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PREAMBLE

The interaction between Ocean Thermal Energy Conversion (OTEC) plants and the oceanic environment in which they will be operating must be considered both in terms of plant design and operation, and in regard to the potential impact of an operating plant on the marine environment. One area of concern is the release of metals from the plant, both inadvertantly as corrosion products or directly through operations such as antifouling control. It is, therefore, important to acquire information on the probable behavior of potential metal pollutants in the area of an operating OTEC plant.

One metal which has been found to be particularly toxic in the marine environment is copper. It is probable that copper will be released from an operating OTEC plant through the corrosion of alloys such as copper-nickel tubes or from anitfouling paints. There is increasing evidence that metals, such as copper, are transported and removed from the water column on particle surfaces. One of the most common particle surfaces, for which there is little data regarding copper adsorption, is calcium carbonate. As copper forms relatively insoluble compounds, such as malachite, with carbonate, it is probable that it also is strongly adsorbed on carbonate mineral surfaces. This study was undertaken in order to determine the degree and rate of copper adsorption from seawater onto the surface of calcium carbonate.

ABSTRACT

The interaction of Cu ions in solution with the surface of calcite has been studied in a range of solutions from pure water to seawater. Observations of the uptake of Cu from solution onto calcite indicates that the process is rapid and strong in both distilled water and seawater.

In distilled water, Cu uptake is directly proportional to the concentration of Cu in solution; $Cu_s = K_s Cu_l$. The average value for K_s is 3.5 ± 1.7. The Cu_s dependence on Cu_l is linear over the entire Cu concentration range studied (0.1 to 200 μM). Results do not indicate the formation of a precipitate of either malachite or copper carbonate. A precipitate of the form $Cu_x\ Ca_{1-x}\ CO_3$ may be deposited onto the calcite surface in distilled water. The value of K_s in distilled water decreased sharply over the solid to solution ratio range of 0.1 to 2 g $CaCO_3$ l^{-1}. This was followed by a small change in K_s for solid to solution ratios in the range of 2 to 10 g $CaCO_3$ l^{-1}.

In seawater, the uptake of Cu is also directly proportional to the concentration of Cu_l up to a limiting value of approximately 13 μM. The average value for K_s in seawater, 0.24 ± 0.06 ($Cu_l \leq 13$ μM), is approximately an order of magnitude less than in distilled water. This is probably the result of smaller Cu_l activity coefficients and increased site competition by other ions in seawater. Attempts to increase the Cu_l concentration above 13 μM resulted in the additional Cu being deposited on the surface of the calcite. A possible explanation for this behavior is the formation of a precipitate of malachite on the calcite surface. The value of K_s decreased slightly with increasing solid to solution ratios in seawater.

INTRODUCTION

The interaction of dissolved transition metals with solid surfaces in natural aquatic environments exerts a strong influence on their transportation, distribution and biologic availability. Most work published in recent years has dealt with the sorption behavior of transition metals on the surfaces of solids such as clays, metal oxides, aluminas and silica. These studies have generally assumed that sorption takes place through an ion-exchange type of reaction (1). They have dealt with such factors as complexing agents in solution (2,3) and changes in adsorption with pH (4,5).

A major solid component of many fresh water and marine environments which has not been carefully investigated for its surface interaction with transition metals is calcium carbonate. Most recent studies of the association of transition metals with calcium carbonate have focused on the transition metal content of biogenic carbonates or on distribution coefficients (K_D) in co-precipitation reactions. Boyle (6), for example, determined the transition metal to calcium mole fractions for Cd, Zn, and Cu in pelagic Foraminifera (calcite), while Lorens (7) determined K_D for Cd, Mn, Co and Sr as a function of calcite precipitation rate from Mg-free seawater. The results of these examinations of biogenic calcium carbonate and experimental co-precipitation measurements of K_D have produced distinctly different results, probably indicative of the different processes of calcium carbonate formation. While these types of studies have provided valuable information on the removal of transition metals from solution by co-precipitation reaction, little is known about the sorption behavior of transition metals on carbonate surfaces. The only study of this type, known to the current authors, was performed in 1959 by Heydemann (8). He studied the loss of copper ions from solution onto clay and calcite surfaces. He found the copper to be adsorbed by clay minerals according to the Freundlich adsorption isotherm, whereas in the case of the calcite surface, the loss of copper ions from solution was attributed to a chemical reaction.

In this investigation, the interaction of Cu with the surface of calcite in a range of solutions from pure water to natural seawater has been chosed for study. The primary reasons for choosing Cu was that it forms strong complexes with carbonate ions in solution, indicating that it may have a strong interaction with calcium carbonate surfaces, and the general environmental interest in the behavior of Cu in natural systems is due to its toxicity.

MATERIALS AND METHODS

Two solutions were used for the Cu adsorption studies. The first was distilled water equilibrated with calcite at a pH of 8.1. The second was filtered (0.4 μm Nuclepore®) surface Gulf Stream seawater with a salinity of 36‰. The seawater was equilibrated with respect to calcite by alkalinity adjustment with HCl and equilibration with atmospheric P_{CO_2}. The pH of the resulting solution was 7.9. During adsorption experiments these pH values varied by less than ± 0.2.

Mallinckrodt® reagent grade $CaCO_3$ was used as the calcite source for all experiments. X-ray diffraction analysis indicated the $CaCO_3$ to be greater than 99% calcite. Absolute surface area of the calcite was determined by the Kr-BET method of de Kanel and Morse (9). It is 0.55 $m^2\ g^{-1}$.

Cu was added to the solution to be studied from a 1,000 ppm atomic absorption standard. Standards for atomic absorption analyses were prepared fresh daily, in the solution being studied. These standards were acidified with dilute nitric acid in order to minimize container surface adsorption. Weakly acidified Cu standards were used in the uptake experiments. The addition of small amounts of these dilute acid solutions caused a negligible (less than 2%) change in the alkalinity of the resulting solution.

Cu analyses were performed using graphite furnace atomic absorption spectrophotometry. Two instruments were employed. A Hitachi-Zeeman effect atomic absorption spectrophotometer, model 170-70 with an autosampler, was used for copper analysis of the distilled water samples. A Perkin Elmer atomic absorption spectrometer, model 403, with a HGA 2100 controller, a D_2 background corrector, and an autosampler was used for copper analysis of the seawater samples. On both units the maximum uncertainty in the 1 to 4 μM Cu concentration range was found to be less than 10%. Cu concentrations greater than 4 μM were determined using dilutions with the solution being studied.

