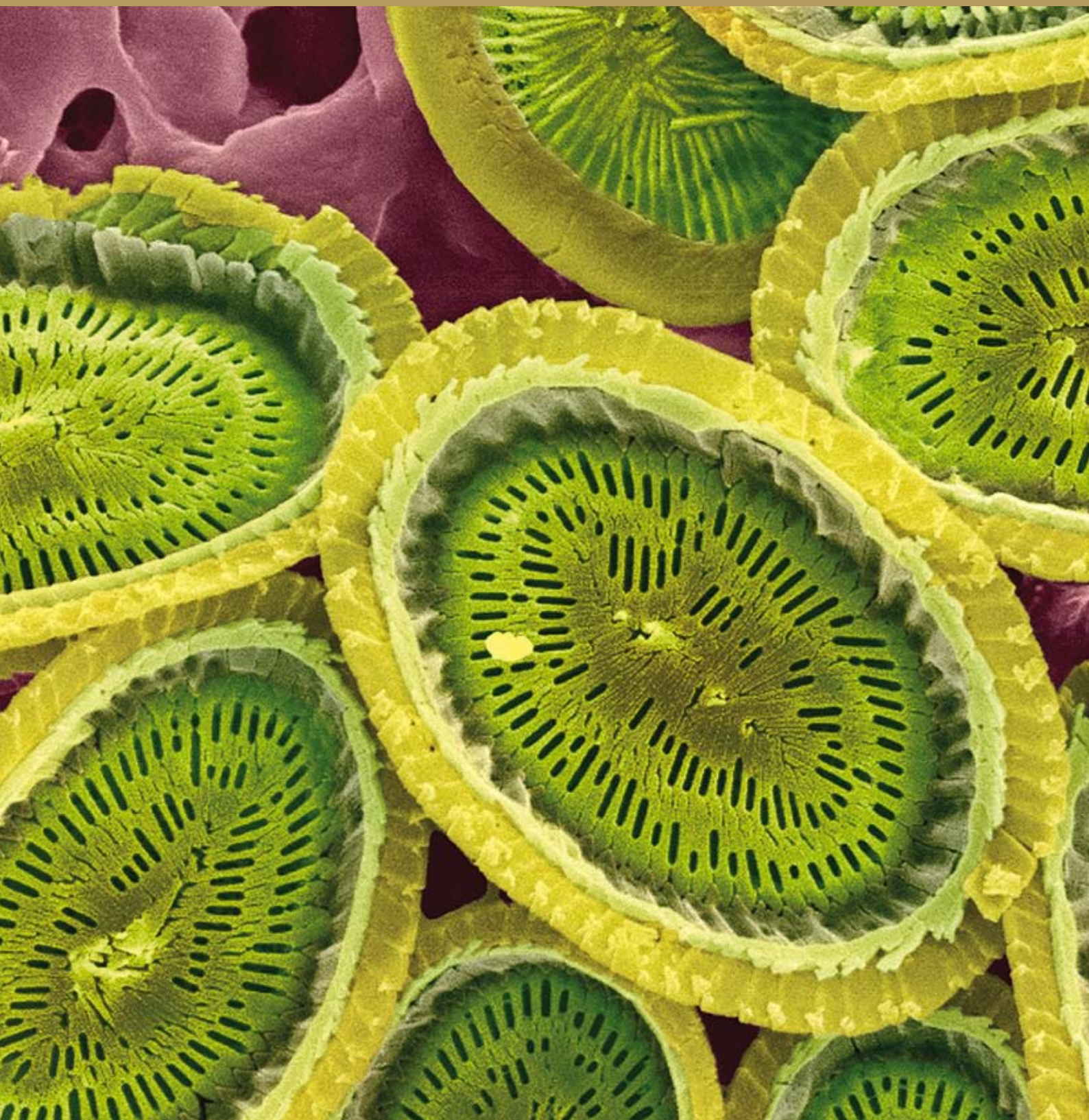
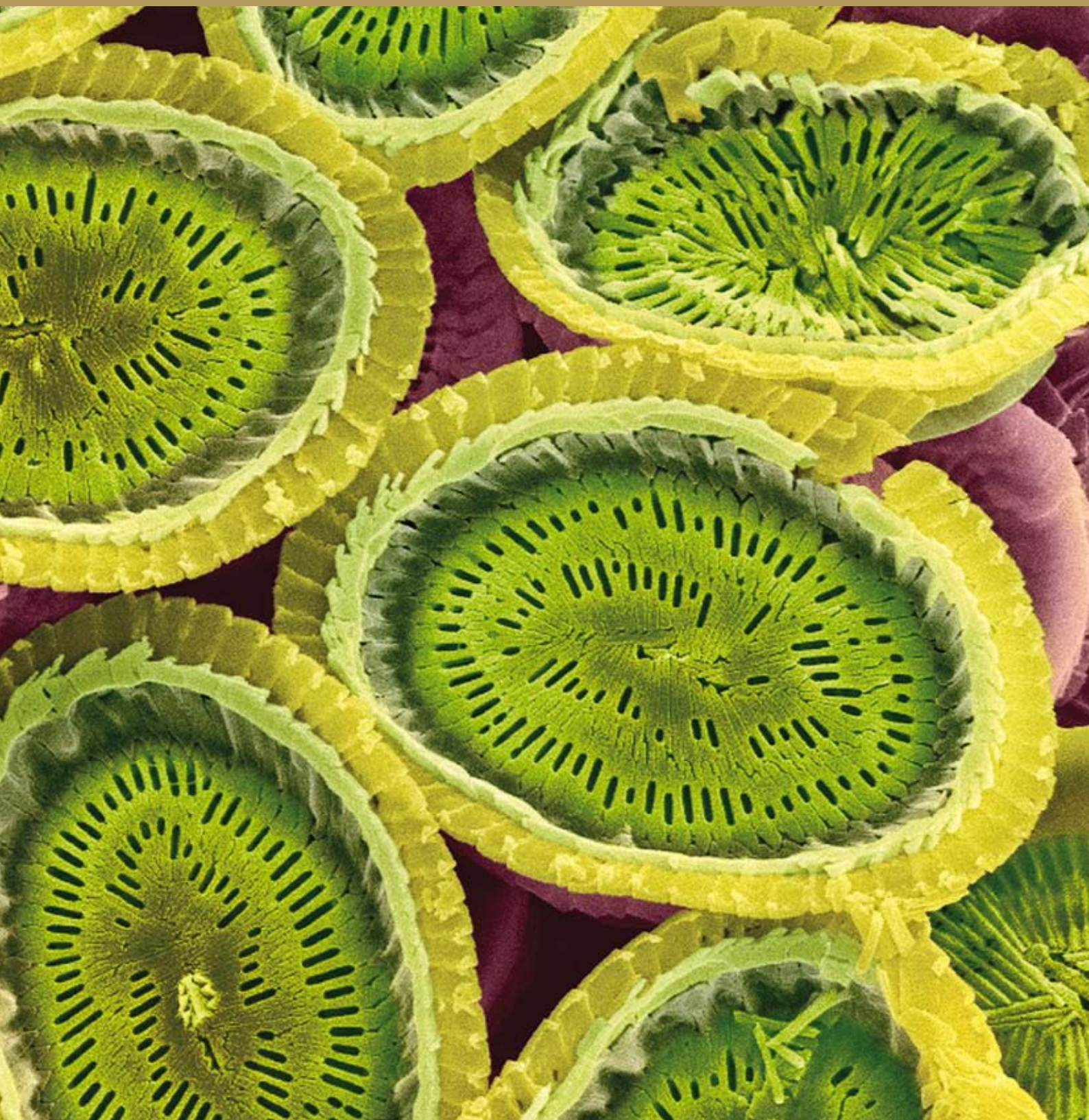


2 How climate change alters ocean chemistry



> Massive emissions of carbon dioxide into the atmosphere have an impact on the chemical and biological processes in the ocean. The warming of ocean water could lead to a destabilization of solid methane deposits on the sea floor. Because of the excess CO_2 , the oceans are becoming more acidic. Scientists are making extensive measurements to determine how much of the humanmade CO_2 is being absorbed by the oceans. Important clues are provided by looking at oxygen.



The oceans – the largest CO₂-reservoir

> The oceans absorb substantial amounts of carbon dioxide, and thereby consume a large portion of this greenhouse gas, which is released by human activity. This does not mean, however, that the problem can be ignored, because this process takes centuries and cannot prevent the consequences of climate change. Furthermore, it cannot be predicted how the marine biosphere will react to the uptake of additional CO₂.

