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The Co-Precipitation of Iron and Trace Metals from Aqueous Solutions

by

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SUMMARY

The oxide facies of most iron-rich sedimentary rocks are thought to have precipitated initially as ferric hydroxide colloids, presumably capable of scavenging trace metals from solution. However, in general the trace metal contents of iron-rich sedimentary rocks are low compared to crustal abundances.

To help define the conditions under which ferric hydroxide will co-precipitate with significant amounts of trace metals, the mechanism of the co-precipitation of trace amounts of Cu(II) with ferric hydroxide has been examined.

The pH's of acid solutions containing Fe(III) and Cu(II) were increased by the addition of small amounts of alkali and the metal concentrations remaining in solution measured for solutions in the pH range 1 - 9. Solutions whose pH's had been raised to near 4.5 precipitated nearly all of their Fe(III) but no Cu(II). Further increases in the pH's of the solutions resulted in precipitation of the Cu(II) in the pH range 5 - 5.5, which is 1.5 pH units below that observed under comparable conditions, but in the absence of Fe(III). These observations are consistent with a mechanism of precipitation involving the formation, at low pH's, of a positively charged ferric hydroxide colloid which can adsorb anions. At higher pH's the charge on the the ferric hydroxide colloid is negative and it is then capable of adsorbing cations.

It is not obvious how ferric hydroxide precipitates formed by this mechanism can be low in both cationic and anionic trace elements, providing an adequate supply of the trace elements is available in the depositional environment. On this basis it seems likely that the low trace metal contents of the iron-rich sedimentary rocks are due to an extremely slow rate of precipitation of the ferric hydroxides, rather than to the chemical environment existing at the time.

Introduction

If the Eh and the pH of a solution containing ferrous or ferric ions is raised then amorphous ferric hydroxide will be precipitated. Under a wide variety of conditions this precipitate forms as a stable colloidal dispersion which has the ability to adsorb positive and negative ions from solution. Thus, it has been suggested that the enhanced trace-element content of manganese - iron oxide concretions of present sea bottoms (James, 1966), and the presence of some trace elements in seawater at concentrations less than saturation (Goldschmidt, 1954; Krauskopf, 1955) are due to the scavaging effects of ferric hydroxide colloids.

There is evidence that iron formations and ironstones formed initially as deposits from marginal seas or water basins of restricted circulation (James, 1966), and, on this basis, it seems likely that the oxide facies originated as colloidal ferric hydroxide. However, in general, the trace element contents of iron-rich sedimentary rocks are low compared to crustal abundances. This may have been due simply to a scarcity of trace elements when the deposits were formed, or, alternatively, an adequate supply of trace elements may have been available in the depositional environment but the conditions of precipitation were such that co-precipitation effects were small.

The present project was designed to evaluate the second possibility be defining the conditions under which iron will co-precipitate from aqueous solutions with trace elements. Initial measurements have been undertaken on solutions at room temperature and pressure and the results presented are those of preliminary investigations into the precipitation of ferric hydroxide with trace amounts of Cu(II), Zn(II), and Ni(II).

Experimental

In most experiments ferric hydroxide and the trace elements were precipitated by slowly raising the pH of a solution containing initially 0.1N HCl, the trace metal cation, and, usually, Fe(III).

The solutions were placed in a plastic jar equipped with a stirrer and a pH electrode, the solution stirred, and 0.5N NaOH added through a capillary tube attached to a peristaltic pump. When the pH reached the required value, the solution was stirred for a further 10 minutes and a 15 ml sample removed to a stoppered plastic bottle and kept for 24 hours. At the end of this time the pH of the solution had settled to a constant value. The pH was recorded and the solution centrifuged for 15 minutes to separate any precipitate which had formed. The contrations of the ions remaining in solution were then determined by Atomic Absorption Spectrophotometry.

A stock solution of Fe(III) was prepared by diluting A.R. ferric chloride solution with A.R. HCl and distilled water to give a solution containing about 1000 ppm Fe and 0.1N HCl. Stock solutions of Cu(II), Co(II), Ni(II), Zn(II), and Pb(II) were prepared similarly using the appropirate metal chloride salt. Solutions for use in the experiments were prepared by dilution of these stock solutions. The alkali used was BDH CVS NaOH, 0.5N.

