A LITERATURE REVIEW OF THE SATURATION STATE OF SEAWATER WITH RESPECT TO CALCIUM CARBONATE AND ITS POSSIBLE SIGNIFICANCE FOR SCALE FORMATION ON OTEC HEAT EXCHANGERS

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SUMMARY

An investigation of available data on the saturation state of seawater with respect to calcium carbonate and its possible significance for scale formation on Ocean Thermal Energy Conversion (OTEC) heat exchangers has been carried out by the University of Miami, under contract with the Biofouling and Corrosion Office at Battelle Pacific Northwest Laboratories for the Department of Energy.

Pertinent oceanographic data is lacking at or near potential OTEC sites for the calculation of the degree of saturation of seawater with respect to calcium carbonate. Consequently, only "extrapolated" saturation values can be used. These indicate that near surface seawater is probably supersaturated, with respect to the calcium carbonate phases calcite and aragonite, at all potential OTEC sites. The deep seawater that would be brought to the surface at the potential Atlantic Ocean sites is also likely to be supersaturated with respect to calcium carbonate. The deep seawater at the potential Pacific Ocean sites may be slightly undersaturated.

The fact that OTEC heat exchangers will be operating in seawater, which is supersaturated with respect to calcium carbonate, means that if nucleation of calcite or aragonite occurs on the heat exchanger surfaces, significant growth rates of calcium carbonate scale may be expected. The potential for calcium carbonate nucleation is highest at cathodic metal surface locations, which are produced as the result of aluminum corrosion in seawater. Consequently, corrosion and scale formation may be closely related. What the possible effects of biofouling may be on this process are not known.

INTRODUCTION

One of the major factors determining the economic feasibility of an Ocean Thermal Energy Conversion (OTEC) facility is the efficiency with which heat can be exchanged across a metallic or plastic interface between seawater and the working fluid, e.g., ammonia. The formation of even relatively thin layers of foreign material on the heat exchanger surfaces can seriously reduce the efficiency of the heat exchange process. If the formation of heat exchanger surface deposits is rapid and their removal excessively expensive, they could render an OTEC facility economically unfeasible.

The three major classes of surface deposits which might be expected to occur on OTEC heat exchangers are: corrosion products, inorganic scale, and biogenic slimes. It is probable that the formation of these different basic classes of materials will be interrelated in a complex manner because of surface microenvironments which differ significantly from the bulk chemical and biological environment of the waters passing through the OTEC heat exchangers. As a starting point for understanding how surface films might form on OTEC heat exchangers, each of these major classes of surface films will be studied independently.

This report is restricted to the consideration of possible carbonate scales and related factors such as magnesium ion interactions with carbonates, which could form on OTEC heat exchangers. If "open" ocean seawater is considered, calcium carbonate is the only major or minor constituent inorganic salt which exhibits natural supersaturation. Until further information becomes available about the chemical nature of the

microenvironments near OTEC heat exchanger surfaces, it seems appropriate to concentrate on the chemistry of calcium carbonate and the possible interactions of magnesium ions in seawater. A detailed discussion of the methods and problems of calculating the saturation state of seawater, with respect to the calcium carbonate phases calcite and aragonite, is presented in Appendix A.

The following discussion is divided into two major areas. The first is the distribution of oceanic calcium carbonate saturation states. It is directed at regions of potential interest in the OTEC program. The second major area, which is discussed, is the reaction kinetics of calcium carbonate in seawater. The latter is principally concerned with the likelihood of calcium carbonate nucleation on OTEC heat exchangers and the rate at which growth of a calcium carbonate scale could occur in the event nucleation takes place.

THE DISTRIBUTION OF OCEANIC CALCIUM CARBONATE SATURATION STATES

The major factors controlling the saturation state of the oceans with respect to calcium carbonate are pressure, temperature and the CO_2 -carbonic acid system. Pressure is the only uniformly "simple" variable in that for the purposes of saturation state calculations, it is directly proportional to the water depth. Temperature is a "simple" variable in deep water (below approximately 1.5 km), but has significant variations in near surface waters where it varies not only with latitude, but also with current, upwelling and seasons.

In addition to the effects of temperature variations on the carbonic acid system, several factors, such as the exchange rate across the air-water

interface, biological activity, and mixing rates with deep water, can affect the carbonate ion concentration in near-surface waters. The major factors causing variations, at a given depth, in the deep ocean are the amount of calcium carbonate dissolution which occurs (changes alkalinity) and the amount of organic matter which is oxidized to CO_2. The increase in alkalinity tends to increase the saturation state, while the CO_2 production tends to decrease the saturation state by lowering the pH. Since the production of CO_2 by oxidation of organic matter is greater than the opposing calcium carbonate dissolution reaction, the net effect is for deep water to become more undersaturated with time.

As a very simplified generalization, the circulation of Arctic deep water can be pictured as a flow from the North Atlantic south around Antarctica, where further deep water is added, and then north through the Pacific Ocean. As a result of this flow pattern, the deep water in the Pacific Ocean has a higher carbonate alkalinity and P_{CO_2} (lower pH) than the Atlantic Ocean deep waters. The Pacific Ocean deep water is, therefore, more undersaturated with respect to calcium carbonate. This general pattern can be observed in figures 1 and 2, which are north-south sections through the Western Atlantic (see inset Figure 1 for sample sites) and Central Pacific (180° longitude) oceans. These profiles are based on GEOSECS (Geochemical Ocean Sections Program) data and were originally plotted by Takahashi (1975). Although his method of calculation was slightly different from that presented in this paper, the results are very similar. Please note that the deep water saturation state in the Pacific Ocean is not very different from that in the Atlantic Ocean until approximately 20°S latitude is reached.
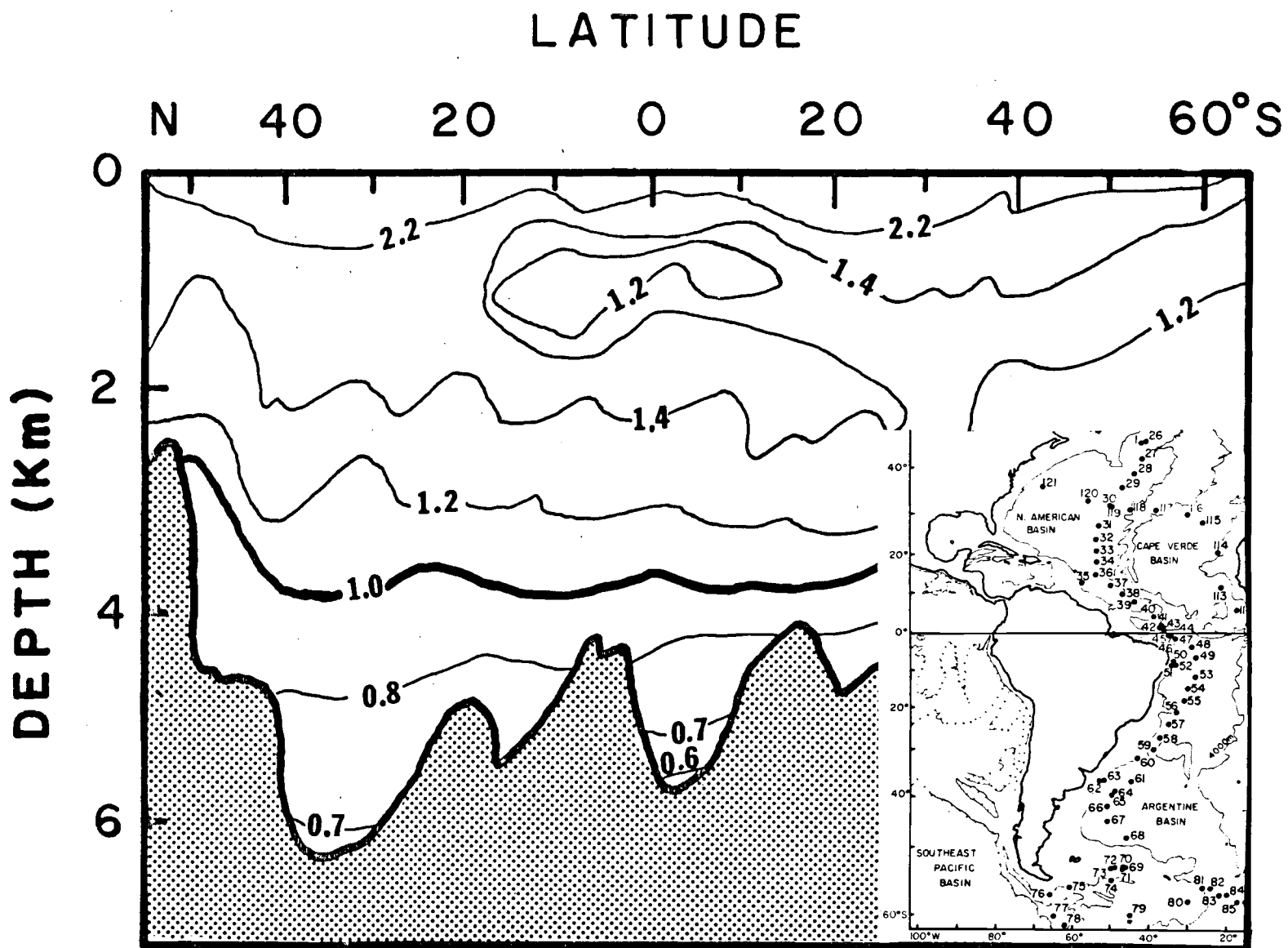
1. The distribution of calcite saturation in the Western Atlantic Ocean along GEOSECS track. (Location shown on insert) Based on Takahashi (1975).