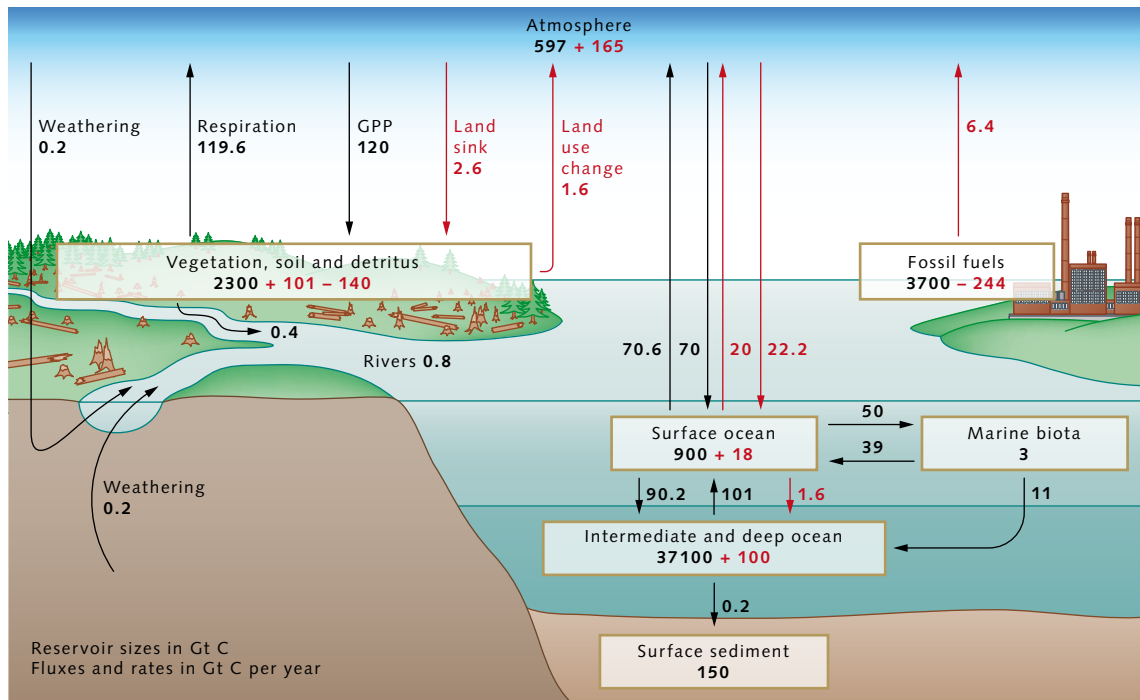
The mutability of carbon

Carbon is the element of life. The human body structure is based on it, and other animal and plant biomass such as leaves and wood consist predominantly of carbon (C). Plants on land and algae in the ocean assimilate it in the form of carbon dioxide (CO₂) from the atmosphere or water, and transform it through photosynthesis into energy-rich molecules such as sugars and starches. Carbon constantly changes its state through the metabolism of organisms and by natural chemical processes. Carbon can be stored in and exchanges between particulate and dissolved inorganic and organic forms and exchanged with the the atmosphere as CO₂. The oceans store much more carbon than the atmosphere and the terrestrial biosphere (plants and animals). Even more carbon, however, is stored in the lithosphere, i.e. the rocks on the planet, including limestones (calcium carbonate, CaCO₃).

The three most important repositories within the context of anthropogenic climate change – atmosphere, terrestrial biosphere and ocean – are constantly exchanging carbon. This process can occur over time spans of up to centuries, which at first glance appears quite slow. But considering that carbon remains bound up in the rocks of the Earth's crust for millions of years, then the exchange between the atmosphere, terrestrial biosphere and ocean carbon reservoirs could actually be described as relatively rapid. Today scientists can estimate fairly accurately how much carbon is stored in the individual reservoirs. The ocean, with around 38,000 gigatons (Gt) of carbon (1 gigaton = 1 billion tons), contains 16 times as much carbon as the terrestrial biosphere, that is all plant and

the underlying soils on our planet, and around 60 times as much as the pre-industrial atmosphere, i.e., at a time before people began to drastically alter the atmospheric CO₂ content by the increased burning of coal, oil and gas. At that time the carbon content of the atmosphere was only around 600 gigatons of carbon. The ocean is therefore the greatest of the carbon reservoirs, and essentially determines the atmospheric CO₂ content. The carbon, however, requires centuries to penetrate into the deep ocean, because the mixing of the oceans is a rather slow (Chapter 1). Consequently, changes in atmospheric carbon content that are induced by the oceans also occur over a time frame of centuries. In geological time that is quite fast, but from a human perspective it is too slow to extensively buffer climate change.

With respect to climate change, the greenhouse gas CO₂ is of primary interest in the global carbon cycle. Today, we know that the CO₂ concentration in the atmosphere changed only slightly during the 12,000 years between the last ice age and the onset of the industrial revolution at the beginning of the 19th century. This relatively stable CO₂ concentration suggests that the pre-industrial carbon cycle was largely in equilibrium with the atmosphere. It is assumed that, in this pre-industrial equilibrium state, the ocean released around 0.6 gigatons of carbon per year to the atmosphere. This is a result of the input of carbon from land plants carried by rivers to the ocean and, after decomposition by bacteria, released into the atmosphere as CO₂, as well as from inorganic carbon from the weathering of continental rocks such as limestones. This transport presumably still occurs today at rates essentially unchanged. Since the beginning of



2.1 > The carbon cycle in the 1990s with the sizes of the various reservoirs (in gigatons of carbon, Gt C), as well as the annual fluxes between these. Pre-industrial natural fluxes are shown in black, anthropogenic changes in red. The loss of 140 Gt C in the terrestrial biosphere reflects the cumulative CO₂ emissions from land-use change (primarily slash and burn agricul-

ture in the tropical rainforests), and is added to the 244 Gt C emitted by the burning of fossil fuels. The terrestrial sink for anthropogenic CO₂ of 101 Gt C is not directly verifiable, but is derived from the difference between cumulative emissions (244 + 140 = 384 Gt C) and the combination of atmospheric increase (165 Gt C) and oceanic sinks (100 + 18 = 118 Gt C).

the industrial age, increasing amounts of additional carbon have entered the atmosphere annually in the form of carbon dioxide. The causes for this, in addition to the burning of fossil fuels (about 6.4 Gt C per year in the 1990s and more than 8 Gt C since 2006), include changes in land-use practices such as intensive slash and burn agriculture in the tropical rainforests (1.6 Gt C annually). From the early 19th to the end of the 20th century, humankind released around 400 Gt C in the form of carbon dioxide. This has created a serious imbalance in today's carbon cycle. The additional input of carbon produces offsets between the carbon reservoirs, which lead to differences in the flux between reservoirs when compared to pre-industrial times. In addition to the atmosphere, the oceans and presumably also land plants

permanently absorb a portion of this anthropogenic CO₂ (produced by human activity).

The ocean as a sink for anthropogenic CO₂

As soon as CO₂ migrates from the atmosphere into the water, it can react chemically with water molecules to form carbonic acid, which causes a shift in the concentrations of the hydrogen carbonate (HCO₃⁻) and carbonate (CO₃²⁻) ions, which are derived from the carbonic acid. Because carbon dioxide is thus immediately processed in the sea, the CO₂ capacity of the oceans is ten times higher than that of freshwater, and they therefore can absorb large quantities of it. Scientists refer to this kind of assimilation of CO₂ as a sink. The ocean absorbs

Fertilizing the ocean with iron

Iron is a crucial nutrient for plants and the second most abundant chemical element on Earth, although the greatest portion by far is locked in the Earth's core. Many regions have sufficient iron for plants. In large regions of the ocean, however, iron is so scarce that the growth of single-celled algae is limited by its absence. Iron-limitation regions include the tropical eastern Pacific and parts of the North Pacific, as well as the entire Southern Ocean. These ocean regions are rich in the primary nutrients (macronutrients) nitrate and phosphate. The iron, however, which plants require only in very small amounts (micronutrients), is missing. Scientists refer to these marine regions as HNLC regions (high nutrient, low chlorophyll) because algal growth here is restricted and the amount of the plant pigment chlorophyll is reduced accordingly. Research using fertilization experiments has shown that plant growth in all of these regions can be stimulated by fertilizing the water with iron. Because plants assimilate carbon, carbon dioxide from the atmosphere is thus converted to biomass, at least for the short term.

