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LOW TEMPERATURE COPPER GEOCHEMISTRY: GITOLOGICAL ASPECTS

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ABSTRACT

The geochemistry of copper at low temperatures is considered with particular reference to the problem of the formation of stratiform copper sulfide ore deposits.

Four approaches are used including low temperature thermodynamic analyses of major copper-bearing aqueous systems; low temperature aqueous experimentation; a review and critical synthesis of analytical data from the major natural copper reservoirs and the construction of dynamic mathematical models of potential ore-forming processes.

Dissolved copper occurs in open ocean water mainly as undissociated cupric carbonate. Copper from continental run-off is largely precipitated in near-shore areas and may be separated from related transition metals. Biological processes are important to the copper economy of freshwater systems but their significance in modifying open ocean copper concentrations is uncertain. The major copper reservoir in the hydrosphere is contained in subsurface waters.

Chloride-rich subsurface waters are also possible carriers of dissolved cuprous copper, which is unstable with respect to water in most natural aqueous systems. Monovalent copper may also be stabilized by ammonia and organic complexes in sedimentary environments.

Cupric salts react with sulfide at low temperature to precipitate cupric sulfides. Direct precipitation of cuprous sulfides only occurs from solutions containing cuprous salts.

Potential ore-forming processes may be investigated by the construction of dynamic mathematical models. Biogenic synsedimentary copper sulfide ores are possible, providing a copper source over and above that in normal open ocean water is available.

Direct application of the data accrued from the discussions of copper geochemistry suggests three systems of immediate interest as potential environments for stratiform copper sulfide ore formation: the sediments of active oceanic ridges, partially connate subsurface water systems, and near shore organic-rich sediments supplied by run-off from adjacent mineralized continental areas.

INTRODUCTION

The purpose of this paper is to provide a geochemical framework for considerations of the mode of formation of stratiform copper sulfide ore deposits. Since these ores are commonly associated mainly with sedimentary, rather than igneous, rocks, the geochemistry of copper in sedimentary environments is emphasized.

The major geochemical problems concerning the origin of stratiform copper

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sulfide ore deposits involve the formation of high copper concentrations in the ores, both in absolute terms and in comparison with related transition metals, and the manner of transport of copper in solution to the depositional environment. A synthesis of actualistic analytical data, low temperature thermodynamic considerations and experimental results is presented in order to give some insight into these problems. Although all three methods are limited in their application, taken together they can be used to examine the potential ore-forming capacities of various natural systems.

The geochemical background to gitological studies is based on investigations of the modern natural environment. High metal concentrations in recent sediments are almost exclusively related to subsurface waters, which often contain an important juvenile component. For example, the copper content of certain oceanic sediments has been related to submarine vulcanism (Boström, 1973). A discussion of the geochemistry of copper in modern geothermal waters is presented in this article. However, the mineral parageneses associated with known hydrothermal systems are not consistent with those from a number of important stratiform copper sulfide deposits. Therefore it is important to consider the possibilities of other, less immediately attractive, potential ore-forming systems, such as seawater.

Ore formation is a dynamic process. The major restriction of the classical geochemical approach is that it can never adequately approximate a changing system. In fact, the absence of kinetic data for reactions in natural systems is probably the single, most important factor limiting our understanding of the low temperature geochemistry of copper. The ore-forming potential of, for example, seawater cannot be realistically considered without reference to the rates of the reactions involved.

In a number of natural sciences, mathematical modelling of natural processes is a well-established technique. This method of study is peculiarly suited to the science of gitology, since the models produced are themselves hypotheses which can be tested and examined with reference to observations. In this article a short discussion of the possibility of modelling ore-forming processes is presented and exemplified with a model for the formation of synsedimentary copper sulfide ores.

DISTRIBUTION OF COPPER IN THE EARTH'S CRUST

Various estimates of the copper concentration of the earth's crust are listed in table 1, and compared with related transition metals. The mean copper content is estimated to be about 50 ppm, rather more than cobalt, but less than nickel and zinc. I have computed the ratios of the mean crustal concentrations of transition metals to the copper concentration. Iron is about 10^3 times as abundant as copper. As can be seen, therefore, the formation of a copper sulfide orebody requires not only the concentration of copper over the mean crustal values, but may also require the separation of copper from Fe, Mn, Zn, Co or Ni.

The older estimates of average metal concentrations of igneous rocks by Clarke and Washington (1924) and Goldschmidt (1937) supposed that copper was relatively concentrated with respect to the crustal estimates. A breakdown of the copper and related transition metal concentrations in various crustal lithologic units, is presented in table 2. The data are abstracted from Parker (1963), and based on the work of Vinogradov (1963) and Turekian and Wedepohl (1961).

TABLE 1. — *Absolute (ppm) and relative concentrations of copper and related transition metals in the earth's crust* (PARKER, 1963; RICKARD, 1970*a*)

	Continental crust	Earth's crust		Igneous rocks		
	Taylor (1964)	Vinogradov (1962)	Mason (1958)	Rankama (1954)	Goldschmidt (1937)	Clarke and Washington (1924)
Cu	55	47	45	55	100	10
Fe	56 300	46 500	50 000	50 000	50 000	50 100
Mn	950	1 000	1 000	1 000	1 000	1 000
Zn	70	83	65	111	40	40
Co	25	18	23	23	40	40
Ni	75	58	80	80	100	200
Fe/Cu	1 025	991	1 112	910	500	501
Mn/Cu	17	17	20	21	10	10
Zn/Cu	1.3	1.8	1.4	2.0	0.4	0.4
Co/Cu	0.5	0.4	0.5	0.4	0.4	0.1
Ni/Cu	1.4	1.2	1.8	1.5	1.0	2.0

Here too I have computed transition metal/copper ratios. Compared to these related transition metals copper is concentrated in granites, felsic granites and granodiorites relative to the crustal mean, even though the absolute concentration in these units is less than the crustal average. In contrast, copper is concentrated in basalts in absolute terms, but is depleted relative to iron, and is not concentrated relative to the other four elements considered. Copper does not show the tendency of cobalt and nickel to be relatively strongly depleted in more acid igneous rocks.

Copper and manganese are strongly concentrated in deep sea clay sediments relative to both the crustal mean and iron, cobalt, nickel and zinc. However, in shales copper and manganese together with the other four elements, approach the average crustal abundance figures. Vine and Tourtelot (1970) reported an average 70 ppm copper from 779 samples of North American black shales.

Although copper is strongly concentrated in deep sea clay sediments relative to the crustal mean, it is not concentrated in near shore sediments. Wedepohl (1960) estimated an average 48 ppm copper in near shore sediments compared with 250 ppm for deep sea clays. According to Chester (1965) the average oceanic pelagic sediment contains about 345 ppm copper. Goldberg and Arrhenius (1958) found a mean copper concentration of 740 ppm for 35 samples of Pacific deep sea clays, and Chester (1965) estimated an average 570 ppm for the Pacific. Copper is less abundant in Atlantic sediments. Wedepohl (1960) found an average 130 ppm in 18 samples of pelagic material from the Atlantic.

Boström and Peterson (1969) presented analyses from sediments on the East Pacific Rise. The average contents Cu, Fe, Mn, Ni, Co and the transition metal/copper ratios are shown in table 3. Copper is actually concentrated on the flanks, where up to 938 ppm copper were detected. However, there is a small but significant copper peak on the actual crest of the rise (reaching 250 ppm Cu). Note that in terms of carbonate-free sediments, the maximum copper concentration recorded was 1 800 ppm, on the flanks of the rise. Boström and Peterson (1969) and Boström (1973) present evidence suggesting that a major fraction of the copper

TABLE 2. — *Absolute (ppm) and relative concentrations of copper and some related transition metals in the major lithologic units of the earth's crust* (PARKER, 1963; RICKARD, 1970*a*)

	Ultramafics		Basalts		Interme-diates	Felsic granites and grano-diorites	Granites		Syenites	Clays and Shales	Shales	Sand-stones	Car-bonates	Deep Sea sediments	
							High Ca	Low Ca						CO_3	clay
	1	2	1	2	2	2	1	1	1	2	1	1	1	1	1
Cu	10	20	87	100	85	20	30	10	5	57	45	–	4	30	350
Fe	94 300	98 500	86 500	85 600	58 500	27 000	29 600	14 200	36 700	33 300	47 200	9 800	3 800	9 000	65 000
Mn	1 620	1 500	1 500	2 000	1 200	600	540	390	850	670	850	–	1 100	1 000	6 700
Zn	50	30	105	130	72	60	60	39	130	80	95	16	20	35	160
Co	150	200	48	45	10	5	7	1	1	20	19	0.3	0.1	7	74
Ni	2 000	2 000	2130	160	55	8	15	4.5	4	95	68	2	20	30	225
Fe/Cu	9 430	4 930	9 940	8 560	1 650	1 350	990	1 420	7 840	580	1 050	7	950	300	260
Mn/Cu	162	75	17	20	34	30	18	39	170	12	19	–	275	33	27
Zn/Cu	5.0	1.5	1.2	1.3	2.1	3.0	2.0	3.9	26.0	1.4	2.1	–	5.0	1.2	0.6
Ni/Cu	200	100	1.5	1.6	1.6	0.4	0.5	0.5	0.8	1.7	1.5	–	5.0	1.0	0.9
Co/Cu	15	10	0.6	0.5	0.3	0.3	0.2	0.1	0.2	0.4	0.4	–	0.03	0.2	0.3

Table 3. — *Average copper and related transition metal contents of sediments from the East Pacific Rise* (Boström and Peterson, 1969). *Figures are for ppm dry weight total sediment.*

	East flank	Crest	West flank
Cu	415	145	490
Fe	40 000	86 000	61 000
Mn	10 000	12 000	19 000
Zn	120	75	155
Co	90	21	130
Ni	290	85	350
Fe/Cu	96	250	125
Mn/Cu	24	82	39
Zn/Cu	0.3	0.5	0.3
Co/Cu	0.2	0.1	0.3
Ni/Cu	0.7	0.6	0.7

(perhaps more than 50 %) is provided by deep-seated mineralizing solutions. Although copper (together with Co, Ni, Mo, Zn and Pb) is less abundant in areas of high heat flow at the ridge crests, this probably mainly reflects variations in residence times for these elements in seawater. The concentrations represent the various rates at which the constituents are precipitated.

Interestingly the sediments in which these metal concentrations occur consist to a large extent of carbonates. The flank sediments are dark brown clays with about 50 % $CaCO_3$; the crest sediments are generally lighter, except at the actual crest, with up to 90 % $CaCO_3$ (average 80 %).

The sediments are also notable for having extremely low Fe/Cu ratios, compared to other lithologic units shown in table 3. The Zn/Cu ratio is also very low.