LATITUDE
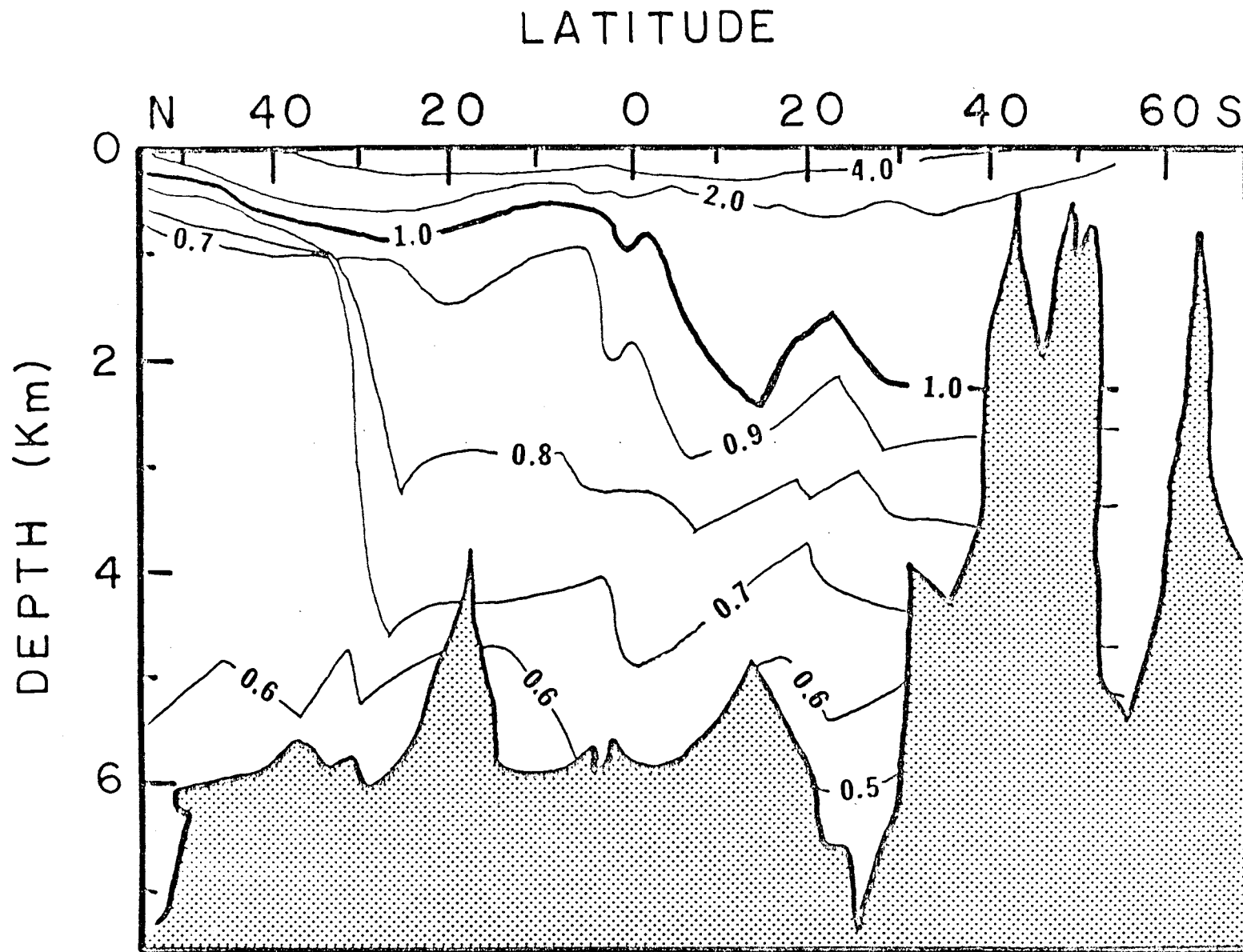
2. The distribution of calcite saturation in the Central Pacific Ocean in a north-south profile along 180° longitude. Based on GEOSECS data as presented by Takahashi (1975).

The saturation state of surface waters in the Western Atlantic and Central Pacific Oceans, along the same lines presented in figures 1 and 2, is shown in Figure 3. Saturation states were calculated using the surface water carbonate molality values of Takahashi (telephone contact, October, 1977) which he calculated from GEOSECS data. The results indicate that there is generally little difference in surface water saturation states in the two oceans at equivalent latitudes.

Figure 4 contains saturation profiles for both calcite and aragonite calculated by the methods presented in this paper for the Central Pacific Ocean over the probable depth range at which an OTEC might be expected to operate (based on the data of Berner and Wilde, 1972). The exact location of this profile is 19°58'N, 169°69'W. This is at approximately the same latitude as Hawaii and about 15° further west. The data of Takahashi (1975) at 35°N indicates that there is little variation in depth of equivalent saturation states in the east-west direction between these longitudes. This saturation profile may, therefore, be a good approximation of the depth distribution of calcium carbonate saturation at the potential Hawaii OTEC site. However, it could be wrong if circulation around the islands seriously disrupts the water masses.

One of the concerns about bringing cold-deep waters to the surface and warming them slightly at an OTEC power plant, has been what effect this would have on the calcium carbonate saturation state. Figure 4 shows the expected change in saturation state caused by bringing water from 1178 m to the surface and warming this water from 3.6°C to 7°C. The water remains undersaturated with respect to aragonite, but changes from slightly undersaturated to slightly supersaturated with respect to calcite.
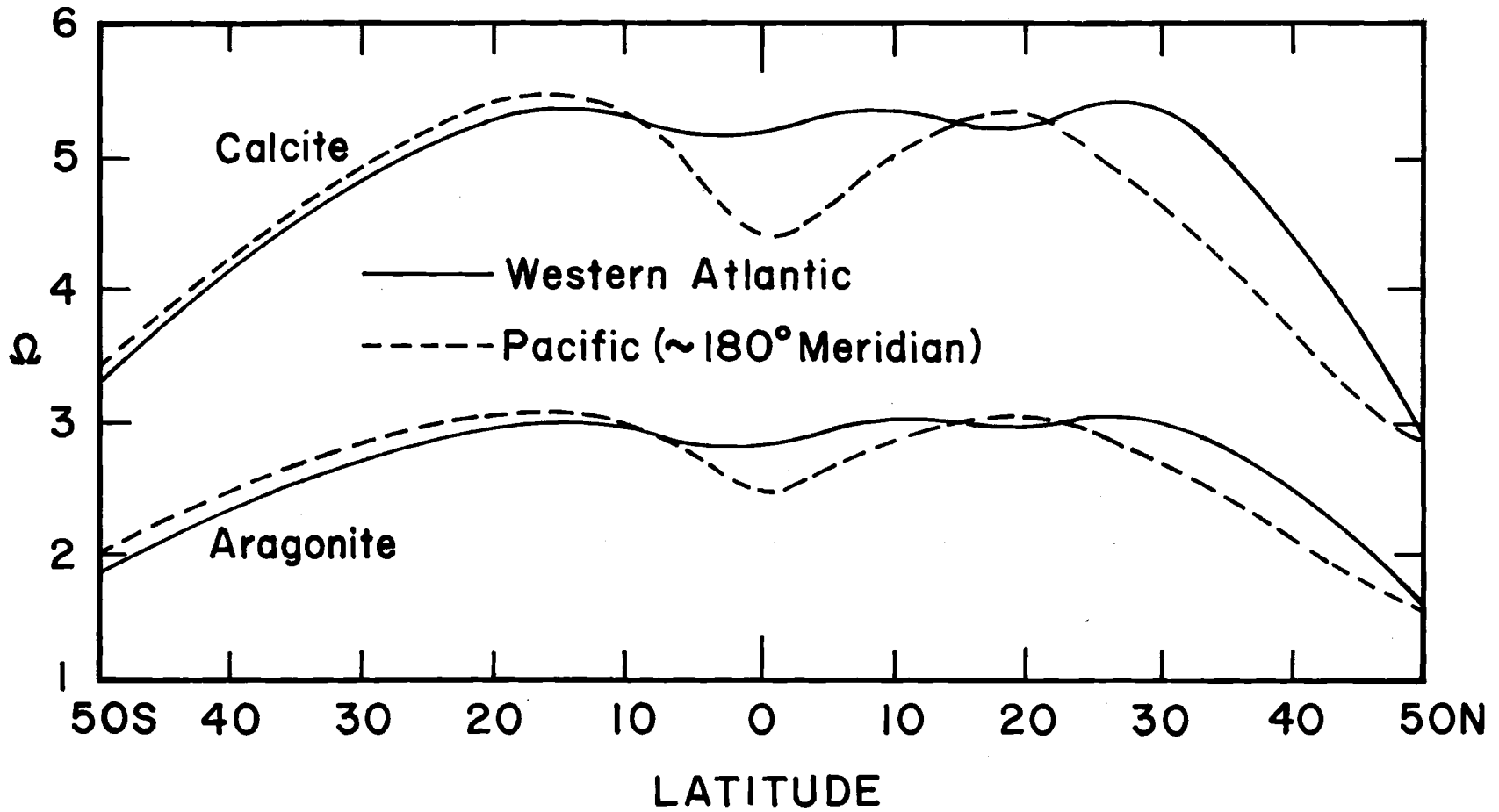
3. The saturation state (Ω) of seawater with respect to calcite and aragonite in the Central Pacific and Western Atlantic Oceans along the same lines as figures 1 and 2.
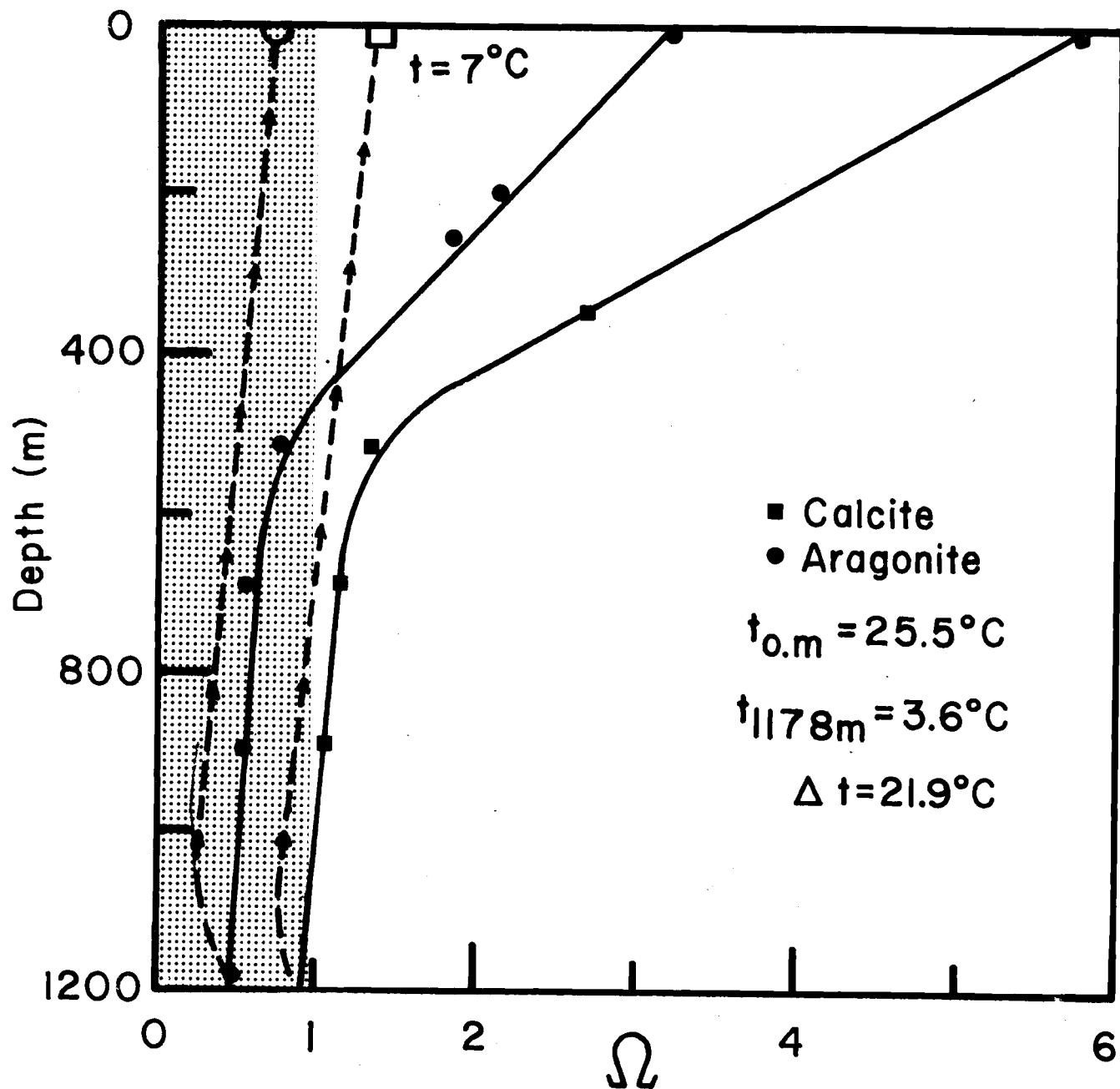
4. The calcite and aragonite saturation state (Ω) in the Pacific Ocean
   approximately 15°C west of Hawaii (based on the data of Berner and
   Wilde, 1972). Dashed lines indicate the effect of bringing water
   from 1178m depth to the surface and warming from 3.6°C to 7°C.
   Stippled area is undersaturated.

