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1963/141

SYNGENESIS OF SULPHIDE OREA: DESORPTION OF ADSORBED METAL IONS AND THEIR PRECIPITATION AS SULPHIDES[1]

K.L. TEMPLE[2] AND N.W. LE ROUX[3]

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2. Division of Plant Industry, C.S.I.R.O., Canberra. Present address, Department of Botany and Bacteriology, Montana State College, Bozeman, Montana.

3. Bureau of Mineral Resources, Geology and Geophysics, Canberra.

ABSTRACT

A distilled-water agar gel was used to separate a saline, sulphate-reducing bacterial culture from metal ions adsorbed on clay or ferric hydroxide. After one to three weeks, the metals were partially desorbed and deposited in the agar as closely banded precipitates of sulphides. Adsorption constitutes one concentrating and separating mechanism. Desorption and sulphide precipitation constitute an additional concentrating and separating mechanism. The application of these results to biogenesis of sulphide ores is discussed.

INTRODUCTION

The work reported here is a continuation of research by the late Dr. Baas Becking and co-workers on the environment of sulphide deposition and the biogenesis of metal sulphides (1, 2). The previous paper of the present series considered the problem of copper toxicity in relation to sulphate-reducing bacteria (Desulphovibrio) (3). Adsorption of metal ions is another potential factor in syngenesis (4, 5). This study was suggested by the adsorption research of Beevers (4), and by discussions with personnel of the Bureau of Mineral Resources, Geology and Geophysics. Experiments were conducted to determine the effect of diffusion between a saline environment where sulphate reduction was taking place and a freshwater environment containing adsorbed metal ions. The purpose was to ascertain the degree of desorption of Fe^{+++}, Cu^{++}, Pb^{++}, and Zn^{++}, and the extent to which these metals would be localized on precipitation as sulphides.

EXPERIMENTAL

Sulphate-reducing culture. - The origin and maintenance of the crude Desulphovibrio culture were as described previously (3). The medium contained 3% NaCl (w/v).

Adsorbed metal ions. - Two local clays, designated "State Circle Shale" and "Black Mountain Kaolinite", were used as adsorbents. The State Circle Shale was taken from the dry bed of the creek west of Dryandra Street, Canberra, A.C.T., where it is exposed in one of the minor Black Mountain faults. Black Mountain Kaolinite was collected from an old quarry on Black Mountain, A.C.T., just south of the road to the television station. Both clays were ground in an iron mortar and pestle. The State Circle Shale was a slightly yellow, gritty material and the Black Mountain Kaolinite was soft and white. A third adsorbent was ferric hydroxide prepared from ammonia and ferric chloride by precipitation.

The adsorbent was shaken with a solution of one of the following:- $\frac{M}{10}$ $FeCl_3$, $\frac{M}{10}$ $Pb(NO_3)_2$, $\frac{M}{10}$ $Cu(NO_3)_2$, or $\frac{M}{10}$ $Zn(NO_3)_2$ (Table 1), and washed with distilled water by decantation until all free metal ion was removed. The amount of metal adsorbed was determined by desorption with 0.2M acetic acid (for the clays) or pH 4 acetate buffer (for the ferric hydroxide) followed by polarographic analysis of the solution. The adsorbents were dried at 110°C before use. (Table 1).

The use of an agar trap. - An agar gel was used to separate the adsorbent with its metal ions from a sulphate-reducing culture whilst permitting diffusion in both directions. It had the advantage that soluble metal ions and soluble sulphide ions meeting in the agar could form an insoluble deposit of metal sulphide in the agar. This deposit could be separated from the adsorbent and the bacterial culture, and could be removed for analysis. The deposit would then be a visible indicator of the formation of metal sulphides.

