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1960/64

BIOGENIC SULPHIDES

by

L.G.M. BAAS BECKING & D. MOORE

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1. SUMMARY

Experiments have been carried out at the laboratory of the Bureau of Mineral Resources in Canberra on the preparation of sulphide minerals by biological methods with the following results:

a. Covellite, digenite, argentite, sphalerite and galena were prepared by bacterial sulphate reduction in artificial seawater on hydrogen and lactate media from carbonates, oxycarbonates and, in the case of silver, from the chloride. Chrysocolla was also used.

b. While nickel and cobalt yielded black sulphides, powder diagrams yielded no identifiable mineral.

c. Rhodochrosite and mercuric carbonate did not produce sulphides.

d. Mixtures of iron and copper oxides always yielded iron sulphides plus covellite. Neither bornite nor chalcopyrite could be obtained.

2. INTRODUCTION

Almost 130 years ago Daubrée, followed by de Sénarmont, (both cited by Clarke, 1916) endeavoured to prepare minerals by chemical methods. "Synthetic" mineralogy has become an integral part of this discipline. Several cases could be cited in which truly biogenic mineralas were obtained; but a systematic approach to biosynthesis of minerals is lacking.

Many biological reactions are in the nature of accumulations, by which is meant a manifold concentration, by the organism, of an element from the outer environment. These reactions cannot be repeated by simple chemical means. Some oxidative reactions, furthered by micro-organisms, may be duplicated in the laboratory. Often, the rate of the chemical reaction is much lower than that of the biological reaction. Reductions of inorganic compounds are known as industrial and laboratory processes and may be carried out under sterile conditions. Exceptions to this are, of course, the reduction of carbon dioxide to sugars, which has never been achieved in the laboratory, and the reduction of sulphates to sulphides, which can only take place in the wet way by very roundabout methods.

In nature, the sulphate reduction is invariably bacterial, whereas the reduction of sulphur to H_2S may be achieved in a variety of ways. In this paper the formation of sulphide minerals by sulphate reduction is considered.

From the positive results obtained it may be concluded that, under certain natural conditions, several sulphide minerals may be formed by sulphate reduction. We are sure that our failure to obtain results with nickel and cobalt salts is rather due to our ineptitude than indicative of some fundamental natural phenomenon. Some of our results are contrary to theory, others cannot be duplicated by chemical means. However, it would be too early to designate sulphate reduction as a main factor in ore formation before we have adduced more arguments. The greatest difficulty seems to be the concentration factor. We know of very few places (e.g. near Pernatty Lagoon, S.A.) where a metal (copper) is present in sufficient quantities in the oxidized form to account for an accumulation of sulphides. This accumulation requires a still unstudied mechanism.

3. BIOLOGICAL AND CHEMICAL APPROACH

"Synthetic" mineralogy probably finds its origin in a publication of W.B. and R.E. Rogers, who, in 1848, described the action of water at a reasonable temperature (60°C), on minerals (cited by Clarke, 1916). They emphasized the role of CO_2 as a solvent. The synthetic mineralogy, as developed by Daubrée (articles in the Comptes Rendus 1849-1864, culminating in his Etude Synthétique de Géologie Experimentale (1876)), as well as the contemporaneous work of H. de Senarmont (1851), is concerned exclusively with high-temperature reactions, and the results cannot be applied to processes taking place in the sedimentary environment. Syntheses "in the wet way" have remained rare. Of the 56 artificial syntheses of simple sulphides mentioned in Dana's handbook (1944), 48 describe thermal reactions and only 8 are concerned with aqueous, low-temperature systems. We cannot help but feel that the support of synthetic mineralogy has been chiefly of use to those studying hydrothermal and magmatic reactions, and that the aqueous environment has been neglected. Possibly this is one of the reasons why, in the study of ore-bodies, there has been, maybe, a slight over-estimation of the magmatic and hydrothermal factors. Moreover, these thermal systems apply to temperatures and pressures which, as independent variables, have been studied only in a few cases (e.g. Allan, Crenshaw Larsen and Johnston, 1912 for the pyrite system, Juza and Bilz, 1932 for the sulphur-sulphide system). About the thermodynamic systems in these regions we are ill-informed. We do not even know whether the free energy and pH concepts, derived for the normal aqueous environment, apply at high temperatures and pressures.