THE COPPER CONTENT OF NATURAL WATERS

The validity of analyses of copper in natural solutions is limited primarily by the difficulty of distinguishing between dissolved and particulate copper. In effect, dissolved copper is defined as that fraction of the total copper that passes through the filter the analyst happens to have available. The problem of meaningful sampling of the hydrosphere provides a further restraint on our understanding of the copper content of natural waters. For example, the mass of the oceans is 1.42×10^{24} g (Poldervaart, 1955). Even if we assume that 100 tons (or 10^8 g) of seawater has been analyzed for copper, this means a sampling of 1 part in about 10^{16}. In lakes and rivers, by similar reasoning, the sampling would be 1 part in about 10^{12}, and for subsurface waters less than 1 part in 10^{15}. Considering the high variability of the copper contents of fresh and subsurface waters and our lack of knowledge about variations in oceanic copper concentrations, the best estimates of copper contents provided in the following sections are rather limited in value.

Rivers and Lakes

In fact, because of its importance in geochemical prospecting and in the control of public water supplies, a considerable number of copper analyses are available for fresh water systems.

TABLE 4. — *Average copper and related transition metal composition (ppb) of streams*
(LIVINGSTONE, 1963; TUREKIAN, 1969; RICKARD, 1970*a*)

Cu	7		
Fe (^{a})	670	Fe/Cu	96
Mn	7	Mn/Cu	1
Zn	20	Zn/Cu	2.9
Co	0.2	Co/Cu	0.03
Ni	0.3	Ni/Cu	0.04

(*a*) Not all soluble; Fe/Cu is thus a maximum.

The mean base metal composition of rivers and lakes is shown in table 4 from Rickard's (1970*a*) compilation. Although there is a considerable dilution of copper in fresh water systems, there is also a primary separation of the transition metals. I have computed transition metal/copper ratios (table 4) for comparison with crustal values (tables 1 and 2). Note that the Fe/Cu ratio is almost a magnitude lower than for any lithologic unit, even though the mean Fe concentration given for fresh water systems includes some particulate iron, and is therefore a maximum figure. The ratios of Mn, Zn and Ni to Cu are also considerably reduced. Interestingly, however, the Co/Cu ratio is similar to that in certain sedimentary rocks.

I have selected a number of analyses of copper in fresh water systems (table 5) to demonstrate the magnitude of the variation in copper contents found in different systems. As can be seen, within the ppb range, there are considerable differences, caused by real regional variations depending on rock type and degree of weathering, seasonal variations, and industrial pollution. It seems probable that continental weathering plays a major part in determining the trace element composition of rivers and lakes (where pollution is not a deciding factor). However, weathering plays a smaller role than might be expected. For example, samples taken from streams draining African copper deposits do not show an especially high copper concentration (table 5).

TABLE 5. — *Copper concentrations (ppb) in streams and lakes*
(from RICKARD's 1970*a* compilation)

Copper content	Location	Notes
0.9	Japan	Stream average
10.5	U.S.S.R.	Stream average
0.07-140	Maine, U.S.A.	440 lakes
0-36	England	Stream range
2.0	Chile	Andean streams, spring
86.4	Chile	Andean streams, summer
5.7-47	Italy	Stream range
10-30	Chambishi, Roan Antelope	Copperbelt streams
6	California, U.S.A.	Average fresh water
8.7	North America and Norway	Average for 35 rivers

Turekian (1969) estimates that the average dissolved copper content of streams and lakes is about 7 ppb. He admits that this is an approximate figure at best, but it may be a long time before a better figure is suggested.

Seawater

The copper content of seawater ranges from 1-20 ppb. An average figure of 3 ppb is often quoted.

Chow and Thompson (1951) listed early copper analyses of seawater. Many of the older analyses are dubious because of the primitive analytical and sampling techniques used.

Slowey and Hood (1971) measured copper, manganese and zinc contents of Gulf of Mexico waters. Their results show that the average total concentration decreases from coastal to open ocean waters, due entirely to the removal of over half the particulate fraction in near-shore waters. The average dissolved copper fraction is constant at 0.9 ppb. Total copper concentrations up to 12.3 ppb were recorded, especially from waters of intermediate depth (e.g. c. 750 m). Particulate copper was defined as the fraction greater than 10 mμ in size for this study. Table 6 shows that up to 35 % of the particulate copper is between 10 mμ and 0.45 μ in size. This figure is interesting because of the common use of 0.45 μ filters for separating out the particulate fraction in other studies. Also interesting is the fact that this 10 mμ-0.45 μ fraction is constant (at 0.14 ppb) in coastal and open ocean waters. The Mn/Cu ratios of table 6 indicate that a separation of Mn and Cu occurs in near-shore areas. In contrast, Zn/Cu ratios remain virtually unchanged. Slowey and Hood (1971) conclude that Mn is supplied by rivers whereas rivers supply only a small fraction of the total Cu and Zn. The increased Cu and Zn contents at intermediate water depths are supposed by them to be caused by copper release from decaying organisms.

TABLE 6. — *Copper concentrations (ppb),* Mn/Cu *and* Zn/Cu *ratios for Gulf of Mexico waters* (after SLOWEY and HOOD, 1971)

	Coastal water (< 100 fathoms)	Open Ocean water
Total Cu (est.)	1.6	1.3
Total particulate Cu	0.71	0.39
Particulate Cu (> 0.45μ)	0.57	0.25
Dissolved Cu (est.)	0.9	0.9
Mn/Cu (total)	2.4	0.3
Zn/Cu (total)	2.6	2.9
Mn/Cu (dissolved)	1.8	0.3
Zn/Cu (dissolved)	3.4	3.4

Fabricand *et al.* (1962) analyzed 27 samples of Atlantic and Pacific water from various depths, and found a surprisingly uniform copper content in all samples, with a maximum of 2.2 ppb. Spencer *et al.* (1970) report results of a detailed study of trace element content with depth from the northeast Pacific Ocean. Total copper varied with depth, from an average 0.7 ppb above 750 m, rising to nearly 3 ppb at 3 500 m. The copper concentration was high near the bottom, at 4 000 m. Zinc showed a similar profile, with a similar sharp rise in the oxygen minimum zone around 750 m.

Rickard (1970*a*) reviewed copper analyses of seawater and found that the total copper content of open ocean water was about 2-4 ppb, of which about half was dissolved. Considerable variations occur, however, and the concentrations range up to over 10 ppb.

Abdullah *et al.* (1972) analyzed copper in seawater off the coast of south-west England. Although falling within the 10 ppb limit, they related high dissolved copper concentrations (< 5 ppb) to run-off from the mineralized zone of Snowdonia. Spencer and Brewer (1969) carefully studied possible biological influences on the copper content of surface waters of the Gulf of Maine and the Sargasso Sea. They found that biological processes exerted only a minimal influence on the copper content of seawater.

Little is known about the copper content of interstitial waters. Presley *et al.* (1967, 1972) found that the dissolved copper content in sulfide-bearing interstitial waters was several magnitudes higher than would be expected from the solubility of simple copper sulfides. Copper concentrations up to 39 ppb have been recorded, indicating most probably that factors other than sulfide solubility control the distribution of copper in the interstitial waters of reduced sediments.

Subsurface Waters

A considerable range of waters of different type and origin occur below the land surface, and are here described by the portmanteau term "subsurface waters." Subsurface waters may be conveniently divided into five types, following the practice of White *et al.* (1963), who originally compiled much of the following data.

Table 7 lists average values of copper contents found by White *et al.* (1963). The ground waters considered are mostly potable. Most connate waters probably consist at least in part of trapped seawater in ancient marine sediments. However, meteoritic waters which have leached out soluble constituents from rocks, probably also form part of the waters listed here. Rittenhouse *et al.* (1969) analyzed the copper content of 823 oil-field waters from the U.S.A. They found concentrations ranging from 1 ppb to 1 ppm, with mean concentrations of 10-100 ppb. The implications of the analyses (that oil field waters contain more copper than spring waters, and that in both cases Na-Ca-Cl types contain about twice as much copper as NaCl types) must be treated cautiously, due to the low number of analyses. However, Davidson (1967) quotes a brine from the Cheleken oil-field, near the Caspian Sea, as containing 0.9-15 ppm copper, and it is apparent that Na-Ca-Cl oil field brines may contain remarkable amounts of trace metals.

Thermal waters connected with recent or active volcanic areas may contain a fraction that is magmatic in origin, but they are generally heavily diluted with meteoritic waters by the time they reach the surface. A summary of mean copper concentrations for some of these waters is shown in table 7. The waters of the non-geyser-NaCl type are probably contaminated with connate waters. White *et al.* (1963) note that 160 ppb Cu were recorded in an acid sulfate-chloride spring near the Kuttara volcano, Hokkaido, Japan, probably occurring as the sulfide. However,

TABLE 7. — *Average copper concentrations (ppb) in subsurface waters*
(WHITE *et al.*, 1963; RICKARD, 1970*a*)

			No. of analyses	Average Cu
Ground waters			38	13
Waters with connate affiliations	Oil field waters	NaCl type	2	170
		Na-Ca-Cl type	2	250
	Springs	NaCl type	4	28
		Na-Ca-Cl type	3	51
Waters with magmatic affiliations	Springs associated with vulcanism	Geyser waters	5	4
		Non-geyser NaCl type	3	207
		Acid SO_4-Cl type	2	95
		Acid SO_4 type	3	35
Waters with metamorphic affiliations	Springs	$NaHCO_3$-boron type	2	155
Miscellaneous waters	Springs associated with epithermal deposits		9	13
	Springs depositing travertine		3	2

according to Ichikuni (1959) the average copper content of Japanese acid springs is only 10 ppb.

The miscellaneous waters of table 7 include those that are apparently associated with epithermal mineral deposition. However, they contain relatively low mean copper concentrations. Even the waters associated with epithermal mercury, manganese and tungsten deposits show only about 12.6 ppb copper, about the same as dilute ground waters.

A number of subsurface solutions with relatively high metal contents and associated with recent metalliferous sediments have been discovered (table 8). These include the well-known Red Sea and Salton Sea brines. The Red Sea brines emanate from a median rift in the Red Sea. The brines occur at a depth of about 2 000 m. The Salton Sea brines occur in extremely thick deltaic sediments at depths greater than 3 000 ft in California. Both areas are in regions where the oceanic active ridge systems extend into the continents. Craig (1966) suggested that both brines mainly consist of meteoritic waters, which leached out the metals from the rocks through which they passed. However, Schoell *et al.* (1972) and Bäcker *et al.* (1972) have provided data which indicate that some brines south of the Discovery and Atlantis II deeps appear to be uncontaminated by South Red Sea surface water.