Iron fertilization is a completely natural phenomenon. For example, iron-rich dust from deserts is blown to the sea by the wind. Iron also enters the oceans with the meltwater of icebergs or by contact

of the water with iron-rich sediments on the sea floor. It is presumed that different wind patterns and a dryer atmosphere during the last ice age led to a significantly higher input of iron into the Southern Ocean. This could, at least in part, explain the considerably lower atmospheric CO₂ levels during the last ice age. Accordingly, modern modelling simulations indicate that large-scale iron fertilization of the oceans could decrease the present atmospheric CO₂ levels by around 30 ppm (parts per million). By comparison, human activities have increased the atmospheric CO₂ levels from around 280 ppm to a present-day value of 390 ppm.

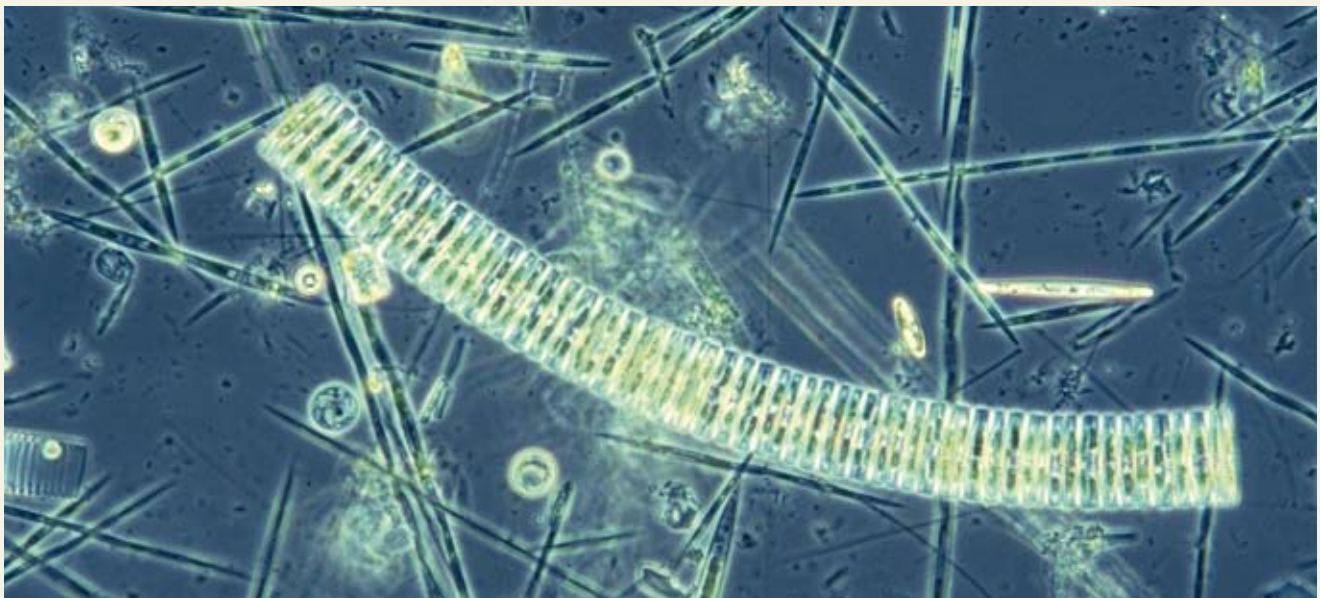
Marine algae assimilate between a thousand and a million times less iron than carbon. Thus even very low quantities of iron are sufficient to stimulate the uptake of large amounts of carbon dioxide in plants. Under favourable conditions large amounts of CO₂ can be converted with relatively little iron. This raises the obvious idea of fertilizing the oceans on a large scale and reducing the CO₂ concentrations in the atmosphere by storage in marine organisms (sequestration). When the algae die, however, and sink to the bottom and are digested by animals or broken down by microorganisms, the carbon dioxide is released again. In order to evaluate whether the fixed

2.2 > Iron is a crucial nutrient for algae, and it is scarce in many ocean regions, which inhibits algal growth. If the water is fertilized with iron there is a rapid increase in algae. Microscopic investigations of water samples taken by the research vessel "Polarstern" clearly show that algae in this iron-poor region proliferate quickly after iron fertilization. Around three weeks after fertilization the marine algal community was dominated by elongate, hard-shelled diatoms.

carbon dioxide actually remains in the ocean, the depth at which the biomass produced by iron fertilization is broken down and carbon dioxide is released must be known, because this determines its spatial and temporal distance from the atmosphere. Normally, 60 to 90 per cent of the biomass gets broken down in the surface water, which is in contact with the atmosphere. So this portion of the biomass does not represent a contribution to sequestration. Even if the breakdown occurs at great depths, the CO_2 will be released into the atmosphere within a few hundred to thousand years because of the global ocean circulation.

There are other reasons why iron fertilization is so controversial. Some scientists are concerned that iron input will disturb the nutrient budget in other regions. Because the macronutrients in the surface water are consumed by increased algal growth, it is possible that nutrient supply to other downstream ocean regions will be deficient. Algal production in those areas would decrease, counteracting the CO_2 sequestration in the fertilized areas. Such an effect would be expected, for example, in the tropical Pacific, but not in the Southern Ocean where the surface water, as a rule, only remains at the sea surface for a relatively short time, and quickly sinks again before the

macronutrients are depleted. Because these water masses then remain below the surface for hundreds of years, the Southern Ocean appears to be the most suitable for CO_2 sequestration. Scientists are concerned that iron fertilization could have undesirable side effects. It is possible that iron fertilization could contribute to local ocean acidification due to the increased decay of organic material and thus greater carbon dioxide input into the deeper water layers. Furthermore, the decay of additional biomass created by fertilization would consume more oxygen, which is required by fish and other animals. The direct effects of reduced oxygen levels on organisms in the relatively well-oxygenated Southern Ocean would presumably be very minor. But the possibility that reduced oxygen levels could have long-range effects and exacerbate the situation in the existing low-oxygen zones in other areas of the world ocean cannot be ruled out. The possible consequences of iron fertilization on species diversity and the marine food chain have not yet been studied over time frames beyond the few weeks of the iron fertilization experiments. Before iron fertilization can be established as a possible procedure for CO_2 sequestration, a clear plan for observing and recording the possible side effects must first be formulated.



human-made atmospheric CO_2 , and this special property of seawater is primarily attributable to carbonation, which, at 10 per cent, represents a significant proportion of the dissolved inorganic carbon in the ocean. In the ocean, the carbon dissolved in the form of CO_2 , bicarbonate and carbonate is referred to as inorganic carbon. When a new carbon equilibrium between the atmosphere and the world ocean is re-established in the future, then the oceanic reservoir will have assimilated around 80 per cent of the anthropogenic CO_2 from the atmosphere, primarily due to the reaction with carbonate. The buffering effect of deep-sea calcium carbonate sediments is also important. These ancient carbonates neutralize large amounts of CO_2 by reacting with it, and dissolving to some extent. Thanks to these processes, the oceans could ultimately absorb around 95 per cent of the anthropogenic emissions. Because of the slow mixing of the ocean, however, it would take centuries before equilibrium is established. The very gradual buffering of CO_2 by

