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REPORT

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APPROACHES TO A QUANTITATIVE ANALYTICAL DESCRIPTION OF LOW FREQUENCY SOUND ABSORPTION IN SEA WATER

Daniel J. Whelan

Approved for Public Release

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APPROACHES TO A QUANTITATIVE ANALYTICAL DESCRIPTION OF LOW FREQUENCY SOUND ABSORPTION IN SEA WATER

10 Daniel J. Whelan

ABSTRACT

The absorption of sound in sea water at low frequency (1-100 kHz) and intermediate frequency (50-500 kHz) ranges can be defined by a series of relaxation phenomena, each of which can be described mathematically by a Debye relationship, of the form

$$\alpha = \Sigma\alpha_i$$

where

$$\alpha_i = \kappa_i \frac{f_{ri}\ f^2}{f^2 + f_{ri}^2}$$

where α_i is the absorption coefficient for the ith process and f_{ri} the relaxation frequency characteristic of that process.

Below 5 kHz, the principal absorption mechanism is attributed to borate and magnesium/carbonate interactions, while in the range 5 to 50 kHz the absorption arises from magnesium sulphate ion pair formation in sea water. The dependence of the various relaxation modes on oceanographic variables is outlined in quantitative terms based on results from deep ocean sound channel experiments and laboratory experiments.

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16. ABSTRACT (if this is security classified, the announcement of this report will be similarly classified):

The absorption of sound in sea water at low frequency (1-100 kHz) and intermediate frequency (50-500 kHz) ranges can be defined by a series of relaxation phenomena, each of which can be described mathematically by a Debye relationship of the form

$$\alpha = \Sigma\alpha_i$$

where $$\alpha_i = \kappa_i \frac{f_{ri} \; f^2}{f^2 + f_{ri}^2}$$

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ABSTRACT (Cont.)

Below 5 kHz, the principal absorption mechanism is attributed to borate and magnesium/carbonate interactions, while in the range 5 to 50 kHz the absorption arises from magnesium sulphate ion pair formation in sea water. The dependence of the various relaxation modes on oceanographic variables is outlined in quantitative terms based on results from deep ocean sound channel experiments and laboratory experiments.

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APPROACHES TO A QUANTITATIVE ANALYTICAL DESCRIPTION OF LOW FREQUENCY SOUND ABSORPTION IN SEA WATER

1. INTRODUCTION

In this report, it is intended to summarize the progress reached in providing an analytical description of sound absorption in sea water over the frequency range, 0.5 to 1000 kHz. As such, this paper is an extension of an earlier paper by the author describing some of the physical and chemical factors which affect the attenuation of low frequency sound in sea water, [1].

Several equations describing the absorption of sound in sea water have been presented over the last thirty years, since Liebermann (1948) found that the absorption coefficient, α, was frequency dependent in the range 100-1000 kHz and could be attributed to perturbations due to ionic relaxation and the effects of shear and volume viscosity changes in the medium [2].

Of the earlier equations put forward, the most comprehensive have been those by Schulkin and Marsh (1962) and by Thorp (1967, 1970) and it was their work [3,4] which, in effect, has set the scene for much of the rationalization of acoustical data obtained from oceanographic experiments since then.

More recently, these equations have been modified - for instance by Mellen and Browning [5,6] and by Fisher and Simmons [7] - but the starting point for most discussions still appears to be those of Thorp and of Schulkin and Marsh.

All of these approaches have their shortcomings but they represent an advance upon which future experiments can be designed and further progress made.

An important outcome of such work must be not only to ultimately define how sound absorption varies with oceanographic parameters in a particular location but also to relate this to practical situations involving acoustical propagation, range-finding and target location.

2. ACOUSTICAL RELAXATION IN SEA WATER

2.1 *Significant Parameters*

For a single relaxation process, the dependence of the sound absorption coefficient, α, on the observing frequency, f, is given by

$$\alpha = \kappa \frac{f_r f^2}{f^2 + f_r^2} \qquad (1)$$

where f_r is the relaxation frequency of the medium. κ is also a characteristic of the medium and is a measure of its chemical compressibility under the influence of the perturbing process.

When $f = f_r$,

$$\alpha = \alpha_r = \tfrac{1}{2}(\kappa . f_r) \qquad (2)$$

If v is the velocity of sound in the medium,

$$v = f_r \lambda_r \qquad (3)$$

where λ_r is the wavelength of the acoustic wave, corresponding to the relaxation frequency, f_r.

Hence, $\alpha_r \lambda_r = \tfrac{1}{2}(\kappa v)$

$$\therefore \quad \kappa = \frac{2(\alpha_r \lambda_r)}{v},$$

and

$$\alpha = \frac{2(\alpha_r \lambda_r)}{v} \cdot \frac{f_r f^2}{f^2 + f_r^2} \qquad (4)$$

It is common to discuss oceanographic acoustical data both in terms of "the excess absorption per wavelength at the relaxation frequency", $(\alpha_r \lambda_r)$, which is also written as $(\alpha\lambda)_r$, and in terms of f_r, the relaxation frequency.

In many instances, especially in the laboratory, it is not possible or not practical to measure the whole acoustical spectrum for a particular relaxational mode; this is especially true in the low-frequency spectrum below 5 kHz in sea water experiments. *In these cases, from a plot of*

$$(\frac{\alpha}{f^2} - \text{vs} - f)$$

or (α - vs - f), the parameters, $(\alpha\lambda)_r$ and f_r, can be evaluated by algebraic methods.

The term, $(\alpha\lambda)_r$, is particularly useful as it gives a sensitive method for deducing the relative intensity of different absorption processes.

The absorption coefficient, α, has the dimensions of attenuation per unit length and, of course, λ, the dimensions of length. $(\alpha\lambda)_r$, therefore, has the units of attenuation even though, somewhat misleadingly, this product is called "the excess absorption per wavelength". This author will, therefore, refer to it as an "excess absorption parameter", henceforth.

In sea water, where the sound velocity is 1.48×10^3 m $\sec^{-1}$, the 1 kHz resonant absorption has a value of $(\alpha\lambda)_r$ of *ca.* 9.7×10^{-5} dB or 1.1×10^{-5} np, as calculated by the Thorp equation, (Section 3.2).

2.2 Units

Various units describing attenuations and attenuation coefficients are used by different authors. While the conversion from one set of units to another is simple to achieve, the need to do it can be annoying.

Throughout this paper, the author will use practical metric units, wherever possible, to describe various parameters, attenuations being described in decibels (dB), attenuation coefficients as decibels per kilometre (dB km^{-1}) and frequencies in units of kHz.

The conversion of attenuation units from nepers to decibels is given in the Appendix.

3. EQUATIONS OF STATE

3.1 The Schulkin and Marsh Equation (1962)

The Schulkin and Marsh equation, (Table 1), attempted to describe acoustic absorption in sea water, over the frequency range 2-25 kHz and beyond, in terms of a relaxation effect from the formation of $MgSO_4$ ion pairs and the viscous absorption of water, both effects being corrected for changes in pressure, temperature and salinity.

Its principal defect appears to have been that, while its general form has sound theoretical justification, it has been found that, at frequencies below 10 kHz, the experimentally observed attenuation coefficients [8,9] were much greater (some 5-fold at 1 kHz) than those calculated using the Schulkin and Marsh equation. As pointed out, this arose because Schulkin and Marsh did not take into account the possibility of additional relaxation mechanisms coming into play at these lower frequencies.

