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Kurt Buch (1881 - 1967) - The historic development of  
the physico-chemical basics of the marine CO<sub>2</sub> system

Bernd Schneider, Wolfgang Matthäus

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## KURT BUCH (1881 – 1967)

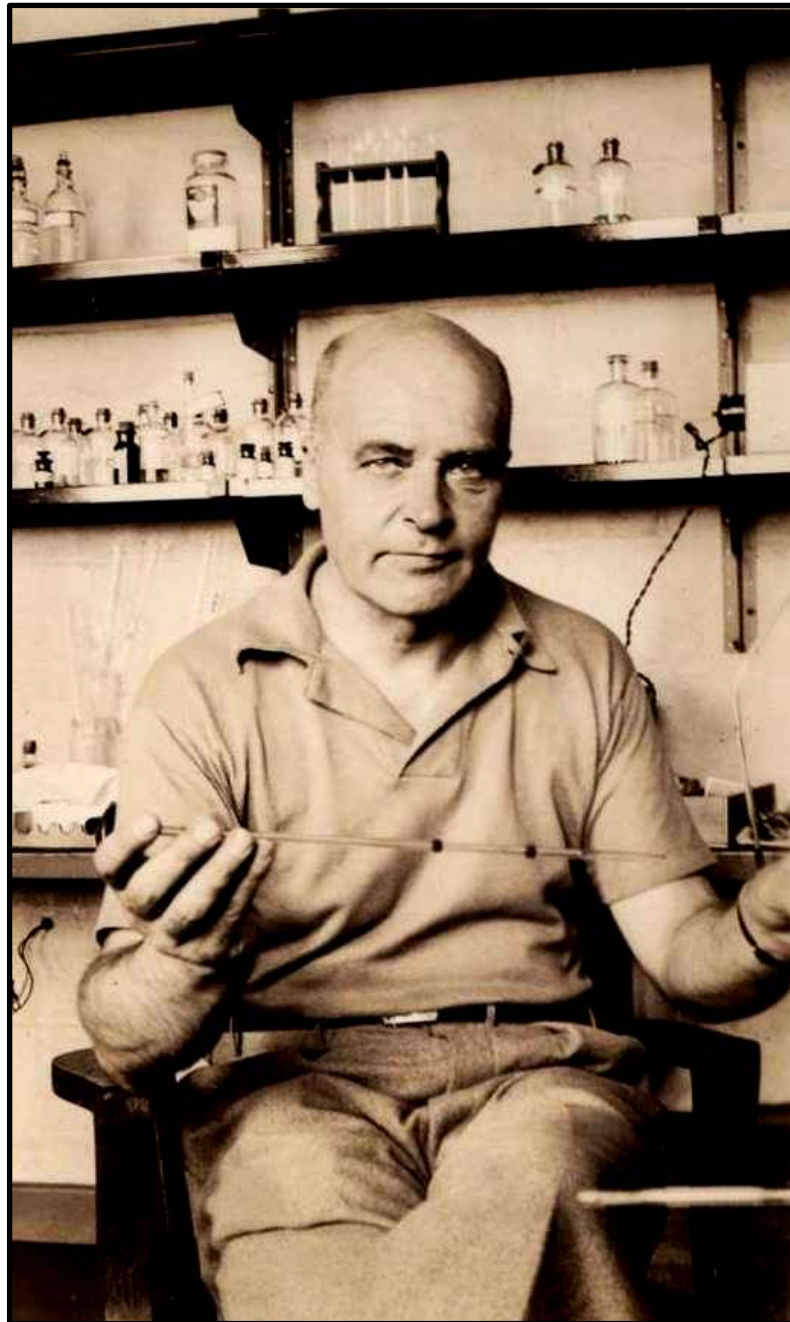
# The historic development of the physico-chemical basics of the marine CO<sub>2</sub> system

BERND SCHNEIDER & WOLFGANG MATTHÄUS

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In memoriam of the Finnish chemical oceanographer  
KURT BUCH (9 May 1881 – 4 January 1967)  
on the occasion of the 140<sup>th</sup> anniversary of his birthday

## Abstract

The review of the research on the marine CO<sub>2</sub> system spans the time between the middle of the 19<sup>th</sup> century and the first years after World War II. We start with the first attempts to determine the amount of air dissolved in seawater and finish with the final physico-chemical characterization of the marine CO<sub>2</sub> system. The development of the latter was significantly influenced by the theoretical and experimental work of the Finnish chemical oceanographer KURT BUCH (1881 – 1967) during the first half of the last century. To appreciate his outstanding achievements in Chemical Oceanography, our retrospect is therefore dedicated to him, at that time chemist at the Finnish Institute of Marine Research in Helsinki.

Our review is aligned along the characteristic variables of the marine CO<sub>2</sub> system which were identified step by step during the historic development of the marine CO<sub>2</sub> research: The acidic extraction with subsequent gasometric measurement of the CO<sub>2</sub> content was introduced after different attempts to determine CO<sub>2</sub> in seawater in the same way as for oxygen or nitrogen had failed. The obtained results which represented the total CO<sub>2</sub> concentration, constituted thus the first major variable of the CO<sub>2</sub> system. The acidification procedure was also used to determine the amount of acid that was required to release CO<sub>2</sub> completely from seawater. Its CO<sub>2</sub> equivalent was called “neutral carbonate” and corresponds to the next variable of the CO<sub>2</sub> system, the alkalinity. In a further step, CO<sub>2</sub> partial pressure measurements in combination with the determination of solubility constants facilitated the determination of the “free CO<sub>2</sub>”. Last but not least the importance of hydrogen ions was recognized and methods were developed to determine the pH. Thus all ingredients for the determination of dissociation constants for carbonic acid were available at the turn of the 19<sup>th</sup>/20<sup>th</sup> century.

On this basis KURT BUCH started lab experiments and extensive field studies around 1911 in order to characterize the state of the marine CO<sub>2</sub> system in the northern Baltic Sea and to relate it to hydrographic and biogeochemical processes. He followed the idea to measure only alkalinity and pH, and to use the dissociation constants for the calculation of total CO<sub>2</sub> and the CO<sub>2</sub> partial pressure. However, due to inadequate dissociation constants the calculations could not be verified by direct measurements. Therefore, upon the initiative of KURT BUCH, a so-called ICES “Working” Commission was set up in 1930 for the revision of the thermodynamics of the marine CO<sub>2</sub> system. In cooperation with H. WATTENBERG (Germany) and H. W. HARVEY (United Kingdom) and assisted by S. GRIPENBERG (Finland) the first and second dissociation constants were determined as functions of temperature and salinity. These constituted the basis for studies of the marine CO<sub>2</sub> system still during the first decade after World War II.

## Kurzfassung

Der Rückblick auf die Geschichte der marinen CO<sub>2</sub>-Forschung umfasst die Zeitspanne von der Mitte des 19. Jahrhunderts bis in die ersten Jahre nach dem Zweiten Weltkrieg. Dabei beginnen wir mit den ersten Versuchen, die Konzentration von Luftbestandteilen im Meerwasser zu bestimmen und spannen den Bogen zur abschließenden physiko-chemischen Charakterisierung des marinen CO<sub>2</sub>-Systems. Letztere Entwicklung wurde während der ersten Hälfte des vergangenen Jahrhunderts maßgeblich von den theoretischen und experimentellen Arbeiten des finnischen chemischen Ozeanographen KURT BUCH (1881 – 1967) geprägt. Um seine herausragenden Verdienste für die Chemische Ozeanographie zu würdigen, widmen wir ihm, der zu jener Zeit als Chemiker am Finnish Institute of Marine Research in Helsinki tätig war, diese Rückschau.

Unsere Betrachtungen bewegen sich entlang der charakteristischen Variablen des marinen CO<sub>2</sub>-Systems, so wie sie Schritt für Schritt während der historischen Entwicklung der marinen CO<sub>2</sub>-Forschung erkannt wurden. Es beginnt mit der Extraktion von CO<sub>2</sub> aus angesäuertem Meerwasser und anschließender gasometrischer Bestimmung des CO<sub>2</sub>-Gehalts, nachdem zuvor Versuche gescheitert waren, CO<sub>2</sub> im Meerwasser in gleicher Weise wie Sauerstoff und Stickstoff zu bestimmen. Die erhaltenen Resultate repräsentierten die Gesamt-CO<sub>2</sub> Konzentration und stellten somit die erste wichtige Variable des CO<sub>2</sub>-Systems dar. Die Prozedur des Ansäuerns wurde auch genutzt, um den Bedarf an Säure zu ermitteln, der erforderlich war, um CO<sub>2</sub> vollständig aus dem Meerwasser freizusetzen. Das entsprechende CO<sub>2</sub>-Äquivalent wurde als „neutral carbonate“ betrachtet und entspricht der nächsten Variablen des CO<sub>2</sub>-Systems, der Alkalinität. Weiterhin ermöglichten Messungen des CO<sub>2</sub>-Partialdrucks in Verbindung mit Löslichkeitskonstanten die Bestimmung des ungebundenen „free“ CO<sub>2</sub>. Schließlich wurde auch die zentrale Bedeutung der Wasserstoffionen erkannt und es wurden Methoden zur pH-Bestimmung entwickelt. Somit waren etwa um die Wende zum 20. Jahrhundert alle Größen verfügbar, die für die Bestimmung der Dissoziationskonstanten der Kohlensäure erforderlich sind.

Auf dieser Basis begann KURT BUCH etwa um 1911 mit Laborexperimenten und Feldstudien, um den Zustand des marinen CO<sub>2</sub>-Systems in der nördlichen Ostsee zu charakterisieren und zu hydrographischen und biogeochemischen Prozessen in Beziehung zu setzen. Er verfolgte dabei die Idee, nur die Alkalinität und den pH-Wert zu messen, um sodann mit Hilfe der Dissoziationskonstanten Gesamt-CO<sub>2</sub> und den CO<sub>2</sub>-Partialdruck zu berechnen. Allerdings konnten die Berechnungen aufgrund ungeeigneter Dissoziationskonstanten nicht durch direkte Messungen verifiziert werden. Auf Initiative von KURT BUCH wurde deshalb 1930 eine sogenannte ICES „Arbeits-Kommission“ zur experimentellen Überarbeitung der Thermodynamik des marinen CO<sub>2</sub>-Systems gebildet. In Zusammenarbeit mit H. WATTENBERG (Deutschland), H. W. HARVEY (Großbritannien) und unterstützt von S. GRIPENBERG (Finnland) wurden die erste und zweite Dissoziationskonstante der Kohlensäure als Funktion von Temperatur und Salzgehalt neu bestimmt. Diese stellten auch noch ein Jahrzehnt nach dem Zweiten Weltkrieg die Basis für die marine CO<sub>2</sub>-Forschung dar.

## 1. Introduction

Early in the history of chemical oceanography, approximately 200 years ago, the main areas of interest were the composition of sea salt and the concentrations of dissolved atmospheric gases. However, while the concentrations of oxygen and nitrogen could be reliably determined, the analysis of CO<sub>2</sub> in seawater was less successful and the results were highly contradictory. The problem lay in the assumption that the methodology for the extraction of CO<sub>2</sub> from seawater was the same as that used in determinations of oxygen and nitrogen, but this ignored the existence of different chemical forms of CO<sub>2</sub> dissolved in seawater (JACOBSEN, 1973a, 1974). Analytical and conceptual progress was achieved by the introduction of an acidification procedure allowing the extraction of total CO<sub>2</sub> from seawater in combination with the determination of the "neutral carbonic acid", also called "neutral carbonate" (TORNØE, 1880b). This procedure defined two major variables of the CO<sub>2</sub> system: the total inorganic CO<sub>2</sub> concentration and alkalinity. Nearly 25 years later, AUGUST KROGH (1904a) was the first to systematically measure the partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) in the ocean, thus adding a third variable describing the marine CO<sub>2</sub> system. Attempts to relate these variables to each other by the mass action law were unsuccessful because the ARRHENIUS' (1884, 1887) concept of the electrolytic dissociation of acids, bases, and salts was not yet known or not taken into account. As a consequence, the existence of hydrogen ions (pH) and their importance in chemical equilibria were not recognized. This limitation was subsequently overcome by the work of SØRENSEN (1909) and PALITZSCH (1911), who introduced pH as a measure of acidity and suggested a set of standard buffer solutions for its colorimetric determination. Hence, the four measurable variables of the marine CO<sub>2</sub> system, i.e., the total inorganic CO<sub>2</sub>, alkalinity, the pCO<sub>2</sub>, and the pH, became accessible and their determination allowed the formulation of chemical equilibria for the dissociation of carbonic acid according to the mass action law.

This was the situation when, in 1910, the Finnish chemist KURT BUCH began his studies, which for several decades thereafter strongly influenced marine CO<sub>2</sub> research and provided the basis for further developments following BUCH's retirement after World War II. It was BUCH who proposed the use of alkalinity and pH, both of which could be easily measured, to investigate the marine CO<sub>2</sub> system and to calculate the remaining variables, especially the pCO<sub>2</sub>, by using the dissociation constants of carbonic acid and the CO<sub>2</sub> solubility constant. BUCH's focus on the pCO<sub>2</sub> reflected his interest in the ocean's role as a sink or source for atmospheric CO<sub>2</sub> and as a buffer against the increase in atmospheric CO<sub>2</sub> caused by anthropogenic emissions. However, the pCO<sub>2</sub> could not be derived with satisfactory reliability from pH and alkalinity measurements, as evidenced by the huge discrepancies between the calculated pCO<sub>2</sub> and the value obtained by direct measurements.

BUCH soon realized that the difference was mainly a consequence of neglecting the effect of salinity on the dissociation constants. Upon his initiative, a commission was established under the umbrella of the International Council for the Exploration of the Sea (ICES) with the intention to determine the effect of temperature and salinity on the dissociation constants of carbonic acid. In a joint effort involving the laboratories of the Finnish Institute of Marine Research (FIMR) in Helsinki, BUCH, together with HERMANN WATTENBERG (Berlin), HILDEBRAND W. HARVEY (Plymouth), and STINA GRIPENBERG (Helsinki), revised experimentally the dissociation constants of carbonic acid as a function of temperature and salinity (BUCH et al., 1932). After these constants were corrected for the effect of borate on the equilibria, they were used by many researchers for several decades thereafter.



In addition to these fundamental investigations, between 1927 and 1938 BUCH initiated annual field measurements of pH, alkalinity, oxygen, and the relevant hydrographic variables within a network of about 70 stations in the northern Baltic Sea (BUCH, 1945). The data collected during that period have allowed assessments of the changes in the biogeochemistry of the Baltic Sea during the last about 100 years (SCHNEIDER et al., 2015). Furthermore, by sampling conducted on board passenger and cargo ships, BUCH investigated the CO<sub>2</sub> system in the surface water of the North Atlantic (BUCH, 1939a, 1939b). He considered this work as complementing WATTENBERG's extensive investigations (WATTENBERG, 1933a-e) during the German "Meteor" Expedition in the South Atlantic (1925-1927). BUCH's wide-ranging activities, comprising theoretical considerations, laboratory studies, and comprehensive field investigations, justify his prominent inclusion in our presentation of the history of marine CO<sub>2</sub> research. The appraisal of his achievements includes his more than 40 publications, an extremely high number for researchers during that time. However, many of those studies were not appropriately acknowledged because they were written in different languages: German, Swedish, or Finnish.

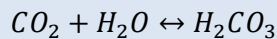
The aim of our retrospective, which concludes with the end of World War II, is to present the history of ideas concerning the chemical nature and transformations of CO<sub>2</sub> in seawater (see also LYMAN, 1972). We show how those ideas developed in parallel with increasingly sophisticated analytical capabilities and progress in theoretical physical chemistry. The result was a chemical model that emerged at the beginning of the last century and continues to provide the basis for the quantitative treatment of the chemical equilibria of CO<sub>2</sub> dissolved in seawater. Only the definitions of pH and alkalinity were later modified, for reasons of thermodynamic consistency. In the reviews published by LYMAN (1972) and DICKSON (1992), the history of field studies on the marine CO<sub>2</sub> system as performed during expeditions or other measurement activities was not addressed. This topic forms the second pillar of our review, as we present selected data from field studies and relate this to the current status of the marine CO<sub>2</sub> system. Finally, we include several Annexes which, through biographies of the involved scientists and descriptions of the equipment, research vessels and expedition routes, provide an illustrative picture of the more than 100 years of research on the marine CO<sub>2</sub> system.

After World War II, a new era began that was characterized by the growing awareness of the rapid and steady increase of atmospheric CO<sub>2</sub> levels and the consequences for the Earth's climate. For researchers in the field of chemical oceanography, this led to a shift in the focus of their work to investigations of the magnitude and mechanisms of the oceanic uptake of anthropogenic CO<sub>2</sub>. In the course of this development, large-scale measurement campaigns were organized within internationally coordinated research programmes, which are characteristic for the recent history of the marine CO<sub>2</sub> research. However, these developments are beyond the scope of this review.

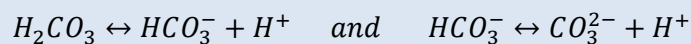
## 2. The early pioneers

In the beginning of the 19<sup>th</sup> century, it was well known that the air does not consist only of oxygen and nitrogen but also of minor constituents such as carbon dioxide. Although the CO<sub>2</sub> share in air amounted to only 0.028 % at that time, its abundance had certainly become evident since it is the gaseous product of any oxidation of organic matter. Hence, the scientific interest in seawater that started with the analysis of its salt constituents and the determination of dissolved air, was consequentially also directed to the question of how much CO<sub>2</sub> is dissolved in seawater. In publications and reports of that time CO<sub>2</sub> was always termed "carbonic acid" because of the acidic reaction upon dissolution in water. This contrasts with the present terminology where "carbonic acid" refers only to the undissociated acid H<sub>2</sub>CO<sub>3</sub> (Box I) and which will be used consistently in the following chapters. In case that the use of "carbonic acid" instead of "CO<sub>2</sub>" is unavoidable, this will be indicated.

Atmospheric gases are physically dissolved in seawater according to their solubility constants which for CO<sub>2</sub> are by a factor of 70 and 30 larger than for N<sub>2</sub> and O<sub>2</sub>, respectively. However, this is not the main difference between the behaviour of these gases in seawater. In contrast to O<sub>2</sub> and N<sub>2</sub>, carbon dioxide reacts with water and forms carbonic acid:



Note that historically the term "carbonic acid" did not refer specifically to H<sub>2</sub>CO<sub>3</sub>, but was equivalent to "CO<sub>2</sub>" in general and included sometimes any chemical form of CO<sub>2</sub> dissolved in seawater and was also used for the atmospheric CO<sub>2</sub>. The reaction of CO<sub>2</sub> with H<sub>2</sub>O is an equilibrium reaction. This means that it does not proceed completely in either direction and that each of the involved species exists in characteristic equilibrium concentrations. The sum of the concentrations of molecular CO<sub>2</sub> and H<sub>2</sub>CO<sub>3</sub> are commonly depicted by CO<sub>2</sub>\* or H<sub>2</sub>CO<sub>3</sub>\* and are also termed "free" CO<sub>2</sub>. In a further step carbonic acid dissociates and releases successively hydrogen ions, H<sup>+</sup>:



As a consequence, seawater contains not only molecular CO<sub>2</sub> but also carbonic acid (H<sub>2</sub>CO<sub>3</sub>), hydrogen carbonate (HCO<sub>3</sub><sup>-</sup>), carbonate (CO<sub>3</sub><sup>2-</sup>) and hydrogen (H<sup>+</sup>) ions. The sum of the CO<sub>2</sub> species is called "total CO<sub>2</sub>". In contrast to pure water, the hydrogen carbonate and carbonate ions in seawater are making up the greater part of the total CO<sub>2</sub>. This is due to the riverine input of bases such as hydrogen carbonate and carbonate which are formed through weathering of limestone (CaCO<sub>3</sub>) and other minerals on the continents. The total concentration of the base equivalents is called alkalinity (for a more precise definition see DICKSON, 1981). Since the alkalinity is a conservative variable, it correlates with salinity.

Box I: What makes carbon dioxide (CO<sub>2</sub>) in seawater different from oxygen (O<sub>2</sub>) and nitrogen (N<sub>2</sub>)?

The earliest determinations of dissolved carbon dioxide in seawater date back to the beginning of the 19<sup>th</sup> century (LICHTENBERG,<sup>1</sup> 1811; VOGEL 1813). Later investigations by FRÉMY<sup>2</sup> (DARONDEAU,<sup>3</sup> 1838a, 1838b), MORREN<sup>4</sup> (1844), LEWY<sup>5</sup> (1846) and PISANI<sup>6</sup> (1855) showed huge differences and were either by far too low to be interpreted as total CO<sub>2</sub> or too high to represent dissolved free

CO<sub>2</sub> (CO<sub>2</sub>\*, Box I). A detailed review of investigations concerning CO<sub>2</sub> in seawater during the first half of the 19<sup>th</sup> century was presented in several publications by OSCAR JACOBSEN (JACOBSEN, 1872, 1873a, 1873b, 1874,<sup>7</sup> 1875) who himself became later on a ground-breaking marine scientist with a high reputation within the marine scientific community (see Annex A I, p. 71).

In the early 19<sup>th</sup> century, researchers dealing with the analysis of dissolved gases in seawater were facing different problems. An appropriate sampling method had to be developed that avoids contamination of the sample with ambient air. Early samplers were constructed in a way that entrapped air bubbles were carried through the water column and dissolved rapidly in the sample especially at high hydrostatic pressure. This led to an overestimation of the dissolved oxygen concentration in deeper water layers and:

*"... even until recently, the absolute quantity of air in sea-water was believed to be much greater in the deep water than on the surface."* (JACOBSEN, 1874, p. 4).

Having realised this problem, JACOBSEN and his assistant HEINRICH BEHRENS<sup>8</sup> constructed a sampler which avoided contamination with ambient air (JACOBSEN, 1873a, 1873b, see A II, p. 80).

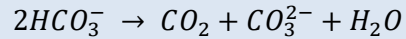
More fundamental obstacles were encountered during investigations of the CO<sub>2</sub> content of seawater. These resulted from insufficient knowledge about the chemical properties of CO<sub>2</sub> in aqueous solutions (Box I). It was assumed that CO<sub>2</sub> dissolved in seawater can be determined in the same way as oxygen and nitrogen (MATTHÄUS, 2010) by extraction through boiling under vacuum and subsequent gasometric analysis. However, through this procedure not only molecular free CO<sub>2</sub> was stripped from the sample, but also CO<sub>2</sub> that is chemically bound as hydrogen carbonate (Box II). Since the latter fraction depends on the experimental conditions such as the boiling time, inconsistent results were obtained. Therefore, early measurements performed in different oceanic regions on the British paddle wheel steamer H.M.S. "Porcupine"<sup>9</sup> (HUNTER,<sup>10</sup> 1870) revealed a huge variability. The data were reported as volume percentage CO<sub>2</sub> in air extracted from the water sample and ranged between less than 10 % and 50 %. Not being aware of chemical nature of CO<sub>2</sub> in seawater, JACOBSEN stated:

*"The carbonic acid [CO<sub>2</sub>, the authors] is only partially expelled by boiling the sea-water for hours in vacuum; the proportion of carbonic acid [CO<sub>2</sub>] found in the expelled gas justifies no conclusion as to the amount in water."* (JACOBSEN, 1872, p. 279).

In terms of absolute concentrations, the reported CO<sub>2</sub> data did not show any similarity with the concentrations of neither dissolved free CO<sub>2</sub> (CO<sub>2</sub>\*) nor total CO<sub>2</sub>. This was in contrast to the determination of oxygen in seawater which was very close to saturation or deviated in a plausible way from saturation with the atmosphere. JACOBSEN (1873a, 1874) was the first who recognized the shortcomings of the practised extraction procedure. He suggested an alternative procedure which was based on

*"... boiling it under the action of a current of air, free from carbonic acid [CO<sub>2</sub>], until a considerable quantity of chloride of sodium is precipitated, upon which the quantity carbonic acid [CO<sub>2</sub>] may be determined in the product".* (JACOBSEN, 1874, p. 11).

Different methods were used to extract dissolved CO<sub>2</sub> from seawater for the subsequent gasometric or titrimetric determination. CO<sub>2</sub> was stripped either through boiling under vacuum or by a flow of CO<sub>2</sub>-free air through the sample. In both cases the chemical equilibrium between the different CO<sub>2</sub> species as given by the dissociation of carbonic acid (Box I) is disturbed. Re-equilibration after removal of CO<sub>2</sub> occurs mainly by the following reaction:



The continuous loss of CO<sub>2</sub> during the extraction procedure is successively replaced on the expense of hydrogen carbonate ions in order to maintain chemical equilibrium. This means that the extracted amount of CO<sub>2</sub> does not represent the concentration of the originally dissolved molecular CO<sub>2</sub>, but it is a fraction of the total CO<sub>2</sub> which depends on the conditions of the extraction procedure. A secondary effect of the continuous formation CO<sub>2</sub> from hydrogen carbonate is the increase of the carbonate ion concentration. This may potentially cause the precipitation of calcium carbonate.

Box II: Why CO<sub>2</sub> extracted from a seawater sample does not represent the concentration of molecular CO<sub>2</sub> in seawater?

In 1881, in a letter to the journal "Nature" it is stated that

*"Jacobsen, by distillation, succeeded in expelling the whole amount of carbonic acid [CO<sub>2</sub>] contained in a quarter litre of sea water..."* (DUNCAN,<sup>11</sup> 1881, p. 213).

The device JACOBSEN used for the distillation and the subsequent titrimetric determination of the extracted CO<sub>2</sub> is shown in Annex A III (p. 82). It was used by him extensively during an expedition in the North Sea (see A V, p. 89)<sup>12</sup> with the German paddle wheel steamer S.M. Aviso "Pommerania"<sup>13</sup> (see A IV, p. 86) in 1872. Almost 100 samples from different depth were analysed for the concentration of extractable CO<sub>2</sub>. Comparing the results with our current knowledge indicates that the amount of CO<sub>2</sub> expelled from the samples was close to the total CO<sub>2</sub> concentration (see Box I). But JACOBSEN was convinced that the CO<sub>2</sub> obtained through distillation, existed as free CO<sub>2</sub> physically dissolved in seawater. This interpretation stimulated a controversial discussion since it was also suggested that the expelled CO<sub>2</sub> originates from the decomposition of bicarbonate. In a report about CO<sub>2</sub> in seawater HERCULES TORNØE<sup>14</sup> wrote:

*"... Jacobsen emphatically opposes Vierthaler's assumption [VIERTHALER, 1867], that the carbonic acid [CO<sub>2</sub>] boiled out of sea-water occurs in that form [bicarbonate]." (TORNØE, 1880b, p. 25).*

Regarding today's knowledge (see Box II), AUGUST VIERTHALER'S<sup>15</sup> view of the release of CO<sub>2</sub> during boiling and distillation was certainly the more realistic one.

Having in mind that some marine organisms form calcium carbonate shells, JACOBSEN furthermore concluded that yet another fraction of dissolved CO<sub>2</sub> must exist which he called "neutral carbonates" or "bound carbonic acid". According to the understanding at that time the

neutral carbonates consist of undissociated molecules, e.g.  $\text{CaCO}_3$ . He assumed that this fraction is not extractable and can be transformed into solid carbonates only by the activity of organisms which form  $\text{CaCO}_3$  shells. First experiments to quantify this fraction were made by JACOBSEN on "Pommerania" during the North Sea Expedition. By evaporation of a large volume of seawater to dryness and release of  $\text{CO}_2$  from the remaining neutral carbonates by acidic decomposition, JACOBSEN found only a surprisingly small amount of non-extractable  $\text{CO}_2$  which amounted only to about 10 % of the extractable "free"  $\text{CO}_2$ . This was the motivation for him to focus his investigations on the determination of the neutral carbonates  $\text{CO}_2$ . He analysed samples taken in different oceanic regions during the oceanographic expedition (see A V, p. 90) of the German steam corvette S.M.S. "Gazelle"<sup>16</sup> (see A IV, p. 86) in 1874-1876 (JACOBSEN, 1888). However, again low concentrations for the neutral carbonates were observed and did not support JACOBSEN's ideas about the importance of this  $\text{CO}_2$  fraction for the formation of biogenic carbonates.

Approximately at the same time (1872-1876) the famous British circumnavigation of the corvette H.M.S. "Challenger"<sup>17</sup> took place which in its chemical part laid the cornerstone for today's knowledge about the main constituents of seawater. Regarding the analysis of dissolved oxygen and nitrogen, JACOBSEN's method was adopted as state-of-the-art:

*"... when Jacobsen, in his capacity as chemist to the German North-Sea Expedition, investigated the quantity of absorbed nitrogen and oxygen in a most masterly manner, and, for the first time, arrived at really reliable results."* (DITTMAR, 1884, p. 140).

For the determination of the free  $\text{CO}_2$ , the distillation method that JACOBSEN introduced during the North Sea Expedition on "Pommerania", was used (see A III, p. 82). However, the results showed huge deviations from JACOBSEN's measurements, a fact that must be attributed to differences in the execution of the distillation procedure. John Y. BUCHANAN,<sup>18</sup> who was in charge for the chemical measurements on board "Challenger", reports:

*"... There is a remarkable difference in the results which I have obtained in the open ocean and those obtained by Dr. Jacobsen in the North Sea. I have found approximately 45 milligrams per litre as a mean amount. Jacobsen found 88.6 milligrams, or about exactly double the quantity."* (BUCHANAN, 1878, p. 463).

