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THE ROLE OF METAL-ALGAL INTERACTIONS IN THE FORMATION OF SEDIMENTARY SULPHIDE DEPOSITS

J. FERGUSON[1] and B. BUBELA[2]

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2. Division of Mineralogy, C.S.I.R.O.

The role of metal-algal interactions in the formation of sedimentary sulphide deposits

J. FERGUSON[1] and B. BUBELA[2]

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ABSTRACT

Experimental studies of the reactions of Cu(II), Pb(II), and Zn(II) in aqueous solutions with organic matter derived from fresh samples of the green filamentous algae *Ulothrix* spp and the green unicellular algae *Chlamydomonas* spp and *Chlorella vulgaris* show that, under suitable conditions, a significant proportion of the metals is removed from solution by sorption onto the particulate organic matter of the algal suspension.

The metal sorption is strongly suppressed by H^+ but is only marginally influenced by the proportion of whole cells in the suspension and by complexing of metals in solution by the soluble organic matter. The presence of relatively small amounts of the cations Na^+ and Mg^{2+} in solution reduces the sorption of Zn(II) to near zero but Pb(II) and Cu(II) sorption occurs to an appreciable extent even in strong brines. This may be a means for the selective precipitation of Pb(II) from brines rich in Pb(II) and Zn(II).

Metal "saturation" values indicate that particulate algal matter of the type used in these experiments could sorb sufficient quantities of metal to form an ore deposit if a weight of organic matter of similar order of magnitude to that of the inorganic sediments in the deposits was available. However, the metal sorption is an equilibrium reaction, and the experimentally determined "enrichment factors" suggest that the "saturation"

values could be approached only in solutions whose metal contents were initially at least two orders of magnitude above those of normal seawater.

INTRODUCTION

A number of sedimentary base-metal sulphide deposits of Precambrian and later ages have organic carbon contents considerably above an average for shales (Table 1), and it appears possible that so-called "organic" processes (KRAUSKOPF, 1955) could have played a significant or perhaps even a critical role in the concentration and transport of the ore metals (BRONGERSMA-SAUNDERS, 1965; ROBERTS, 1973).

There is little direct evidence on the primary source of the organic carbon but it has been suggested that, for some deposits at least, it was derived from a large population of algae growing in the overlying waters (BRONGERSMA-SAUNDERS, 1965; ROBERTS, 1973). This hypothesis is particularly pertinent in the case of deposits of Precambrian age, when higher forms of life are unlikely to have been well established.

A wide variety of mechanisms for concentration of metals in sediments by living organisms and their decay products have been postulated (e.g. KRAUSKOPF, 1955; LEE and HOADLEY, 1967). They include i) direct incorporation into the sediments of metals concentrated by living organisms

(BRONGERSMA-SAUNDERS, 1965 on the origins of the Kupferschiefer, Germany), ii) the sorption of metal ions from solution onto particulate organic or organic-inorganic matter, iii) the sorption of soluble metal-organic complexes from solution onto particulate inorganic or organic matter, iv) the sorption of metals from pore waters by organic materials in sediments, v) the "solubilization", as metal-organic complexes, of metals dispersed in sediments, and their subsequent transport and concentration in veins and fissures (ROBERTS, 1973, on the origins of Woodcutters Prospect, Australia).

To date the limitations of the above processes are not well defined. Most of the available quantitative data relates to the trace metal contents of living algae (e.g. VINOGRADOV, 1953; BLACK and MITCHELL, 1952; NICHOLLS *et al.*, 1959) and to the metal complexing abilities of humic and fulvic acids (e.g. SCHNITZER and HANSEN, 1970; RASHID, 1971) and natural humic materials, e.g. peats (COLEMAN *et al.*, 1956; SZALAY, 1958; BEEVERS, 1966).

Comparatively little data is available, however, on the metal complexing abilities of the organic matter of dead, but not extensively decomposed, algal cells (WASSERMAN, 1949; WILLIAMS, 1958). Organic matter of this type may be present in significant amounts in the waters of depositional basins and could contribute to metal concentration by reactions ii), iii) and, to a lesser extent, iv) and v).

This paper reports the results of an investigation of the interactions of Cu(II), Pb(II), Zn(II) and, to a lesser extent Cd(II), in aqueous solutions with fresh particulate organic matter of the green filamentous algae *Ulothrix* spp. and the green unicellular algae *Chlamydomonas* spp. and *Chlorella vulgaris* (hereafter "*Ulothrix*", "*Chlamydomonas*" and "*Chlorella*"). The amounts of metals sorbed[3] from solution have been measured and the effects of varying a number of chemical factors, including pH, salinity and metal concentrations in solution, determined. The results are interpreted in terms of the mechanisms of the metal sorption reactions and their possible role in metal concentration in sediments.

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[3] Throughout this paper the non-specific term "metal sorption" will be used to describe the processes by which metal is removed from solution onto particulate organic matter.

MATERIALS AND METHODS

Collection and Culture of Algae

Ulothrix spp. used in these experiments are the major component of an almost monoalgal natural population obtained from a site at the base of Corin Dam, A.C.T., where it "blooms" in acid groundwaters enriched in Fe, Mn, Cu, Zn, nitrate and phosphate (HALDANE *et al.*, 1970). Fresh, bright green algae were collected and freed as far as possible from extraneous organic and inorganic matter. The long (up to 1 metre) filaments were then washed several times by decantation with distilled water and stored at -20°C.

Chlamydomonas spp. were grown at room temperature under Osram MCFE fluorescent lights in a liquid medium (STANIER *et al.*, 1971) adjusted to pH 3.5 with H_2SO_4. Inoculation with a portion of the natural algal population described above resulted in selective growth of the unicellular alga *Chlamydomonas* which was a minor (<5% of the unit cell count) component of the inoculum. After 1-2 weeks growth the cells were harvested by centrifugation, washed twice with distilled water and stored at -20°C or freeze dried overnight in a Martin-Christ Freeze Dryer (sample temperature -30°C; condenser temperature -70°C; pressure 1×10^{-3} mm Hg).

Chlorella vulgaris (pure culture) was grown at room temperature under Osram MCFE fluorescent lights in a vigorously agitated liquid medium (KESSLER and CZYGAN, 1970) through which 5% CO_2 in nitrogen was bubbled continuously. The cells were collected and stored as for *Chlamydomonas*.

Preparation of Algal Suspensions

The following techniques, which are described in detail by NORRIS and RIBBONS (1971), were used to prepare homogeneous suspensions of the algae, suitable for handling by conventional volumetric procedures.

1) Aqueous suspensions of the algal cells were hand homogenized (HH) in a Thomas Tissue Grinder (Teflon piston model).

2) Cooled suspensions of the algal cells were treated with ultrasonic radiation (500W, 22 ± 3kHz) minute using a Fisher Ultrasonic Probe.

3) *Ulothrix* filaments were mechanically chopped (MC) to small lengths in a Sorval Omni-Mixer Type O.M.

4) Cooled suspensions of the algal cells were broken by high pressure extrusion in a French press (FP) under 2000 atmospheres pressure.

Suspensions for routine experiments were prepared as follows:

Ulothrix. The natural material was chopped to a pasty consistency, diluted with distilled water, and 10.0 ml aliquots of the suspension pipetted into plastic jars and deep frozen. Immediately before use the samples were thawed, diluted with distilled water and the coagulated algae re-suspended by treatment with ultrasonic radiation for 1 minute.

Chlamydomonas and *Chlorella*. A weighed amount of freeze-dried powder (or a suitable aliquot of the deep frozen material) was suspended in distilled water, hand homogenized to destroy aggregates of cells, and made up to volume. *Chlamydomonas* suspensions were then passed three times through the French press. *Chlorella* suspensions were used without further treatment.

Suspensions used to check the effects of the proportion of "whole cells" of *Chlamydomonas* and *Chlorella* on metal sorption were hand homogenized to produce a minimum of damage to the cells, or were passed through the French press up to 3 times. This procedure was most successful with *Chlorella* and suspensions containing < 5 to > 95% ruptured cells were prepared. *Chlamydomonas* suspensions contained a proportion of cells which were strongly resistant to rupture by the French press and no more than about 50% breakage could be achieved. The naturally occurring *Ulothrix* contained small amounts of sediment particles which prevented the use of the French press. The proportion of cells broken by mechanical chopping was estimated to be between 10 and 40%.