However, in their original paper, Schulkin and Marsh did point out that each term in their equation should have a temperature, salinity and pressure (depth) dependence, the bracketed pressure-dependent term in their equation (Table 1) being based on previously published laboratory data obtained by Fisher (1958). This term has the form

$$(1 - 6.54 \times 10^{-4}\ p)$$

where p is the pressure in atmospheres.

Calculations based on subsequent work from Fisher's laboratory published in 1965 [10] have suggested that, at least in the frequency range 100-500 kHz, the pressure-dependent term can be approximated by a linear term

$$(1 - 8.62 \times 10^{-4}\ p)$$

for pressures down to a depth of *ca*. 2000 m [11]. This compares with an experimentally determined pressure correction

$$(1 - 12.3 \times 10^{-4}\ p)$$

which Clay and Medwin have suggested [12] on the basis of work by Bezdek [13], which was carried out at depths down to 3300 metres off the coast of California from measurements at 75 kHz. In fairness, however, it should be borne in mind that the Schulkin and Marsh equation was developed from a consideration of data primarily outside the range of the author's calculations [11] and in a frequency domain less than that used in Bezdek's experiments.

3.2 The Thorp Equation (1967)

From all accounts in the literature [1], it appears that the Thorp equation (Table 2) provides a reasonable first order description of the dependence of the absorption coefficient, α, and frequency, f. This is especially true at low frequency, 350 Hz - 3.5 kHz, and it is a tribute to Thorp and Browning's perspicacity that, in their original report under Thorp's direction [4], they recognized that the low frequency anomaly in the Schulkin

---

<u>Footnote</u>: 1 atmosphere = pressure equivalent of 10.06 metre of sea water at 4°C, 35 ppt salinity (Appendix), 14.696 psi or 1.0133 bar.

and Marsh equation could be attributed to an unidentified relaxation process with a resonant frequency less than 5 kHz. This relaxation has been subsequently associated with perturbations in the boric acid/borate equilibria in sea water [1] and is quite sensitive to changes in pH, alkalinity, temperature and boron concentration.

The deficiency of the Thorp equation appears to be that, strictly speaking, it applies only to deep ocean sound channel acoustics presumably at 4°C and 35‰ salinity [5,6] and, as presented, does not contain terms to allow for temperature, pressure, salinity and molecular variations which occur in the oceans of the world.

Fortunately, the changes prompted by these variations are often small in the region of interest and, for this reason, the Thorp equation has enjoyed considerable status.

3.3 The Fisher-Simmons Equation (1977)

Of the various approaches to the problem of sound absorption near 1 kHz in sea water, and its dependence on frequency, one of the most comprehensive has been that of Fisher and Simmons [7]. They based their approach on laboratory work per se rather than on field experiments.

These authors studied the low- and medium- frequency portion of the sound absorption spectrum in Lyman-Fleming sea water (pH 8.0, S 35‰) [14] scanning over an experimentally accessible frequency range from 6- to 350-kHz, using a harmonic oscillator fitted into an accurately engineered 200 litre spherical glass resonator as the acoustic probe.

Their results, obtained at atmospheric pressure over a small temperature range, 4°-36°C, were coupled with those of Fisher [10], Pinkerton [15] and Litovitz and Carnevale [16] to produce a sound absorption equation (Table 3) which agrees to within a factor of perhaps 20% with that from the Thorp equation.

A comparison of results predicted from the Schulkin-and-Marsh equation, the Thorp equation and the Fisher-Simmons equation for a select range of frequencies is given in Table 4.

4. LOW FREQUENCY ACOUSTICAL DATA AND OCEANOGRAPHIC VARIABLES

4.1 Oceanographic Variables

From an inspection of Table 5, it is clear that variations in acoustical parameters do occur in different oceans, a fact which is hardly surprising if indeed acoustical properties arise from physicochemical perturbations in chemical equilibria [1]. For this reason, a summary is given in Table 6 of the variations in pH, temperature and salinity which occur in the deep axis (SOFAR) sound channels of the oceans for which the acoustic field data discussed in this paper have been obtained; these data are taken from the paper by Schulkin and Marsh [17].

These locations, all in Northern Hemisphere waters, present a wide spectrum of variations.

Unfortunately, while Materials Research Laboratories have similar data concerning waters around Australia [18], the Marine Environment Group has access to very little supporting acoustical data. However, from the generalizations which can be made from Northern Hemisphere studies, some predictions can be made about the Australian situation. These will be the subject of a separate report.

4.2 Low Frequency Acoustic Properties in the Ocean

As outlined earlier, the various developments aimed at adapting the Thorp equation to a general equation of state assume that the absorption of acoustical energy can be accounted for by a summation of terms which individually describe the various relaxation phenomena contributing to the absorption process, that is,

$$\alpha = \Sigma_i \alpha_i \tag{5}$$

where

$$\alpha_i = \kappa_i \frac{f_{ri} f^2}{f_{ri}^2 + f^2} \tag{6}$$

α being the overall absorption coefficient observed at frequency, f, and α_i, f_{ri} and κ_i having their usual significance (Section 2) with respect to the particular relaxation process, i, under consideration. While κ_i, in principle, can be resolved into components incorporating S, T and p effects, it is best regarded as an operational variable at this juncture.

In order to advance further discussion, one must consider the low frequency component of the overall absorption, commonly associated with the presence of boric acid in sea water and given by

$$\alpha_b = \frac{\kappa_b f_{rb} f^2}{f_{rb}^2 + f^2} \tag{7}$$

where the subscript b identifies the low frequency (boric acid) component, f_{rb} is the relaxation frequency characteristic of this absorption and, on classical grounds

$$\kappa_b = \frac{2(\alpha\lambda)_{rb}}{v} \tag{8a}$$

or

$$(\alpha\lambda)_{rb} = \tfrac{1}{2} v \kappa_b \tag{8b}$$

In addition, it is further assumed that:

(i) the velocity of sound in various water masses at the SOFAR channel is constant; the effects of this approximation (Table 6) should be checked in any detailed analysis, and

(ii) the value of κ is independent of pressure (depth), in as far as correlation analyses involving f_{rb} and $(\alpha\lambda)_{rb}$ take care of these variations.

It is these two parameters which, in effect, determine the magnitude of α_b and several attempts have been made to correlate these parameters with variations in the oceanographic properties.

4.2.1 Mellen and Browning (1976-78)

Mellen and Browining, in a series of papers surveying the variations in low-frequency in various oceans [5,6,19], expressed the low-frequency component of the Thorp equation in the usual form,

$$\alpha_b = A_{MB} \frac{f_{rb} f^2}{f^2 + f_{rb}^2} \tag{9}$$

where α_b is in units of dB km^{-1} and the frequencies, f_{rb} and f, are in kHz.

They proposed that, at least over the pH-range 7.5-8.5 encountered, the parameter A_{MB} should be nominally pH dependent and characteristic of the water body, and the relaxation frequency, f_{rb}, should be nominally independent of pH but temperature dependent, the respective expressions being

$$A_{MB} = 0.11 \times 10^{pH-8} \text{ dB (km kHz)}^{-1} \tag{10}$$

and

$$f_{rb} = 10^{(t-4)/100} \text{ (kHz)} \tag{11}$$

where t is the temperature in °C.