The Matupi harbour solutions are hot, acid springs associated with a volcanic-

TABLE 8. — *Copper and associated transition metal contents of selected metal-depositing geothermal fluids (ppm)*

	Red Sea Brines (^{a})		Salton Sea Brines (^{b})		Matupi Harbour (^{c}) Thermal Spring	Lake Kivu (^{d}) hydrothermal waters (est.)
	Atlantis II 56 °C brine	Discovery 44 °C brine	I.I.D. No. 1	I.I.D. No. 2		
Cu	0.3	0.1	8	3	0.06	0.2
Fe	80	3	2 290	2 000	108	45
Mn	80	50	1 400	1 370	20	1.2
Zn	5	0.8	540	500	1.35	7
Co	0.2	0.1	–	–	–	0.01
Ni	–	0.3	–	–	–	0.03
Fe/Cu	267	30	286	667	1 800	225
Mn/Cu	267	500	175	457	333	6
Zn/Cu	17	80	68	167	23	35
Co/Cu	0.7	1	–	–	–	0.05
Ni/Cu	–	3	–	–	–	0.15

(^{a}) BREWER and SPENCER (1969).
(^{b}) WHITE (1968).
(^{c}) FERGUSON and LAMBERT (1972).
(^{d}) DEGENS and KULBICKI (1973).

exhalative-sedimentary environment. They contain much less copper than the Red Sea and Salton Sea brines, but have been considerably diluted by near-surface waters (Ferguson and Lambert, 1972). Degens and Kulbicki (1973) have estimated the compositions of metalliferous hydrothermal solutions, emanating from the African Western Rift, and debouching into Lake Kivu.

All these solutions are associated with metal enrichments in sediments. The Red Sea brines overlay precipitates containing up to 3.3 % Cu (Hendricks *et al.*, 1969). Pipe scales from the Salton Sea brines contain up to 43.6 % Cu (Skinner *et al.*, 1967). The Matupi harbour sediments are actually depleted in copper, but enriched in Fe and Mn. Copper is also not especially abundant in the sediments of Lake Kivu (up to about 170 ppm, Degens and Kulbicki, 1973).

In fact, in terms of both mineral parageneses and copper concentrations in most of the precipitates, these mineralizing solutions are rather disappointing with regard to the formation of stratiform copper sulfide deposits.

THE BIOGEOCHEMISTRY OF COPPER

Copper plays an extremely important role in the physiology of many, if not all animals and plants. Many specific copper compounds have been isolated and identified. One of the most important is haemocyanin, the blue respiratory pigment responsible for oxygen transport in the blood of marine invertebrates such as molluscs and crustaceans.

Rickard (1970) reviewed the biogeochemistry of copper. The copper contents of marine plankton have been analyzed by Nicholls *et al.* (1959) and Presley *et al.* (1972). Nicholls *et al.* suggested that for any given chemical element there will eventually be found at least one planktonic species capable of spectacularly concentrating it. A selection of the results of Nicholls *et al.* (1959) is given in table 9.

Table 9. — *Copper content (ppm) in the ash of some marine plankton* (after NICHOLLS *et al.*, 1959)

Group	Specific organism	Copper in ash (ppm)
Coelenterata	*Cyanea capillata*	13
Ctenophora	*Beröe cucumis*	700
Mollusca Pteropoda	*Limacina retroversa*	30
	Clione limacina	70
Mollusca Cephalopoda	*Ommastrephes illicebrosa*	2 700
Arthropoda Copepoda	*Centropages typicus* and *hamatus*	1 350
	Calanus finmarchicus	300
Arthropoda Euphausiacea	*Euphausia krohnii*	600
Chaetognatha	*Sagitta elegans*	1 100
Tunicata	*Salpa fusiformis*	500

The copper enrichment factor for the marine cephalopod quoted is about 90 000. Noddack and Noddack (1939) estimated that the average enrichment factor for copper in marine organisms over seawater is 7 500. This is equivalent to stating that the average copper concentration of all dry marine organic matter is about 22.5 ppm.

Martin and Knauer (1973) made a detailed study of plankton composition. Their results are summarized in table 10. The highest copper concentration found was 104 ppm in a microplankton sample from Hawaii. The samples were of mixed species, and thus did not demonstrate any spectacular concentrations as found by Nicholls *et al.* (1959). The plankton samples are generally characterized by low Fe/Cu, Mn/Cu, Ni/Cu (and Co/Cu) ratios, and by a high Zn/Cu ratio. The microplankton contained the highest Cu contents. In contrast, phytoplankton from Monterey Bay contained generally low Cu concentrations in the organic fraction (1.9-14.8 ppm). Interestingly, about 20 % of the total copper was found in the silica fraction. The average copper content of phytoplankton and zooplankton, as measured by Martin and Knauer, does not greatly exceed 10 ppm.

TABLE 10. — *Mean values of copper and associated transition metals (ppm dry weight) for plankton* (MARTIN and KNAUER, 1973). *Cobalt was not detected in any sample (i.e. less than 1.0 ppm)*

	Monterey Bay			Hawaii		Oregon
	Euphausids	Copepods	Radiolarians	Zooplankton	Microplankton	Microplankton
Cu	15.6	10.5	6.5	11.5	57.5	45.8
Fe	92	197	315	100	1 985	745
Mn	3.6	4.4	6.4	4.3	15.0	7.4
Zn	69	113	110	180	780	970
Ni	3.8	2.0	3.7	8.4	11.6	5.7
Fe/Cu	5.9	19	49	8.7	35	16
Mn/Cu	0.2	0.4	1	0.4	0.3	0.2
Zn/Cu	4.2	11	17	16	14	21
Ni/Cu	0.2	0.2	0.6	0.7	0.2	0.1

However, these average copper values are of the order of one magnitude lower than the copper concentration of recent marine sediments. Presley *et al.* (1972) found about 13 ppm Cu in marine plankton from a reducing fjord, and noted that this gives an enrichment factor of 0.277 over the whole sediment copper concentration. In this case too copper was well correlated with organic carbon in the sediment.

From the gitological point of view, interest in copper biochemistry does not lie in the average copper content of marine organisms, but rather in those organisms which specifically concentrate copper to exceptionally high amounts. This further implies that in considering the possibility of the development of high copper concentrations in sediments by assimilatory biological processes, it is necessary to consider the ecological factors that control the development of the specific, copper-concentrating organisms. Virtually no work has been done on this aspect of the relationship between copper distribution in sediments and ecology, although Brongersma-Sanders (1969) has considered broader aspects of this type of relationship with references to the origin of the Kupferschiefer deposits.

THE FORM OF COPPER IN NATURAL WATERS

Seawater

In normal surface seawater

$$M_{SO_4^{2-}} = 0.028, \quad M_{Cl^-} = 0.54, \quad M_{HCO_3^-} = 0.0024, \quad M_{CO_3^{2-}} = 0.00027$$

and $pH = 8.15$.

Garrels and Thompson (1962) estimate that

$$\gamma_{SO_4^{2-}} = 0.12, \quad \gamma_{Cl^-} = 0.64, \quad \gamma_{HCO_3^-} = 0.68 \text{ and } \gamma_{CO_3^{2-}} = 0.20 \text{ at } 25\,°C,$$

1 atm pressure and at an ionic strength of 0.7.

Under these conditions the chloride and sulfate activities are insufficient to form major copper chloride or copper sulfate complexes. In the absence of ligands other than chloride, for example, copper would exist mainly as Cu^{2+} (71.6 %), with only 26.7 % $CuCl^+$, 1.68 % $CuCl_2^0$ and 0.01 % $CuCl_3^-$.

However, as is shown in figure 1, undissociated cupric carbonate ($CuCO_3^0$) is the dominant dissolved copper phase at $pH = 8.15$ and $\log\{HCO_3^-\} = -2.79$, the conditions in normal seawater. In fact, the seawater environment falls in the middle of the $CuCo_3^0$ field in figure 1, and it would require considerable inaccuracies in the data used to form any other dissolved inorganic copper species.

Garrels and Thompson (1962) suggest that activity coefficients for neutral species, such as $CuCO_3^0$, should lie around unity. Knowing the activity of copper in seawater, we can then examine if dissolved copper is in equilibrium with any solid phase in normal oxidized open ocean water.

Reference to figures 2, 3, 4, 5 and 6, demonstrates that four solid copper phases are most important in oxidized environments at non-extreme pH values. These are all cupric compounds, and include the oxide (tenorite), oxycarbonate (malachite), oxychloride (paratacamite) and oxysulfate (brochantite). In this analysis, phases such as azurite, antlerite and chalcanthite are included. Thermodynamic data are not available for metastable oxycarbonates, oxychlorides or oxysulfates. Par-

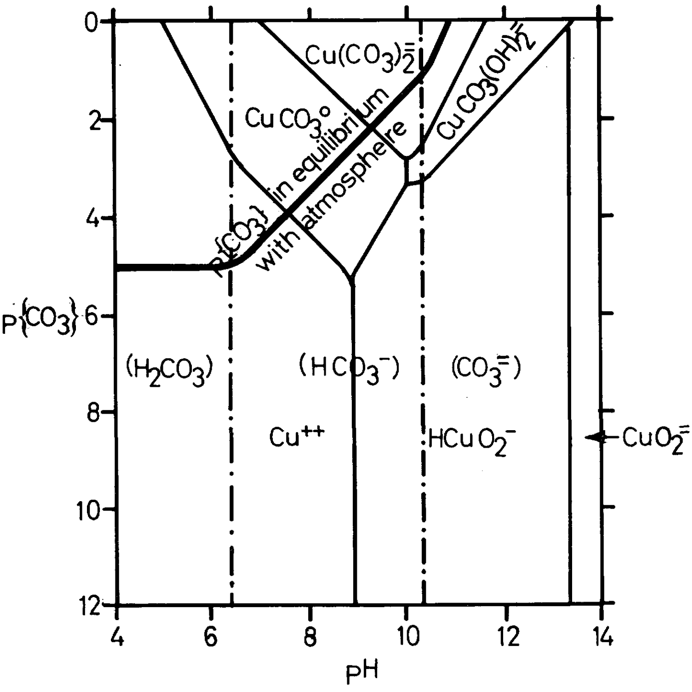


FIG. 1. — *Relationships between dissolved copper carbonate species as a function of the negative logarithm of the total dissolved carbonate activity (p*$\{CO_3\}$*) and pH at 25 °C and 1 atm pressure (Rickard, 1970a). p*$\{CO_3\}$ *in equilibrium with the atmosphere (*$P_{CO_2} = 10^{-3.5}$*) for different pH values is marked. At pH = 8.15 (normal ocean water)* $CuCO_3^0$ *is the dominant species.*

atacamite is assumed to approximate to atacamite, although no thermodynamic data are available for this polymorph. Cu(OH)Cl, possibly equivalent to the mineral mellanothallite, is also excluded for the lack of quantitative data, but is not expected to be important in these systems. A large number of oxysulfates of copper are known, but in the absence of further information, it must be assumed that these do not significantly modify the brochantite-aqueous Cu^{2+} and brochantite-tenorite stability boundaries.