At the beginning of this century, after the work of the (chiefly) French chemists, it was comfortably concluded that the composition of the inorganic environment was pretty well known. This was an opportune thought, as attention could be diverted to the more "modern" things. We know now that this conclusion was highly premature. The period of this old-fashioned "bread-and butter" chemistry is by no means over: free iodine, iodates, nitrous oxide, perchlorate, and hydrogen peroxide, as found since, are only an expression of the whim of the investigator and not a systematic attempt to catalogue, as it were, the inorganic environment. Synthetic mineralogy will remain highly one-sided if such a survey remains incomplete, apart from the fact of our predilection for thermal reactions, which has also been detrimental to the development of our knowledge of the sedimentary environment.

In one of his many prophetic statements Pasteur said that it seemed to him that the influence of the infinitely small (organisms) was infinitely great. A century ago geology was a comfortably "sterile" science, in spite of palaeontology and apart from a few inopportune and disobliging exceptions like coal mines and coral reefs. Under the influence of such masters as Winogradsky and Beijerinck this picture has changed completely. It may be said that the pendulum has swung to the other extreme position; there is a tendency now to ascribe a number of geological processes to microbial action without a thorough investigation of the geochemical and geobiological factors involved. Vague statements as to the virtues of micro-organisms in geological happenings are of very little use to us. On the contrary, as they are discursive, and often not based on experiment, they give welcome fuel to those critics, who, subconsciously perhaps, want to maintain the "sterile" status quo ante. There is ample experimental evidence to show that many sedimentary processes are abiological; the oxidation of pyrite to ferrous sulphate and of the iron monosulphides to sulphur and hematite have been shown to take place spontaneously under sterile conditions: there is no need to invoke bacterial action to account for them. A synthetic mineralogy, based upon biological reactions, has to take this into account.

A systematic approach to a "biological" mineralogy has not been made. The biological formation of limestone by coral animals and by coral algae was proposed before Darwin wrote his classical monograph and both aragonite and calcite were soon recognized as biological products. A special bacillus was thought by Drew (1914) to be active in lime deposition and his "Bacillus calcic" has since haunted geological literature, although a special lime-depositing bacterium does not exist. Alderman (1956-57) has shown that dolomite may be precipitated by the photo-synthetic action of plants. The biological origin of the Texas sulphur deposits was proposed by Tan Tek Hok, as long ago as 1927; this opinion has since been confirmed. Miller (1950) succeeded in preparing various metal sulphides by sulphate reduction. He failed to obtain copper sulphide and no specific minerals were identified. Much more scattered evidence may be adduced, but a systematic approach has been lacking.

4. BIOLOGICAL AND CHEMICAL PROCESSES

As stated above, happenings in the aqueous sedimentary environment are partly biological, partly chemical. There are, amongst the geobiological processes, many that may be reproduced in the laboratory by chemical means. In the absence of bacteria many oxidations may proceed, albeit with reduced velocity, such as the oxidation of ferrous to ferric sulphate (unpublished) and oxidation of sulphur. Certain reductions are also spontaneous, e.g. the formation of H_2S from sulphur (de Rey-Pailhade, 1906). This reduction is exothermic, and the beneficial effect of sulphur dust in the treatment of plant disease has been ascribed to this process. There are, however, biogenic reactions that cannot be easily reproduced in the laboratory: for instance, the photosynthetic carbon dioxide assimilation has eluded, thus far, any attempts at reproduction *in vitro*.

Amongst those that require unusual substances, acting at boiling temperature, in order to proceed, we may mention the reduction of sulphate to sulphuretted hydrogen. We realize, since 1895, that bacterial agencies carry out this reduction at room temperature. Keeping in mind the enormous quantities of ferrous sulphides occurring in the black muds in estuaries and elsewhere, it appears that this reaction is of prime geochemical importance. Before the discovery of the causative organism, in 1895, by Beijerinck, the handbook on hygiene and on water treatment ascribed the occurrence of these sulphides to the decomposition of proteins; but, contrary to the opinion of some recent biochemists, proteins are very scarce in the natural aqueous environment. Most of the bacteria in these environments live on a minimum diet, and the juicy culture media, usually prepared by the bacteriologist, containing glucose, or peptone (or even more complicated substances in medical bacteriology), are hardly ever met with in the natural environment. This is why those forms that may develop without organic substances (the autotrophs) come to the fore in the natural environment.