Physical and Chemical Examination of Algal Suspensions

Morphology and cell counts. The algal suspensions were examined microscopically and cells counted using a Petrof-Hauser Bacterial Counter in conjunction with a Leitz Ortholux Microscope.

Centrifugation. In most experiments the organic matter in the algal suspensions was separated into "particulate" and "soluble" fractions (see Results) by centrifugation for

30 minutes at 198,400 x g in a Beckman Model L2 Preparative Ultracentrifuge. A number of separations of *Ulothrix* suspensions were made by centrifuging the sample for 15 minutes at 14,400 x g in an I.E.C. International Portable Refrigerated Centrifuge. Experiments showed that the amounts of metals and organic matter sedimented under these conditions were only marginally smaller than those sedimented at the higher speed.

Major element analyses of the dry algal materials (Table 3) were carried out by the Australian Microanalytical Service, Melbourne. Organic carbon results are precise to better than ± 1% of the reported values.

Dissolved organic carbon in the supernatant of centrifuged algal suspensions was determined by the method of BRADY (1914) as modified by BUSH (1970). The apparatus was calibrated using aqueous solutions of A.R. glucose. Precision is ± 3% of the reported values.

Trace element contents of *Ulothrix* ashed at 800°C were determined by direct reading atomic emission spectrometry. Precision is better than ± 10% of the reported values.

Inorganic cations in the algal supernatants were determined by atomic absorption spectroscopy using a Varian AA-5 spectrophotometer. Precision is ± 3% for concentrations > 1 mg.1^{-1} and ± 10% for concentrations < 1 mg.1^{-1}.

Inorganic anions in the algal supernatants (Table

4) were determined by standard wet chemical microtechniques (GOLTERMAN and CLYMO, 1971). Inorganic phosphate was determined by the method of CHEN *et al.*, (1956).

Reactions of Metals with Algal Suspensions

An aliquot of the algal suspension was pipetted into a 25 ml volumetric flask and the pH brought to the required value by the addition of 0.2 M sodium acetate/acetic acid (NaOAc/HOAc) or sodium acetate/HCl buffer (VOGEL, 1951). In experiments without buffers the pH was adjusted approximately at this stage with dilute HNO_3 or NaOH. The metal was then added in the form of a stock solution (adjusted to pH 4-5) of the A.R. grade metal chloride or nitrate in distilled water. Final pH adjustments of solutions without buffers were made at this stage and the suspensions made up to volume and shaken overnight on a mechanical shaker. The solutions were then centrifuged and a portion of the supernatant removed and its metal content determined by atomic absorption spectroscopy.

Two types of "blanks" were prepared. In "distilled water" blanks the aliquot of the algal suspension was replaced by distilled water. "Algal supernatant" blanks were prepared by first centrifuging a portion of the algal suspension under the conditions to be used for the sample separation. An aliquot of this supernatant was used in place of the algal suspension and the solution prepared, shaken or allowed to stand overnight and centrifuged as for the sample. Precision of measurements of metal concentrations in blank and sample supernatants is ± 3%.

RESULTS

Physical and Chemical Compositions of Algal Suspensions

In the following sections concentrations of organic materials in the algal suspensions are expressed in terms of their "total (C_t), "particulate" (C_p) and "soluble" (C_s) organic carbon contents. C_p is defined as the organic carbon sedimented by centrifuging the algal suspension at 198,400 x g for 30 minutes and C_s is the organic carbon remaining in the supernatant. Values of C_t and C_p were calculated from the freeze-dried weight of the algae, their organic carbon contents (Table 3) and experimentally determined C_s concentrations.

Data given in Table 2 show that for *Chlamydomonas* and *Chlorella* the proportion of soluble organic carbon increases with increasing degree of cell breakage. There are indications (see later) that, in some systems, a portion of this soluble organic matter is not in true solution but coagulates and is sedimented under the conditions of the metal sorption experiments. This process is most obvious in *Chlorella* FP x 3 suspensions, whose bright green chlorophyll-rich supernatants are decolourized by centrifugation after reaction with added metal ions.

The specific conductances of supernatants of

Chlamydomonas and *Chlorella* (Table 4) are almost independent of the proportion of visibly broken cells in the suspension, which indicates that the apparently whole cells are readily permeable to simple ions. This holds for most of the individual ions listed in Table 4, the most notable exceptions being magnesium and copper in *Chlorella* and copper in *Chlamydomonas* supernatants. It is likely that, in these cases, the additional amounts of metals released into the supernatant by breaking the cells are present in metal-organic compounds of relatively high stability (e.g. chlorophyll in *Chlorella* FP x 3 supernatants) and therefore do not participate significantly in equilibria involving simple metal ions. Experiments involving the sorption of small amounts of added Cu(II) by *Chlorella* and *Chlamydomonas* suspensions provided further evidence that the indigenous Cu(II) remained in the supernatant as "background".

A major anion in *Chlorella* and *Chlamydomonas* supernatants is phosphate, which may reflect the concentrations (0.64 and 0.925 $g.l^{-1}$ respectively) of this ion in the growth media (KETCHUM, 1939). Consideration of the "ion balance" of data in Table 4 indicates an excess of anions in *Chlamydomonas* and *Chlorella* and an excess of cations in *Ulothrix* supernatants. The counterions in each case may be, respectively, organic acids or bases.

Reactions of Metals with Algal Suspensions

When suspensions of *Ulothrix*, *Chlamydomonas*, or

Chlorella were shaken with aqueous solutions of Cu(II), Pb(II), Zn(II) or Cd(II) under suitable conditions it was found that, in some systems, metal sorption by the particulate organic matter was accompanied by three other reactions: 1) precipitation of inorganic metal salts, 2) precipitation of metal-containing soluble organic matter and 3) formation of soluble metal-organic complexes.

Experimentally, reactions 1) and 2) can be extremely important as they contribute directly to the total amounts of metal removed from solution by the algal suspension. To allow for the contributions of these reactions to the total amounts of metal removed from solution by the algal matter, the amount of metal sorbed from solution per 1000 g of particulate organic carbon ($[M(II)]_{sorbed}$) has been calculated by subtracting the metal concentration in the supernatant of the algal suspension from the metal concentration in the "algal supernatant" blank, and dividing this value by the concentration of C_p in the suspension.

Generally, the combined contributions of reactions 1) and 2) (given by subtracting the metal contents of the "algal supernatant" blanks from those of the "distilled water" blanks) are less than 5% of the total amount of metal removed from solution.

Reaction 1) is, however, quantitatively significant in the systems Pb(II)/*Chlamydomonas* and Pb(II)/*Chlorella* where extensive precipitation of Pb(II) and an accompanying decrease in the inorganic phosphate content of the supernatant blank occurs. This reaction may also be important in the system Cu(II)/*Chlorella* at high concentrations ($\gtrsim$ 0.6 mmoles.l^{-1}) of the metal in solution, but at low concentrations (Table 5) the amounts of metal involved are negligible compared to metal sorption by the particulate organic matter.

Pb(II) is also precipitated from algal supernatant blanks of *Ulothrix* but the amounts involved (*ca* 20% of the total metal removed from solution) were insufficient to allow identification of the precipitated material. In view of the small amounts of phosphate, sulphate and chloride present in these solutions it is unlikely that reaction 1) is involved to a significant extent and the precipitated material is probably a Pb(II)-organic complex.

Reaction 2) can account for up to 15% of the total metal removed from solution in the Zn(II)/*Chlorella* and Cu(II)/*Chlorella* systems, where French pressing the suspensions results in a marked increase in both the "soluble" organic carbon contents and the amounts of metals precipitated from the "algal supernatant" blanks (Table 5). In both systems the reaction is accompanied by decolouration of the green chlorophyll-rich supernatant.

Reaction 3), although not capable of contributing directly to the removal of metals from solution, was examined experimentally to assess its ability to influence the metal sorption reactions by complexing a proportion of "free" metal ions in solution.