Four simultaneous equations may be written for the equilibria of these stable cupric compounds:

$$CuO + H_2O = Cu^{2+} + 2\,OH^- \quad : \log K = -20.11 \quad (1)$$

$$Cu_2(OH)_2CO_3 = 2\,Cu^{2+} + 2\,OH^- + CO_3^{2-} \quad : \log K = -34.19 \quad (2)$$

$$Cu_2(OH)_3Cl = 2\,Cu^{2+} + 3\,OH^- + Cl^- \quad : \log K = -34.75 \quad (3)$$

$$Cu_4(OH)_6SO_4 = 4\,Cu^{2+} + 6\,OH^- + SO_4^{2-} \quad : \log K = -68.81 \quad (4).$$

Solving these equations independently of $\{Cu^{2+}\}$ for pH = 8.15 and the anionic activities of normal seawater demonstrates that the oxycarbonate is the stable phase in open ocean water.

The inorganic reaction controlling the solubility of copper in seawater is then

$$Cu_2(OH)_2CO_3 + HCO_3^- + H^+ = 2\,CuCO_3^0 + 2\,H_2O:\ \log K = -2.6$$

$$\text{At pH} = 8.15 \text{ and } \log\{HCO_3^-\} = -2.79,\quad \log\{CuCO_3^0\} = -6.77.$$

Since $\gamma_{CuCO_3^0} = 1$, this is equivalent to a dissolved copper concentration of about 10.8 ppb. This is about one magnitude greater than the observed copper concentration of normal open ocean water. Furthermore, the highest recorded dissolved copper contents from seawater do not exceed this figure. In other words, the oceans

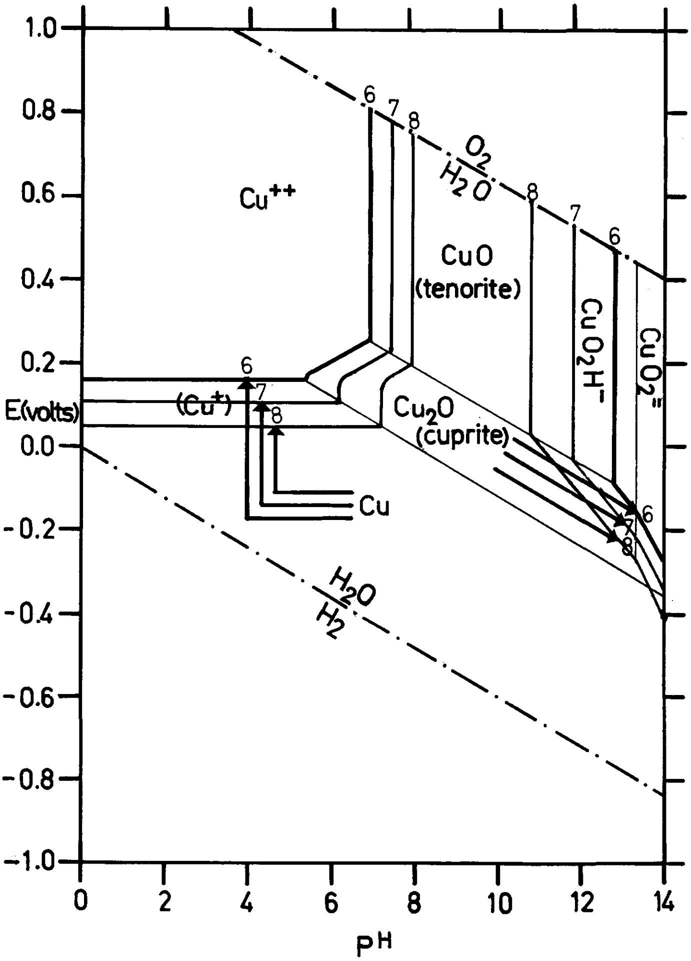


FIG. 2. — *Potential-pH diagram for the* Cu—H_2O—O_2 *system at 25 °C and 1 atm pressure (Rickard, 1970a). The extent of solid stability fields at* pCu = *6,7 and 8 are shown. At pH = 8.15 in oxidizing environments tenorite is in equilibrium with* $\{Cu^{2+}\} < 10^{-8}$. *Helgeson (personal communication) considers that* $\Delta G^0_{Cu^+} = +16.93$ *(rather than +12.0) and* $\Delta G^0_{Cu^{2+}} = +15.39$ *(rather than +15.53) are better values. The overall effect of these changes is to depress the* Cu^+ *field of dominance reducing its geochemical importance.*

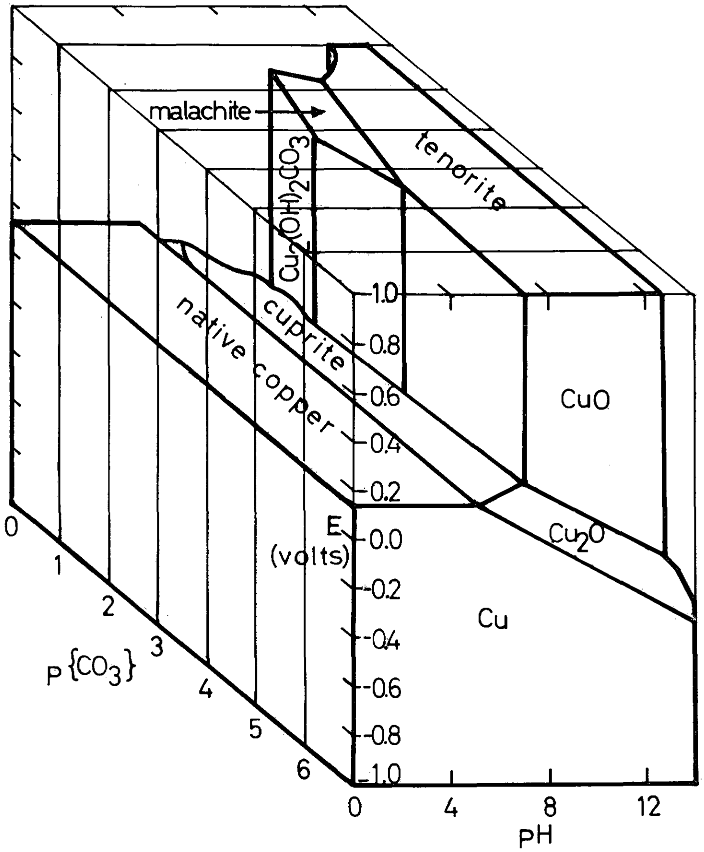


FIG. 3. — *Relationships in the* $Cu—H_2O—O_2—CO_2$ *system as a function of pH,* $p\{CO_3\}$ *and E at* $p\{Cu\} = 6$*, 25 °C and 1 atm pressure (Rickard, 1970a). At* $p\{CO_3\} < 0.9$ *tenorite is not stable.*

are generally undersaturated with respect to malachite, the stable solid copper phase under seawater conditions.

Rickard (1970*a*) discussed a variety of factors that may control or modify the dissolved copper content of ocean waters.

The types of solid compounds used in the thermodynamic studies do not reflect all the possible solid copper forms that may occur in the oceans. Rickard (1970*a*) considered copper in solid solution with such compounds as Fe and Mn oxides and oxyhydroxides, and various silicates. He presented physicochemical and oceanographic evidence suggesting that the effect of these compounds on the dissolved copper contents was either negligibly small or very local.

Removal of copper by adsorption on to inorganic particulate matter was also considered. Krauskopf (1956) had shown that copper was adsorbed in high quantities on manganese and iron oxide and clays. Basu (1958) demonstrated that copper exchanged with hydrogen on clays far more readily than manganese and zinc, but it was the least easily desorbed. Gorlich and Gorlich (1958) showed that copper was adsorbed on calcium carbonate and natural limestone particles.

However, adsorption on inorganic particles is not entirely satisfactory as a process for controlling oceanic copper contents. Intuitively it would seem that far more copper should be adsorbed by inorganic particles in freshwater (c. 7 ppb Cu) and ground water (c. 13 ppb) systems, compared with seawater (c. 0.9 ppb Cu). Since most particulate matter is brought to the oceans by streams, it would seem reasonable to suppose that they would adsorb much copper during their long voyage from the erosional site to the sea. Furthermore, much of this copper would be in a solid form (see discussion on freshwater systems below), and would redissolve on reaching the undersaturated seawater environment. Temple and Leroux (1964) proposed that desorption of copper ions, through competitive displacement of Na^+ for Cu^{2+}, may occur on the passage from fresh to saline environments. Thus it appears as if adsorption on inorganic particulate matter does not control the open ocean copper content. Although much of the copper in near-shore waters may be associated with inorganic particulate matter, it is deposited or redissolved at this point, and does not affect the oceanic dissolved copper content.

As has been mentioned above, the influence of biological processes on the copper content of seawater is unknown. Plankton commonly concentrate copper several thousand times (dry weight) over seawater. However, the sea water reservoir of copper for organisms is almost infinite.

Taking 4×10^{18} g as the mass of all living and undecayed organic matter (both terrestrial and oceanic, Poldervaart, 1955) with a mean copper concentration of 20 ppm, then the biosphere contains about 8×10^{13} g Cu. This is an overestimate

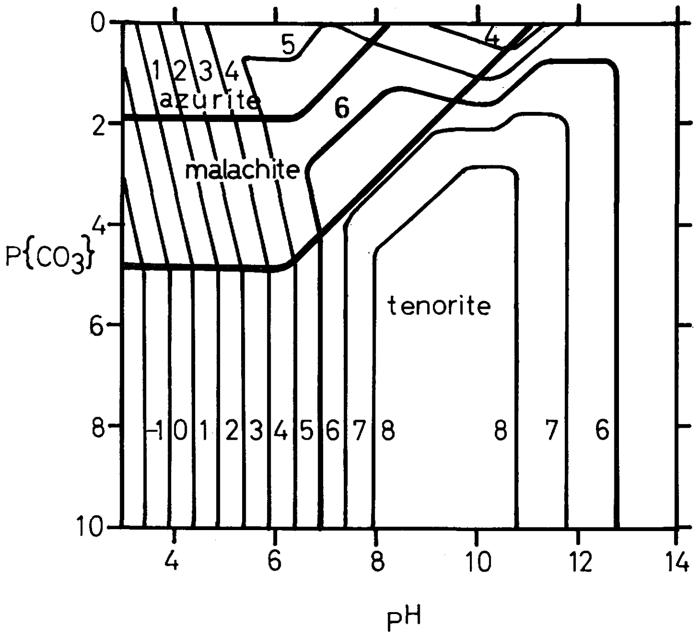


FIG. 4. — *$p\{\mathrm{Cu}\}$ values in equilibrium with tenorite, malachite and azurite in terms of $p\{\mathrm{CO_3}\}$ and pH at 25 °C and 1 atm pressure (Rickard, 1970a). At $p\{\mathrm{Cu}\} > 6$ azurite is not stable and at $p\{\mathrm{Cu}\} > 7$ malachite is not stable even at low $p\{\mathrm{CO_3}\}$* values.