The change in calcite saturation state due to changes in temperature and pressure for a water sample of constant composition initially in equilibrium with calcite is presented in Figure 5. The effects of temperature and pressure are presented independently and in combination. The temperature and pressure are presented independently and in combination. The temperature data at various depths in the Central Pacific Ocean of Berner and Wilde (1972) were used. The relative changes in saturation state can be used to determine approximate effects for general situations of bringing deep water to the surface at other locations.

It is important to remember that the supersaturation can go from 1 to infinity, while the undersaturation can go only from 0 to 1. The relative changes in saturation state in a plot such as the one presented in Figure 4 can, therefore, be somewhat misleading. As will be discussed in the next section of this paper, rates of reaction tend to follow the log of the saturation state. For this reason, it may be more useful to consider the log of the saturation state versus water depth if potential reactivity of the water is of primary concern. This has been done in Figure 6 for the data presented in Figure 4.

Unfortunately, very little applicable data exists at potential OTEC sites for the determination of saturation state profiles. The data of Munier (1977) at the St. Croix biofouling and corrosion experiment test site indicate an average July pH of 8.20 at approximately 20 m water depth. The water temperature is 27°C and the salinity is 35.5°/oo. From these considerations, a good guess for titration alkalinity is 2.40 meq/l. The calculated saturation states with respect to calcite and aragonite are respectively 5.23 and 2.97. These values are close to those reported
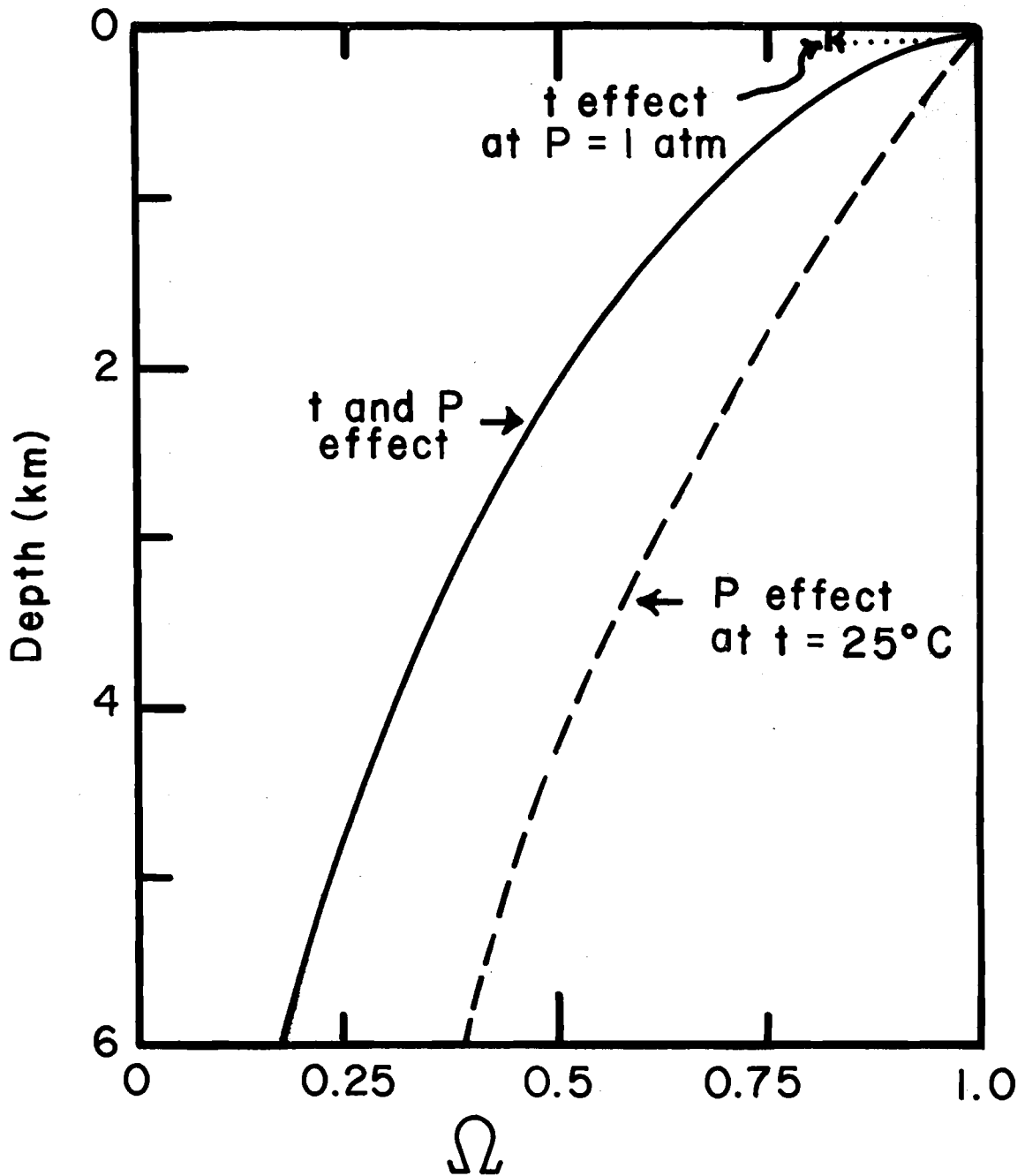
5. The effect of pressure and temperature on the saturation state
    (Ω) of a water sample of constant composition and in equilibrium
    with calcite at 25°C and 1 atmosphere pressure. The temperature
    versus depth data of Berner and Wilde (1972) for the Central
    Pacific Ocean were used.
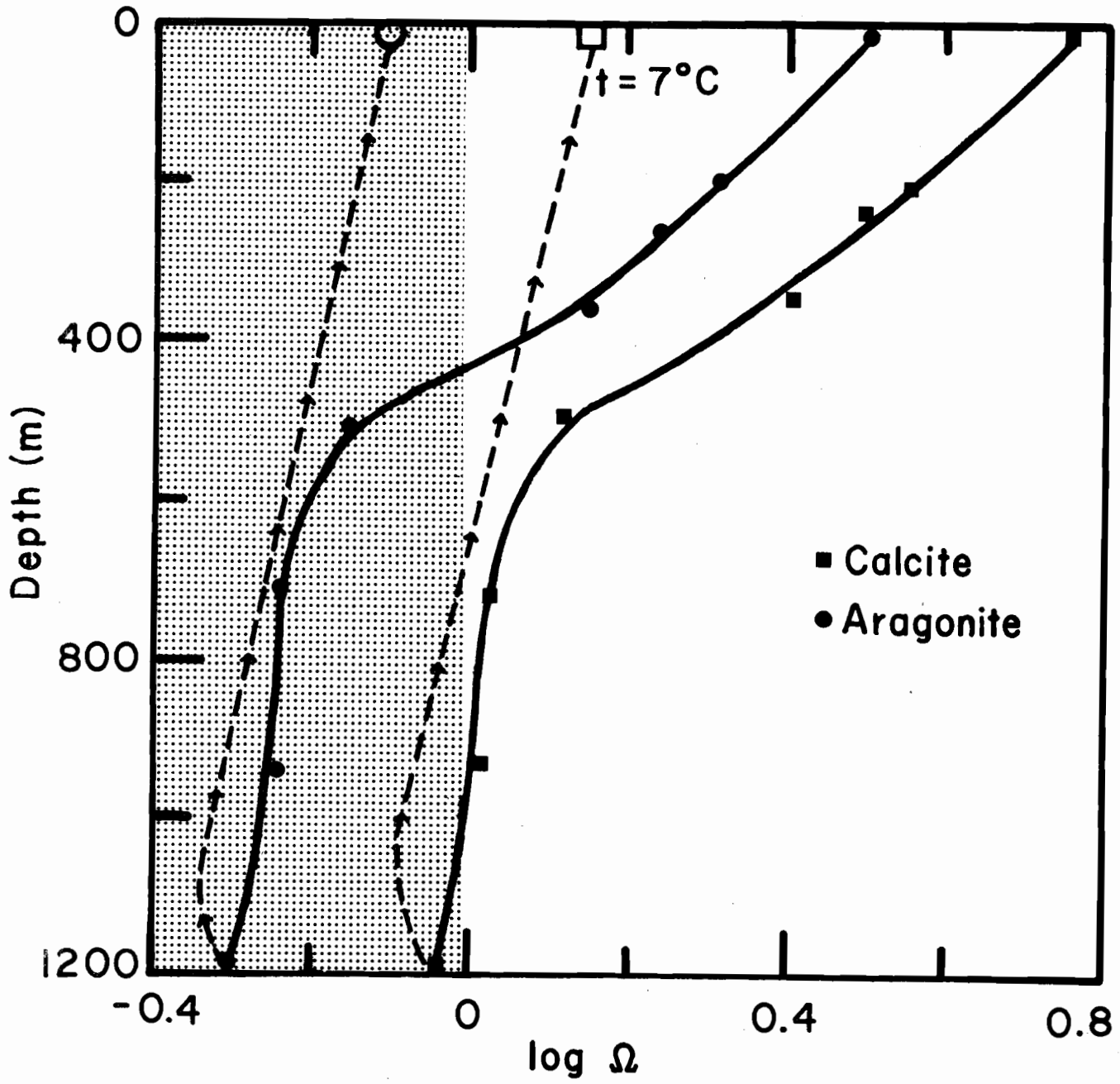
6. Figure 4 replotted as the log of Ω versus depth.

for Central Pacific and Western Atlantic Oceans.

