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SIMULATION OF SEDIMENTARY ORE-FORMING PROCESSES: CONCENTRATION OF Pb AND Zn IN ORGANIC AND Fe-BEARING CARBONATE SEDIMENTS

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Auszug

Anreicherungen von Pb bis zu 0.5% und Zn bis zu 1% wurden in Karbonatsedimenten, welche organische Substanz sowie Fe enthielten, in Sedimentationsversuchen experimentell erzeugt. Die Metalle wurden zusammen mit wasserhaltigen Fe-Oxiden (wahrscheinlich Lepidocrocit), organischer Substanz und einer Reihe von Ca-und Mg-Karbonaten aus einer hoch salinaren Pb- und Zn- reichen Lösung, welche ein kräftiges Wachstum der Grünalge *Chlorococcus* sp. unterstützte, abgelagert.

Blei war überwiegend mit den Karbonaten sowohl der Suspension als auch des Sediments assoziiert. Der Bleigehalt der zwei wichtigsten Karbonate nimmt von Aragonit zu Monohydrocalcit ab. Der Zn-Gehalt war korrelierbar mit dem Fe-Gehalt der aus Einzelheiten bestehenden Substanz in der Lösung und in den Sedimenten. Die Komplexierung von Pb und Zn in Lösung in Beziehung mit organischen Substanzen und die direkte Ausfällung von Pb- und Zn-Karbonaten und/oder Hydroxiden lieferte höchstens einen zweitrangigen Beitrag zum Konzentrationsprozess der Metalle.

Abstract

Concentrations of Pb up to 0.5% and Zn up to 1.0% have been produced in organic and Fe-bearing carbonate sediments formed in a simulated sedimentary system. The metals, together with hydrated ferric oxides (probably lepidocrosite), organic matter, and a variety of calcium and magnesium carbonate phases were deposited from a highly saline Pb and Zn-rich brine supporting a vigorous growth of the green alga *Chlorococcus* sp.

Pb is associated mainly with carbonate phases suspended in the brine and incorporated in the sediments, the Pb content of the two major carbonate phases decreasing in the order aragonite > monohydrocalcite. Zn is correlated with the Fe content of the particulate matter of the brine and the sediments. Complexing of Pb and Zn in solution with particulate organic matter, and the direct precipitation of Pb and Zn carbonates and/or hydroxides, make, at most, a secondary contribution to the overall concentrating process.

Introduction

In a previous communication (BUBELA and FERGUSON, 1973) we described the construction of a fibreglass tank of about 4 m^3 capacity which facilitates the investigation, under monitored conditions, of some chemical, mineralogical, and biological processes which take place in sediments.

As part of a program to apply experimental sedimentary systems to problems of the genesis of sedimentary Pb-Zn deposits we have used the apparatus to simulate an aerobic, highly saline, shallow-water, carbonate environment supplied with appreciable quantities of hydrated ferric oxides and dissolved Pb and Zn. The system was allowed to evolve for 8 months, and in this time: (i) a thriving algal population became established in brine overlying indigenous sediments; (ii) calcium and magnesium carbonate phases were precipitated from the brine; and (iii) a carbonate "crust" enriched in Pb and Zn, and containing considerable quantities of organic matter and hydrated ferric oxides, was deposited.

The present paper describes results of chemical analysis and supporting experiments on the supernatant brine and carbonate crust. They have been used to define the environment of deposition and the major reactions leading to the concentration and distribution of Pb and Zn in the system. Relevance to the formation of certain types of Pb-Zn deposits in carbonate rocks is briefly considered.

Methods

Experimental Sedimentary System

The major features of the experimental sedimentary system are presented schematically in Fig. 1. It comprised several layers of sediment, the topmost of which was nesquehonite, $MgCO_3.3H_2O$, saturated with and overlain by a concentrated (25% solids) brine collected at Port Alma, Queensland (hereafter the "Port Alma" brine). This brine contained significant amounts of organic matter and Fe, lesser amounts of Mn and Zn, but little Pb (Table 1). Immediately after introduction of the Port Alma brine and sediments into the system sufficient Pb and Zn were added to the brine overlying the sediments (hereafter the "supernatant" brine) to raise their concentrations to 15 PPM each. The system was then allowed to stand for a total of 8 months, and during this period losses of brine by evaporation, and of Pb and Zn to the underlying sediments, were compensated for by periodic additions of Port Alma brine containing Pb and Zn.

Samples

Samples of the supernatant brine were collected at intervals of about 1 month during the experiment, and their pH and Ca, Mg, Pb, and Zn contents determined. HCO_3^- was also determined on a sample collected after 3 months. Towards the end of the experiment two 1-litre samples were collected for a comprehensive analysis of their particulate and solution components. As a control, samples of the Port Alma brine were collected and analysed before and after the experiment. To test the homogenity of the brine two samples were collected from the large (200 litre) storage container, and their Fe and Mn contents determined. One sample was also analysed in detail. A sample collected before the experiment was analysed for Ca and Mg and its pH determined.

Total particulate matter in the brine samples was sedimented by centrifugation at 100,000 x g for 60 minutes in a Beckman Model L2 Preparative Ultracentrifuge. The particulate fractions of the Port Alma and supernatant brines were not homogeneous, and comprised two and three layers, respectively. The particulate matter from the supernatant brine consisted of a white solid overlain by a red-brown, fine-grained material which was in turn overlain by a semi-liquid mucilaginous layer coloured bright green by suspended algal cells. In the case of the Port Alma brine the white solid was absent, and the mucilaginous layer was light brown.

Two attempts to isolate pure phases from the particulate matter from the supernatant brine were made using differential centrifugation at the speeds shown in Table 2. This resulted in the isolation of five (A1, A2, A3, A4, A5) and four (B1, B2, B3, B4) fractions respectively. All of these fractions contained at least some algal mucilage, and, because of the small quantities available and their complex mineralogy, further fractionation was not attempted.

Samples of the carbonate crust were collected after 5 and 7 months, and their mineralogy determined. The later sample was sorted into three fractions of differing grain size by "panning" in acetone. The coarsest material ("spheres") comprised mainly small (0.15 mm in diameter), concentrically zoned spheres, most of which appeared to have an organic nucleus (DAVIES *et al.*, in preparation). The two finer fractions ("matrix 1" and "matrix 2") were fine-grained and amorphous.