5. SULPHATE REDUCTION

(a) General

Desulphovibrio desulfuricans or *Clostridium desulfuricans* is the chief agent in the reduction of sulphates. It is an anaerobe. Baas Becking and Wood (1955) found that it cannot occur under a pH of 4.2 (peat bogs), and Kaplan (private communication) found it at pH's well over 10 in mud from Searles Lake, California. The highest electrode potential at which it may develop is + 110 millivolts, a number since confirmed by more extensive tests. It may actually generate potentials as low as -500 millivolts. There is evidence that, in this case, the cause of these low potentials is not the sulphuretted hydrogen but an addition compound of ferrous sulphide and sulphuretted hydrogen (Baas Becking, 1956). Like all *Clostridium*-like organisms, the microbe is a spore former and, under certain conditions, highly thermotolerant. Like *Clostridium pastorianum* it is able to reduce atmospheric nitrogen to the ammonia level. Its development is apparently inhibited in brines rich in magnesium salts, and selenates (maybe because of a competitive action) also inhibit the reduction (Postgate, 1955).

In the highmoor waters of Tasmania sulphate reducers were not encountered. This is apparently due to the almost total absence of sulphate in these waters, for addition of sulphate to the moor waters yielded sulphate reduction. Certain strains of the sulphate reducers are able to persist and develop in an inorganic medium, if hydrogen is provided. This autotrophic existence is probably more common than has been assumed. Most experimental work has been carri out with organic media, lactate or acetate being most suitable hydrogen donors. Figure 1 shows the development of a purified culture of sulphate reducers in a hydrogen atmosphere on filtered seawater (Gunnamatta Bay, N.S.W.) to which some ammonium magnesium phosphate was added. It is also possible to generate hydrogen in the seawater by means of steelwool or of zinc wire (Figure 2). If the presence of iron compounds in the medium is undesirable, the steelwool may be wrapped in cellophane and evacuated to remove the air. The iron compounds, insoluble at the pH of seawater, will remain inside while the hydrogen will diffuse out. In our work we made use of a strain capable of developing either on hydrogen or on organic matter; this was isolated from estuarine mud at Port Hacking, N.S.W. After three transfers on a steelwool medium the culture was used for the production of metal sulphides. Although, in laboratory bacteriology, the use of pure cultures is indicated, in the study of natural processes (Winogradsky, 1945) such a practice may lead to erroneous results, as in nature we usually find an assemblage of microbes instead of one actor. In our work this assemblage has probably been reduced to few, and maybe to one component, owing to the special nature of the medium into which they were repeatedly transferred. Recent work on the oxidation of pyrite (unpublished) has shown the complexity of the assemblage of iron and sulphur bacteria taking part in this process. It is likely, however, that sulphate reduction, as far as the number of organisms is concerned, is more like a monologue than a play.

(b) Ferrous Sulphide from Metallic Iron

In active cultures with steelwool prepared with artificial seawater, black sulphide is formed within one week at $30^{\circ}C$. The artificial seawater, which may be sterilized by heat, was prepared as follows:

Tapwater	100 g
NaCl	3 g
Ammonium magnesium phosphate	.075 g
Potassium sulphate	.350 g
Soil extract	5 ml
Calcium carbonate	10 g

(natural seawater is saturated with lime)

After autoclaving, the suspension was shaken for 24 hours, the lime was allowed to settle and the supernatant decanted. The solution showed a pH of 8.2, total base 2.5 10^{-3}n, like seawater. An adequate supply of both sulphate and bicarbonate was present. For a 250 ml stoppered bottle, lg. of steelwool, degreased with carbon tetrachloride, was added. The black sulphides formed oxidize rapidly in air with the formation of iron oxide and sulphur (see also Verhoop, 1940). When these sulphides were dehydrated by repeated treatment with absolute alcohol, a black powder was obtained, which could be kept for weeks in a sealed tube. In a moist atmosphere it oxidized rapidly and even the manipulations necessary for the preparation of the X-ray photograph caused enough change to prevent an interpretation of the powder diffraction pattern. Iron powder may be substituted for steelwool, although the reaction is slower, probably owing to the reduction in surface. When using organic media (artificial seawater) with 1% sodium lactate or acetate, iron was added to the medium as strengite or as hematite. The phosphate was the more successful.

(c) Pyrite and Marcasite from the Monosulphides

This process is an oxidation and considered by us as a hydrogen donation to an external acceptor. However, experiments on this process are still under way and it would be premature to report on them here.