An important step towards the determination of well-defined quantities of the marine  $\text{CO}_2$  system was achieved during the Norwegian North Atlantic Expeditions with steamer „Vøringen“<sup>19</sup> (Fig. 1) between 1876 and 1878. Again, JACOBSEN's method to determine the concentration of free  $\text{CO}_2$  by distillation was questioned. In a report (TORNØE 1880a, 1880b) HERCULES TORNØE, the chief chemist at those expeditions, expressed his concerns:

*"... on repeating the operation with the same sample of water, the results were always found to vary, and frequently indeed considerably;"* and *"Partly for this reason,... I was led to question the trustworthiness of Jacobsen's method."* (TORNØE, 1880b, p. 27).

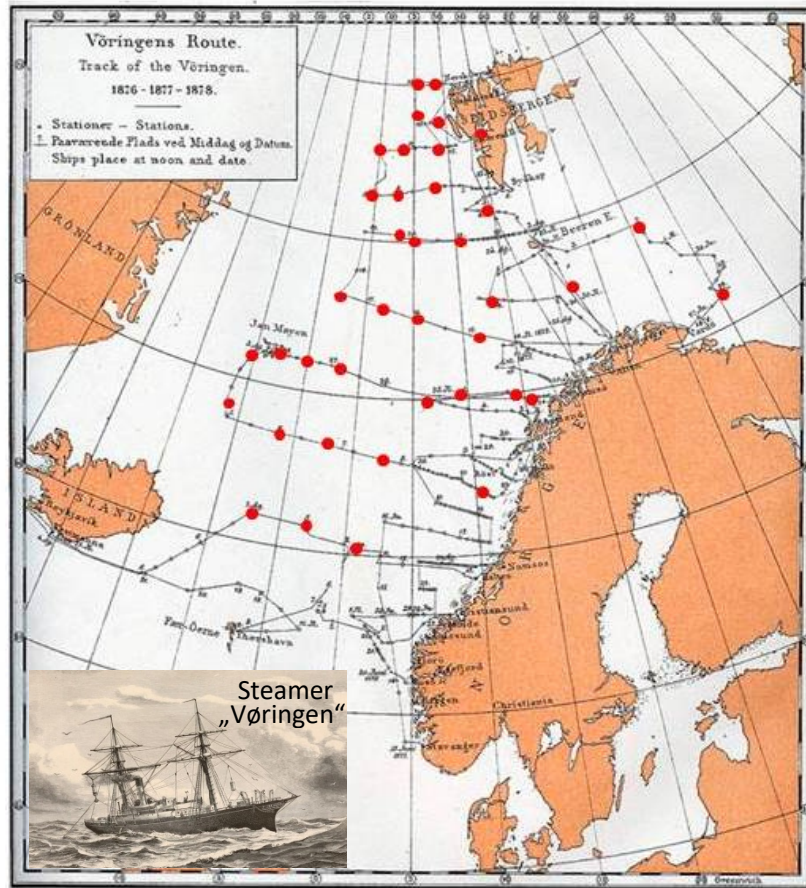


Fig. 1: Cruise of the steamship „Vøringen“ during the Norwegian North Atlantic Expeditions between 1876 and 1878 and the station network (from WILLE, 1882). Red dots mark the locations where samples for CO<sub>2</sub> analyses were taken.

Two observations were then the key to suggest a new methodological approach and to develop new ideas about the chemical nature of CO<sub>2</sub> in seawater:

*"Quite accidentally, I was one day led to investigate the effect of sea-water as a reagent on litmus and rosolic acid, and found its reaction, to my great surprise, distinctly alkaline"* (TORNØE, 1880b, p. 27).

This finding which was already described thirty years before by von BIBRA<sup>20</sup> (1851), conflicted with JACOBSEN's view that CO<sub>2</sub> in seawater mainly exists as free CO<sub>2</sub> which upon the addition of an indicator dye must have given an acidic response. Similar to AUGUST VIERTHALER's hypothesis (VIERTHALER, 1867), TORNØE thus concluded that also neutral carbonates – equivalent to "neutral bound carbonic acid" – such as carbonates or bicarbonates of calcium must exist and must have been decomposed during JACOBSEN's extraction procedure by boiling and distillation in a stream of CO<sub>2</sub>-free air. He could confirm this by lab experiments with dissolved soda (Na<sub>2</sub>CO<sub>3</sub>) which also released significant amounts of CO<sub>2</sub> by distillation. This could only be explained by the decomposition of Na<sub>2</sub>CO<sub>3</sub> which was believed to exist as undissociated neutral carbonate molecules in the solution. Regarding JACOBSEN's approach to determine free CO<sub>2</sub> in seawater, TORNØE (1880b) concludes:

*"... that all carbonic acid [CO<sub>2</sub>] determinations hitherto attempted with the object of measuring the carbonic acid [CO<sub>2</sub>] present in sea-water were faulty."* (TORNØE, 1880b, p. 28).

Therefore, TORNØE (1880b) used a quite different analytical approach<sup>21</sup> (see A III, p. 83) during the second Norwegian North Atlantic Expedition in 1877 (Fig. 1). For the determination of the neutral carbonates a defined amount of sulfuric acid was added to the seawater samples. The released CO<sub>2</sub>, originating from carbonate and bicarbonate was then expelled by a CO<sub>2</sub>-free stream of air during boiling. The amount of sulfuric acid that was not consumed by reaction with carbonate and bicarbonate, was determined by titration with a sodium hydroxide solution (back-titration). Hence, the amount of acid used for the formation of CO<sub>2</sub> could be calculated and was ascribed to the abundance of neutral carbonates. From today's view, this procedure was some kind of alkalinity titration. According to our understanding of the marine CO<sub>2</sub> system, the results of TORNØE's back titration represent approximately the sum of carbonate ion (CO<sub>3</sub><sup>2-</sup>) plus half of the hydrogen ion (HCO<sub>3</sub><sup>-</sup>) concentration when ignoring other contributions to alkalinity such as borate.

However, the term "alkalinity" was not used by TORNØE. It was introduced by WILLIAM DITTMAR<sup>22</sup> who analysed the composition of seawater collected during the "Challenger" Expedition. Having in mind the idea that sea salt consists of chemical bonds between acids and bases, he compared the concentrations of chloride and sulphate - representing the acid component in sea salt – with those of the major cations which originate from the corresponding bases (hydroxides). He found consistently a surplus of the bases and called it alkalinity and according to the requirement for a charge balance attributed it to the concentration of carbonates, hence to the "neutral carbonates". This definition of the alkalinity does not account for the complex acid-base interaction in seawater, nevertheless, it was adopted by many researchers still in the beginning of the 20<sup>th</sup> century.

TORNØE's apparatus for the determination of neutral carbonates CO<sub>2</sub> was also used for the determination of the total CO<sub>2</sub>. Therefore, the expelled CO<sub>2</sub> was absorbed by a barium hydroxide solution with a defined concentration. Titrating the excess barium hydroxide with oxalic acid then allowed the calculation of the total CO<sub>2</sub> concentration of the seawater sample. The difference between the total CO<sub>2</sub> and the concentration of neutral carbonates was ascribed to "acidic carbonate" contained in bicarbonate. Hence, bicarbonate contributes to both the neutral carbonates and the acidic carbonate. This view of the marine CO<sub>2</sub> system has some similarity with a more recent concept that distinguishes between basic and acidic CO<sub>2</sub> in seawater (WALIN<sup>23</sup> et al., 2014). Despite the analytical and conceptual progress achieved by TORNØE (1880b), a shortcoming exists in his view of the marine CO<sub>2</sub> system. This is the missing distinction between acidic carbonate as part of bicarbonate and free CO<sub>2</sub> which originates from the equilibrium with the atmospheric CO<sub>2</sub>.

No.	Temp.	Neutralbunden Kulsyre	Surtbunden Kulsyre	Alkalinity	Tot. CO <sub>2</sub>	pCO <sub>2</sub>
	°C	Mgr./Litre [mg-CO <sub>2</sub> /L]	Mgr./Litre [mg-CO <sub>2</sub> /L]	μmol/kg	μmol/kg	μatm
6	10.5	54.3	40.4	2404	2096	235
8	8.2	53.4	41.5	2363	2100	255
10	8.6	53.5	44.8	2367	2175	382
13	7.6	53.8	40.9	2380	2095	226
17	9.6	54.2	41.8	2399	2124	264
18	8.0	54.2	41.4	2398	2115	236
21	2.8	52.6	46.8	2331	2079	224
25	3.0	52.2	40.7	2308	2054	202
26	3.0	52.2	41.6	2308	2074	225
27	3.0	53.4	42.4	2361	2118	224
<b>Mean</b>				<b>2362</b>	<b>2155</b>	<b>247</b>

Excerpt (only surface water data) of a table presenting data from the second Norwegian North Atlantic Expedition in 1877 (first four columns, TORNØE, 1880b, Table II, p. 33). The concentrations for "neutralbunden Kulsyre"<sup>24</sup> (neutral carbonates) are used to calculate the alkalinity (multiplication with 2 and division through the molar weight of CO<sub>2</sub> and the seawater density). The total CO<sub>2</sub> results from the sum of "neutralbunden" and "surtbunden Kulsyre"<sup>25</sup> (acidic carbonate) divided by the molar weight of CO<sub>2</sub> and the seawater density. Assuming a salinity of 35 psu (salinity was not reported) the alkalinity/salinity ratios vary between 66.0 and 68.7 and fit perfectly into the range of oceanic values (63 - 69) which are based on current high precision analytical methods. Based on the alkalinity and total CO<sub>2</sub> data, we calculated the CO<sub>2</sub> partial pressure. The variability is considerable and probably due to both analytical errors and natural variability as well. However, the mean value stands in a reasonable relation to the pre-industrial CO<sub>2</sub> content of the atmosphere (270 ppm).

Box III: TORNØE's measurements of acidic and neutral carbonates ("acidic bound and neutral carbonic acid") in seawater of the North Atlantic in 1877 and its "modern" interpretation.

When using TORNØE's measurements of the neutral carbonates for the calculation of the alkalinity we found a surprising agreement with our current knowledge about the alkalinity in ocean surface waters (Box III). The range of alkalinity-salinity ratios matched almost perfectly current observations. Furthermore, the calculations of the surface water CO<sub>2</sub> partial pressure from total CO<sub>2</sub> and alkalinity which react very sensitive on small analytical errors, were consistent with the atmospheric CO<sub>2</sub> content in pre-industrial times (Box III). Obviously, the lack of modern analytical instruments was compensated for by analytical skill and accurateness. TORNØE's method to determine defined fractions of CO<sub>2</sub> in seawater constituted a significant progress in characterizing the chemical nature of CO<sub>2</sub> dissolved in seawater. The approach to use determinations of the total CO<sub>2</sub> and alkalinity for the characterization of the marine CO<sub>2</sub> system is even nowadays practiced.



### 3. New insights by progress in physical chemistry

The Norwegian North Atlantic Expeditions were the last ones of a series of oceanographic expeditions that were performed within less than a decade: "Pommerania" (1871/72); "Challenger" (1872/76); "Gazelle" (1874/76) and "Vøringen" (1876/78). Significant steps both analytically and conceptually towards a chemical model of the marine CO<sub>2</sub> system were achieved by these activities. The second pillar, on which further progress was based, is given by the development of new ideas and concepts in theoretical physical chemistry by the end of the 19<sup>th</sup> century.

#### 3.1 Application of the mass action law to CO<sub>2</sub> equilibria in seawater

The term "chemical equilibrium" became central importance for the interpretation of chemical reactions and this was also reflected in the characterization of the chemical nature of CO<sub>2</sub> dissolved in seawater. The Danish physiologist AUGUST KROGH (see A I, p. 72) summarized in the article "On the tension of carbonic acid in natural waters and especially in the sea" (KROGH, 1904a) the progress that had been achieved at the beginning of the 19<sup>th</sup> century. At that time the dispute about the existence of free CO<sub>2</sub> (equivalent to CO<sub>2</sub><sup>\*</sup>, see Box I) in seawater was finally settled. It was recognized that CO<sub>2</sub> in seawater is partly also physically absorbed as free CO<sub>2</sub> in a similar way as it was observed for oxygen and nitrogen. The term "carbonic acid tension" was introduced, which in our current terminology is identical with the equilibrium partial pressure of CO<sub>2</sub>, the pCO<sub>2</sub>. Since these terms are used in an inconsistent way in the historic literature, we will only use the term "CO<sub>2</sub> partial pressure" and its abbreviation "pCO<sub>2</sub>" throughout the following chapters.

KROGH (1904a) investigated the coefficient of absorption (equivalent to the solubility constant,  $k_0$ ) which describes the relationship between CO<sub>2</sub> partial pressure and the concentration of the free CO<sub>2</sub>. Using acidified seawater and thus eliminating all CO<sub>2</sub> species other than free CO<sub>2</sub>, KROGH (1904a) determined absorption coefficients at different temperatures by measurements of the total CO<sub>2</sub> and the pCO<sub>2</sub> (see below). Direct measurements of the free carbonic acid in seawater were not possible at that time and also nowadays methods for routine determinations of that fraction do not exist. A comparison of the absorption coefficients as determined by KROGH (1904a) with the currently used  $k_0$  as a function of temperature (WEISS,<sup>26</sup> 1974) shows surprisingly small differences (maximum <2.5 %) (Fig. 2). This underlines again the trustworthiness of the simple, but well-thought-out analytical methods and their careful execution more than hundred years ago.

Together with measurements (TORNØE, 1880b) of "neutral carbonates" that was now called "alkalinity", and of total CO<sub>2</sub>, measurements of the CO<sub>2</sub> partial pressure facilitated the calculation of all CO<sub>2</sub> species existing in seawater (see Box I): free CO<sub>2</sub> (CO<sub>2</sub><sup>\*</sup>), hydrogen carbonate ions (HCO<sub>3</sub><sup>-</sup>) and carbonate ions (CO<sub>3</sub><sup>2-</sup>). This was the basis for applying the mass action law to the equilibrium between these variables of the marine CO<sub>2</sub> system.

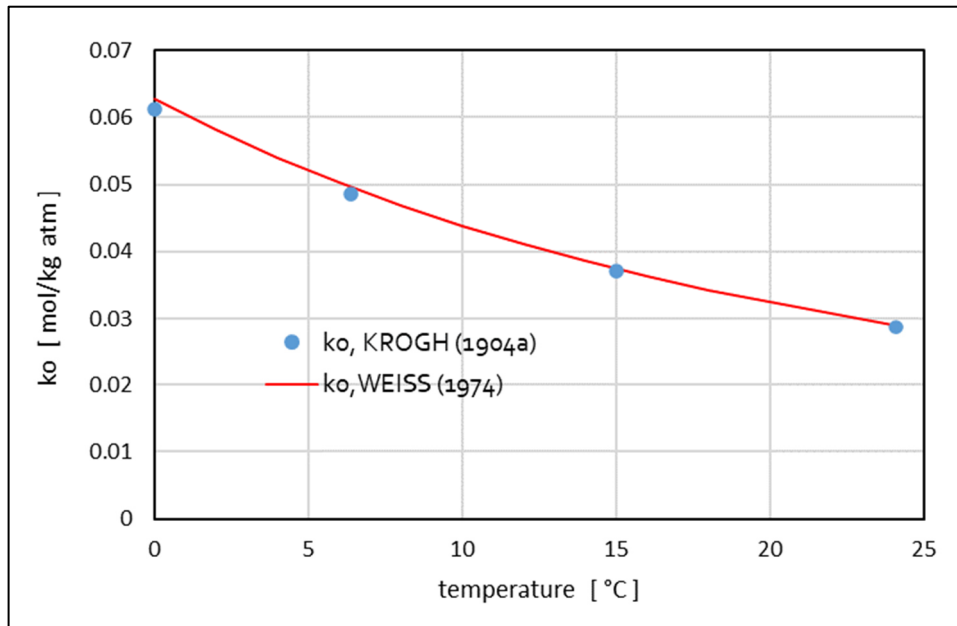


Fig. 2: Carbon dioxide solubility constant (absorption coefficient) in seawater,  $k_0$ , (blue dots) as function of temperature determined by KROGH (1904a) and compared to measurements by WEISS (1974) (red line) at a salinity of 35 psu.

The mass action law which controls the relationship between the concentrations of reacting chemical species and those of the reaction products, was discovered already in 1864 by the Norwegian chemists CATO MAXIMILIAN GULDBERG<sup>27</sup> and PETER WAAGE.<sup>28</sup> However, it took ten more years until its importance was recognized by the work and the publications of the Dutch physical chemist van't HOFF<sup>29</sup> and others. In 1886, the Swedish physicist AXEL HAMBERG<sup>30</sup> postulated an equilibrium for the reaction between free  $\text{CO}_2$  and normal carbonates (e.g.  $\text{CaCO}_3$ ) forming acidic carbonates (bicarbonates) (HAMBERG, 1886). This corresponds to the formation of  $\text{HCO}_3^-$  by the reaction of  $\text{CO}_2$  with  $\text{CO}_3^{2-}$  (buffer reaction, Box II). To test the applicability of the mass action law, KROGH (1904a) performed lab experiments with seawater that was adjusted to  $p\text{CO}_2$  between  $70 \mu\text{atm}$  and  $29\,500 \mu\text{atm}$  by spiking with pure  $\text{CO}_2$ . He calculated the concentrations of normal carbonate and bicarbonate on the basis of measurements of the total  $\text{CO}_2$  and the alkalinity. The equilibrium constants calculated for the different  $p\text{CO}_2$  differed only by a few percent from each other at low  $p\text{CO}_2$  ( $<295 \mu\text{atm}$ ), however, larger discrepancies existed at higher  $p\text{CO}_2$ . Furthermore, the results were not consistent with those obtained by HAMBERG (1885). KROGH suspected that this was due to the contribution of non-carbonate bases to the alkalinity:

*"..., and even very slight differences of this kind will prove disastrous for a computation of the tension [ $p\text{CO}_2$ ]. I am inclined to think that some error of this kind must have infected the otherwise so remarkably accurate experiments of HAMBERG. At least they do not agree, when treated theoretically, either with my own or indeed among themselves." (KROGH, 1904a, p. 366).*

Here KROGH anticipates the later discovery of the borate contribution to alkalinity. However, from today's perspective, the failure of the mass action law when applying it to the chemistry of

CO<sub>2</sub> dissolved in seawater was mainly the consequence of an inadequate conception of aqueous acid-base systems and its tight connection to the electrolytic dissociation. The role of hydrogen ions as “carrier” of the acidity was not yet discovered and salts, considered as the chemical bond between an acid and a base, such as calcium carbonate and calcium bicarbonate (CaH<sub>2</sub>C<sub>2</sub>O<sub>6</sub>), were considered to exist as undissociated molecules.

Nonetheless, investigations of CO<sub>2</sub> in seawater continued and more precise analytical methods were established. The latter refers especially to the determination of the alkalinity. The acid addition method was maintained, but the back-titration of the acid excess was executed by iodometry (PALMQVIST,<sup>31</sup> 1891). OTTO PETTERSSON<sup>32</sup> (1894) reports alkalinity data for waters from the Gullmar Fjord at the west coast of Sweden which shows a distinct dependency on salinity. Approximating this relationship by a linear regression (Fig. 3) yields an equation that shows clear

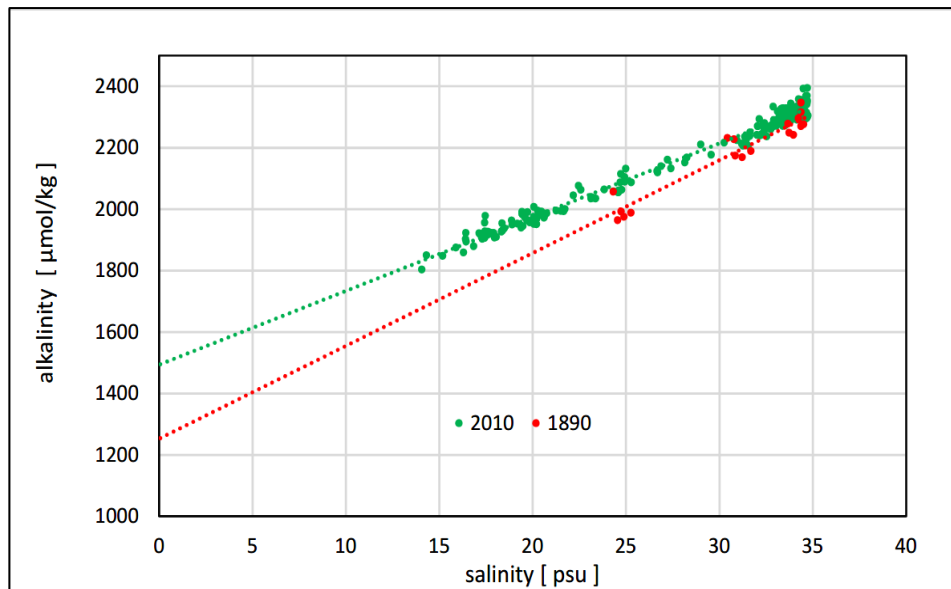


Fig. 3: Alkalinity in the Kattegat/Skagerrak area as a function of salinity in 1890 (red) and in 2010 (green) as measured by PALMQVIST (1891) and within the Swedish Environmental Monitoring Programme, respectively. The corresponding linear regression lines indicate the alkalinity in river water ( $S = 0$  psu) and in ocean water at  $S = 35$  psu.

similarities to the alkalinity-salinity relationship obtained from current Baltic Sea monitoring data (National Swedish Environmental Monitoring Programme, SMHI<sup>33</sup>). Extrapolation of the two equations to oceanic salinity ( $S = 35$  psu) yields almost identical values: 2328 μmol/kg vs. 2310 μmol/kg. This finding conforms to our expectation that the oceanic alkalinity did not change during the last centuries. The intercepts of the regression lines ( $S = 0$  psu) represent the mean alkalinity in river water flowing into the Baltic Sea. They show a difference of about 250 μmol/kg which may be questioned because of the rather limited number of historical data. Still, it is in line with the detection of an increasing alkalinity trend in the Baltic Sea during the 20<sup>th</sup> century (MÜLLER et al., 2016).

Extensive field studies were performed in 1895/96 during a research cruise of the Danish schooner H.M.S. "Ingolf"<sup>34</sup> in arctic waters around Iceland. Samples for the analysis of dissolved atmospheric gases including CO<sub>2</sub> were taken at numerous stations (Fig. 4). The data for total CO<sub>2</sub> and alkalinity are presented in a cruise report (KNUDSEN, 1899) by the well-known Danish physicist and oceanographer MARTIN KNUDSEN.<sup>35</sup> Unfortunately, he detected a contamination by the glass bottles used for storage of the samples.

*"...most unfortunately it came to my knowledge too late that sea-water, when subject to storing, had such an influence on glass, that it could dissolve perceptible quantities of the alkali of this latter, which makes the alkalinity determinations unreliable."* (KNUDSEN, 1899, p. 95).

Measurements of the total CO<sub>2</sub> were based on expelling CO<sub>2</sub> (A III, p. 83) from the acidified sample by boiling at low pressure in a flow of hydrogen that was generated within the sample by adding a piece of iron (PETTERSSON, 1894, KNUDSEN, 1899). CO<sub>2</sub> was then obtained from the analysis of the volume loss of the expelled gases after absorption of CO<sub>2</sub> by a sodium hydroxide solution. A large number of analysis (130) were performed during the "Ingolf" Expedition, however, a comparison with nowadays knowledge indicated that these were mostly erroneous.

AUGUST KROGH also contributed to the development of analytical methods and investigations of the surface water pCO<sub>2</sub>. He introduced the so-called headspace method for the determination of the pCO<sub>2</sub> which is based on the analysis of air in the headspace of the sample bottle that is at equilibrium with the seawater (KROGH, 1904a). The CO<sub>2</sub> content was then determined by a modification of the gasometric method which was state-of-the-art at that time (A III, p. 85). KROGH's field studies during an expedition to the Island of Disko west of Greenland in 1902 were initially only the by-product of biological investigations:

*"I intended to study the respiratory exchange of the organisms of the Arctic sea, ... At the same time I had in view the determination of the tensions [pCO<sub>2</sub>] in the surface-water of the sea and especially ascertaining as to whether the carbonic acid [CO<sub>2</sub>] was really in equilibrium with the atmosphere. The results ... appeared to me to be so interesting that I devoted most of my time to it during my stay in Greenland, and I have since my return pursued it further."* (KROGH, 1904a, p. 334/335).

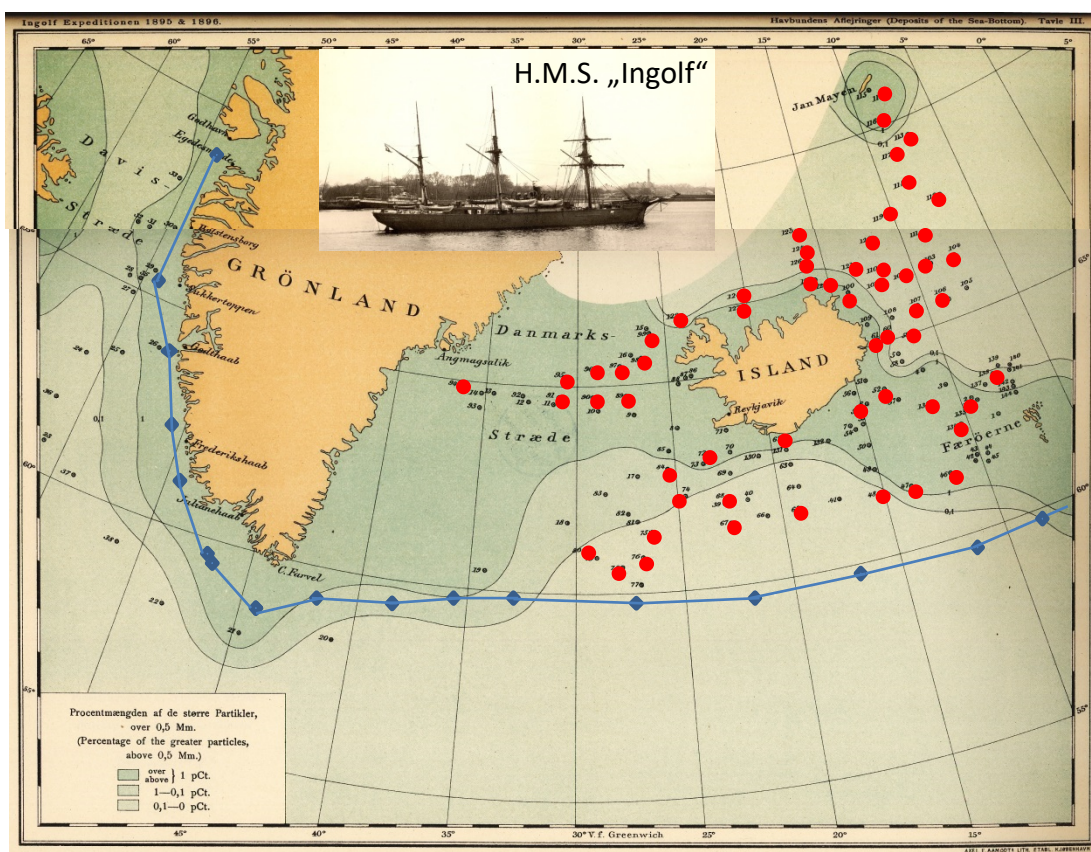


Fig. 4: Cruise of the Danish H. M. S. "Ingolf" during the expedition in 1895/1896 and the station network (from BOEGGILD, 1900, Vol. 1, Part 3, Table III, modified). Red dots mark the locations where samples for CO<sub>2</sub> analyses were taken by KNUDSEN (1899). Blue rhombs mark the positions where KROGH performed CO<sub>2</sub> measurements during a cruise in summer 1902 (KROGH, 1904a).

Samples were taken at 18 stations along the route between Scotland and the west coast of Greenland (Fig. 4, blue rhombs) and the pCO<sub>2</sub> measurements were the very first that have ever been performed in ocean waters. We emphasize this here because measurements of the pCO<sub>2</sub> play currently a central role for estimating the ocean's uptake of anthropogenic CO<sub>2</sub>. This was reason for the establishment of global pCO<sub>2</sub> measurement programmes, mainly based on automated measurement systems on so called "Voluntary Observing Ships" (VOS), during the last 30 - 40 years. A huge amount of data was collected during recent years and it is now possible to construct high resolution monthly pCO<sub>2</sub> fields for the world oceans. Comparing these with historic pCO<sub>2</sub> measurements facilitates the assessment of changes in the cycling of CO<sub>2</sub> between the oceans and the atmosphere that have possibly happened during the last hundred years.

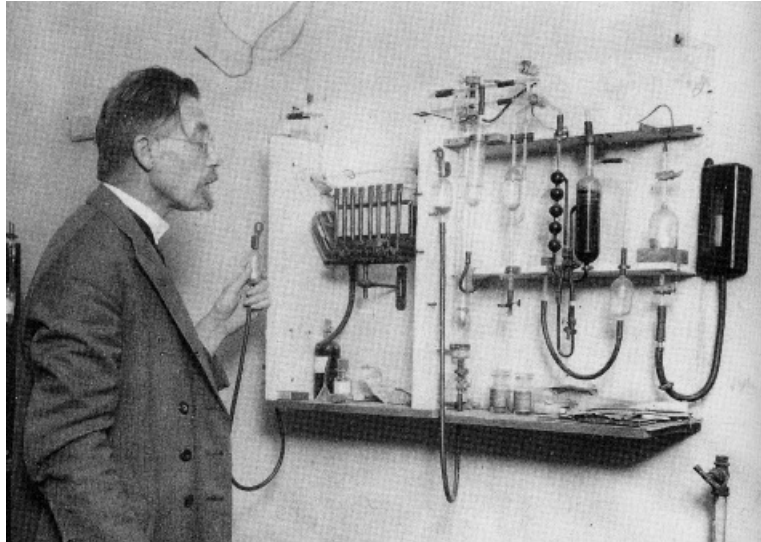


Fig. 5: AUGUST KROGH in front of his measuring device in 1928 (from SCHMIDT-NIELSEN, 1995).