It is strongly recommended that serious consideration be given to determining calcium carbonate saturation profiles at potential OTEC sites or at least at and during biofouling and corrosion experiments.

THE REACTION KINETICS OF CALCIUM CARBONATE IN SEAWATER

In order to have a predictive understanding of how rapidly carbonate scale may be deposited on OTEC power plant heat exchangers, it is necessary to determine how fast reactions associated with calcium carbonate formation from seawater proceed. In this section of the report current information on this topic is reviewed in three sub-sections. The first is directed at general considerations of the topic. The second sub-section is a discussion of the relationship between the chemistry of initial formation of calcium carbonate (nucleation) on a heat exchanger and corrosion chemistry. The third sub-section examines how fast a thickening of a calcium carbonate scale might occur as a function of seawater chemistry.

GENERAL CONSIDERATIONS

From a thermodynamic standpoint, whenever a system is not in its lowest free energy state, a net reaction should occur which moves the system towards that state. As a general rule, the rate at which the system approaches a given configuration decreases as the degree of disequilibrium decreases. The fact that there is no universal relationship between chemical reaction rate and the degree of disequilibrium, and that real systems are usually heterogeneous means that almost every reaction must be studied individually.

The reaction kinetics between different calcium carbonate phases and seawater have proven to be especially complex. It is possible to divide the reaction kinetics of calcium carbonate with seawater into four major areas: dissolution, homogeneous precipitation, heterogeneous precipitation and phase transformation. The two areas which have received the most research attention in recent years are dissolution (e.g., Berner and Morse, 1974; Morse, 1977; Plummer and Wigley, 1976) and phase transformation (e.g., Jackson and Bischoff, 1971; Katz et al., 1972) kinetics. Unfortunately, both of these areas of investigation can contribute little directly to the problem of calcium carbonate deposition from seawater.

Two types of precipitation of a solid from solution can occur. The first, and least common, type is homogeneous precipitation in which the solid forms directly and spontaneously from a supersaturated solution. The other type of precipitation from solution is heterogeneous precipitation in which precipitation occurs on pre-existing nuclei. Heterogeneous precipitation can be subdivided into two major types, depending on whether or not the precipitation occurs on nuclei of the same phase or on nuclei of a different phase (e.g., calcium carbonate precipitation on aluminum OTEC heat exchanger tubes). For the purposes of this report homogeneous nucleation and heterogeneous nucleation of calcium carbonate on another phase will be treated differently from heterogeneous precipitation on the same phase or crystal growth.

NUCLEATION KINETICS

Several investigators have carried out theoretical calculations (e.g., Berner, 1971; Wollast, 1971) and attempted to measure the

relationship between calcium carbonate supersaturation and the rate of homogeneous nucleation (e.g., Pytkowicz, 1965, 1973). The calculations of Berner (1971) indicate that a supersaturation, relative to calcite, on the order of a billion is necessary for homogeneous precipitation. Pytkowicz (1965, 1973) set a lower limit on the relationship between nucleation time and calcium carbonate supersaturation. In his experiments it was found that rapid precipitation (minutes to hours) does not occur until added carbonate concentrations on the order of ten times those found in surface seawater are used. While these findings are probably not the result of "pure" homogeneous precipitation, they definitely indicate that homogeneous precipitation of calcium carbonate will not occur at supersaturations found in the "open" ocean.

Since homogeneous precipitation of calcium carbonate appears to be most unlikely under conditions to be encountered within an OTEC power plant and would, in any event, not lead directly to deposits on OTEC heat exchangers, the major concerns for the OTEC project are the ability of heat transfer surfaces to act as nucleation sites for the heterogeneous precipitation of calcium carbonate, and the rate of growth of the calcium carbonate from seawater onto the heat exchanger surfaces once nucleation has occurred. It is likely that these processes will occur at different rates and that one of them will be the primary cause of reduced heat exchange efficiency.

The ability of heat exchanger surfaces to act as nucleation sites for the deposition of carbonate from seawater is strongly dependent on

the chemistry of the heat exchanger surfaces. Areas of heat exchanger
surfaces become cathodic during corrosion. When this occurs, a more
basic microenvironment is established on the surface which acts as a
site for carbonate nucleation.

Among the candidate materials for heat exchanger tubes are aluminum
alloys. These alloys are known to corrode in seawater. Aluminum corrosion
produces strongly alkaline conditions at the metal surfaces, which are
functioning as cathodes due to the reduction of oxygen:

$$O_2 + 4e^- + 2H_2O \rightleftharpoons 4OH^- \qquad (1)$$

In a pitting situation, as much as 95 to 98% of the total surface behaves
this way. Thus, there is a tendency to precipitate calcium carbonate
scales all over the tube by the following mechanism:

$$HCO_3^- + OH^- \rightleftharpoons H_2O + CO_3^{--} \qquad (2)$$

$$Ca^{++} + CO_3^{--} \rightleftharpoons CaCO_3 \qquad (3)$$
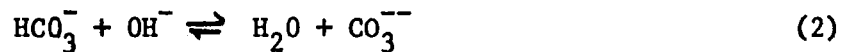
This process has been studied as a function of corrosion potential
using a constant current circuit to determine the total electrical
current discharged. Experiments were run for various time periods ranging
from one to four weeks. Seawater was changed daily. (It was not possible
to have continuously flowing seawater, as several samples were connected
in a series circuit, and different areas were used to produce a variety
of current densities and potentials, using a single current source). The
results, shown in figures 7 and 8, are based on the results of Kole (1973).
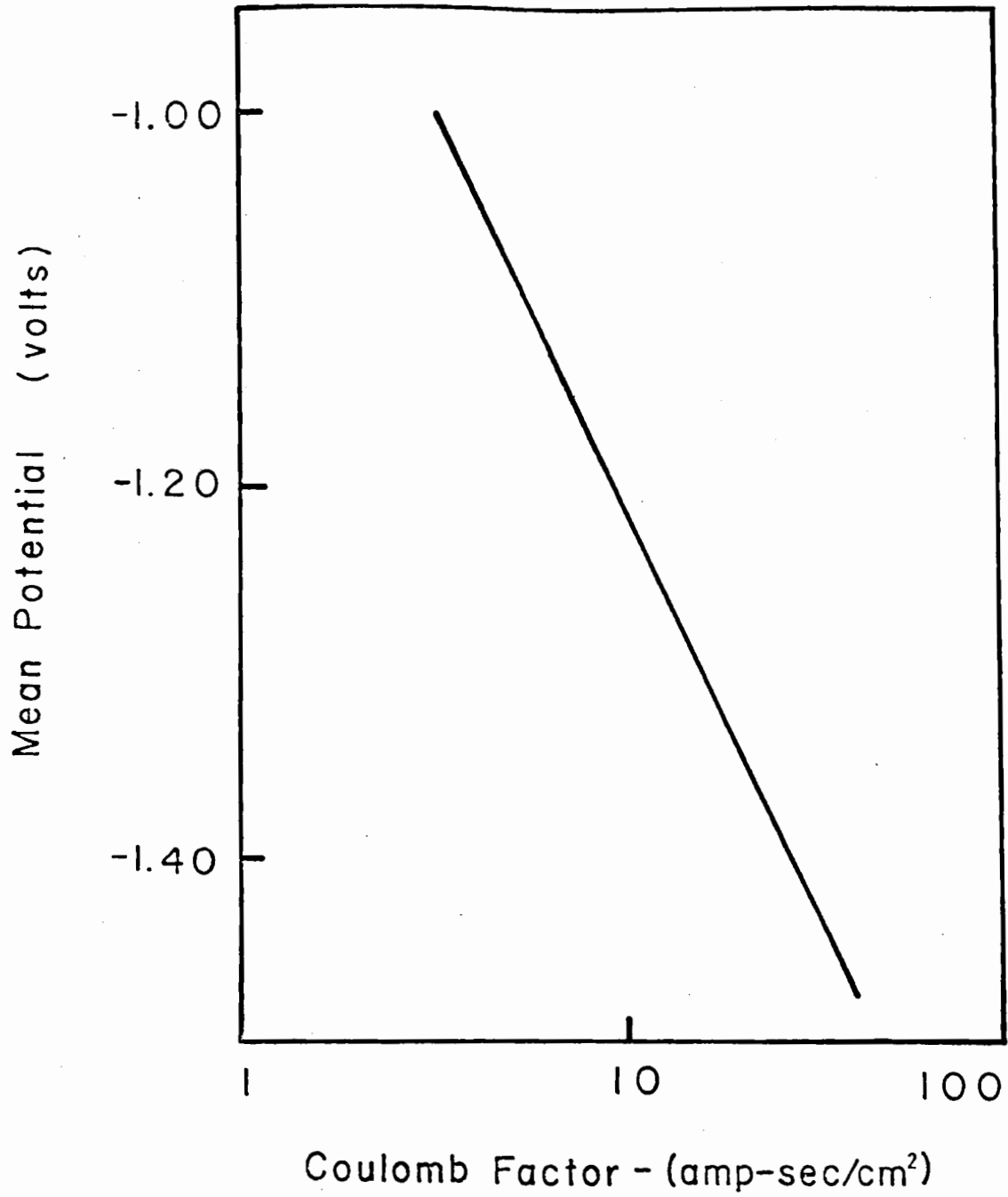
7. Coulomb factor versus mean potential for aluminum(after Kole,1973).
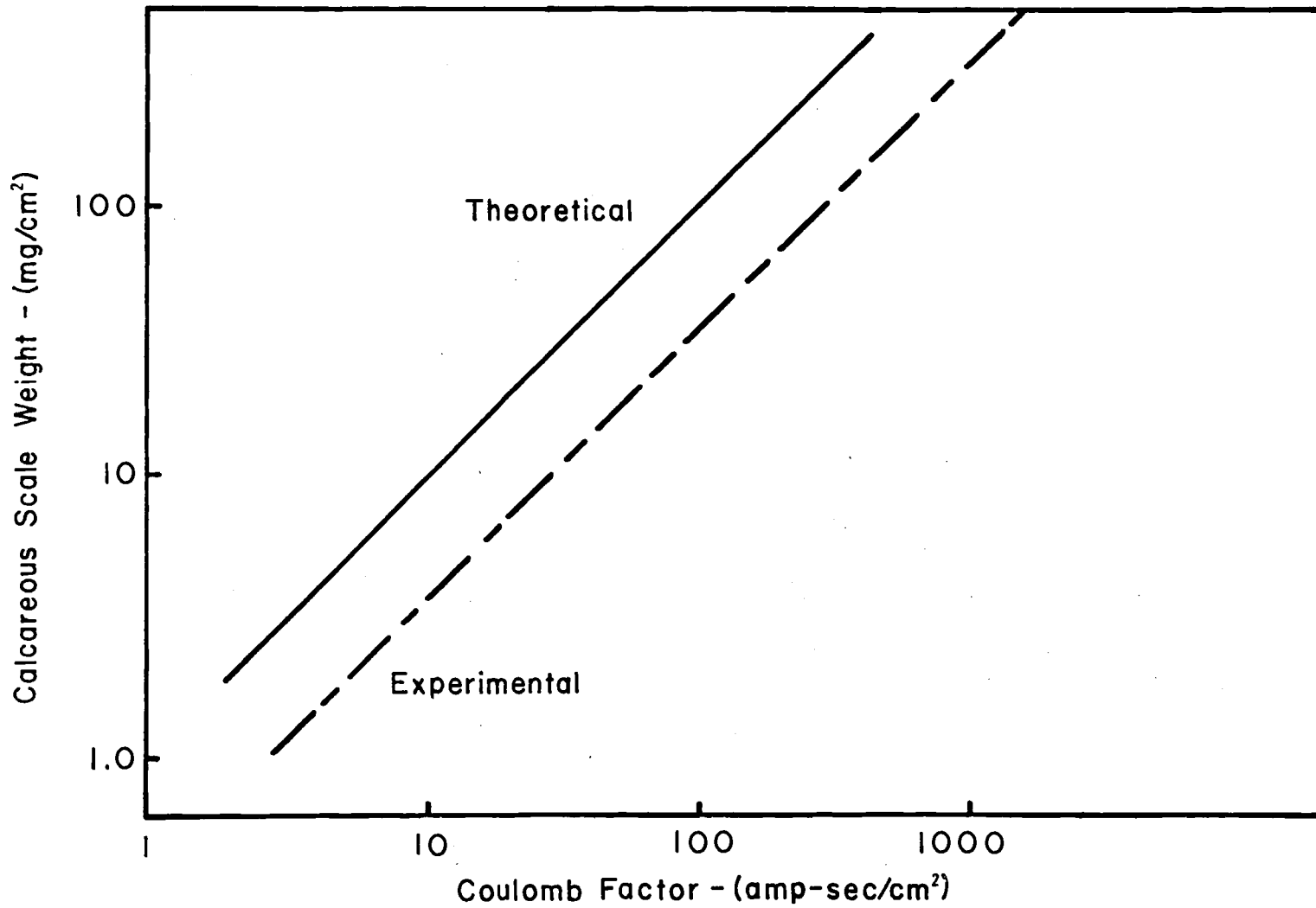
8. Theoretical and experimental relationship of calcareous scale weight versus coulomb factor (after Kole, 1973). Experiments were carried out on steel, galvanized sheet and aluminum.