(d) Covellite from Malachite via Copper

Miller (1950) failed to obtain sulphate reduction in the presence of copper hydroxy carbonate. We used copper phosphate, without success, but in our experiments, malachite apparently yielded only little soluble copper and the toxic effect was minimized. Using malachite, metallic copper appeared in both steelwool acetate and lactate cultures within three days incubation at 30°C. A black precipitate appeared after 5-7 days. This precipitate was digested with 10% acetic acid and centrifuged and washed five times. The X-ray powder pattern was that of covellite.

Table 1. Powder data for Covellite

Data from the literature

d/n	3.26	3.03	2.81	2.71	1.89	1.73	1.56
I	12	20	60	14	100	10	30

From hydrogen,
15.4.59

d/n	3.19	3.03	2.78	2.71	1.89	1.73	1.56
I	10	50	40	10	100	5	10

Bateman (1950) postulates its supergene formation from H_2S and copper sulphate. This cannot occur as a biological process, as copper sulphate is highly toxic to life.

(e) Covellite from Chrysocolla

Pernatty Lagoon (S.A.) contains a strong brine from which acid-insoluble black sulphides may be separated. When this Lagoon was visited (May, 1958 with Mr. Haddon King and Mr. D. O'Driscoll) the abundance of copper and of manganese ore in the surrounding hills appeared to be most striking. The copper was chiefly present as silicate (chrysocolla). On a lactate medium with artificial seawater chrysocolla proved to be sufficiently insoluble to allow sulphate reduction to take place. After a few weeks a copious black precipitate was formed, which consisted of covellite. The abundance of chrysocolla in the region could result in the formation of a large amount of covellite if the water level should rise, and anaerobic conditions prevail. This is the only case observed by us where enough oxidized ore was present to allow for an appreciable accumulation of sulphide to be formed under appropriate conditions.

(f) Digenite from Cuprous Oxide

Chalcocite may be prepared by the action of heat upon H_2S and cuprous salts (de Sénarmont, 1951). Existing claims for its preparation in the wet way have been discredited. Bacteria, though not causing the formation of chalcocite, actually form the cuprous-cupric sulphide digenite when cuprous oxide is subjected to sulphate reduction. A lactate medium was used and the formation of the digenite preceded without the visible intermediate of native copper. The cuprous oxide was prepared by the reduction of an alkaline copper sulphate solution in the presence of tartrate by glucose. The reaction takes slightly longer than the formation of covellite from malachite (about 10 days at $30^{\circ}C$). The X-ray powder diffraction patterns (see also Figure 3) were convincing.

Table 2. Powder data for digenite

Data from the literature

d/n	3.20	2.78	2.17	1.96	1.67	1.39	1.25	1.13	1.07
I	20	30	10	100	20	10	10	20	10

Culture

25.6.59

d/n	3.19	2.75	2.16	1.95	1.67	1.38	-	1.13	1.06
I	30	30	5	100	20	5	-	10	5

(g) Argentite

Both from the chloride and from the carbonate silver sulphide was formed on acetate and on lactate media. The typical purple colour of native silver appeared first, although the cultures were placed in a dark incubator. With the increase in sulphide the native silver seemed to decrease. The sulphide was extracted with ammonia and washed several times after centrifuging, and the powder spectrogram obtained. About the identity of the product formed with argentite there is no doubt, as the following results show:

Table 3. Powder data for argentite

Data from the literature

d/n	3.40	3.08	2.83	2.59	2.43	2.37	2.21	2.08	1.71
I.	40	40	80	100	80	60	10	10	10

Black precipitate

25.6.59

d/n	3.42	3.08	2.85	2.60	2.45	2.39	2.22	2.09	1.72
I.	10	20	20	100	60	20	10	10	10

Though several authors agree about the presence of argentite in supergene environments, Bateman (1950, p.39) holds that argentite and acanthite represent respectively the high and low-temperature forms of Ag_2S with an inversion point at 179°C. According to him much of what is called argentite in the supergene environment is really acanthite. Nevertheless, bacteria undoubtedly prepare argentite from silver chloride and silver carbonate at low temperatures.

(h) Galena

This is probably the easiest sulphide to make ny bacterial sulphate reduction. It is formed within four days at 30°C in media containing either hydrogen, lactate, or acetate. Both the carbonate and the hydroxycarbonate may serve as a source of lead. The precipitate is easily cleaned in weak acid after removal of the carbonate with 10% KOH. The identification is certain, as the following table shows:-

Table 4. Powder data for galena

Data from literature

d/n	3.42	2.96	2.08	1.79	1.71	1.36	1.33	1.22
I.	80	100	90	90	80	70	90	90

Precipitate

25.6.59

d/n	3.41	2.95	2.10	1.79	1.71	1.36	1.33	1.21
I.	80	100	60	40	20	10	20	10

Bateman contests the supergene formation of galena.