Results

Fig. 1 shows concentration versus pH curves for two solutions; one containing initially 0.1N HCl and 2.5 ppm Cu(II) (Curve 3); and the containing initially 0.1N HCl, 85 ppm Fe(III), and 2.0 ppm Cu(II) (curves 1 and 2).

The "sigmoid" shapes of the curves are typical of many types of precipitation reaction and the pH at which the rate of decrease of the metal concentration in solution is most rapid characterises the curve. In the present experiments this pH has been approximated by recording the pH at which the metal concentration in solution is reduced to half its initial value; this value is referred to as "$pH_{1/2}$" below.

The metals precipitate over a somewhat wider pH range than would be expected from solubility product relationships. It is likely that this is the result of incomplete sedimentation of the metal hydroxides by the centrifugation process. Colloidal ferric hydroxide particles range in size from those small enough to be inseparable by all but the most sophisticated techniques, up to those which can be readily removed from solution by centrifugation or ultra-filtration. I· the present experiments the ferric hydroxide formed at low pH's could be only partially centrifuged down, but as the pH was increased a greater proportion of the colloidal material could be separated, until, at pH 4 - 5 the colloids coagulated and could be separated completely.

Buffers were not used to control the pH's of the solutions and, although they were allowed to equilibrate for 24 hours before final pH readings were taken, large "drifts" in the pH's of near neutral solutions occurred before the metal hydroxides could be separated. Buffers were not used because of the need to keep the solution free of large anions such as sulphate, acetate, or phosphate, which are known (Gordon, 1959) to facilitate the precipitation of Fe(III) as basic salts of large particle sizes. This property also influenced the choice of the Fe(III) salt used in the experiments. Ferric chloride was chosen because Cl^- is known to be less efficient in forming basic salts, than the anions mentioned above (Remey, 1956), but it has the disadvantage that α-$Fe_2O_3 . H_2O$ is precipitated from solution, rather than the more commpnly found β - $Fe_2O_3 . H_2O$.

The precipitation of Fe(III) from aqueous solutions is a complicated reaction. The nature of the precipitate and its ability to adsorb ions mainly depends on the concentrations and types of ions in solution, the temperature, and the rate of precipitation (Remey, 1956). In view of the large number of potential variables in the experimental systems the measured $pH_{1/2}$'s of the trace metals in solutions containing Fe(III) have been compared to $pH_{1/2}$'s measured under comparable experimental conditions, but in the absence of Fe(III) Fig. 2. shows graphs of $pH_{1/2}$ versus the initial concentration of metal in solution (M_I) for Co(II), Ni(II), Cu(II), Pb II), and Zn(II) in the concentration range 1 - 1000 ppm. The graphs are straight lines and can be extrapolated to lower concentrations ($>$ 1 ppm) than can be achieved experimentally.

Discussion

Although it has been known for many years that colloidal ferric hydroxide can scavenge trace metal ions from aqueous solutions, it is only recently that the mechanisms of the processes have been studied in detail. Harvey (1937) has shown that ferric hydroxide forms in acid solutions as a positively charged colloid and, if the pH of the solution is then increased, the charge on the colloid decreases till the isoelectric point is reached at pH about 5, above which the colloid is negatively charged. On this basis it would be expected that ferric hydroxide will adsorb negatively charged ions at low pH's and positively charged ions at higher pH's. This has been confirmed experimentally (Skirrow, 1965; Joyner, 1967, Kim, 1969).

The results presented in Figs. 1 and 2 indicate that a similar mechanism of precipitation operates in the present experiments. It can be seen from Fig. 1 that at pH's near 4.5 greater than 90% of the Fe(III) has been precipitated, but almost all of the Cu(II) remains in solution. This is consistent with the formation of positively charged colloidal ferric hydroxide. At higher pH's the Cu(II) is precipitated, the value of the $pH_{1/2}$ depending on the concentration of Cu(II) and on whether or not Fe(III) was present in solution. For example it can be interpolated on Fig. 2 that a solution containing 2.0 ppm Cu(II) has a $pH_{1/2}$ of 6.7, whereas a solution containing initially 85 ppm Fe(III) in addition to the Cu(II), has a $pH_{1/2}$ of only 5.3. On this basis it is likely that the charge on the ferric hydroxide colloid changed from positive to negative somewhere in the pH range 4.5 - 5.3.