Mineralogical determinations

Minerals were identified from XRD diagrams obtained with a Phillips P.W. 10/10 Diffractometer. An Fe-rich fraction of the Port Alma brine used for identification of the Fe minerals was washed with distilled water and dried over silica gel. Other particulate fractions from the Port Alma and supernatant brines were air or freeze dried and identified directly. Carbonate crust samples were washed with acetone and air-dried.

Chemical analyses

Analytical procedures will be described in detail elsewhere (BURELA *et al.*, in prep.).

Crust samples were washed with acetone, others were pressed between sorbent papers and air or freeze-dried overnight.

Pb, Zn, Fe, and Mn analyses of the brines are estimated to be precise to ± 5%, and Ca, Mg, and Sr are probably to ± 3%. Analyses of other inorganic components were carried out by Australian Mineral Development Laboratories (Adelaide), and precision is probably better than ± 5%.

The Na contents of the sediment samples were assumed to be derived from brine salts, and were used to recalculate analytical results to a salt-free basis. Sediment samples containing large amounts of mucilage (A4, A5, B4) had high salt contents (up to 70% of the total weight), and analytical precision may be as low as ± 15% for these.

Results

1. Formation of Calcium and Magnesium Carbonates

Chemical changes in the superantant brine (Table 3)

Data summarising the major trends observed during the experiment are given in Table 3.

The Port Alma brine changed little in pH or Ca and Mg contents while stored for the duration of the experiment (Table 3), but in this period a number of major changes occurred in the supernatant brine in the sedimentary system.

(1) Evaporation of the superantant brine and its replacement by fresh Port Alma brine resulted in a gradual increase in salinity. The theoretical concentration factor of 1.21 calculated by volume changes is closely approached by experimental factors of 1.17 and 1.16 based on measurements of Na^+ and Cl^- concentrations, which suggests that only limited interchange of the concentrated supernatant brine with interstitial water in the sediments had occurred.

(2) In the initial stages of the experiment (< 3 months) the pH of the brine rose relatively sharply from its initial value

of 6.9 to 8.1, and then declined slowly, until after 7.5 months it had reached a value of 7.65.

(3) The HCO_3^- concentration, compared to that of the Port Alma brine stored for 8 months, increased 10-fold in less than 3 months, and remained near this level till the end of the experiment.

(4) The concentration of Ca^{2+} declined to almost one-third of its original value, whereas the Mg^{2+} concentration was marginally higher than that calculated from volume changes due to evaporation.

(5) Changes (1) and (4) caused an increase in the Mg : Ca molar ratio from its initial value of 18.4 to 63 after 7.5 months.

Changes generally similar to (2), (3), and (4) could be induced experimentally in samples of the Port Alma brine by shaking them with excess solid nesquehonite (Table 3), although if the nesquehonite was centrifuged off after a short time (< ½ hour) the pH remained higher and the calcium content became lower than the corresponding values for the supernatant brine in the sedimentary system.

Mineralogy and chemical composition of precipitated carbonates (Tables 2 and 4).

The chemical changes outlined above resulted in the slow precipitation of a complex assemblage of carbonate and other phases, whose mineralogy and chemical composition varied considerably during the course of the experiment (DAVIES *et al.*, in preparation).

After 7 months the sediment crust, whose composition was probably an average of the various sediments deposited up to that time, contained monohydrocalcite as its major calcium carbonate mineral (Table 4). It was the only carbonate mineral detected in the "spheres" fraction of the crust, and chemical analyses confirmed that Mg-rich phases were present in this fraction in, at most, trace amounts. The finer fractions (matrix 1 and matrix 2) contain the calcium magnesium carbonates huntite and (?) protohydromagnesite (DAVIES and BUBELA, 1973), but in the earlier (5 months) sample nesquehonite was also detected, which suggests that diagenesis of some of the Mg-rich components of the crust occurred during the experiment.

The analytical data given in Table 3 indicate that particulate matter separated from the supernatant brine 7.5 months after the start of the experiment probably contained both carbonate and non-carbonate calcium and magnesium-rich components. Like the crust, the coarsest fractions were the most calcium-rich, but in this case aragonite was the dominant mineral, and Mg-rich phases, probably including high-magnesium calcite, were also present. Fractions A1, A2, and A3 also contained unidentified phases which, from the anlytical data in Table 3 and the position of a characteristic XRD peak in the region 31 to 31.5° 2θ, were probably calcium magnesium carbonates. Their concentrations, relative to those of aragonite, differed in the order A1 < A2 < A3. XRD diagrams of fraction A4 showed only halite peaks.

2. Concentrations of Organic Matter (Tables, 1, 2 and 4).

Soluble organic matter, the major organic component of the Port Alma brine (Table 1), was present in concentrations some 2 to 3 orders of magnitude above those in seawater (*ca* 0.5 PPM dissolved organic carbon; MENZEL and RYTHER, 1970). Particulate organic matter in the Port Alma brine was mainly algal mucilage which sedimented as a viscous brown syrup containing little recognizable organic debris.

Within 1 to 2 months of the start of the experiment a thriving population of the motile green unicellular alga *Chlorococcus* sp. had developed in the supernatant brine resulting, after 7 months, in a 10-fold increase in its particulate organic carbon content (Table 1). This particulate matter consisted mainly of whole algal cells, the remains of such cells, and an unidentified organism.

The carbonate "crust" contained 4.4% organic carbon overall, a significant proportion of which was present as easily recognizable whole cells and cell fragments within the crust.

3. Distribution of Fe and Mn

Fe occurred in the supernatant and Port Alma brines predominantly in the particulate form (Table 1). No crystalline Fe minerals could be detected by XRD in samples of the sediment "crust" or particulate matter from the supernatant brine. However, poorly crystallized lepidocrosite (γ-FeOOH) was detected in a comparatively Fe-rich sample of particulate matter from the Port Alma brine, and it seems likely that this was the major Fe-containing mineral in the sedimentary system.

The Fe contents of two samples of the Port Alma brine, collected after the experiment, differed significantly (19.4 and 80.0 PPM; Table 1). This was probably due to the accumulation of particulate Fe in the lower parts of the storage container. Calculations, based on the total amount of Ca deposited from the brine, the average Ca and Fe contents of the crust, and the amount of Fe remaining in the supernatant brine at the end of the experiment, indicate that the stock Port Alma brine had an average Fe content of 30 to 40 PPM.

The bulk of the Fe in the supernatant brine sedimented with the finer fractions of the particulate matter (Table 5), and one of the fractions (B3; Table 2) contained almost 5% Fe. Most of the Fe in the carbonate "crust" was also contained in the finer fractions (Table 5), but the concentrations (*ca.* 1% Fe; Table 4) were lower.