As a preliminary investigation a pyrex tube, length 120 mm., i.d. 14 mm., was prepared with a column of 3% agar in the centre, saturated H_2S water at one end and 10^{-2}M Pb $(NO_3)_2$ at the other. In a few days a number of dark bands developed in the agar; these bands lay at right angles to the length of the tube, and PbS was identified in them by X-Ray powder-diffraction photography. After this preliminary experiment, similar banded precipitates were developed in agar columns, this time with a sulphate-reducing culture at one end and State Circle Shale with adsorbed Fe^{+++}, Cu^{++}, Pb^{++}, or Zn^{++} at the other end.

Procedure and results. - Fig. 1 illustrates the procedure adopted for quantitative experiments. A column of melted 3% distilled water agar approximately 95 mm. long was poured into a 25 mm. i.d. pyrex, rubber joined tube. (Fig. 1). The rubber sleeve connecting the two pieces of pyrex tubing was put on to facilitate the removal of the agar at the end of the experiment but in fact was found to be an unnecessary addition. A single tube would have been adequate. When the agar had solidified, it was pushed nearly to the top of the lower tube and the space above the agar was filled with a sulphate-reducing culture so that no air remained in contact with the culture. The tube was inverted, and a slurry of adsorbent with attached metal ions (in distilled water) was added. A small air space was left above the slurry to keep it aerobic. The tubes were allowed to stand at room temperature for up to four weeks. Table 1 shows the composition of the contents of each tube.

The clay slurries settled in a few hours, leaving a clear aqueous solution on top and a few millimetres of clay resting on the agar. At the end of six days there was a visible precipitate in the agar of tubes 2, 3, 6, 7, 9, 11 and 12, i.e., those containing copper and lead. After three weeks all tubes had banded precipitates in the agar and no further visible change took place after 28 days. The photograph (Plate 1) was then taken. Tube 12 had already been opened and was not photographed. The mark at the left side of each tube indicates the top of the agar column. In tube 7 the top of the agar is hidden by the rubber sleeve. The horizontal banding of the precipitates was visible to the unaided eye in most cases, and by hand lens in all cases, but is not generally apparent in the photograph (Plate 1). A description from top to bottom of each tube follows.

Tube 1 - A clear aqueous layer.
Clay with a dark band next to the agar.
Faintly blue, almost clear agar for 8 mm.
A dark zone for another 18 mm. grading to clear agar.
A very diffuse lower dark boundary in the agar.

Tube 2 - A clear aqueous layer.
Clay.
A very dark zone in the agar for 10 mm.
A fairly sharp boundary, followed by clear agar.

Tube 3 - A clear aqueous layer.
Clay with a thin dark band at the bottom.
Clear agar for 1.5 mm.
A dark brown precipitate for 9 mm.
A very sharp upper boundary and a 6 mm. diffuse lower boundary.
Clear agar.

Tube 4 - A clear aqueous layer.
Settled clay.
Clear agar for 4 mm.
A broad white band for 11 mm.
A sharp lower boundary.
Clear agar.

Tube 5 - A clear aqueous layer.
Clay with a thick dark zone at the bottom.
A thin blue band at the top of the agar followed by a light blue band for 4 mm.
Dark blue for 46 mm. diffusing to clear agar.

Tube 6 - A clear aqueous layer.
Clay.
A very finely banded dark zone for 11 mm. succeeded by a pale green zone for 15 mm., all with fairly sharp boundaries.
Clear agar.

Tube 7 - A clear aqueous layer.
A large zone of dark precipitate in the aqueous layer above the clay.
Clay with a dark precipitate.
A black zone in the agar (behind rubber sleeve).
Clear agar.

Tube 8 - A clear aqueous layer.
Clay.
Clear agar for 10 mm.
A broad-banded, white precipitate for 9 mm.
Sharp boundaries.
Clear agar.

Tube 9 - A clear aqueous layer.
A thin, irregular deposit of ferric hydroxide adsorbent.
Blue agar for 1 mm. and clear agar for 6 mm.
Irregular brown and blue bands for 21 mm.
A very sharp lower boundary.
Clear agar.

Tube 10 - A clear aqueous layer.
A thin, irregular deposit of ferric hydroxide.
Dark blue agar becoming diffuse at 10 mm.
A visible precipitate in the agar for another 14 mm. with a sharp lower boundary.
Clear agar.