KROGH was well aware of the importance of the ocean for regulating the atmospheric CO<sub>2</sub>, with reference to his pCO<sub>2</sub> measurements (Fig. 5; see also A III, p. 85), he states:

*"... a copious absorption of carbonic acid [CO<sub>2</sub>] took place in a very considerable area of the North-Atlantic and Davis Strait during the first half of September 1903." (KROGH, 1904a, p. 403)*

and:

*"...the amount of loose and free carbonic acid [CO<sub>2</sub>] in the ocean is many times greater than in the air. If differences in tension [pCO<sub>2</sub>] are found the interchange of the gas between the sea and the atmosphere will therefore have by far the greater influence on the latter." (KROGH 1904a, p. 401).*

Investigations on the CO<sub>2</sub> gas exchange between air and water were performed by the Danish physiologist CHRISTIAN BOHR,<sup>36</sup> the father of the famous physicist and later NOBEL Prize winner NIELS BOHR.<sup>37</sup> C. BOHR performed lab studies on the dynamics of the CO<sub>2</sub> gas exchange and determined evasion and invasion coefficient which characterize the velocity of the release and uptake of CO<sub>2</sub> by over- and undersaturated waters, respectively (BOHR, 1899). KROGH, at that time assistant of C. BOHR, used these coefficients to estimate the effect of anthropogenic emissions on the CO<sub>2</sub> concentrations in seawater in the coupled atmosphere-ocean system (KROGH, 1904b). He showed that the annual CO<sub>2</sub> production by combustion of coal would cause a doubling of the atmospheric CO<sub>2</sub> concentration within about 1000 years in case that the oceans don't take up any of the anthropogenic CO<sub>2</sub>. But when taking into account the oceanic sink for CO<sub>2</sub> and assuming that the uptake occurs according to BOHR's invasion coefficient, KROGH concluded from his calculations:

*"If therefore our present consumption of coal should constitute a surplus-production of carbonic acid [CO<sub>2</sub>] and destroy a state of perfect equilibrium*

*between the atmosphere and the sea, we shall in a few years reach such a tension-difference [pCO<sub>2</sub> difference] that the ocean can absorb the surplus as rapidly as it is produced, and ... the percentage of carbonic acid [CO<sub>2</sub>] in air will ... rise about 0.005 % or probably less.” (KROGH, 1904b, p. 422).*

This statement is implicitly based on some unrealistic assumption such as a perfectly mixed ocean, and on a somewhat inconsequent idea of the establishment of a steady state (*sliding equilibrium*). Therefore, KROGH’s estimate of the fate of CO<sub>2</sub> produced by combustion of coal is an unrealistic scenario. Nonetheless, it demonstrates KROGH’s ability to see the big picture behind the CO<sub>2</sub> measurements: the global cycling of CO<sub>2</sub> between the ocean and the atmosphere, an issue which after hundred years is still – and even more urgent than before – a scientific and environmental challenge.

Based on his atmospheric and oceanic pCO<sub>2</sub> measurements, KROGH finally speculated that

*“...the atmospheric percentage of carbonic acid must at present be on the increase.” (KROGH, 1904b, p. 424)*

but then conceded:

*“... that the observational evidence, upon which my far-reaching conclusion is based, must be regarded as insufficient, and I have made out the case chiefly as a plea for a thorough investigation of the problem. In our times, when the greater part of the ocean is traversed day by day, throughout the year, by innumerable steamers, it ought to be possible to undertake such an investigation, which must of course be of an international character.” (KROGH, 1904b, p. 424/425).*

In the meantime KROGH’s vision has become widespread practice within international research and data acquisition networks which are aiming at an assessment of the ocean’s role for the fate of anthropogenic CO<sub>2</sub> emissions.

### **3.2 Discovery of the electrolytic dissociation leads to a new acid-base concept**

A major step forward in the understanding of acid-base equilibria and thus of the marine CO<sub>2</sub> system was achieved when the discovery of the electric conductivity of aqueous solutions of salts was explained by the electrolytic dissociation. The theoretical concept was developed by the Swedish physicist and physical chemist SVANTE ARRHENIUS (see A I, p. 73) (ARRHENIUS, 1884, 1887) and had also consequences for the chemical interpretation of acids and bases. According to ARRHENIUS, acids and bases are substances which upon dissolution in water dissociate and thereby release hydrogen or hydroxyl (hydroxide) ions, respectively. Since the dissociation must follow the mass action law and is thus characterized by the dissociation constant, a measure for the strength of an acid was obtained. The understanding of the acid-base chemistry was further advanced by the discovery of the electric conductivity of pure water. This could only be explained by the dissociation of water molecules into hydrogen and hydroxyl ions. Hence water can act as both an acid and a base and this property is characterized by the product of the concentrations of the hydrogen and of the hydroxyl ions (ion product of water,  $k_w$ ) which is a constant that only depends on temperature and salinity.

These physico-chemical findings date back to the last decade of the 19<sup>th</sup> century, but it took several years until they were adopted by chemical oceanographers. In a comprehensive and in-depth article about CO<sub>2</sub> in seawater published in 1904 KROGH still considered the marine CO<sub>2</sub> system to be adequately represented by three variables: free CO<sub>2</sub>, bicarbonate and normal carbonate. The first publication that accounts for the electrolytic dissociation of acids, bases and salts was published by the Scottish chemist CHARLES FOX<sup>38</sup> (FOX, 1909) who complains that:

*"It is regrettable that the Ionic Theory has not yet been adopted as the basis for classifying Oceanographic results ... It is also unwarrantable and opposed to the facts, to describe salts ... as existing [molecules] dissolved in sea-water. The Ionic Theory makes it clear that ... the positive ions Na\*, K\*, Ca\*, Mg\*\* etc. must be in simultaneous equilibrium with each and all the negative ions Cl', (Br', I'), SO<sub>4</sub>'', HCO<sub>3</sub>' etc.;"* (FOX, 1909, p. 6).

Furthermore, FOX suggested expressing the alkalinity as hydroxide ion equivalents instead of considering it as the amount of CO<sub>2</sub> necessary to form carbonates from the base excess. This definition comes close to the exact definition that evolved in the coming decades (see Box I). But despite this progress FOX developed ideas about the chemical equilibria which led to the fallacious conclusion that seawater must be slightly acidic:

*"The Ocean therefore as a whole is in equilibrium with an excess of CO<sub>2</sub> in the Atmosphere of about 3 ‰ [parts per 10,000]; and there is thus a corresponding small residual H\*-concentration (acidity) due to the small amount of CO<sub>2</sub> H<sub>2</sub>O in the solution, ..."* (FOX, 1909, p. 13).

FOX performed comprehensive lab measurements<sup>39</sup> to establish quantitative relationships between the CO<sub>2</sub> partial pressure, total CO<sub>2</sub> and alkalinity. For practical use, the results and interpolated values were presented in tables (FOX, 1909). Furthermore, an attempt was made to derive equilibrium constants according to the mass action law. However, the calculations were based on an incorrect usage of the mass action law and still did not account in a proper way for role of hydrogen ions. Therefore, the obtained "constants" had no physico-chemical meaning.

It was the Danish chemist SØREN SØRENSEN<sup>40</sup> who during his biochemical studies discovered the importance of hydrogen ions (H<sup>+</sup>) for many chemical reactions including acid-base equilibria. He introduced the pH as a measure for the hydrogen ion concentration (SØRENSEN, 1909). In the same publication he reviewed different methods to determine the pH. Early and somewhat exotic attempts were based on the catalytic effect of hydrogen ions on the rate of certain chemical reaction which did not consume or produce hydrogen ions. An example is the splitting (inversion) of cane sugar into glucose and fructose which depends on the concentration of hydrogen ions. Since the reaction is accompanied by the change of optical properties (rotation of polarized light) which can easily be recorded by a polarimeter, a method for the determination of the hydrogen ion concentration was obtained. However, the practicability of this method and similar others is limited to a narrow pH range and may be affected by the chemical composition of the test solution. SØRENSEN therefore suggested to use colorimetric methods which are based on the colour change of certain organic compounds upon changes in pH. To assign a certain colour nuance of a particular indicator to a pH value, standard (buffer) solutions with a defined pH were used. This principle for the determination of a pH value is still practiced by the use of pH paper. But it is also the basis for spectrophotometric pH measurements which were further



developed during the last decades and represent currently the state-of-the-art in chemical oceanography.

Due to the progress in electrochemistry at the beginning of the 20<sup>th</sup> century, electrometric (nowadays: "potentiometric") pH measurements were introduced. The electromotive force exerted by hydrogen ions at a platinum/hydrogen electrode – the precursor of the later HARNED<sup>41</sup> Cell<sup>42</sup> – provided a measure for the hydrogen ion concentration, hence, for the pH. Compared to the colorimetry, the electrometric method allowed for an increased precision, however, it was rather laborious and not well suited for routine analysis. But since it constituted an absolute reference method, it could be used for assigning pH values to standard solutions. These are essential for calibration of other pH measurement methods such as the colorimetry. SØRENSEN (1909) determined the pH of standard solutions which were prepared from different buffer substances, in a way that the range between pH = 1 and pH = 13 was sub-divided into increments of about 0.3 – 0.4 pH units. Furthermore, SØRENSEN determined the ion product of water,  $k_w$  (SØRENSEN, 1909), by electrometric measurements. A value of  $k_w = 0.72 \times 10^{-14} \text{ mol}^2/\text{L}^2$  (at 18 °C) was obtained which is close to the value currently used ( $0.57 \times 10^{-14} \text{ mol}^2/\text{L}^2$ ). This number is more than a theoretical constant; it defines the pH of a neutral solution, where the concentration of hydrogen ions equals that of hydroxyl ions and sets the threshold between acidic (pH < 7) and basic (pH > 7) solutions.

Whereas SØRENSEN developed a general concept for pH measurements, his assistant SVEN PALITZSCH<sup>43</sup> focused on pH measurements of seawater. He described precisely the composition and preparation of standard solutions and the use of suitable indicators for colorimetric pH measurements in the range between pH = 7.95 and pH = 8.35 (PALITZSCH, 1911). This range of pH values were encountered during an expedition with the Danish research vessel "Thor"<sup>44</sup> in the North Atlantic and the Mediterranean Sea. The uncertainty of the measurements was estimated to be +/-0.04 pH units. PALITZSCH (1911) introduced also the "salt factor" to correct the pH measurements for effect of dissolved salts on the colour response of the indicator.

#### 4. KURT BUCH – the father of the modern view of the marine CO<sub>2</sub> system

With the recognition of the importance of hydrogen ions for many chemical transformations, the definition of the pH scale and the development of analytical methods for the determination of the pH, the pre-requisites for a theoretically well-founded understanding of acid-base systems were given. Furthermore, together with the methods for the determination of total CO<sub>2</sub>, alkalinity and the CO<sub>2</sub> partial pressure, the basics for the exact thermodynamic description of the marine CO<sub>2</sub> system were thus available. The four variables together with the dissociation constants for carbonic acid are still the basis for the experimental and computational characterization of the state of marine CO<sub>2</sub> system. However, knowledge about the chemical thermodynamics in strong ionic media such as seawater and about the complexity of the marine acid-base system was still fragmentary and prevented a precise theoretical treatment of the marine CO<sub>2</sub> system.

ERNST RUPPIN<sup>45</sup> (1910) was one of the first who accounted for the dissociation of acids and for the role of hydrogen ions when applying the mass action law to the marine CO<sub>2</sub> system. In a comprehensive treatise about the meaning of alkalinity, he showed that seawater at equilibrium

with calcium carbonate must be slightly alkaline at the given atmospheric concentration of CO<sub>2</sub>. His calculations, which included the equilibria of the CO<sub>2</sub> system and the ion product of water, yielded a hydroxyl ion concentration (pH) that was consistent with values derived from electrometric measurements of the hydrogen ion concentration. RUPPIN (1910) also contributed to the collection of field data for alkalinity and total CO<sub>2</sub>. He performed two cruises with the first German research vessel "Poseidon" in the central and western Baltic Sea and in the North Sea. The alkalinity for the Baltic Sea showed a distinct relationship to salinity (KRÜMMEL,<sup>46</sup> 1907) and similar to the findings by PALMQUIST (1891) (Fig. 3), the mean alkalinity for the central Baltic Sea was distinctly below today's level (about 200 µmol/kg). Likewise, the extrapolation of the AT-S relationship to S = 35 psu (Fig. 3) yielded again almost exactly the currently observed alkalinity of North Atlantic surface water.

#### 4.1 Early studies

These were the starting conditions for the Finnish chemist KURT BUCH (see A I, p. 74), at that time chemical assistant at the hydrographic-biological working group of the Finnish Society of Science, when he started investigations on the marine CO<sub>2</sub> system in 1910 after his studies of basic physical chemistry. The first systematic investigation which included the determination of pH, total CO<sub>2</sub> and alkalinity were performed in a fjord at the southwest coast of Finland (Pojowiek).<sup>47</sup> Four measurement campaigns were performed in 1911/1912 in order to investigate the horizontal and vertical distribution of various hydrochemical variables in a salinity gradient caused by mixing of river water with water from the Gulf of Finland (BUCH, 1914). The results for the vertical distribution of the measured variables were presented by a series of isoline plots. An example is given in Fig. 6 which shows the typical oxygen depletion (60 % saturation) and concurrent pH decrease (<7.0) in the deeper water layers as consequence of intense organic matter decomposition.

BUCH (1914) also suggested to use the pH and total CO<sub>2</sub> data to calculate the CO<sub>2</sub> partial pressure on the basis of the first dissociation constant for carbonic acid (see Box I). However, he did not report details of the calculations and provided only some preliminary results. He referred to pending investigations and we suspect that he encountered difficulties in obtaining realistic pCO<sub>2</sub> values by the calculations. From today's perspective the reasons for the shortcoming are obvious and set the direction for the future research on CO<sub>2</sub> in seawater: (1) The dissociation constant for carbonic acid had only been determined for solutions in pure water at a certain temperature (e.g., WALKER & CORMACK, 1900) and not in electrolyte solutions such as seawater at different temperatures and (2) The second dissociation step of carbonic acid was considered to be negligible and ignored.

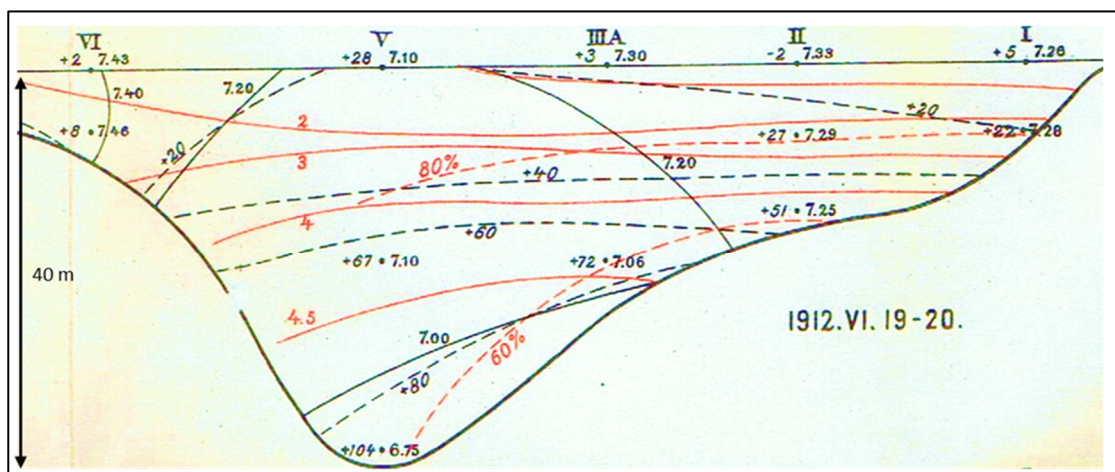


Fig. 6: The inner part of the Pojowiek (Gulf of Finland) with isolines for O<sub>2</sub> concentration (mL/L, solid red), O<sub>2</sub> saturation (% , dashed red), pH (solid black) and lowering of pH (dashed black). The latter was calculated with reference to the surface water pH and corrected for the higher salinity (alkalinity) in the deeper water layers (from BUCH, 1914).

Even when using current dissociation constants for the calculation of the pCO<sub>2</sub> from each of the three pairs of variables (total CO<sub>2</sub>-alkalinity; total CO<sub>2</sub>-pH; alkalinity-pH) determined by BUCH (1914), values for the pCO<sub>2</sub> are obtained which are beyond any reasonable range. This indicates the necessity for improved quality of the analytical method when using measurements for the calculation of any other variables.

The latter aspect was also highlighted by JOHNSTON<sup>48</sup> (1916) who reviewed and assessed the methods used for the determination of the various CO<sub>2</sub> species in solutions containing carbonates. Although he did not refer specifically to seawater, his conclusions apply also to the analysis of the marine CO<sub>2</sub> system:

*"In principle the only absolutely reliable methods are those for the total base combined with the carbonic acid [CO<sub>2</sub>] and for the total CO<sub>2</sub> present in solution; in practice they yield accurate results provided that due attention is paid to the conditions discussed... . these two determinations suffice in general to characterize the solution with respect to either its content of free CO<sub>2</sub>, the proportion of carbonate to bicarbonate, or the degree of alkalinity or acidity [pH]."* (JOHNSTON, 1916, p. 975).

In the same paper, JOHNSTON demonstrates how to calculate the variables of the CO<sub>2</sub> system such as the pCO<sub>2</sub> and pH from measurements of total CO<sub>2</sub> and alkalinity using the dissociation constants, k<sub>1</sub> and k<sub>2</sub>, suggested by JAMES WALKER<sup>49</sup> and WILLIAM CORMACK<sup>50</sup> (1900).

These ideas and concepts were picked up in the dissertation of KURT BUCH (1917a) (see Fig. 7) which was motivated by the hope

*"... durch Anwendung auf das Meerwasser der für die elektrolytische Dissoziation verdünnter Lösungen geltenden Gesetze, eine Berechnung der Kohlensäure-tension [pCO<sub>2</sub>] ... ausführen zu können."*

[„... that by adopting the laws of electrolytic dissociation in diluted solutions to seawater ... calculations of the carbonic acid tension [ $p\text{CO}_2$ ] will be possible.“]<sup>51</sup> (BUCH, 1917a, preface, p. 3).

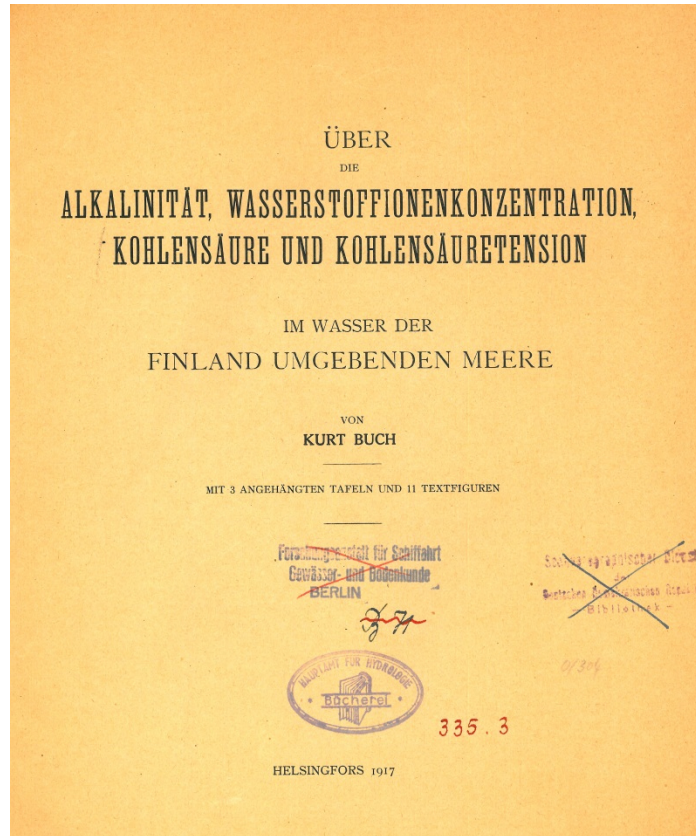


Fig. 7: Front page of the dissertation of KURT BUCH (from BUCH, 1917a).

To achieve this, BUCH performed systematic laboratory investigations which included measurements of total  $\text{CO}_2$ , alkalinity, pH and the  $p\text{CO}_2$ . These studies were complemented by comprehensive field measurements of these four variables of the  $\text{CO}_2$  system in the Gulfs of Finland and Bothnia. In this context, the various analytical methods were examined and partly refined in order to increase the accuracy, especially for the determination of the  $p\text{CO}_2$ . Measurements of total  $\text{CO}_2$  and of alkalinity were based on established techniques (PETTERSSON, 1894; KNUDSEN, 1899). Special emphasis was put on pH measurements and on the temperature dependency of the pH of seawater and of standard solutions. In addition to the colorimetric pH determination that was carefully elaborated by SØRENSEN (1909), BUCH used a spectrophotometric method for seawater pH measurements. Since photo detectors did not exist at that time, the measurement of light intensities was based on the properties of polarized light generated by a so-called NICOL<sup>52</sup> Prism (MARTENS<sup>53</sup> & GRÜNBAUM,<sup>54</sup> 1903). It is noteworthy that this spectrophotometric pH measurements were soon replaced by different potentiometric techniques, but became state-of-the-art again in the nineties of the last century – of course with high-tech spectrophotometers.

BUCH performed different series of experiments with seawater at salinities and alkalinities typical for the northern Baltic Sea. Total CO<sub>2</sub> concentration, alkalinity, the pCO<sub>2</sub> and pH were determined at selected alkalinities and presented as isoline plots. An example is given in Fig. 8 which shows the isolines for total CO<sub>2</sub> and hydrogen ion concentrations in a two-dimensional pCO<sub>2</sub>-alkalinity field. Due to the lack of precise mathematical descriptions and in the absence of computers to handle these, such graphics were a common tool in those times to estimate quantitatively the relationships between the properties of complex chemical/physical systems.

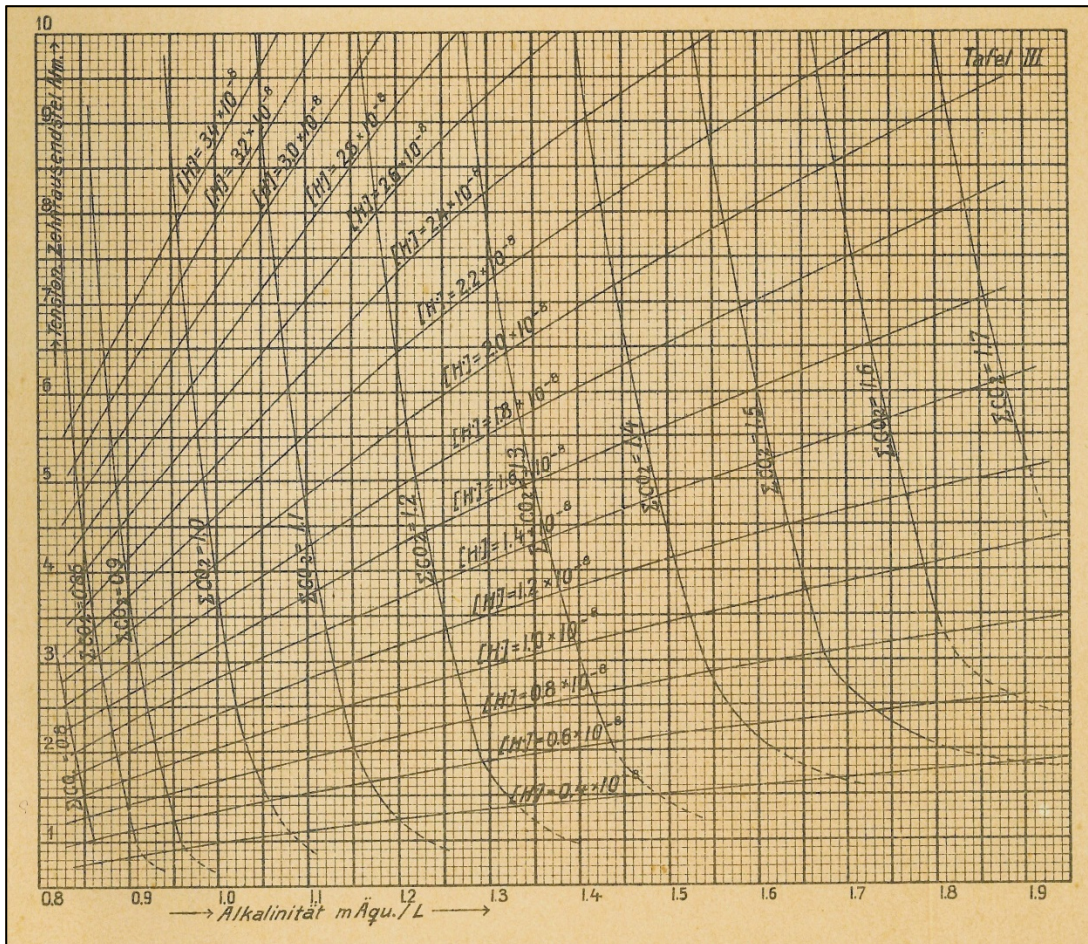


Fig. 8: Isolines for total CO<sub>2</sub> and hydrogen ion concentrations presented in a pCO<sub>2</sub> (tension)-alkalinity (mequ./L) diagram as obtained from systematic laboratory experiments (from BUCH, 1917c, Table III). In the absence of theoretically based mathematical formulations, BUCH used empirical diagrams for the determination of the pCO<sub>2</sub> on the basis of alkalinity data in combination with total CO<sub>2</sub> or hydrogen ion concentration (pH) measurements.

Using the carbonic acid dissociation constants,  $k_1$  and  $k_2$ , determined for pure diluted Na<sub>2</sub>CO<sub>3</sub>/NaHCO<sub>3</sub> solutions by MICHAELIS<sup>55</sup> & RONA<sup>56</sup> (1914) and AUERBACH<sup>57</sup> & PICK<sup>58</sup> (1911), respectively, BUCH tested the internal thermodynamic consistency between the four variables measured during his lab experiments with seawater. However, this attempt failed. Approximate agreement between measured and theoretically calculated concentrations of HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> was only obtained when assuming an unrealistic low degree of dissociation of the respective salts. BUCH (1917b) concedes:

*"... dass die theoretischen und experimentellen Funktionen dem Verlaufe nach gleichartig waren, dass aber das experimentell erhaltene Gleichgewichtssystem im Verhältnis zum anderen eine systematische Verschiebung aufwies ..."*

[„... that the shape of the theoretical and experimental functions were similar, but that the experimentally obtained system of equilibria showed a systematic bias in relation to the theoretical ones ...”] (BUCH, 1917b, p. 94).

From today's perspective this “systematic bias” is a consequence of several factors. First of all, the dependency of the equilibrium constants on salinity was not taken into account and this shortcoming could only partly be compensated for by the assumption of incomplete dissociation of carbonate salts. But it is also important, that the contribution of borate to the alkalinity was not yet discovered. Due to these circumstances, BUCH's initially expressed hope for a thermodynamically consistent quantitative characterization of the marine CO<sub>2</sub> system could not be fulfilled. Hence graphical representations such as those shown in Fig. 8 were the only way to compute any variables of the CO<sub>2</sub> system from measured quantities.

The second part of BUCH's dissertation deals with the presentation and interpretation of field measurements. In 1911, 1912 and 1914, BUCH participated in the first regular Finnish hydrographic and hydrochemical monitoring cruises in the northern Baltic Sea including the Gulfs of Bothnia and Finland. High resolution pH depth profiles were determined at more than 70 stations (Fig. 9). The measurements were performed immediately after sampling on board the research vessel “Nautilus”<sup>59</sup> (see A IV, p. 88) using SØRENSEN's (1909) colorimetric method. Samples were also taken for the later determination of alkalinity and total CO<sub>2</sub>. Similar to previous investigations by RUPPIN (1910) in the central and western Baltic Sea, the alkalinity data showed a distinct relationship to salinity. This behaviour was attributed to conservative mixing between the river water and Baltic Sea water alkalinity. Accordingly, extrapolation of the alkalinity/salinity functions to zero salinity yielded values which were consistent with direct alkalinity measurements in the adjacent rivers. An apparent dependency on salinity, but less pronounced, was also found for pH. BUCH recognized that this was primarily due to the buffer effect of alkalinity on pH which varied with salinity.