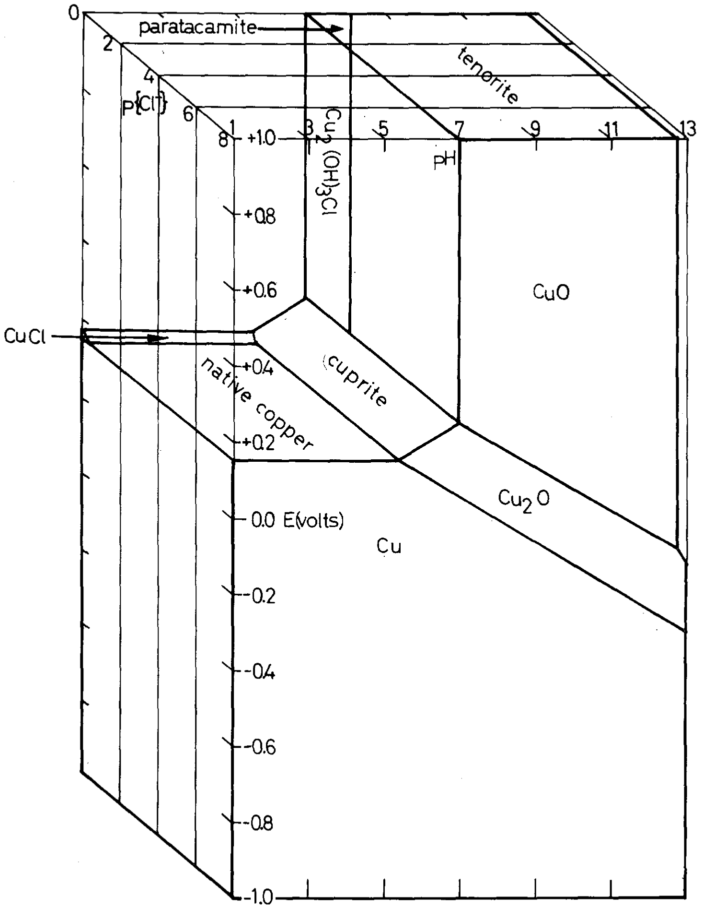


FIG. 5. — *Relationships in the* $Cu—H_2O—O_2—Cl$ *system as a function of pH,* $p\{Cl\}$*, and E at* $p\{Cu\} = 6$*, 25 °C and 1 atm pressure (Rickard, 1970a). Paratacamite is taken as the representative oxychloride, and it becomes stable at* $p\{Cl\} < 2$*.* CuCl *appears on the diagram at very high chloride concentrations.*

since oceanic living and undecayed organic matter probably makes up no more than 70 % of the total, and 20 ppm Cu is a maximum average figure. Since the oceans contain about 280×10^{13} g Cu (Rickard, 1970*a*) copper associated with living and undecayed organic matter makes up less than 2.5 % of the total oceanic copper. It seems unlikely therefore that removal by organisms is the process causing the low dissolved copper content of seawater.

This conclusion is supported by the measurements of Spencer and Brewer (1969). However, the data of Slowey and Hood (1971) suggest that organisms may locally modify the total and dissolved oceanic copper content, and may be the major causes of fluctuations (between 1 and 20 ppb) in the total copper concentrations in seawater.

Copper is complexed readily by a variety of organic compounds. However, Stumm and Morgan (1970) and Dyrssen (personal communication, 1970) have shown by equilibrium computations, that considerable organic ligand concentrations are required for organic copper complexes to become important. Such concentrations may be available in organic sedimentary environments, and possibly, seasonally, in freshwater and local marine systems. In sulfide-bearing organic sediments, these complexes may explain the surprisingly high dissolved copper contents (up to 39 ppb) recorded by Presley *et al.* (1967, 1972) in the interstitial waters.

It is important to note that all the copper compounds discussed with reference to seawater contain cupric copper.

Cuprous ion is highly unstable with respect to water under normal oceanic

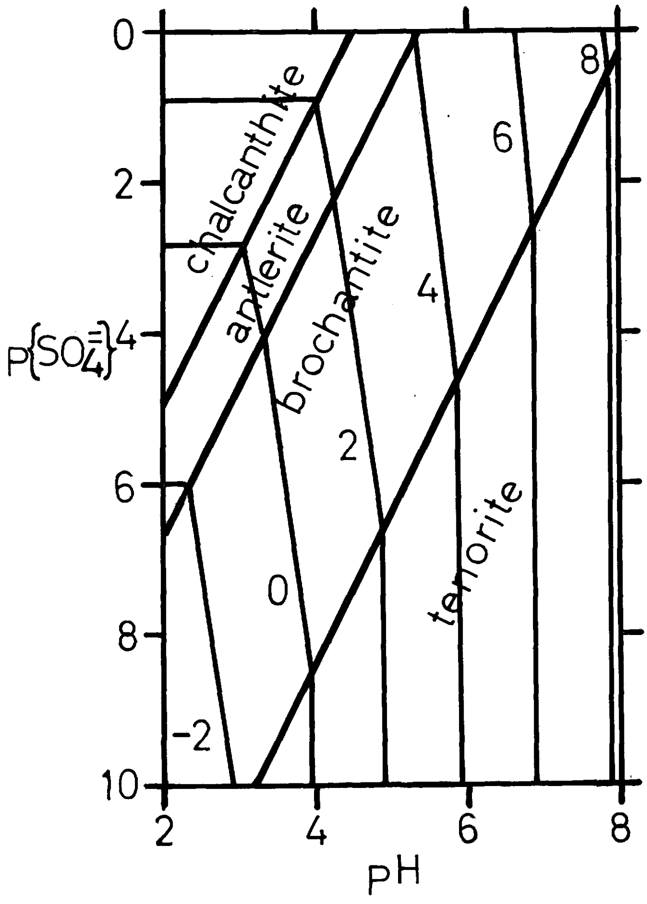


FIG. 6. — *Values of* $p\{\mathrm{Cu}\}$ *in equilibrium with tenorite, brochantite, antlerite and chalcanthite at various* $p\{\mathrm{SO_4}\}$ *values, 25 °C and 1 atm pressure (Rickard, 1970a). Brochantite is the important oxysulfate, and affects the solubility of* Cu^{2+} *at* $p\{\mathrm{Cu}\} < 6$ *and* $pH < 7$ *at low* $p\{\mathrm{SO_4}\}$ *values.*

oxidation conditions. Furthermore, solid cuprous oxides, hydroxides, oxycarbonates, oxysulfates and oxychlorides are either unknown or unstable with respect to the cupric equivalent in normal seawater.

Cuprous copper can be stabilized by complexation. Rickard (1970*b*) considered copper complexation by ammonia in the absence of sulfide and showed that the diamminecuprous ion, $[Cu(NH_3)_2]^+$, increases markedly the solubility of stable cupric solids at concentrations as low as about 1 ppm ammonia. Ammonia production in sediments in the absence of sulfide production is well known in sediments, and the sedimentary microbial ecologic succession (aerobic respiration - nitrate-reduction - sulfate-reduction - methane production) well established. Thus it is possible for dissolved cuprous copper to be supplied to the sulfide zone of sediments. In fact, the presence of high ammonia concentrations could raise dissolved copper contents into the ppm range.

In summary, copper mainly occurs in seawater as undissociated cupric carbonate. Copper is undersaturated with respect to the stable solid, malachite. Adsorbed copper on inorganic particulate matter may be important in near shore areas. Biologic processes may locally modify the copper content of ocean water. In sediments complexation by dissolved organic compounds may be important, and cuprous copper may be stabilized by ammonia complexes.

Freshwater

The average dissolved copper content of streams and lakes is about 7 ppb (Turekian, 1969), or about a magnitude greater than the oceanic concentration.

Riley (1939) pointed out that only about 20 % of all available copper in freshwaters is in the ionic form. A major part of all fresh particulate eroded matter from the lithosphere is primarily deposited in freshwater systems. De Grys (1962) noted that this particulate matter adsorbs much of the available dissolved copper in solution. Since some of this adsorbed soluble copper may become available to the solution it may be assumed that adequate total soluble copper concentrations are available in many freshwater systems to satisfy the requirements of the major solid copper phases under neutral conditions.

The equilibria then controlling copper solubilities have been shown in equations (1) to (4) above, and the conditions needed to satisfy equilibria between these solid phases may be calculated. Rickard (1970*a*) showed that these relationships demonstrate that malachite is stable relative to tenorite at pH = 7 in aqueous environments open to atmospheric carbon-dioxide. Brochantite becomes stable with respect to malachite where

$$\log\{SO_4^{2-}\} > -2.37.$$

Its stability with respect to malachite is described by the relationship

$$2\log\{CO_3^{2-}\} - \log\{SO_4^{2-}\} - 2\log\{OH^-\} = 0.43$$

The solution to this equation is demonstrated graphically in figure 7. Note that in solutions in equilibrium with atmospheric CO_2, brochantite becomes stable with respect to malachite at pH = 5.5-6.5 at sulfate concentrations of 1-100 ppm, but inhibitive sulfate concentrations are required at pH = 7 and above. Riley (1939) showed that between 12 and 27 % of the available copper in Connecticut lakes was in the sestonic fraction. Seasonal variation is probably the greatest single

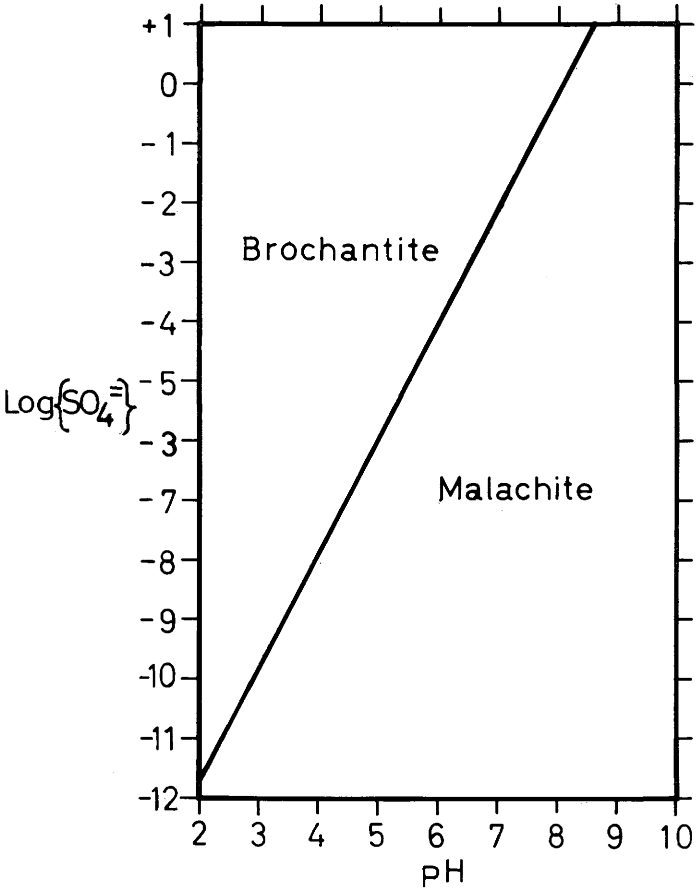


FIG. 7. — *The graphical solution to the equation: 2 log* CO_3^{2-} *— log* SO_4^{2-} *— 2 log* $OH^- = 0.43$ *defining the malachite-brochantite equilibrium, at* $P_{CO_2} = 10^{-3.5}$*, 25 °C and 1 atm pressure Rickard, 1970a). Between pH = 7 and 8, malachite is the stable phase at* $\{SO_4^{2-}\} < 10^{-2}$.

factor controlling the copper content of freshwaters. In particular, increased stream flow during the spring melting means dilution of copper and adsorption on fresh particulate matter; increases in the organic crop in lakes mean fixation of copper in living organisms, and subsequent declines in the organic crop are concomitant with the release of copper into solution. The biological influence on copper in lakes is large, not only through the growth and decay of organisms but also because of the extreme concentration variations of many biologically-related ligands which affect copper solubility.