Initial experiments indicated that Cu has a high affinity for the surface of reaction vessels. At the low Cu concentrations employed in this study, a significant adsorption of copper onto the surface of containers was encountered, a problem noted by several other researchers (5, 10, 11, 12, 13). Reaction vessels constructed from a variety of different materials including Teflon®, Nalgene®, polypropylene, and pyrex glass, were tested by adding known amounts of dissolved Cu. Teflon®, polypropylene, and Nalgene® containers all exhibited similar affinity for Cu. This adsorption was found to be approximately 40 percent in the distilled water solution and 20 percent in seawater. The adsorption was relatively constant from container to container and was independent of the total Cu concentration over the range studied. The adsorption was rapid during the first hour, but slowed and remained relatively constant for the next 24 hours. The pyrex glass surface had a larger affinity for the Cu ions, and a greater variability between similar reaction vessels. Also, the Cu concentration in solution did not attain a steady state for time periods of up to 48 hours, in pyrex glass containers. For these reasons, pyrex glass reaction vessels were considered to be undesirable and were not employed in these studies.

Desorption off the walls of the reaction vessels was also investigated. The container-surface equilibrated Cu solutions were diluted or replaced with the medium being studied and allowed to stir for 3 hours. In all solutions there was no detectable desorption from the container surface to the solution.

Suspension of the calcite was maintained by stirring with Teflon®-coated magnetic stirring bars or by continuous shaking of the solution. The results obtained were independent of the mixing procedure or the plastic reaction vessels used. This indicated that grinding by the stir bars was not a significant problem. In all uptake experiments, sufficient time was allowed prior to calcite addition for container surface adsorption to pass through the rapid uptake phase (one to three hours). The initial Cu concentration was determined in each case just prior to adding the desired amoung of calcite.

The solution was separated from the solid phase by centrifugation. Centrifuge tubes were prerinsed with the solution to decrease container surface adsorption. Aliquots of the centrifuged solution were acidified with dilute nitric acid. A comparison of Cu concentrations of centrifuged solution with filtered solutions of the same sample were found to be consistent within the limits of the precision of the Cu determinations.

Two methods were used for the uptake experiments. The method used most frequently was the addition of the desired amount of calcite to the Cu-containing solution. The Cu concentration in solution (Cu_1) was measured immediately before and one-half hour after the addition of the calcite. The uptake of Cu from solution onto calcite was determined by the amount of Cu lost from the solution. Measurements were generally done in triplicate. A second method used was to increase either the total Cu concentration or the solid to solution ratio each half hour. In this way, a series of uptake results could be obtained from one experiment. The Cu concentration in solution was determined as previously mentioned. The total Cu (dissolved plus that on $CaCO_3$), Cu_T, was determined using one or more of the following three methods: 1) when the total Cu concentration was not increased during the uptake experiment, Cu_T was assumed to be the same as the Cu concentration before the addition of calcite; 2) by acid digestion of an aliquot of the total solution (solid plus solution); 3) by using the Cu concentration of a similar blank reaction vessel (one void of solid calcite). The results obtained from sample to sample were independent of the experimental procedure used and the method used for determining Cu_T.

RESULTS

One of the major objectives of this study was to investigate the kinetics of Cu sorption from solution onto calcite. Initial experiments indicated that the sorption of Cu onto calcite from distilled water and seawater in equilibrium with calcite is rapid. Table 1 presents the percent of Cu removed from solution onto suspended calcite as a function of time for four typical samples. The solutions had a range of Cu concentrations from 1 to 20 μM and solid to solution ratios from 0.1 to 10 g $CaCO_3$ l^{-1}, the practical working limits. In distilled water, the sorption reaction of Cu onto calcite is completed, or over 90% completed, during the first three minutes of interaction. For this rapid process, an accurate time dependence for Cu sorption from distilled water could not be established during the first three minutes using the methods employed. The results obtained for Cu sorption from seawater exhibit a greater variability, with the extent of sorption being close to constant after 15 minutes. Checks for up to 150 hours were made of this constancy. Based on these results, a reaction time of one-half hour, at least twice that required to reach steady-state, was chosen as the time for determination of the equilibrium sorption concentration.

The uptake of Cu from the distilled water medium onto calcite is presented in Figure 1 and Table 2. The solid to solution ratio used in these experiments was 1 g $CaCO_3$ l^{-1}.

The Cu adsorbed onto calcite, Cu_s (μmole Cu m^{-2} $CaCO_3$), increases linearly with the equilibrium concentration of Cu remaining in the solution, Cu_l (μM), over a three order of magnitude change in the Cu_T concentration. The ratio of the adsorbed Cu to the equilibrium Cu concentration in solution, $K_s = Cu_s/Cu_l$, has a mean value of 3.5($\pm$ 1.7) for these samples. The line presented in Figure 1 represents the least squares fit for the log-log plot of Cu_s as a function of Cu_l. This line has a slope of 0.90 and a coefficient of correlation of 0.95. The stippled area represents the equilibrium Cu concentration for malachite ($Cu_2(CO_3)(OH)_2$) solubility. The uncertainty in

Cu_l is due to the variation in the pH of the solutions, which causes a variation in the activity coefficient of Cu^{2+}. A K_{sp} for malachite, calculated from free energies of formation, of 4.5×10^{-33} (14,15) was used (see note). This was then combined with the activity of the CO_3^{2-} ion and the activity coefficient of Cu^{2+} (see discussion) over the experimental pH range determine the range in Cu_l shown by the stippled area.

K_{sp} (malachite) $= \bar{a}_{Cu^{2+}} \bar{a}_{CO_3^{2-}} = [\overline{Cu}^{2+}] [\overline{CO}_3^{2-}] (\gamma_{Cu^{2+}} \gamma_{CO_3^{2-}})$ where a_i, [i], and γ_i are respectively the thermodynamic activity concentration and total activity coefficient of component i. The $\bar{}$ indicates equilibrium values.

Figure 2 and Table 3 present data for the sorption of Cu onto calcite in a seawater medium with a solid to solution ratio of 1 g $CaCO_3$ l^{-1}. A large increase in Cu_s was observed at a Cu_l concentration of approximately 13 μM. This major removal of Cu from solution can only be accounted for by the formation of a precipitate on the surface of the calcite since the total Cu_s concentration exceeds that needed for monolayer coverage by a large amount (see Discussion). This loss of Cu from solution does not occur in blank solutions, e.g., solutions with the same Cu concentration in the absence of suspended calcite. At lower dissolved Cu concentrations, sorption increases in a close to linear manner up to a maximum of 13 μM Cu, although in some runs major deviations from linearity were found at Cu_l concentrations of 6 μM. These values approximately bracket the range of uncertainty in Cu_l for equilibrium with malachite. The mean value for K_s over this range of concentrations is 0.24 ± 0.06. The line presented in Figure 2 represents the least squares fit for the log-log plot of Cu_s as a function of Cu_l up to 13 μM Cu_l. This line has a slope of 1.17 and a coefficient of correlation of

0.97. Samples at solid to solution ratios greater than 1 g $CaCO_3$ l^{-1} presented in Figure 2 were normalized to a solid to solution ratio of 1 g $CaCO_3$ l^{-1} by the use of the best fit line given in Figure 3B. The stippled area in Figure 2 represents the malachite equilibrium concentration of Cu (see Discussion). The Cu_l range represents an uncertainty in the activity coefficient of copper in seawater from 0.010 to 0.006.