For the determination of the pCO<sub>2</sub>, BUCH used the empirical graphs which were obtained from his laboratory studies (Fig. 8). The mean pCO<sub>2</sub> obtained from the measurements of alkalinity and pH in spring and autumn (1911- 1914) showed a distinct seasonal variability. In both the Gulfs of Finland and Bothnia, as well at stations in the northern central Baltic, higher pCO<sub>2</sub> were observed in autumn. Ignoring the effect of vertical mixing and organic matter mineralization, BUCH attributed this to higher temperatures in autumn. Taking into account data for atmospheric CO<sub>2</sub> concentrations, BUCH finally concluded that at least during spring the northern Baltic Sea

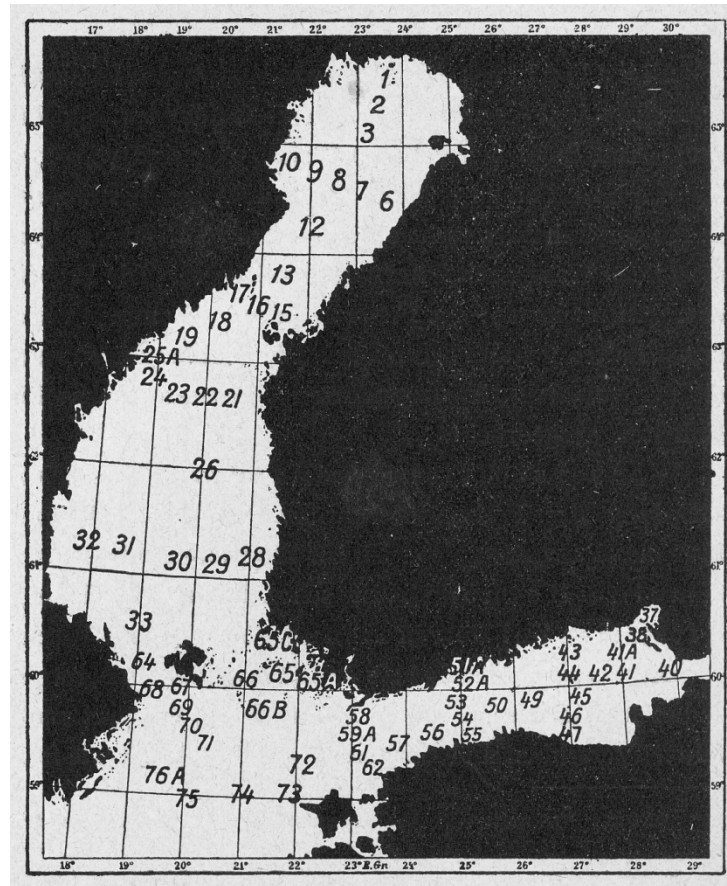


Fig. 9: Station network of the Finnish Monitoring Programme used by BUCH for his investigations in the 1910s (from BUCH, 1917b, p. 13).

including its Gulfs must absorb CO<sub>2</sub> from the atmosphere. Further considerations concerning the CO<sub>2</sub> exchange between atmosphere and sea were published in different articles (BUCH, 1922, 1924, 1926, 1928a).

During the ten years that followed his dissertation, BUCH published few studies concerning nitrogen compounds in seawater (BUCH, 1920, 1923), but any relevant contributions to research concerning the marine CO<sub>2</sub> system are missing. Likewise, no reports exist about the continuation of the Finnish marine monitoring programme that served as the basis for BUCH's CO<sub>2</sub> studies already in 1911. Possibly the Finnish Civil War of 1918<sup>60</sup> in which BUCH was allegedly actively involved (LINDBERG,<sup>61</sup> 1970), and the following societal and political instability had impaired scientific activities. It was not until 1928 that BUCH published a further study relevant for investigations of the marine CO<sub>2</sub> system. It was related to the practicability of the so-called quinhydrone method for pH measurements in seawater (BUCH, 1928b, 1928c). In further publications, he emphasized the importance of temperature for colorimetric pH measurements (BUCH, 1929a, 1929b, 1929c) and states:

*"In determining the pH of sea-water, sufficient regard has hitherto not been paid to the influence exercised by temperature. As a rule, the temperature has been ignored entirely;"* (BUCH, 1929a, p. 267).

Based on comprehensive laboratory investigations he derived temperature correction terms for different indicator dyes and gave detailed practical instruction on how to perform colorimetric pH determinations.

#### 4.2 Establishment of a consistent set of dissociation constants

In 1930, BUCH published an article consisting of two parts about "Die Kohlesäurefaktoren des Meerwassers" ("The components of carbonic acid in seawater"; see BUCH, 1930a, 1930b) that can be considered as a benchmark for the research concerning the marine CO<sub>2</sub> system. Taking into account the state-of-the-art in physical chemistry (e.g. DEBYE<sup>62</sup>-HÜCKEL<sup>63</sup> Theory<sup>64</sup>) the chemical equilibria between the CO<sub>2</sub> species in seawater were formulated and interpreted in terms of well-defined thermodynamic properties. The underlying ideas constitute still nowadays the basis for the theoretical treatment of the marine CO<sub>2</sub> system and its sound presentation clearly reflects BUCH's former studies in pure physical chemistry. But beyond the theoretical considerations, BUCH aimed at making practical use of the relationships between the measurable variables (what he called "Kohlensäurefaktoren") for investigating the marine CO<sub>2</sub> system through field studies. His particular interest was related to the determination of the surface water pCO<sub>2</sub> with view to the sea as sink or source for atmospheric CO<sub>2</sub>. He derived a formula which facilitated the simplified calculation of the pCO<sub>2</sub> based on measurements of solely pH, temperature and salinity whereby the alkalinity is obtained from regional alkalinity-salinity relationships.

It follows a critical review of the analytical methods and the recognition that:

*"Die meisten Messmethoden ergeben nicht das, was theoretisch erwünscht wäre, ... Deshalb können wir uns nicht ganz von der „Empirie“ befreien."*

[„Most of the measurement methods do not provide what is theoretically required... Therefore, we cannot liberate ourselves entirely from empiricism”]  
(BUCH, 1930a, p. 60).

As a consequence he states:

*"Für uns handelt es sich aber in erster Linie darum, die Beziehungen unter genauer Angabe der Arbeitsweise quantitativ überall durch dieselben Zahlen festzustellen, und in zweiter Linie darum, die Zahlen theoretisch zu deuten."*

[„In the first place, we must establish relationships (between the "Kohlensäurefaktoren") which are based on precisely characterized methods and reproducible results, and secondly to interpret theoretically the results.”]  
(BUCH, 1930a, p. 60).

An example is the use of "concentration" instead of the thermodynamically correct quantity "activity" for the description of chemical equilibria according to the mass action law. BUCH considered also the effect of anions of weak acids other than carbonic acid on the determination of the alkalinity. Taking into account related investigations including his own measurements, he concluded that a potential influence on the alkalinity measurement is too small to have a measurable effect on the acid-base equilibrium in seawater. This was a misinterpretation since it was very soon shown that borate contributes significantly to the alkalinity of seawater and that



its negligence was partly responsible for inconsistencies in calculations of the CO<sub>2</sub> equilibria in seawater.

Furthermore, BUCH reports some measurements which he used to determine exemplary the dissociation constants of carbonic acid and involved activity coefficients. He used the results to calculate the relative distribution of the individual CO<sub>2</sub> species over a pH range between 4 and 5. It followed considerations about the buffer properties and the uptake capacity of seawater for atmospheric CO<sub>2</sub>. Finally, based on his experimental studies, he outlined the objectives for future research which mainly referred to the accurate characterization of the carbonic acid dissociation constants over the full salinity and temperature range encountered in seawater. According to his perception, this will not only increase our knowledge about the thermodynamic properties of CO<sub>2</sub> in seawater, but beyond that it will contribute to:

*„... Studium der hydrographischen Lage und der Wasserumsetzung, Untersuchung des allgemeinen Stoffwechsels im Meere, der speziellen Lebensbedingungen der Organismen im Meere, des Einflusses auf den atmosphärischen CO<sub>2</sub>-Gehalt und indirekt damit auf die Lebenstätigkeit zu Lande.“*

[„... studying hydrographic conditions and water mass transformations, investigations of living conditions for marine organisms, the influence on the atmospheric CO<sub>2</sub> concentrations and, through this indirectly on life activity on the continents.“] (BUCH, 1930a, p. 74).

The theoretical considerations and experimental studies presented in that paper constituted the background for a cooperative effort to establish generally accepted standards for the theoretical treatment of the marine CO<sub>2</sub> system and for state-of-the-art analytical methods. A commission of experts (“Arbeitskommission”) was installed in 1930 by the International Council for the Exploration of the Sea (ICES). ICES, founded in 1899, was already an established international organization in those years, dedicated to international cooperation in marine research (a short history of ICES and BUCH’s activities within ICES see A VI). The commission consisted of KURT BUCH (Finnish Institute of Marine Research, [FIMR], Helsinki), HERMANN WATTENBERG (FRIEDRICH-WILHELMS-University, Berlin) (see A I, p. 75), HILDEBRAND WOLFE HARVEY (Marine Biological Association, Plymouth) (see A I, p. 76), assisted by STINA GRIPENBERG (FIMR) (see A I, p. 77). The objectives were outlined in “Nature” (BUCH et al., 1931a, 1931b):

*“With the object of extending recent researches by one of us (K. B.) concerning the first and second apparent dissociation constants  $K_1'$  and  $K_2'$  of carbonic acid in sea-water of varying salinity, and of developing suitable analytical methods of estimating ‘excess base’ (Alkalinität) and pH on board research vessels, collaboration was arranged by the International Council for the Exploration of the Sea.“* (BUCH et al., 1931b, p. 411).

The joint practical work of the Commission which took place at the laboratories of the Finnish Institute of Marine Research, lasted from spring to autumn 1930. The results were presented in a comprehensive report edited by ICES in 1932 (BUCH et al., 1932). It started with the definition of dissociation constants for CO<sub>2</sub> in seawater which differed by the use of concentration units, activity units or various combinations of these in the formulation of the mass action law. The

authors also addressed problems concerning the determination of the hydrogen ion activity and the implications for the best choice of the pH scale. These questions have occupied marine chemists until the recent past, when a general agreement on the so-called “total hydrogen ion concentration” scale was found.

However, the main achievement was the determination of the first and second dissociation constants of carbonic acid,  $K_1'$  and  $K_2'$ , at salinities between 0 and about 40. Depending on the use of varying combinations of activity and concentration units, different constants were defined – unfortunately not in a consistent terminology. In those years, the “apparent dissociation constants” which refer to concentration units for  $\text{CO}_2$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  and to activity units for  $\text{H}^+$ , was mainly used. Based on samples with a defined alkalinity and total  $\text{CO}_2$ ,  $K_1'$  and  $K_2'$  were derived from measurements of pH and  $\text{pCO}_2$ . Simple equations were fitted to the experimental data and yielded  $K_1'$  and  $K_2'$  as functions of salinity. Likewise, measurements were performed at different temperatures and together with other investigations (e.g. HASSELBALCH,<sup>65</sup> 1910-11; KENDALL,<sup>66</sup> 1916; WARBURG,<sup>67</sup> 1922), yielded the temperature dependency of  $K_1'$  and  $K_2'$ . The results were summarized in interpolation tables showing  $K_1'$  and  $K_2'$  at temperatures from 0 °C to 30 °C and salinities from 0 psu to 40 psu.



Fig. 10: KURT BUCH (right) and captain WOLTER MATTSSON (Finnish steamship S/S “Astræa”) at the Gefion Fountain in Copenhagen in 1933 (Photo reproduced with the kind permission of ROLF MATTSSON/Finland).

The ICES Commission that set for the first time standards for the physico-chemical characterization of the marine  $\text{CO}_2$  system, was headed by KURT BUCH. He was obviously the mastermind behind the experimental activities and theoretical considerations which he already outlined some years before (BUCH, 1930a). The contributions by the other members is not specified, however, it is very likely that WATTENBERG’s input was based on his oceanic studies of the  $\text{CO}_2$  system and in particular of the dissolution of  $\text{CaCO}_3$  in seawater during the “Meteor” Atlantic Expedition (1925 - 1927) (see Section 4.4). The role of HILDEBRAND W. HARVEY, who

published a textbook "Biological chemistry and physics of sea water" (HARVEY, 1928), may have been related to the biological aspects of the studies of CO<sub>2</sub> in seawater. References to any specific research activities could not be found in the report of the ICES Commission. Finally, STINA GRIPENBERG (Fig. 11), a research assistant at the FIMR, was involved in the work of the commission. She assisted in the laboratory work and contributed to the evaluation of the measurements. Despite GRIPENBERG continued her research on the marine CO<sub>2</sub> system e.g., by developing improvements for the alkalinity titration (GRIPENBERG, 1932, 1936), her later scientific achievements were related to the chemical and physical characterization of sediments in the northern Baltic Sea. This was also the topic of her dissertation (GRIPENBERG, 1934, 1939) which she completed in 1934. She was the first woman who received a doctoral degree in chemistry at the University of Helsinki.



Fig. 11: ROLF WITTING,<sup>68</sup> the first director of the Finnish Institute of Marine Research from 1918 to 1936, and STINA GRIPENBERG; photo taken probably in the late 1920s/early 1930s (Photo reproduced with the kind permission of FIMR Helsinki).

Despite the obvious progress achieved by the ICES Commission, a problem emerged when comparing the second dissociation constants determined in natural and in artificial seawater. Significant discrepancies between the values existed which could not be explained by any missing constituent in the artificial seawater. However, just one year after the work of the ICES Commission, GOLDSCHMIDT<sup>69</sup> et al. (1931) reported concentrations of boron in seawater which were much higher than previously believed. Since boron, existing in seawater as dissociable boric acid, may contribute to alkalinity, BUCH (1933a, 1933b) recalculated the second dissociation constant for natural seawater. Hereby, the previously observed discrepancy in K<sub>2</sub> with respect to artificial seawater could widely be explained, but K<sub>2</sub>' still remained a matter of discussion. BUCH (1938) states:

*"The first constant of the carbonic acid for different salinities and temperatures has been satisfactorily determined. But the chemical oceanographers have not*

*yet accepted a fixed value for the second constant, about which several investigations have been published.”* (BUCH, 1938, p. 5).

This was reason for BUCH to repeat the measurements for the determination of  $K_2'$  and to combine the results with those from previous investigations for an update of  $K_2'$  as a function of salinity (BUCH, 1938). Together with a similar function for the dependency of  $K_1'$  on salinity, these were then generally accepted and marked to some extent the termination of efforts to characterize the marine CO<sub>2</sub> system by measurable variables for many years.

#### 4.3 Continuation of alkalinity and pH monitoring in the northern Baltic Sea.

Investigations of the alkalinity and pH in the frame of the oceanographic Monitoring Programme of the FIMR which started in 1911, continued until the onset of World War II. Measurements were performed once a year mainly during summer at about 70 station stations (similar to those in Fig. 9) in the Gulfs of Bothnia and Finland, and in the northern Gotland Sea. The results and conclusions about the physical and biological control of the marine CO<sub>2</sub> system were summarized in a book (BUCH, 1945). It comprises extensive tables and many graphs which characterize the mean horizontal and vertical distribution of alkalinity and pH together with hydrographic variables for the time period 1927-1938. The tables also include mean data for the CO<sub>2</sub> partial pressure, total CO<sub>2</sub> and calcium carbonate saturation which were calculated from alkalinity and pH using the dissociation constants for carbonic acid previously updated by BUCH et al. (1932) and BUCH (1938).

The distributions of the surface water pCO<sub>2</sub> at different seasons are presented by isoline plots. An example for the spatial distribution for April/May 1938 is given in Fig. 12. In general, the values are clearly below saturation with the atmospheric CO<sub>2</sub> which was at a level of about 320 ppm in those years (3.2 parts per 10,000, common unit for atmospheric CO<sub>2</sub> in those years) (CALLENDAR,<sup>70</sup> 1940). This is characteristic for the situation in spring when intense biological production consumes CO<sub>2</sub>. BUCH's data has been used by SCHNEIDER & KUSS (2004) to estimate the net biomass production in the Gotland Sea at the beginning of the last century and to compare it with current eutrophication driven production rates. The data indicated an increase by a factor of about 3 during the last approximately seventy years.

BUCH also addressed the role of the sea as a sink or source for anthropogenic CO<sub>2</sub>. According to the investigations by CALLENDAR (1940), the atmospheric CO<sub>2</sub> had increased by about 10 % since the onset of the industrial emissions. Assuming that an equilibrium existed for the distribution of CO<sub>2</sub> between the sea and the atmosphere in pre-industrial times, BUCH concluded that the oceans must have become on average a sink for atmospheric CO<sub>2</sub>. With respect to the Baltic Sea he states:

*“In den Ostseegewässern schwanken die Tensionen [pCO<sub>2</sub>] im Laufe des Jahres auf beiden Seiten der Gleichgewichtslage. Auch hier ist eine resultierende Wanderung Atmosphäre → Meer zu erwarten.”*

[“In the waters of the Baltic Sea, the tensions [pCO<sub>2</sub>] fluctuate between both sides of the equilibrium. Also here, we can expect a resultant flux atmosphere → sea.”] (BUCH, 1945, p. 199).

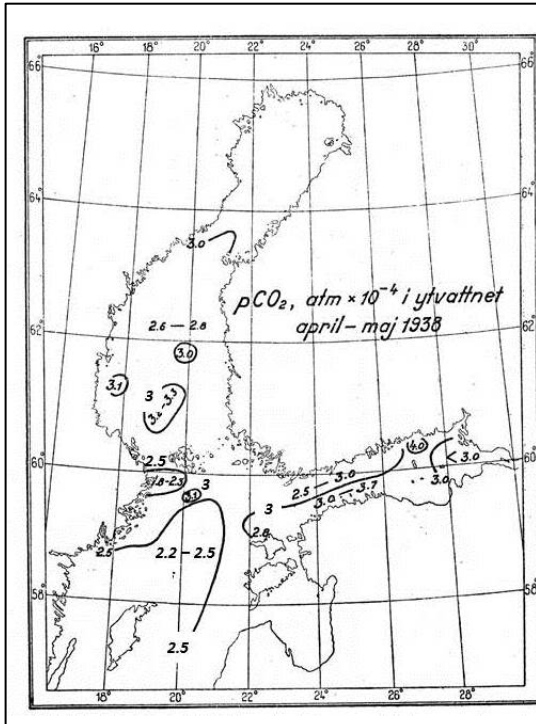


Fig. 12:  $pCO_2$  isolines in the surface water of the northern Gotland Sea and the Gulfs of Finland and Bothnia in April/May 1938 (from BUCH, 1945, modified).

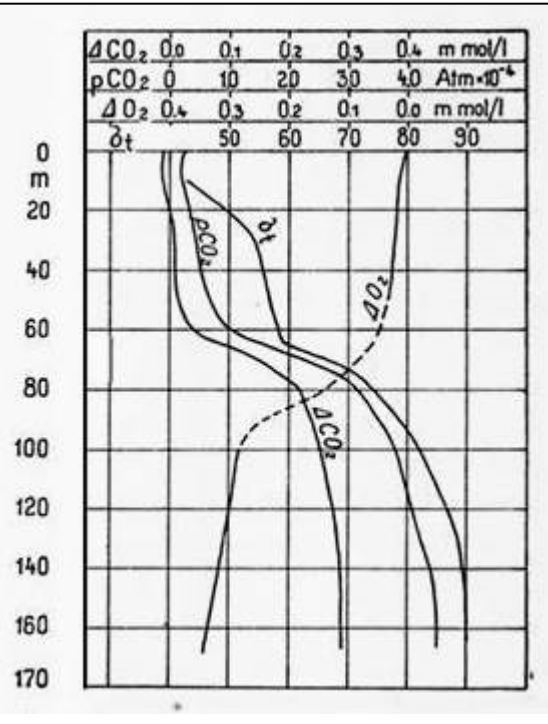


Fig. 13: Mean profiles of density  $\sigma_t$ ,  $pCO_2$ , total  $CO_2$  excess ( $\Delta CO_2$ ) and  $O_2$  depletion ( $\Delta O_2$ ) averaged over the years 1927-1938 for the Fårö Deep (from BUCH, 1945, modified).

New findings were also obtained from the analysis of the  $CO_2$  system in the deep water of the Baltic Sea. Based on the measurements of pH and alkalinity, the concentrations of total  $CO_2$  were calculated. The data were used to determine the total  $CO_2$  excess,  $\Delta CO_2$ , caused by the mineralization of organic matter. Mean values of about 300  $\mu mol/L$  were observed for  $\Delta CO_2$  in the bottom water of the northern Gotland Sea and coincided with the consumption of almost the entire oxygen content (Fig. 13). This indicates that oxygen depletion and  $CO_2$  accumulation was a common phenomenon in the Baltic Sea deep water already eighty years ago. However, due to eutrophication currently observed accumulations of  $CO_2$  are much larger and may reach values of up to 500  $\mu mol/L$  after longer periods of stagnation (SCHNEIDER et al., 2010) and is accompanied by the total exhaustion of oxygen and the formation of hydrogen sulfide.

BUCH also analyzed the stoichiometry of  $CO_2$  accumulation, oxygen consumption and the release of phosphate during organic matter mineralization. He used the relationships to infer the surface water organic matter production in coastal waters of the Gulf of Finland on the basis of the phosphate consumption during an algae bloom. To illustrate the magnitude of the productivity he expressed it in terms of harvested potatoes, a method that was obviously not unusual in those times:

*"Als Kohlehydrat berechnet ergäbe sich 2.3 g/m<sup>3</sup> Trockensubstanz und als Kartoffel mit 25 % Trockensubstanz berechnet ergäbe sich 9 g/m<sup>3</sup>. ..., so ergäbe sich eine Ernte von 1800 kg/ha."*

[„Expressed as carbohydrates, this corresponds to 2.3 g/m<sup>3</sup> dry substance and converted to the amount of potatoes with 25 % dry substance 9 g/m<sup>3</sup> are obtained. ...., this would yield a harvest of 1800 kg/ha.”] (BUCH, 1945, p. 198).

These are a few examples which demonstrate the broad approach of BUCH's studies of the marine CO<sub>2</sub> system. It covered improvements of analytical methods, further development of the theoretical background, extensive field studies including the assessment of the CO<sub>2</sub> gas exchange and the control by biochemical processes. The potential of the latter aspect has been disregarded during the decades following BUCH's activities, but has gained timeliness during recent years in connection with eutrophication studies in the Baltic Sea (e.g., SCHNEIDER & MÜLLER, 2018).

#### 4.4 BUCH's oceanic studies

BUCH's studies of the marine CO<sub>2</sub> system were not confined to the Baltic Sea, but included some measurement campaigns in the North Atlantic. But before presenting these, we must first pay attention to HERMANN WATTENBERG's studies of the CO<sub>2</sub> system during the German Atlantic Expedition aboard the survey vessel "Meteor"<sup>71</sup> (Fig. 14) that lasted from 1925 to 1927. This was certainly one of the most important and extensive oceanographic expedition that had taken place since the famous British "Challenger" Expedition in 1872-1876. The focus was on the hydrography of southern Atlantic Ocean, in particular on the water transport between the northern and southern hemisphere. A tremendous amount of data was collected on 14 zonal cross sections and provided insight in the biogeochemistry and water mass circulation patterns of the Atlantic Ocean. The interdisciplinary composed scientific staff included chemical oceanographers which were headed by HERMANN WATTENBERG (see Section 4.2), a young chemist who had finalized his dissertation only two years before the start of the expedition.

The measurements of pH formed the basis for the investigations of the CO<sub>2</sub> system (see A III, p. 85). All water samples taken during the expedition were analysed for pH and resulted in a total of almost 7000 data points. WATTENBERG justifies the focus on pH measurements by:

*"..., war es von jeher das Ziel theoretischer und experimenteller Untersuchungen, an denen K. Buch den größten Anteil hat, aus dem pH die freie und auch die gebundene Kohlensäure berechnen zu können ... Aber das pH für sich gibt schon ein ganz brauchbares Mittel an die Hand, Alter und Herkunft von Wasserarten sowie biologische und geologische Vorgänge im Meere zu erkennen und zu verfolgen."*

[„... it was always the goal of theoretical and experimental investigations which were to the most part performed by K. Buch, to calculate the free and bound carbonic acid from the pH ... But also the pH as such provides a useful tool to identify and to trace the age and origin of water masses, as well as biological and geological processes in the sea.”] (WATTENBERG, 1933a, p.234).

Using graphical representations (such as shown in Fig. 8) for the relationship between the CO<sub>2</sub> partial pressure and pH for a given alkalinity, the pCO<sub>2</sub> was determined for each sample. The results were used to characterize the distribution of the pCO<sub>2</sub> between about 15° N and the Antarctic Peninsula by isoline plots for different depth levels (WATTENBERG, 1933b). This was the first coherent large scale mapping of the surface water pCO<sub>2</sub> which is unique and was never again repeated in such a way in chemical oceanography until very recently. The data was carefully interpreted in terms of biological and physical conditions and indicated that biological processes are the major control for both the seasonal and the horizontal pCO<sub>2</sub> distributions. Varying characteristics of the vertical distribution of total CO<sub>2</sub> could be explained by the circulation of water masses, while – vice versa – information about the ocean circulation could be inferred from the distribution patterns of the total CO<sub>2</sub> in the sub-surface water.

Another goal of the investigations concerned the conditions under which the huge deposits of CaCO<sub>3</sub> in marine sediments can be formed. Experiments were performed with water from different depth in order to investigate the solubility of CaCO<sub>3</sub> in seawater and its dissolution or precipitation in dependency on the water depth. Based on pH measurements and using the thermodynamics of the equilibria between dissolved CO<sub>2</sub> (CO<sub>2</sub>\*) and solid CaCO<sub>3</sub>, WATTENBERG derived a formula that facilitated the determination of the state of saturation in terms of a CaCO<sub>3</sub> excess or deficit (WATTENBERG, 1933c). The results showed that surface water in general is strongly supersaturated with regard to CaCO<sub>3</sub> and that a trend towards undersaturation exists with increasing water depth. These are findings which could partly explain the geographical distribution of CaCO<sub>3</sub> deposits in marine sediments. The biogeochemical investigations during the "Meteor" Expedition were not confined to studies of the CO<sub>2</sub> system. They included another focus: Oxygen was determined in all samples and more than half of the samples were also analysed for phosphate. The data which can be considered as the complement to the CO<sub>2</sub> data,





performed on passenger liners. An example is the crossing of the North Atlantic between Copenhagen and Boston when BUCH followed an invitation for studies at Woods Hole Oceanographic Institution (WHOI). It is worth to dedicate a few words to this visit because at that year, 1933, ALFRED C. REDFIELD,<sup>73</sup> a senior biologist at WHOI, had just finalized his famous studies "On the proportions of organic derivatives in sea water and their relation to the composition of plankton" (REDFIELD, 1934) which revealed the relationship between the concentrations of phosphate, nitrate, CO<sub>2</sub> and O<sub>2</sub> in deeper water layers and the bulk elemental composition of organic matter produced by photosynthesis. He concluded that the corresponding ratios C:N:P:O<sub>2</sub>, since then known to every oceanographer as "REDFIELD Ratios", are within certain limits universal for the composition of marine phytoplankton. On the other hand, REDFIELD calculated the total CO<sub>2</sub> concentration in deeper water layers from pH measurements using the approach and tables by BUCH et al. (1932), while BUCH (1939a, 1939b) was well aware of the importance of nutrients for the CO<sub>2</sub> exchange between the ocean and the atmosphere:

*"... which depends partly on temperature and salinity, but partly also on biological activity, mainly attributable to phyto-plankton in the surface water and to bacteria in the depth. The biological production depends in its turn on substances which limit it, viz., nutrient salts, phosphates, nitrogen, and so forth ...."* (BUCH, 1939b, p. 38.)

It is therefore very likely, even if not documented, that BUCH and REDFIELD met at Woods Hole for discussions about common scientific interests.

Since BUCH used so-called "ships of opportunity" for his oceanic studies, sampling was restricted to surface waters. The on-board measurements comprised the determination of pH, the pCO<sub>2</sub> and atmospheric CO<sub>2</sub> content whereas the alkalinity titration was performed after return in the home lab. In contrast to WATTENBERG who focused his view on the dissolution and precipitation of CaCO<sub>3</sub> (WATTENBERG, 1933b, 1936), BUCH's interest was mainly in the CO<sub>2</sub> air-sea gas exchange and the role of the ocean for regulating the atmospheric CO<sub>2</sub> content:

*"In conjunction with similar investigations ...these investigations were intended to extend the knowledge of carbonic acid [CO<sub>2</sub>] equilibrium and of the exchange of carbon dioxide between the sea and the atmosphere in the North Atlantic, ..."* (BUCH, 1939a, p. 28).

Low pCO<sub>2</sub> and uptake of atmospheric CO<sub>2</sub> were observed in different regions of the North Atlantic. As a consequence of plankton growth, the pCO<sub>2</sub> in June 1935 on the route between Copenhagen and Boston showed in general values below the atmospheric level. Extreme low pCO<sub>2</sub> were observed in arctic waters close to the ice boundary during measurements on a ferry along the route Narvik – Svalbard in August 1936 (BUCH, 1936). This could be explained by the combined effect of low temperature and low salinity on the solubility and dissociation of carbonic acid in seawater. BUCH further concluded that the uptake of atmospheric CO<sub>2</sub> in these regions is the cause for lower CO<sub>2</sub> concentrations in polar air masses. His interest in the interaction between the ocean and the atmosphere is also reflected in his attempt to estimate the role of the ocean for the uptake of industrial CO<sub>2</sub> emissions. Therefore, he used annual anthropogenic CO<sub>2</sub> emission rates estimated by GOLDSCHMIDT (1933) which amounted to 4.1 Gt-CO<sub>2</sub>/yr. For comparison: A recent study by GÜTSCHOW et al. (2019) report a similar emission rate for 1950 (6.6 Gt-CO<sub>2</sub>/yr.) but an almost ten times higher rate for 2017 (36 Gt-CO<sub>2</sub>/yr.). Based on the

distribution of total CO<sub>2</sub> between the ocean and the atmosphere and assuming long-term equilibrium, BUCH estimated that the effect of the anthropogenic emissions at that time on the atmospheric CO<sub>2</sub> concentration is only minor and that a doubling of the concentration will take about 3000 years (BUCH, 1939b, p. 33).