At $t = 4^\circ C$ in sea water 35‰ salinity and pH 8.0, equation [9] reduces to the first term of the Thorp equation, (Section 3.2).

From equations [8] and [10], one can arrive at an expression for the excess absorption factor, $(\alpha\lambda)_r$, based on Mellen and Browning's value of A_{MB}; if one assumes a value of the speed of sound of 1.48 km sec^{-1} (Table 6 and References 20-22) and remembers the correct units for A_{MB}, then

$$(\alpha\lambda)_{rb} = \tfrac{1}{2}\,(A_{MB}\ v)$$

$$= \tfrac{1}{2}\,(0.11 \times 10^{pH-8} \times 1.48 \times 10^{-3})\ \ \mathrm{dB}$$

$$= 8.14 \times 10^{-5} \times 10^{pH-8} \qquad (12)$$

This may be compared with values, quoted later, proposed by other authors.

4.2.2 Simmons (1975)

From laboratory work and field data leading up to the Fisher-Simmons Equation (Section 2.3), Simmons suggested that the low frequency relaxation parameter, f_{rb}, is temperature dependent [22,23] and fits an equation of the form

$$f_{rb} = 0.9 \times (1.5)^{t/18} \qquad (13a)$$

which can be transformed simply to

$$f_{rb} = 0.9 \times 10^{t/100} \qquad (13b)$$

where t is in °C and f_{rb} is in kHz

Equation 13 yields values for f_{rb} very similar to those calculated from equation 11, as proposed by Mellen and Browning, over the temperature range 4° to 25°C.

The magnitude of the excess absorption factor, $(\alpha\lambda)_r$, from Simmons' data is also comparable to that from other sources. Simmons assigned a value to κ_b in equation 7 equal to 1.2×10^{-4} dB/(m.kHz), applicable to Lyman-Fleming sea water, from which

$$(\alpha\lambda)_{rb} = \tfrac{1}{2} \times 0.12 \times 1.48 \times 10^{-3}$$

$$= 8.89 \times 10^{-5}\ \ \mathrm{dB}$$

where the speed of sound is expressed in units of km. msec^{-1}

In plotting log f_{rb} - vs - t, Simmons also found that his laboratory data from Lyman-Fleming sea water (pH 8.0, S 35‰) fitted on the same curve as deep ocean data from the Atlantic Ocean, the Pacific Ocean and the Red Sea - results which imply that f_{rb} has only a very small pressure dependence, up to pressures of 120 atmospheres. No comparable relationship can be deduced about the absorption coefficient, however, from the available data.

4.2.3 *Fisher and Simmons (1977), Schulkin and Marsh (1978) and Lovett (1979)*

The original work of Mellen and Browning (Section 4.2.1) drove home the fact that that the operational terms in equations, κ_b and f_{rb} (and therefore α_b and $(\alpha\lambda)_{rb}$), vary from ocean to ocean, observations which have been supported by extensions of Simmons' work reported by Fisher and Simmons [7], and by reassessment of existing data by Schulkin and Marsh [23] and by Lovett [24].

From a statistical analysis of the acoustical oceanographic data, Schulkin and Marsh ascertained that the excess absorption factor, $(\alpha\lambda)_r$, followed pH quite closely (Tables 7, 8), the direct effects of temperature and depth (pressure) at the deep axis sound channel appearing to be incidental and occurring only in as far as they affected the pH profile. In addition, they noted that, to a reasonable approximation, the relaxation frequency depends on salinity and temperature and expressed their findings in terms of two equations,

$$(\alpha\lambda)_{rb} = 2.69 \times 10^{0.69\mathrm{pH} - 6} \times 10^{-4} \ \mathrm{dB} \qquad (14)$$

and

$$f_{rb} = 6.1 \times \left(\frac{S}{35}\right)^{\frac{1}{2}} \times 10^{f(T)} \qquad (15)$$

where $f(T) = 3 - (1051/T)$, T being expressed in $^{\circ}$K, and S is the salinity, %o.

Lovett believes the pH data from the North Pacific Ocean, which were apparently used to relate the dependence of acoustical parameters to pH changes, are in error [24,25] because the pH data were measured at laboratory temperature and pressure and had not been corrected for in-situ temperature and pressure at the deep axis sound channel. On the basis of corrected data, Lovett proposed [24] that the Schulkin and Marsh equation for the excess absorption factor is better accommodated by the relationship,

$$(\alpha\lambda)_{rb} = 1.22 \times 10^{-4} \times 10^{0.72\mathrm{pH} - 6} \ \mathrm{dB}$$

and has produced a synoptic map for the Pacific Ocean, predicting how low-frequency acoustic absorption may be expected to vary from region to region. A variant of this chart is shown in Figure 3.

In passing, it may be mentioned that two of the most important groups of experiments in the South Pacific in the area of low frequency sound absorption have been the OPERATION KIWI experiments of 1973. Figure 3 indicates that the original approach used in assessing the features of these experiments and defining microstructural scattering elements [19] were probably oversimplified as the excess absorption factor, $(\alpha\lambda)_{rb}$, over the area of the KIWI experiments, alters significantly across the Southern Pacific [19, 24-26].

4.3 Low Frequency Sound Absorption in Perspective

The deep ocean experiments of Mellen and Browning, the correlations of Schulkin and Marsh and the laboratory observations of Fisher and Simmons are particularly valuable as they systematise the present state of knowledge on how low frequency sound absorption varies from ocean to ocean and they signal a definite advance in practical oceanographic research [26]. Although each author has produced slightly different sets of equations relating the experimental parameters of equations 7 and 8, namely, κ_b, $(\alpha\lambda)_{rb}$ and f_{rb}, to oceanographic variables, these equations are based on similar experimental data and they predict comparable values for a given set of conditions within the ocean. Differences do exist but these probably lie within the limitations of the accuracy of the original data.

Some time ago, Mellen and Browning attempted to relate changes in low frequency sound absorption with changes in borate anion concentration at the molecular level [1,5,25]. This was proposed on the premise that, with increasing pH, both the excess absorption factor, $(\alpha\lambda)_r$, and the absorption coefficient, α, increase and the relative concentration of borate to boric acid also increases [27]. Despite all that has been written so far, it has not been established unequivocally that the observed attenuation is due to boric acid/borate relaxation per se; the boric acid/borate system and its interaction with the other ions which occur in sea water still need to be defined, as does the role that these interactions have on low frequency acoustical attenuation. In short, the picture is far from complete and it is far from simple.

It has been observed [7] that, for a five-fold increase in the analytical concentration of boric acid/borate in Lyman-Fleming sea water, the absorption coefficient, α, increases only some 30% at constant pH and constant temperature. One may have expected, a priori, a much greater increase in α were a simple boric acid/borate interaction responsible for the acoustical attenuation at the (unstated) observing frequencies.

Why the discrepancy? This apparent anomaly may be rationalized descriptively by assuming that only certain configurations of the boric acid/borate species present in sea water contribute to the absorption process and that these configurations are concentration dependent. Unfortunately, the practical limitations of laboratory experiments do not lend themselves to the investigation of acoustic effects at lower boron concentrations than those occurring in sea water.