Tube 11 - A clear aqueous layer.
A thin, irregular deposit of ferric hydroxide.
A thin dark blue agar zone.
A blue zone for 10 mm. and green for another 15 mm.
A diffuse lower boundary.
Clear agar.

Tube 12 - A clear aqueous layer.
A thin, irregular deposit of ferric hydroxide.
Grey-brown agar for 25 mm. with a very sharp lower boundary.
Clear agar.

The metal in the agar was determined as follows: The agar column was removed, rinsed, and dried at 110°C. 20 ml. of concentrated HNO_3 were added and the mixture gently evaporated to dryness. After cooling, 10 ml. of 30% H_2O_2 were added and the mixture was again evaporated to dryness. The residue was dissolved in about 10 ml. of conc. HNO_3 and 100 ml. of distilled water, and diluted to 200 ml. in a volumetric flask. Samples containing lead were also treated with concentrated ammonium acetate solution to dissolve any lead sulphate which might have been formed. Iron was determined colorimetrically using Ferron (6), and zinc was determined colorimetrically using dithizone (7). Copper and lead were determined polarographically (8). The analytical results are given in Table 1.

DISCUSSION OF RESULTS

Adsorption and desorption. - The phenomenon of adsorption in itself is not a topic of this paper, and its relevance to syngenetic theory has been discussed by others (4, 5). The order of desorption was Zn > Cu > Fe > Pb. This suggests a simple competitive displacement, presumably by Na^+ from the culture medium. Desorption by this means would occur when adsorbed metal ions were transferred from a fresh water to a salt water environment. The order of desorption from ferric hydroxide was Cu > Zn > Pb. This differentation could form the basis of a separating device, for the degree of adsorption of Cu^{++} was approximately the same on ferric hydroxide as on clays, but the desorption from ferric hydroxide was much greater.

Trapping desorbed metal ions. - The tubes may be conceived as limited diffusion systems for the following reasons. Na^+ was free to diffuse from the bacterial culture throughout the agar and aqueous upper layer. The same is true for $S^=$ and SH^- ions except that these would be immobilized on encountering Fe^{+++}, Cu^{++}, Pb^{++} or Zn^{++}. Metal ions set free by the Na^+ replacement could diffuse in any direction initially. However, these ions would meet $S^=$ or SH^- ions when diffusing in the direction of the bacterial culture. In consequence of the low solubility of metal sulphides, all desorbed metal would eventually be precipitated, and would be most likely to do so in the agar column.

The system did in fact behave as indicated above for the most part. The clear agar zone at the bottom of each agar column, considered in conjunction with the presence of excess sulphide in the bacterial medium, shows that no metal ions reached the lower part of the agar. The absence of darkening or visible precipitate in the upper aqueous layer, and the presence of a precipitate in the upper part of the agar, show that sulphide did not diffuse throughout the tube, and that sulphide and metal ions did meet in the upper part of the agar column. Tube 7 is an exception; the visual appearance indicated a large amount of PbS in the upper aqueous layer. It is possible that the thin dark zone at the bottom of most of the clay deposits in the tubes was caused by an accumulation of sulphide. In all tubes there was a definite displacement of metal towards the sulphate-reducing zone. Agar was used to give a visual demonstration of this displacement, and provided a convenient means of removing the metal sulphide for analysis. In a natural environment, the sulphate-reducing zone itself would serve as the trap, or an intervening layer of unconsolidated sediment could also serve this purpose.

All four tubes with ferric hydroxide probably had some iron sulphide associated with the desorbed metal sulphide in the agar. This can also be deduced from the bicoloured effect in these tubes. It is possible that some zinc was extracted from the rubber, but none could have come from the rubber of the lower stopper since it would have been trapped by the medium, and no tubes had any white bands of ZnS near the rubber sleeves.

Positive qualitative tests for metal ions in the upper aqueous layer showed that the experiment did not continue long enough for complete trapping.