The Mn contents of the two samples of the Port Alma brine, collected after the experiment, did not differ greatly, possibly because they contained a high proportion of soluble Mn (Table 1). Comparison of the data for the supernatant and Port Alma brines (Table 1) indicates that this soluble fraction was significantly depleted during the experiment, which suggests that it was probably the source of most of the Mn in the carbonate crust.

No strong correlation between Fe or Mn and the major elements (Ca, Mg, organic C) of the "crust" or the particulate matter of the brine is evident from the data in Tables 2 and 4.

4. Distribution of Pb

About one quarter of the Pb in the supernatant brine was in the particulate form (Table 1). This particulate, Pb, and the Pb in the carbonate "crust", were present in marginally higher concentrations in the coarser fractions (up to 1.5 and 0.4%, respectively; Tables 2 and 4), but the total amounts of Pb in each of the fractions A1 to A4 were similar (Table 5).

Graphs of data in Tables 2 and 3 indicate that the Pb contents of the particulate brine and sediment "crust" fractions correlate with their Ca + Mg contents (Fig. 2), but not with their Fe, Mn or organic C contents. The correlations with [Ca] + [Mg] is non-linear, and may therefore reflect differences in the mineralogy of the calcium and magnesium phases.

Data in TAble 2 show that points at the upper and lower extremes of the curves in Fig. 2 correspond to samples containing predominantly Ca or Mg, respectively. By using the slopes of the tangents of the curve for the particulate matter for the brine, and a process of iteration, the relative dependence of the concentrations of Ca and Mg on the concentrations of Pb (Fig. 3) has been estimated as 9×10^{-3} moles Pb per mole of Ca, and 4×10^{-3} moles Pb per mole Mg. Data on the sediment "crust" are less complete, but because of the existence of an almost completely Mg-free fraction ("spheres") it could be calculated that the dependence of [Pb] on [Ca] and [Mg] is approximately equal to 2×10^{-3} moles Pb per mole of Ca or Mg. It is probable that aragonite and monohydrocalcite are the major Ca-containing minerals in the brine and crust, respectively, and, on this basis, their relative ability to remove Pb from solution is aragonite > monohydrocalcite.

5. Distribution of Zn.

Slightly more than 50% of the Zn in the supernatant brine is in the particulate form (Table 4), and both this particulate Zn and the Zn in the sediment "crust" correlate with the respective Fe contents (Fig. 4). The two sets of Zn/Fe ratios lie on the same curve, which suggests that the ability of the ferric hydroxides to react with Zn did not vary greatly during the experiment.

Discussion

Comparison with Natural Environments

The sedimentary system used in these experiments was designed to simulate a highly saline, shallow-water environment supporting vigorous algal growth, and depositing a variety of carbonate phases. Comparison of the major physical and chemical parameters of the experimental system with those of analogous present-day environments - e.g., the Coorong in South Australia - indicates that the artificial system is, in many respects, a realistic model of such environments.

Thus the rate of carbonate precipitation in the sedimentary system (60 cm per 100 years) is similar to that in one of the "ephemeral" lakes of the Coorong (50 cm per 100 years; SKINNER *et al.*, 1963), and the organic carbon and Fe contents of the sediment 'crust' are comparable to those found in various Coorong lakes (0.19 to 2.42% C, and 0.13 to 1.36% Fe; G.F. TAYLOR, pers. comm.). Furthermore, the high salinities and Mg : Ca molar ratios developed in the supernatant brine are well within the ranges found in the Coorong lakes (up to 38% total dissolved solids, and 1.1 to 362 Mg : Ca molar ratios; G.F. TAYLOR, pers. comm.). The particulate organic carbon concentration developed in the supernatant brine is, however, some 4 to 5 orders of magnitude above that in the open ocean (0.005 PPM particulate organic C; MENZEL and RYTHER, 1970). Few data appear to be available on the organic carbon contents of naturally occurring brines, but in view of observations of dense algal "blooms" in salt-fields (e.g., HANSGIRG, 1887; HOF and FREMY, 1933), the organic carbon concentrations in the simulated system do not seem abnormally high. The absence of sulphide, from the upper sediments and supernatant brine, of the sedimentary system, despite the development of sulphide concentrations up to 250 PPM in sediments below the nesquehonite layer, also reflects conditions in certain Coorong lakes where H_2S-rich sediments are overlain by aerobic sediments and brine (TAYLOR, 1972).

In most natural environments carbonate precipitation is probably induced by changes in the CO_2 flux caused by metabolic processes (CLOUD, 1965). Inorganically induced precipitation - e.g., by the influx of high bicarbonate groundwaters (VON DER BORCH, 1965) -

is comparatively less common. In the experimental sedimentary system, carbonate precipitation, at least in the initial stages, probably resulted mainly from an increase in the CO_3^{2-} concentration in the supernatant brine induced by equilibration with the nesquehonite forming the top layer of the indigenous sediments. Thus the pH and total alkalinity (mainly HCO_3^-) increases by the reaction:

$$MgCO_3 + H^+ \rightleftharpoons Mg^{2+} + HCO_3^- \tag{1}$$

producing, initially, a solution of pH 8.5 supersaturated with respect to calcium and magnesium carbonate phases. As the experiment progressed, and the algal population in the supernatant brine became firmly established, the inorganically produced carbonate may have been supplemented by the photosynthetic activities of the algae. Compared to laboratory investigations of carbonate precipitation (e.g., KITANO and HOOD, 1965) the rates of precipitation of carbonates from the supernatant brine are low. Both this slow rate of precipitation and the formation of monohydrocalcite, rather than the more commonly precipitated aragonite, may be related to the high concentrations of organic matter in the system (e.g., KITANO and HOOD, 1965; DUEDALL and BUCKLEY, 1971; CHAVE, 1970). LIPPMAN (1973) has suggested that high CO_3^{2-} concentrations in solution also favour calcite formation.

As the experiment proceeded the precipitation of carbonate phases was accompanied by a gradual decrease in the pH of the solution, which suggests that reaction (1) was strongly inhibited by the formation of the sediment "crust" and possibly by diagenetic changes within the nesquehonite layer. The final pH of 7.65 is 0.25 units below that at which carbonate precipitation in oceans ceases (CLOUD, 1965). This may have been a result of the much higher alkalinity and ionic strength (which will reduce the value of the dissociation constant for the reaction $HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$; HARNED and SCHOLES, 1941) of the supernatant brine in the system.