Approximately 50% of the corrosion current resulted in scale formation. This is a function of the relative diffusion of the hydroxyl ions away from the surface in relation to the reaction time for carbonate precipitation. These results are only an indication of what might happen in an OTEC plant. On the other hand, a noncorrodible metal, such as titanium, will collect a deposit by this mechanism only if a galvanic cell exists in which it is a cathodic element. In areas of turbulence, the accumulation of alkali which will result in calcareous deposits is unlikely. However, in "dead" spots such a buildup will be enhanced due to the low diffusion rates of hydroxyl away into the bulk solution.

The data of Ailor (1970) and Groover et al. (1969) summarized data for many aluminum alloys in flowing natural seawater. These data, reported by Craig (1974), are presented in Figure 9. They indicate that the corrosion potentials of aluminum alloys fall within the range where scale formation is likely. Indeed, when the samples are cleaned to remove the corrosion products, considerable effervescence is always observed, giving testimony to the presence of calcium carbonate scales laid down during the corrosion process.

In addition to nucleation of calcium carbonate associated with the corrosion of the OTEC heat exchanger surfaces, calcium carbonate nucleation could be brought about on the heat exchanger surfaces by biologic activity. This could occur either directly, by calcium carbonate secreting organisms, or indirectly, in highly supersaturated microenvironments that result from organic deposition and decay. It is, however, quite possible that biogenic coatings on the heat exchanger surfaces could have the opposite effect by creating a barrier between the seawater and the metallic heat
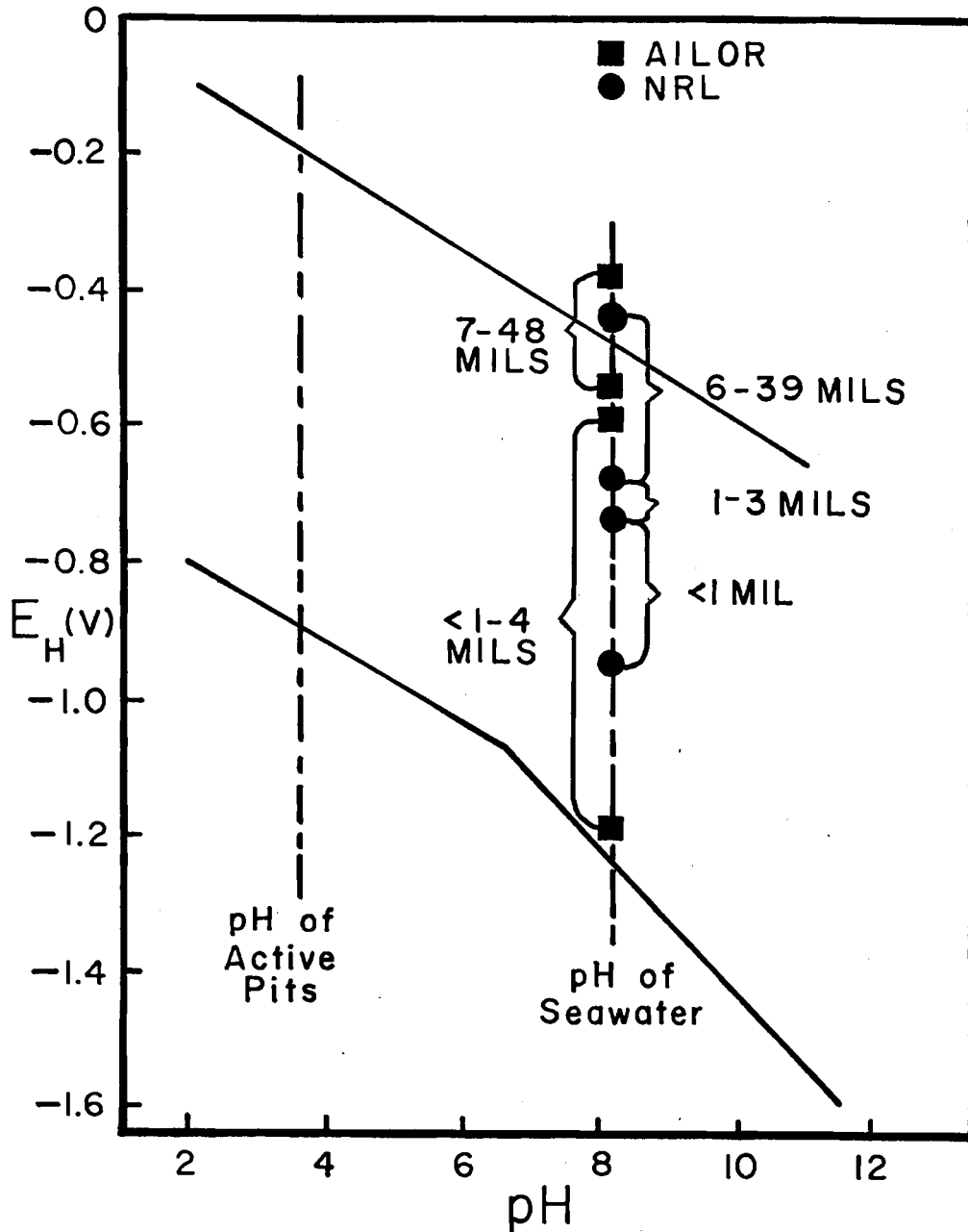
9. Maximum pit depths found for various aluminum alloys. Points are plotted at the average corrosion potential measured during the study with values converted to the standard hydrogen electrode. These points are portrayed at the typical pH value of surface seawater (after Craig, 1974). AILOR and NRL refer respectively to the data of Ailor (1970) and Groover et al (1969) for many aluminum alloys in flowing, natural seawater for periods of several months.

exchanger surface, on which nucleation of calcium carbonate would not be likely.

Thus, the formation of calcium carbonate nuclei on OTEC heat exchanger surfaces is a definite possibility. Whether such nucleation will occur or not will depend on a very complex interplay between several competing processes. It is unlikely that the nucleation problem can be resolved from a theoretical basis. Only direct experimentation can indicate which process will win out as the dominant one in coating OTEC heat exchanger surfaces. Different processes may dominate in the cold deep water from those in the warm shallow water, where biofouling should be more important.

Nucleation of calcium carbonate on the surface of an OTEC heat exchanger could result in the formation of a very thin film of calcium carbonate of less than 5 μm (0.2 mils) that would not significantly inhibit heat transfer. It is the outward growth of this film beyond 5 μm that could result in the formation of a layer of calcium carbonate of sufficient thickness to retard heat transfer beyond acceptable limits for an OTEC power plant. The relation between heat transfer inhibition, and the thickness of a biofouling layer and solid calcium carbonate layer is presented in Figure 10 (letter from Bell, October, 1977).