Exploratory measurements, using a cupric ion-selective electrode, of the extent of reaction 3) in the system Cu(II)/*Ulothrix*, indicated that the amounts of Cu(II) complexed by the soluble organic matter are of a similar order of magnitude to the amounts sorbed by the particulate matter of the suspension. To determine the effects of this complexing on the amounts of metal sorbed, aliquots of the algal suspension were centrifuged, the supernatant removed, and the particulate organic matter resuspended. It was found that the amounts of Cu(II), Pb(II), and Zn(II) sorbed by this material differed little from those sorbed by the untreated suspension (Table 6, experiments 1, 2 and 3).

Metal Sorption by Particulate Organic Matter

Data on metal sorption reactions are summarized in Tables 5 and 8 and Figures 1 to 3. Most data refer to *Ulothrix* suspensions, which were available in much greater quantities than the cultured algae. There is, however, no evidence from exploratory measurements that the reactions of *Chlamydomonas* and *Chlorella* are fundamentally different from those of *Ulothrix*.

1. *Dependence of* $[M(II)]_{sorbed}$ *on pH*

$[M(II)]_{sorbed}$ is strongly dependent on the pH of the suspension (Fig. 1).

At pH values above 6 precipitation and supersaturation effects resulting from metal hydroxide formation make data unreliable and the shape of the $[M(II)]_{sorbed}$ against pH curve in this range could not be determined. By analogy with graphs of pH against Pb(II) (BEEVERS, 1966) or UO_2^{2+} (SZALAY, 1958) sorbed on peat preparations, it might be expected that the linear portion of the graph would be followed by a region where $[M(II)]_{sorbed}$ is independent of pH. However, if the metal-organic matter reaction products are unstable at high pH, then $[M(II)]_{sorbed}$ may reach a maximum and decline with further increases in the pH of the solution (e.g. RANDHAWA and BROADBENT, 1965).

In view of the sensitivity of $[M(II)]_{sorbed}$ to changes in pH of the solution, most experiments were carried out with suspensions maintained at pH 5.6 by the addition of NaOAC/HOAC buffer.

2. *Effects of inorganic ions in solution on* $[M(II)]_{sorbed}$ (Table 6).

Data in Table 6 show that Zn(II) sorption, as compared with Pb(II) and Cu(II) sorption, is considerably more sensitive to the presence of added salts in solution. Thus Zn(II) sorption is depressed to near zero by the addition of 200 $mmoles.l^{-1}$ NaCl or $Mg(NO_3)_2$ to the solution (experiment 7), and in the presence of as little as 16 $mmoles.l^{-1}$ NaOAC + HOAC buffer $[M(II)]_{sorbed}$ is 15 to 20% lower than in a similar unbuffered solution (experiment 6). Cu(II) sorption, on the other hand, is only marginally decreased by the addition of up to 200 mmoles.l^{-1} of NaCl to the solution, and more than 50% of the amount sorbed from distilled water solutions can be sorbed from seawater or strong brine solutions (experiment 8).

The relative metal complexing abilities of the metal ions with most ligands is Cu(II) > Zn(II) (IRVING and WILLIAMS, 1948), and it is unlikely, therefore, that the decreases in metal sorption are a result of the formation of metal-inorganic species in solution which are less readily sorbed by particulate organic matter. It is most likely a result of "competition" by the added cations with the metal ions in solution for the available sorption sites on the particulate organic matter. On this basis the lower value of $[Zn(II)]_{sorbed}$ in buffered solutions can be attributed to the competition of Na^+ in the NaOAC/HOAC buffer and the comparatively greater effect of 200 mmoles.l^{-1} $Mg(NO_3)_2$, as compared to NaCl of 10 times the concentration, on Cu(II) sorption (experiments 8 and 9) reflects the relative complexing abilities of Mg^{2+} and Na^+.

3. *Effects of proportion of "whole" cells on* $[M(II)]_{sorbed}$

The data in Table 7 indicate that, for *Chlamydomonas* and *Chlorella*, $[M(II)]_{sorbed}$ is not strongly dependent on the proportion of visibly ruptured cells in the suspension. This implies that, even in apparently "whole" cells, the great majority of metal sorption sites are readily accessible to the metals in the bulk of the solution. This might be expected if, as the conductivity data imply, the cells are readily permeable to simple ions.

4. *Dependence of* $[M(II)]_{sorbed}$ *on* $[M(II)]_{solution}$

Graphs of $[M(II)]_{sorbed}$ against [M(II)] remaining in solution ($[M(II)]_{solution}$) are approximately linear at low concentrations (Fig. 2), but as $[M(II)]_{solution}$ increases, $[M(II)]_{sorbed}$ tends towards a "saturation" value (Table 8). Similar behaviour has been noted for the sorption of Pb(II) and UO_2^{2+} on peats (BEEVERS, 1966; SZALAY, 1958) and data for these systems can be described mathematically by the Langmuir isotherm.

If the present data obey this relationship then plots of $\frac{1}{[M(II)]_{sorbed}}$ against $\frac{1}{[M(II)]_{solution}}$ should be linear (CASTELLAN, 1964), and the intercept of the y-axis will give a value for the reciprocal of the concentration of metal sorbed at infinitely high concentrations of metal in solution ($[M(II)]_{saturation}$).

For the systems Pb(II) and Cu(II)/*Ulothrix* (Fig. 3a) and Cu(II)/*Chlamydomonas* these plots are linear over the experimentally accessible range of $\frac{1}{[M(II)]_{solution}}$ and graphical extrapolation gives a common value of about 500 mmoles.1000 g C_p^{-1}

for $[M(II)]_{saturation}$. This agrees reasonably with the data obtained experimentally for Cu(II) and Pb(II)/*Ulothrix* at the highest accessible concentrations of these metals in solution (Table 8).

Significant deviations from linearity occur at high values of $[M(II)]_{solution}$ in graphs of data for the systems Zn(II) and Cd(II)/*Ulothrix* (Fig. 3b), Zn(II)/*Chlamydomonas* and Zn(II) and Cu(II)/*Chlorella*. Extrapolation of the low concentration linear portion of the graph gives $[M(II)]_{saturation}$ values near 100 mmoles.1000 g C_p^{-1} for the Zn(II) and Cd(II) systems (Table 9) whereas the higher concentration data extrapolate to values ranging from 250 to 500 mmoles.1000 g C_p^{-1} (Fig. 3a and b and Table 9). These latter values could not be confirmed experimentally for *Ulothrix* systems as the amounts of Zn(II) and Cd(II) sorbed increase significantly with increasing $[M(II)]_{solution}$ up to the highest accessible concentrations (Table 8). Low-concentration data for Cu(II)/*Chlorella* extrapolate to a value of 400 mmoles.1000 g C_p^{-1} for $[M(II)]_{saturation}$, which is similar to the values obtained for the Cu(II)/*Ulothrix* and Cu(II)/*Chlamydomonas* systems. The data at higher concentrations of $[M(II)]_{solution}$, however, extrapolate to 1200 mmoles.1000 g C_p^{-1} which is uniquely high for the present systems and may indicate the simultaneous precipitation of Cu(II) phosphates.

Metal sorption from dilute solutions can be expressed in terms of "enrichment factors" (E.F.) which are obtained from the slope of the tangent to the graphs of

$[M(II)]_{sorbed}$ against $[M(II)]_{solution}$ at $[M(II)]_{solution} = 0$ (SZALAY, 1958).

The relative values of E.F. for the algae used in this investigation with various metals are Pb(II) > Cu(II) > Cd(II) > Zn(II) for *Ulothrix* and Cu(II) > Zn(II) for *Chlamydomonas* and *Chlorella* (Table 9). This apparent relative order of stabilities of the metal-algal species was confirmed for *Ulothrix* by "competition" reactions, which showed that the metal highest in the series was preferentially sorbed from bimetallic solutions.

The E.F.s for *Ulothrix* with Pb(II) and Zn(II) differ by 1 to 2 orders of magnitude (Table 9) but, in contrast, those for Zn(II) with *Ulothrix*, *Chlamydomonas* and *Chlorella* all lie in the narrow range 700 to 950 1.1000 g C_p^{-1}. The data for Cu(II) with the three algae are complicated by the possibility of metal-phosphate precipitation in the Cu(II)/*Chlorella* system, but E.F.s for Cu(II)/*Ulothrix* and Cu(II)/*Chlamydomonas* are sufficiently close to indicate they may also be relatively independent of the particular alga used.