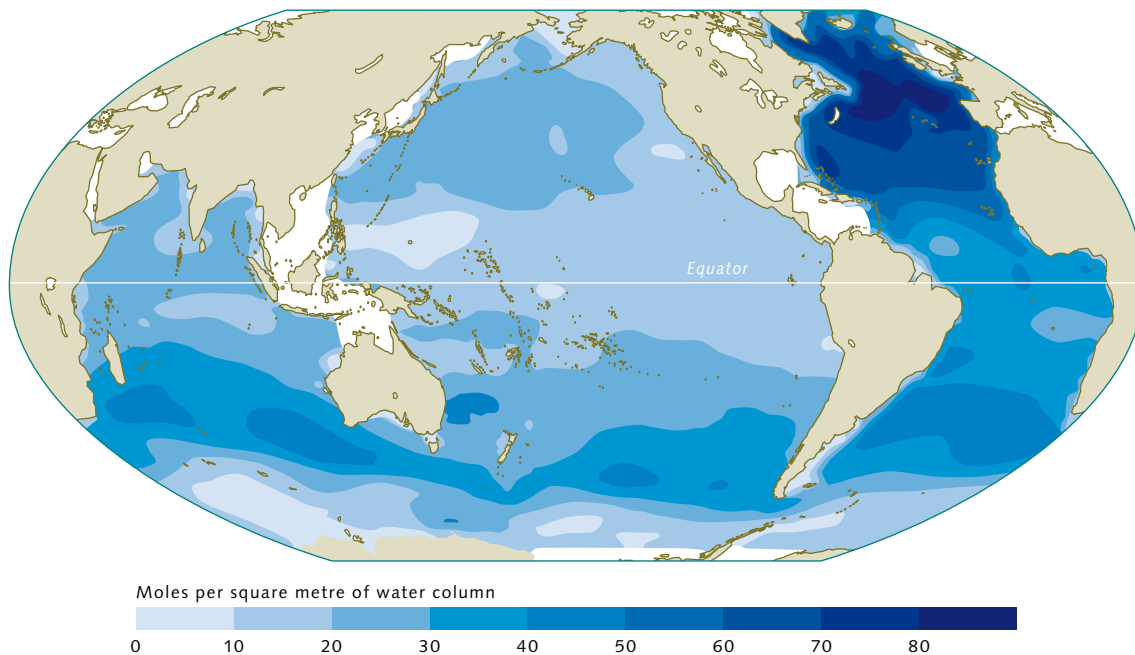
the reaction with carbonate sediments might even take millennia. For today's situation this means that a marked carbon disequilibrium between the ocean and atmosphere will continue to exist for the decades and centuries to come. The world ocean cannot absorb the greenhouse gas as rapidly as it is emitted into the atmosphere by humans. The absorptive capacity of the oceans through chemical processes in the water is directly dependent on the rate of mixing in the world ocean. The current oceanic uptake of CO_2 thus lags significantly behind its chemical capacity as the present-day CO_2 emissions occur much faster than they can be processed by the ocean.

Measuring exchange between the atmosphere and ocean

For dependable climate predictions it is extremely important to determine exactly how much CO_2 is absorbed by the ocean sink. Researchers have therefore developed a

2.3 > Cement plants like this one in Amsterdam are, second to the burning of fossil fuels, among the most significant global sources of anthropogenic carbon dioxide. The potential for reducing CO_2 output is accordingly large in these industrial areas.





2.4 > The world ocean takes up anthropogenic CO₂ everywhere across its surface. The transport into the interior ocean, however, primarily takes place in the North Atlantic and in a belt between 30 and 50 degrees south latitude. The values indicate the total uptake from the beginning of the industrial revolution until the year 1994.

variety of independent methods to quantify the present role of the ocean in the anthropogenically impacted carbon cycle. These have greatly contributed to the present-day understanding of the interrelationships. Two procedures in particular have played an important role:

The first method (atmosphere-ocean flux) is based on the measurement of CO₂ partial-pressure differences between the ocean surface and the atmosphere. Partial pressure is the amount of pressure that a particular gas such as CO₂ within a gas mixture (the atmosphere) contributes to the total pressure. Partial pressure is thus also one possibility for quantitatively describing the composition of the atmosphere. If more of this gas is present, its partial pressure is higher. If two bodies, such as the atmosphere and the near-surface layers of the ocean, are in contact with each other, then a gas exchange between them can occur. In the case of a partial-pressure difference between the two media, there is a net exchange of CO₂. The gas flows from the body with the higher partial pressure into that of lower pressure. This net gas exchange can be calculated when the global distribution of the CO₂ partial-pressure difference is known. Consider-

ing the size of the world ocean this requires an enormous measurement effort. The worldwide fleet of research vessels is not nearly large enough for this task. A significant number of merchant vessels were therefore outfitted with measurement instruments that automatically carry out CO₂ measurements and store the data during their voyages or even transmit them daily via satellite. This "Voluntary Observing Ship" project (VOS) has been developed and expanded over the last two decades and employs dozens of ships worldwide. It is fundamentally very difficult to adequately record the CO₂ exchange in the world ocean, because it is constantly changing through space and time. Thanks to the existing VOS network, however, it has been possible to obtain measurements to provide an initial important basis. The database, covering over three decades, is sufficient to calculate the average annual gas exchange over the total surface of the oceans with some confidence. It is given as average annual CO₂ flux density (expressed in mol C/m²/year), that is the net flux of CO₂ per square meter of ocean surface per year, which can be integrated to yield the total annual CO₂ uptake of the world ocean.

Our present picture is based on around three million measurements that were collected and calculated for the CO₂ net flux. The data were recorded between 1970 and 2007, and most of the values from the past decade were obtained through the VOS programme. Regions that are important for world climate such as the subpolar North Atlantic and the subpolar Pacific have been reasonably well covered. For other ocean regions, on the other hand, there are still only limited numbers of measurements. For these undersampled regions, the database is presently insufficient for a precise calculation. Still, scientists have been able to use the available data to fairly well quantify the oceanic CO₂ sink. For the reference year 2000 the sink accounts for 1.4 Gt C.

This value represents the net balance of the natural carbon flux out of the ocean into the atmosphere and, conversely, the transport of anthropogenic carbon from the atmosphere into the ocean. Now, as before, the annual natural pre-industrial amount of 0.6 Gt C is flowing out of the ocean. Conversely, around 2.0 Gt C of anthropogenic carbon is entering the ocean every year, leading to the observed balance uptake of 1.4 Gt C per year. Because of the still rather limited amount of data, this method has had to be restricted so far to the climatological CO₂ flux, i.e., a long-term average over the entire observation period. Only now are studies beginning to approach the possibility of looking at interannual variability for this CO₂ sink in especially well-covered regions. The North Atlantic is a first prominent example. Surprisingly, the data shows significant variations between individual years. Presumably, this is attributable to natural climate cycles such as the North Atlantic Oscillation, which have a considerable impact on the natural carbon cycle. Understanding such natural variability of the ocean is a prerequisite for reliable projections of future development and change of the oceanic sink for CO₂.

The second method attempts, with the application of rather elaborate geochemical or statistical procedures, to calculate how much of the CO₂ in the ocean is derived from natural sources and how much is from anthropogenic sources, although from a chemical aspect the two are basically identical, and cannot be clearly distin-

guished. Actually, several procedures are available today that allow this difficult differentiation, and they generally provide very consistent results. These methods differ, however, in detail, depending on the assumptions and approximations associated with a particular method. The most profound basis for estimating anthropogenic CO₂ in the ocean is the global hydrographic GLODAP dataset (Global Ocean Data Analysis Project), which was obtained from 1990 to 1998 through large international research projects. This dataset:

- includes quality-controlled data on a suite of carbon and other relevant parameters;
- is based on analyses of more than 300,000 water samples;
- contains data that were collected on nearly 100 expeditions and almost 10,000 hydrographic stations in the ocean.

All of these data were corrected and subjected to multi-level quality control measures in an elaborate process. This provided for the greatest possible consistency and comparability of data from a number of different laboratories. Even today, the GLODAP dataset still provides the most exact and comprehensive view of the marine carbon cycle. For the first time, based on this dataset, reliable estimates have been made of how much anthropogenic carbon dioxide has been taken up from the atmosphere by the ocean sink. From the beginning of industrialization to the year 1994, the oceanic uptake of anthropogenic carbon dioxide amounts to 118 ± 19 Gt C. The results indicate that anthropogenic CO₂, which is taken up everywhere across the ocean's surface flows into the ocean's interior from the atmosphere primarily in two regions. One of these is the subpolar North Atlantic, where the CO₂ submerges with deep-water formation to the ocean depths. The other area of CO₂ flux into the ocean is a belt between around 30 and 50 degrees of southern latitude. Here the surface water sinks because of the formation of water that spreads to intermediate depths in the ocean.