## 5. New challenges for the marine CO<sub>2</sub> research after World War II

With the outbreak of World War II marine research was widely closed down except that it could provide military profit. Due to the naval warfare it was impossible to execute any field studies through expeditions. Regarding chemical oceanography on a European level, this was more than just a temporal break in the research activities; it was also the beginning of a new era. In 1945, BUCH published the book "Kolsyrejämvikten i Baltiska Havet" ("Carbon dioxide equilibria in the Baltic Sea", BUCH, 1945) which can be considered as a kind of account of his scientific life's work concerning the theoretical treatment and the characterization of the state of the marine CO<sub>2</sub> system in the northern Baltic Sea. In 1951, the year of his retirement, BUCH (1951) published final calculations of the dissociation constants taking into account data (HARNED & SCHOLLES, 1941; HARNED & DAVIS, 1943) which were not available for his previous estimates. However, for average marine conditions this resulted in only minor corrections. A few further publications appeared thereafter (e.g. BUCH, 1960a, 1960b, 1960c; see also A VII), but were not related to own original research activities. Still, BUCH remained closely connected to CO<sub>2</sub> research within the marine and atmospheric science community. An example is his engagement for the establishment of a Scandinavian station network for the detection of increasing atmospheric CO<sub>2</sub> concentrations (FONSELIUS<sup>74</sup> & KOROLEFF,<sup>75</sup> 1955).

The career of HERMANN WATTENBERG, who became the Director of the Institute of Marine Research in Kiel in 1944, ended tragically. He died during a bomb attack together with eight staff members of the Institute, among them was HANNA WITTIG<sup>76</sup> who worked on the distribution of alkalinity and calcium in the Baltic Sea (WITTIG, 1940). This was certainly a painful loss for the oceanographic community in Germany and beyond. In memory of WATTENBERG, BUCH wrote:

*"Die Katastrophe, die am 24. Juli 1944 über das Institut für Meereskunde der Universität Kiel hereinbrach ..., bedeutet durch den Tod von Prof. Dr. Hermann WATTENBERG einen unersetzlichen Verlust für die gesamte internationale Meeresforschung"*

[„The catastrophe which stroke the Institute of Marine Research of the University Kiel on July 24, 1944, ... caused due to the death of Prof. Dr. Hermann WATTENBERG an irreplaceable loss for the entire international marine research community“] (BUCH, 1949, p. 7).

Different appraisals emphasized WATTENBERG's ability for and promotion of interdisciplinary marine research, e.g., BUCH (1949) cites a statement that WATTENBERG gave in his inaugural lecture:

*"...dass die Erforschung des Meeres ... von Natur aus hervorragend geeignet, ja geradezu bestimmt ist, in ihrem Bereich die spezialistische Zersplitterung in einzelne Wissenszweige aufzuheben. Wirkliche Meeresforschung ist ... die einheitliche Erfassung eines Organismus, dessen Glieder und Funktionen miteinander unlösbar verbunden sind."*

[ "... that the exploration of the sea is ideally suited and even virtually destined, to overcome the specialized fragmentation of its research issues into scientific disciplines. Real marine research means ... coherent comprehension of an organism whose constituents and functions are inseparably connected with each other." ] (WATTENBERG, 1944, Inaugural Lecture, see BUCH, 1949, p. 10).

The new start of marine research after the War set different developments in motion which impacted the marine research activities in the following decades. The major motivation for fostering intense studies of the marine CO<sub>2</sub> lied in the perception of the ocean's role for mitigating the increase of the atmospheric CO<sub>2</sub> by anthropogenic emissions and thus for the change of the Earth's climate.

In 1824, the French mathematician JOSEPH FOURIER<sup>77</sup> presented some general ideas about the temperature of the Earth and about the absorption of longwave radiation by the atmosphere (FOURIER, 1824). It was then EUNICE FOOTE<sup>78</sup>, an American scientist, who for the first time linked the atmospheric CO<sub>2</sub> to the temperature of the atmosphere (Fig. 15). Based on some simple experiments with water vapour and CO<sub>2</sub>, she concluded:

*"An atmosphere of that gas would give to our earth a high temperature; and if, as some suppose, at one period of its history, the air had mixed with it a larger proportion than at present, an increased temperature ... must have necessarily resulted ... The highest effect of the sun's rays I have found to be in carbonic acid [CO<sub>2</sub>] gas " (FOOTE, 1856, p. 383).*

A few years later, in 1861, the Irish physicist JOHN TYNDALL<sup>79</sup> published a paper on the Earth's atmosphere warming which was the basis for the later "hot-house theory" (TYNDALL, 1861; cf. also ARRHENIUS, 1908, p. 51). He found that water vapour is the strongest absorber of radiant heat and, together with CO<sub>2</sub>, is mainly controlling the temperature of the Earth's atmosphere.

These early studies did not consider possible effects of anthropogenic CO<sub>2</sub> emissions and were not aware of ocean's role for regulating the atmospheric CO<sub>2</sub>. These aspects were taken up by SVANTE ARRHENIUS (ARRHENIUS, 1896a, Bihang; 1896b) who published for the first time a plausible physical model that explained how gases in Earth's atmosphere trap heat.<sup>80</sup> He called it "hot-house theory" of the atmosphere, which later on was termed "greenhouse effect" (ARRHENIUS, 1908).

382 *On the Heat in the Sun's Rays.*

ART. XXXI.—*Circumstances affecting the Heat of the Sun's Rays;*  
by EUNICE FOOTE.

(Read before the American Association, August 23d, 1856.)

My investigations have had for their object to determine the different circumstances that affect the thermal action of the rays of light that proceed from the sun.

Several results have been obtained.

First. The action increases with the density of the air, and is diminished as it becomes more rarified.

The experiments were made with an air-pump and two cylindrical receivers of the same size, about four inches in diameter and thirty in length. In each were placed two thermometers, and the air was exhausted from one and condensed in the other. After both had acquired the same temperature they were placed in the sun, side by side, and while the action of the sun's rays rose to 110° in the condensed tube, it attained only 88° in the other. I had no means at hand of measuring the degree of condensation or rarefaction.

The observations taken once in two or three minutes, were as follows:

Exhausted Tube		Condensed Tube.	
In shade.	In sun.	In shade.	In sun.
75	80	75	80
76	82	78	95
80	82	80	100
83	86	82	105
84	88	85	110

This circumstance must affect the power of the sun's rays in different places, and contribute to produce their feeble action on the summits of lofty mountains.

Secondly. The action of the sun's rays was found to be greater in moist than in dry air.

In one of the receivers the air was saturated with moisture—in the other it was dried by the use of chlorid of calcium.

Both were placed in the sun as before and the result was as follows:

Dry Air.		Damp Air.	
In shade.	In sun.	In shade.	In sun.
75	75	75	75
78	88	78	90
82	102	82	106
83	104	82	110
82	105	82	114
88	108	92	120

ART. XXXII.—*Review of a portion of the Geological Map of the United States and British Provinces by Jules Marcou,\** By WILLIAM P. BLAKE.

GEOLOGICAL maps of the United States published in Europe and widely circulated among European geologists, are necessarily regarded by us with no small degree of attention and curiosity. This is more especially true, when such maps embrace regions of which the geography has only recently been made known and the geology has never before been laid down on a map with any approach to accuracy.

The recent geological map and profile by M. J. Marcou, which has appeared in the *Annales des Mines* and in the *Bulletin of*

\* Carte Géologique des Etats-Unis et des Provinces Anglaises de l'Amérique du Nord par Jules Marcou. *Annales des Mines*, 5<sup>e</sup> Série, T. vii, p. 329. Published also with the following:  
Résumé explicatif d'une carte géologique des Etats-Unis et des provinces anglaises de l'Amérique du Nord, avec un profil géologique allant de la vallée du Mississippi aux côtes du Pacifique, et une planche de fossiles, par M. Jules Marcou *Bulletin de la Société Géologique de France*, Mai, 1856, p. 813.

Marcou's Geological Map of the United States. 383

The high temperature of moist air has frequently been observed. Who has not experienced the burning heat of the sun that precedes a summer's shower? The isothermal lines will, I think, be found to be much affected by the different degrees of moisture in different places.

Thirdly. The highest effect of the sun's rays I have found to be in carbonic acid gas.

One of the receivers was filled with it, the other with common air, and the result was as follows:

In Common Air.		In Carbonic Acid Gas.	
In shade.	In sun.	In shade.	In sun.
80	90	80	90
81	94	84	100
80	99	84	110
81	100	85	120

The receiver containing the gas became itself much heated—very sensibly more so than the other—and on being removed, it was many times as long in cooling.

An atmosphere of that gas would give to our earth a high temperature; and if as some suppose, at one period of its history the air had mixed with it a larger proportion than at present, an increased temperature from its own action as well as from increased weight must have necessarily resulted.

On comparing the sun's heat in different gases, I found it to be in hydrogen gas, 104°; in common air, 106°; in oxygen gas, 108°; and in carbonic acid gas, 125°.

Fig. 15: Paper of EUNICE FOOTE dated 23 August 1856.

According to his calculations a doubling (fourfold) of the atmospheric CO<sub>2</sub> results in a temperature increase by 4 (8) °C. With respect to the ocean's role as a sink of carbon dioxide he states:

*"Although the sea, by absorbing carbonic acid [CO<sub>2</sub>], acts as a regulator of huge capacity, which takes up about five-sixths of the produced carbonic acid [CO<sub>2</sub>], we yet recognize that the slight percentage of carbonic acid [CO<sub>2</sub>] in the atmosphere may by the advances of industry be changed to a noticeable degree in the course of a few centuries."* (ARRHENIUS, 1908, p. 54).

BUCH (1939b) was also aware that a certain fraction of the industrial CO<sub>2</sub> emissions must stay in the atmosphere despite the huge uptake capacity of the oceans (see Section 4.4). However, he and others (CALLENDAR, 1940) did not link it to potential effects on the Earth's climate. Still, there was an interest to obtain further evidence for increasing atmospheric CO<sub>2</sub> concentrations. In 1954, upon an initiative of KURT BUCH, a network of stations for the determination of atmospheric CO<sub>2</sub> was established in Scandinavia. In 1954/55 air was sampled at 15 stations in Sweden, Finland, Denmark and Norway with a temporal resolution of 10 days (FONSELIUS et al., 1956). The data indicated an increase of the CO<sub>2</sub> concentrations since BUCH's measurements in 1935/36 (BUCH, 1939a, 1939b) but

*"... it is impossible to say at present whether this increase is just a fluctuation in the regional CO<sub>2</sub>-climate or if it represents a steady increase since 1935."*  
(FONSELIUS et al., 1956, p. 178).

This problem was solved a few years later when CHARLES D. KEELING<sup>81</sup> started the famous CO<sub>2</sub> time series measurements at the Mauna Loa Observatory (3400 m a.s.l.) on Hawaii in 1958 (KEELING, 1960). Since then the so-called KEELING Curve, showing the increase of the atmospheric CO<sub>2</sub>, is a standard chart in atmospheric and climate research. But it has also stimulated physical and chemical oceanography since the role of the ocean for the fate of the anthropogenic CO<sub>2</sub> is one of the key questions for the future development of the atmospheric CO<sub>2</sub> concentrations and thus of climate change. It has also stimulated research on the marine CO<sub>2</sub> system worldwide with a distinct shifting of the activities from northern Europe to the global marine research community. This is also reflected in the decline of CO<sub>2</sub> studies of the Baltic Sea which due to KURT BUCH were the starting point for many new ideas and concepts, but were no longer considered as relevant for investigating the uptake of anthropogenic CO<sub>2</sub>.

However, in the early nineties a revival of CO<sub>2</sub> studies in the Baltic Sea was initiated by the Institute for Baltic Sea Research (IOW) in Warnemünde (Germany) and since then continuously intensified. Beyond the importance for the uptake of anthropogenic CO<sub>2</sub>, it was recognized that investigations of the marine CO<sub>2</sub> system provide an excellent tool to study biogeochemical processes which are linked to the production and decomposition of organic matter and thus to eutrophication. This aspect is reflected in the title of a book "Biogeochemical processes in the Baltic Sea – Observations through carbon dioxide glasses" (SCHNEIDER & MÜLLER, 2018) which presents the major achievements concerning the marine CO<sub>2</sub> research at the IOW during the past two decades.

## Summary

After the Introduction (Chapter 1), Chapter 2 describes the early attempts, around 1870/80, to determine the concentrations of atmospheric gases dissolved in seawater. While the approach based on vacuum extraction and gas gasometric measurements (JACOBSEN, 1874, 1875) was successful for oxygen and nitrogen, it did not yield consistent data for CO<sub>2</sub>. The results obtained with other extraction methods, such as evaporation and distillation, were contradictory and led to heated discussions regarding the chemical nature of extractable CO<sub>2</sub> and of the fraction controlling the biogenic formation of calcium carbonate. Progress in the reproducibility and interpretability of CO<sub>2</sub> determinations was achieved by TORNØE (1880b), who extracted CO<sub>2</sub> from acidified seawater and was thus able to estimate the total CO<sub>2</sub> concentration, a major variable describing the marine CO<sub>2</sub> system. TORNØE then used the same acidification procedure to determine the amount of acid needed to release CO<sub>2</sub> completely from the sample. The resulting CO<sub>2</sub> equivalents based on acid consumption were designated "neutral carbonates" and corresponded to half of the alkalinity, another key variable of the marine CO<sub>2</sub> system. During extensive field studies in the North Atlantic, TORNØE investigated the marine CO<sub>2</sub> system in both the surface and the deeper water layers. The total CO<sub>2</sub> and alkalinity data generated in those studies are consistent with our current view on the biogeochemical control of the marine CO<sub>2</sub> system thus demonstrating the quality of the historic data.

Chapter 3 presents another variable of the marine CO<sub>2</sub> system, the CO<sub>2</sub> partial pressure (pCO<sub>2</sub>). AUGUST KROGH, a Danish physiologist, developed a method for determining the pCO<sub>2</sub> ("CO<sub>2</sub> tension") based on the CO<sub>2</sub> content of a gas phase at equilibrium with seawater (KROGH, 1904a). In experiments with acidified seawater containing only the species CO<sub>2</sub> and H<sub>2</sub>CO<sub>3</sub> ("free CO<sub>2</sub>"), KROGH determined solubility constants (KROGH, 1904a; FOX, 1905) relating the concentration of free CO<sub>2</sub> to the CO<sub>2</sub> tension. The existence of a defined concentration of free CO<sub>2</sub> led to the conclusion that an equilibrium exists between the CO<sub>2</sub> species in seawater which results from the reaction of free CO<sub>2</sub> with CO<sub>3</sub><sup>2-</sup> ("normal carbonates") in which bicarbonate is formed. However, attempts to characterize this equilibrium by a reaction constant according to the mass action law were only partly successful (KROGH, 1904a). In field studies conducted in the North Atlantic, KROGH performed the very first pCO<sub>2</sub> measurements in ocean surface waters. He also recognized the role of the oceans in regulating the atmospheric CO<sub>2</sub> level, including the uptake of CO<sub>2</sub> produced by the combustion of coal (KROGH, 1904b).

The second part of Chapter 3 deals with the discovery of the hydrogen ion as a measure of acidity, which derived from ARRHENIUS' theory of electrolytic dissociation and its implication that, upon their dissolution in water, acids release hydrogen ions. SØRENSEN (1909) defined the pH scale as a measure of the hydrogen ion concentration and developed both colorimetric and electrometric (HARNED Cell) methods enabling its determination. To measure the pH of seawater, PALITZSCH (1911) used different indicator dyes that allowed a colorimetric determination of the pH within the natural range of seawater; the method has a precision of ±0.04 pH units. From this and the above-described work, all four variables that characterize the marine CO<sub>2</sub> system, i.e., total CO<sub>2</sub>, alkalinity, pCO<sub>2</sub> and pH were accessible.

Chapter 4 is dedicated almost exclusively to the achievements of KURT BUCH. The first section (4.1) provides an overview of his early activities, including his dissertation at the University of Helsinki. BUCH (1933a) carried out field studies at a coastal station in the Gulf of Finland and between 1911 and 1914 participated in an ongoing Finnish hydrographic and hydrochemical

monitoring program that collected data from more than 70 stations in the northern Baltic Sea. Alkalinity and pH were measured and the results interpreted in terms of hydrographic and biogeochemical processes. BUCH also attempted to study the marine CO<sub>2</sub> system by confining the measurements to alkalinity and pH and to use the dissociation constant of carbonic acid to calculate the total CO<sub>2</sub> concentration and the pCO<sub>2</sub>. However, due to the use of inadequate dissociation constants and insufficient knowledge of the role of salinity in chemical equilibria, this approach failed. The total CO<sub>2</sub> and pCO<sub>2</sub> calculated from the alkalinity and pH could not be validated by measurements. Therefore, the theoretical calculations were replaced by empirical graphical representations of the relationships between the variables of the CO<sub>2</sub> system.

Section 4.2 is a tribute to BUCH's role in the establishment of a coherent set of dissociation constants characterizing the thermodynamics of the marine CO<sub>2</sub> system. Upon his initiative, an ICES Working Commission was set up in 1930 with the goal of reconsidering the thermodynamics of the marine CO<sub>2</sub> system. Through their extensive laboratory studies at the Finnish Institute of Marine Research, BUCH and his colleagues H. WATTENBERG (Germany) and H. W. HARVEY (United Kingdom), with the assistance of S. GRIPENBERG (Finland), were able to determine the first and second dissociation constants as functions of salinity and temperature. The results were presented as interpolation tables (BUCH et al., 1932), which were used until the 1950s in calculations related to the marine CO<sub>2</sub> system. Substantial correction proved to be necessary only for the second dissociation constant, based on the recognition of the importance of borate as a carrier of alkalinity (BUCH, 1933).

Section 4.3 addresses BUCH's extensive field studies, which started in 1911 (Section 4.1). However, due to methodological shortcomings BUCH considered only the data from 1927-1938 as sufficiently reliable for publication. Nonetheless, the pH and alkalinity measurements performed annually at ~70 stations during those 11 years constitute a unique data set that is unparalleled in the history of marine CO<sub>2</sub> research. In BUCH (1945), the temporal means of pH and alkalinity together with the values for total CO<sub>2</sub> and pCO<sub>2</sub>, calculated from pH and alkalinity, are presented as tables and isoline plots for each station and water depth. The interpretation of the surface water data included considerations about the Baltic Sea (oceans) as a sink for the increasing CO<sub>2</sub> caused by anthropogenic emissions, a subject of discussion already at the beginning of the last century. The deep-water accumulation of total CO<sub>2</sub> was related to oxygen depletion and to the increase in the phosphate concentrations, resulting in stoichiometric relationships for the production/mineralization of organic matter.

Section 4.4 presents BUCH's oceanic research activities together with the investigations of HERMANN WATTENBERG during the German "Meteor" Expedition of 1925-1927. WATTENBERG, later the director of the Institute for Marine Research in Kiel (Germany), studied the marine CO<sub>2</sub> system along 14 zonal transects in the South Atlantic (WATTENBERG, 1933). Using measurements of pH and alkalinity, he determined the horizontal and vertical distributions of pCO<sub>2</sub>. However, his main interest was related to calcium carbonate saturation in both surface and deep waters. BUCH conducted his oceanic studies from on board cargo ships and passenger liners, including during a journey from Copenhagen to Boston on the occasion of a visit to the Woods Hole Oceanographic Institution. His investigations focused on the surface pCO<sub>2</sub> and his continued study of the ocean as a sink or source of atmospheric CO<sub>2</sub>. Based on rough calculations of the ocean's capacity for the uptake of anthropogenic CO<sub>2</sub> and on rates of anthropogenic CO<sub>2</sub> emissions (GOLDSCHMIDT, 1933), he estimated the future development of the atmospheric CO<sub>2</sub> concentration.

Chapter 5 focuses on the years after World War II, which in many respects were a turning point for studies of the marine CO<sub>2</sub> system. This was mainly due to the increasing recognition of the consequences of anthropogenic emissions for atmospheric CO<sub>2</sub> concentrations and thus for the Earth's climate. With this knowledge, research into the role of the oceans as a sink for anthropogenic CO<sub>2</sub> and thus as a modulator of climate change took on a new urgency for chemical oceanographers, in particular for those working on the marine CO<sub>2</sub> system.

A comprehensive reference list and a wealth of additional information can be found in the Annotations while the Annexes provide further information and illustrative material concerning the history of the research into the marine CO<sub>2</sub> system.

### **Acknowledgement**

The authors are deeply grateful to MATTI PERTILÄ (Helsinki) for organizing access to the publications of KURT BUCH that appeared in Finnish journals and for additional information and historic photos. We also thank EEVA-LIISA POUTANEN (Helsinki), who provided biographical information on STINA GRIPENBERG, including a photo. The support of RUTH ANDERSON (ICES), for providing ICES documents, of ROLF MATTSSON (Helsinki), for the photo of K. BUCH together with captain O. MATTSSON, and of CARL ARTUR SVANSSON (Gothenburg) for translating a paper from Swedish into English is gratefully acknowledged. Finally, the authors thank the librarians of the Leibniz-Institute for Baltic Sea Research Warnemünde, OLIVIA DIEHR and MELANIE REHBEIN, for their gracious assistance in the often-difficult task of accessing historical papers and books.



## Annotations

- 1 FRIEDRICH DAVID LICHTENBERG (1774 – 1847), German pharmacist; about 1803 principal of the Pharmaceutical Society in Berlin, run a drugstore in Danzig from 1806 to 1837.
- 2 EDMOND FRÉMY (1814 – 1894), French chemist; entered 1831 the laboratory of the first chemical oceanographer JOSEPH LOUIS GAY-LUSSAC (1778 – 1850) (cf. WALLACE, 2004) and became assistant there in 1833; in 1850 he succeeded GAY-LUSSAC in the chair of chemistry at the National Museum of Natural History in Paris; from 1879 to 1891 he became director of the Museum.
- 3 BENOÎT-HENRY DARONDEAU (1805 – 1869), French hydrographer; participant of the voyage around the world on board the French corvette “La Bonité” in 1836/1837.
- 4 JEAN FRANÇOIS AUGUSTE MORREN (1804 – 1870), French physicist; 1830 professor of physics and chemistry and 1838 dean of the Royal College of Angers/France, 1841-1854 professor of physics in Rennes, 1854-1870 professor of physics in Marseille.
- 5 BERGNART CARL LEWY (1817 – 1863), Danish pharmacist and chemist; 1835-1838 study of chemistry at the Polytechnic College of Education in Copenhagen; 1840 assistant in the laboratory of the French chemist JEAN-BAPTISTE ANDRÉ DUMAS (1800 – 1884) in Paris; 1847-1851 professor of chemistry in Bogotá/Colombia.
- 6 FÉLIX PISANI (1831 – 1920), French chemist and mineralogist; studied chemistry in Paris at a private school for chemistry run by the French organic chemist CHARLES FRÉDÉRIC GERHARDT (1816 – 1856).
- 7 The JACOBSEN paper of 1874 is the English translation of the paper “Ueber die Luft des Meerwassers” (JACOBSEN, 1873a) republished for the U.S. Coast Survey.
- 8 THEODOR HEINRICH BEHRENS (1842 – 1905), German chemist; 1869-1874 assistant of the marine biologist VICTOR HENSEN (1835 – 1924) at the Physiological Institute of the Kiel University; from 1874 onwards professor of mineralogy, geology and mining at the Polytechnic School of Delft/Netherlands.
- 9 H.M.S. “Porcupine”, built in 1844, was a Royal Navy wooden paddle wheel steamer and served as a survey ship. In 1869, H.M.S. “Porcupine” carried out scientific explorations in the North Atlantic (cf. CARPENTER et al., 1869-1870).
- 10 JOHN HUNTER, at that time chemical assistant of the Queen’s College in Belfast; later professor of mathematics and natural philosophy at the University of King’s College in Windsor/Nova Scotia.
- 11 PETER MARTIN DUNCAN (1821 – 1891), English palaeontologist; professor of geology at the King’s College in London in 1870, and shortly afterwards appointed professor of geology at Cooper’s Hill College near Egham/Surrey.
- 12 On further details of the “Pommerania” Expedition cf. MATTHÄUS (2011).

- 13 S.M. Aviso "Pommerania", built as dispatch steamer between Stralsund and Stockholm in 1864, was commandeered by the Navy in 1870 (cf. MATTHÄUS, 2016).
- 14 DAVID HERCULES TORNØE (1856 – 1907), Norwegian chemist; in summer 1877 participant of the Norwegian North-Atlantic Expeditions 1876-1878 on board steamer „Vøringen“ for the investigation of the physical and biological conditions of the North Atlantic. From 1899 to 1901 assistant professor of physical chemistry under PETER WAAGE (1833 – 1900) at the University of Kristiania (see Annot. 28).
- 15 AUGUST VIERTHALER (1838 – 1901), Austrian chemist; professor of chemistry at the Imperial and Royal Austro-Hungarian Navy Academy in Trieste, dealt with chemical analyses of river and seawater near Split (Croatia) and Cetinje (Montenegro).
- 16 S.M.S. „Gazelle“, frigate of the Prussian Navy, built in the 1850s.
- 17 H.M.S. „Challenger“, Royal Navy wooden corvette, built in 1858; undertook the first global marine research expedition during 1873-1876.
- 18 JOHN YOUNG BUCHANAN (1844 – 1925), Scottish chemist and oceanographer; chemist of the "Challenger" Expedition 1873-1876. In the 1870s, BUCHANAN dealt intensively with carbon dioxide in seawater (BUCHANAN, 1873/1874, 1874).
- 19 Steamship „Vøringen“, build in 1861; chartered from a private owner for the Norwegian North-Atlantic Expedition 1876-1878.
- 20 ERNST VON BIBRA (1806 – 1878), German naturalist and writer.
- 21 The approach is based on an apparatus used by the German chemist and metallurgist WILHELM BORCHERS (1856 – 1925) (BORCHERS, 1878) and devised by the German chemist ALEXANDER MARTIN HUBERT CLASSEN (1843 – 1934) for determining carbon dioxide in carbonates.
- 22 WILHELM (WILLIAM) DITTMAR (1833 – 1892), German-born chemist; from 1861 to 1869 chief assistant in the chemical laboratory at Edinburgh University; from 1874 onwards professor of chemistry at the Andersonian College in Glasgow.
- 23 STEN GÖSTA WALIN (\*1938), Swedish oceanographer; 1964-1972 Department of Meteorology of the Stockholm University under BERT BOLIN (1925 – 2007); 1973 professor of oceanography at the Göteborg University.
- 24 Neutral carbonates (also: carbonic acid forming carbonates).
- 25 Acidic carbonates (also: carbonic acid forming bicarbonates).
- 26 RAY F. WEISS, geochemist; professor of geochemistry at the Scripps Institution of Oceanography, La Jolla/USA; specialist in trace gases in the atmosphere and in the oceans.
- 27 CATO MAXIMILIAN GULDBERG (1836 – 1902), Norwegian mathematician and chemist; pioneer in

physical chemistry; together with PETER WAAGE, he discovered and developed the "law of mass action" between 1864 and 1879 (GULDBERG & WAAGE, 1864).

- 28 PETER WAAGE (1833 – 1900), Norwegian chemist; professor of chemistry at the University of Kristiania (Oslo), brother-in-law of C. M. GULDBERG.
- 29 JACOBUS HENRICUS van't HOFF (1852 – 1911), Dutch physical chemist. He highly influenced the theoretical chemistry of his time and was a pioneer in chemical affinity, equilibrium, kinetics and thermodynamics (van't HOFF, J. H., 1884). First winner of the NOBEL Prize in chemistry in 1901. 1896-1911 professor at the Prussian Academy of Sciences in Berlin.
- 30 AXEL HAMBERG (1863 – 1933), Swedish geographer and physicist. In 1883, he participated as hydrographer in the Greenland-Expedition of the Arctic explorer ADOLF ERIK NORDENSKIÖLD (1832 – 1901) (HAMBERG, 1885). 1907-1928 professor of geography at the Uppsala University.
- 31 AUGUSTA PALMQVIST (1861 – 1930) was a student of OTTO PETERSSON. She worked on measurements of atmospheric carbon dioxide and on the design of equipment needed for such analyses during the 1880s and early 1890s (PETERSSON & PALMQVIST, 1887; TROILI-PETERSSON, 1897, 1898).
- 32 SVEN OTTO PETERSSON (1848 – 1941), Swedish chemist and oceanographer; father of oceanography in Sweden; 1881 professor of chemistry at the Stockholm University. He made improvements on the existing apparatus for measuring CO<sub>2</sub> in fluids and in the air (PETERSSON & HÖGLAND, 1889), worked out methods to determine carbon dioxide by gasometric analysis and reported values from some of the main deep stations in the Baltic proper.
- 33 Swedish Meteorological and Hydrological Institute
- 34 H.M.S. "Ingolf", Danish schooner-rigged steam gunboat, launched in 1876.
- 35 MARTIN HANS CHRISTIAN KNUDSEN (1871 – 1949), Danish physicist and oceanographer; 1912-1941 professor of physics at the Copenhagen University. 1902-1948 head of the ICES Service Hydrographique. He developed methods for defining the properties of seawater and was in charge of the Standard Seawater Service from 1908-1948.
- 36 CHRISTIAN BOHR (1855 – 1911), Danish physiologist, father of NIELS BOHR. 1886 professor of physiology at the Copenhagen University, in 1903 he described the "BOHR effect" whereby hydrogen ions and carbon dioxide heterotopically decrease hemoglobin's oxygen-binding affinity.
- 37 NIELS HENRIK DAVID BOHR (1885 – 1962), Danish physicist; made fundamental contributions to understanding atomic structure and quantum theory, founded the Institute of Theoretical Physics at the University of Copenhagen in 1920; 1922 NOBEL Prize in physics.
- 38 CHARLES J. J. FOX, British chemist; studied chemistry under the Scottish chemist WILLIAM RAMSAY (1852 – 1916) in London and the German chemist RICHARD WILHELM HEINRICH ABEGG (1869 – 1910) in Breslau. The Swedish physicist and oceanographer VAGN WALFRID EKMAN (1874 – 1954) (physics) and FOX (chemistry) were scientific assistants in the Central Laboratory

of ICES in Kristiania founded in 1902 and headed by the Norwegian marine scientist and polar explorer FRIDTJOF NANSEN (see Annot. 86). FOX left the Central Laboratory in 1907.

