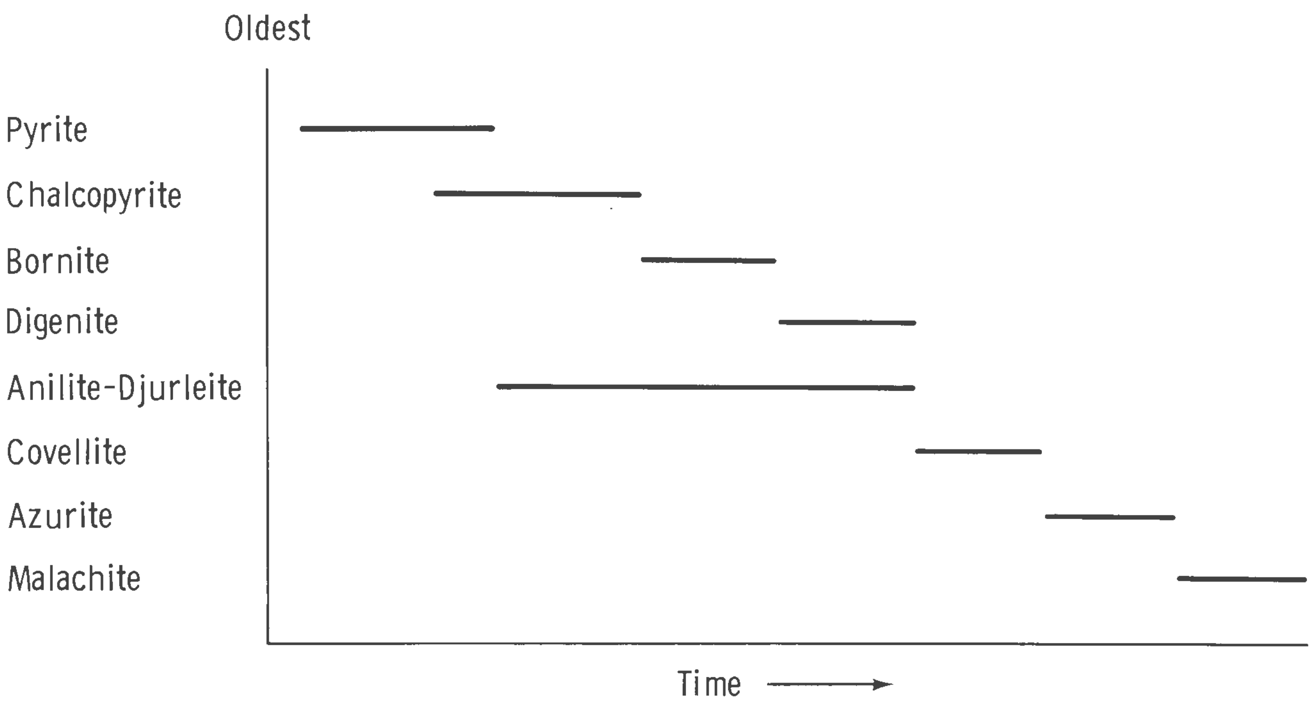

FIGURE 14.—Paragenetic sequence for copper carbonates and copper sulfides in the study area.

CONCLUSIONS

The major conclusions reached from this study are:

1.) Pyrite, chalcopyrite, bornite, digenite, anilite and djurleite, covellite, azurite, and malachite occur as spore replacements and as vertical stringers in greenish-gray shales and dolomites in the upper Wellington Formation and the Ninnescah Shale of south-central Kansas.

2.) Electron microprobe studies indicate that the minerals in the copper-sulfur system exhibit varied chemistry ranging in composition from anilite ($Cu_{1.75}S$) to djurleite ($Cu_{1.96}S$).

3.) The paragenetic sequence of the ore mineralization is pyrite-chalcopyrite-bornite-digenite-anilite-djurleite-covellite-azurite-malachite.

4.) The zoning sequence is interpreted as indicating a progressively less copper-rich mineralizing fluid as distance from the copper source increases.

5.) The source of copper could have been either the Wichita Mountains in southern Oklahoma or, as suggested by several workers, a geopressured brine from sediments of the Ouachita Mountains in southeastern Oklahoma.

6.) However, the model for copper mineralization favored in this report views the rocks associated with the Central North American Rift System, especially the basalts, gabbros, and their derivative sedimentary equivalents, as the ultimate source of the copper. By one of several mechanisms the copper was introduced into the Permian sea and adsorbed on the reduced sediments (clays). At a later time, oxygenated groundwaters solubilized the copper and reprecipitated and concentrated it downdip in a reduced environment.

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