(i) Sphalerite

The active bacterial culture used in these experiments developed on artificial seawater without organic matter, when zinc wire was supplied (Figure 2). White blobs formed on the wire after 3 weeks at ca. 20°C. These blobs developed H_2S when treated with acid and formed gas with sodium azide-iodine. Apparently a sulphide was formed which was assumed to be sphalerite, as the occurrence of wurtzite is unlikely at these low temperatures. As free zinc does not occur in nature, the experiment has little geobiological significance. It only shows that the strain of sulphate reducers used by us is able to utilize hydrogen and it provides us with a method for the culture of sulphate-reducing bacteria if the use of iron has to be avoided.

(j) Sphalerite from Smithsonite

Although a sulphide was formed within a week at 30°C on organic media, its identity with sphalerite could not, at first, be established, as the sulphide is soluble in weak acid. Because of this, a large amount of smithsonite remained in the precipitate. Using older cultures and gravity separation, followed by repeated centrifugation, we finally obtained a light grey material which yielded a rather blurred powder diffraction pattern with the characteristics of sphalerite. According to Bateman (op cit), however, this mineral is never of supergene origin.

Table 5. X-ray Powder data for Sphalerite

Type specimen

d/n	3.95	3.12	2.70	1.91	1.63	1.56	1.35	1.24	1.21
I.	30	100	70	90	90	30	70	80	30
	1.11	1.04							
	90	70							

From culture

d/n	3.12	2.70	1.91	1.63	1.35	1.24
I.	100	40	100	90	10	20
	1.10	1.04				
	20	20				

(k) Negative or uncertain results

Though copious black precipitations were formed when nickel carbonate was incubated in organic media and though positive sulphide tests were obtained on these precipitates, we have been unable to prepare an identifiable powder diagram from them. Cobalt carbonate behaved in a similar way.

Mercuric carbonate could not be reduced to cinnabar by bacteria. In this case no H_2S was formed. The toxicity of the mercury may account for this.

Although copious sulphate reduction occurred in cultures with rhodochrosite, neither alabandite nor hauerite was present in the precipitates. As will be stated in the discussion of the results, the electrode potential generated by the bacteria must have been too high to allow for the formation of these sulphides. As this conclusion is entirely based on free energy values and not on experimentation, the absence of the manganese sulphides in the final preparation may equally well have been due to our inexpert handling of the samples.

(l) Failure to Produce Bornite and Chalcopyrite

Using organic media and combinations of cuprous oxide or malachite to which we added either haematite or lepidocrocite, the black precipitates formed never showed the powder spectra of the copper-iron sulphides, but only the spectrum of covellite. These experiments, carried out at 30°C, were repeated under a variety of external conditions with the same results. This is important as both bornite and chalcopyrite are classed as hypogene.

The pioneer work on the formation of sulphides was done by Miller (1950), who obtained sulphides of antimony, bismuth, cobalt, cadmium, iron, lead, nickel, and zinc by sulphate reduction, the latter two with difficulty. No positive identification of the products was made, apart from titration of the liberated H_2S after acid treatment. Miller failed to obtain sulphate reduction in the presence of malachite, while we found this compound to be a suitable source for covellite. The discrepancy in our results may be due to a difference in strains or to a difference in culture media. Miller used 1% NaCl whereas we used 3%, and, in his cultures, the sulphate concentration was about 6-10 times higher than in the artificial seawater used in our work; he used higher lactate concentrations as well. The influence of the chloride and the sulphate concentration has to be investigated further. As appears from this paper, unidentifiable sulphides were formed from nickel and cobalt salts. Without a proper X-ray identification the work has little significance.

6. DISCUSSION

The formation of native copper and of native silver as a "half-way house" between the oxidized and the reduced state is significant. Silver is definitely supergene (Clarke, 1916, p.649) and may very well be formed in a way similar to that appearing in our experiments. The formation of native silver from its sulphides is called "a reduction" by Clarke, although it is definitely an oxidation. At very low potentials, below the potential region of the sulphide, there may be another zone in which native silver is stable: this region should be definitely magmatic, however.

In order to obtain an overall picture of our results the electrode potentials of the reaction sulphide-sulphate were calculated from the free energy data (Latimer, 1952). The equilibrium lines for 25°C are drawn within the confines of the natural aqueous environment as outlined by Baas Becking, Kaplan, and Moore (in press) and by Baas Becking and Moore (unpubl.). Table 7 shows the nature of these equilibria.