5. *Influence of* $[C_p]$ *on* $[M(II)]_{sorbed}$

The dependence of $[M(II)]_{sorbed}$ on the concentration of organic matter in the systems Cu(II), Pb(II) and Zn(II)/*Ulothrix* was studied using suspensions containing constant total M(II) concentrations but with $[C_p]$ varying in the range 143 to 714 mg.1^{-1}. Under these conditions a change in $[C_p]$ will result in a change in $[M(II)]_{solution}$, and the effects of this change will be superimposed on any variations in $[M(II)]_{sorbed}$ that result from the change in $[C_p]$. However, if the change in $[M(II)]_{solution}$ is the only effect operating then graphs of $\frac{1}{[M(II)]_{sorbed}}$ against $\frac{1}{[M(II)]_{solution}}$ should have similar slopes to those in Fig. 3a, the data for which were obtained under analogous conditions but with constant $[C_p]$.

For Pb(II)/*Ulothrix* the slopes of the lines are 0.059 and 0.047 1.1000 g C_p^{-1} for varying and constant $[C_p]$ respectively, which indicates only a marginal dependence of $[M(II)]_{sorbed}$ on $[C_p]$. A much stronger dependence on $[C_p]$ is evident from the data on the Cu(II) and Zn(II)/*Ulothrix* systems. The slopes are Cu(II), 1.1 and 0.31; Zn(II), 1.7 and 1.5 1.1000 g C_p^{-1} for the varying and constant $[C_p]$ respectively, and this suggests that increasing $[C_p]$ decreases the ratio $\frac{[M(II)]_{sorbed}}{[M(II)]_{solution}}$ for these metals. The differences in the slopes indicate that this effect increases in the order Pb(II) < Cu(II) < Zn(II).

DISCUSSION

In most of the metal algae systems used in this investigation the major process by which metal ions are removed from solution involves the sorption of metal ions onto particulate organic matter. Precipitation of inorganic metal salts and the formation of insoluble metal-organic species with soluble organic matter are quantitatively important in some systems but there are indications that these reactions are unlikely to be as significant in natural metal-organic systems. Thus, the precipitation of metal-phosphates is limited to reactions of the cultured algae *Chlorella* and *Chlamydomonas*, whose P contents are high compared with naturally occurring *Ulothrix* and to a wide variety of marine phytoplankton (0.3 to 0.4% of freeze-dried weight; FUJITA, 1971). The additional soluble organic matter present in French pressed suspensions of *Chlamydomonas* and *Chlorella* may contain some particulate organic matter which has been converted to a colloidal state by the cell breaking technique, as well as truly soluble organic matter released from the broken cells. The similar values of $[M(II)]_{sorbed}$ obtained for the hand homogenized and French pressed suspensions indicate that the additional soluble organic matter had similar metal sorption properties to the bulk of the particulate matter. This suggests that most of the additional soluble organic matter in the algal suspensions, and in particular the metal-containing organic matter precipitated from *Chlamydomonas* and *Chlorella* algal supernatant blanks, is particulate organic matter rendered soluble by the French pressing technique.

From a geochemical point of view metal sorption by particulate organic matter appears to provide a relatively direct mechanism for the concentration of metals from dilute solutions and their possible subsequent incorporation in sediments. Chemically, however, the metal sorption reaction is complex and, like the reactions of metals with humic and fulvic acids, the total amounts of metals sorbed reflect the sum of differing types of interaction of the metal with a wide variety of chemically dissimilar complexing sites.

In the systems Zn(II) and Cd(II)/*Ulothrix*, Zn(II)/*Chlamydomonas*, and Zn(II)/*Chlorella* deviations from the Langmuir isotherm have been detected. This isotherm is suitable for predicting the chemisorption of dissolved molecules onto a sorbent surface when a monolayer is formed, but if multilayer sorption occurs a more elaborate equation is needed (CASTELLAN, 1964). It is suggested that the deviations from the Langmuir isotherm observed in these metal-algae systems result from the formation, at high concentrations of M(II) in solution, of mixed and/or multinuclear metal-organic complexes whose M(II) : C_p ratio is higher than those of the complexes which exist in more dilute solutions. The observed dependence of $[M(II)]_{sorbed}$ on $[C_p]$ for *Ulothrix* suspensions may also result partly from changes in the M(II) : C_p ratios of the complexes formed. On this basis the Zn(II)/*Ulothrix* reaction should be most sensitive to changes in $[C_p]$ and the Pb(II)/*Ulothrix* system the least. This is, in fact, observed experimentally.

The formation of mixed and/or multinuclear metal-organic complexes may be relatively common in the reactions of metals with natural organic materials. SCHNITZER and HANSEN

(1970) noted that a number of divalent metal ions formed 1 : 1 molar complexes with fulvic acids in solutions of 0.1 ionic strength and pH between 3 and 5. With increase in pH from 3 to 5 and lowering of the ionic strength to zero the metal : fulvic acid ratios rose above 1, this effect being greatest for those metals whose 1 : 1 complexes have the highest stability constants. Consideration of the "saturation" values obtained for the present systems (Table 9) suggests an analogous situation. The common values near 100 mmoles.1000 g C_p^{-1} obtained by extrapolation of data from suspensions containing low concentrations of Zn(II) and Cd(II) indicate that complexes with similar, well-defined stoichiometries are formed by the organic matter of the three algae. The metal : C_p ratio, however, is only about one-twentieth that of the 1 : 1 molar metal-fulvic acid complexes detected by SCHNITZER and HANSEN. With the exception of Cu(II)/*Chlorella*, the remaining data extrapolate to "saturation" values near 500 mmoles.1000 g C_p^{-1}. Again the constancy of this saturation value indicates the formation of well-defined complexes with similar stoichiometries. In the Cu(II) and Pb(II)/algal systems these high M(II) : C_p complexes seem to be dominant over the entire experimentally accessible concentration range.

The enrichment factors and results of metal competition reactions in the system M(II)/*Ulothrix* both suggest that the relative stabilities of the metal-organic complexes are Pb(II) > Cu(II) > Cd(II) > Zn(II). This order, and the order of stability constant of bivalent metal-fulvic acid complexes given by SCHNITZER and SKINNER (1967), differ from the expanded Irving-Williams series (BASOLO and PEARSON, 1958) which is UO_2(II) > Be(II) > Cu(II) > Ni(II) > Co(II) > Pb(II) > Zn(II) > Cd(II) > Fe(II) > Mn(II) > Ca(II). A feature of the M(II)/*Ulothrix* series is the greater stability of the Pb(II) complexes compared with the Cu(II) complexes. This reversal of the order of stabilities has been noted in the sorption of metals by peat (BEEVERS, 1966), but not in the metal-fulvic acid systems examined by SCHNITZER and SKINNER. In the latter systems, however, an increase in the pH of the solution from pH 3.0 to 5.0 produces a larger increase in the stability constants of the Pb(II)/fulvic acid complexes than in those of the Cu(II)/fulvic acid complexes. This suggests that the reversal of the relative stabilities of the Cu(II) and Pb(II) complexes may be confined to the high M(II) : C_p ratio complexes.

The data on metal sorption by *Ulothrix* suspensions show that Zn(II) sorption is inhibited to a much greater extent by the presence of added cations in solution than is Cu(II) and Pb(II) sorption. Although this observation is consistent with the relative positions of Cu(II) and Zn(II) in the Irving-Williams series, the effectiveness of weakly complexing cations, such as Na^+, in suppressing Zn(II) sorption is perhaps unexpected. Further indications that Zn(II) complexes with naturally occurring organic matter may be relatively unstable are the reversal of the relative stabilities of Zn(II) and Cd(II) complexes with *Ulothrix*, and the greater stability of fulvic acid complexes of the non-transition metal Ca(II) compared with the Zn(II) complexes (SCHNITZER and SKINNER, 1967; SCHNITZER and HANSEN, 1970). It is not evident if, as with Pb(II), this effect is confined to the high Zn(II) : C_p ratio complexes.