- 39 FOX also designed an apparatus for the complete extraction and estimation of dissolved gases in seawater (FOX, 1905, cf. A III, p. 84), but OTTO PETERSSON was of the opinion that the apparatus was too complicated for general use (SMED, 2005).
- 40 SØREN PETER LAURITZ SØRENSEN (1868 – 1939), Danish biochemist; studied medicine and chemistry at the Copenhagen University; he introduced the concept of pH as measure for acidity; from 1901 to 1938 he was head of the chemical department of the Carlsberg Laboratory in Copenhagen.
- 41 HERBERT SPENCER HARNED (1888 – 1969), U.S. American chemist; studied chemistry at the University of Pennsylvania in Philadelphia/USA; served in the Chemical Warfare Service of the U.S. Army during World War I; from 1928-1957 professor of chemistry at Yale University in New Haven; from 1943-1945 group leader for the Manhattan Project (Project for research and development of first nuclear weapons); from 1950-1965 consultant for the Oak Ridge National Laboratory (for details cf. STURTEVANT, 1980).
- 42 HARNED Cell, originally developed by HERBERT S. HARNED and co-workers in the 1930s for primary pH measurements (cf. HARNED & ROBINSON, 1928).
- 43 SVEN PALITZSCH (1882 – 1959), Danish chemist; from 1905-1919 assistant of SØRENSEN at the Carlsberg Laboratory in Copenhagen; he became known as specialists on examination hydrogen ion concentrations in seawater.
- 44 R/V "Thor", Danish steam trawler, built in 1899; between 1903 and 1927 research vessel of the Danish Ministry of Agriculture and Fishing; carried out two expeditions to the Mediterranean Sea in 1908-1910 funded by the Carlsberg Foundation (NIELSEN, 1912).
- 45 ERNST RUPPIN, German chemist; from 1902 onwards assistant at the Kiel Hydrographic Laboratory directed by OTTO KRÜMMEL from 1902 to 1911.
- 46 JOHANN GOTTFRIED OTTO KRÜMMEL (1854 – 1912), German geographer and oceanographer; 1883-1911 professor of geography at the Kiel University; pioneer of the oceanography in Germany; 1902-1911 member of the Central Bureau of the International Council for the Exploration of the Sea (ICES) in Copenhagen.
- 47 Pojowiek (Pojoviken) near Hanko; the only fjord of Finland is 15 km long and is considered as small model of the Baltic Sea.
- 48 JOHN JOHNSTON (1881 – 1950), Scottish born chemist; 1908-1916 Geophysical Laboratory of the Carnegie Institution of Washington; in 1920 he became the first Sterling professor at the Yale University in New Haven/USA.
- 49 JAMES WALKER (1863 – 1935), Scottish chemist; his main research interest was in physical chemistry; spent several years in Germany, working among others with WILHELM OSTWALD (1853 – 1932); 1894-1908 appointed professor of chemistry at the University College in

Dundee (today University of Dundee) and 1908-1928 professor of chemistry at the University of Edinburgh.

- 50 WILLIAM CORMACK, chemist at the University College in Dundee/Scotland.
- 51 Quotations in German are generally translated into English. The translation attached in brackets is not a literal one but reflects the content of the paragraph.
- 52 WILLIAM NICOL (1770 – 1851), Scottish geologist and physicist; invented the first device for obtaining plane-polarized light in 1828, the so-called NICOL Prism.
- 53 FRIEDRICH FRANZ MARTENS (1873 – 1939), German physicist; 1892 study of mathematics and natural sciences at Rostock University/Germany; 1905/06 assistant professor at the Rostock University; from 1906 onwards Handels-Hochschule Berlin, Institute of Physics.
- 54 FRITZ GRÜNBAUM, German physicist; Handels-Hochschule Berlin, Institute of Physics.
- 55 LEONOR MICHAELIS (1875 – 1949), German-American biochemist; in 1903 study of medicine and in 1908 professor at the Berlin University; 1922-1926 professor of biochemistry in Nagoya/Japan; in 1926 JOHNS-HOPKINS-University in Baltimore/USA and from 1929-1941 ROCKEFELLER Institute of Medical Research in New York.
- 56 PETER RONA [until 1892 PETER ROSENFELD] (1871 – 1945), German physician and physiologist; as successor of L. MICHAELIS he was professor of medical chemistry at the Berlin University and director of the chemical department of the Pathological Institute from 1921 until the coming of the Nazis in 1933.
- 57 FRIEDRICH AUERBACH (1870 – 1925), German chemist; senior civil servant in the Imperial Health Office of Germany in Berlin.
- 58 HANS PICK (1884 – ?), from 1910 onwards scientific assistant in the Imperial Health Office of Germany in Berlin.
- 59 Steamship "Nautilus", Finnish research vessel, built in 1903 for ichthyologic and marine research; used by the Finnish Institute of Marine Research from 1903 to 1933.
- 60 Finnish Civil War (from January to May 1918); Finland was independent since 6 December 1917 and fought for the leadership and control during the country's transition from a Grand Duchy of the Russian Empire to an independent state.
- 61 JARL JOHAN LINDBERG (1921 – 2008), Finnish chemist, one of the last students of KURT BUCH; from 1952 onwards assistant, 1959-1969 docent of physical chemistry and from 1969 to 1987 professor of polymer chemistry at the Helsinki University. He published a paper on the life of BUCH (LINDBERG, 1970).
- 62 PETER JOSEPH WILLIAM DEBYE (1884 – 1966), Dutch physical chemist; 1935-1939 director of the Kaiser-Wilhelm-Institute for Physics and professor of theoretical physics at the FRIEDRICH-WILHELMS-University at Berlin; NOBEL Prize in chemistry in 1936 for his contributions to the

study of molecular structure; after leaving Germany in early 1940, DEBYE became a professorship at the Cornell University in Ithaca, New York, and chaired the chemistry department for 10 years.

- 63 ERICH ARMAND ARTHUR JOSEPH HÜCKEL (1896 – 1980), German chemist and physicist; pioneer in quantum chemistry; as assistant to DEBYE he developed an improvement of SVANTE ARRHENIUS' theory of electrical conductivity in electrolyte solutions in 1923.
- 64 DEBYE-HÜCKEL Theory, proposed by PETER DEBYE and ERICH HÜCKEL; describes the electrostatic interactions of ions in electrolyte solutions; the theory is regarded as a major forward step in the understanding of electrolytic solutions.
- 65 KARL ALBERT HASSELBALCH (1874 – 1962), Danish physician and chemist; was a pioneer in the use of pH measurement in medicine together with CHRISTIAN BOHR (see Annot. 36).
- 66 JAMES PICKERING KENDALL (1889 – 1978), British chemist; in 1912, he worked with SVANTE ARRHENIUS on electrolytes in the NOBEL Institute for Physical Chemistry in Stockholm; 1915-1926 professor of chemistry at Columbia University, New York, interrupted by World War I; 1928-1959 professor of chemistry at the Edinburgh University as successor of JAMES WALKER (see Annot. 49).
- 67 ERIK JOHAN WARBURG (1892 – 1969), Danish physician; professor of medicine at the Copenhagen University from 1931 to 1962.
- 68 ROLF JOHAN WITTING (1879 – 1944), Finnish oceanographer and politician; founder of physical oceanography in Finland; studied geophysics and geography at the Helsinki University; 1902-1910 assistant at the Finnish Institute of Marine Research (FIMR); 1918-1936 first Director of the FIMR; member of the Finnish Parliament; 1934-1936 deputy minister and 1940-1943 Minister of Foreign Affairs.
- 69 VICTOR MORITZ GOLDSCHMIDT (1888 – 1947), Norwegian geochemist; 1914-1929 professor of mineralogy at the University in Kristiania; 1929-1935 professor at the University of Göttingen/Germany; discovered the so-called GOLDSCHMIDT Tolerance Factor in 1926.
- 70 GUY STEWART CALLENDAR (1898 – 1964), British steam engineer and inventor; in 1938, he developed the theory that rising carbon dioxide concentrations in the atmosphere are linked to global temperature, today known as CALLENDAR Effect; he assessed the climate sensitivity value at 2 °C.
- 71 Survey vessel „Meteor“, launched in 1915, intended to become a gunboat for the Imperial German Navy, commissioned as a military ship for the German Reichsmarine in 1924, undertook the German Atlantic Expedition between 1925 and 1927 and a North Atlantic Expedition in 1937/38.
- 72 FRITZ JAKOB HABER (1868 – 1934), German chemist; 1911-1933 director of the Kaiser-Wilhelm-Institute for Physical Chemistry and Electrochemistry in Berlin, invented the HABER-BOSCH Process.

- 73 ALFRED CLARENCE REDFIELD (1890 – 1983), American oceanographer; 1921-1956 professor of physiology at the Harvard University in Cambridge/Mass.; discovered the so-called REDFIELD Ratio, the ratio between nutrients in plankton and ocean water.
- 74 STIG HENRIK FONSELIUS (1921 – 2003), Swedish chemical oceanographer; student of KURT BUCH, studied chemistry at the University of Helsinki. Later he studied atmospheric chemistry especially the carbon dioxide in the atmosphere at the International Meteorological Institute in Stockholm under the leadership of CARL-GUSTAF ROSSBY (1898 – 1957). From 1959 to 1987, he worked at the Hydrographic Department of the Board of Fisheries, later SMHI Oceanographic Laboratory in Göteborg. For some details see also ROZWADOWSKI (1998).
- 75 FOLKE ANDRÉ KOROLEFF (1918 – 2003), Finnish chemical oceanographer; student of KURT BUCH. Finnish Institute of Marine Research, Helsinki.
- 76 HANNA WITTIG (1910 – 1944), German chemist; from 1938 onwards assistant at the Institute of Marine Research in Kiel.
- 77 JEAN BAPTISTE JOSEPH FOURIER (1768 – 1830), French mathematician and physicist; initiating the investigation of FOURIER series; from 1795 onwards professor on analysis and mechanics at the École Polytechnique in Paris as successor of the Italian mathematician and astronomer JOSEPH-LOUIS DE LAGRANGE (1736 – 1813).
- 78 EUNICE NEWTON FOOTE (1819 – 1888), American physicist and inventor. She conducted a series of experiments that demonstrated the interactions of the sun's rays on different gases like carbon dioxide, common air and hydrogen.
- 79 JOHN TYNDALL (1820 – 1893), Irish physicist; studied under ROBERT BUNSEN (1811 – 1899) at the University of Marburg/Germany and received there a doctor's degree. Beginning in the late 1850s, he studied the action of radiant energy on the constituents of air (TYNDALL, 1872).
- 80 Already in 1893, ARVID GUSTAF HÖGBOM (1857 – 1940) investigated the increase of the temperature of the atmosphere by fossil burning (HÖGBOM, 1895). ARRHENIUS incorporated the most important parts in his paper from 1896 (ARRHENIUS, 1896b), but with respect to the "greenhouse effect" HÖGBOM was hardly referred to, cf. CRAWFORD (1996).
- 81 CHARLES DAVID KEELING (1928 – 2005), American oceanographer; 1956-2005 Scripps Institution of Oceanography, La Jolla/California; he showed that carbon dioxide levels in the atmosphere were rising steadily what later became known as the "KEELING Curve".
- 82 HEINRICH ADOLPH MEYER (1822 – 1889), merchant, factory owner and sponsor of German oceanography; carried out the earliest systematic investigations of the oceanographic conditions in the western Baltic Sea during the late 1850s.
- 83 GUSTAV KARSTEN (1820 – 1900), German physicist; from 1847 to 1894 professor of physics and mineralogy at the Kiel University. He was one of the leading German marine scientists of the 19<sup>th</sup> century.

- 84 GEORGES AIMÉ (1810 – 1846), French physicist; studied the Mediterranean Sea between 1838 and 1846, invented oceanographic instruments, devices and methods.
- 85 HEINRICH GEORG VON BOGUSLAWSKI (1827 – 1884), German hydrographer; from 1874 onwards section-chief in the Hydrographic Office of the Imperial Admiralty in Berlin.
- 86 FRIDTJOF WEDEL-JARLSBERG NANSEN (1861 – 1930), Norwegian polar explorer, oceanographer and diplomat. Between 1893 and 1896, he drifted across the Arctic Ocean aboard research vessel "Fram". Later he contributed to the development of oceanographic equipment, NOBEL Peace Prize in 1922.
- 87 SHALE JACK NISKIN (1926 – 1988), American engineer and inventor.
- 88 JENS SMED (1914 – 2016), Danish physicist, ICES hydrographer in 1946; 1948-1984 head of the ICES Service Hydrographique as successor of MARTIN KNUDSEN. He developed ICES as a regional oceanographic data centre.
- 89 OSCAR FRITHIOF NORDQUIST (1858 – 1925), Finnish hydrographer. He accompanied ADOLF ERIK NORDENSKIÖLD (1832 – 1901) in the voyage of the S.S. "Vega" through the Northeast Passage in 1879.
- 90 For details of the foundation of ICES cf. WENT (1972) and ROZWADOWSKI (2002).
- 91 The background of the Finnish participation in ICES before Finland gained independence is described by MÄLKKI (1990).
- 92 VIKTOR THEODOR HOMÉN (1858 – 1923), Finnish physicist and politician; professor of applied physics at the Helsinki University; as member of a passive resistance movement in Finland, HOMÉN was arrested and exiled at Novgorod in Russia in 1904, however returned home in February 1905, from 1908 to 1913 member of the Parliament of Finland.
- 93 HEIKKI JUHANI SIMOJOKI (1906 – 1990), Finnish geophysicist; 1945-1956 Finnish Institute of Marine Research; 1967-1972 professor of geophysics at the Helsinki University.
- 94 HAAKEN HASBERG GRAN (1870 - 1955), Norwegian marine botanist; from 1897 onwards, he dealt with marine zoology under JOHAN HJORT (see Annot. 98) and together with hydrographer FRIDTJOF NANSEN (see Annot. 86); from 1905 to 1940 professor of botany and director of the University Botanical Garden in Kristiania; GRAN was among the founders of ICES.
- 95 ERNST SCHREIBER (1896 – 1980), German marine botanist; 1925-1936 curator of bontology at the Biologische Anstalt Helgoland (BAH); later professor at the University in Frankfurt am Main/Germany.
- 96 ALF KLEM (1903 – 1941), Norwegian biologist.
- 97 BIRGITHE RUUD FØYN (1900 – 1985), Norwegian planktologist; in 1928 assistant of H. H. GRAN.



- 98 JOHAN HJORT (1869 – 1948), Norwegian fisheries scientist and oceanographer; 1900-1916 director at the Norwegian Institute of Marine Research in Bergen; 1921-1939 professor of marine biology at Oslo University. He was among the founding fathers of ICES, Norwegian delegate at ICES from 1902 to 1938 and from 1938 to 1948: president of ICES.
- 99 TORBJØRN GAARDER (1885 – 1970), Norwegian chemist, pioneer of biochemistry in Norway, University of Bergen. He also dealt with carbon dioxide in seawater and other fluids (GAARDER, 1926).
- 100 ARTHUR EDWARD JAMES WENT (1910 – 1980), Irish fisheries biologist and historian; 1966-1969 president of ICES.
- 101 EMORY D. ANDERSON (\*1939), American fisheries biologist; National Marine Fisheries Service (NMFS), Northeast Fisheries Science Center, Woods Hole/USA; 1989-1993 general secretary of ICES.
- 102 HELEN M. ROZWADOWSKI, professor of history and maritime studies at the University of Connecticut in Avery Point/USA.
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**Annex A I**

Scientists concerned with the investigation of the carbon dioxide system in seawater during the 19<sup>th</sup> and the first half of the 20<sup>th</sup> century

**OSCAR JACOBSEN (1840 – 1889)**

(Photo: Archive of the Rostock University)

GEORG OSCAR FRIEDRICH JACOBSEN (born on 25 June 1840 in Ahrensburg/Germany; died on 24 August 1889 in Rostock/Germany), German chemist and first German chemical oceanographer.

JACOBSEN started studies in pharmacy and chemistry at the Kiel University in 1864. He worked as assistant at the chemical laboratory of the University under AUGUST FRIEDRICH CARL HIMLY (1811 – 1885) from 1865 to 1872. In 1868, he made his doctorate in organic chemistry. From 1873 to 1889, he was professor of chemistry at the Rostock University and had a decisive part in the development of chemical research in Rostock.

JACOBSEN was the first German chemist interested in both the chemical analysis of the salts and the amount and composition of atmospheric air dissolved in seawater – mainly oxygen, nitrogen and carbon dioxide. He participated in two cruises of S.M. Aviso "Pommerania" for investigations in the Baltic and North Sea in 1871 and 1872 (MATTHÄUS, 2011). Moreover, he was working on the development of methods for chemical analysis suitable for use on board of vessels, on the construction of improved sampling bottles and on the importance of salinity for physical processes in the sea. In 1872, he was the first who started systematic investigations of carbon dioxide in the North Sea. For more details on O. JACOBSEN cf. MATTHÄUS (2010).



**AUGUST KROGH (1874 – 1949)**

(Photo from Wikipedia, 2019)

SCHACK AUGUST STEENBERG KROGH (born on 15 November 1874 in Grenaa/Denmark; died on 13 September 1949 in Copenhagen/Denmark), Danish physiologist, was a pioneer in comparative physiology. He investigated the carbon dioxide system in natural waters including seawater in the North Atlantic in 1902.

He attended the University of Copenhagen in 1893, studied medicine and later zoology and gained his doctorate in 1903. In 1897, he became assistant at the Institute of Medical Physiology in Copenhagen. KROGH began lecturing in the University of Copenhagen in 1908. From 1916 to 1945 KROGH was professor of zoophysiology at the University of Copenhagen.

In 1902, KROGH was invited to take part in an expedition to Greenland during which he investigated the general relationship between CO<sub>2</sub> in the atmosphere and in the ocean.

In 1920, KROGH was awarded the Nobel Prize in Medicine and Physiology. For details cf. also LILJESTRAND (1950) and SCHMIDT-NIELSEN (1995).





**SVANTE ARRHENIUS (1859 – 1927)**

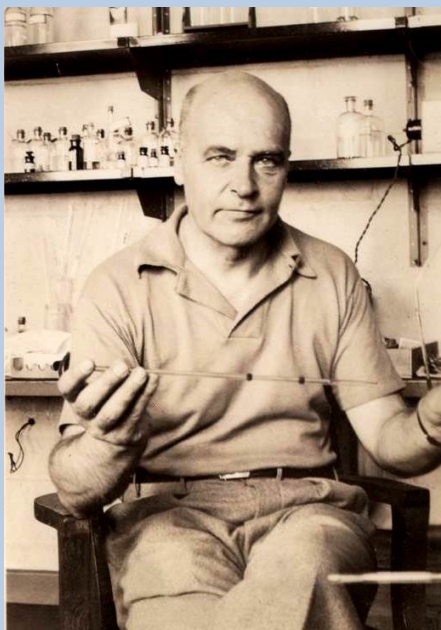
in 1909 (Photo from OSTWALD, 1909)

SVANTE AUGUST ARRHENIUS (born on 19 February 1859 near Uppsala/Sweden; died on 2 October 1927 in Stockholm/Sweden), Swedish physicist and chemist, one of the founders of the science of physical chemistry.

From 1876 onwards ARRHENIUS studied mathematics and natural sciences at the Universities of Uppsala and Stockholm. In 1884, he gained his doctorate based on a paper on electrolytic dissociation (ARRHENIUS, 1884). Between 1884 and 1890, he worked under the most famous physical chemists of that time like WILHELM OSTWALD (1853 – 1932) in Riga und Leipzig, FRIEDRICH WILHELM KOHLRAUSCH (1840 – 1910) in Würzburg, LUDWIG BOLTZMANN (1844 – 1906) in Graz and JACOBUS HENRICUS van't HOFF (1852 – 1911) in Amsterdam. In 1891, he became lecturer and from 1895 onwards professor of physics at the Stockholm University. From 1905 to 1927, he was director of the Nobel-Institute of Physical Chemistry at Stockholm.

His most important scientific work was the development of the theory of the electrolytic dissociation (ARRHENIUS, 1884). He identified for the first time the importance of atmospheric carbon dioxide for the climate of the earth (ARRHENIUS, 1896a, 1896b, 1908).

In 1903, ARRHENIUS was awarded the Nobel Prize in Chemistry. For further details cf. RIESENFELD (1931) and CRAWFORD (1996).



**KURT BUCH (1881 – 1967)**

(Photo: Earth Science Center of the Göteborg University/Sweden)

KURT KARL WILHELM BUCH (born on 9 May 1881 in Helsingfors/Finland; died on 4 January 1967 in Herrljunga/Sweden), Finnish chemical oceanographer, has a decisive part in investigation of the carbon dioxide system in seawater.

The family of KURT BUCH originates from Thuringia (Germany). His father became Finnish citizen in 1885. In 1899, KURT BUCH started studies in medicine and later in chemistry at the University in Helsinki. He finished his study in chemistry in 1904. Thereafter, he became an assistant at the Agricultural Chemistry laboratory of the University of Helsinki, headed by the chemist ARTHUR RINDELL (1852 – 1936). Through RINDELL he came for the first time in contact with problems concerning chemical equilibria and the aqueous carbon dioxide system.

After two years in the laboratory, he went to Germany and continued studies in physical chemistry at the University of Breslau. After returning in 1908, he worked seven years in a hydrographic-biological research group of the Finnish Society of Sciences dealing with investigations of the carbon dioxide content and partial pressure of seawater. In 1917, he finished his doctor thesis (BUCH, 1917a). In 1918, the Finnish Institute of Marine Research was founded and BUCH was appointed head of the chemical department (1919 – 1935). In 1928, he was invited by ICES to take part in a working group to develop chemical methods for the determination of nutrients in seawater and, in 1931, asked to lead a commission for investigations on the chemical equilibria within the marine CO<sub>2</sub> system.

BUCH was appointed assistant professor in chemistry at the Helsinki University in 1927 and professor of chemistry at the Åbo Academy in Turku (1934 – 1942). In 1935, he was invited by the Woods Hole Oceanographic Institution for investigations on oceanographic-chemical problems and, in 1941, he gave lectures in Hamburg, Kiel and Berlin in Germany. During the World War II and afterwards BUCH finalized his laboratory investigations on carbon dioxide equilibria in seawater and on related biochemical metabolisms in the Baltic Sea, mostly at the Finnish Institute of Marine Research.

BUCH was appointed member of the Finnish Society of Sciences in 1933 and became their chairman in 1952/53. For further details on K. BUCH cf. LINDBERG (1970).



**HERMANN WATTENBERG (1901 – 1944)**

(Photo reproduced with the kind permission of Schleswig-Holsteinische Landesbibliothek Kiel)

KARL FRIEDRICH HERMANN WATTENBERG (born on 16 April 1901 in Berlin/Germany; died on 24 July 1944 in Kiel/Germany), German marine chemist, advocate for interdisciplinary cooperation in marine research, contributed to investigations of the carbon dioxide system in seawater.

WATTENBERG studied chemistry in Hannover and Munich from 1919 onwards. In 1923, he finished his doctor thesis in inorganic and analytical chemistry. In 1924, he became assistant at the Technical College in Danzig. He participated in the German "Meteor" Expedition 1925-1927. Later he was research assistant at the chemical institute of the Munich University and at the Institute of Marine Research in Berlin where he expanded his expertise in nutrient chemistry, in the calcium carbonate saturation and in the carbon dioxide system of seawater.

In 1931, WATTENBERG became member of the ICES-commission for investigations on the thermodynamics of the marine carbon dioxide system. The commission, headed by KURT BUCH, worked for three months in Helsinki in spring 1931. He got his postdoctoral lecture qualification in 1934. From 1934 onwards he acted as head of the Marine Chemistry Laboratory of the Kiel University. His research field was then mainly focused on the Baltic Sea. In 1938 WATTENBERG was appointed as a professor and head of the hydrographic-chemical department at the Institute of Marine Research in Kiel, founded in 1937. In 1944, he became director of the institute. For more details on H. WATTENBERG cf. BÖHNECKE (1944), BUCH (1949) and EHRHARDT (1986).



**HILDEBRAND WOLFE HARVEY (1887 – 1970)**

(Photo from COOPER, 1972)

HILDEBRAND WOLFE HARVEY (born on 31 December 1887 in London/Great Britain; died on 26 November 1970 in Plymouth/Great Britain), British marine chemist, had part in investigation of the carbon dioxide system in seawater.

In 1906, HARVEY entered the Downing College in Cambridge and studied natural sciences, finished his master's degree in 1924 and awarded the degree of Sc. D. in 1937. In 1921, he joined the staff of the Marine Biological Association of the United Kingdom at Plymouth as administrative and hydrographic assistant, and worked there until 1958 when he retired. In 1928, he published his first book on "Biological chemistry and physics of sea water" (HARVEY, 1928). In 1931, HARVEY was invited to the ICES-Committee for investigation on the carbonic dioxide system in seawater headed by KURT BUCH.

In the following years he dealt mainly with questions of the biological productivity in the sea. In 1945, he published the monograph "Recent advances in chemistry and biology of sea water" (HARVEY, 1945). In his book "The chemistry and fertility of sea waters" published in 1955 he summarized the results of his investigations in relation to the physical oceanography, biological productivity and the carbon dioxide system (HARVEY, 1955).

In 1952, he was awarded the ALEXANDER AGASSIZ Medal of the United States National Academy of Sciences. For more details on H. W. HARVEY cf. COOPER (1972).



**STINA GRIPENBERG (1891 – 1979)**

(Photo: Earth Science Center of the Göteborg University/Sweden)

HEDVIG CHRISTINA AUGUSTA GRIPENBERG (born on 6 August 1891 in Elimäki/Finland; died on 23 March 1979 in Paris/France), Finnish chemical oceanographer, analytical chemist, participated in investigations on the carbon dioxide system in seawater.

STINA GRIPENBERG started to study chemistry at the Åbo Akademi in Turku, later at the University of Helsinki. In 1923, she became chemical assistant at the Finnish Institute of Marine Research in Helsinki. In 1926, STINA GRIPENBERG visited marine scientific laboratories in Monaco, Plymouth and the United States. She finished her doctor thesis on the chemical composition of Baltic Sea sediments at the University of Helsinki in 1934 (GRIPENBERG, 1934, 1939). She was the first female doctor in the chemistry department. Though being employed at the Finnish Institute of Marine Research, she also worked at several occasions in Sweden. In 1931, GRIPENBERG became member of the ICES-commission for investigation on the thermodynamics of the carbon dioxide system in seawater. In 1937/38, she performed studies on the analysis of organic carbon in marine sediments at the Scripps Institution of Oceanography in San Diego/USA.

GRIPENBERG headed the Oceanographic Institute in Gothenburg at the time when the Swedish "Albatross" deep sea expedition took place in 1947/48. In 1957-1958 she returned to the Finnish Institute of Marine Research.

## Annex A II

### The problem of obtaining uncontaminated water samples for analysis of carbon dioxide dissolved in seawater

As mentioned in Chapter 2, problems existed in the 19<sup>th</sup> century in obtaining samples for analysis of gases dissolved in seawater. An appropriate sampling method which avoided contamination of the sample by the ambient air was lacking.

During the investigations by JACOBSEN (1873b) at the Baltic Sea Expedition aboard "Pommerania", simple glass bottles were used which were developed by the merchant and factory owner HEINRICH ADOLPH MEYER<sup>82</sup> (MEYER, 1871; KARSTEN,<sup>83</sup> 1873). The closed bottle (Box A, left) used for water sampling at shallow depths was submerged, opened at the desired sampling depth and lifted up after no longer air bubbles raised to the water surface. This sampling method was sufficient for identification of salinity but inadequate for the analysis of dissolved gases in seawater (JACOBSEN, 1873b).

In order to investigate whether the air content of seawater increases with depth – as earlier investigations seemed to show (DARONDEAU,<sup>3</sup> 1838b; AIMÉ,<sup>84</sup> 1843) – JACOBSEN, assisted by HEINRICH BEHRENS,<sup>8</sup> constructed a special rubber water sampler which avoided contact of the sample with air (Box B, Fig. 2).