Table 7. Equilibria for the oxidation of various sulphides

$$\text{Met S} + 4H_2O \rightleftharpoons \text{Met SO}_4 + 8H^+ + 8e^-$$

	E_0 in millivolt	$E_{pH=8}$ in millivolt	pH below which sulphide soluble
HgS	+ 525	+060	
Ag_2S	" 482	+015	
Cu S	" 436	-045	
NiS	" 375	-110	
CoS	" 360	-130	
PbS	" 298	-160	
ZnS	" 305	-170	2.07
MnS	" 163	-310	
CaS	" 094	-370	9.05

Figure 4? 5 represents this graphically.

The outline of bacterial sulphate reduction, as established from previous experiments and from field observations, is indicated by a hatched line. The smaller, hatched area represents the values obtained in the sulphate reductions described in this paper. It may be seen at a glance that, under the conditions of our experiments, no manganese sulphide could be formed. The absence of cinnabar formation may be ascribed to the toxicity of the mercury, and we cannot account for the absence of nickel and cobalt sulphides. It should be stated that the black precipitates originating from nickel and cobalt carbonate yielded H_2S on acidification, while copious gas was formed after addition of sodium azide-iodine. Sulphides were, therefore, present. All sulphides in the diagram are acid-stable within the natural environment, sphalerite and oldhamite excepted. The use of mineral acid in the purification of sphalerite should be avoided, therefore. The region for the calcium sulphide is very small and only with intense sulphate reduction under alkaline conditions may the presence of this compound (in the absence of heavy metal) be expected. We know from practical experience that the iron sulphide (probably the hydrate) becomes soluble below a pH of 5.8! This shows that the value for troilite, as given in the literature, and as used in Figure 5, is of little use to us, as this compound probably does not occur in the aqueous environment.

Of the seven mineral species formed from fairly insoluble oxidized compounds by sulphate reduction, only the metallic silver will get a hearty welcome from all geologists. Bateman (loc. cit., p.486) states "there are no sedimentary copper deposits free from controversy" and, according to him, the Mansfield deposits are hydrothermal (loc. cit., p.177, 526). Argentite, as stated above, is considered to be a high temperature form, stable above 179°C. We should have found acanthite in our experiments. As remarked before, the attempts to produce synthetic sulphides have been confined, for the largest part, to hydrothermal or to magmatic temperatures. It may be that a renewed attempt to obtain sulphides under "sedimentary" conditions (avoiding "outlandish" substances and acidities) will be fruitful. But the microbiologist is also at fault. It is not so long ago that the microbial world was referred to by the geologist as "carbonaceous matter". The change in attitude has been too abrupt and it could be continuously remembered that vague statements as to the prowess of microbes are almost useless. These statements should be backed up by deliberate experiments; and these experiments have, in the main, not been carried out.

The seven reductions reported upon in this paper were carried out under "unnatural" conditions: at 30°C, often with 1% lactate or acetate. Sometimes substances were used that are not recognized as mineral species (e.g., silver carbonate). And even if these few experiments could be repeated at lower temperatures and with more "natural" nutrients, the meagre evidence presented by the authors should not be used as a convincing argument for the syngenetic origin of orebodies. There are countless common sulphides which remain unstudied, and, moreover, our negative results do not allow of rigid interpretation. The only conclusion that can be reached is that our results probably clash with current geological concepts. We are certain that this clash is due to insufficient experimental evidence. It seems to us that a renewed chemical and microbiological study of the sedimentary environment is desirable. One of the chief problems confronting us is concerned with the accumulation of metals. We know that the black mud is a phosphate - and probably a uranium - trap. We have only a vague inkling about these accumulations. With the heavy metals dissipated in oceans as they are, it is their mode of concentration that remains the chief problem. Once accumulated, we are certain that the microbes will do the rest.

The experiments are being continued.

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Figure 1

Sulphate reducing bacteria growing on hydrogen. The tube to the left is filled with hydrogen by the tube on the right. Formation of black iron sulphide at a distance both from the hydrogen and the air-meniscus. The medium is filtered sterile seawater, to which is added some ammonium magnesium phosphate.

Figure 2

Formation of zinc sulphide from zinc wire. The medium is filtered, sterile, seawater with the addition of ammonium magnesium phosphate. Bacteria develop on the hydrogen generated by the zinc.