GROWTH KINETICS

Although a number of studies have been made on the growth rate of calcium carbonate from supersaturated solutions other than seawater (e.g., Reddy and Nancollas, 1971; Nancollas and Reddy, 1971; Nancollas and Reddy, 1974; Nancollas, 1975), the results are generally not applicable
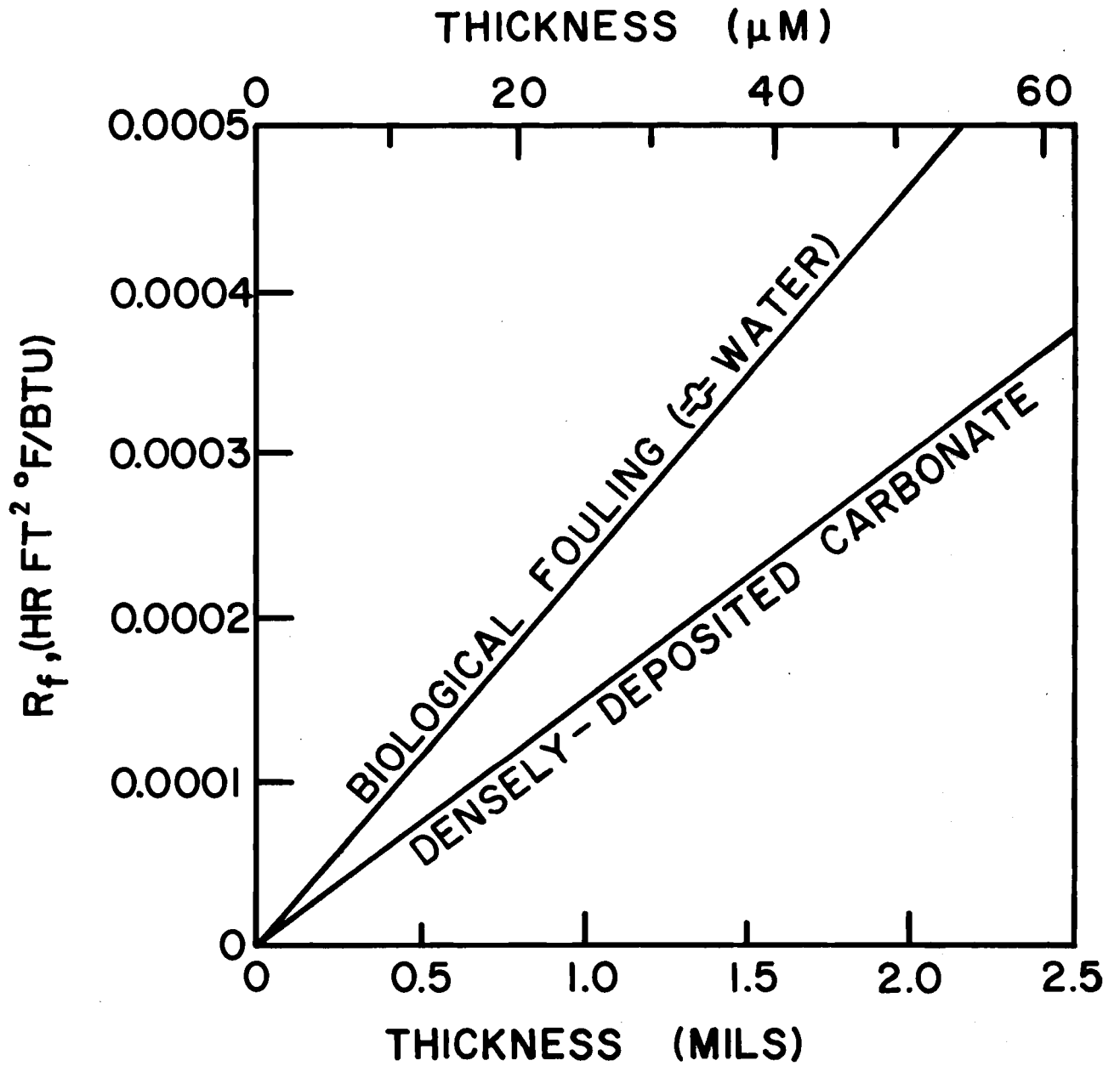
10. The relation between heat transfer, and the thickness of biofouling and solid calcium carbonate layers on heat exchanger surfaces. (Letter from Bell, October, 1977).

to calcium carbonate growth kinetics in seawater. This is because it has been found that magnesium has a strong effect on calcite growth kinetics (e.g., Weyl, 1965; Pytkowicz, 1965, 1973; Bischoff, 1968; Lippman, 1973; Berner, 1975), and organics (e.g., Chave, 1965; Chave and Suess, 1967, 1970; Berner, et al., 1977) and phosphates (e.g., Raistrick, 1949; Reddy and Nancollas, 1973; Berner, et al., 1977) have been shown to be inhibitors of both calcite and aragonite dissolution. Variations in organic and phosphate concentrations occurring in the ocean can cause changes in precipitation rates in excess of an order of magnitude (Berner, et al., 1977). Biofouling in OTEC heat exchangers could result in micro-environments in which variations in these parameters could exceed those found in seawater. So again, the need for direct experimental results will be necessary in order to elucidate the relationship between seawater chemistry and possible calcium carbonate scale buildup.

Perhaps the only data that are useful in getting an approximate idea of how the rate of calcium carbonate deposition would vary as a function of saturation state are those of Berner (1975). Approximate fits to the data are presented in Figure 11. The values of constants were modified to be consistent with those of this paper. It was also assumed that his relative rate units were the same for calcite and aragonite (he used "arbitrary rate units"). The rates were normalized to the different surface areas of the calcite and aragonite samples. When the rates of dissolution are plotted relative to the aragonite saturation state, which in effect normalizes the reaction rates of
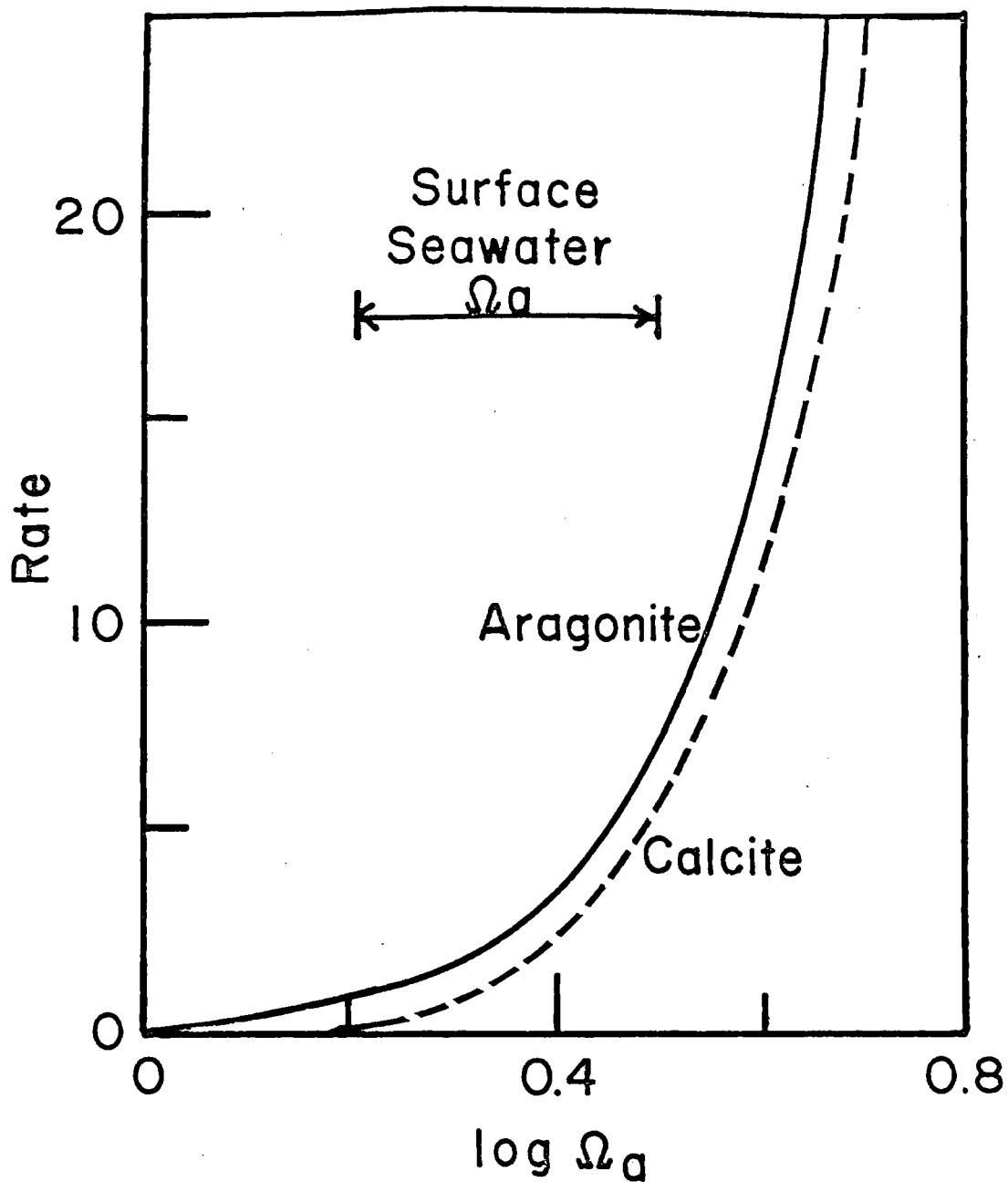
11. The relationship between log Ω_a and the precipitation rates of calcite and aragonite based on the data of Berner (1975).

calcite and aragonite to the same calcium carbonate ion molal product, the rates of dissolution of calcite and aragonite are found to be very close in artificial seawater. Another way of putting this is that calcite and aragonite would have approximately the same rate of growth, per unit surface area, in the same seawater sample if no organic or phosphate inhibitors are present. Further experimentation in this area is necessary, but from the plots of the rate of precipitation versus the log of the saturation state it is apparent that large changes of growth rate occur over relatively small changes in saturation state. These results indicate that if calcium carbonate nuclei form on the surface of OTEC heat exchangers, scale buildup can be expected.

CONCLUSIONS AND RECOMMENDATIONS

Although detailed data on the calcium carbonate saturation state of seawater at potential OTEC sites is lacking, it seems very probable that all warm water heat exchangers will encounter seawater that is supersaturated with respect to the calcium carbonate phases calcite and aragonite. It also appears probable that the deep waters, even when brought to the surface and warmed, will be less supersaturated than the surface waters. The only possibility for heat exchangers encountering undersaturated waters may be in the Pacific Ocean deep waters.

The formation of calcium carbonate scale on OTEC heat exchangers will depend on the surface microenvironment which is established on the heat exchangers. This will involve a complex interplay of corrosion and biofouling. If calcium carbonate nucleation on the heat exchanger surfaces does occur, both calcite and aragonite can grow on the nuclei to

form scale deposits. This could severely inhibit heat transfer. The rate of this growth will again be dependent on the environment in the heat exchangers.

Having made the basic theoretical estimates that strongly indicate the _possibility_ of calcium carbonate scale fromation on OTEC heat exchangers, it is now necessary to carry out direct experiments. These experiments should be aimed at two primary objectives. The first is the determination of the conditions, if any, under which nucleation of calcium carbonate on OTEC power plant heat exchangers is likely to occur. The second is determination of the rate at which scale thickening would proceed under OTEC power plant operating conditions. It is also recommended that the saturation state of seawater with respect to calcium carbonate used in any biofouling and corrosion experiments be carefully monitored.

ACKNOWLEDGEMENTS

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APPENDIX A

CALCULATION OF CALCIUM CARBONATE SATURATION STATE

GENERAL CONSIDERATIONS

In order to facilitate the discussion of methods for calculating

the saturation state of seawater with respect to calcium carbonate,

initial consideration will be given to pure calcium carbonate phases

($CaCO_3$). The usual method of expressing the saturation state of a

solution with respect to a solid phase is as the ratio Ω of the ion

activity (a) product to the thermodynamic solubility constant (K). For

the calcium carbonate phase calcite, the expression for the saturation state

is defined as (e.g. Morse and Berner, 1972) :

$$\Omega_c = \frac{a_{Ca^{++}} \, a_{CO_3^{--}}}{K_c} \qquad (1)$$

Where the subscript "c" denotes calcite. A subscripted "a" will be

used in the same manner to denote aragonite. If Ω is greater than 1

the solution is supersaturated, less than 1 undersaturated and equal to

1 in equilibrium with respect to calcite.