In comparing the metal complexing abilities of the fresh algal materials used in this study with those of living algae and humic materials (Table 9) the sensitivity of the E.F.s, and to a lesser extent the saturation values, to the experimental conditions under which they were obtained must be taken into account. It is evident that detailed comparison of the E.F.s and saturation values given in Table 9 is not justified, but some feeling for the relative metal complexing abilities of the various materials can be obtained.

The saturation values of *Ulothrix*, *Chlamydomonas* and *Chlorella* for metal sorption are about 2 to 10 times lower than values for the uptake of Cu(II) by marine humic acids (RASHID, 1971), and at least 3 times lower than a minimum value for the removal of Cu(II) from solution by fresh organic matter from the marine brown alga *Ascophyllum nodosum* (WASSERMAN, 1949). Nonetheless, if saturation values of this order (which correspond to about 10% Pb, 3% Cu, and 3% Zn) were attained by the organic matter present in sedimentary ore-forming environments, then a weight of organic matter of similar order of magnitude to that of the inorganic sedimentary materials would be needed to sorb sufficient metals to form a sedimentary ore deposit. The organic carbon contents of those deposits at the present day amounts to only 0.1% to 10% of this amount. In view of DEUSER's (1971) conclusion that only 4% of the organic carbon primarily produced in the Black Sea is fixed in the sediment, however, this does not seem an unreasonable circumstance.

Consideration of the values of the E.F.s for metal sorption by *Ulothrix*, *Chlamydomonas*, and *Chlorella* suggest that the saturation values are unlikely to be approached in solutions whose metal contents are of a similar order of magnitude to those of average seawater. If, however, metal concentrations in the water of the sedimentary basin had been raised by some mechanism to near 1 $mg.l^{-1}$, then the E.F.s given in Table 9 indicate that particulate algal materials could sorb 2.5% Pb(II) and 0.3% Cu(II). The present data indicate that Zn(II) will not be sorbed under the highly saline conditions which probably existed in most environments of ore deposition, but insufficient data are available to determine if this degree of selectivity is specific to *Ulothrix*. If it is a feature of a wide variety of algal materials then it may provide a mechanism for the selective precipitation of Pb(II) from brines rich in Pb(II) and Zn(II).

CONCLUSIONS

1) Metal sorption by particulate organic matter is quantitatively the main reaction by which metals are removed from solution by suspensions of *Ulothrix*, *Chlamydomonas*, and *Chlorella*. The precipitation of insoluble metal-organic and metal-inorganic compounds from metals and soluble organic and inorganic materials derived from the algae is experimentally important but may not occur to a significant extent under natural conditions.

2) Chemically the metal sorption process is complex and involves the formation, to varying degrees, of at least two types of metal complex with differing metal : organic carbon ratios. Under the experimental conditions of this study two types of complex were detected in the reactions of Zn(II) and Cd(II), but only the complexes with the higher metal : organic carbon ratios were detected in Pb(II) and Cu(II) systems.

3) The chemical characteristics of metal sorption by the fresh algal materials used in these experiments are similar in some respects to those of the reactions of metals with humic materials. There are indications in both cases that mixed and/or multinuclear metal-organic complexes are formed and that the Pb(II) complexes are stabilized and Zn(II) complexes destabilized, compared with complexes of these metals with most ligands. In metal sorption from saline solutions by *Ulothrix* this results in the

suppression of Zn(II) sorption to zero, but this degree of selectivity has not been demonstrated for other algal materials.

4) If the "saturation" values of the algal materials used in this study were attained, a quantity of organic material of similar order of magnitude to that of the inorganic sediments would be required to sorb sufficient metals to form a sedimentary ore deposit. In the light of data on the organic carbon budgets of modern euxinic basins this does not seem unreasonable,but the magnitude of the enrichment factors indicates that the saturation values could be approached only in solutions already enriched in metals.

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JAMES FERGUSON and BOHDAN BUBELA, Baas Becking Geobiological Laboratory, B.M.R. Building, P.O. Box 378, Canberra City, A.C.T., 2601, Australia.

TABLE 1. Organic carbon contents of some low-grade metamorphosed sedimentary sulphide ore deposits

Deposit	Type	Organic Carbon %	Age	Reference
McArthur River: HYC deposit	Stratiform Pb/Zn	0.1 to 13	Middle Proterozoic	LAMBERT and SCOTT (in prep).
Mount Isa: No. 7 orebody	Stratiform Pb/Zn	0.1 to 1.0	Middle Proterozoic	CROXFORD (1963)
Copperbelt: N. Rhodesia overall	Stratiform Cu	trace to 1.9	Upper Proterozoic	MENDELSOHN (1961)
Kupferschiefer: Mansfield	Stratiform Cu/Pb/Zn	Up to 9	Upper Permian	TRASK (1925)
Woodcutters	Vein-type Pb/Zn	Up to 1.6	Lower Proterozoic	ROBERTS (1973)

TABLE 2. Effects of homogenizing techniques on the physical and chemical compositions of algal suspensions

Algae	Homogenizing Technique	Morphology[1]	Proportion of whole[2] cells (%)	Centrifugation conditions	Total freeze-dried weight $g.l^{-1}$	C_t $g.l^{-1}$	C_s $g.l^{-1}$	Calc. C_p $g.l^{-1}$
Ulothrix	Mechanical chopping	Short filaments[3] mainly 14-35 μ in length. Cell "husks" and fragments	60-90[4]	198,400 x g	9.8	4.42	0.85_5	3.57
Chlamydomonas	Hand homogenization (HH)	Whole cells about 10 μ in diameter	> 95	198,400 x g	10.0	4.64	0.57	4.07
	French press (FP) X 1	Whole cells plus cell fragments	50	198,400 x g	10.0	4.64	1.20	3.44
	X 3	"	70					
Chlorella	Hand homogenization	Whole cells about 10 μ in diameter	> 95	198,400 x g	10.0	4.51	0.43_5	4.07_5
	French press X 2	Whole cells plus cell fragments	< 5	198,400 x g	10.0	4.51	1.62	2.89

1. From microscopic examination.
2. i.e. Cells not visibly ruptured. The freezing and/or freeze-drying procedures to which the cells had been previously subjected can, in themselves, damage the cells.
3. Individual cells are approximately 7μ x 3μ.
4. Estimated by microscopic examination of suspensions.

TABLE 3. Major element contents of algae
Values are percent of freeze-dried pellets

Algae	Fraction	C	H	N	S	P	Ash at 700°C
Ulothrix	Total	45.13	6.24	5.52	0.5	0.16	9.6[1]
	MC 14,400 x g	43.45	7.15	5.63	0.5	0.2	n.d.[3]
Chalamydomonas	Total	46.37	6.50	8.38	1.2	3.1	9.0
	HH 198,400 x g	49.43	7.35	8.94	n.d.	2.4	n.d.
	FP X 2 198,400 x g	49.45	7.28	9.08	n.d.	2.9	n.d.
Chlorella	Total	45.07	6.80	7.95	0.6	3.4	n.d.
	HH 198,400 x g	48.99	7.48	8.57	n.d.	2.25	n.d.
	FP X 2 198,400 x g	48.02	7.53	7.46	n.d.	2.26	n.d.
Chlorophyceae[2]	Total	46	6	5.6	n.d.	n.d.	n.d.

1. Metal content of ash: Fe, 9.2; Mn, 0.37; Ca, 2.0; Mg 5.0; Ti, 0.07; V, 22 ppm; Y, 115 ppm; Zr, 100 ppm; Ba, 1100 ppm; Co, 190 ppm; Ni, 160 ppm; Cr, 140 ppm; Cu, 900 ppm; Sc, 220 ppm; Sr, 50 ppm.