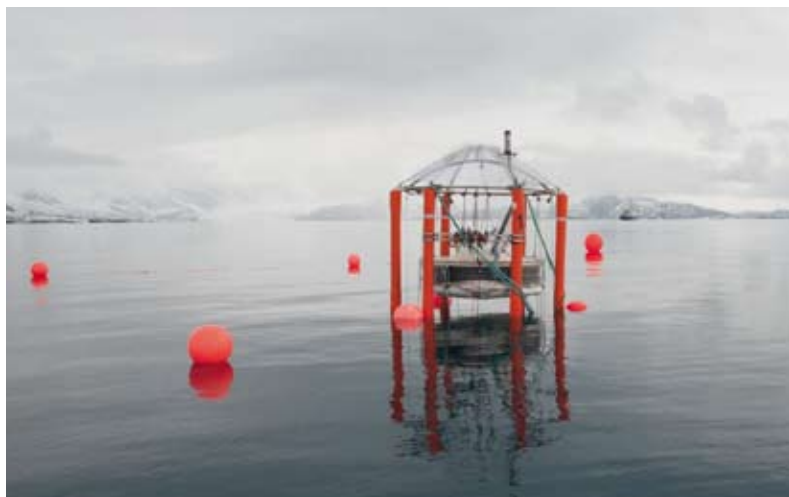
The CO₂ input derived from the GLODAP dataset to some extent represents a snapshot of a long-term transition to a new equilibrium. Although the anthropogenic carbon dioxide continuously enters the ocean from the

surface, the gas has not penetrated the entire ocean by any means. The GLODAP data show that the world ocean has so far only absorbed around 40 per cent of the carbon dioxide discharged by humans into the atmosphere between 1800 and 1995. The maximum capacity of the world ocean of more than 80 per cent is therefore far from being achieved.

How climate change impacts the marine carbon cycle

The natural carbon cycle transports many billions of tons of carbon annually. In a physical sense, the carbon is spatially transported by ocean currents. Chemically, it changes from one state to another, for example, from inorganic to organic chemical compounds or vice versa. The foundation for this continuous transport and conversion is made up of a great number of biological, chemical and physical processes that constitute what is also known as carbon pumps. These processes are driven by climatic factors, or at least strongly influenced by them. One example is the metabolism of living organisms, which is stimulated by rising ambient temperatures. This temperature effect, however, is presumably less significant for the biomass producers (mostly single-celled algae) than for the biomass consumers (primarily the bacteria), which could cause a shift in the local organic carbon balance in some regions. Because many climatic interactions are still not well understood, it is difficult to predict how the carbon cycle and the carbon pumps will react to climate change. The first trends indicating change that have been detected throughout the world ocean are those of water temperature and salinity. In addition, a general decrease in the oxygen content of seawater has been observed, which can be attributed to biological and physical causes such as changes in current flow and higher temperatures. It is also possible that changes in the production and breakdown of biomass in the ocean play a role here.

Changes in the carbon cycle are also becoming apparent in another way: The increasing accumulation of carbon dioxide in the sea leads to acidification of the



2.5 > In order to determine the effect of increasing atmospheric CO₂ concentrations on the ocean, an international research team enriched seawater with CO₂ in floating tanks off Spitsbergen, and studied the effects on organisms.

oceans or, in chemical terms, a decline in the pH value. This could have a detrimental impact on marine organisms and ecosystems. Carbonate-secreting organisms are particularly susceptible to this because an acidifying environment is less favorable for carbonate production. Laboratory experiments have shown that acidification has a negative effect on the growth of corals and other organisms. The topic of ocean acidification is presently being studied in large research programmes worldwide. Conclusive results relating to the feedback effects between climate and acidification are thus not yet available. This is also the case for the impact of ocean warming. There are many indications for significant feedback effects here, but too little solid knowledge to draw any robust quantitative conclusions.

We will have to carry out focussed scientific studies to see what impact global change will have on the natural carbon cycle in the ocean. It would be naïve to assume that this is insignificant and irrelevant for the future climate of our planet. To the contrary, our limited knowledge of the relationships should motivate us to study the ocean even more intensely and to develop new methods of observation.

The consequences of ocean acidification

> Climate change not only leads to warming of the atmosphere and water, but also to an acidification of the oceans. It is not yet clear what the ultimate consequences of this will be for marine organisms and communities, as only a few species have been studied. Extensive long-term studies on a large variety of organisms and communities are needed to understand potential consequences of ocean acidification.

How climate change acidifies the oceans

Carbon dioxide is a determining factor for our climate and, as a greenhouse gas, it contributes considerably to the warming of the Earth's atmosphere and thus also of the ocean. The global climate has changed drastically many times through the course of Earth history. These changes, in part, were associated with natural fluctuations in the atmospheric CO₂ content, for example, during the transitions from ice ages to interglacial periods (the warmer phases within longer glacial epochs). The drastic increase in atmospheric CO₂ concentrations by more than 30 per cent since the beginning of industrialization, by contrast, is of anthropogenic origin, i.e. caused by humans.

The largest CO₂ sources are the burning of fossil fuels, including natural gas, oil, and coal, and changes in land usage: clearing of forests, draining of swamps, and expansion of agricultural areas. CO₂ concentrations in the atmosphere have now reached levels near 390 ppm (parts per million). In pre-industrial times this value was only around 280 ppm. Now climate researchers estimate that the level will reach twice its present value by the end of this century. This increase will not only cause additional warming of the Earth. There is another effect associated with it that has only recently come to the attention of the public – acidification of the world ocean.

There is a permanent exchange of gas between the air and the ocean. If the CO₂ levels in the atmosphere increase, then the concentrations in the near-surface layers of the ocean increase accordingly. The dissolved carbon dioxide reacts to some extent to form carbonic

acid. This reaction releases protons, which leads to acidification of the seawater. The pH values drop. It has been demonstrated that the pH value of seawater has in fact already fallen, parallel to the carbon dioxide increase in the atmosphere, by an average of 0.1 units. Depending on the future trend of carbon dioxide emissions, this value could fall by another 0.3 to 0.4 units by the end of this century. This may appear to be negligible, but in fact it is equivalent to an increased proton concentration of 100 to 150 per cent.

The effect of pH on the metabolism of marine organisms

The currently observed increase of CO₂ concentrations in the oceans is, in terms of its magnitude and rate, unparalleled in the evolutionary history of the past 20 million years. It is therefore very uncertain to what extent the marine fauna can adapt to it over extended time periods. After all, the low pH values in seawater have an adverse effect on the formation of carbonate minerals, which is critical for many invertebrate marine animals with carbonate skeletons, such as mussels, corals or sea urchins.

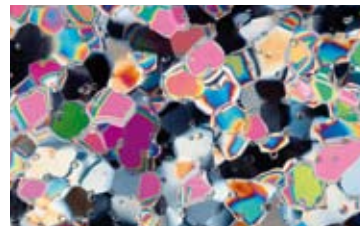
Processes similar to the dissolution of CO₂ in seawater also occur within the organic tissue of the affected organisms. CO₂, as a gas, diffuses through cell membranes into the blood, or in some animals into the hemolymph, which is analogous to blood. The organism has to compensate for this disturbance of its natural acid-base balance, and some animals are better at this than others. Ultimately this ability depends on the genetically determined efficiency of various mechanisms of pH and ion regulation,

The pH value

The pH value is a measure of the strength of acids and bases in a solution. It indicates how acidic or basic a liquid is. The pH scale ranges from 0 (very acidic) to 14 (very basic). The stronger an acid is the more easily it loses protons (H⁺), which determines the pH value. Practically expressed, the higher the proton concentration is, the more acidic a liquid is, and the lower its pH value is.



2.6 > By studying ice cores scientists want to discover which organisms live in the ice. Air bubbles in Antarctic ice cores also provide clues to the presence of trace gases in the former atmosphere, and to past climate. The ice cores are drilled using powerful tools. For more detailed study they are analysed in the laboratory. When ice crystals are observed under a special polarized light, their fine structure reveals shimmering colours.



which depends on the animal group and lifestyle. In spite of enhanced regulatory efforts by the organism to regulate them, acid-base parameters undergo permanent adjustment within tissues and body fluids. This, in turn, can have an adverse effect on the growth rate or reproductive capacity and, in the worst case, can even threaten the survival of a species in its habitat.

The pH value of body fluids affects biochemical reactions within an organism. All living organisms therefore strive to maintain pH fluctuations within a tolerable range. In order to compensate for an increase in acidity due to CO_2 , an organism has two possibilities: It must either increase its expulsion of excessive protons or take up additional buffering substances, such as bicarbonate

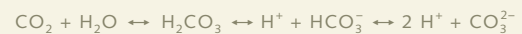
ions, which bind protons. For the necessary ion regulation processes, most marine animals employ specially developed epithelia that line body cavities, blood vessels, or the gills and intestine.