It has also been found that, in Lyman-Fleming sea water, the low frequency acoustical properties are also affected by total carbonate concentration at constant pH, [28]. This reasserts the premise that a simple perturbation to the boric acid/borate equilibrium is insufficient to explain the molecular basis of low frequency absorption. While the key interaction may well be

$$B(OH)_3 + OH^- \rightleftharpoons \left[B(OH)_3(OH^-)\right] \rightleftharpoons B(OH)_4^- \qquad (16)$$

various proton-transfer steps or side-reactions may influence not only the observed relaxation frequency but also the magnitude of the observed perturbation. This could be a fruitful area for closer investigation.

5. MAGNESIUM/CARBONATE RELAXATION IN SEA WATER

Up till recently, only two relaxation mechanisms in sea water in the frequency range 1-100 kHz had been identified - the low frequency absorption due to boric acid interactions (Section 4) and the intermediate relaxation due to $MgSO_4$ ion pair formation. In an investigation of the low frequency absorption in sea water at pH values (*ca*. pH 9) higher than usually encountered in the ocean (pH 7.3-8.5), Simmons found that, at pH 9.0 and at frequencies above 5 kHz, the observed absorption coefficient was greater, by a factor of *ca*. 2, than that calculated on the basis of the previously-defined boric acid and magnesium sulphate interactions, [29].

Subsequent experiments led to a series of comparisons being made on the acoustical absorption at low frequency from solutions at pH 8.5-9.0 from

(i) sea water

(ii) $MgCl_2$ - $NaHCO_3$ (sulphate free), and

(iii) $MgCl_2$ - $NaHCO_3$ - $CaCl_2$

and it was concluded that this additional attenuation could be attributed to Mg^{2+} - $CO_3{}^{2-}$ interactions in sea water.

The observed contribution of this relaxation to the observed attenuation can be described by equation 6,

$$\alpha_i = \frac{\kappa_i f_{ri} f^2}{f^2 + f_{ri}{}^2} \quad (\mathrm{dB\ km^{-1}}) \qquad (6)$$

where, at 20°C,

$$\kappa_4 = 0.03 \times 10^{pH-8} \qquad (17)$$

and

$$f_{r4} \simeq 20 \text{ kHz} \qquad (18)$$

the subscript '4' being assigned to this relaxation.

Over the temperature range 0-25°C, it was found that at atmospheric pressure,

$$f_{r4} = 2.821 \times 10^{10} \times \exp(-6160/T) \text{ kHz} \qquad (19a)$$

which transforms to

$$f_{r4} = 2.821 \times 10^{10} \times 10^{-2675/T} \qquad (19b)$$

where T is the temperature in ^{o}K

with an apparent energy of activation of 12.2 kcal mole^{-1}.

This may be compared with values calculated from data in the same paper for the relaxation frequencies for the boric acid process, f_{rb}, and the magnesium sulphate process, f_{rm}, thus

$$f_{rb} = 1260 \times \exp(-1975/T) \qquad (20a)$$

$$= 1260 \times 10^{-858/T} \qquad (20b)$$

with $E_{act} = 3.92$ kcal.mole^{-1}

and

$$f_{rm} = 1.229 \times 10^{7} \exp(-3415/T) \qquad (21a)$$

$$= 1.229 \times 10^{7} \times 10^{-1483/T} \qquad (21b)$$

with $E_{act} = 6.79$ kcal mole^{-1},

where f_{ri} are in kHz and T in ^{o}K.

The contribution of each of these three terms to the observed sound absorption at 1 kHz, 20 kHz and 50 kHz on the basis of equation 5 is given in Table 9 .

6. MAGNESIUM SULPHATE ION PAIR RELAXATION

In the early fifties, Wilson and Leonard [30] and Kurtze, Tamm and Kaiser [31], using acoustical resonator techniques, established that magnesium sulphate was responsible for the absorption of sound in sea water over the frequency range 50-500 kHz, the sound absorption curve for 0.014 m $MgSO_4$ in pure water superimposing that obtained from natural sea water.

Eigen and Tamm proposed that this sound absorption is due to molecular relaxation arising from the formation of $MgSO_4$ ion pairs with varying degrees of hydration in solution [32], a concept which has been analysed kinetically in considerable detail[33-35] and is also consistent with results from electrical conductance,[36], from H^1 nmr proton exchange [37] and from laser Raman spectroscopy [38].

The analytical concentration of Mg^{++} (free and associated) in sea water (35‰ salinity) is 0.052 m and that of SO_4^{--} is 0.028 m [39], implying that only portion of the total Mg^{++} and total SO_4^{--} present in sea water is involved in the sound absorption process, [40]. This is hardly surprising as sea water can be regarded as a multi-electrolyte solution, in which many ionic interactions occur [41].

How do the laboratory measurements of the acoustical absorption due to $MgSO_4$ in water compare to those observed in the deep ocean sound channel?

The Thorp term [4] from (Table 2) referring to the intermediate frequency sound absorption term attributed to $MgSO_4$ is given by

$$\alpha_m = \frac{44\ f^2}{4100 + f^2}\ \text{dB km}^{-1} \qquad (22a)$$

which transforms to

$$\alpha_m = (0.6875) \times \frac{64\ f^2}{f\ + 64^2} \qquad (22b)$$

The Thorp equation applies to deep ocean sound channel transmission at 4°C and 35%o salinity. From equation 22b, one infers

$$f_{rm} = 64\ \text{kHz}$$

and can calculate $(\alpha\lambda)_{rm}$ thus

$$(\alpha\lambda)_{rm} = \tfrac{1}{2}\,\kappa_m\,v \qquad (4)$$

$$= \tfrac{1}{2} \times 0.6875 \times 1.48 \times 10^{-3}\ \text{dB}$$

$$= 5.09 \times 10^{-4}\ \text{dB}$$

κ being in units of (dB km^{-1} kHz^{-1}) and v in units of km millisec^{-1}.

This compares with laboratory experiments which predict, from equation 21, values of f_{rm} of 55 kHz (4°C), 107 kHz (20°C) and 130 kHz (25°C). f_{rm} equals 64 kHz at 7°C, on this basis.

Atkinson and Petrucci [33] in a detailed and sophisticated study of the acoustic absorption spectrum of magnesium sulphate in water determined the excess absorption factor at 25°C at various concentrations, (Table 10). From their work, it appears that both the relaxational absorption frequency, f_{rm}, and the excess absorption parameter, $(\alpha\lambda)_{rm}$, are concentration dependent.

If both these dependencies are linear with concentration - and independently obtained evidence suggests they are [31b] - then one can calculate that, at an effective concentration of 0.014 m $MgSO_4$ (the concentration of $MgSO_4$ in pure water which gives an absorption equivalent to that observed in sea water [30,31]) and at 25°C,

$$(\alpha\lambda)_{rm} = 5.5_3 \times 10^{-4} \text{ dB}$$

and $$f_{rm} = 127 \text{ kHz},$$

values which compare with those calculated [11] from data obtained from the Thorp equation and adjusted to 25°C of

$$(\alpha\lambda)_{rm} = 6.8 \times 10^{-4} \text{ dB}$$

and $$f_{rm} = 130 \text{ kHz}$$

The reasonably close agreement between these two sets is pleasantly surprising even though it is probably fortuitous. However, it does serve to reinforce the premise that the absorption over this frequency range is molecular in origin and can be attributed qualitatively and quantitatively to $MgSO_4$ ion pair relaxation.