2. VINOGRADOV (1953).

3. Not determined.

TABLE 4. Inorganic constituents of supernatants from algal suspensions centrifuged at 198,400 x g
Concentrations in $mg.l^{-1}$

Algae	C_t $g.l^{-1}$	C_s $g.l^{-1}$	K sp. at 20°C $\mu\Omega^{-1}.cm^{-1}$	K	Na	Ca	Mg	Fe	Mn	Cu	Pb	Zn	PO_4^{3-}	Cl^-
Ulothrix	4.42	0.85_5	234	34.5	2.5	0.65	4.6	0.7	0.3	0.55	0.05	0.25	2.43	<5
Chlamydomonas														
HH	4.64	0.57	178	9.5	10.2	3.5	4.45	2.4	0.3	1.4	0.4	0.3	122	
FP X 2	4.64	1.20	194	10.5	7.1	3.55	4.9	2.4	0.3	8.0	0.4	0.45	130	<5
Chlorella														
HH	4.51	0.435	680	185	52	1.05	9.5	2.5	0.3	0.3	0.4	0.3	450	
FP X 3	4.51	1.62	735	185	68	3.55	34.5	1.9	0.5	8.0	0.4	0.5	n.d.[2]	<5

1 Concentrations are approximately 10 times those used in metal sorption experiments

2 Not determined.

TABLE 5. Metal concentrations in blanks and suspensions of *Chlorella.* pH = 5.6 [NaOAc + HOAc] = 16 mmoles.l^{-1} [C_p] = 451 mg.l^{-1}

	[M(II)] in mmoles.l^{-1}				
	Distilled water Blank	Supernatant blank		Suspension	
		HH	FP x 2	HH	FP x 2
Cu(II)	0.318 ± 0.009	0.309 ± 0.01	0.263 ± 0.008	0.132 ± 0.004	0.142 ± 0.004
Zn(II)	0.317 ± 0.009	0.320 ± 0.01	0.300 ± 0.009	0.225 ± 0.007	0.217 ± 0.007

TABLE 6. Effects of organic and inorganic matter in solution on $[M(II)]_{sorbed}$ by particulate organic matter derived from *Ulothrix*. Suspensions centrifuged at 14.400 x g. pH = 5.6

Experiment No.	Metal	$[C_p]$ $mg.l^{-1}$	C_s $mg.l^{-1}$	[NaOAc + HOAc] $m.moles.l^{-1}$	Added salts $m.moles.l^{-1}$	[M(II)] added $m.moles.l^{-1}$	[M(II)] removed $m.moles\ 1000g\ C_p^{-1}$
1.	Cu(II)	357	85	16	-	0.482	348 ± 50
		357	10	16	-	0.482	362
2.	Pb(II)	357	85	16	-	0.145	270 ± 20
		357	10	16	-	0.145	262
3.	Zn(II)	357	85	16	-	0.327	198 ± 60
		357	10	16	-	0.327	180
4.	Cu(II)	357	85	0	-	0.504	340 ± 50
		357	85	16	-	0.504	353
5.	Pb(II)	357	85	0	-	0.135	216 ± 20
		357	85	8	-	0.135	208
		357	85	16	-	0.135	243
		357	85	40	-	0.135	203
6.	Zn(II)	357	85	0	-	0.598	218 ± 60
		286	68	8	-	0.601	171
		286	68	16	-	0.601	155
7.	Zn(II)	357	85	16	-	0.382	203 ± 60
		357	85	16	200 NaCl	0.382	< 20
		357	85	16	200 $Mg(NO_3)_2$	0.382	21
		357	85	16	Seawater	0.382	21
		357	85	16	Red Sea Brine	0.382	< 20
8.	Cu(II)	357	85	20	-	0.587	374 ± 50
		357	85	20	51 NaCl	0.587	374
		357	85	20	103 NaCl	0.587	368
		357	85	20	205 NaCl	0.587	354
		357	85	20	510 NaCl	0.587	320
		357	85	20	1540 NaCl	0.587	286
		357	85	20	3080 NaCl	0.587	286
		357	85	16	-	0.491	374
		357	85	16	Seawater[1]	0.491	353
		357	85	16	Red Sea Brine[2]	0.491	191
		357	85	16	200 $Mg(NO_3)_2$	0.491	208
9.	Pb(II)	357	85	16	-	0.135	243 ± 20
		357	85	16	200 $Mg(NO_3)_2$	0.162	182

1. Na^+ 0.46 M; Cl^-, 0.54M; Mg^{2+}, 0.06 M; Ca^{2+}, 0.01M; SO_4^{2-}, 0.03 M.

2. Solution containing the major ions in the approximate concentrations found in the hot brine in the Atlantis (II) Deep in the Red Sea (i.e. without trace metals). ($moles.kg^{-1}$) NaCl, 4.007; 0.048 KCl; 0.128 $CaCl_2$; 0.031 $MgCl_2$; 0.0016 NaBr; 0.0087 Na_2SO_4. (Brewer and Spencer, 1969).

TABLE 7. Dependence of $[M(II)]_{sorbed}$ on proportion of whole cells in the suspension

$[NaOAc + HOAc]$ = 16 mmoles l^{-1}. pH = 5.6. All samples centrifuged at 198,400 x g for 30 minutes

Algae	Pre treatment	Organisms ml^{-1}	Percent whole cells	C_t mg l^{-1}	C_p mg l^{-1}	C_s mg l^{-1}	[Cu(II)] added mmoles.l^{-1}	[Cu(II)] sorbed mmoles 1000 g C_p^{-1}	[Zn(II)] added mmoles.l^{-1}	[Zn(II)] sorbed mmoles 1000 g C_p^{-1}
Chlamydomonas	HH	14.4×10^8	> 95	232	203	28	0.315	388	0.306	140
	FP x 1	9.8×10^8	70	232	-	-	-	-	-	-
	FP x 2	9.3×10^8	65	232	172	60	0.315	402	0.306	150
	FP x 3	7.4×10^8	50	232	-	-	-	-	-	-
Chlorella	HH	30.6×10^8	> 95	451	407	43	0.315	430	0.306	230
	FP x 1	5.5×10^8	20	-	-	-	-	-	-	-
	FP x 2	0.5×10^8	< 5	451	289	162	0.315	419	0.306	290

TABLE 8. Experimental "saturation" values for Cu(II), Pb(II), Zn(II) and Cd(II) sorbed by particulate organic carbon derived from *Ulothrix*. [NaOAc + HOAc] = 16 mmoles l^{-1} pH=5.6. $[C_p]$ = 357 $mg.l^{-1}$

	$[M(II)]_{solution}$ mmoles l^{-1}	$[M(II)]_{sorbed}$ mmoles 1000 g C_p^{-1}	
Cu(II)	0.810	542	± 100
	1.110	551	
	1.1330	547	
	2.030	573	
Pb(II)	0.639	540	± 100
	0.760	564	
Cd(II)	0.675	120	± 100
	0.853	124	
	1.600	177	
	1.775	187	
Zn(II)	1.020	140	± 100
	1.328	130	
	1.910	200	± 100
	2.217	200	

TABLE 9. Enrichment factors and saturation values for Cu(II), Pb(II) and Zn(II) in natural organic materials

$$\text{E.F.} = \frac{\text{mmoles M(II)}.1000\ \text{g}\ C_{org}^{-1}}{\text{mmoles M(II)}.1^{-1}}$$

	Metal	E.F. $(1.1000\ g\ C_{org}^{-1})$	Saturation value $(\text{mmoles}.1000\ g\ C_{org}^{-1})$	Notes
Metal contents of living algae				
Marine brown algae				
(BLACK and MITCHELL, 1952)	Cu	500 to 5,300	-	1
	Pb	3,400 to 44,000	-	1
	Zn	4,300 to 13,000	-	1,2
Metal sorption from aqueous solutions by fresh particulate algal matter				
Ulothrix (This work)	Cu	3,300	500	3,7
	Pb	25,400	500	3,7
	Zn (dilute)	700	100	3,4,7
	(conc)	-	500	3,4,7
	Cd (dilute)	750	100	3,4,7
	(conc)	-	500	3,4,7.
Chlamydomonas (This work)	Cu	4,400	500	5,7
	Zn (dilute)	950	100	4,5,7
	(conc)	-	300	4,5,7
Chlorella (This work)	Cu (dilute)	9,700	400	4,5,7
	(conc)	-	1,200	4,5,7
	Zn (dilute)	970	80	4,5,7
	(conc)	-	250	4,5,7
Ascophyllum nodosum (a marine brown alga; WASSERMAN, 1949).	Cu	-	1,400	6,12
Metal sorption from aqueous solutions by humic materials				
Peat (BEEVERS, 1966)	Cu	178,000	-	8,12
	Pb	40,000	ca 800	6,9,12
	Zn	14,000	-	10,12
Marine humic acids (RASHID, 1971)	Cu	-	900 to 5,600	11,12
Maximum metal contents of organic-rich sediments				
Walvis Bay, South-west Africa (CALVERT and PRICE, 1970).	Cu	56,000	-	1,13
	Pb	150,000	-	1,13
	Zn	180,000	-	1,13