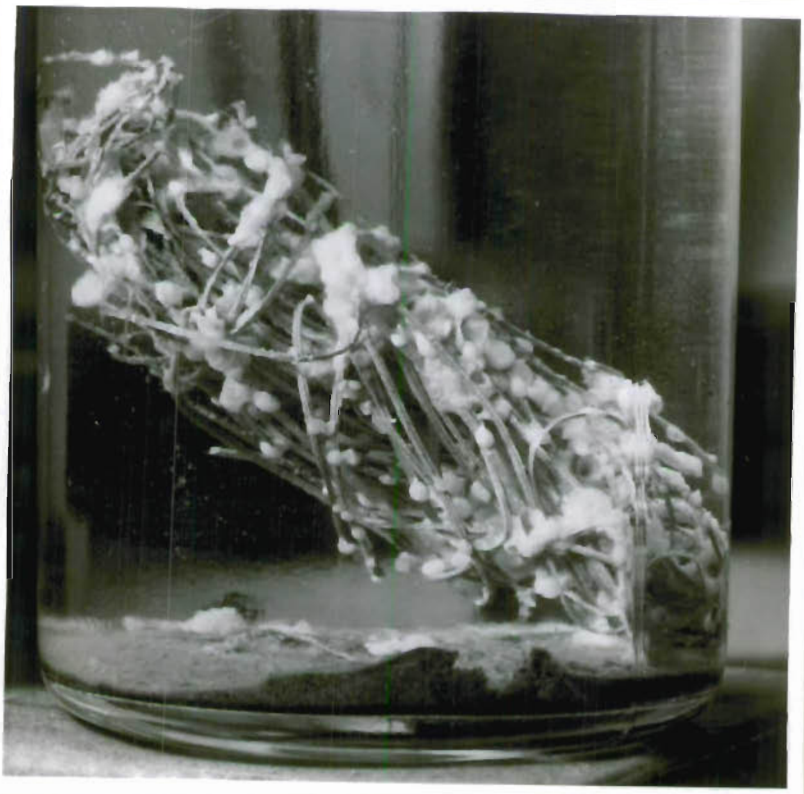

Figure 3

Minerals generated from the carbonates by sulphate reduction in hydrogen or lactate containing seawater. The X-ray powder diagrams were prepared by means of a copper target, except for the sphalerite, where a cobalt target was used. The lines in the sphalerite diffraction diagram are less well defined owing to the admixture of other substances. The photographs were taken by Messrs. Bayly and Thomas in the laboratory of Mr. Roberts, B.M.R. The black inked line indicates the centres of the diagrams.

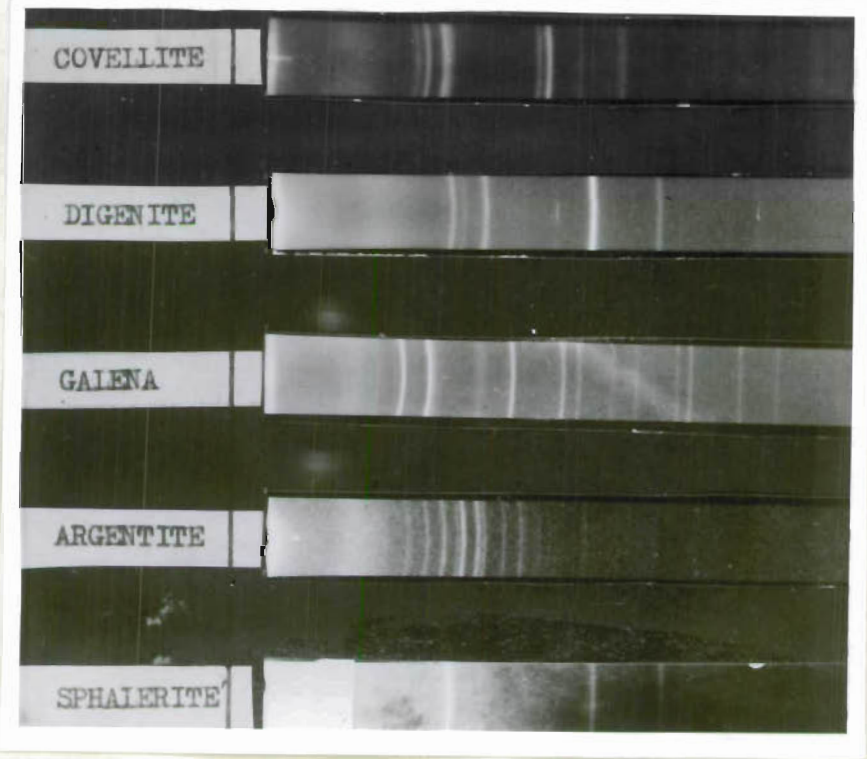

Figure 4

Equilibrium lines between sulphides and sulphates. See Table 7. The upper hatched line shows the limit of sulphate reduction, the hatched area represents values encountered normally. The outer boundary represents the limit of the natural aqueous milieu.