7. SUMMARY

The absorption of sound in sea water can be defined by a series of relaxation phenomena each of which can be described mathematically by a Debye relationship of the form

$$\alpha = \Sigma_i \, \alpha_i$$

where $$\alpha_i = \kappa_i \frac{f_{ri} \, f^2}{f^2 + f_{ri}^{\,2}}$$

where α_i, κ_i, f_{ri} have been previously defined.

The principal absorption at low frequency is attributed to borate- and magnesium/carbonate interactions (Sections 4 and 5) while, at intermediate frequencies, the absorption arises from $MgSO_4$ ion-pair formation in sea water, (Table 11).

The magnitude of the various parameters describing the sound absorption is determined by oceanographic variables - temperature, pressure (depth), salinity, pH and molecular environment - and can be described in quantitative terms based on results from deep ocean sound channel experiments and from laboratory experiments, (Table 12). The available evidence supports the premise that the sound absorption phenomenon can be ascribed to chemical interactions.

The initial approach of Thorp [4] in defining absorption pragmatically in terms of a previously undefined low frequency absorption term was remarkably successful and will probably continue to be the basis of most future discussion. However, there is a weakness in this type of approach in the treatment of data obtained in the field. For this reason, the approaches of Mellen and Browning, Fisher and Simmons, Schulkin and Marsh, and Lovett in defining the subtle changes in acoustic parameters which occur with changes in environment represent a significant step forward, more particularly so when one finds the changes observed in field experiments correlate with those observed in the laboratory.

8. ACKNOWLEDGEMENT

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APPENDIX

CONVERSION FACTORS

Nepers/Decibels

Attenuations are frequently expressed in neper (np) or decibel (dB) units.

The neper is a natural logarithmic unit corresponding to an attenuation in acoustic pressure to 1/e of its initial or reference value, defined by the equation,

$$N(\text{np}) = \ln (p/p_o)$$

The decibel unit is a decimal logarithmic unit corresponding to an attenuation in acoustic intensity to 1/10 of its initial or reference value defined by the equation,

$$N(\text{dB}) = 10 \log_{10} (I/I_o)$$

Since sound intensity is proportional to the square of the sound pressure,

$$N(\text{dB}) = 20 \log_{10} (p/p_o)$$

Therefore,

$$\frac{N(\text{dB})}{N(\text{np})} = \frac{20 \log_{10} (p/p_o)}{\log_e (p/p_o)}$$

$$= \frac{20 \log_{10} (p/p_o)}{\log_{10} (p/p_o) \times \log_e 10}$$

$$= \frac{20}{2.3026}$$

$$= 8.686$$

i.e.

$$N(\text{dB}) = N(\text{np}) \times 8.686$$

Pressure

Density of sea water = 1.027 g cm^{-3} = 1027 kg m^{-3}
(4°C, 35 ppt S)

Pressure

1 atmos. = 1.013×10^{6} dyne cm^{-2}
= 1.013×10^{5} newton m^{-2}
= 1.0336 kg wt. cm^{-2}

is the pressure equivalent to 10.33 metre of pure water at 4°C or 10.06 metre of sea water (4°C, 35 ppt salinity).

Derivation:

From elementary hydrostatics,

p(pressure) = h(depth) × (density) × g(gravity)

L.H.S. = p(newton m^{-2})
= p(kg wt. cm^{-2}) × 9.80 (newton/kg wt.) × 10^{4} (cm^{2}/m^{2})
= $9.80 \times 10^{4} \times$ p (kg wt. cm^{-2})

R.H.S. = h(metre) × 1027 (kg m^{-3}) × 9.80 (m sec^{-2})

$\therefore$ h(metre) = 9.737 p (kg wt. cm^{-2})
= 9.737 × 1.0366 p (atmos.)
= 10.06 p (atmos.)

TABLE 1

SCHULKIN AND MARSH EQUATION (1962)

$$\alpha = \left(\frac{SA\, f_r\, f^2}{f_r^2 + f^2} + \frac{B\, f^2}{f_r} \right) (1 - 6.54 \times 10^{-4} P)$$

where α is the sound absorption coefficient, (dB km^{-1}),

A is a constant for the ionic relaxation processes in the sea, 20.32×10^{-3} dB/(kHz. ppt. km),

B is a constant relating to viscous changes in sea water evident at higher frequencies, 29.36×10^{-3} dB/(kHz. km),

S is the salinity (parts per thousand, ppt)

f is the frequency in kHz,

f_r is the temperature dependent relaxation frequency, given by

$$f_T = 21.9 \times 10^{6 - 1520/T} \quad \text{kHz}$$

T is the temperature, ^{o}K and

P is the pressure (km cm^{-2} or atmosphere)

When S = 35%o and T = 277.2 ^{o}K, this equation reduces to

$$\alpha = \left(\frac{50.929\, f^2}{f^2 + 5127} + 4.10 \times 10^{-4}\, f^2 \right) (1 - 6.54 \times 10^{-4} P)$$

and

$$f_T = 71.6 \quad \text{kHz}$$

TABLE 2

THORP EQUATION

$$\alpha = \frac{0.11\ f^2}{1 + f^2} + \frac{44\ f^2}{4100 + f^2} + 3.0 \times 10^{-4} f^2$$

where α is in dB km^{-1}, and

f is in kHz

The first term predominates at lower frequencies and has been attributed, in the past, to boric acid - borate relaxation, the second term refers to the magnesium sulphate relaxation reaction and the third term,to the relaxation of pure water, observed at high frequency.

The Thorp Equation refers to sound absorption in the deep ocean sound channel (SOFAR) axis, presumably at $4^{\circ}C$ and 35%o salinity sea water.

TABLE 3

FISHER - SIMMONS EQUATION

1. The observed absorption coefficient, α, can be expressed as the sum of three frequency dependent terms, $\alpha 1$, $\alpha 2$, $\alpha 3$.

i.e.
$$\alpha = \sum_{i=1}^{3} \alpha i$$

2. These variables have been derived from laboratory data obtained by Fisher and Simmons in Lyman-Fleming sea water at pH 8.0, 35%o salinity.

3. Boric Acid Term

$$\alpha 1 = A1 \frac{f_1 f^2}{f_1^2 + f^2} \quad \mathrm{dB\ km^{-1}}$$

where $A1 = 0.0894 + 2.05 \times t \times 10^{-3} - 4.53 \times 10^{-5} t^2 \quad \mathrm{dB\ km^{-1}\ kHz^{-1}}$

$$f_1 = 1.32 \times T \times \exp[(-1700/T)] \quad \mathrm{kHz}$$

4. Magnesium Sulphate Term

$$\alpha 2 = A2 \ P2 \frac{f_2 f^2}{f^2 + f_2^2} \quad \mathrm{dB\ km^{-1}}$$

where $A2 = 4.88 \times 10^{-1} + 6.53 \times 10^{-3} t \quad \mathrm{dB\ km^{-1}\ atm^{-1}}$

$f_2 = 1.55 \times 10^4 \times T \times \exp(-3052/T) \quad \mathrm{kHz}$

$P2 = 1 - 1.03 \times 10^{-3} p + 3.7 \times 10^{-7} p^2 \quad \mathrm{atm}$

TABLE 3

(Continued)