The dependence of adsorption and coprecipitation on solid surface area to solution volume ratios has recently come under investigation. It has generally been assumed that the sorption capacity should be directly proportional to solid surface area. However, the anticipated linear relationships have not been found in coprecipitation experiments (18, 19, 20) and in the adsorption of Am^{3+} onto calcite (12). The dependence of the sorption of Cu onto calcite on the solid to solution ratio has been determined in this study for seawater and distilled water solutions. This dependence is presented in Table 4 and 5 and Figure 3. In the distilled water experiment, a sharp decrease in K_s in the solid to solution ratio range from 0 to 2 g $CaCO_3$ l^{-1} was observed. A small or experimentally undetectable decrease occurs from 2 to 10 g $CaCO_3$ l^{-1}. Results obtained in seawater indicate that a similar trend in K_s with solid to solution ratio occurs. Solid to solution ratios less than 1 g $CaCO_3$ l^{-1} could not be studied in seawater because the sorption of Cu onto calcite was small and the change in Cu_l was less than the deviation in the measurement of Cu.

Note: A K_{sp} of 1.7×10^{-34} has been reported by Sillen and Martel (16), and a value of 3.5×10^{-34} has been reported by Symes and Kester (17). These lower K_{sp} values shift the stippled area shown in Figure 1 to 0.19 - 0.32 μM Cu_l and to 0.27 - 0.47 μM Cu_l, respectively.

DISCUSSION

The average value obtained for K_s in distilled water (3.5 $\pm$ 1.7) is approximately 15 times greater than the average value obtained in seawater (0.24 $\pm$ 0.06, for Cu_1 up to 13 μM). This difference in K_s is believed to be due to a combination of factors involved in the sorption process in the two solutions. First, the activity coefficient of Cu in distilled water is greater than that in the seawater. In distilled water saturated with $CaCO_3$ ($I \approx 1 \times 10^{-3}$) the activity coefficient of Cu can be calculated from the fraction of free copper in solution and the activity coefficient of the free ion, obtained from the Davies form of the Debye - Hückel limiting law. The fraction of free Cu in solution is calculated by assuming the total dissolved Cu is partitioned among the following four forms (21, 22):

$$Cu(T) = [Cu^{+2}] + [CuOH^{+}] + [Cu(OH)_2] + [CuCO_3].$$

$CuHCO_3^{+}$ has been neglected in the partitioning of Cu^{2+} because the stability constant for this complex, 6×10^2 (22), is small compared with the stability constant for $CuCO_3$, 7×10^6 (22). The contribution by $CuHCO_3^{+}$ to the fraction of free Cu in the distilled water solution is less than 3 percent in the pH range from 7.5 to 8.4. A total activity coefficient of Cu^{2+} of 0.036 in the distilled water medium was calculated for a pH of 8. Values reported for the activity coefficient of Cu in seawater range from 2×10^{-3} (23) to 3×10^{-2} (24). The intermediate value of 6×10^{-3} given by Millero and Schreiber (25) has been chosen for the total activity coefficient of Cu^{2+} in the seawater medium. This difference in the total activity coefficient of Cu in the two solutions would result in a lower Cu activity in seawater for a given concentration. This could account for the difference in the amount of uptake of Cu onto the calcite surface.

A second major difference between the two solutions is the presence of a large number of other ions in seawater, Magnesium, for example, is known to compete for adsorption sites on the calcite surface (12, 26). This site competition could lower the uptake of Cu onto the calcite surfaces in seawater. Site competition, along with the other differences between the two solutions (ionic strength, calcium concentration, etc.), could contribute to the lower level of Cu onto calcite in seawater and cause a different Cu compound to be deposited on the calcite surface.

The linear increase in Cu_s for a three order of magnitude change in the total Cu concentration, in distilled water at a solid to solution ratio of 1 g $CaCO_3$ 1^{-1} was presented in Figure 1. The slope of the line obtained indicates that the uptake of Cu onto calcite is directly proportional to Cu_1 and follows the dependence given by $Cu_s - K_s Cu_1$. The value obtained from the y - intercept gives $K_s - 3.4$.

The maximum concentration of Cu adsorbed onto the calcite surface represents an uptake equivalent to approximately three monolayers of Cu ions. This large an uptake of Cu ions cannot be explained by simple adsorption behavior. The uptake of Cu onto calcite continues to increase in a linear manner through the malachite equilibrium Cu concentration shown in the stippled area. This increase continues for two orders of magnitude in Cu_1 above the malachite solubility. It is, therefore, unlikely that the formation of malachite on the calcite surface can explain the uptake of copper from the distilled water medium. The formation of $CuCO_3$ on the calcite surface is a possibility, but the K_{sp} for $CuCO_3$ (15) is not exceeded at even the highest Cu concentrations employed.

Considering all of the experimental evidence, the uptake appears to be the result of the formation of a coprecipitate of copper with calcium and carbonate ions. A precipitate of the form $Cu_x Ca_{1-x}CO_3$ is proposed for the uptake of copper onto calcite in the distilled water medium. An exact value for x cannot be postulated from the experimental data at this time. A value on the order of 0.1 seems reasonable based on the activities of Cu^{2+}, Ca^{2+}, and CO_3^{2-} in the solutions employed, and on the solubilities of $CuCO_3$ and $CaCO_3$ (13). This value corresponds to a distribution coefficient on the order of 6×10^2 in the solutions with a copper concentration of 10 μM at a pH of 8. This value for K_D is in reasonable agreement with the value obtained by Lorens (20) for the Zn distribution coefficient in calcite, 217×10^3.