The formation of aragonite rather than monohydrocalcite in the latter stages of the experiment may have been induced by the high Mg : Ca molar ratios in the solution at that stage (e.g., KITANO, 1964).

Mechanisms of metal deposition

Mechanisms by which Pb and Zn could be removed from the supernatant brine and incorporated in the sediments include: 1) Direct precipitation of the metals from solution as metal carbonates and/or hydroxides, 2) sorption or complexing of the metals to particulate organic matter or hydrated ferric oxides, 3) sorption (coprecipitation) of the metals with carbonate phases, and, in the early stages of the experiment, 4) sorption of the metals by nesquehonite in the topmost layers of the indigenous sediments.

Mechanism (4) was shown to be feasible by shaking excess nesquehonite with a sample of Pb or Zn-spiked Port Alma brine. The

Pb and Zn were rapidly sorbed, and after 16 days, the initial concentrations in the brine of 15 PPM each had been reduced to < 3 PPM. However, the relative rapidity of this process, together with data on the decrease in the Pb and Zn concentrations in the supernatant brine 0.5 months after the start of the experiment (4 and 6 PPM, respectively) allows an upper limit of 30% of the total to be placed on the amounts of Pb and Zn removed from solution by this mechanism.

The solubility product of lead carbonate is about $10^{-13.2}$ (SILLEN and MARTELL, 1964). Assuming that the activity coefficient of Pb in the supernatant brine is determined mainly by complexing with Cl^- ions in solution, and therefore lies in the range 0.01 to 0.001 (C.J. DOWNES, pers. comm. 1974), it can be calculated that during the experiment the superantant brine was probably supersaturated with respect to lead carbonate. The strong correlation of [Pb] with [Ca]+[Mg] indicates, however, that most of the Pb co-precipitated with the calcium and magnesium carbonates, rather than precipitating directly from solution as lead carbonate. The apparently greater ability of Pb to coprecipitate with aragonite rather than with monohydrocalcite, is consistent with the observation that lead carbonate and aragonite are isostructural (DANA, 1932).

Zinc carbonate is 2 to 3 orders of magnitude more soluble ($K_{sp} \approx 10^{-10.8}$; SILLEN and MARTELL, 1964) than lead carbonate, but the activity coefficient of Zn in high Cl^- solutions is 1 to 2 orders of magnitude higher than that of Pb (C.J. DOWNES, pers. comm. 1974).

On this basis it is open to question if the supernatant brine in the sedimentary system was supersaturated with respect to zinc carbonate. The coprecipitation of Zn with calcite and aragonite from saline solutions containing organic matter (KITANO *et al.*, 1970), and the sorption of Zn from solution onto pre-formed dolomite (BEEVERS, 1966), have been demonstrated experimentally, but there is no evidence that such processes made a significant contribution to the concentration of Zn in the carbonate crust. The Zn appears to have sedimented mainly in association with hydrated ferric oxides. This has resulted in the abnormally high Zn : Fe ratios (*ca.* 1 : 2) but the nature of the association is not clear. BEEVERS (1966) has noted that the sorption of metals by ferric hydroxides is greatly enhanced by high salt concentrations in solution.

The relative importance of the organic and inorganic components of sedimentary basins in the concentration and accumulation of metals in sediments is largely unknown. For a wide variety of sediments their trace metal contents can be most readily correlated with their organic carbon contents. This has been taken as indicative that the metals were concentrated mainly by so-called "organic processes" (KRAUSKOPF, 1955) in which the metals are sorbed onto organic matter or organic-inorganic complexes (e.g., organo-clays). Experimental studies where sorption of metals by organic and inorganic materials were measured under comparable conditions are few, but the results tend to confirm that organic matter, especially that rich in humic and fulvic components, is considerably more efficient in sorbing metals than are clays, silts, carbonates, and hydrated ferric oxides (BEEVERS, 1966). On the other hand, JENNE (1968) has suggested that the distribution and concentration of trace metals in soils is controlled mainly by their sorption onto ferric hydroxides, and ROBERTS (1973) has postulated that, although the depositional environment of Woodcutters Pb-Zn Prospect, N.T., Australia, was probably rich in organic matter, Pb and Zn were removed from solution by co-precipitation with calcite, magnesium-calcite, and aragonite.

In the present experiments, Pb and Zn were removed from solution mainly in association with the carbonates and hydrated ferric oxides, rather than the particulate organic matter. For Pb, the dominance of co-precipitation with carbonates as the mechanism by which the metal is fixed in the sediments appears to be a function of the moderately high concentrations of Pb in the carbonate phases (up to 1.5%) as well as their much higher rates of precipitation compared to the organic matter. For Zn, the high concentrations of the metal associated with the ferric hydroxides, together with the likely inhibition of zinc-organic complexing by the high salt concentrations in solution (FERGUSON and BUBELA, 1974), may be the major factors controlling its precipitation behaviour.

It seems feasible that the differing mechanisms of precipitation of Pb and Zn could have led to a more rapid rate of precipitation of one or other of the metals, and the consequent formation of Pb or Zn enriched "bands" within the crust. However, the ratio of Pb to Zn deposited during the experiment (0.7) is near unity, and no evidence for spatial separation of Pb and Zn in the sediment "crust" was obtained.

Implications for Ore Genesis

The experimental sedimentary system used in this investigation has simulated a number of features characteristic of an evaporitic, aerobic, shallow-water marine environment of restricted circulation and containing abundant Pb and Zn but no sulphide in the overlying water. Environments of this type may have been sites for the deposition of certain sedimentary Pb-Zn ores whose predominantly carbonate host rocks usually include algal reefs and contain abundant iron sulphides, stromatolites, and organic matter.

Considerable experimental evidence demonstrates that a wide variety of inorganic and organic sedimentary materials can remove metal ions from solution, and, further, there are indications that at least some types of material have the capacity to concentrate sufficient quantities of metals to form an ore deposit (e.g., FERGUSON and BUBELA, 1974; RASHID and LEONARD, 1973). It is far from certain, however, that these capacities will be realized under normal sedimentary conditions, and metal-concentrating processes of this type may be important only in environments already enriched in metals, or in providing a metal-enriched sediment from which ore-forming solutions may be derived (e.g., ROBERTS, 1973).