5. Water Term

$$\alpha 3 = A3 \quad P3 \quad f^2 \quad \text{dB km}^{-1}$$

where $A3 = (485 - 20.6t + 0.414t^2 - 3.02 \times 10^{-3} t^3) \times 10^{-6}$
$\text{dB km}^{-1} \, (\text{atm})^{-1} \, (\text{kHz})^{-2}$

$$P3 = 1 - 3.84 \times 10^{-4} p + 7.57 \times 10^{-8} p^2$$

6. Units

$$f \text{ kHz}, \; T \, {}^{o}K, \; t \, {}^{o}C, \text{ and } p \text{ atmos}$$

At a depth of 900 m in sea water, 35%o S and $4^{o}C$,

$$\alpha 1 = \frac{0.077 f^2}{f^2 + 0.63}$$

$$\alpha 2 = \frac{31.77 f^2}{5028 + f^2}$$

$$\alpha 3 = 3.96 \times 10^{-4} \; f^2$$

TABLE 4

A COMPARISON OF THE SOUND ABSORPTION CHARACTERISTICS PREDICTED FROM VARIOUS EQUATIONS OF STATE

(a) 4°C, 35%o Salinity

(b) Depths : 900 metre, 1300 metre

(c) Frequency : 0.5, 1, 5, 10, 50, 100, 500 kHz

Part 1

900 m depth (Pacific)

Attenuation Coefficient (dB km^{-1})

Frequency (kHz)	Schulkin-Marsh (1962)	Thorp (1967)	Fisher-Simmons (1977)
0.5	2.4×10^{-3}	2.5×10^{-2}	2.3×10^{-2}
1	9.7×10^{-3}	6.6×10^{-2}	5.4×10^{-2}
5	2.4×10^{-1}	3.8×10^{-1}	2.4×10^{-1}
10	9.6×10^{-1}	1.2×10^{0}	7.4×10^{-1}
50	1.7×10^{1}	1.7×10^{1}	1.2×10^{1}
100	3.6×10^{1}	3.4×10^{1}	2.5×10^{1}
500	1.4×10^{2}	1.2×10^{2}	1.3×10^{2}

TABLE 4

(Continued)

Part 2

1300 m depth (Atlantic)

Attenuation Coefficient (dB km^{-1})

Frequency (kHz)	Schulkin-Marsh (1962)	Thorp (1967)	Fisher-Simmons (1977)
0.5	2.3×10^{-3}	2.5×10^{-2}	2.3×10^{-2}
1	9.4×10^{-3}	6.6×10^{-2}	5.3×10^{-2}
5	2.3×10^{-1}	3.8×10^{-1}	2.3×10^{-1}
10	9.3×10^{-1}	1.2×10^{0}	7.1×10^{-1}
50	1.6×10^{1}	1.7×10^{1}	1.1×10^{1}
100	3.5×10^{1}	3.4×10^{1}	2.4×10^{1}
500	1.4×10^{2}	1.2×10^{2}	1.3×10^{2}

Note: Fisher and Simmons (Ref. 7) have carried out similar comparisons for sound absorption at the following stations:

(4°C, 0 m depth), (4°C, 5000 m depth) and (20°C, 0 m depth).

TABLE 5

VARIATIONS TO THE THORP EQUATION TERMS, OCEAN BY OCEAN

References: 19, 23-26

Ocean Area	Temp. °C	Salinity %o	pH (mean)	Frequency Absorption Terms ($dB\ km^{-1}$)	
				Low	Intermediate ($f < 10$ kHz)
Atlantic ($30-40^{o}N$)	4.65	35.7	8.09	$\frac{(1)\ (0.11)\ f^2}{1 + f^2}$	$0.011\ f^2$
Pacific ($30-40^{o}N$)	3.72	34	7.70	$\frac{(1)\ (0.055)\ f^2}{1 + f^2}$	$0.011\ f^2$
Mediterranean	14	38	8.19	$\frac{(0.15)\ (1.7)\ f^2}{(1.7)^2 + f^2}$	$0.0066\ f^2$
Red Sea	22	40	8.20	$\frac{(0.15)\ (1.5)\ f^2}{(1.5)^2 + f^2}$	$0.0077\ f^2$
Gulf of Aden	14.3	36	7.83	$\frac{(1.2)\ (0.078)\ f^2}{(1.2)^2 + f^2}$	$0.0066\ f^2$
Tasman Sea (SOFAR Channel)					
1. Subtropical			7.9	$\frac{(1)\ (0.07)\ f^2}{1 + f^2}$	$0.011\ f^2$
2. Subantarctic			7.9	$\frac{(0.09)\ (1)\ f^2}{1 + f^2}$	$0.011\ f^2$

TABLE 6

OCEANOGRAPHIC VARIABLES AT VARIOUS SOUND CHANNEL AXIS STATIONS

Ocean Area and Location	Month	Axis Depth (m)	Temp. (^oC)	Salinity (%o)	Sound Speed (km sec^{-1})	pH (average)
Atlantic ($30-40^oN$, $50-60^oW$)	Feb.	1320	4.65	35.0	1.492	8.09
Pacific ($30-40^oN$, $150-160^oW$)	Mar.	890	3.72	34.1	1.479	7.70
Baffin Bay ($70-80^oN$, $60-70^oN$)	July	50	-1.49	33.7	1.441	8.02
Mediterranean ($30-40^oN$, $10-20^oE$)	Aug.	150	14.18	38.7	1.511	8.19
Red Sea ($20-30^oN$, $30-40^oE$)	Nov.	190	22.06	40.5	1.537	8.20
Gulf of Aden ($10-20^oN$, $50-60^oE$)	May	300	14.31	35.7	1.511	7.83

TABLE 7

CORRELATION OF ACOUSTIC PROPERTIES WITH OCEAN VARIABLES; EXCESS ABSORPTION FACTOR, $(\alpha\lambda)_{rb}$, AND RELAXATION FREQUENCY, f_{rb}, WITH OCEAN FACTORS (REF. 23)

	Correlation Coefficients			
Ocean Factor	$(\alpha\lambda)_{rb}$	$\log\ (\alpha\lambda)_{rb}$	f_r	$\log\ (f_r)$
pH	0.96	0.97	0.39	0.39
Salinity	0.58	0.48	0.81	0.83
Temperature	0.26	0.21	0.63	0.68
Channel depth	0.16	0.16	0.30	0.31

TABLE 8

COMPARISON OF OBSERVED AND CALCULATED EXCESS ABSORPTION FACTORS $(\alpha\lambda)_{rb}$ AND RELAXATION FREQUENCIES (f_{rb}), FOLLOWING SCHULKIN AND MARSH [17]

	$((\alpha\lambda)_{rb} \times 10^5$, dB)		(f_{rb}, kHz)	
Ocean Area	Meas.	Calc.	Meas.	Calc.
Atlantic	9.6	10.25	1.0	1.0
Pacific	5.0	5.30	1.0	1.0
Baffin Bay	9.6	9.21	1.0(?)	0.8
Mediterranean	11.3	12.07	1.7(?)	1.3
Red Sea	12.8	12.25	1.5	1.8
Gulf of Aden	7.1	6.78	1.2	1.4

TABLE 9

RELATIVE CONTRIBUTION OF MAGNESIUM CARBONATE TERM TO THE OBSERVED SOUND ABSORPTION COEFFICIENT

Assume

(i) $\alpha = \alpha_b + \alpha_{Mg-CO_3} + \alpha_{MgSO_4}$

(ii) Thorp equation (Table 2) adequately describes the contributions of α_b and α_{MgSO_4}