The uptake of Cu onto calcite in seawater indicates a dependence on Cu_1 (Figure 2) different than with distilled water. The linear increase of Cu_s with increasing Cu_1 occurs up to approximately 13 μM Cu. Attempts to increase Cu_1 by using high initial Cu concentrations results only in additional sorption of Cu onto the surface of the calcite. The limiting solution concentration at a Cu_1 of 13 μM is within the range of the equilibrium Cu concentration calculated for malachite, based on $K_{sp} = 4.5 \times 10^{-33}$ and pH - 7.9, as shown in the stippled area of Figure 2. The values for K_{sp} reported by Sillen and Martel (16), and by Symes and Kester (17) are lower and would shift the equilibrium Cu malachite solubility to approximately 3 μM, at pH - 7.9, which is lower than that observed in this study. The observed variation in the final pH of seawater solutions ranged from 7.9 to 7.6. At a pH of 7.65 the calculated Cu concentration in equilibrium with malachite is within the observed values using the K_{sp} value of Symes and

Kester (17) or Sillen and Martel (16). Thus, the precipitation of malachite on the surface of calcite appears to be the most likely process for the removal of Cu in seawater at Cu_l concentrations greater than 13 μM. For Cu_l concentrations less than 13 μM, the line obtained from Figure 2 shows a Cu_s uptake dependence on Cu_l similar to that obtained in distilled water, $Cu_s - K'_s Cu_l$. The value of K'_s obtained from the y - intercept (0.18) is slightly less than the average ratio of Cu_s to Cu_l (0.24) obtained for Cu_l concentrations less than 13 μM.

The effect of surface area on the amount of Cu removed from solution was investigated in both distilled water (Figure 3A) and seawater (Figure 3B). In distilled water the loss of Cu from solution per unit of surface area shows a 4-fold decrease from 0 to 2 g $CaCO_3$ l^{-1}. This sharp drop in uptake was followed by a small (if any) decrease in the sorption per unit of surface area. A similar decrease in the growth rate constant for calcite crystallization was reported by Reddy and Gailland (19). Am^{3+} adsorption on calcite has also been found not to be linearly dependent on the solid surface area to solution volume ratio (12). One possible explanation for this behavior centers around a surface nucleation process. Nucleated sites are formed on the surface of the calcite and preferential uptake occurs on these sites. The number of sites which become nucleated on the calcite surface is a function of both the total surface area and the Cu concentration in solution. For a given solid to solution ratio, more sites become nucleated at higher Cu concentration, but the percent uptake remains relatively constant. At low solid to solution ratios, there is a greater chance of nucleation at more sites per unit of surface area, compared with higher solid to solution ratios. Preferred sorption at the nucleated sites results in a larger uptake per unit surface area at lower solid to solution ratios. This difference in uptake may be similar to polynuclear versus mononuclear growth mechanisms on surfaces (27). In the case of seawater (Figure 3B), the possibility of a similar mechanism exists, but there is insufficient data to draw a conclusion on the uptake of Cu onto calcite as a function of solid to solution ratio.

CONCLUSION

The results of this study on the uptake of Cu from solution onto calcite indicate a rapid uptake in both distilled water and seawater. The uptake is complete, or nearly complete, in 15 minutes or less in both solutions. The average value obtained for K_s in distilled water (3.5 ± 1.7) is approximately 15 times greater than the average value obtained for K_s in seawater (0.24 ± 0.06 at Cu_l concentrations ≤ 13 μM). This difference is attributed to the difference in the activity coefficient of Cu in the two solutions and the competition for adsorption sites by other ions, such as Mg, in seawater.

Two different processes are proposed for the uptake of Cu in these solutions. In distilled water, the uptake is directly proportional to the copper concentration in solution, Cu_l. The Cu_s dependence on Cu_l remains linear throughout the entire Cu concentration range studied and does not indicate the formation of a precipitate of either malachite or $CuCO_3$. Because this uptake represents the equivalent of over three monolayers of Cu^{2+} ions on the calcite surface, at the high Cu concentrations, a precipitate of the form $Cu_x Ca_{1-x}CO_3$ may be deposited onto the calcite surface in the distilled water medium.

In seawater, the Cu_s dependence on Cu_l remains close to linear up to a Cu_l concentration of approximately 13 μM. An increase in the Cu_l concentration to higher values causes the additional Cu to be deposited on the surface of the solid. A value of Cu_l equal to 13 μM is in the range of Cu_l concentrations predicted from the equilibrium malachite solubility in seawater. The formation of a precipitate of malachite on the calcite surface may, therefore, explain the adsorption pattern of Cu onto calcite in seawater.

The dependence of K_s on the solid to solution ratio was investigated in distilled water from 0.1 to 10 g $CaCO_3$ l^{-1}. A sharp decrease in K_s from 0.1 to 2 g $CaCO_3$ l^{-1} was observed, followed by a small change in K_s from 2 to 10 g $CaCO_3$ l^{-1}. This decreasing adsorption with increasing surface area can be explained by a surface nucleation process. More adsorption sites per unit surface area are nucleated at low solid to solution ratios than with high solid to solution ratios. Preferred uptake occurs on the nucleated sites resulting in a larger value of K_s at low solid to solution ratios. There is evidence for a very slight decrease in K_s with increasing solid to solution ratios in seawater.

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FIGURE CAPTIONS

FIGURE 1. The uptake of copper onto calcite in distilled water at a solid to solution ratio of 1 g $CaCO_3$ l^{-1}. The stippled area represents the equilibrium copper concentration for malachite solubility for a pH range from 7.5 to 8.4.

FIGURE 2. The uptake of copper onto calcite in seawater at solid to solution ratios ranging from 1.0 to 10.0 g $CaCO_3$ l^{-1}. The stippled area represents the equilibrium copper concentration for malachite solubility (pH = 7.85) for a range in the total activity coefficient of copper from 0.006 to 0.010.

KEY: ■ 1.0, ▼ 3.0, ▲ 5.0, ◆ 5.5, ● 5.8, + 7.5, X 10.0 g $CaCO_3$ l^{-1}.

FIGURE 3. K_s as a function of solid to solution ratio in A. distilled water and B. seawater.