Copper in freshwater systems is therefore mainly in three forms: inorganic precipitates (particularly malachite, but also brochantite); adsorbed on inorganic particulate matter; fixed in living and undecayed organic matter. Ashry (1973) has shown that copper in Egyptian Nile sediments is preferentially bound to clay-sized carbonate particles, confirming the theoretical considerations of Rickard (1970*a*).

On reaching the oceans, the nature of the stream copper is significantly modified. The solid phases are precipitated in near-shore areas or dissolved, the adsorbed copper is deposited or desorbed, the organic copper is precipitated or decomposed. Only the finest fraction of the most resistant particulate copper reaches open ocean waters.

Subsurface Waters

The variations in chemistry and temperatures of subsurface waters make it impossible to generalize about the nature of the copper present.

Helgeson (1969) has shown that adequate thermodynamic data are available to permit the evaluation of minimal approximations of the solubilities of a number of significant copper sulfides, oxides, silicates, sulfates and carbonates in multicomponent hydrothermal systems up to about 300 °C in the presence of abundant chloride. These calculations, although limited by a lack of detailed thermochemical information about a variety of important mineral phases, demonstrate that the solubilities of stoichiometric covellite, chalcocite, chalcopyrite and bornite are adequate in high temperature brines to account for the formation of copper ore deposits. The dissolved copper in these systems is in the form of copper chloride complexes.

Generally, the proportion of copper in negatively-charged chloride complexes increases with temperature and chloride activity. Furthermore, cuprous copper is stabilized in these chloride complexes.

THE GEOCHEMICAL COPPER CYCLE

Table 11 represents estimates of the average copper concentrations and masses in various geochemical units. Over 99 % of all terrestrial copper occurs in the lithosphere, mainly in mafic igneous and metamorphic rocks. Only about 4 % of lithospheric copper is contained in sediments. However, the average oceanic sedimentary copper concentration is about double the concentration in oceanic and continental mafic rocks, and about five times that of continental granites.

In the hydrosphere, subsurface waters constitute the most important copper reservoir, although the masses of copper in this reservoir and in oceanic water are similar. A significant mass of copper is associated with the biosphere. Although insignificant in long term copper cycles, biological processes are important in short term local redistributions of copper in the hydrosphere. Spencer and Brewer (1969), for example, found no significant seasonal variation in the copper content of surface waters of the Gulf of Maine and the Sargasso Sea that could be attributed to biological processes. Although certain organisms are able to concentrate copper to a great extent, they are operating on what is, essentially, an infinite reservoir of copper in the oceans. Thus high copper concentrations may be localized within organic debris, and within local sediments, but the overall effect of biological processes on the copper content of open ocean waters is negligible.

A summary of the geochemical copper cycle is presented in figure 8. The cycle within the hydrosphere is open, and subject to additions through the contamination

TABLE 11. — *Average copper concentrations and masses in various geochemical units* (RICKARD, 1970*a*)

	Unit mass ($\times 10^{15}$ tons)	Mean copper concentration (ppb)	Mass of copper ($\times 10^{10}$ tons)
Oceanic Rocks			
Sediments	217	140 000	3 000
Mafic rocks	4 400	80 000	38 300
Sedimentary Rocks			
Sandstones	280	100	3
Shales	750	45 000	3 375
Limestones	290	4 000	116
Evaporites	30	20 000	6
Subsurface waters	201	20	0.4
Fresh water	0.3	7	0.000 21
Sea water	1 420	2	0.28
Atmospheric water	0.5	1	0.000 036
Ice	35	1	0.003 5
Continental Igneous and Metamorphic Rocks			
Granitic	10 500	30 000	31 500
Mafic	8 700	87 000	75 700
Living and undecayed organic matter	0.004	20 000	0.000 8

of subsurface waters by magmatic activity and by direct introduction of copper into oceanic sediments through submarine vulcanism. Boström (1973) has presented evidence suggesting that a considerable proportion of the copper contained in active oceanic ridge sediments has a deep-seated origin.

Boström's data support Wedepohl's (1960) and Rickard's (1970*a*) conclusion that continental run-off is not as important in the deep sea copper economy as submarine vulcanism. Although some 70×10^{-9} g Cu . cm^{-2} . yr^{-1} are supplied to the oceans by streams (Rickard, 1970*a*) about 60 % of this is received by the Atlantic Ocean north of 10°S (Schutz and Turekian, 1965). However, the total copper content in Atlantic deep sea pelagic sediments is 3 or 4 times less than in similar Pacific sediments, although the total and dissolved copper concentrations of Atlantic and Pacific seawater are similar.

Considerable evidence is available to suggest that most stream copper is precipitated in near-shore areas. Normally, considerable dilution by other particulate matter occurs and the mean near-shore sediment copper concentration is only 43 ppm.

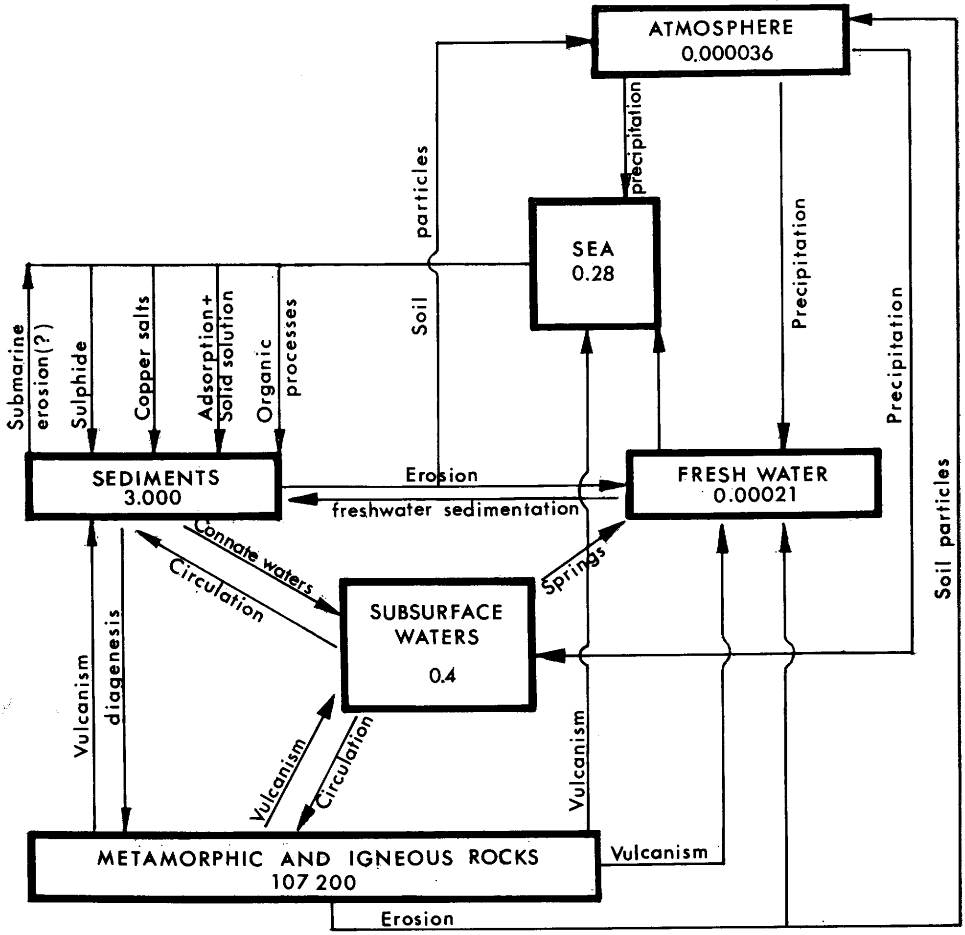


FIG. 8. — *Major units and relationships in the geochemical copper cycle (Rickard, 1970a). Figures represent masses of copper in 10^{10} metric tons.*

GITOLOGICAL IMPLICATIONS OF COPPER GEOCHEMISTRY

Sulfide Ore Formation Models

Dynamic mathematical models of gitological processes are a relatively new method of investigating ore formation conditions, although simplistic mass balance considerations have been an intrinsic feature of economic geology since the beginnings of scientific interest in the subject. By comparison with other natural sciences, it is obvious that the construction of more refined and detailed models will become an important aspect of future gitological studies.

The major aspects of model-making in natural science are demonstrated in figure 9. Observations and measurements from the natural environment are refined and simplified to that the processes involved can be described by a number of mathematical relationships. The solutions to these relationships usually require further approximations before the model is defined. The degree of simplification required at this time depends essentially on the pre-mathematical approximations and assumptions and the speed and data-handling capacity of the computational technique employed. Once constructed, the model is used to examine the investigated system, and the results obtained checked against the original observations. Corrections to the model are then made until it most nearly approximates the natural system, within the limits of the techniques used.

A basic error of approach, which has been widely made in other natural sciences, involves making models for the sake of making models; that is, without any clearly defined purpose. In gitology, it is essential that the model-making purpose is delineated precisely. Any model of ore-formation at the present time must include a series of implicit controversial assumptions, and unless the model is directed towards some specific goal, the results are meaningless. Brief consideration of the model-making scheme of figure 9 demonstrates a number of weak links that are peculiar to the subject of ore genesis.