A mechanism for concentration. - At this preliminary stage, the results are relevant to the problem of a mechanism for the concentration of metals in sediments. The adsorption process is one mechanism for concentrating dissolved ions. Desorption followed immediately by precipitation as sulphide promises a further degree of concentration. To be effective, this mechanism would require an anaerobic sulphate-reducing zone in a saline water basin very near the point of entrance of fresh water carrying adsorbed metals. Alternatively, the presence of fresh water sediments containing adsorbed metals and the subsequent invasion by saline water and formation of an anaerobic layer could result in displacement of metals towards the anaerobic zone and their precipitation as sulphides.

A mechanism for separation. - Adsorption and desorption followed by fixation of the metal as an insoluble sulphide is also a mechanism for the separation of metals in solution. This mechanism is evident in the present experiment but its potential has barely been suggested. The variety of colloids, with their adsorptive properties, occurring naturally in fresh waters is considerable and should be more fully investigated. Not only metal ratios, but zonation and lensing could be effected by desorption in the vicinity of sulphide. Diffusion, settling rates, turbulence, flow, and possibly other physical factors could also be important in a separating or concentrating mechanism. Experiments being carried out by one of us (N.W.L.) with mixtures of metals and analysis of separate bands of precipitates could yield further information on this aspect of biogenesis.

Identity of the agar precipitate. - It has been clearly demonstrated that metal ions in the vicinity of sulphate-reducing cultures form corresponding sulphides (2). Accordingly, it was considered superfluous to identify each precipitate as the sulphide. However, a similar tube was set up and an X-Ray photograph taken to show that PbS was precipitated in the agar.

SUMMARY AND CONCLUSIONS

Clays or ferric hydroxide with adsorbed Fe^{+++}, Cu^{++}, Pb^{++}, or Zn^{++} in distilled water were separated from a saline culture of sulphate-reducing bacteria by a column of 3% agar in distilled water. This system allowed diffusion of soluble components. Adsorbed metals were displaced, presumably by Na^{+}, in amounts which were characteristic of the metal ion and adsorbent. Desorbed metals were precipitated as sulphides in the upper part of the agar column. The percentage recovery of adsorbed metal as sulphide in the agar was greatest for Cu^{++} and Zn^{++}, and least for Pb^{++}. The experiment served as a model of a fresh water system containing adsorbed metals in juxtaposition to a saline system containing active sulphate-reducing bacteria. Taking into account the fact that adsorbents exist in the natural environment having better adsorption qualities than those used in this experiment, the amount of metal adsorbed could be greater than the figures quoted in this paper. Adsorption followed by desorption near a zone of sulphide ions could act as a concentrating and separating mechanism.

The authors are not qualified to evaluate the likelihood of such circumstances occurring in present or past geologic times, but offer their results as a part of the biochemical picture to be considered in syngenesis of sulphide ores.

ACKNOWLEDGEMENTS

The authors are indebted to J.R. Beevers, of the Bureau of Mineral Resources, Geology and Geophysics, for preparing the adsorbed metal samples, and for the polarographic analyses.

X-Ray identifications were carried out by S.C. Goadby, of the Bureau of Mineral Resources.

We also wish to acknowledge the friendly assistance of many individuals who helped introduce us to the topic of sulphide ore formation, and in particular W.M.B. Roberts and J.R. Beevers, for their discussion and suggestions.