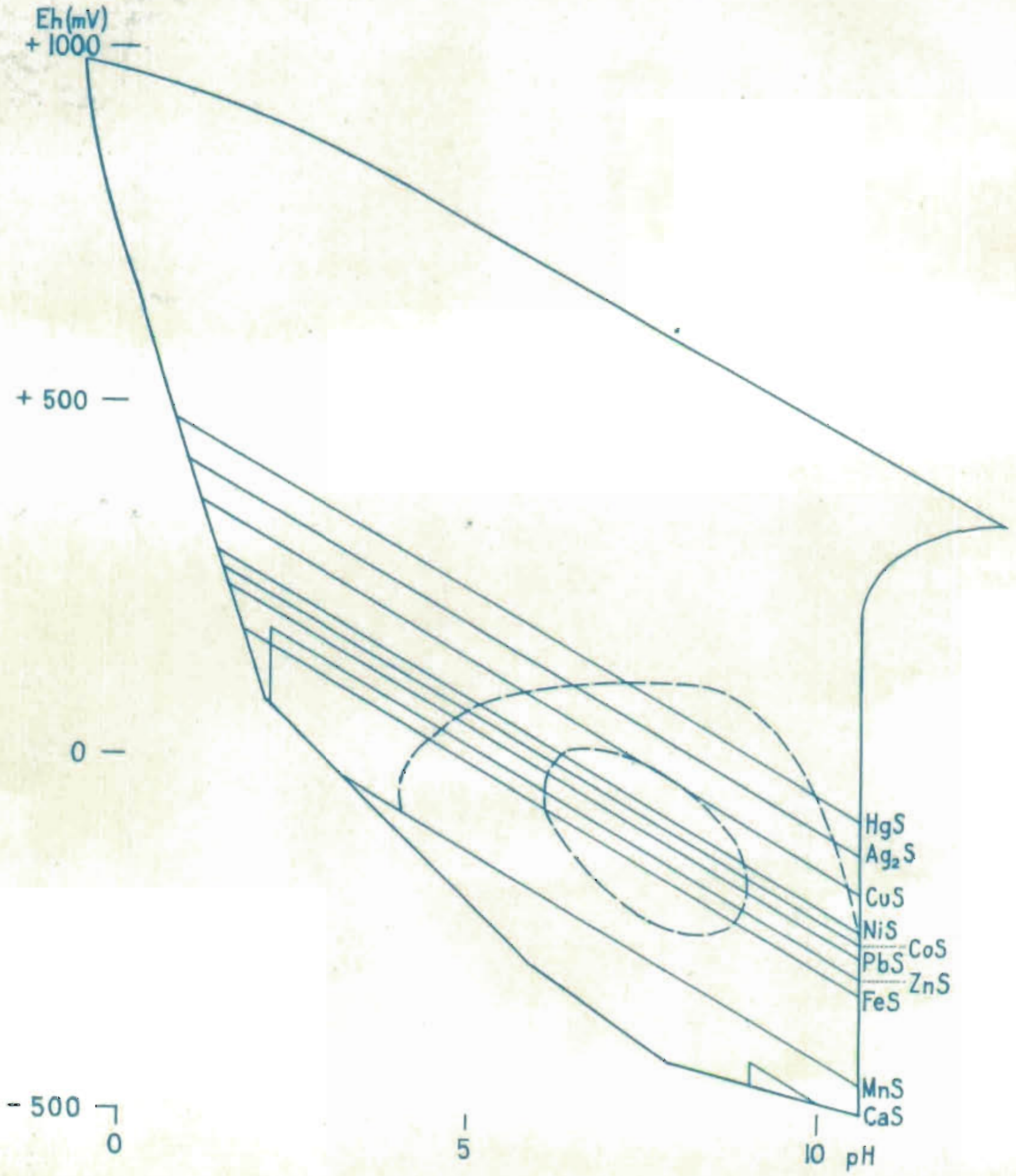

Figure 4