In the highly metal-enriched sedimentary environment used in these experiments, Pb and Zn concentrations of about 0.5% developed in the sediments, which is equivalent to a concentration factor of about 200 to 300. The direct formation of an ore deposit under these conditions would require Pb and Zn concentrations in solution of about 50 PPM, which, amongst known present-day metal-rich brines are exceeded only by the hot, highly saline brines of the Salton Sea (540 PPM Zn, 102 PPM Pb; WHITE, 1968), and are significantly higher than those of the Red Sea (up to 11.03 PPM Zn, 0.56 PPM Pb; BROOKS *et al.*, 1969). The concentration factors are, however, less than an order of magnitude below the value of 1000 postulated by ROBERTS (1973) as sufficient for the preliminary concentration of 1 PPM Pb and Zn from solution into the carbonate host rocks of Woodcutters Prospect.

The concentration factors from solution to sediment obtained in the sedimentary system (200 to 300) are, in general, considerably smaller than those obtained in experimental investigations of metal-sediment interactions. They do not, however, preclude the primary formation of metal concentrations of ore grade in this way, and appear more than adequate for the preliminary concentration of metals in sediments.

The Pb and Zn in the experimental sedimentary system have been deposited, apparently without spatial differentiation, in an organic and Fe-bearing carbonate layer overlying the indigenous sediments, but it is conceivable that a wide variety of distributions and textures of metal sulphides could form from this deposit during diagenesis and metamorphism. The metals may be converted to sulphides *in situ* as the sediments become anaerobic, and bacterial sulphate reduction commences, giving rise to a stratiform deposit. Alternatively, during early diagenesis the metals may be expelled from unstable carbonate phases, and concentrated in veins and interstices where metal sulphides would subsequently form as veinlets and "cement" between the carbonate grains. If massive mobilization of the metals-e.g., as metal-organic complexes-takes place, a vein-type deposit may result.

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Table 1. *Soluble and total particulate trace metal and organic carbon concentrations in the Port Alma and supernatant brines.*

Concentrations in PPM. Total particulate matter is that sedimented by centrifugation at 100,000 x g for 1 hour. n.d. = not determined.

Brine	Time[1]		Fe	Mn	Pb	Zn	C_{org}
Port Alma	7.5	Soluble	1.2	2.5	<0.2	2.0	170
		Total particulate	18.2	1.0	<0.2	<0.2	50
		Total	19.4	3.5	<0.4	2.0	220
	>8	Total	80.0	4.1	n.d.	n.d.	n.d.
Supernatant	7.5	Soluble	2.0	0.6	12.6	8.8	120
		Total particulate	16.4	0.7	4.1	11.1	480
		Total	18.4	1.3	16.7	19.9	600

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[1] Time in months after establishment of the sedimentary system.

Table 2. *Chemical composition and mineralogy of particulate matter fractionated from the supernatant brine 7.5 months after establishment of the sedimentary system.*

Results are in percent, and have been adjusted to a salt-free basis.
n.d. = not determined.

Separation A[1]	Mineralogy[2]	Ca	Sr	Mg	Fe	Mn	Pb	Zn	C_{org}
A1 (<100 x g)	Aragonite, Mg - calcites, "Calcium magnesium carbonates"[3]	25.5	1.83	5.02	0.31	0.030	1.25	0.34	1.6
A2 (500 x g)	Aragonites; Mg - calcites; "Calcium magnesium carbonates"[3]	27.5	1.81	6.14	0.73	0.13	1.54	1.30	5.3
A3 (3,000 x g)	?Aragonite, Mg - calcites, "Calcium magnesium carbonates"[3]	9.14	0.27	10.01	3.24	0.21	0.73	2.38	5.1
A4 (14,400 x g))	Only halite peaks in XRD diagrams	1.81	0.050	5.47	3.07	0.072	0.29	1.36	10.3
A5 (100,000 x g))		0.2	0.12	0.2	0.29	0.0079	0.021	0.077	10.8
Separation B									
B1 (<100 x g)	n.d.	15.3	n.d.	5.5	0.20	0.029	0.75	0.32	n.d.
B2 (3,000 x g)	n.d.	2.78	n.d.	5.06	2.35	0.18	0.29	1.78	n.d.
B3 (14,400 x g)	n.d.	1.52	n.d.	9.10	4.73	0.16	0.41	2.24	n.d.
B4 (100,000 x g)	n.d.	0.2	n.d.	0.2	0.42	0.005	0.03	0.16	n.d.

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[1] Centrifugation speeds in brackets.

[2] Based on analytical and XRD data. Halite was detected in all fractions.

[3] Unidentified carbonate phases characterized by a broad peak in the region 31 to 31.5° 2θ, which is co-incident with the region where the calcium magnesium carbonates, dolomite and huntite, have diffraction peaks.

Table 3. *Changes in the pH and major constituents of the Port Alma and supernatant brines*

Results are in PPM and include contribtions from suspended particulate matter.
n.d. = not determined.

Brine	Time	pH	Ca	Mg	Sr	Na[6] %	Cl[6] %	HCO_3
Port Alma	0[1]	6.9	800[3]	10,600[3]	n.d.	n.d.	n.d.	n.d.
	8[1,4]	6.95	900	10,020	42	7.70	14.34	150
Port Alma	4 hrs[2]	8.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Nesquehonite	1 day[2]	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1500
	16 days[2]	7.95	100	10,060	n.d.	n.d.	n.d.	n.d.
Supernatant	3[1]	8.1	n.d.	n.d.	n.d.	n.d.	n.d.	1500
	7.5[1,2,5]	7.65	320[7,8]	12,200[7,8]	32[8]	8.925	16.76	1600

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[1] Time in months after establishment of the sedimentary system.

[2] Laboratory bench experiment in which a sample of the Port Alma brine was shaken for 15 minutes with solid nesquehonite and the excess removed by centrifugation. Time after removal of the nesquehonite.

[3] By titration; other Ca and Mg analyses by atomic absorption spectroscopy.

[4] K, 0.14%; Ba, 1 PPM; SO_4, 1.39%; NO_3, 0.4 PPM; PO_4, 0.3 PPM; I, 0.5 PPM; Br, 350 PPM.

[5] K, 0.17%; Ba, 1 PPM; SO_4, 1.59%; NO_3, 0.7 PPM; PO_4, 0.4 PPM; I, 0.75 PPM; Br, 400 PPM.

[6] Na supernatant/Na Port Alma = 1.16; Cl supernatant/Cl Port Alma = 1.17. Concentration factor calculated from volume changes = 1.21.