The ion transport systems used to regulate acid-base balance are not equally effective in all marine animal groups. Marine organisms are apparently highly tolerant of CO_2 when they can accumulate large amounts of bicarbonate ions, which stabilize the pH value. These organisms are usually also able to very effectively excrete protons. Mobile and active species such as fish, certain crustaceans, and cephalopods – cuttlefish, for instance – are therefore especially CO_2 -tolerant. The metabolic rates of these animals can strongly fluctuate and reach

When carbonate formation loses equilibrium

The atmospheric gas carbon dioxide (CO_2) dissolves very easily in water. This is well known in mineral water, which often has carbon dioxide added. In the dissolution process, carbon dioxide reacts with the water molecules according to the equation below. When carbon dioxide mixes with the water it is partially converted into carbonic acid, hydrogen ions (H^+), bicarbonate (HCO_3^-), and carbonate ions (CO_3^{2-}). Seawater can assimilate much more CO_2 than fresh water. The reason for this is that bicarbonate and carbonate ions have been perpetually discharged into the sea over aeons. The carbonate reacts with CO_2 to form bicarbonate, which leads to a further uptake of CO_2 and a decline of the CO_3^{2-} concentration in the ocean. All of the CO_2 -derived chemical species in the water together, i.e. carbon

dioxide, carbonic acid, bicarbonate and carbonate ions, are referred to as dissolved inorganic carbon (DIC). This carbonic acid-carbonate equilibrium determines the amount of free protons in the seawater and thus the pH value.



In summary, the reaction of carbon dioxide in seawater proceeds as follows: First the carbon dioxide reacts with water to form carbonic acid. This then reacts with carbonate ions and forms bicarbonate. Over the long term, ocean acidification leads to a decrease in the concentration of carbonate ions in seawater. A 50 per cent decline

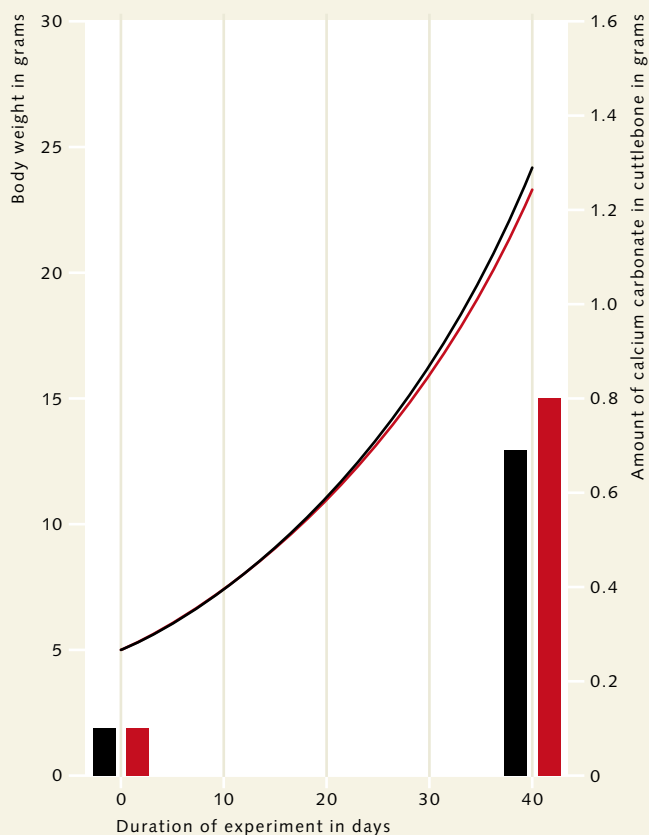


2.7 > Studies of the coral *Oculina patagonia* show that organisms with carbonate shells react sensitively to acidification of the water. Picture a shows a coral colony in its normal state. The animals live retracted within their carbonate exoskeleton (yellowish). In acidic water (b) the carbonate skeleton degenerates. The animals take on an elongated polyp form. Their small tentacles, which they use to grab nutrient particles in the water, are clearly visible. Only when the animals are transferred to water with natural pH values do they start to build their protective skeletons again (c).

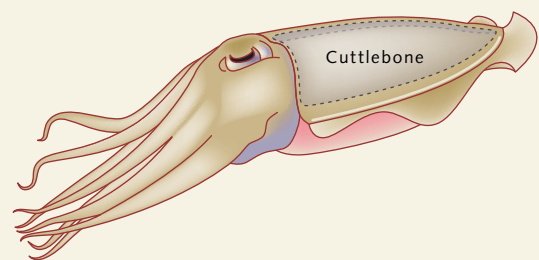
of the levels is predicted, for example, if there is a drop in pH levels of 0.4 units. This would be fatal. Because carbonate ions together with calcium ions (als CaCO_3) form the basic building blocks of carbonate skeletons and shells, this decline would have a direct effect on the ability of many marine organisms to produce **biogenic** carbonate. In extreme cases this can even lead to the dissolution of existing carbonate shells, skeletons and other structures.

Many marine organisms have already been studied to find out how acidification affects carbonate formation. The best-known examples are the warm-water corals, whose skeletons are particularly threatened by the drop in pH values. Scientific studies suggest that carbon dioxide levels could be reached by the middle of this century

at which a net growth (i.e. the organisms form more carbonate than is dissolved in the water), and thus the successful formation of reefs, will hardly be possible. In other invertebrates species, such as mussels, sea urchins and starfish, a decrease in calcification rates due to CO_2 has also been observed. For many of these invertebrates not only carbonate production, but also the growth rate of the animal was affected. In contrast, for more active animal groups such as fish, salmon, and the cephalopod mollusc *Sepia officinalis*, no evidence could be found as to know that the carbon dioxide content in the seawater had an impact on growth rates. In order to draw accurate conclusions about how the carbon dioxide increase in the water affects marine organisms, further studies are therefore necessary.



2.8 > Active and rapidly moving animals like the cephalopod mollusc (cuttlefish) *Sepia officinalis* are apparently less affected by acidification of the water. The total weight of young animals increased over a period of 40 days in acidic seawater (red line) just as robustly as in water with a normal pH and CO_2 content (black line). The growth rate of the calcareous shield, the cuttlebone, also proceeded at very high rates (see the red and black bars in the diagram). The amount of calcium carbonate (CaCO_3) incorporated in the cuttlebone is used as a measure here. The schematic illustration of the cephalopod shows the position of the cuttlebone on the animal.



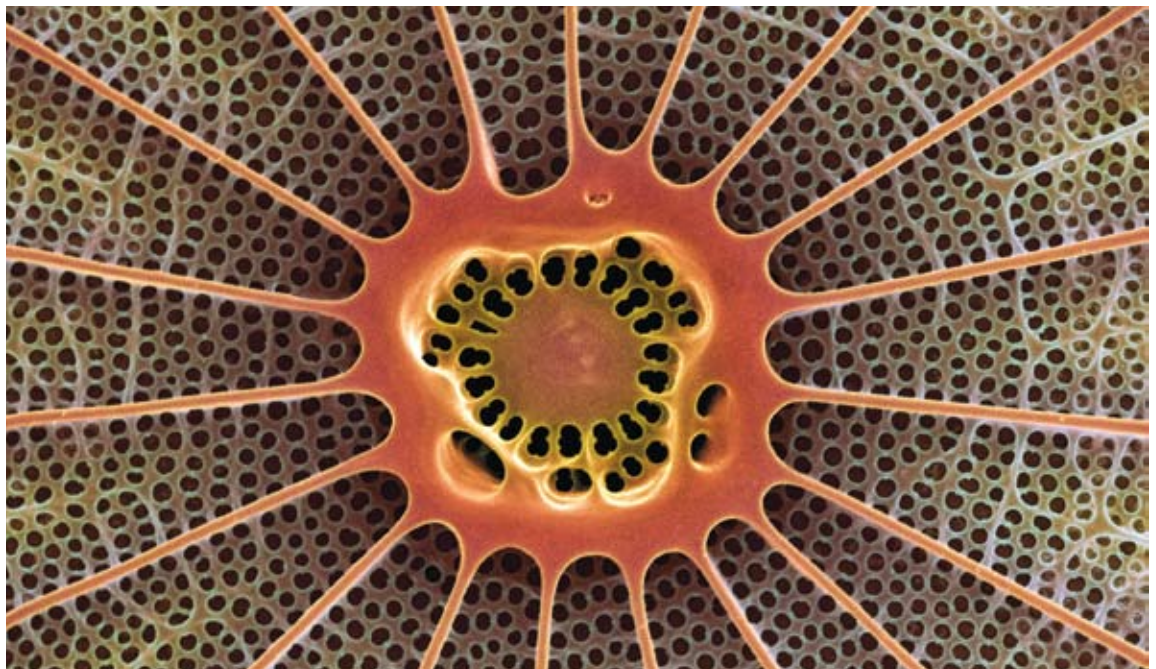
very high levels during exercise (hunting & escape behaviour). The oxygen-consumption rate (a measure of metabolic rate) of these active animal groups can reach levels that are orders of magnitude above those of sea urchins, starfish or mussels. Because large amounts of CO_2 and protons accumulate during excessive muscle activity, active animals often possess an efficient system for proton excretion and acid-base regulation. Consequently, these animals can better compensate for disruptions in their acid-base budgets caused by acidification of the water.