The present study, although far from complete, has provided no evidence that the chemical environment could modify the mechanisms of precipitation of ferric hydroxide in such a manner as to produce precipitates low in both cationic and anionic trace metals. It is well known that the formation of chemically pure precipitates is favoured by a slow rate of precipitation. It seems likely that in natural systems, where the pH and Eh conditions of the environment may change extremely slowly, the rate of deposition of ferric hydroxide colloids determines their trace metal contents.

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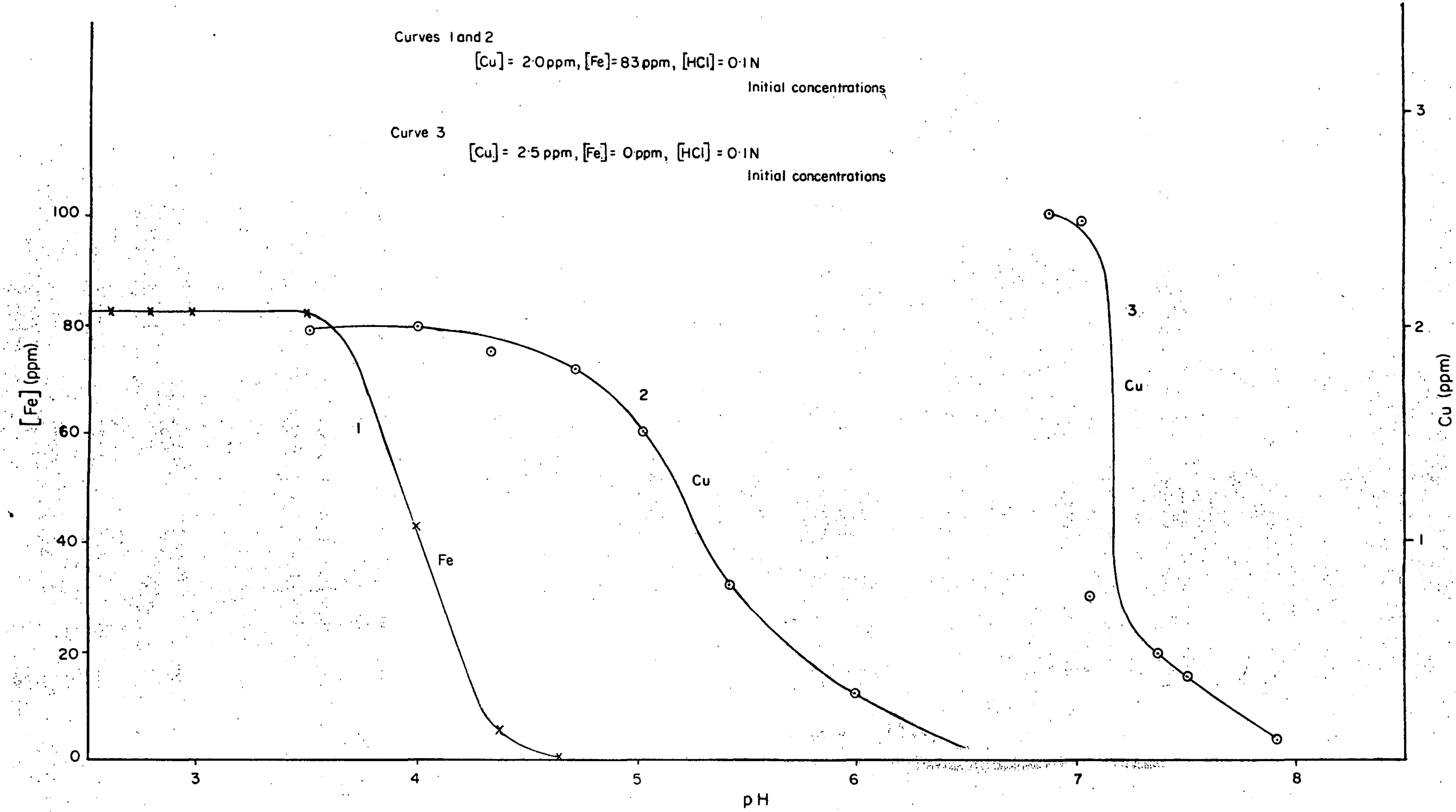