[7] Concentrations expected from experimental concentration factor of 1.165: Ca, 1070 PPM; Mg, 11,660 PPM.

[8] Contributions from particulate matter as determined by centrifugation: Ca, 36 PPM; Mg $\leq$ 100 PPM; Sr < 5 PPM.

Table 4. *Chemical composition of fractions of carbonate "crust" collected 7 months after establishment of the sedimentary system.*

Results are in percent, and have been adjusted to a salt-free basis.

Fraction	Mineralogy	Ca	Mg	Fe	Mn	Pb	Zn
"Spheres"	Monohydrocalcite	38.8	0.2	0.35	0.074	0.43	0.37
"Matrix 1")	Huntite and	13.9	13.1	0.43	0.14	0.34	0.56
"Matrix 2")	(?)protohydromagnesite[1]	13.7	14.1	0.91	0.23	0.36	0.94

Overall $C_{org} = 4.4\%$

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[1] DAVIES and BUBELA, 1973.

Table 5. *Relative contributions of fractions from separation A to the total particulate matter in supernatant brine.*

Concentrations in PPM. n.d. = not determined.

	Concentration fraction in brine	% of total particulate matter in brine	Ca	Mg	Fe	Mn	Pb	Zn
A1	82	3.2	21	4	0.3	0.02	1.03	0.30
A2	55	2.1	15	3	0.4	0.07	0.85	0.72
A3	94	3.7	8	9	3.0	0.20	0.69	2.24
A4	337	13.4	6	18	10.3	0.24	0.98	4.58
A5	1,950	77.4	1	1	5.6	0.16	0.41	1.50
Total a)[1]	2,520	100	51	34	19.6	0.69	3.96	9.34
b)[2]	n.d.	-	36	<100	16.4	0.7	4.1	11.1

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[1] Sum of concentrations in each of the fractions A1 to A5

[2] Total concentrations obtained experimentally by difference in concentrations before and after centrifugation at 100,000 x g.

Legends for Figures

Fig. 1. Major features of part of the simulated sedimentary system. By the end of the experiment the nesquehonite in the layer below the crust had been converted to other carbonate phases (DAVIES *et al.*, in preparation).

Fig. 2. Relationship of [Pb] to [Ca] + [Mg]

□ Suspended in brine; separation A
△ Suspended in brine; separation B
○ Sediment crust

Fig. 3. Relationship of [Pb] to [Ca] and [Mg] calculated by iteration of data in table 3.

□ and ▨ Suspended in brine; separation A
△ and ▲ Suspended in brine; separation B

Fig. 4. Relationship of [Zn] to [Fe]

□ Suspended in brine; separation A
△ Suspended in brine; separation B
○ Sediment crust

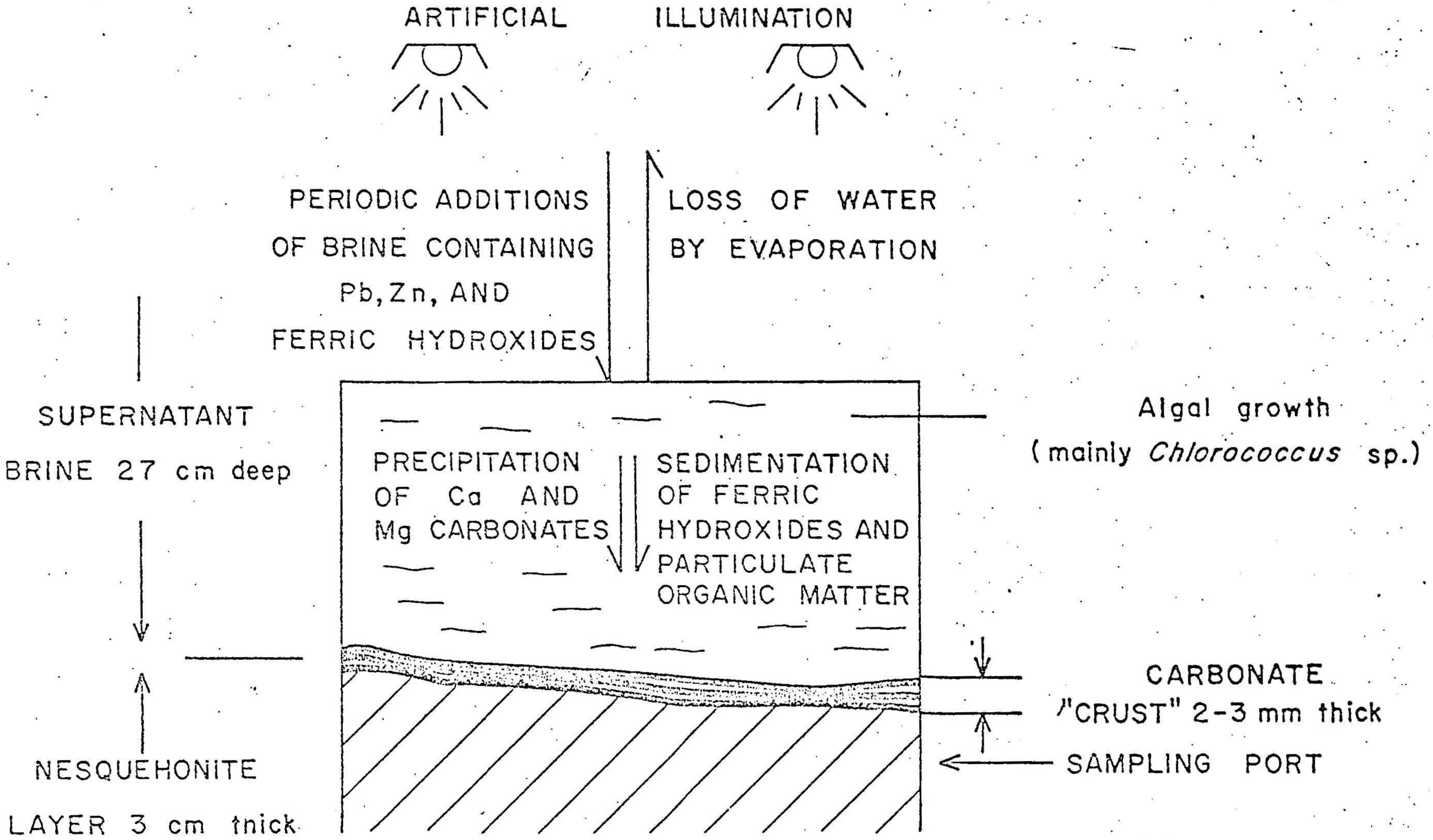

ARTIFICIAL ILLUMINATION
PERIODIC ADDITIONS OF BRINE CONTAINING Pb, Zn, AND FERRIC HYDROXIDES
LOSS OF WATER BY EVAPORATION
SUPERNATANT BRINE 27 cm deep
Algal growth (mainly *Chlorococcus* sp.)
PRECIPITATION OF Ca AND Mg CARBONATES
SEDIMENTATION OF FERRIC HYDROXIDES AND PARTICULATE ORGANIC MATTER
CARBONATE "CRUST" 2-3 mm thick
SAMPLING PORT
NESQUEHONITE LAYER 3 cm thick