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TABLE 1

Composition of tube contents and amount of metal precipitated in the agar

Tube No.	Adsorbent	Weight of Adsorbent*	Adsorbed metal	Percent of Metal Adsorbed	Amount of Metal Adsorbed g	Amount of Metal in agar g	Percent in agar
1	State Circle Shale	3.000	Fe^{+++}	0.26	0.00780	0.00156	20.0
2	State Circle Shale	3.000	Cu^{++}	0.18	0.00540	0.00225	41.7
3	State Circle Shale	3.000	Pb^{++}	0.87	0.02610	0.00357	13.7
4	State Circle Shale	3.000	Zn^{++}	0.17	0.00510	0.00267	52.4
5	Black Mountain Kaolinite	3.000	Fe^{+++}	0.24	0.00720	0.00306	42.5
6	Black Mountain Kaolinite	3.000	Cu^{++}	0.16	0.00480	0.00204	42.5
7	Black Mountain Kaolinite	3.000	Pb^{++}	0.57	0.01710	0.00040	2.3
8	Black Mountain Kaolinite	3.000	Zn^{++}	0.14	0.00420	0.00400	95.3
9	Ferric Hydroxide	1.000	Pb^{++} Cu^{++}	0.26, 0.028	0.00260, 0.00028	0.00023, 0.00021	8.9, 75.0
10	Ferric Hydroxide	1.000	Zn^{++}	0.033	0.00033	0.00027	81.8
11	Ferric Hydroxide	1.000	Cu^{++}	0.16	0.00160	0.00133	83.2
12	Ferric Hydroxide	1.000	Pb^{++}	0.52	0.00520	0.00088	16.9