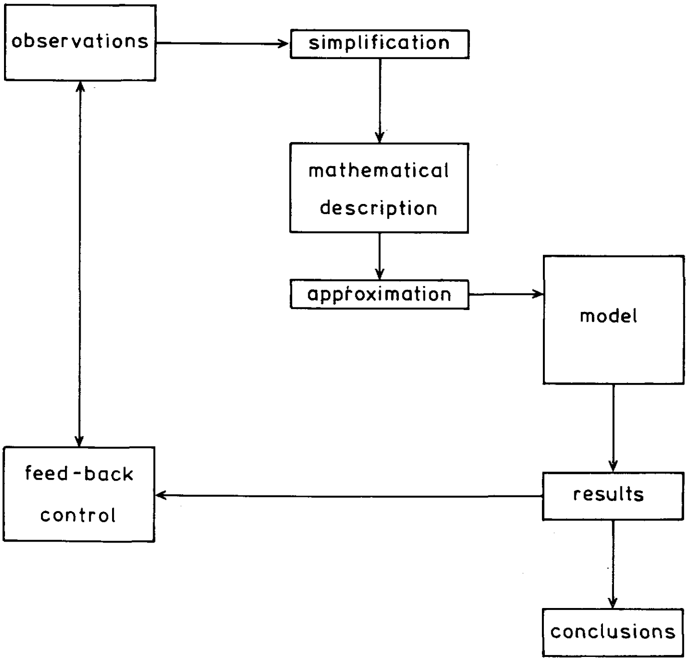


FIG. 9. — *Major operations in the construction of dynamic mathematical models of natural systems. The model itself is essentially a hypothesis, which can be tested with reference to observations. Hypotheses for the genesis of ore deposits can thus be critically examined by this method. Complex natural systems can be most closely approximated using analog computor techniques.*

Gitological modelling is particularly suited to examining the limiting conditions for various ore-forming processes in different environments. In a number of systems, sufficient data are now available for assumptions to be chosen such that maximum and minimum results are obtained. Increased information (in part due to the results of the model-making process itself) will mean that these limits can be increasingly narrowed to some worthwhile approximation to the system.

Synsedimentary Sulfide Ore Formation Models

Ecologic models of the modern natural aqueous environment are well established. The immediate overlap between these ecologic models and gitology lies in the field of synsedimentary sulfide ore formation. Because of this close connection, models of this potential ore-forming system have been the first constructed in gitology. At the present time, no detailed dynamic models of other potentially important sulfide ore-forming systems have been made. Thus, this section is limited to a discussion of models involving biogenic sulfide production.

TABLE 12. — *Calculated formation times for selected stratiform sulfide ores* (after TRUDINGER *et al.*, 1972)

Ore deposit	Total sulfide sulfur (g.m^{-2})	Formation time (yr.)	Average rates of sulfide precipitation (a) (g S.m^{-2}.yr^{-1})
McArthur River	1.9×10^7	$4.1\text{-}16.5 \times 10^5$	11.5-46
Mt. Isa (No. 10/25 ore body)	6×10^5	$0.6\text{-}\ 1.5 \times 10^4$	10-40
Copperbelt (Roan Antelope)	6×10^5	$1.5\text{-}\ 6 \times 10^5$	1-4
Kupferschiefer (Mansfield)	2.3×10^4	$1.9\text{-}\ 7.5 \times 10^3$	3-12

(a) Computed maximum sulfide fluxes from modern sediments do not normally exceed about 10 g S . m^{-2} . yr^{-1}, although, locally, about 100 g S . m^{-2} . yr^{-1} has been recorded in polluted environments (RICKARD, 1973*a*).

Trudinger *et al.* (1972) considered rates of ore deposition for a variety of stratiform sulfide ore deposits for which origins involving microbial sulfide production in sediments have been widely advocated. They considered the metal, sulfide, and organic carbon contents of these ores as well as their approximate dimensions. They assumed that the metals were precipitated from seawater (rather than from within the sediment itself), and assumed 1 cm of lithified ore would take between 75 and 300 yrs to accumulate (by analogy with the Black Sea and Red Sea brines). The results of their computations are summarized in table 12.

The results demonstrate that both the time of formation and the rate of sulfide production are possible if a biogenic hypothesis for ore-formation is assumed. However, their model did not convincingly demonstrate the applicability of the biogenic hypothesis to these ores. They note that the sulfide production has to be continued at a high rate for very long periods of times and that most of the sulfide produced must be fixed as metal sulfides.

A more detailed model of this process was presented by Rickard (1973*a*), based on the work of Berner (1971) on the rate of sulfide production in sediments. Rickard (1973*a*) was primarily interested in how much metal sulfide could be produced in a sediment by bacterial processes. This approach is based on the development of a series of mathematical relationships describing the various processes involved in the system. A number of assumptions were implicit in the model, but these were chosen so as to maximize the results. The Berner-Rickard model includes diffusion as a rate-limiting step. The equations used are summarized in table 13. Equations 1, 2 and 3 (table 13) are used in the development of equation 4. Under the conditions

$$x \rightarrow \infty, \quad C_s \rightarrow C_{s\infty}$$

$$x = 0, \quad C_s = 0$$

and

$$\frac{\partial C_s}{\partial t} = 0$$

the solution to equation 4 is

$$C_s = C_s(1 - e^{-(k/\sigma)x})$$

where

$$C_{s\infty} = \frac{ZC_{co}\sigma^2}{D_s k + \sigma^2}$$

Substituting this relationship in equation 5 (table 13) and simplifying gives

$$J_{so} = -\phi Z C_{co} \sigma$$

In other words, the sulfide flux at the top of the reduced zone in the sediment can be described in terms of the porosity, a stoichiometric constant relating sulfide produced to organic matter utilized, the metabolizable organic carbon content and the sedimentation rate. The maximum amount of metal fixed as sulfide in the sediment can then be found by equation 6 (table 13). For copper (as $CuFeS_2$), a concentration of 1% requires a sulfide flux of at least 10^{-12} g S . cm^{-2} . sec^{-1} at slow sedimentation rates ($\sigma = 10^{-10}$ cm . sec^{-1}). The maximum sulfide flux for this model is about 10^{-10} g S . cm^{-2} . sec^{-1} for maximum metabolizable organic carbon concentrations and minimum sedimentation rates. Under these circumstances, there is no effective limit to the amount of metal sulfide that could be produced apart from the obvious limitations due to the relative densities of the metal-bearing solid reactants and the organic matter requirements. It is not possible to form pure metal sulfide deposits directly by this model.

Rickard (1973*a*) examined the effect of an additional flux of dissolved metal to the sediment. A series of simple relationships were developed based on the assumption of diffusion as the rate-controlling process. In normal seawater, the dissolved copper concentration is about 2 ppb, and sediment copper concentrations of the order of 300 ppm could be obtained by this model. Furthermore, a steady state concentration of about 100 ppm dissolved copper in seawater would be required to utilize all the sulfide produced (fixed as $CuFeS_2$).

The model was applied to various natural systems by Rickard (1973*a*) and was found to give results in agreement with known data. Although the model is a very

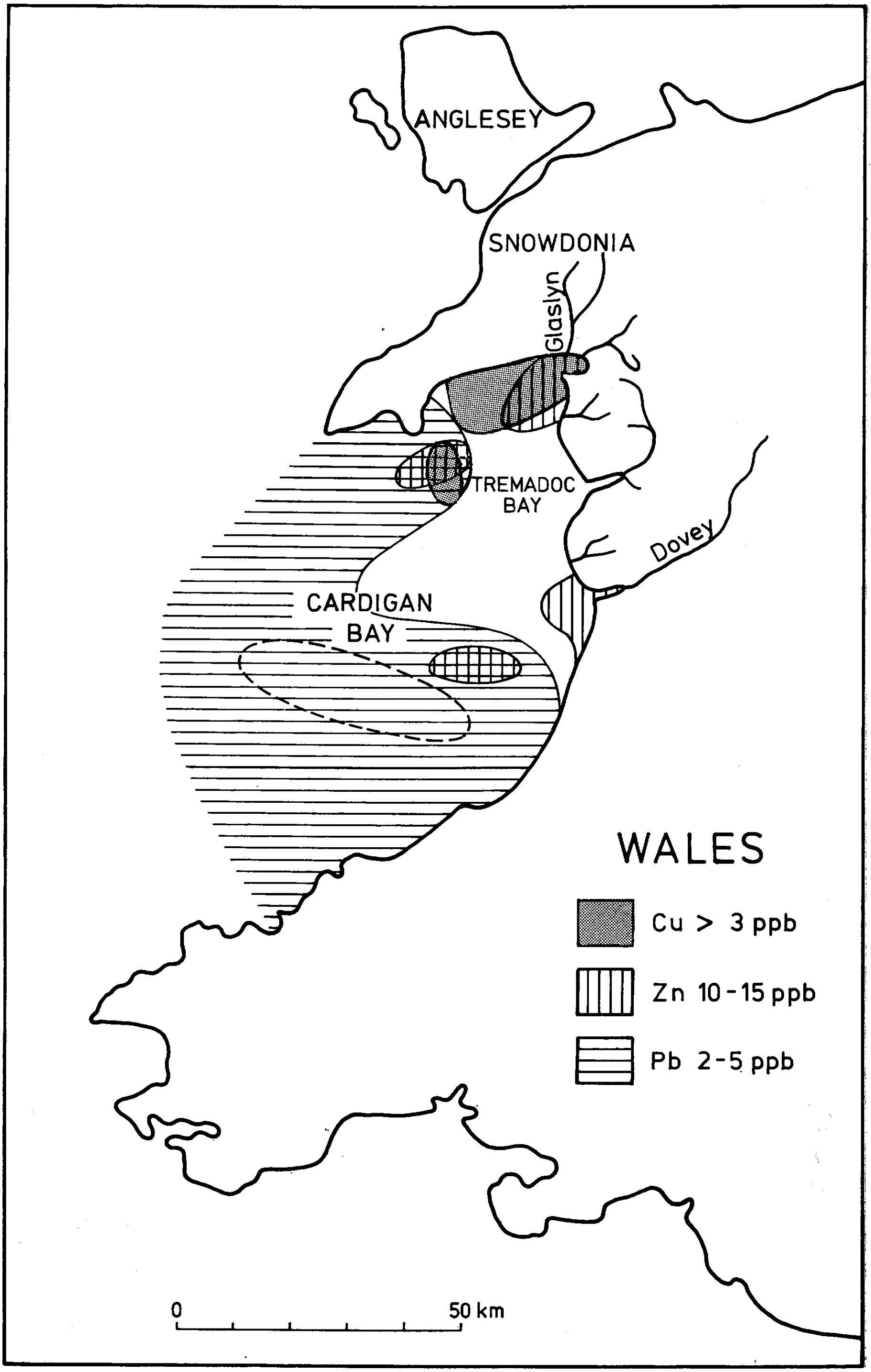
TABLE 13. — *Summary of mathematical relationships used in Rickard's (1973) model for synsedimentary metal sulfide formation*