Fig. 1

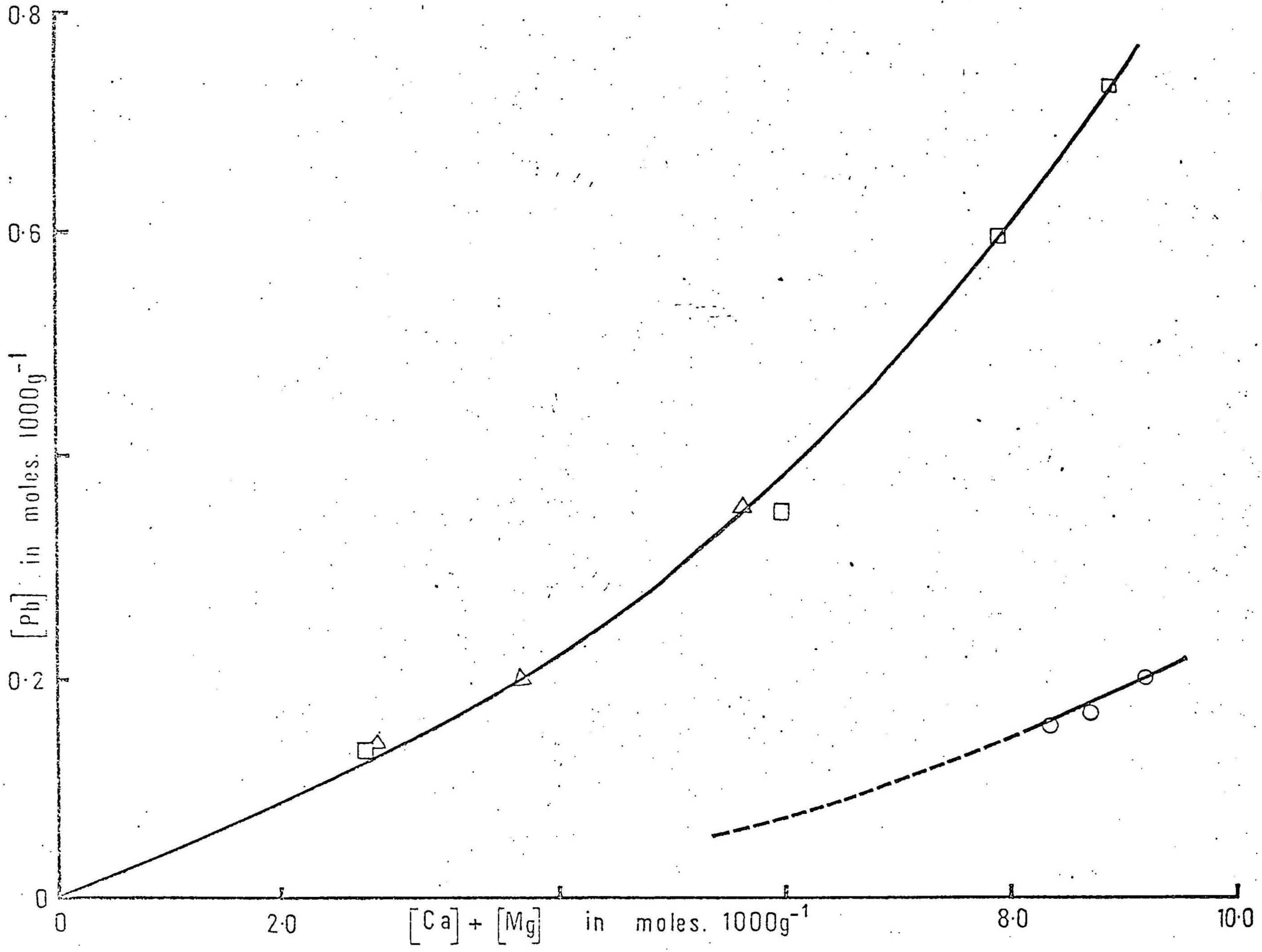


Fig. 2

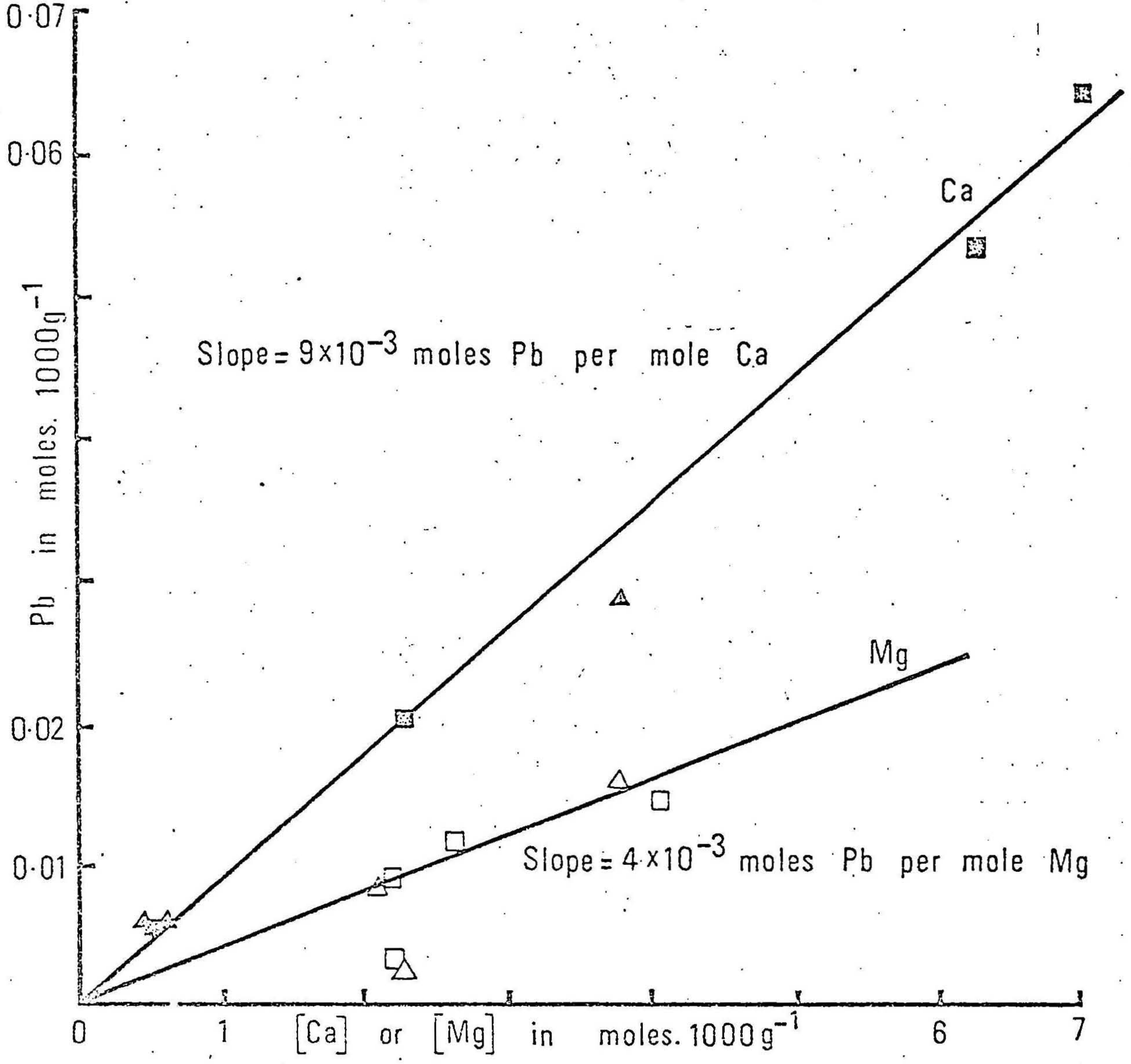
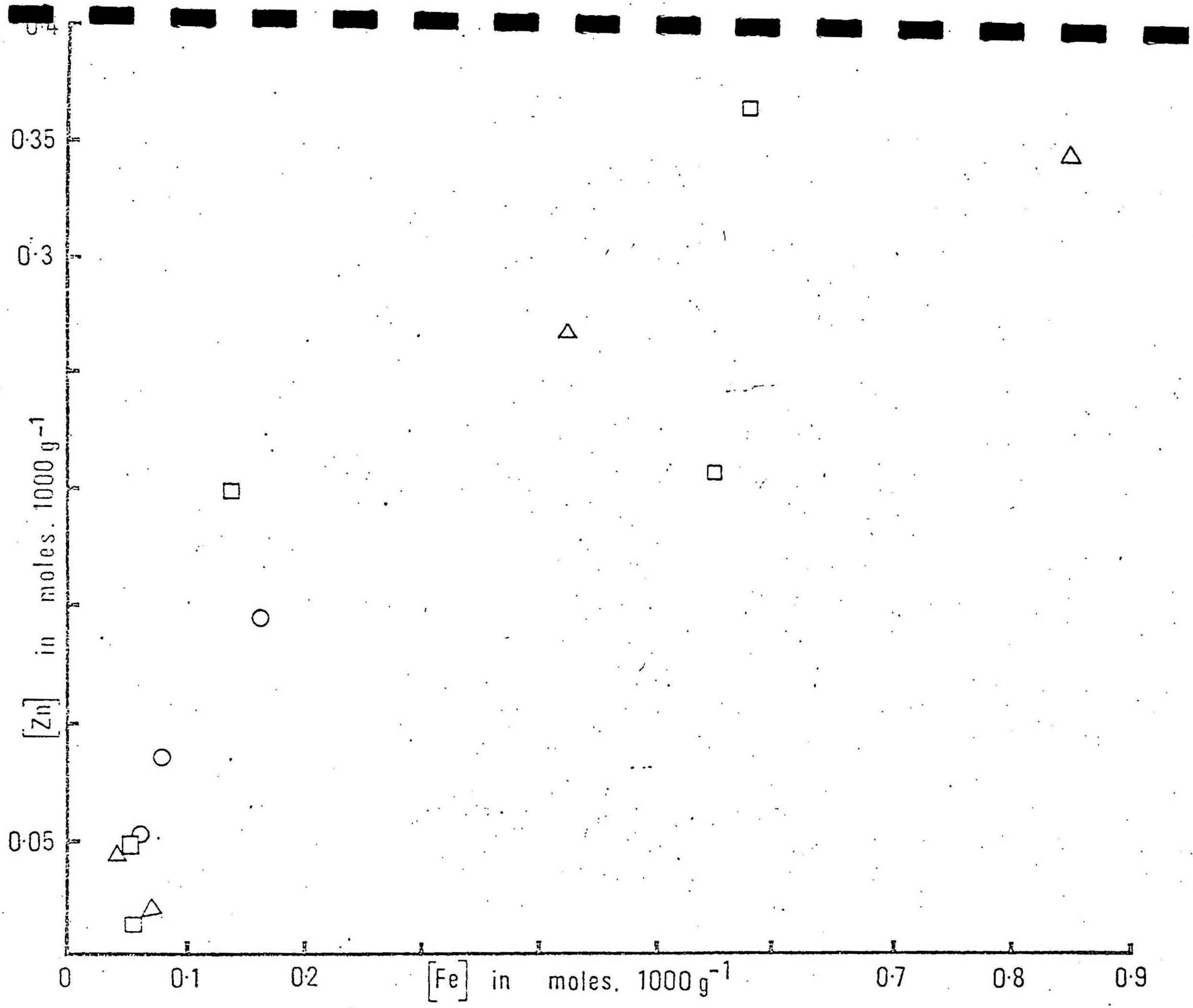

0·07
0·06
0·02
0·01
Pb in moles. 1000g⁻¹
Ca
Mg
Slope = 9×10⁻³ moles Pb per mole Ca
Slope = 4×10⁻³ moles Pb per mole Mg
0
1
6
7
[Ca] or [Mg] in moles. 1000 g⁻¹

Fig.3


0·4
0·35
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0·05
[Zn] in moles. 1000 g^{-1}
0
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0·2
0·7
0·8
0·9
[Fe] in moles. 1000 g^{-1}

Fig. 4