Because of the difficulties in precisely calculating the total ion

activity coefficient (γ) of calcium and carbonate ions in seawater and

the effects of temperature and pressure on the activity coefficients, a

semiempirical approach has been generally adopted by chemical ocean-

ographers for calculating saturation states. This approach utilizes the

apparent solubility constant (K'), which is the equilibrium ion molal

(m) product. In this approach:

$$\Omega = \frac{m_{Ca^{++}} \, m_{CO_3^{--}}}{K'} \tag{2}$$

the ratio of K to K' is then:

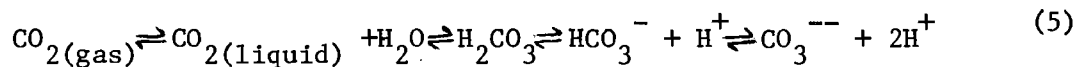$$\frac{K}{K'} = \gamma_{Ca^{++}} \, \gamma_{CO_3^{--}} \tag{3}$$

CALCULATION OF CALCIUM AND CARBONATE TOTAL MOLALITIES

The total ion molal calcium concentration in seawater can be calculated, in "open" ocean seawater samples, directly from high precision salinity measurements, using the relationship:

$$m_{Ca^{++}} = 0.01027 \left[\frac{S}{35} \right] \tag{4}$$

Where S is salinity in parts per thousand. This relationship can be expected to be constant under "open" ocean conditions to within at least 0.5% and is independent of temperature and pressure.

The calculation of the total ion molal carbonate concentration is more complex than for calcium, because it is part of the carbonic acid system. The following reactions take place between CO_2 and carbonic acid in seawater:

$$CO_{2(gas)} \rightleftharpoons CO_{2(liquid)} + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \rightleftharpoons CO_3^{--} + 2H^+ \tag{5}$$

Because the dissolved CO_2 is almost completely hydrated, generally only one equilibrium constant is used to describe the reaction between gaseous carbon dioxide and H_2CO_3. The thermodynamic and apparent equilibrium constants for the above reactions are:

$$K_o = \frac{a_{H_2CO_3}}{P_{CO_2}} \quad ; \quad K'_o = \frac{m_{H_2CO_3}}{P_{CO_2}} \tag{6}$$

Where P_{CO_2} is the partial pressure of CO_2 gas.

$$K_1 = \frac{a_{HCO_3^-} \; a_{H^+}}{a_{H_2CO_3}} \quad ; \quad K_1' = \frac{m_{HCO_3^-} \; a_{H^+}}{m_{H_2CO_3}} \tag{7}$$

$$K_2 = \frac{a_{CO_3^{--}} \; a_{H^+}}{a_{HCO_3^-}} \quad ; \quad K_2' = \frac{m_{CO_3^{--}} \; a_{H^+}}{m_{HCO_3^-}} \tag{8}$$

Using the above equations it is possible to calculate $m_{CO_3^{--}}$ if any two of the four possible analytic quantities for the carbonic acid system are known. These four analytic quantities are:

1. Total CO_2 defined as:

$$\Sigma CO_2 = m_{H_2CO_3} + m_{HCO_3^-} + m_{CO_3^{--}} \tag{9}$$

2. Carbonate alkalinity defined as:

$$A_c = m_{HCO_3^-} + 2m_{CO_3^{--}} \tag{10}$$

3. P_{CO_2}

4. pH

Carbonate alkalinity is not a directly analyzable quantity, but it can be derived from the titration alkalinity (A_t) by a relationship which is temperature and pressure dependent. pH is also variable with pressure and temperature. In addition, pH can be defined several ways depending on which buffer system is used, whether liquid junction potentials are considered, and what definition of ionic strength is used. The values of the apparent dissociation constants and calcium carbonate solubility constants are dependent on exactly what definition of seawater pH is used and what standardization technique was used (e.g. Bates, 1974; Hansson 1973;

Mehrbach et al, 1973).

Although virtually every combination of the four carbonic acid system analyzable variables has been used, the easiest pair from both an analytical and calculation standpoint is pH and alkalinity. When this pair is used, the equation relating total carbonate molality to pH and carbonate alkalinity is:

$$m_{CO_3^{--}} = \frac{A_c}{2 + \left(\frac{10^{-pH}}{K_2'} \right)} \qquad (11)$$

If for the moment, it is assumed that there is negligible error in the apparent constants, transformation of titration alkalinity to carbonate alkalinity, determination of calcium molality, and the pressure and temperature corrections, the sensitivity of the saturation state calculation to probable analytical errors can be determined using Equation (11). It will be assumed that the maximum error is the sum of the errors attributable to pH and alkalinity errors. It is very easy to measure alkalinity to within 5% and it can be measured with proper equipment and reasonable care to within better than 0.4%. Since the carbonate molality is directly related to the alkalinity, the uncertainity in carbonate molality caused by alkalinity measurement is the same as the alkalinity measurement error. It is extremely difficult to measure pH to better than 0.01, even if a Zirino (1975) cell is used with seawater buffers. Without a great deal of care, errors in pH on the order of 0.05 can easily occur. In the range of pH values encountered in the ocean, an error of 0.01 in pH causes approximately a 2% error in the carbonate molality. The range in probable carbonate ion molality directly

attributable to analytical uncertainty is on the order of 3% to 15%. A factor of five in the probable error between "state of the art" measurements and those easily carried out by investigators lacking special training in this area of research, points up the dangers in using data where little is known about the exact techniques which were used.

The in situ pH can be calculated by making the appropriate temperature and pressure corrections on the measured pH. Temperature corrections are made using the equation of Harvey (1963).

$$pH_{t_2} = pH_{t_1} + x(t_1 - t_2) \qquad (12)$$

For the general case where the pH is measured at $25°C(t_1)$ and the in situ temperature $(t_2 = t_{is})$ is less than 20°C, the values of x given by Harvey (1963) yield Equation (13).

$$pH_{t_{is}} = pH_{25} - 0.0097(20 - 25) - 0.0105(t_{is} - 20) \qquad (13)$$

Once the pH at the in situ temperature has been calculated, the actual in situ pH can be calculated by correcting the pH for the effect of pressure by use of Equation (14) which was derived from the data presented by Culberson and Pytkowicz (1968, Table 4).

$$pH_{is} = pH_{t_{is}} - (P \times 10^{-4}) [4.28 - 0.04 \, t_{is} - 0.4(pH_{t_{is}} - 7.8)] \qquad (14)$$

Where P is pressure in atmospheres in excess of 1 atmosphere.

In order to calculate the in situ carbonate alkalinity, it is first necessary to calculate the in situ alkalinity contribution of boric acid to the analyzed quantity, titration alkalinity. This is done by initially calculating the concentration of boric acid via the boron to chlorinity ratio of Culkin (1965) and a general salinity-molecular weight conversion formula.

$$^{m}B(OH)_3 = \frac{(1.21 \times 10^{-5})\ S}{1 - \left(\frac{S}{1000}\right)} \tag{15}$$

The next step is to calculate the first apparent dissociation constant of boric acid in seawater (K_B') under _in situ_ conditions. K_B' can be calculated at the _in situ_ temperature using the equation of Edmond (1970) which is based on the data of Lyman (1957).

$$-\log K_{B'_{t_{is}}} = \left(\frac{2291.90}{t_{is} + 273}\right) + 0.01756(t_{is} + 273)$$

$$-3.3850 - 0.32051 \left(\frac{S}{1.80655}\right)^{1/3} \tag{16}$$

The change in $-\log K_B'$ due to pressure (generally designated in oceanographic literature as pK_B') can be calculated using the equation of Culberson and Pytkowicz (1968).

$$\Delta (-\log K_B') = 1.809 \times 10^{-3})\ P - (4.515 \times 10^{-6})\ (t_{is} + 273)P$$

$$- (1.69 \times 10^{-7})P^2 + (1.759 \times 10^{-12})(t_{is} + 272)^2P^2 \tag{17}$$

From these considerations the _in situ_ first apparent dissociation constant for boric acid in seawater is:

$$K_{B'_{is}} = 10^{-\ [(-\log K_{B'_{t_{is}}}) - \Delta (-\log K_B')]} \tag{18}$$

The carbonate alkalinity is calculated by the relationship of Skirrow (1965).

$$A_{c_{is}} = A_t - \frac{K_{B'_{is}}\ ^{m}B(OH)_3}{K_{B'_{is}} + 10^{-pH}} \tag{19}$$

It is also necessary to calculate the _in situ_ value for the second

apparent dissociation constant of carbonic acid in seawater. Its value

at the in situ temperature can be calculated using the equation of

Mehrbach et al (1973):

$$-\log K'_{2_{t_{is}}} = 5371.9645 + 1.671221 \, (t_{is} + 273) + 0.22913 \, S +$$

$$18.3802 \log (S) - 128375.28/(t_{is} + 273) - 2194.3055 \log (t_{is} + 273)$$

$$-(8.0944 \times 10^{-4})(t_{is} + 273)S - 5617.11 \log(S)/(t_{is} + 273)$$

$$+ 2.136 \, S/(t_{is} + 273) \tag{20}$$

The change in $-\log K'_2$ due to pressure, near $34.8^o/oo$ salinity, is

given by Culberson and Pytkowicz (1968) as:

$$\Delta(-\log K'_2) = - 0.015 + (8.39 \times 10^{-4}) \, P - (1.908 \times 10^{-6})(t_{is} + 273)P$$

$$+ (1.82 \times 10^{-7})(t_{is} + 273)^2 \tag{21}$$

From these considerations the in situ second apparent dissociation con-

stant of carbonic acid in seawater is:

$$K'_{2_{is}} = 10^{-[(-\log K'_{2_{t_{is}}}) - \Delta(-\log K'_2)]} \tag{22}$$

The total carbonate ion molal concentration can now be determined

using Equation (11). At this point, the only parameter lacking for

calculation of the saturation state of calcium carbonate in seawater are

the in situ values of the apparent solubility products of calcite and

aragonite.

CALCULATION OF APPARENT CALCIUM CARBONATE SOLUBILITY PRODUCTS

The precise determination of the solubility of calcite and aragonite

in seawater has proven to be one of the more elusive quests of low

temperature geochemists. The two most recent determinations of apparent

calcite solubility (Ingle et al, 1973; Berner, 1976) differ by approximately

40% at 2°C. One approach to making a decision as to which values are most likely to be correct, is to compare the apparent solubility products which can be calculated from thermodynamic equilibrium constants and total activity coefficients, with measured apparent solubility products.

The extent of disagreement on solubility arrived at by the two different approaches and within each approach, is summarized in Table 1. Only the values presently in most contention have been used.