(iii) Deep ocean sound channel, 4°C, 35%o salinity, pH 8.

$$\therefore \quad \alpha_b = \frac{0.11\ f^2}{1 + f^2} \quad \text{(dB/km)}$$

$$\alpha_{MgSO_4} = \frac{44\ f^2}{4100 + f^2} \quad \text{(dB/km)}$$

$$\alpha_{Mg-CO_3} = \frac{0.03\ .\ 6\ .\ f^2}{36 + f^2} \quad \text{(dB/km)}$$

$$= \frac{0.18\ f^2}{36 + f^2}$$

f(kHz)	α_b	α_{MgSO_4}	α_{Mg-CO_3}	$\alpha = \Sigma \alpha_i$
1	0.055	0.011	0.005	0.07
20	0.110	3.91	0.17	4.19
50	0.110	16.7	0.18	17.0

TABLE 9

(Continued)

Note 1: The Thorp Equation was used here for illustrative purposes only. Originally, it was formulated on the basis of experimental observations and should therefore include contributions from all relaxation phenomena. Expressed another way, it states that the total intermediate and low frequency absorption can be summarized by two terms. Practice has assigned these terms to boric acid and $MgSO_4$ relaxations.

Note 2: Ca^{++} competes with Mg^{++} in the formation of $Mg^{++} - CO_3^{--}$ complexes, reducing this component of the sound attenuation coefficient in sea water by a factor of 2, in relation to Equation 6. This reduction has not been allowed for in this calculation.

TABLE 10

RELAXATION PARAMETERS IN AQUEOUS $MgSO_4$ AT 25°C, FOLLOWING ATKINSON AND PETRUCCI (REF. 33)

Concentration (M)	0.09889	0.1493	0.1965
f_r (kHz)	133	137	140
$(\alpha\lambda)_r$ (dB)	3.91×10^{-3}	5.91×10^{-3}	7.82×10^{-3}

TABLE 11

SOUND ABSORPTION IN SEA WATER

Key Equations

(a) $$\alpha = \sum_i \alpha_i = \sum_i \kappa_i \frac{f_{ri} \; f^2}{f_{ri}^2 + f^2}$$

(b) α = Function (Oceanographic Variables)

(c) $$(\alpha\lambda)_{ri} = \tfrac{1}{2} (\kappa_i \, v)$$

Equations of State

(a)	Schulkin and Marsh (1962)	(Sect. 3.1)
(b)	Thorp	(Sect. 3.2)
(c)	Fisher and Simmons	(Sect. 3.3)
(d)	Mellen and Browing	(Sect. 4.2.1)

Chemical Relaxation

(a)	Boric Acid - Borate	(Sect. 4.2)
(b)	Magnesium - Carbonate	(Sect. 5)
(c)	Magnesium Sulphate	(Sect. 6)
(d)	Water	(Tables 1, 2, 3)

Excess Absorption Parameter, $(\alpha\lambda)_{ri}$

(a)	Definition	(Sect. 2.2)
(b)	Low Frequency Term : Borate	
(i)	Mellen and Browing	(Equation 12)
(ii)	Simmons	(Sect. 4.2.2)
(iii)	Schulkin and Marsh	(Equation 14)
(iv)	Lovett	(Equation 15)

TABLE 11

(Continued)

(c) Low Frequency Term : Mg-CO_3	(Sect. 5)
(d) Intermediate Frequency Term : $MgSO_4$	(Sect. 6)
(i) Thorp	(Sect. 6)
(ii) Atkinson and Petrucci	(Table 10)

Relaxation Frequency, (f_{ri})

(a) Low Frequency Term : Borate	
(i) Mellen and Browning	(Equation 11)
(ii) Simmons	(Equation 13)
(iii) Schulkin and Marsh	(Equation 15)
(iv) Mellen, Browning, Simmons	(Equation 20)
(b) Low Frequency Term : Mg-CO_3	(Sect. 5)
Mellen, Browning, Simmons	(Equation 19)
(c) Intermediate Frequency Term : $MgSO_4$	
(i) Fisher and Simmons	(Table 3)
(ii) Mellen, Browning, Simmons	(Equation 21)
(iii) Atkinson and Petrucci	(Table 10)
(iv) Thorp	(Equation 22)

T A B L E 12

COMPARISON OF $(\alpha\lambda)_{rb}$- AND f_{rb}- VALUES CALCULATED BY DIFFERENT AUTHORS FOR DIFFERENT OCEAN WATERS

Body of Water	Experimental		Mellen-Browning		Schulkin-Marsh		Lovett
	$(\alpha\lambda)_{rb} \times 10^5$ dB	f_r kHz	$(\alpha\lambda)_{rb} \times 10^5$ dB	f_r kHz	$(\alpha\lambda)_{rb} \times 10^5$ dB	f_r kHz	$(\alpha\lambda)_{rb} \times 10^5$ dB
Gulf of Aden	7.12	1.2	5.50	1.27	6.69	1.35	5.21
Northern Pacific	4.08	1.0	4.07	0.99	5.27	0.96	4.06
North Atlantic	9.64	1.0	10.14	1.01	10.28	1.00	8.15
Baffin Bay	9.21	1.0(?)	8.52	0.88	9.55	0.83	7.14