For obtaining samples unaffected by ambient air

*"...a sac, a, of non-vulcanized caoutchouc is prepared [and] ... is tightly stretched over the trumpet-shaped end of the brass neck, b, ... Overlying it rests a similarly-shaped somewhat overlapping bell, c. By means of a three-armed ring, d, turning in a screw cut in the neck, b, the bell, c, can ... be made to press down upon the caoutchouc cover. The neck, b, has a slightly conic horizontal bore to receive a carefully finished stop-cock, e, ... The fork, f, acts as a lever for so turning the stop-cock that the apparatus, with the position of the fork indicated in the illustration [see Box B, Fig. 2], is open and becomes closed by pressing down the fork ... The whole rests upon a varnished iron trevet, h... A floater ... is attached at i to the handle of the fork f, and on the other side at k a sinker is suspended from a short line." (JACOBSEN, 1974, p. 9/10).*

Later on, the mechanic LUDWIG STEGER from Kiel simplified the construction and the sampler could be used without the floater (Box B, Figs. 3 and 4).

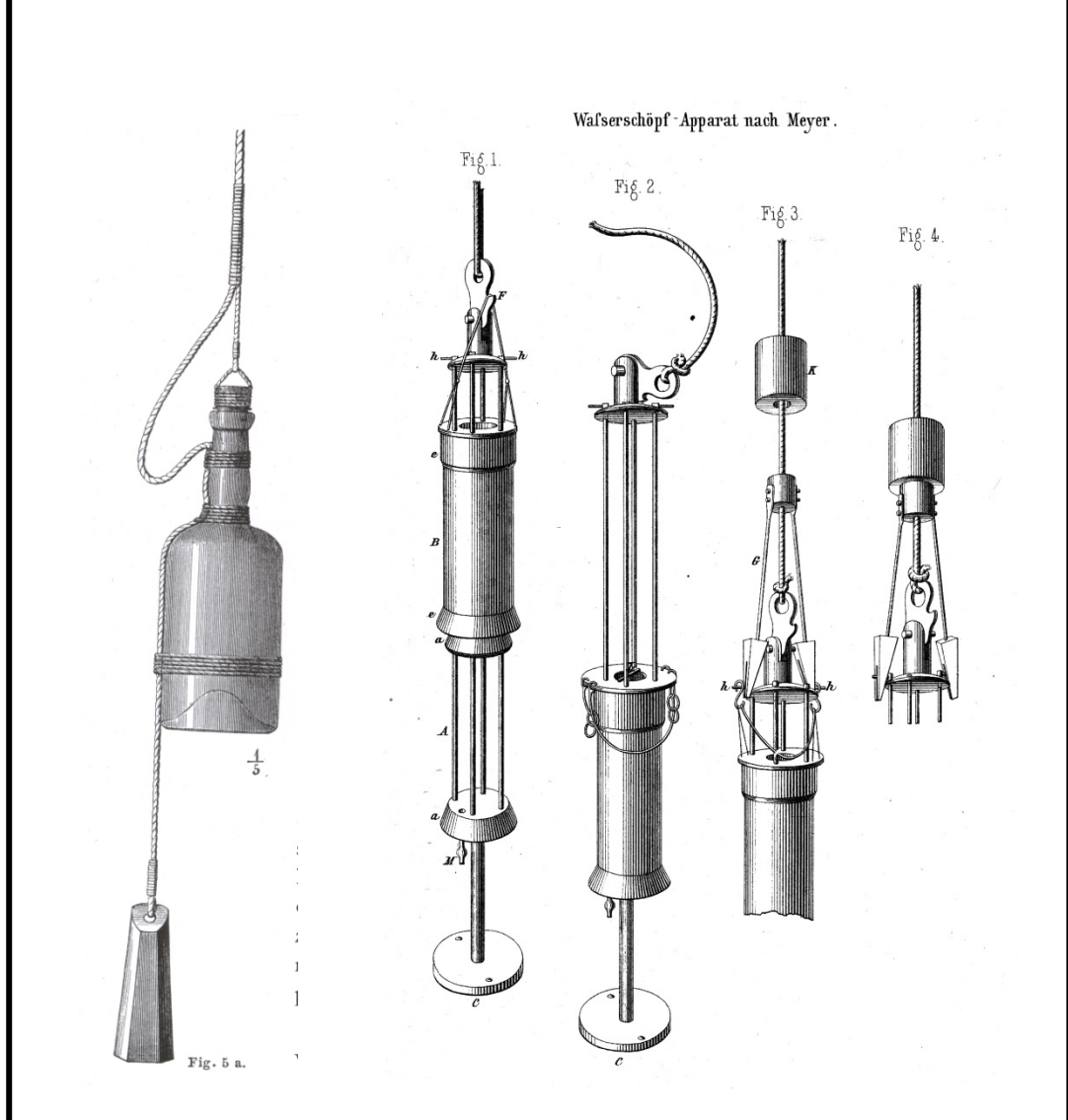
Before lowering the apparatus the sac a was filled

*"... to one-fifth of its volume with mercury [and has the position in Fig. 3 during lowering] ... As soon as the sinker touches the bottom the floater opens the stop-cock and the caoutchouc sac, expanding by the intruding water, will assume its proper shape [Box B, Fig. 4]. At the moment it leaves the bottom the apparatus is again hermetically closed." (JACOBSEN, 1974, p. 10)*

and an uncontaminated water sample was obtained.

## Box A

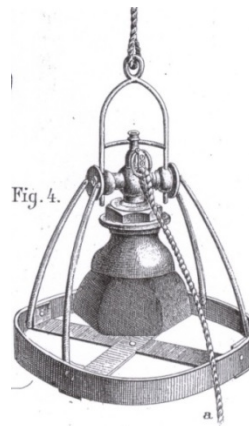
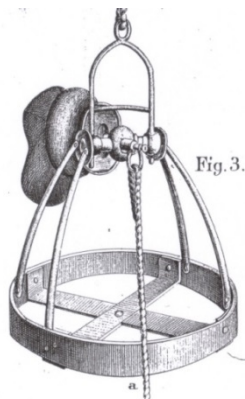
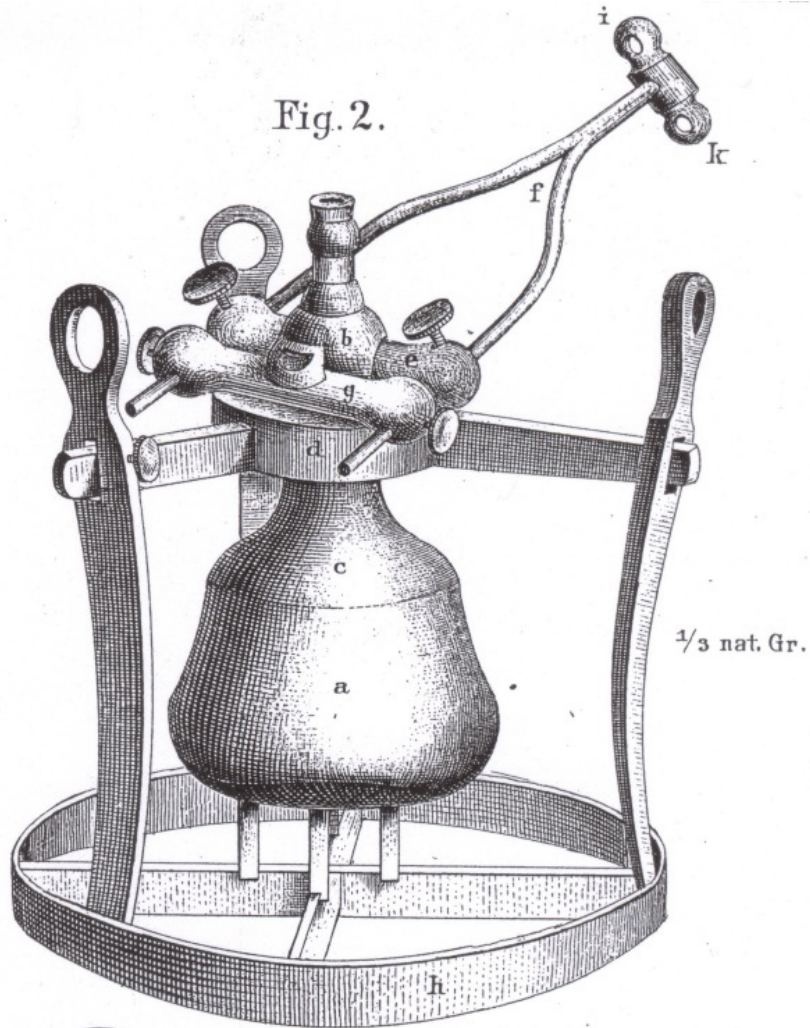
*Water samplers developed by H. A. MEYER and used by OSCAR JACOBSEN during the expeditions of S.M. Aviso „Pommerania“ in the Baltic Sea in 1871 (left) (from KARSTEN, 1973) and in the North Sea in 1872 (right, Figs. 1-4) (from ANON., 1889).*



However, experiments showed that avoiding contact of the water sample with air enclosures could also be achieved by more simple constructed water bottles like those designed by MEYER (1875) (see Box A, Figs. 1-4). MEYER's water bottle worked successfully during the North Sea cruise of "Pommerania" in 1872 (JACOBSEN, 1873b, 1875), was tested with success during the famous "Challenger" circumnavigation (1872-1876) (BUCHANAN,<sup>18</sup> 1878) and used during the voyage of S.M.S. "Gazelle" (1874-1876) (see MEYER, 1875; v. BOGUSLAWSKI,<sup>35</sup> 1884; KRÜMMEL,<sup>46</sup> 1886, 1907; ANON., 1889). Later on, it was even delivered to the United States and Russia (MEYER, 1875).

## Box B

*Sophisticated rubber sampler for contamination-free sampling of seawater for the analysis of dissolved atmospheric gases, designed by JACOBSEN and BEHRENS and constructed by mechanic LUDWIG STEGER (above, Fig. 2). The principle of sampling operation (below, Fig. 3 and 4) (from JACOBSEN, 1875).*

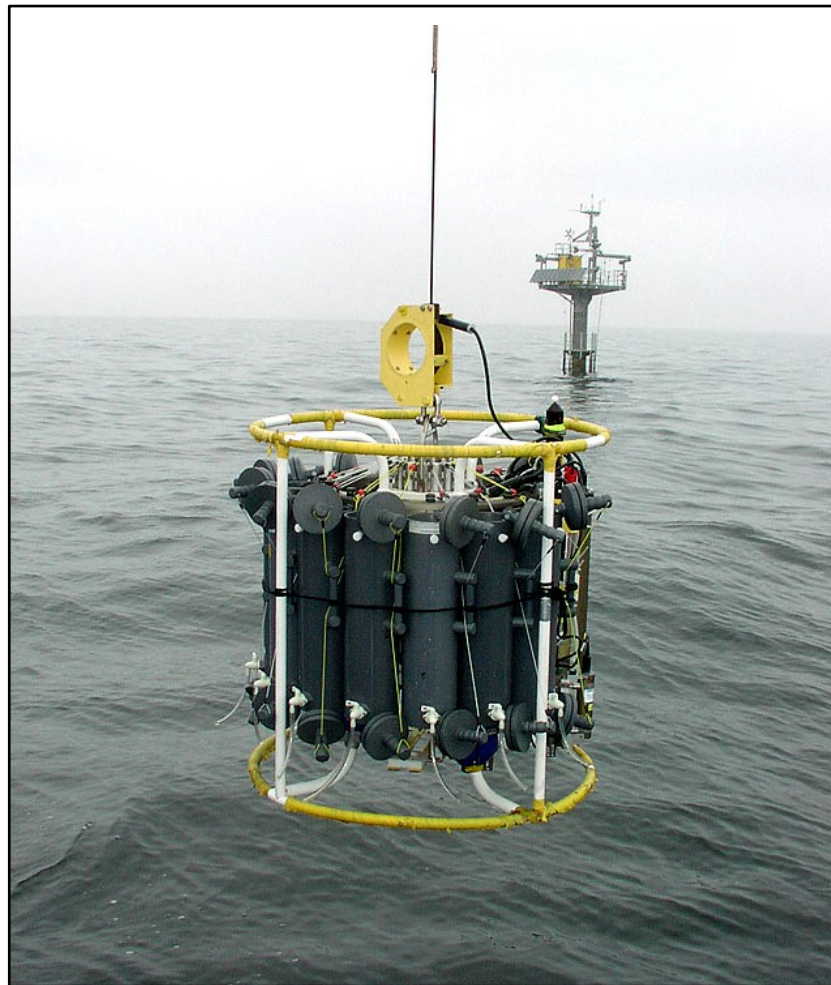




Since then, the sampling techniques suitable for the subsequent analysis of dissolved gases, e.g. CO<sub>2</sub>, have hardly changed. A modification, called NANSEN water bottle, was designed by the Norwegian oceanographer FRIDTJOF NANSEN<sup>86</sup> in 1894 and frequently used since then. The NANSEN bottle was improved by the American inventor SHALE JACK NISKIN<sup>87</sup> in 1966 through replacing the metal bottle by a plastic tube with a lid at both sides. Opening and closing of the lids occurs either manually or is controlled by a computer. Nowadays, an array of NISKIN water bottles which also holds a CTD probe ("rosette", Box C) is mainly used.

### Box C

*CTD probe with NISKIN water bottles mounted in a circular frame (rosette). In the background the German automated measuring station "Arkona Sea" (IOW Photo gallery).*



## Annex A III

Equipment for the determination of the content of carbon dioxide in seawater used between 1870 and 1905

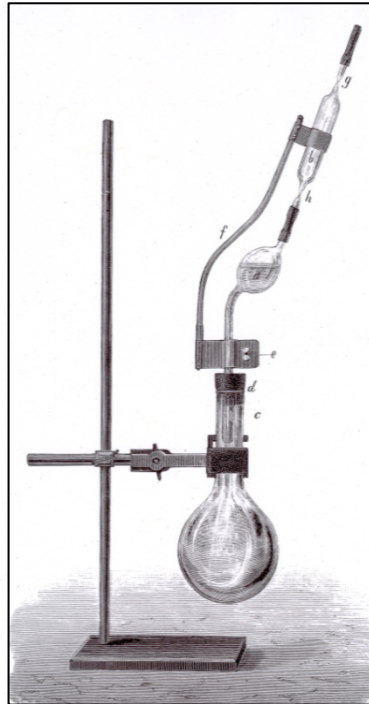


Fig. 1: Apparatus for extraction of dissolved oxygen and nitrogen gases for use on board of ships, designed by JACOBSEN and BEHRENS (from TORNØE, 1880a) (unsuitable for carbon dioxide).

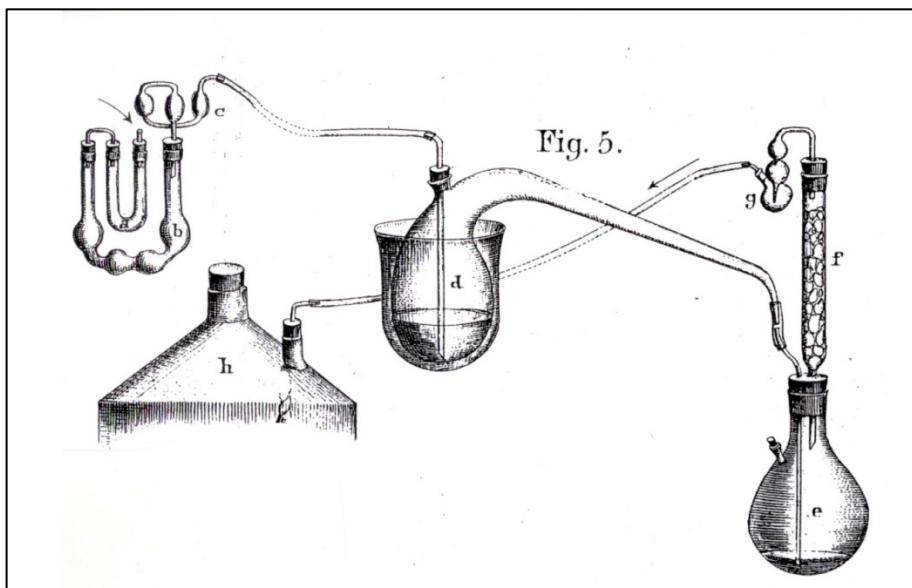


Fig. 2: Arrangement for the extraction of CO<sub>2</sub> from a seawater sample through boiling in a stream of CO<sub>2</sub>-free air and subsequent titrimetric determination, designed by OSCAR JACOBSEN in 1872 (from JACOBSEN, 1875).

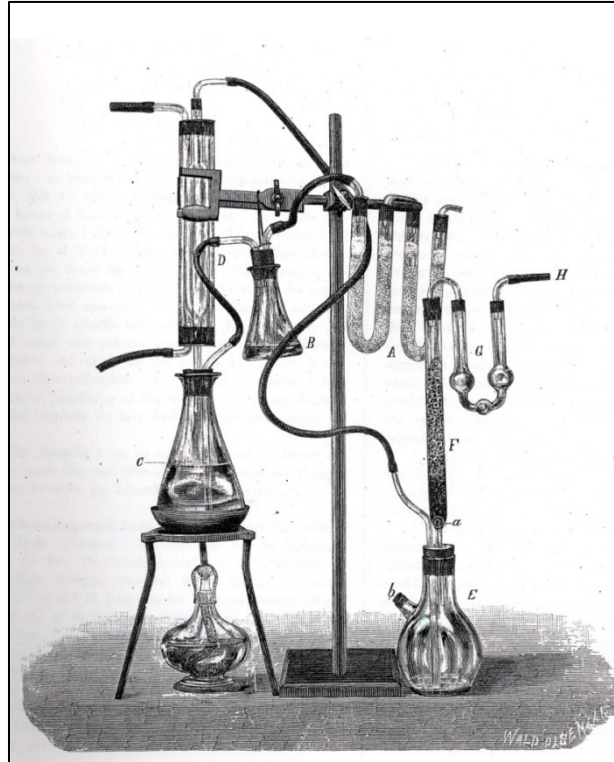


Fig. 3: Apparatus for the simultaneous determination of total CO<sub>2</sub> and "neutral carbonates" (alkalinity) in seawater by acid addition used by TORNØE, (from TORNØE, 1880b).

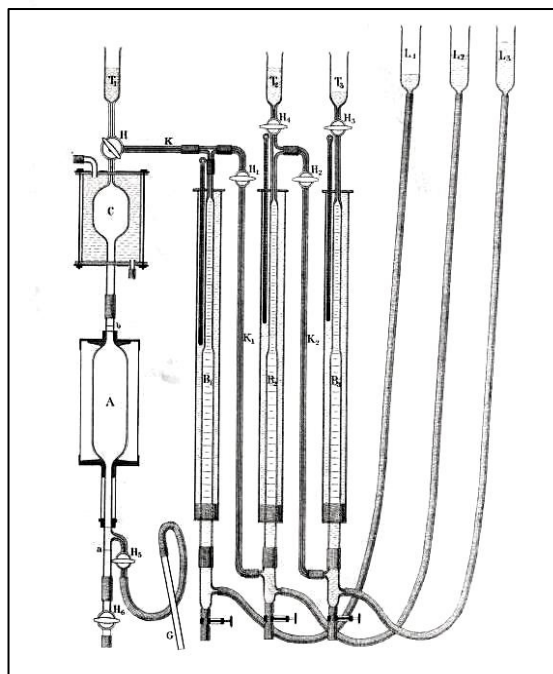


Fig. 4: Apparatus for the simultaneous determination of the content of oxygen, nitrogen and carbon dioxide in seawater used by MARTIN KNUDSEN (from KNUDSEN, 1899, Vol. 1, Plate II).

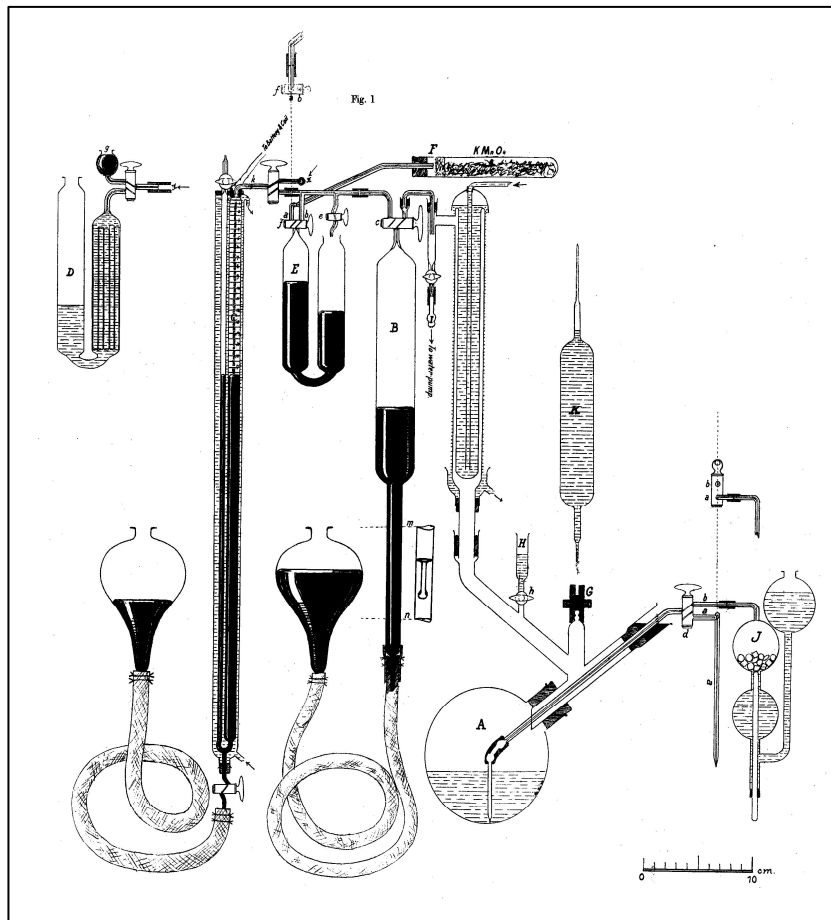


Fig. 5: Apparatus for the simultaneous determination of the content of oxygen, nitrogen and carbon dioxide in seawater designed by CHARLES FOX in 1904 (from FOX, 1905).

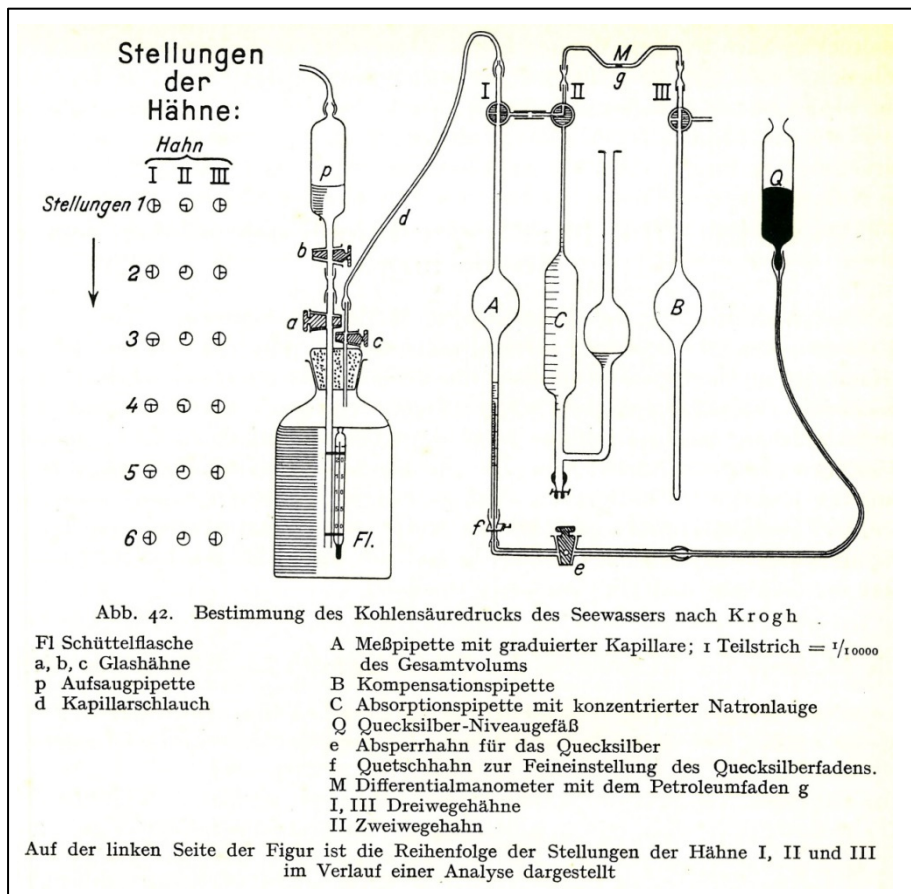


Fig. 6: Apparatus for determination of the CO<sub>2</sub> partial pressure of seawater according to KROGH (1904a) used during the German Atlantic Expedition 1925-1927 (from WATTENBERG, 1933a, p. 254).

## Annex A IV

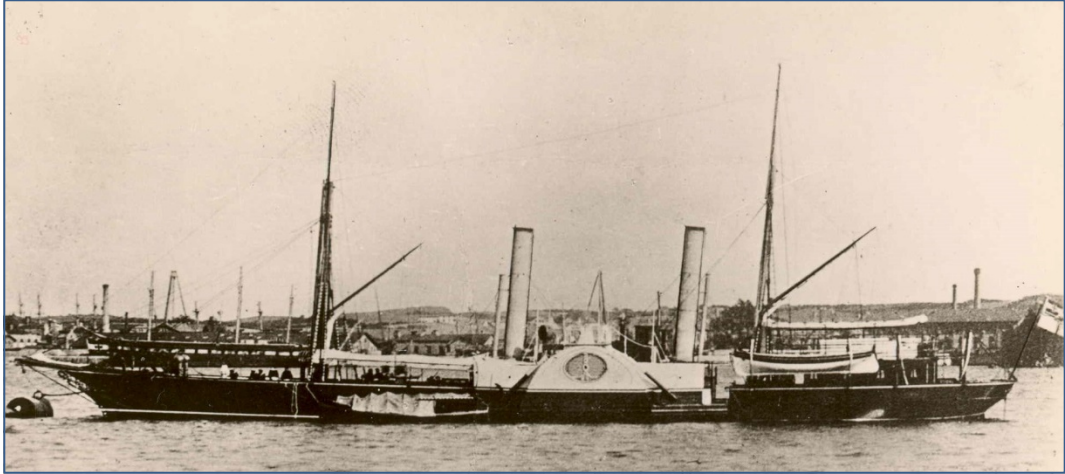
Research vessels participating in investigations of the marine CO<sub>2</sub> system

Fig. 1: Paddle-wheel steamer of the Imperial German Navy S.M. Aviso "Pommerania" chartered by the "Commission for the Scientific Investigation of the German Seas" in Kiel for the North Sea Expedition 1872 (Photo from about 1880, reproduced with the kind permission of Bilddienst Wilhelmshavener Zeitung).

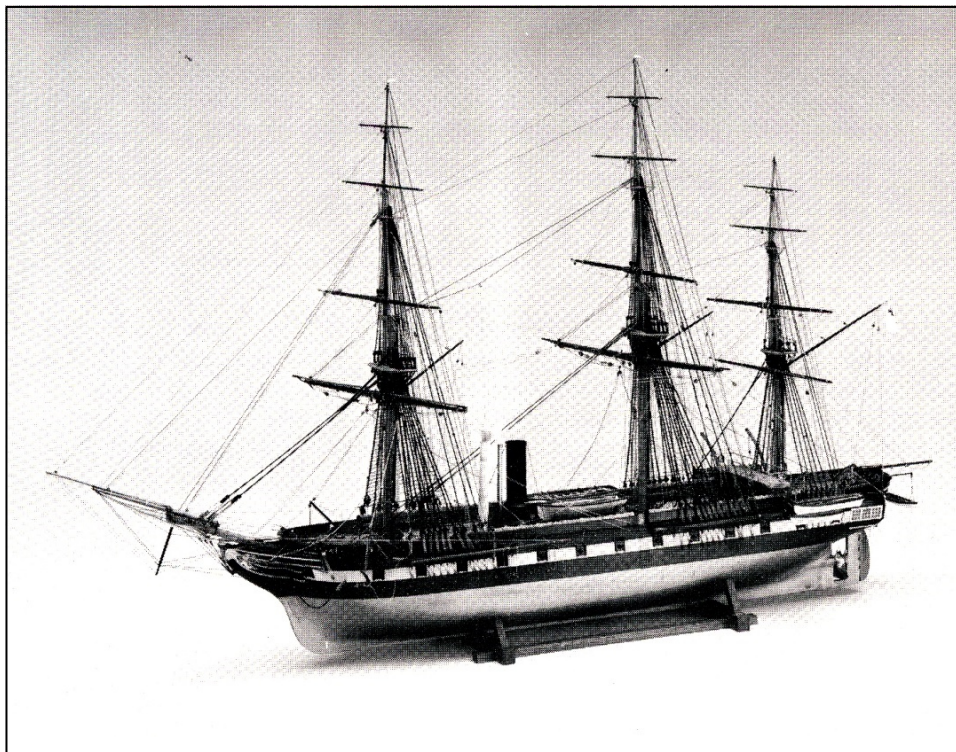


Fig. 2: Model of the German steam corvette S.M.S. "Gazelle" of the Imperial German Navy used during the sailing around the world in 1874-1876, Deutsches Schiffahrtsmuseum Bremerhaven (from RÖHR, 1981).