The values of K_c at 25°C and 5°C presented by Jacobson and Langmuir (1974) and by Berner (1976) were used. The value of $\gamma_{CO_3^{--}}$ at 25°C and 5°C of Pytkowicz (1975), and the values for $\gamma_{Ca^{++}}$ at 25°C of Pytkowicz (1975) and Berner (1965) were utilized for the activity coefficients. $\gamma_{Ca^{++}}$ was calculated at 5°C from both values at 25°C using the temperature correction of Berner (1971). Values of K_c' range at 25°C from 5.0×10^{-7} to 6.3×10^{-7} and at 5°C from 4.8×10^{-7} to 8.0×10^{-7}. As if this were not bad enough, K_c' values calculated from solubility products and activity coefficients give a decrease in apparent solubility with decreasing temperature, while measured K_c' values increase with decreasing temperature.

The opposite change in calculated and measured apparent solubilities for calcite with temperature is especially perplexing. An examination of this reveals how convoluted the whole area has become. The problem, to a large extent, is associated with the temperature coefficient for $\gamma_{Ca^{++}}$. The temperature coefficient for $\gamma_{Ca^{++}}$ of Berner (1971) was calculated from the data of Berner(1965) and Li(1967). It is based on differences between

TABLE 1

CALCULATED AND MEASURED VALUES OF K_c'

PARAMETERS USED		$K_c' \times 10^7$	
K_c	γ_{Ca}^{++}	25°C	5°C
Jacobson & Langmuir (1974)	Pytkowicz (1975)	5.5	5.0
Jacobson & Langmuir (1974)	Berner (1965)	6.3	5.7
Berner (1976)	Pytkowicz (1975)	5.1	4.8
Berner (1976)	Berner (1965)	5.9	5.4
K_c' measured by Ingle et al (1973)		5.0	5.8
K_c' measured by Berner (1976)		5.9	8.0

The value for $\gamma_{CO_3}^{--}$ at 25°C and 5°C of Pytkowicz (1975) and the temperature coefficient for $\gamma_{Ca.}^{++}$ of Berner (1971) were also used in the calculation of K_c' from K_c.

calculated K_c and measured K_c' values at that time, as well as estimates

at that time of $\gamma_{CO_3}{}^{--}$ at different temperatures. Consequently, any

attempt to test the consistency of recently reported K_c and K_c' values

at temperatures other than 25°C is circular since it rests on an activity

coefficient variation with temperature which is based on the same types

of measurements done at an earlier time. What is needed for comparisons

at other than 25°C is a temperature coefficient for $\gamma_{Ca}{}^{++}$ which is based

on measurements independent of the carbonate system.

The following discussion will be directed at the differences in the

recently reported values for K_c' calcite of Ingle et al (1973) and

Berner (1976). As a start, it will be assumed that the data in both

studies could be closely reproduced by other investigators following the

same procedures.

In the study of calcite solubility by Ingle et al (1973) both

reagent grade and Iceland spar calcite were studied in seawater (35°/oo

salinity) at different temperatures. An airtight saturometer was used

for solubility measurements (Weyl, 1961). Starting undersaturations

were small enough so that pH changes of less than 0.2 were observed.

However, in the experiments started in supersaturated seawater, pH

changes as large as 0.8 occurred.

Berner (1976) took a new approach to the determination of K_c' of

calcite in seawater. His basic argument was that it is extremely

difficult, if not impossible, to obtain good solubility data on calcite

in seawater because, in precipitation from supersaturation, pure calcite

does not form. Instead, a low magnesium calcite is formed and the

solubility of the low magnesium calcite, not pure calcite, is measured.

This argument had previously been advanced by Weyl (1965) from his saturometry results and was clearly demonstrated by Berner (1975) in his study of the role of magnesium in the crystal growth of calcite and aragonite. To avoid this problem, Berner (1976) measured the solubility of calcite and aragonite in distilled water. He then measured the solubility of aragonite, which does not suffer from the magnesium problem, in seawater at various temperatures. The K_c' of calcite was obtained by assuming that the difference in solubility of calcite and aragonite was constant. His experimental method for the determination of K' was quite different from that which Ingle et al (1973) used. Instead of using a saturometer, a sample of the calcium carbonate to be studied was stirred in a solution kept at constant P_{CO_2} by bubbling a gas of constant composition through it. He then measured pH, alkalinity and $m_{Ca^{++}}$. From the data presented by Ingle et al (1973) and Berner (1976) it is impossible to determine the exact solid to solution ratios. A reasonable guess might be that the ratio was on the order of 10 to 100 times higher in the experiments of Ingle et al (1973) than in Berner's experiments.

There appear to be two primary possibilities for the differences in the results. The first is that the differences are a result of the different experimental techniques used to measure K_c'. The second possibility is that Ingle et al (1973) measured the solubility of a low magnesium calcite. The main difficulty with this argument is that the K_c' values obtained from undersaturation agree quite well with those obtained from supersaturation. It is possible that, while pure calcite was dissolving, a low magnesium calcite of lower solubility was forming on

soluble in seawater than pure calcite. If a guess is made that the least soluble phase contains 5 mole percent magnesium, and the value for K_c' of Ingle et al (1973) at 25°C is used, then $K_{mc}' = 5.43 \times 10^{-7}$. If Berner's (1975) thermodynamic values are used with $\gamma_{Ca^{++}} = 0.20$, $\gamma_{Mg^{++}} = 0.25$ and $\gamma_{CO_3^{--}} = 0.030$, the difference between the calculated free energy of formation and that determined by Berner (1975) is only approximately 0.1 kcal/mole. This is probably well within the accuracy of the data. Although this is certainly not conclusive evidence that low magnesium calcite of approximately 5 mole percent magnesium is being formed in the experiments of Ingle et al (1973), it certainly reinforces the possibility.

If low magnesium calcite forms as a surface phase which controls the solubility of calcite in seawater, it may be incorrect to use the solubility of pure calcite in trying to understand the deposition of calcitic carbonates in the sea. It could turn out that Ingle et al (1973) and Berner (1976) are both correct in their own way. Berner's values could be correct in a thermodynamic sense (i.e., the solubility of calcite if no different surface phase forms), while the results of Ingle et al (1973) could be correct in the empirical sense (i.e., calcite will always come to their equilibrium value due to formation of a low magnesium calcite surface phase). This possibility has recently been reinforced by the experimental work of Morse (1977) and the deep sea observations of Broecker and Takahashi (1977).

At this time the best approach appears to be use of the value of $K_{c_{25°}}'$ given by Ingle et al (1973) and $K_{a_{25°}}'$ of Berner (1976). The temperature and salinity effects of Ingle (1975) appear to be the most reasonable in light of recent considerations of the possible size of the

temperature coefficient for $\gamma_{Ca}++$(Millero, personal communication). If this path is followed, the proper way to calculate K'_a as a function of temperature in seawater is to first calculate K'_c at the desired tempera- ture and salinity. The equation given by Ingle (1975) for this is:

$$K'_{c_{t_{is}}} = [-34.452 - 39.866\ S^{1/3} + 110.21\ \log(S) -$$
$$(7.5752 \times 10^{-6})(t_{is} + 273)^2] \times 10^{-7} \qquad (25)$$

The next step in the calculation of K'_a is to assume that the K'_a to K'_c ratio is approximately temperature independent. This is justified by the observation that the measured change of the ratio in distilled water, between 25° and 5°C, is only 0.0022 per degree. The total change in the ratio over this temperature range is very close to the uncertainty in the values of the constants (based on data of Berner, 1976). The value of K'_a at _in situ_ temperature is therefore:

$$K'_{a_{t_{is}}} = 1.76\ K'_{c_{t_{is}}} \qquad (26)$$

The equation developed by Ingle (1975) will be used in determining the effect of pressure on the apparent solubility products for calcite and aragonite. This equation is:

$$R(t_{is} + 273)\ \ln(K'_{is}/K'_{t_{is}}) = -\ \Delta \overline{V}P + (1/2)\Delta \overline{K}P^2 \qquad (27)$$

Where $\Delta \overline{V}$ is the change in the partial molal volume for dissolution of calcite or aragonite in seawater and $\Delta \overline{K}$ is the compressibility of the reaction, $-(\partial \Delta \overline{V} / \partial P)_{t_{is}}$.

Both $\Delta \overline{V}$ and $\Delta \overline{K}$ change with temperature and they must be calculated for the _in situ_ temperature before use of Equation (27). The appropriate

temperature corrections, based on the data of Ingle (1975), are:

$$\Delta \overline{K} = [2.529 + 0.369(25 - t_{is})] \times 10^{-3} \qquad (28)$$

$$\Delta \overline{V}_{c_{t_{is}}} = -35.5 - 0.53(25 - t_{is}) \qquad (29)$$

$$\Delta \overline{V}_{a_{t_{is}}} = -38.3 - 0.53(25 - t_{is}) \qquad (30)$$

From the above considerations all calculations necessary to determine the in situ saturation state of seawater can be carried out. A sample calculation using the methods described in this section is presented in Table 2.

TABLE 2

SAMPLE CALCULATION OF CALCIUM CARBONATE SATURATION STATE IN SEAWATER

Step 1. Data: The pH at 25°C is 7.85. The titration alkalinity at 25°C is 2.38 meq/l. The sample was collected at 3400 m water depth where the in situ temperature was 2.0°C. The salinity is 34.6°/oo.

Step 2. Pressure = (3400 m)/(10 m/atm) = 340 atm

Step 3. Using Equation (13) the pH at 2°C is calculated to be 8.09.

Step 4. An in situ pH = 7.95 is calculated by use of Equation (14).

Step 5. The molality of boric acid calculated by Equation (15) is 4.35×10^{-4}.

Step 6. The value of $K'_{B_{is}}$ calculated from equations (16), (17) and (18) is $10^{-8.73}$.

Step 7. The in situ carbonate alkalinity determined by use of Equation (19) is 2.32 meq/l.

Step 8. The in situ value of the second apparent dissociation constant of carbonic acid in seawater calculated by equations (20), (21) and (22) is $10^{-9.33}$.

Step 9. The total carbonate ion molal concentration can now be calculated via Equation (11) to be 9.04×10^{-5}.

Step 10. The total calcium ion molal concentration can be calculated from Equation (4) to be 1.015×10^{-2}.

Step 11. From steps 9 and 10 the calcium carbonate total molal product is 9.18×10^{-7}.

Step 12. The value of K'_c at t_{is} is calculated using Equation (25) to be 4.69×10^{-7} and from this value K'_a at t_{is} is calculated using Equation (26) to be 8.26×10^{-7}.

Step 13. The values of $\Delta \overline{V}$ and $\Delta \overline{K}$ are corrected to t_{is} by use of equations (28), (29) and (30). Using these values in Equation (27) yields $K'_{c_{is}} = 9.87 \times 10^{-7}$ and $K'_{a_{is}} = 18.13 \times 10^{-7}$.

Step 14. From Equation (2), $\Omega_c = 0.93$ and $\Omega_a = 0.50$.