TABLE 1

COPPER UPTAKE ON CALCITE WITH TIME

A		B		C		D	
Cu_T = 2.8 μM in DW		Cu_T = 1.1 μM in DW		Cu_T = 3.7 μM in SW		Cu_T = 3.7 μM in SW	
$CaCO_3(s)$ =0.1 g/1		$CaCO_3(s)$ = 1 g/1		$CaCO_3(s)$ = 1 g/1		$CaCO_3(s)$ = 10 g/1	
Medium D W		Medium D W		Medium S W		Medium S W	
TIME	% Cu ADSORBED	TIME	% Cu ADSORBED	TIME	% Cu ADSORBED	TIME	% Cu ADSORBED
0 min	0	0 min	0	0 min	0	0 min	0
3 "	39	3 "	59	15 "	9	15 "	31
10 "	26	6 "	64	40 "	6	40 "	34
30 "	31	15 "	67	135 "	6	135 "	33
45 "	23	30 "	70	250 "	12	250 "	44
60 "	38	60 "	64	24 hrs	18	24 hrs	36
150 "	26	180 "	71	50 "	8	50 "	38
300 "	36	300 "	69	75 "	8	75 "	37
				150 "	16	150 "	44
MEAN (> 3 min)		MEAN (> 3 min)		MEAN (> 0 min)		MEAN (> 0 min)	
31 ± 6%		68 ± 3%		10 ± 5%		37 ± 5%	

TABLE 2

COPPER UPTAKE ON CALCITE FROM DISTILLED WATER

TOTAL Cu (ppb)	PERCENT UPTAKE	K_s (μ mole Cu m^{-2}) (μ mole Cu l^{-1})$^{-1}$	NUMBER OF REPLICATES
0 - 100	62.4 ± 7.6	3.0 ± 1.2	22
100 - 500	64.2 ± 11.4	3.9 ± 2.3	25
500 - 1,000	70.9 ± 8.5	4.9 ± 1.8	16
1,000 - 2,000	55.4 ± 13.2	2.6 ± 1.3	15
2,000 - 5,000	53.0 ± 11.7	2.3 ± 1.0	8
5,000 - 15,000	60.0 ± 0.8	2.7 ± 0.1	4
TOTAL AVERAGE	63.7 ± 12	3.5 ± 1.7	90

All experiments conducted with a solid to solution ratio of 1 g calcite per liter.

TABLE 3

COPPER UPTAKE ON CALCITE FROM SEAWATER

Total Cu µmole Cu l^{-1}	Cu Remaining in Solution µmole Cu l^{-1}	Percent Uptake	K_s (µmole Cu m^{-2})(µmole Cu l^{-1})$^{-1}$
1.64	1.48	9.6	0.19
2.30	2.01	12.5	0.27
3.34	2.83	15.3	0.32
3.72	3.34	10.2	0.21
10.24	9.02	11.8	0.24
11.65	9.95	14.6	0.31
14.43	13.23	8.3	0.16
18.90	14.05	25.7	0.63
19.50	15.75	19.2	0.44
23.92	17.56	26.6	0.66
23.94	14.87	37.9	1.11
289.13	9.29	96.8	54.8
308.66	9.92	96.8	54.8
308.66	5.98	98.1	92.0
308.66	13.23	95.7	40.6

All experiments conducted with a solid to solution ratio of 1 g calcite per liter.

TABLE 4

COPPER UPTAKE ON CALCITE IN DISTILLED WATER: DEPENDENCE ON SOLID TO SOLUTION RATIO

Suspended Calcite $g\ l^{-1}$	Range of Total Cu $\mu mole\ Cu\ l^{-1}$	Percent Uptake	K_s $(\mu mole\ Cu\ m^{-2})(\mu mole\ Cu\ l^{-1})^{-1}$	Number of Replicates
0.10	1.45 to 13.67	30.6 ± 5.9	8.1 ± 2.1	7
0.20	2.83	47.12	8.2	1
0.40	2.83	57.2	6.1	1
0.50	1.81 to 19.18	67.7 ± 8.0	8.3 ± 3.0	7
0.75	2.77 to 29.72	49.9 ± 7.7	2.5 ± 0.7	5
0.80	2.83	62.2	3.7	1
1.00	0.16 to 236.22	64.0 ± 12.0	3.5 ± 1.7	90
2.00	2.99, 21.73	54.0	1.1	2
3.00	2.80 to 32.02	63.4 ± 3.0	1.0 ± 0.2	5
4.00	2.99, 21.73	74.5	1.4	2
5.00	1.45 to 28.33	87.2 ± 2.2	2.5 ± 0.5	7
6.00	2.99, 21.73	80.3	1.4	2
8.00	2.99, 21.73	81.1	1.1	2
10.00	2.13 to 21.73	89.1 ± 5.9	2.1 ± 1.4	7

TABLE 5

COPPER UPTAKE ON CALCITE IN SEAWATER: DEPENDENCE ON SOLID TO SOLUTION RATIO

Suspended Calcite $g\ l^{-1}$	Range of Total Cu $\mu mole\ Cu\ l^{-1}$	Percent Uptake	K_s $(\mu mole\ Cu\ m^{-2})(\mu mole\ Cu\ l^{-1})^{-1}$	Number of Replicates
1	1.64 to 14.43	11.7 ± 2.5	0.24 ± 0.06	7
3	1.39, 3.34	18.7	0.15	2
3.1	11.65	24.9	0.19	1
5	3.34	35.8	0.20	1
5.5	11.65	31.6	0.15	1
5.8	3.65	26.9	0.12	1
7.5	3.34, 11.65	38.6	0.15	2
10	1.70 to 14.41	36.9 ± 3.4	0.11 ± 0.01	9

The following data tables are supplements to Table 2 and Table 4 and are submitted for use by the reviewers. They are not intented for publication in the original paper.

DATA TO GO WITH TABLE 2

Cu_T µmole l^{-1}	Cu_s µmole m^{-2}	Cu_l µmole l^{-1}	Percent Uptake	K_s (µmole Cu m^{-2}) (µmole Cul^{-1})$^{-1}$
0.16	0.17	0.06	60	2.86
0.28	0.34	0.09	67	3.82
0.36	0.43	0.13	65	3.30
0.47	0.49	0.20	57	2.43
0.55	0.57	0.24	57	2.39
0.58	0.63	0.24	59	2.62
0.63	0.63	0.28	55	2.25
0.68	0.60	0.35	49	1.72
0.68	0.95	0.16	77	5.91
0.72	0.86	0.25	65	3.44
0.82	0.80	0.38	54	2.11
0.94	0.80	0.50	53	1.60
1.10	1.37	0.35	68	3.93
1.13	1.15	0.50	56	2.29
1.26	1.43	0.47	63	3.05
1.35	1.43	0.57	58	2.51