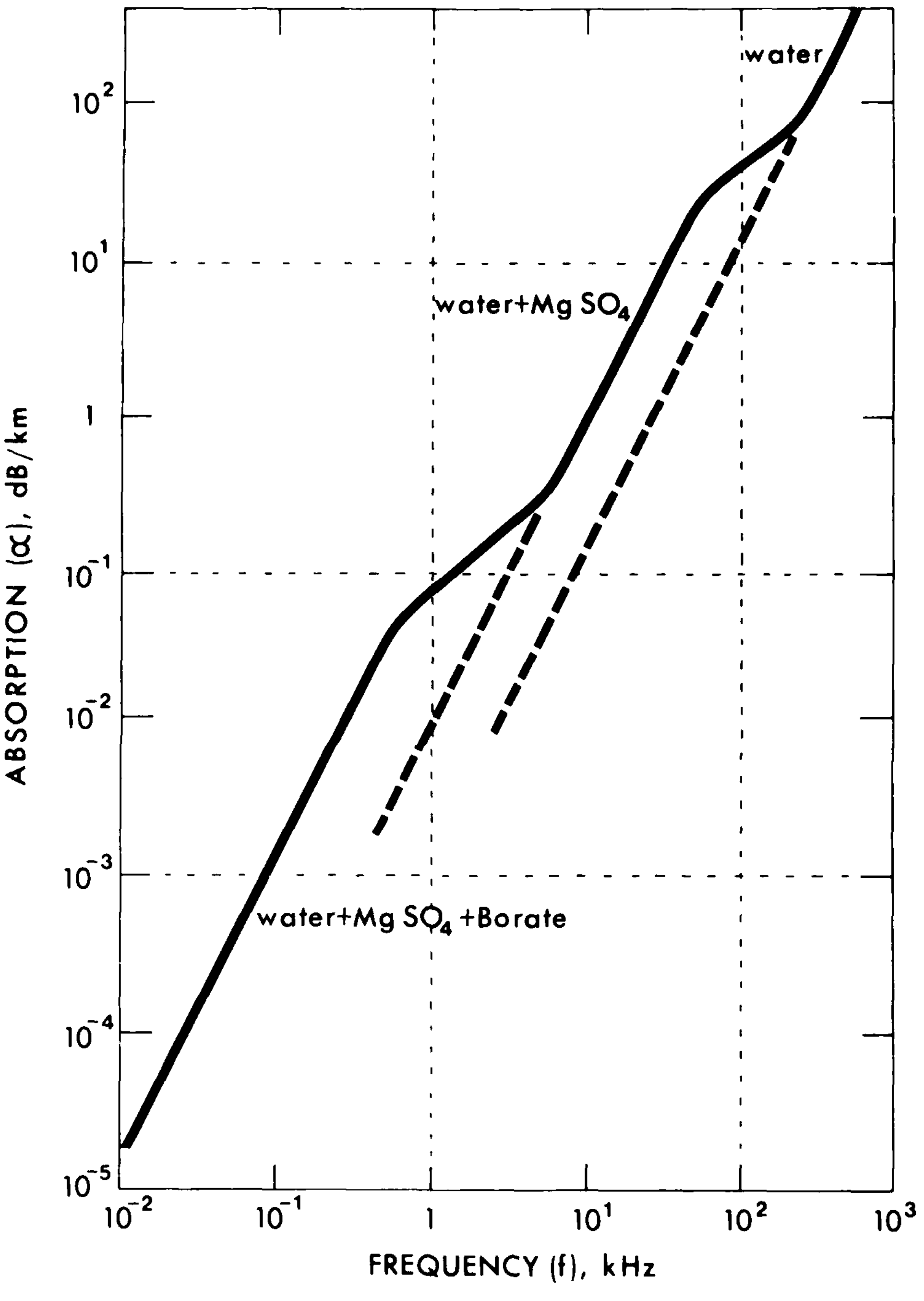

FIG. 1 - Sound Absorption in sea water of 35‰ salinity at 4°C, calculated by the Thorp Equation, (Section 4), for SOFAR Channel

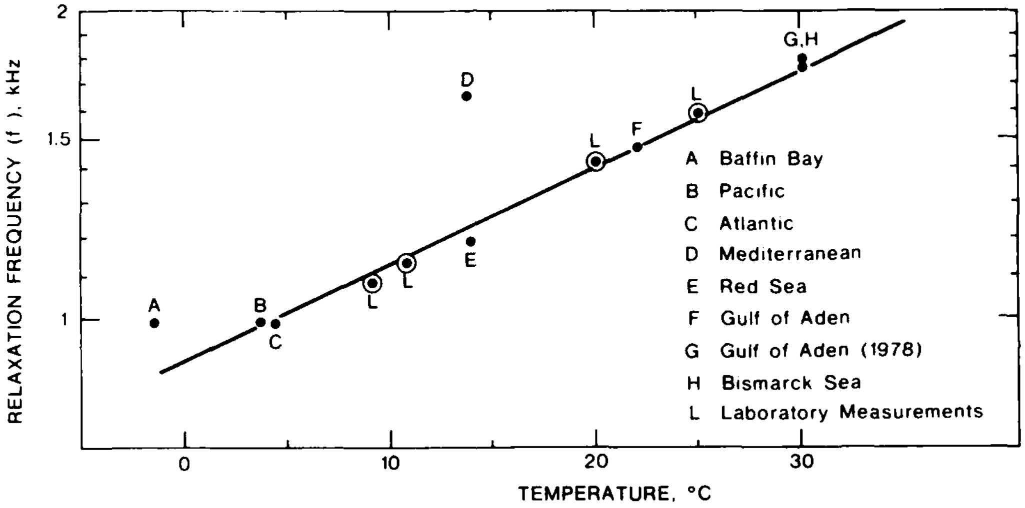

FIG. 2 - Relaxation frequency for boric acid reaction in sea water as a function of temperature. Laboratory data are circled dots (Ref. 12). Ocean data (Ref. 5, 23) are plain dots.

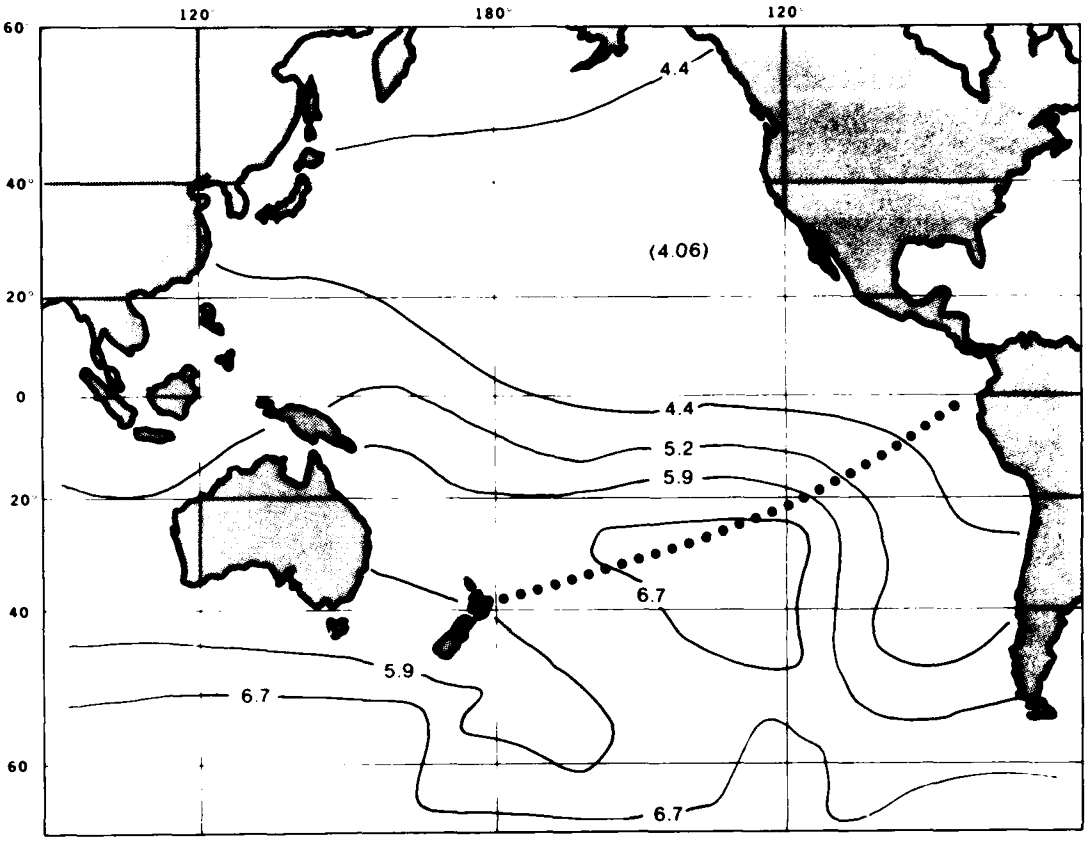

FIG. 3 - Contour plot of the value of the "Excess Absorption Parameter", $[(\alpha\lambda)_{rb} \times 10^5\ \mathrm{dB}]$, in the Pacific Ocean, after Lovett (Ref. 24). Note the dotted path indicates the path of the KIWI experiments of 1973.

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