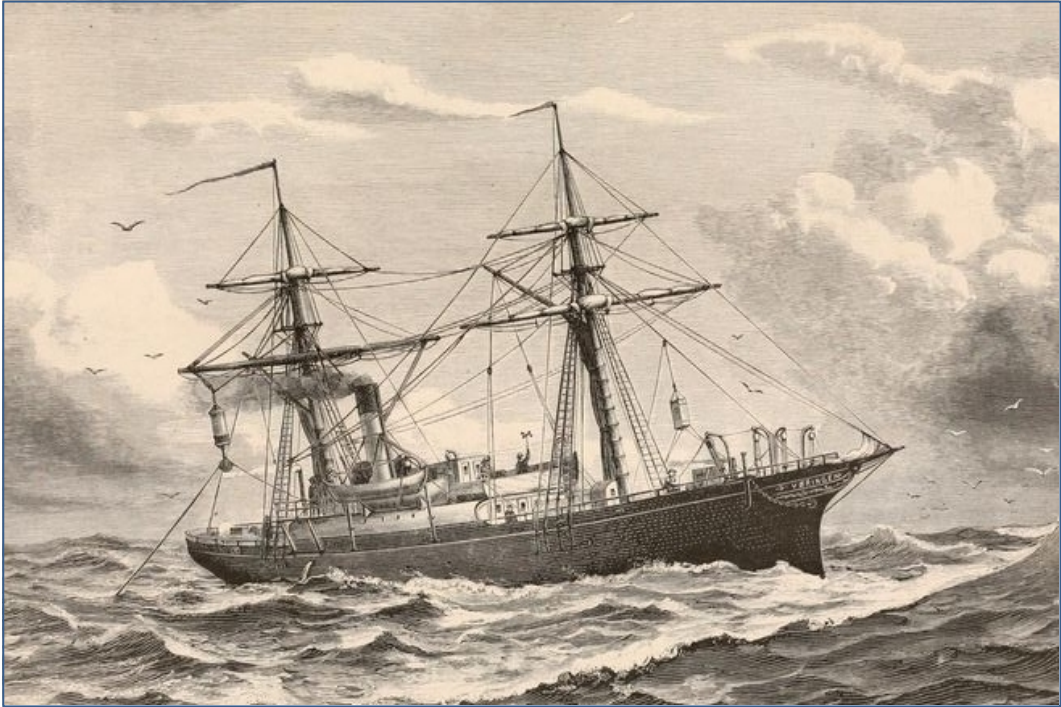


Fig. 3: Steamship S.S. „Vøringen“ chartered from a private owner for the Norwegian North-Atlantic Expeditions 1876-1878 (Photo from WILLE, 1882).



Fig. 4: The Danish naval schooner H. M. S. "Ingolf" used for the Danish "Ingolf"-Expedition in 1895/1896 (from ANON, 1899a).



Fig. 5: Finnish research vessel „Nautilus“ used for marine research and monitoring by the Finnish Institute of Marine Research between 1903 and 1933 (Photo: Finnish Environment Institute Helsinki).



Fig. 6: German Navy survey vessel "Meteor" used for the German Atlantic Expedition 1925 - 1927 (from Wikipedia, 2020).



## Annex A V

Cruise tracks and station plans of expeditions performed by the previously shown research vessels (red dots mark the locations where samples for CO<sub>2</sub> analyses were taken)

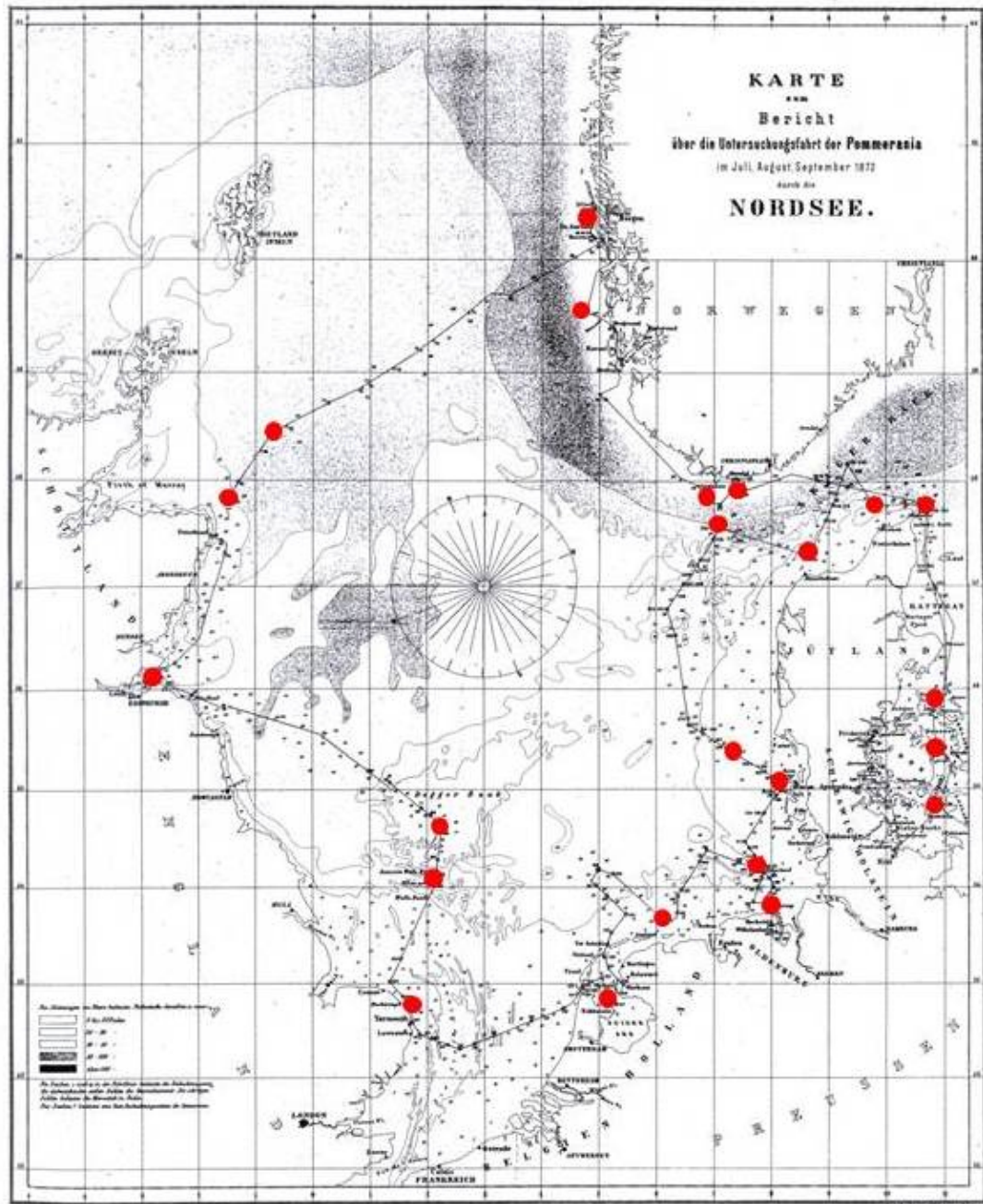


Fig. 1: Cruise track of the German paddle wheel steamer S.M. Aviso „Pommerania“ during the North Sea Expedition in 1872 and station network (from MEYER et al., 1875).

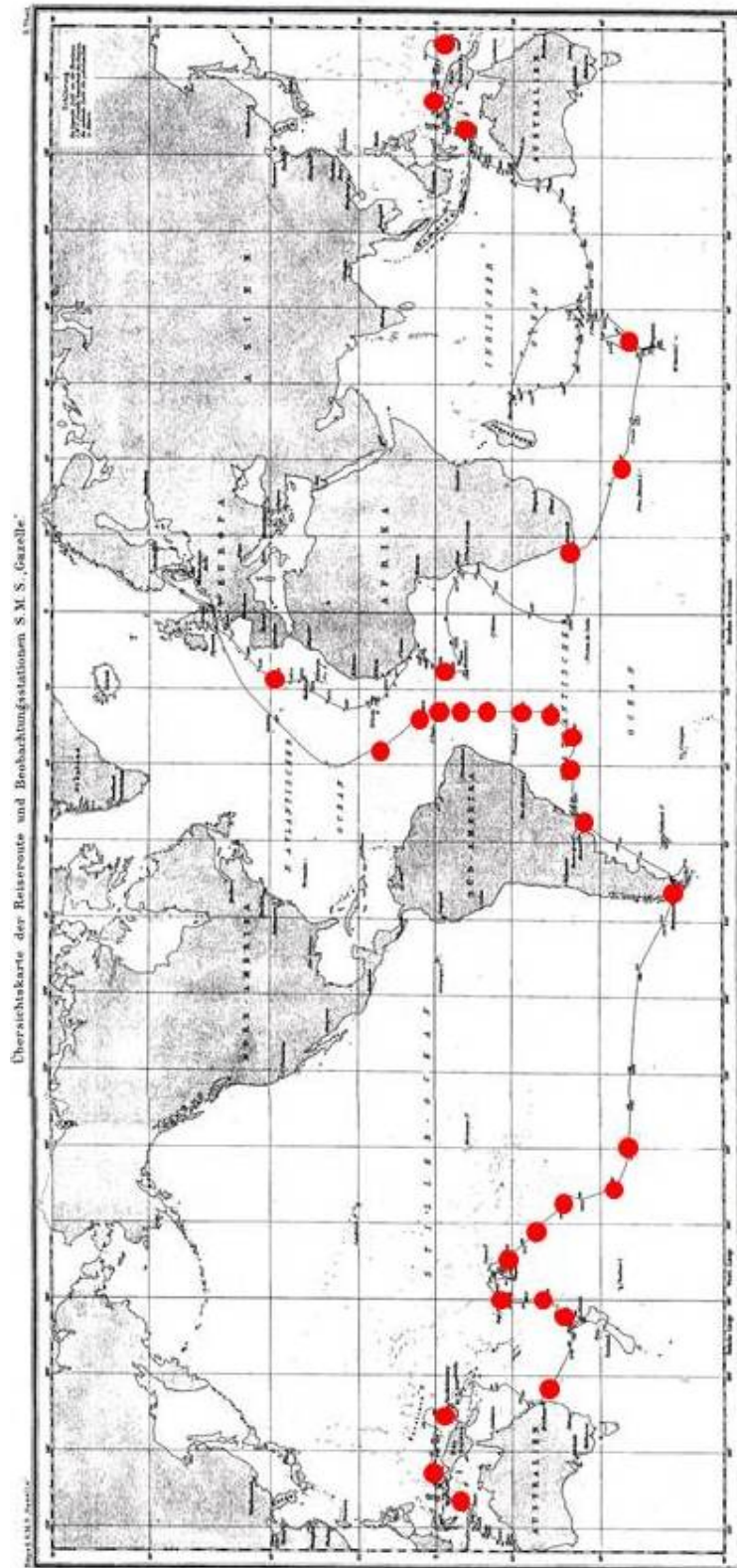


Fig. 2: Voyage and station plan of the German steam corvette S.M.S. "Gazelle" around the world in 1874-1876 (from ANON., 1888, II. Theil, Table B, p. 67/68; modified).

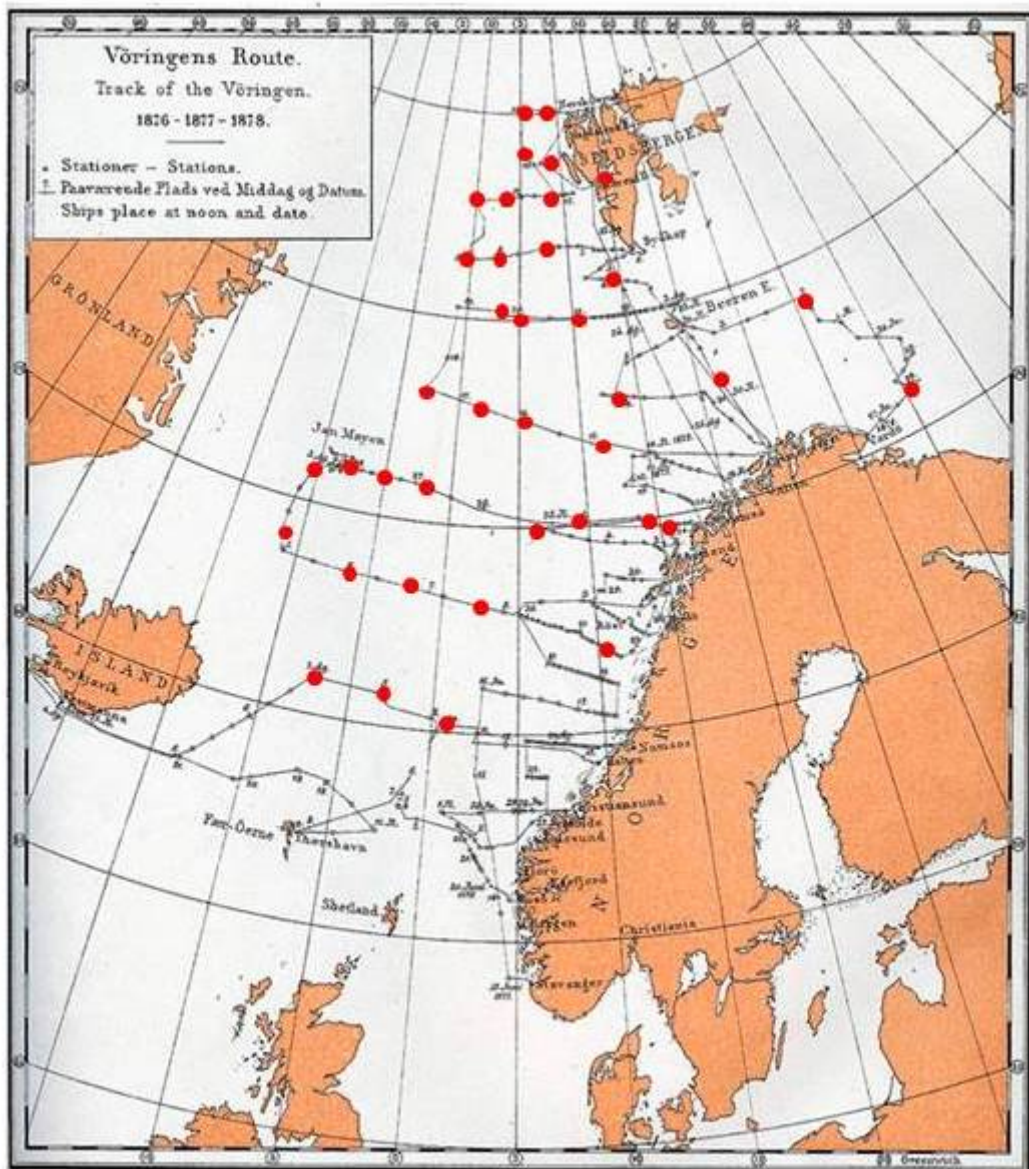


Fig. 3: Cruise track of the steamship „Vøringen“ during the Norwegian North-Atlantic Expeditions between 1876 and 1878 and station network (from WILLE, 1882).

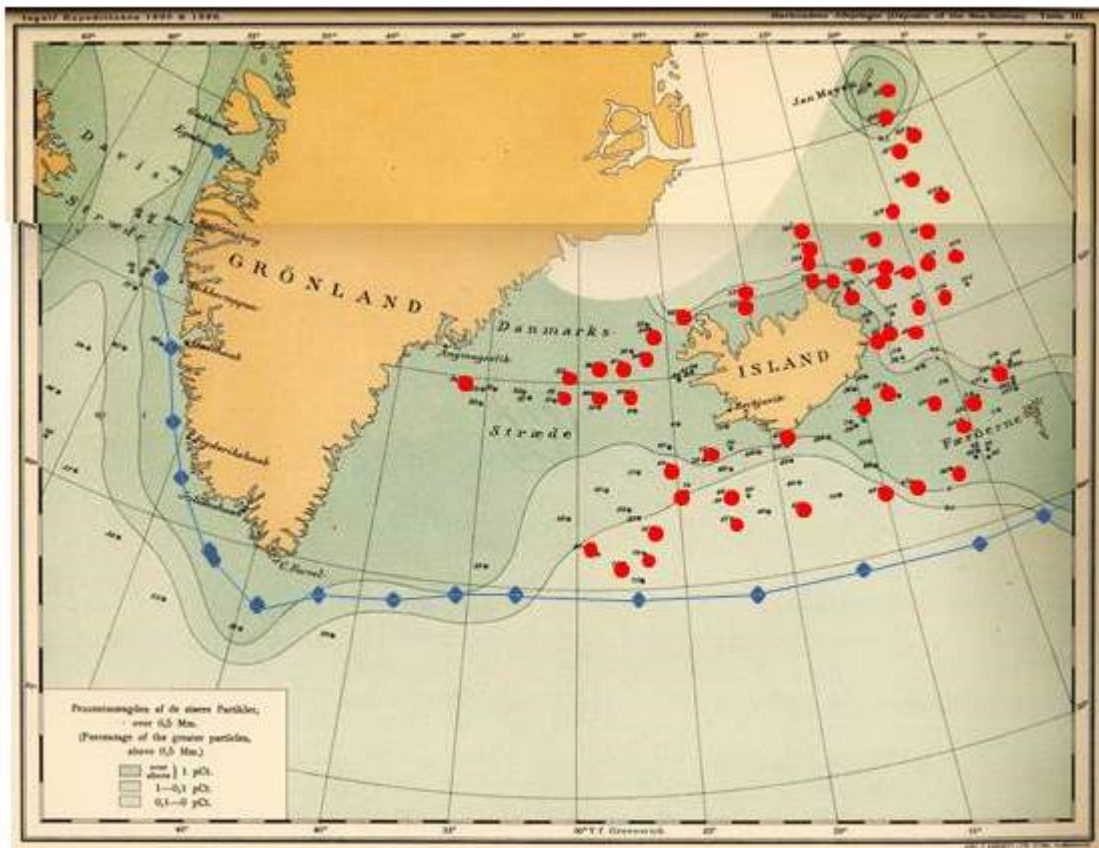


Fig. 4: Cruise track of the Danish H. M. S. "Ingolf" during the expedition in 1895/1896 and station network (from BOEGGILD, 1900, Vol. 1, Part 3, Table III, modified). Red dots mark locations where samples for CO<sub>2</sub> analyses were taken by KNUDSEN (1899). Blue rhombs mark the positions where KROGH performed CO<sub>2</sub> measurements during a cruise on board of the sailing vessel "Peru" in summer 1902 (KROGH, 1904a, p. 403).

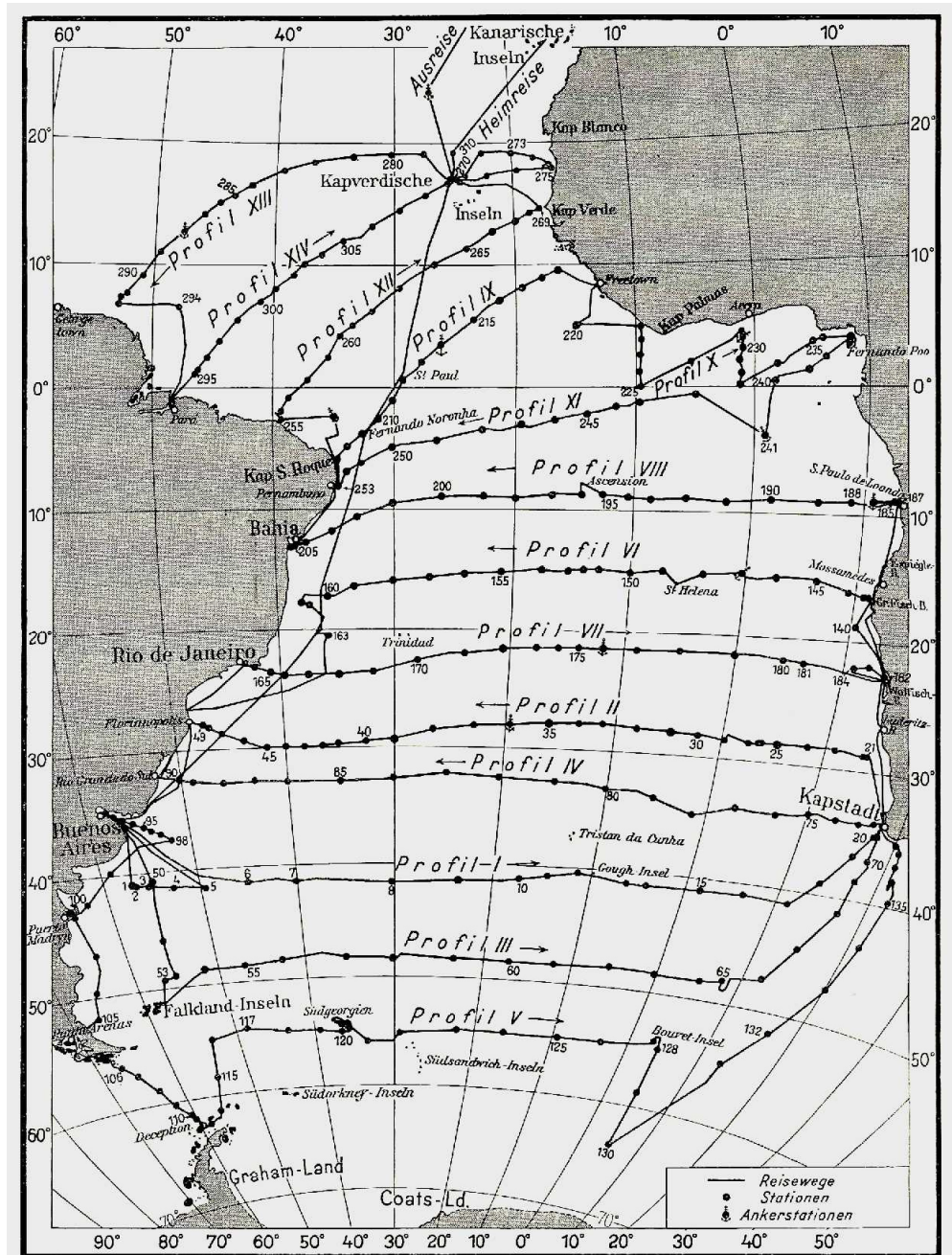


Fig. 5: Cruise track of the survey vessel "Meteor" during the German Atlantic Expedition 1925 - 1927 and station network (from WATTENBERG, 1933b, p. 232).

## ANNEX A VI

### KURT BUCH and the International Council for the Exploration of the Sea (ICES)

At the end of the 19<sup>th</sup> century, marine scientists realized that international cooperation in marine investigations is highly desirable (SMED,<sup>88</sup> 1990) and is the only way to learn about the sea and its inhabitants. Activities of the Swedish oceanographer OTTO PETTERSSON<sup>32</sup> resulted in an invitation of the Swedish Government for the First International Conference for the Exploration of the Sea in Stockholm in June 1899 (ANON., 1899b). The conference stated that it is desirable to start international investigations already in May 1901. In the same month, the Second International Conference for the Exploration of the Sea was held in Kristiania (ANON., 1901). The hydrographer OSCAR NORDQUIST,<sup>89</sup> head of the Finnish delegation at the Kristiania conference, was in charge of the first Finnish hydrographical expedition in the Gulf of Bothnia in 1887.

The Kristiania conference again recommended starting seasonal cruises already in 1901. Each member country should provide a steamer specially constructed for scientific fishery research. The Third International Conference for the Exploration of the Sea (ICES) took place in Copenhagen in July 1902 (ANON., 1903). ICES – the oldest international scientific organization – was then formally founded.<sup>90</sup> Already in 1902, a detailed programme for hydrographic investigations was implemented without delay owing to the experience of the member countries from national observation programmes in the late 19<sup>th</sup> century.

Although at that time not an independent state but an autonomous Grand Duchy under the Russian Empire, Finland is one of the founding members of ICES (SMED, 2003).<sup>91</sup> THEODOR HOMÉN,<sup>92</sup> secretary of the Finnish Meteorological Commission, and the hydrographer OSCAR NORDQUIST were Finnish delegates of the inaugural meeting in Copenhagen in 1902. The meeting set up three committees among them the Committee for the Baltic with NORDQUIST as convener.

Finland had started hydrographical work in 1887 (NORDQUIST, 1888). In 1898, observations were carried out in the Archipelago Sea and the Gulf of Bothnia four times a year in August, October and December 1898 and in April/May 1899 (SIMOJOKI,<sup>93</sup> 1978).

During 1911 to 1914, BUCH participated in the first regular Finnish hydrographic and hydrochemical monitoring cruises in the northern Baltic Sea including the Gulfs of Bothnia and Finland.

In the early 20<sup>th</sup> century, ICES mainly focused on fisheries research. Nevertheless, the activities of BUCH in the framework of ICES were significant. Due to his experience in analysis of dissolved nitrogen compounds (BUCH, 1914/1915, 1920, 1923) he was invited to take part in two meetings on the analysis of phosphates and nitrogen compounds in sea water in 1928 in Copenhagen and Oslo (ICES, 1929; BUCH, 1929a) and presented a paper (BUCH, 1929a). During the expert meeting in Oslo standard methods were tested and recommendations were given for the analysis of nutrients in seawater (Fig. 1).

The most important contribution of BUCH to the ICES work was the investigation of the carbonic acid equilibrium system. In 1930, the ICES Annual Meeting in Copenhagen proposed to set up an ICES expert team consisting of K. BUCH, H. W. HARVEY and H. WATTENBERG and assisted by S.

GRIPENBERG. Background for this initiative was a report of BUCH on the state-of-the-art concerning the investigations of the marine CO<sub>2</sub> system presented during the Annual Meeting (BUCH, 1930a, 1930b). The recommended two-month joint investigations of the experts were carried out at the chemical laboratory of the Institute for Marine Research in Helsinki in spring 1931 and were completed by BUCH and GRIPENBERG in September/October (BUCH et al., 1932).



Fig. 1: ICES expert meeting in Oslo in October 1928 to standardize methods for nutrient analysis in seawater. From left H. H. GRAN,<sup>94</sup> H. W. HARVEY, E. SCHREIBER,<sup>95</sup> A. KLEM,<sup>96</sup> B. R. FØYN,<sup>97</sup> K. BUCH, H. WATTENBERG, J. HJORT<sup>98</sup> and T. GAARDER,<sup>99</sup> (Photo: Department of Biology, University of Oslo).

Later BUCH worked in the Sub-Committee for evaluating the chemical nomenclature to be used in the publications of the Council that was set up in 1934 (JACOBSEN et al., 1938). The recommended nomenclature was largely consistent with a proposal of the Association d'Océanographie Physique from 1936.

Although KURT BUCH and his colleagues performed fundamental investigation on the marine CO<sub>2</sub> system during the 1930s under the umbrella of ICES the results were hardly mentioned in general ICES publications (cf. WENT,<sup>100</sup> 1972; ANDERSON,<sup>101</sup> 2002; ROZWADOWSKI,<sup>102</sup> 2002). Only JOHN LYMAN<sup>103</sup> appreciated the investigation of BUCH in a general history of the knowledge on the carbon dioxide system in seawater (LYMAN, 1972). A detailed description of the life of KURT BUCH and an appraisal of his overall scientific activities is summarized by one of his last students, J. JOHAN LINDBERG<sup>61</sup> (LINDBERG, 1970).

## Annex A VII

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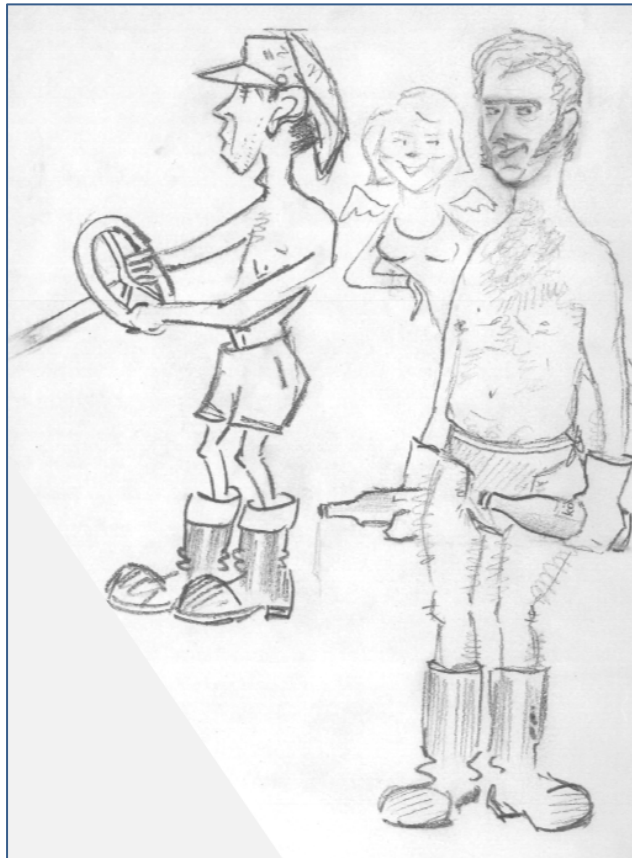
**Anecdote accredited to KURT BUCH*****What is an oceanographer?***

A sailor is mostly out at sea, away from home but thinking of his family, mostly.

A scientist is mainly bodily at home but his mind is in the laboratory, mostly not thinking of his family.

***An oceanographer is the combination of both.***

Anecdote handed over by STIG FONSELIUS, student of KURT BUCH at the late 1940s at the University of Helsinki (from ROZWADOWSKI, 1998).



Oceanographers hard working at sea at the winch and during sampling  
(Sketch by A. Zubin, 1972).

Schneider, B., Matthäus, W.:  
Kurt Buch (1881 - 1967) - The historic  
development of the physico-chemical  
basics of the marine CO<sub>2</sub> system.

## CONTENT

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Summary

Acknowledgement

Annotations

References

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