2-1

DATA TO GO WITH TABLE 2 CONT'D

Cu_T µmole l^{-1}	Cu_s µmole m^{-2}	Cu_l µmole l^{-1}	Percent Uptake	K_s (µmole Cu m^{-2}) (µmole Cu l^{-1})$^{-1}$
1.37	1.78	0.39	71	4.55
1.40	1.43	0.61	56	2.35
1.40	1.80	0.41	71	4.40
1.46	1.92	0.41	72	4.68
1.51	1.95	0.44	72	4.43
1.53	1.86	0.50	67	3.72
1.78	1.70	0.85	52	1.99
1.86	2.06	0.71	62	2.91
2.16	2.38	0.85	61	2.80
2.27	2.41	0.95	58	2.55
2.32	2.58	0.90	61	2.87
2.49	2.46	1.13	54	2.18
2.52	2.95	0.90	64	3.28
2.80	3.01	1.15	59	2.62
2.83	3.46	0.93	67	3.73
2.99	2.34	1.70	43	1.38
2.99	4.12	0.72	76	5.72
3.43	4.81	0.79	77	6.09
3.83	4.44	1.39	64	3.20

2-2

DATA TO GO WITH TABLE 2 CONT'D

Cu_T μmole l^{-1}	Cu_s μmole m^{-2}	Cu_1 μmole l^{-1}	Percent Uptake	K_s (μmole Cu m^{-2}) (μmole Cu l^{-1})$^{-1}$
3.89	4.50	1.42	64	3.17
4.57	5.15	1.73	41	2.98
4.77	6.93	0.96	80	7.21
4.80	4.55	2.30	52	1.98
5.35	6.73	1.65	69	4.08
5.41	5.13	2.60	52	1.97
5.50	6.47	1.92	65	3.37
5.83	7.82	1.53	74	5.12
4.77	6.93	0.96	80	7.22
6.70	9.02	1.92	72	4.69
7.18	10.19	1.57	78	6.47
7.35	10.82	1.40	81	7.73
8.03	11.10	1.92	76	5.78
8.60	11.45	2.30	73	4.98
8.60	12.43	1.76	79	7.04
9.13	12.31	2.36	74	5.21
9.61	13.23	2.33	76	5.67
10.39	10.02	4.88	53	2.05

DATA TO GO WITH TABLE 2 CONT'D

Cu_T µmole l^{-1}	Cu_s µmole m^{-2}	Cu_l µmole l^{-1}	Percent Uptake	K_s (µmole Cu m^{-2})(µmole Cul^{-1})$^{-1}$
10.39	15.15	2.06	80	7.34
12.23	18.38	2.13	83	8.65
12.60	13.31	5.28	58	2.52
12.61	16.38	3.59	71	4.56
13.20	17.61	3.53	73	4.99
14.17	14.75	6.06	57	2.43
14.61	17.67	4.90	66	3.61
14.96	19.90	4.02	73	4.96
15.07	19.24	4.47	70	4.30
15.51	20.64	4.16	73	4.97
16.57	19.21	6.00	64	3.20
16.85	13.89	9.21	45	1.51
16.91	20.93	5.40	68	3.88
17.29	18.61	7.06	59	2.63
18.35	16.52	9.26	50	1.78
18.65	25.62	4.55	76	5.63
18.90	22.91	6.30	67	3.64
20.98	25.14	7.13	66	3.52

2-4

DATA TO GO WITH TABLE 2 CONT'D

Cu_T μmole l^{-1}	Cu_s μmole m^{-2}	Cu_1 μmole l^{-1}	Percent Uptake	K_s (μmole Cu m^{-2}) (μmole Cul^{-1})$^{-1}$
21.73	12.51	14.54	32	0.86
22.52	16.61	13.39	41	1.24
23.10	25.65	8.99	61	2.85
25.83	19.61	15.03	42	1.30
28.35	19.18	17.80	37	1.08
28.39	31.10	11.28	60	2.76
31.04	35.36	11.59	63	3.05
32.41	38.08	11.47	65	3.32
33.07	28.63	17.40	48	1.65
37.56	45.98	12.27	67	3.75
40.22	38.11	19.26	52	1.98
44.09	24.05	30.87	30	0.78
45.28	40.29	23.12	49	1.74
49.39	47.56	21.86	53	2.18
59.06	64.42	23.62	60	2.73
87.21	96.92	33.91	61	2.86
102.20	111.50	40.88	60	2.73
135.53	144.54	56.03	59	2.58
236.22	257.70	94.49	60	2.73

DATA TO GO WITH TABLE 4

Suspended Calcite $g\ l^{-1}$	Cu_T $\mu mole\ l^{-1}$	Cu_s $\mu mole\ m^{-2}$	Cu_l $\mu mole\ l^{-1}$	Percent Uptake	K_s $(\mu mole\ Cu\ m^{-2})(\mu mole\ Cu\ l^{-1})^{-1}$
0.1	1.45	9.16	0.94	34.8	9.70
0.1	2.83	16.03	1.95	31.1	8.21
0.1	2.83	16.32	1.94	31.7	8.43
0.1	3.24	22.62	2.00	38.3	11.31
0.1	6.83	36.65	4.82	29.5	7.61
0.1	10.93	53.54	7.98	26.9	6.71
0.1	13.67	51.54	10.83	20.7	4.76
0.2	2.83	12.17	1.50	47.2	8.13
0.4	2.83	7.37	1.21	57.2	6.08
0.5	1.81	3.72	-0.79	56.5	4.73
0.5	3.35	7.67	1.23	62.9	6.25
0.5	3.94	8.59	1.57	60.0	5.45
0.5	5.78	15.52	1.51	73.8	10.27
0.5	9.84	28.00	2.14	78.2	13.07
0.5	12.74	33.84	3.43	73.1	9.86
0.5	19.18	48.50	5.84	69.5	8.30

4-1

<u>DATA TO GO WITH TABLE 4 CONT'D</u>

Suspended Calcite g l^{-1}	Cu_T µmole l^{-1}	Cu_s µmole m^{-2}	Cu_l µmole l^{-1}	Percent Uptake	K_s (µmole Cu m^{-2})(µmole Cu l^{-1})$^{-1}$
0.75	2.77	2.56	1.72	38.1	1.49
0.75	12.11	14.20	6.25	48.4	2.27
0.75	15.13	21.65	6.20	59.0	3.49
0.75	21.06	26.00	10.33	50.9	2.52
0.75	29.72	38.14	13.67	52.9	2.79
0.8	2.83	4.01	1.07	62.2	3.74
1	SEE DATA TO GO WITH TABLE 2				
2	2.99	1.52	1.32	55.8	1.15
2	21.73	10.32	10.06	52.2	1.03
3	2.80	1.04	0.96	61.2	1.08
3	6.06	2.30	2.27	62.6	1.01
3	20.00	8.33	6.25	68.7	1.33
3	23.75	9.09	8.76	63.1	1.04
3	32.02	11.95	14.14	61.6	0.84
4	2.99	0.95	0.90	70.0	1.06
4	21.73	7.80	4.25	79.0	1.84
5	1.46	0.46	0.20	86.0	2.24
5	2.83	0.86	0.46	93.9	1.89