TABLE 9 (cont'd)

	Metal	E.F. ($l.1000\ g\ C_{org}^{-1}$)	Saturation value ($mmoles.1000\ g\ C_{org}^{-1}$)	Notes
Maximum metal contents of organic-rich sediments				
Black shales (VINE and TOURTELOT, 1970)	Cu	1,670,000	-	1,14
	Pb	3,300,000	-	1,14
	Zn	23,000,000	-	1,14

1. Conditions are presumably those of normal seawater, for which metal concentrations are assumed to be Cu, 0.01 $mg.l^{-1}$; Zn, 0.01 $mg.l^{-1}$ (GOLDBERG, 1963) and Pb, 0.001 $mg.l^{-1}$. The Pb value is near the middle of the range quoted by RILEY (1965).
2. Measured Zn concentration in the associated seawater; 0.009 to 0.02 $mg.l^{-1}$.
3. pH = 5.6; $[C\ ] = 357\ mg.l^{-1}$; $[NaOAc + HOAc] = 16\ mmoles.l^{-1}$.
4. Deviations from the Langmuir isotherm occurred at high (> 5 to 20 $mg.l^{-1}$) concentrations of M(II) in solution.
5. pH = 5.6; $[C_p] = 407\ mg.l^{-1}$; $[NaOAc + HOAc] = 16\ mmoles.l^{-1}$.
6. pH = 4.3 to 4.5; $[C_{org}] = 5.600\ mg.l^{-1}$; $[M(II)]_{solution} = 320\ mg.l^{-1}$. Under these conditions the "saturation" value may not have been attained and the figure quoted is probably a minimum value.
7. E.F.s obtained from slopes of tangents at infinitely low $[M(II)]_{solution}$ (see text).
8. pH > 4; $[C_p] = 14.7\ mg.l^{-1}$; $[M(II)]_{solution} = 1.3\ mg.l^{-1}$.
9. pH > 4; $[C_p] = 117\ mg.l^{-1}$. E.F.s calculated from graphical data given by the author
10. pH > 4; $[C_p] = 14.7\ mg.l^{-1}$; $[M(II)]_{solution} = 3.6\ mg.l^{-1}$.
11. pH 7.0.
12. $[C_{org}]$ calculated from original data assuming, after CALVERT and PRICE (1970), that $C_{org} \times 1.7$ = dry organic matter.
13. The E.F.'s refer to the samples in the set which contain the maximum amount of the particular element under consideration. They have been calculated from the total metal content of the sample as, in the authors' view, the contribution of terrestrial components to the trace metal contents is small.
14. Calculated assuming $C_{org} = 3.0\%$. The E.F.s refer to the 95th percentile of 20 sets of black shale samples.

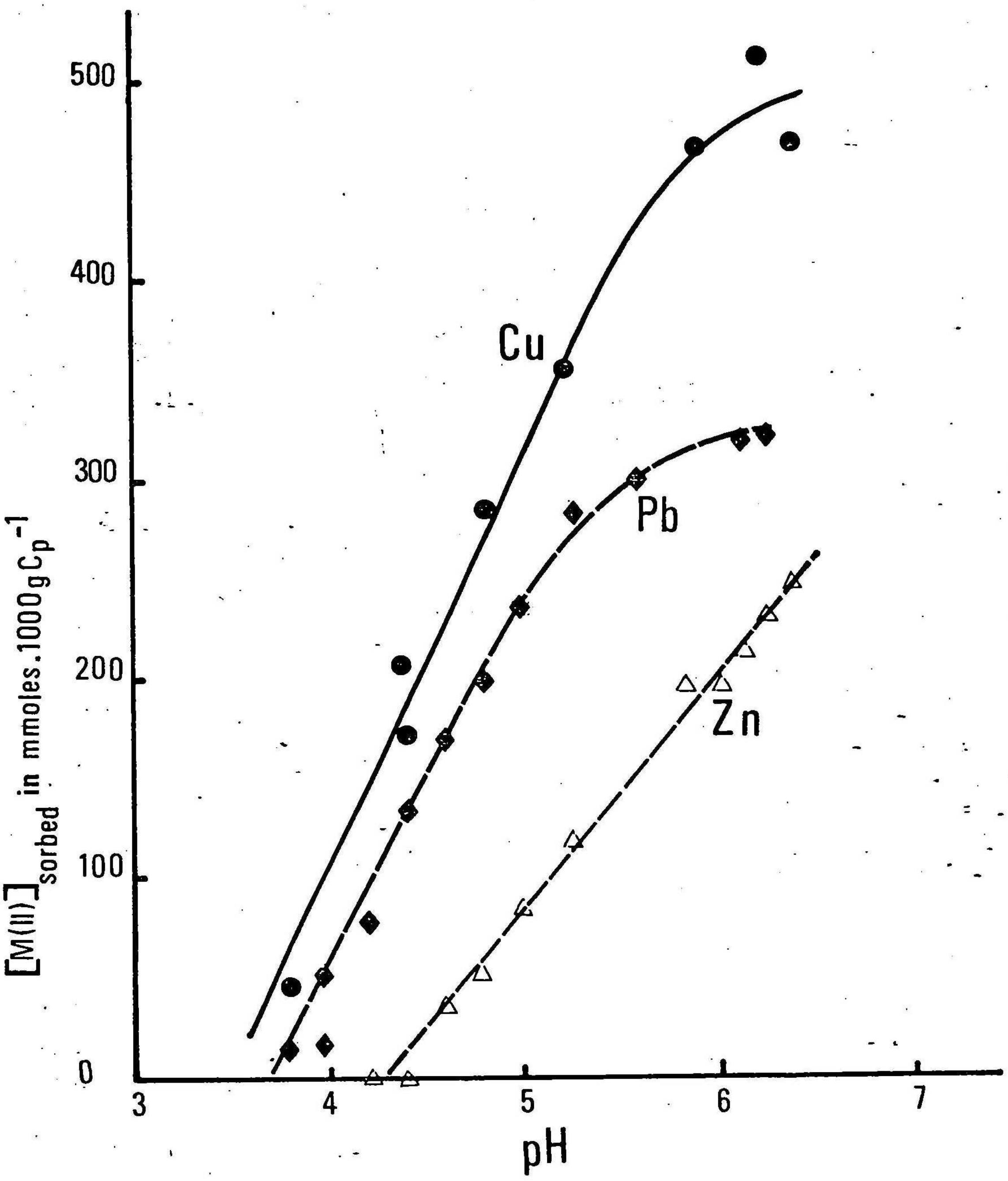
LEGENDS FOR FIGURES

Fig. 1. Dependence of $[M(II)]_{sorbed}$ on pH for particulate organic-matter of *Ulothrix*. $[C_p]$ = 357 mg.l^{-1}; [NaOAc + HOAc] or [NaOAc + HCl] = 16 mmoles.l^{-1}. Total metal added to suspensions : Cu(II), 0.628 mmoles.l^{-1}; Pb(II), 0.193 mmoles.l^{-1}; Zn(II), 0.607 mmoles.l^{-1}.

Fig. 2. Evaluation of "enrichment factors" from graphs of $[M(II)]_{solution}$ against $[M(II)]_{sorbed}$.