Benthic invertebrates (bottom-dwelling animals without a vertebral column) with limited ability to move great distances, such as mussels, starfish or sea urchins, often cannot accumulate large amounts of bicarbonate in their body fluids to compensate for acidification and the excess protons. Long-term experiments show that some of these species grow more slowly under acidic conditions. One reason for the reduced growth could be a natural protective mechanism of invertebrate animal species: In stress situations such as falling dry during low tide, these organisms reduce their metabolic rates. Under normal conditions this is a very effective protection strategy

that insures survival during short-term stress situations. But when they are exposed to long-term CO_2 stress, this protective mechanism could become a disadvantage for the sessile animals. With the long-term increase in carbon dioxide levels in seawater, the energy-saving behaviour and the suppression of metabolism inevitably leads to limited growth, lower levels of activity, and thus a reduced ability to compete within the ecosystem.

However, the sensitivity of a species' reaction to CO_2 stressor and acidification cannot be defined alone by the simple formula: good acid-base regulation = high CO_2 tolerance. There are scientific studies that suggest this is not the case. For example, one study investigated the ability of a species of brittlestar (echinodermata), an invertebrate that mainly lives in the sediment, to regenerate severed arms. Surprisingly, animals from more acidic seawater not only re-grew longer arms, but their calcareous skeletons also contained a greater amount of calcium carbonate. The price for this, however, was reduced muscle growth. So in spite of the apparent positive indications at first glance, this species is obviously adversely affected by ocean acidification because they

2.9 > Diatoms like this *Arachnoidiscus* are an important nutrient basis for higher organisms. It is still uncertain how severely they will be affected by acidification of the oceans.



can only efficiently feed and supply their burrows in the sediment with oxygenated seawater if they have fully functioning arms.

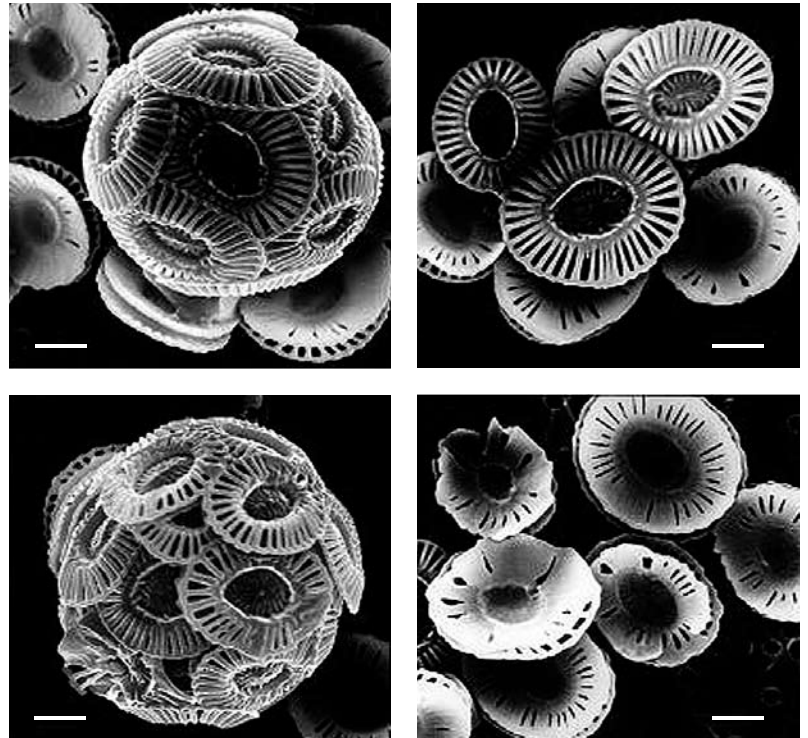
Even fish can be impaired. Many adult animals are relatively CO₂ tolerant. Early developmental stages, however, obviously react very sensitively to the CO₂ stressor. A strong impairment of the sense of smell in seawater with low pH values was observed in the larval clownfish. These animals are normally able to orientate themselves by a specific odour signal and, after their larval phase, which they spend free-swimming in the water column, to find their final permanent habitat on coral reefs. In the experiment, fish larvae that were raised in seawater with a pH value lowered by about 0.3 units, reacted significantly less to the otherwise very stimulating odour of sea anemones with which they live in symbiosis on reefs. If behavioural changes caused by CO₂ occur during a critical phase of the life cycle, they can, of course, have a strong impact on the reproductive success of a species.

It is not yet known to what extent other marine organisms are impacted by these kinds of effects of ocean acidification. Other studies on embryonic and juvenile stages of various species have shown, however, that the early developmental stages of an organism generally respond more sensitively to CO₂ stress than the adult animals do.

Threat to the nutrition base in the oceans – phytoplankton and acidification

The entire food chain in the ocean is represented by the microscopic organisms of the marine phytoplankton. These include diatoms (siliceous algae), coccolithophores (calcareous algae), and the cyanobacteria (formerly called blue algae), which, because of their photosynthetic activity, are responsible for around half of the global primary productivity.

Because phytoplankton requires light for these processes, it lives exclusively in surface ocean waters. It is therefore directly affected by ocean acidification. In the future, however, due to global warming, other influenc-



2.10 > These electron micrographs clearly illustrate that increased CO₂ concentrations in the water can disturb and lead to malformation in calcareous marine organisms, such as the coccolithophorid *Emiliana huxleyi* shown here. The upper pictures reflect CO₂ concentrations in the water of 300 ppm, which is slightly above the pre-industrial average CO₂ level for seawater. The bottom photographs reflect a CO₂ content of 780 to 850 ppm. For size comparison, the bars represent a length of one micrometre.

ing variables such as temperature, light or nutrient availability will also change due to global warming. These changes will also determine the productivity of autotrophic organisms, primarily bacteria or algae, which produce biomass purely by photosynthesis or the incorporation of chemical compounds. It is therefore very difficult to predict which groups of organisms will profit from the changing environmental conditions and which will turn out to be the losers.

Ocean acidification is of course not the only consequence of increased CO₂. This gas is, above all, the elixir of life for plants, which take up CO₂ from the air or seawater and produce biomass. Except for the acidification problem, increasing CO₂ levels in seawater should

2.11 > The clownfish (*Amphiprion percula*) normally does not react sensitively to increased CO₂ concentrations in the water. But in the larvae the sense of smell is impaired.



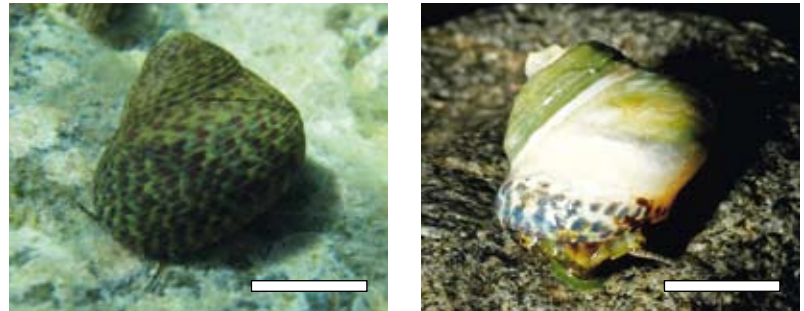
therefore favour the growth of those species whose photosynthetic processes were formerly limited by carbon dioxide. For example, a strong increase in photosynthesis rates was reported for cyanobacteria under higher CO₂ concentrations. This is also true for certain coccolithophores such as *Emiliana huxleyi*. But even for *Emiliana* the initially beneficial rising CO₂ levels could become fatal. *Emiliana* species possess a calcareous shell comprised of numerous individual plates. There is now evidence that the formation of these plates is impaired by lower pH values. In contrast, shell formation by diatoms, as well as their photosynthetic activity, seems to be hardly affected by carbon dioxide. For diatoms also, however, shifts in species composition have been reported under conditions of increased CO₂ concentration.