DATA TO GO WITH TABLE 4 CONT'D

Suspended Calcite $g\ l^{-1}$	Cu_T $\mu mole\ l^{-1}$	Cu_s $\mu mole\ m^{-2}$	Cu_l $\mu mole\ l^{-1}$	Percent Uptake	K_s $(\mu mole\ Cu\ m^{-2})(\mu mole\ Cu\ l^{-1})^{-1}$
5	3.28	1.04	0.43	87.0	2.44
5	5.61	1.81	0.63	88.8	2.87
5	10.16	3.33	1.01	90.1	3.30
5	13.73	4.43	1.54	88.8	2.87
5	20.33	6.33	2.91	85.7	2.17
6	2.99	0.69	0.72	75.8	0.95
6	21.73	5.59	2.98	84.9	1.88
8	2.99	0.53	0.68	77.4	0.78
8	21.73	4.18	3.01	84.7	1.39
10	2.13	0.37	0.08	96.3	4.73
10	2.99	0.44	0.60	80.0	0.73
10	3.62	0.62	0.22	93.9	2.81
10	7.93	1.32	0.58	92.6	2.26
10	12.02	1.98	1.10	90.8	1.80
10	15.59	2.41	2.36	84.8	1.02
10	21.73	3.36	2.93	85.1	1.15