Process	Relationship
1. Use of metabolizable organic carbon by sulfate-reducing bacteria	$\frac{\partial C_c}{\partial t} = -k C_c - \sigma \frac{\partial C_c}{\partial x}$
2. Rate of sulfide production	$\frac{d C_s}{d t} = Z k C_c$
3. Diffusion	$\frac{\partial C_s}{\partial t} = D_s \frac{\partial^2 C_s}{\partial x^2}$
4. Sedimentary sulfide production	$\frac{\partial C_s}{\partial t} = D_s \frac{\partial^2 C_s}{\partial x^2} Z k C_{co} e^{-(k/\sigma)x} -$ $-\sigma \frac{\partial C_s}{\partial x}$
5. Sulfide flux	$J_s = -D_s \phi \frac{\partial C_s}{\partial x}$
6. Metal sulfide produced	$J_{so} = M C_m \sigma (1-\phi)$

Symbols

C_c = metabolizable organic carbon.
t = time.
k = bacterial rate-constant.
σ = sedimentation rate.
x = depth in sediment.
Z = stoichiometric constant.
C_s = sulfide concentration.
D_s = whole sediment diffusion coefficient.
J_s = sulfide flux.
C_m = metal concentration.
ϕ = porosity.
C_{co} = C_c at $x = 0$.
$C_{s\infty}$ = C_s at $x \rightarrow \infty$.
J_{so} = J_s at $x = 0$.

crude approximation, it does demonstrate that adequate sulfide is commonly available in normal sedimentary environments to produce potential copper sulfide ore deposits, provided there is an adequate supply of the metal. For example, a copper concentration of 1-2 % over a thickness of 10 cm could be obtained from the coincidence in time and space of a submarine metal-rich solution and a sulfidized bottom water.


ANGLESEY
SNOWDONIA
Glaslyn
TREMADOC BAY
Dovey
CARDIGAN BAY
WALES
Cu > 3 ppb
Zn 10-15 ppb
Pb 2-5 ppb
0
50 km

Potential Copper Sulfide Ore-forming Environments

The synsedimentary system modelled in the previous section has certain specific geochemical characteristics. In the absence of a submarine supply, the metal-bearing solution is primarily seawater, and the metals are initially transported by streams.

Normal seawater is far too deficient in copper to act as a potential ore fluid. The model described in the previous section showed that maximum copper concentrations of the order of 300 ppm are to be expected in marine sediments. Seawater can have local high copper concentrations, perhaps up to 20 ppb total copper. However, more than about 11 ppb dissolved copper is improbable since malachite precipitates. In a near shore system with a low sedimentation rate and a high dissolved seawater copper content (10 ppb total copper) a maximum 0.3 dry wt. % Cu could be formed according to the model. If it is further assumed that part of the sedimentation is as particulate copper (malachite) then copper concentrations approaching ore grades may be produced. For such a system to be applicable many unusual features must coincide. In particular, an organic matter rich sediment (probably a black clay) must be deposited very slowly (1 cm/1 000 yrs) in a near shore area fed by a river containing high copper concentrations in solution, with perhaps only a small total particulate load. Peculiar current systems, for example a slow moving mass of water in the centre of a bay, might assist the process. Unusual "vortex-like" currents in the middle of Cardigan Bay, Wales, have been suggested by Abdullah *et al.* (1972) as the cause of high seawater lead and zinc concentrations.

The nature of the deposits thus formed can be examined by reference to transition metal ratios in such systems. Rivers contain on average low Fe/Cu ratios relative to lithologic units. Zinc is commonly associated with organic matter, and thus should be relatively concentrated in organic rich sediments. The ore formed by this process would thus probably contain chalcopyrite, rather than pure copper sulfides, and be associated with sphalerite. It is possible that this type of situation could be more meaningfully examined with respect to Kupferschiefer-type ores.

A summary of the more important features of seawater copper, lead and zinc concentrations in Cardigan Bay is presented in figure 10. The data are extracted from Abdullah *et al.* (1972). A synthesis of the data for this bay shows a strong zonation of metals in the near shore waters. Particularly noticeable is the almost complete separation of copper from lead. Copper is concentrated in the Tremadoc Bay area around the outflow dominated by the river Glaslyn. Lead in this area is at almost open ocean concentrations, but is concentrated up to 5 ppb in the centre of Cardigan Bay, where the copper concentration is down to almost open ocean levels. Zinc follows copper in the Tremadoc Bay zone, but similar concentrations (15 ppb) are found at the mouth of the river Dovey and in the centre of Cardigan Bay.

FIG. 10. — *Copper, lead and zinc distributions in the water of Cardigan Bay (March, 1971), compiled from data extracted from Abdullah* et al. *(1972). The drainage system from the weakly mineralized Snowdonia region is marked. Copper and lead are particularly well separated, and zinc does not follow copper exclusively. The dashed line delineates an area with lead concentrations of 3-5 ppb, controlled by "vortex-like" currents in the centre of the bay. The run-off is characterized by containing negligible industrial and domestic effluent.*

This separation, especially of copper and lead, might be of importance in any discussions of stratiform copper sulfide ore formation; it is particularly interesting in the context of Kupferschiefer-type ores. It must be emphasized that there are no data concerning any metal zonation in the sediments related to the seawater variations, but at these low concentrations such an effect may not be measurable anyway. Even so, any proposed sedimentary metal zonation related to seawater as the metal-bearing fluid must be primarily related to metal zonation in the water itself. In this context, the distribution of copper, lead and zinc in the near shore waters of Cardigan Bay may be extremely significant, especially since the relatively high metal concentrations in this area are due to run-off from a weakly mineralized continental area. The reasons for the separation of copper and lead are not known. It is apparent that copper is mainly precipitated on entering the bay, but the reasons for the lead distribution are not clear.

High copper concentrations are present in Pacific pelagic sediments. Boström (1973) reported up to 1 800 ppm, on a carbonate-free basis, from active ridge sediments. Copper sulfide rich rocks have been found on the Carlsberg Ridge and native copper has been reported from the basalt-sediment boundary in the Atlantic and Indian Oceans (Boström, 1973). Nagle *et al.* (1973) report another find of native copper associated with a spilite-keratophyre association of possible marine affiliation from the Lesser Antilles. Even though the spilite-copper ore association is now well documented, there are still some geochemical problems connected with it (Boström, 1973).

From a geochemical point of view, there seem to be three major problems associated with the formation of copper sulfide bodies of the type found in the Central African Copperbelt: the high copper concentrations, the abundance of cuprous sulfides and the relative paucity of iron sulfides.

The only solution containing adequately high copper contents even approaching that intuitively necessary for the formation of Copperbelt-type ores are the Salton Sea brines. These are associated with a paragenesis which appear widely divergent from the stratiform copper sulfide ores. However, subsurface brines vary considerably in composition. The aforementioned Cheleken brine, for instance, contains up to 15 ppm copper, even though it is mainly associated with lead deposition. It seems therefore, by a process of elimination, that subsurface waters, not necessarily of magmatic origin, could contain sufficient copper and sufficiently unusual Fe/Cu ratios to account for the formation of this type of orebody.

Rickard (1972, 1973*b*) demonstrated experimentally that if sulfide is added to a cupric salt, a cupric sulfide precipitates at low temperature. As in many metal redox reactions, the rate of precipitation is far greater than the rate of reduction, and when the precipitate is formed, it is very slow to be reduced. Reduction can take place during late diagenetic or low-grade regional metamorphic conditions. However, a cuprous salt is required for the direct precipitation of cuprous sulfides. Cuprous copper is not abundant in the hydrosphere because of the instability of cuprous ions in water. It is possible for cuprous ions to be stabilized by complexing (e.g. with ammonia), but this must be an essentially small scale process in sedimentary environments. However, cuprous ions can be complexed in concentrated chloride solutions, especially at higher temperatures. Thus in those stratiform copper sulfide ores where cuprous sulfides (chalcocite, djurleite, digenites, etc.) are major minerals, it is unlikely that seawater or freshwater are major copper-transporting agents. However, it is possible to transport monovalent copper in brines.

CONCLUSIONS

A simple and direct approach to aspects of low temperature copper geochemistry relevant to the formation of stratiform copper sulfide ores has been presented in the above discussions. Excluding the copper-rich massive pyrite ores, the stratiform copper sulfide ores of interest have two major characteristics: (1) a high concentration of copper and (2) a varying degree of separation of copper from related transition metals.

Concentration factors of the order of 10^3 are required to produce a copper ore from the normal background crustal copper contents. In certain lithologic units, these concentration factors are reduced to as little as 10^2, on average. These low concentration factors are associated with deep sea clay sediments. Boström's (1973) work has further shown even higher concentrations of copper (up to 1 800 ppm, on a carbonate-free basis) associated with active submarine ridges in the Pacific. Concentration factors lower than 10 would be required to produce ores from such systems. The proposition that some stratiform copper ores would be likely to be associated with such systems is supported by discoveries of native copper and copper-sulfide-rich rocks in modern marine environments and the widespread copper ore-spilite association.

No other lithologic systems of immediate interest to copper sulfide ore formation are apparent from the general analysis of the crustal distribution of the element. Natural waters containing relatively high copper contents are known, however. Many geothermal fluids associated with modern metal enrichments do not seem to be entirely consistent with the requirements for stratiform copper sulfide ore formation. However, subsurface waters vary greatly in composition, and it is chemically feasible for solutions, possibly of connate and meteoritic, rather than magmatic, origins to provide the copper concentrations necessary for ore formation.

Although seawater is normally an unsatisfactory copper ore-forming fluid, dynamic models of sedimentary systems reveal that it is possible to produce copper sulfide concentrations of interest in local areas where the copper concentration is anomalously high (10 ppb). Higher copper concentrations (up to 5 ppb) are known in near shore waters associated with run-off from weakly mineralized continental areas. These copper concentrations are further associated with a separation of copper from related transition metals. In particular copper is rapidly removed in near-shore areas by precipitation, and this feature of copper geochemistry has been substantiated by both theoretical considerations and actual observations. Furthermore, the Fe/Cu, Mn/Cu, Zn/Cu and Ni/Cu ratios are generally very low in streams compared to lithologic units, implying a possibility for a general relative copper enrichment in stream-fed near shore environments.

The immediate relevance of the biophilic nature of copper to ore-formation processes is not apparent from present analytical data. Although copper is concentrated to a high degree in certain specific organisms, populations of marine organisms have copper contents such that they effectively dilute some sedimentary copper concentrations. It seems possible that relatively homogeneous populations of copper concentrating organisms could be produced in certain ecosystems which could effect a sediment copper enrichment. A more detailed investigation of the ecology of individual copper concentrations would seem to be necessary before their relevance to problems of ore genesis can be evaluated.

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