Fig. 3. Linear Langmuir isotherm plots of the dependence of $[M(II)]_{sorbed}$ on $[M(II)]_{solution}$ for particulate organic matter of *Ulothrix*. $[C_p]$ = 357 mg.l^{-1}; [NaOAc + HOAc] = 16 mmoles.l^{-1}; pH = 5.6

FIGURE 1



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M(P+)148

FIGURE 2

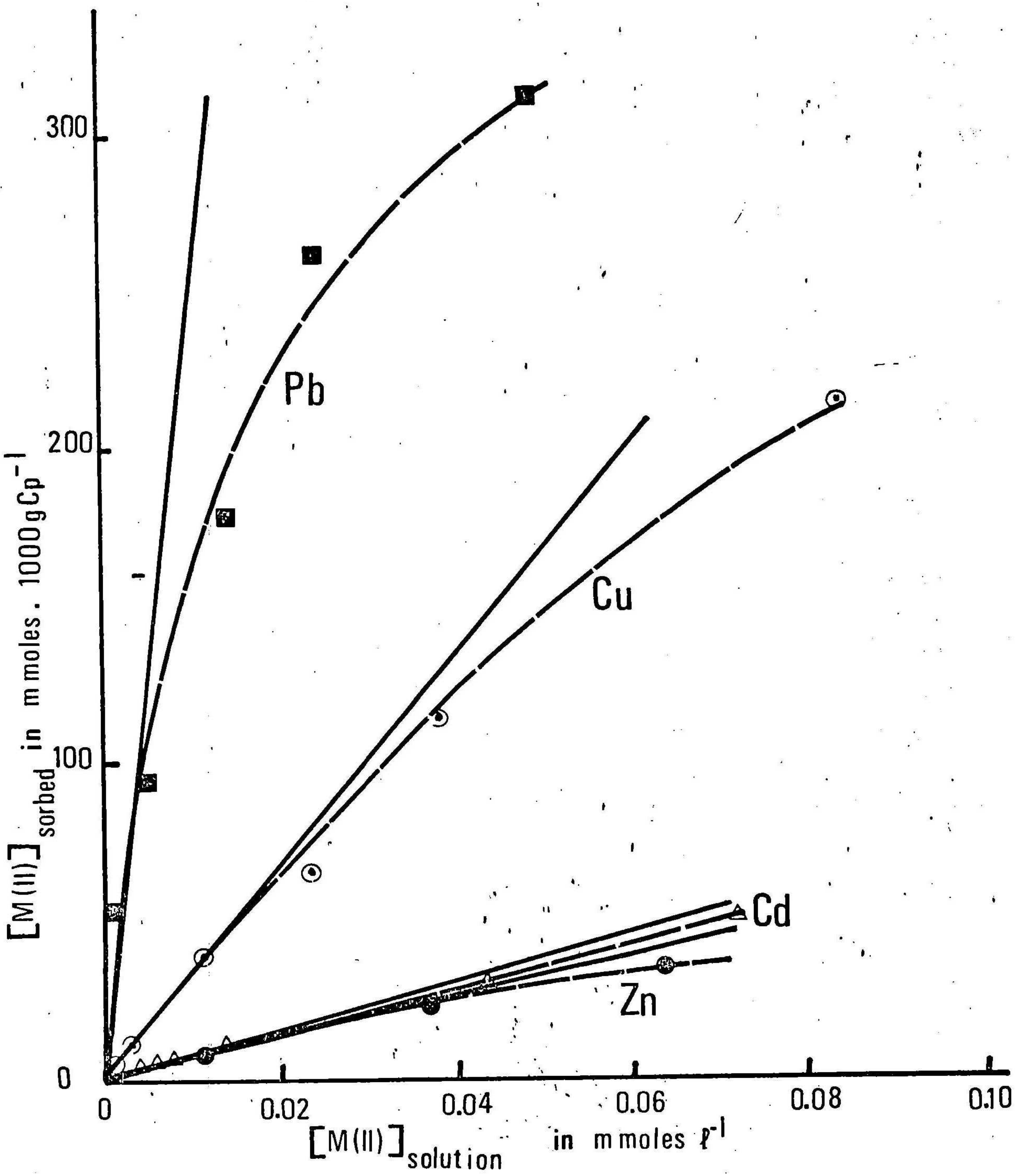
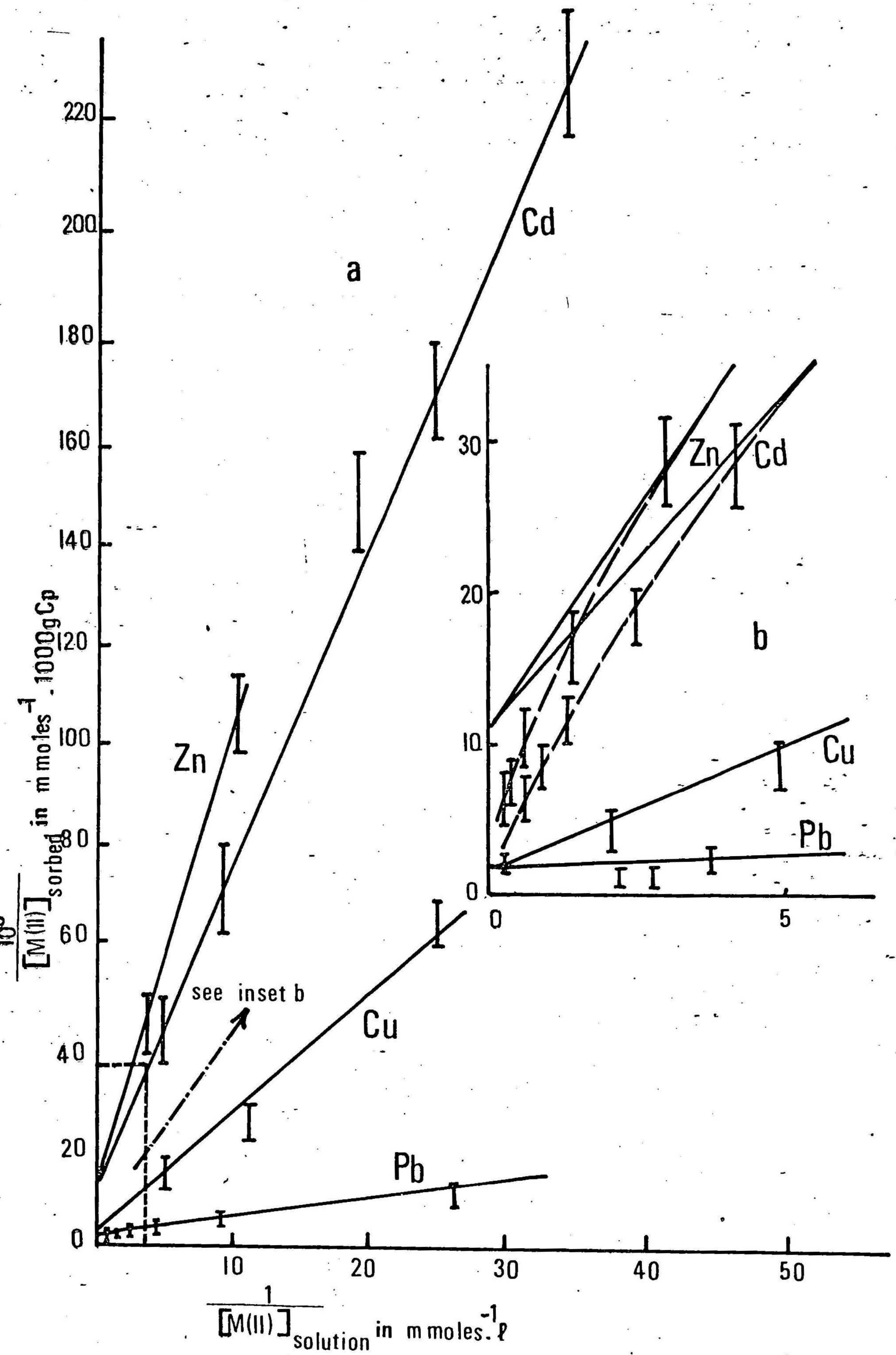

[M(II)]sorbed in mmoles . 1000 g Cp-1
300
200
100
0
0
0.02
0.04
0.06
0.08
0.10
[M(II)]solution in mmoles l-1
Pb
Cu
Cd
Zn

FIGURE 3


a
b
Cd
Zn
Cu
Pb
see inset b
220
200
180
160
140
120
100
80
60
40
20
0
10
20
30
40
50
30
20
10
0
0
5
$\frac{10^3}{[M(II)]_{sorbed}}$ in m moles^{-1} . 1000g Cp
$\frac{1}{[M(II)]_{solution}}$ in m moles^{-1} ℓ