4-3

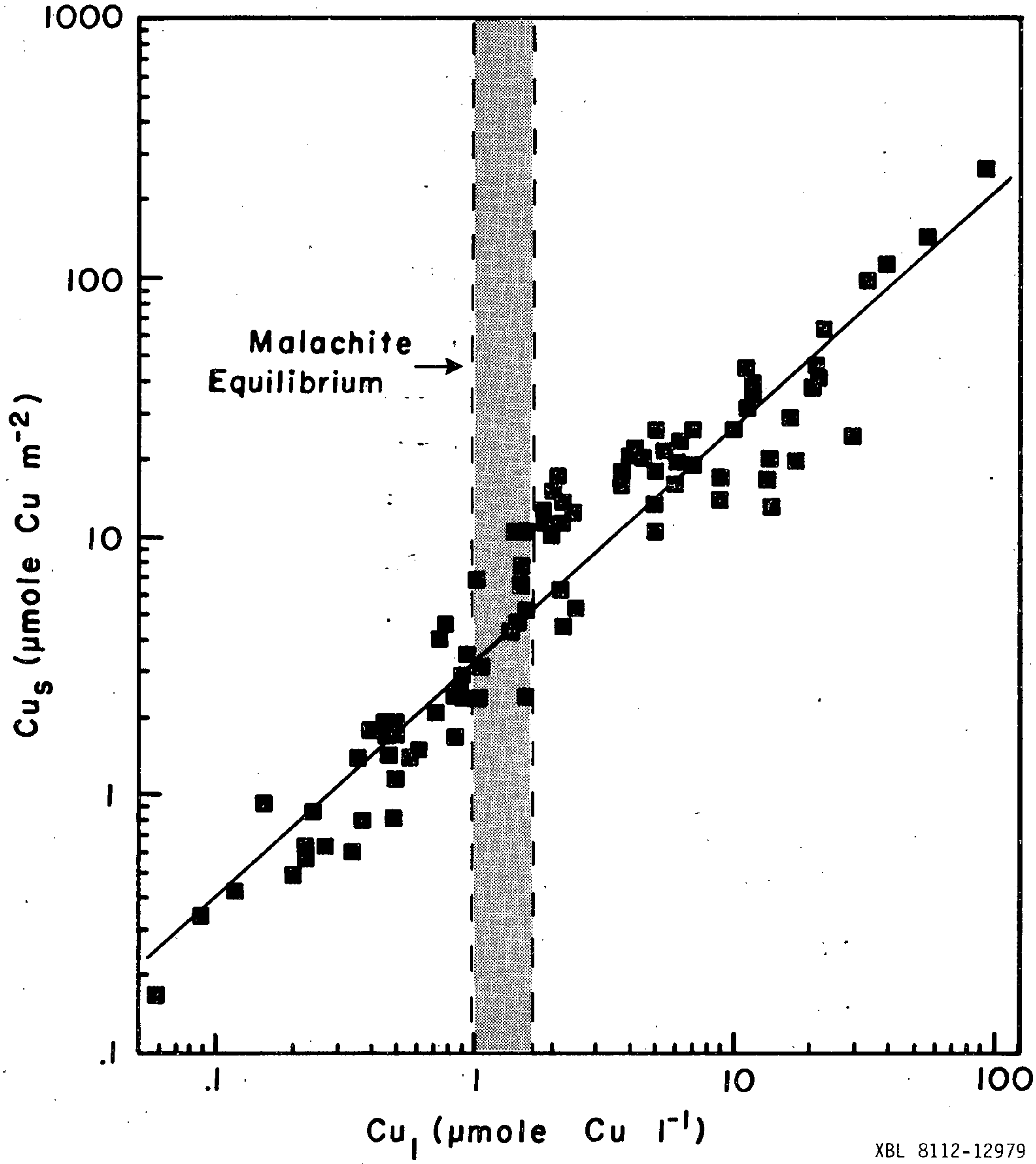

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Fig. 1

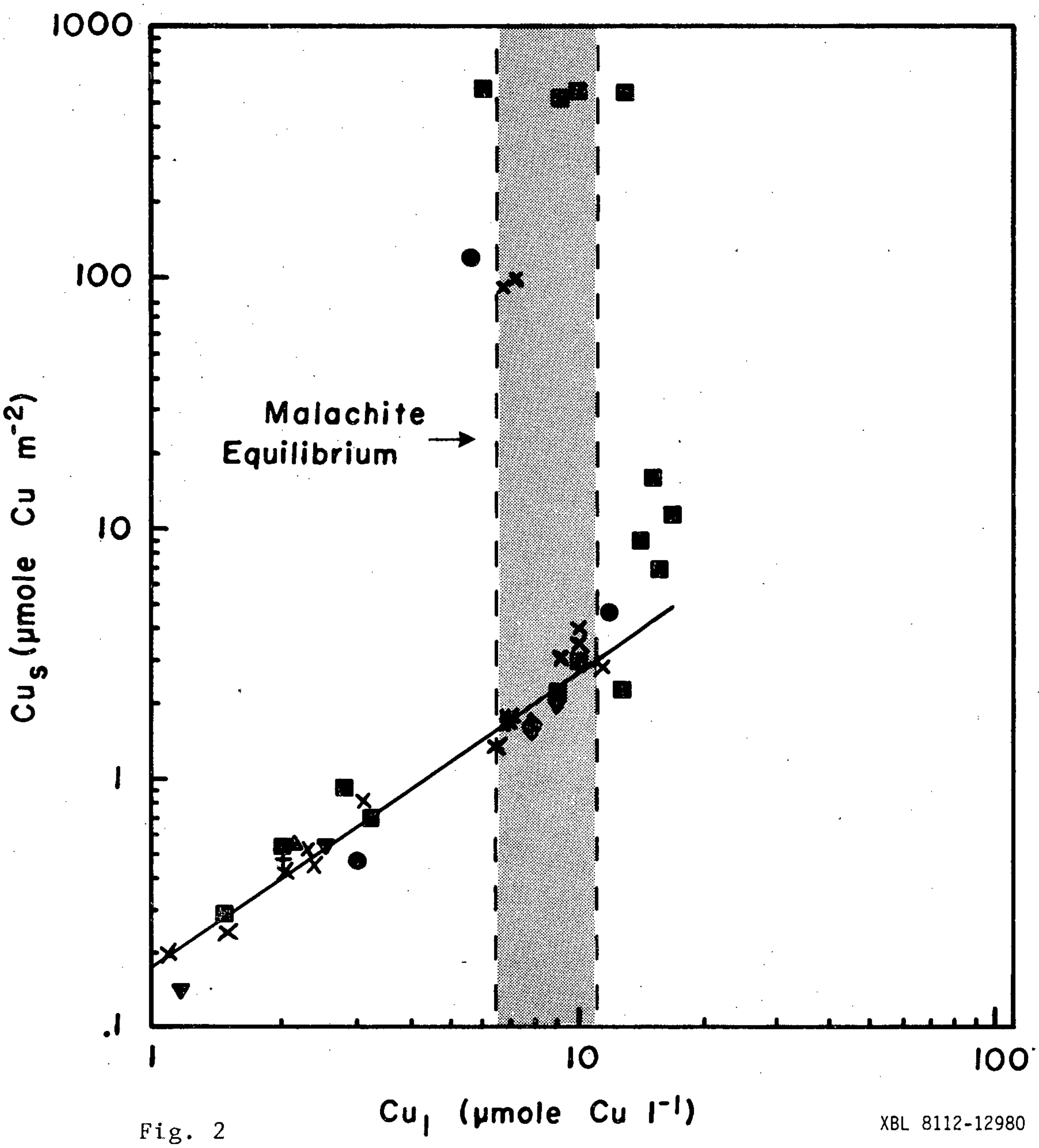

Fig. 2

XBL 8112-12980

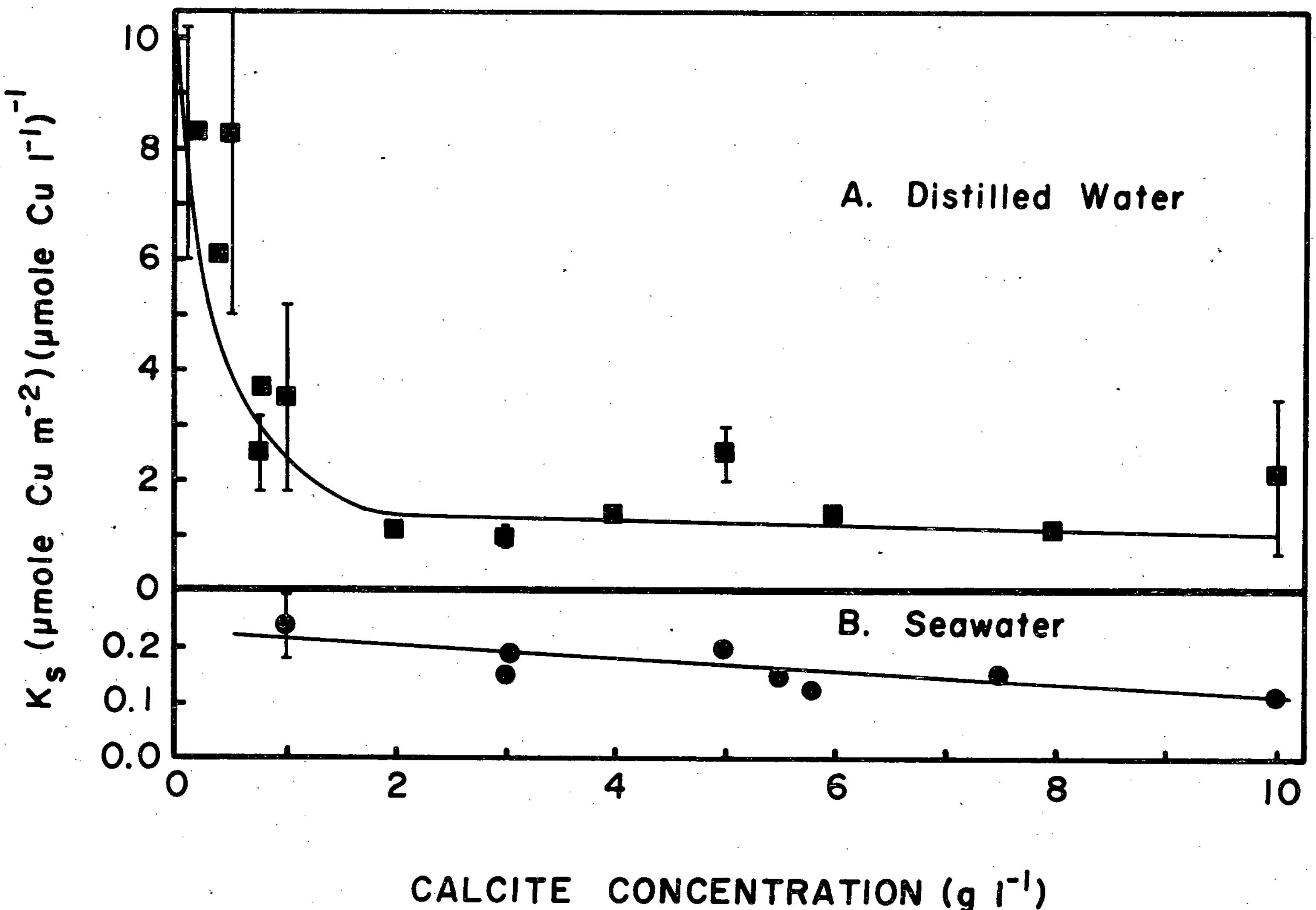

Fig. 3

XBL 8112-12981

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