Fig. 1 Initial concentration versus pH curves for solutions containing Fe (III) and Cu (II)

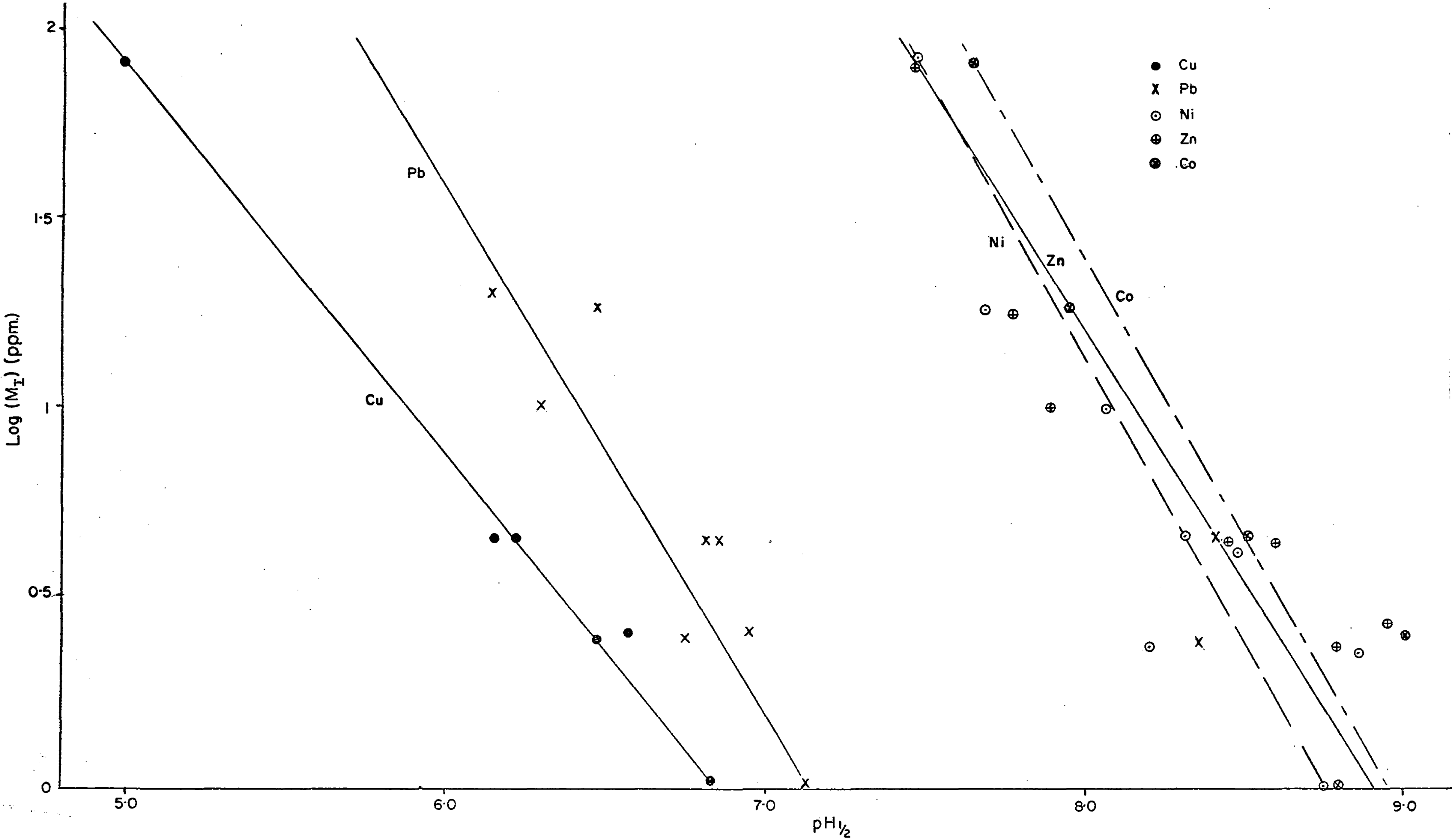

Fig. 2 Log (Initial Trace Element Concentration) versus pH½ for solutions containing Cu(II), Co(II), Ni(II), Zn(II), and Pb(II) in the absence of Fe(III)

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