* grams dry weight at 110°C

PROCEDURE FOR CONDUCTING DESORPTION AND PRECIPITATION OF METAL IONS

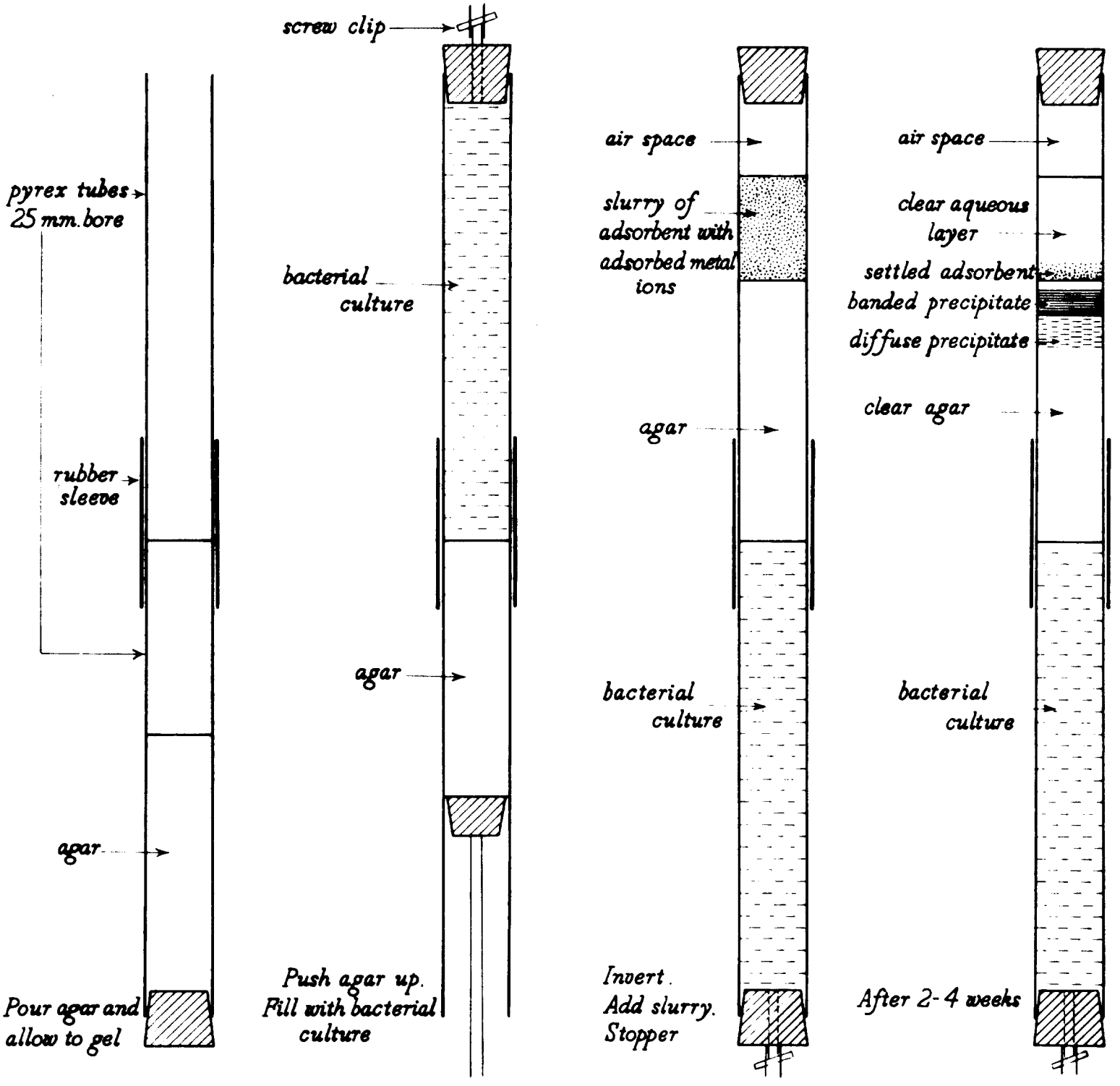
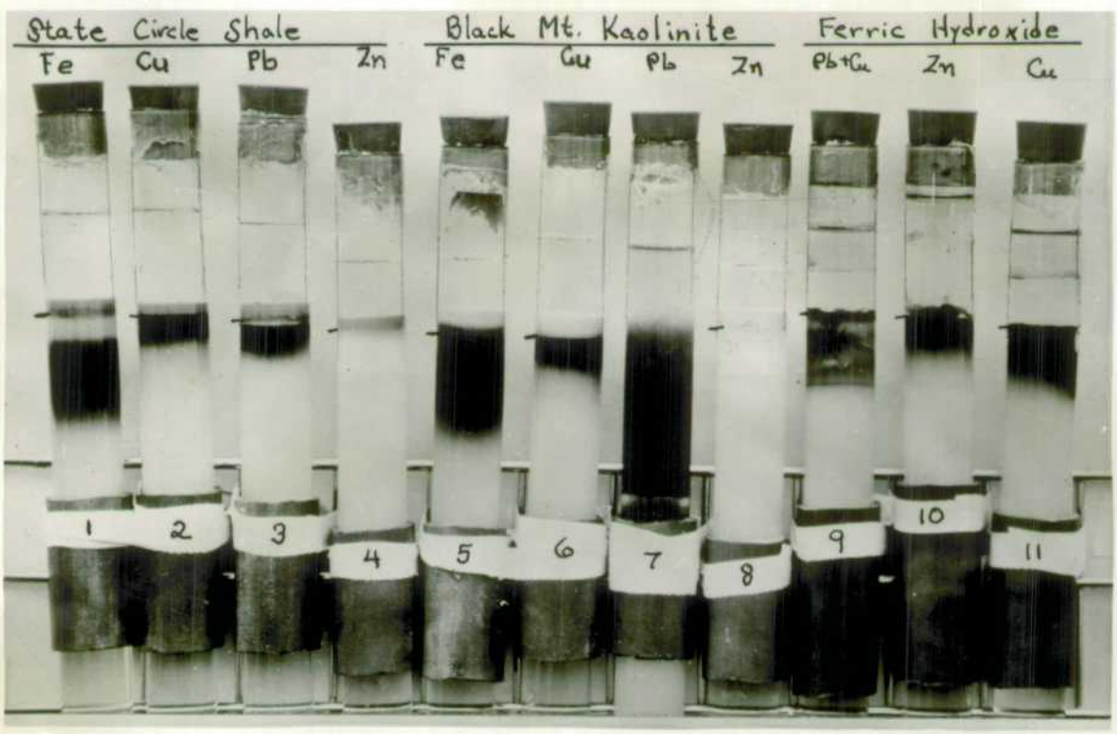


PLATE 1.


State Circle Shale
Fe
Cu
Pb
Zn
Black Mt. Kaolinite
Fe
Cu
Pb
Zn
Ferric Hydroxide
Pb+Cu
Zn
Cu
1
2
3
4
5
6
7
8
9
10
11