Challenge for the future: Understanding acidification

In order to develop a comprehensive understanding of the impacts of ocean acidification on life in the sea, we have to learn how and why CO₂ affects various physiological processes in marine organisms. The ultimate critical challenge is how the combination of individual processes determines the overall CO₂ tolerance of the organisms. So far, investigations have mostly been limited to short-term studies. To find out how and whether an organism can grow, remain active and reproduce successfully in a more acidified ocean, long term (months) and multiple-generation studies are necessary.

The final, and most difficult step, thus is to integrate the knowledge gained from species or groups at the ecosystem level. Because of the diverse interactions among species within ecosystems, it is infinitely more difficult to predict the behaviour of such a complex system under ocean acidification.

In addition, investigations are increasingly being focused on marine habitats that are naturally characterized by higher CO₂ concentrations in the seawater. Close to the Italian coast around the island of Ischia, for instance, CO₂ is released from the sea floor due to vol-



2.12 > Low pH values in the waters around Ischia cause corrosion of the shells of calcareous animals such as the snail *Osilinus turbinata*. The left picture shows an intact spotted shell at normal pH values of 8.2. The shell on the right, exposed to pH values of 7.3, shows clear signs of corrosion. The scale bars are equal to one centimetre.

canic activity, leading to acidification of the water. This means that there are coastal areas directly adjacent to one another with normal (8.1 to 8.2) and significantly lowered pH values (minimum 7.4). If we compare the animal and plant communities of these respective areas, clear differences can be observed: In the acidic areas rock corals are completely absent, the number of specimens of various sea urchin and snail species is low, as is the number of calcareous red algae. These acidic areas of the sea are mainly dominated by seagrass meadows and various non-calcareous algal species.

The further development of such ecosystem-based studies is a great challenge for the future. Such investigations are prerequisite to a broader understanding of future trends in the ocean. In addition, deep-sea ecosystems, which could be directly affected by the possible impacts of future CO₂ disposal under the sea floor, also have to be considered.

In addition, answers have to be found to the question of how climate change affects reproduction in various organisms in the marine environment. Up to now there have been only a few exemplary studies carried out and current science is still far from a complete understanding. Whether and how different species react to chemical changes in the ocean, whether they suffer from stress or not is, for the most part, still unknown. There is an enormous need for further research in this area.

Oxygen in the ocean

> Scientists have been routinely measuring oxygen concentrations in the ocean for more than a hundred years. With growing concerns about climate change, however, this parameter has suddenly become a hot topic. Dissolved oxygen in the ocean provides a sensitive early warning system for the trends that climate change is causing. A massive deployment of oxygen sensors is projected for the coming years, which will represent a renaissance of this parameter.

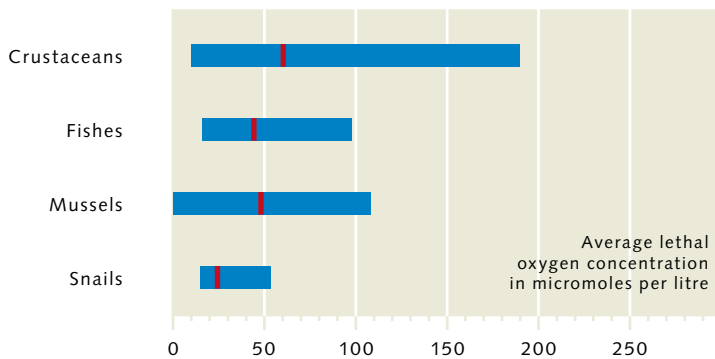
Oxygen – product and elixir of life

Carbon dioxide, which occurs in relatively small amounts in the atmosphere, is both a crucial substance for plants, and a climate-threatening gas. Oxygen, on the other hand, is not only a major component of the atmosphere, it is also the most abundant chemical element on Earth. The emergence of oxygen in the atmosphere is the result of a biological success model, photosynthesis, which helps plants and bacteria to convert inorganic materials such as carbon dioxide and water to biomass. Oxygen was, and continues to be generated by this process. The biomass produced is, for its part, the nutritional foundation for consumers, either bacteria, animals or humans. These consumers cannot draw their required energy

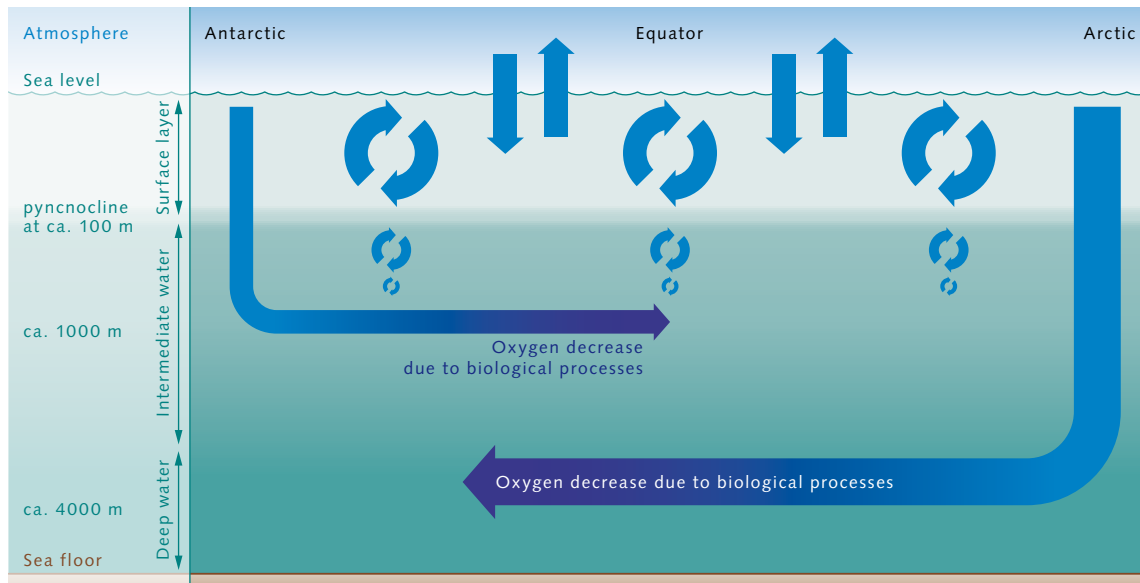
from sunlight as the plants do, rather they have to obtain it by burning biomass, a process that consumes oxygen. Atmospheric oxygen on our planet is thus a product, as well as the elixir of life.

Oxygen budget for the world ocean

Just like on the land, there are also photosynthetically active plants and bacteria in the ocean, the **primary producers**. Annually, they generate about the same amount of oxygen and fix as much carbon as all the land plants together. This is quite amazing. After all, the total living biomass in the ocean is only about one two-hundredth of that in the land plants. This means that primary producers in the ocean are around two hundred times more productive than land plants with respect to their mass. This reflects the high productivity of single-celled algae, which contain very little inactive biomass such as, for example, the heartwood in tree trunks. Photosynthetic production of oxygen is limited, however, to the uppermost, sunlit layer of the ocean. This only extends to a depth of around 100 metres and, because of the stable density layering of the ocean, it is largely separated from the enormous underlying volume of the deeper ocean. Moreover, most of the oxygen generated by the primary producers escapes into the atmosphere within a short time, and thus does not contribute to oxygen enrichment in the deep water column. This is because the near-surface water, which extends down to around 100 metres, is typically saturated with oxygen by the supply from the atmosphere, and thus cannot store additional oxygen from biological production. In the inner ocean, on the



2.13 > Marine animals react in different ways to oxygen deficiency. Many species of snails, for instance, can tolerate lower O_2 levels than fish or crabs. The diagram shows the concentration at which half of the animals die under experimental conditions. The average value is shown as a red line for each animal group. The bars show the full spectrum: some crustaceans can tolerate much lower O_2 concentrations than others.



2.14 > Oxygen from the atmosphere enters the near-surface waters of the ocean. This upper layer is well mixed, and is thus in chemical equilibrium with the atmosphere and rich in O_2 . It ends abruptly at the pycnocline, which acts like a barrier. The oxygen-rich water in the surface zone does not mix readily

with deeper water layers. Oxygen essentially only enters the deeper ocean by the motion of water currents, especially with the formation of deep and intermediate waters in the polar regions. In the inner ocean, marine organisms consume oxygen. This creates a very sensitive equilibrium.

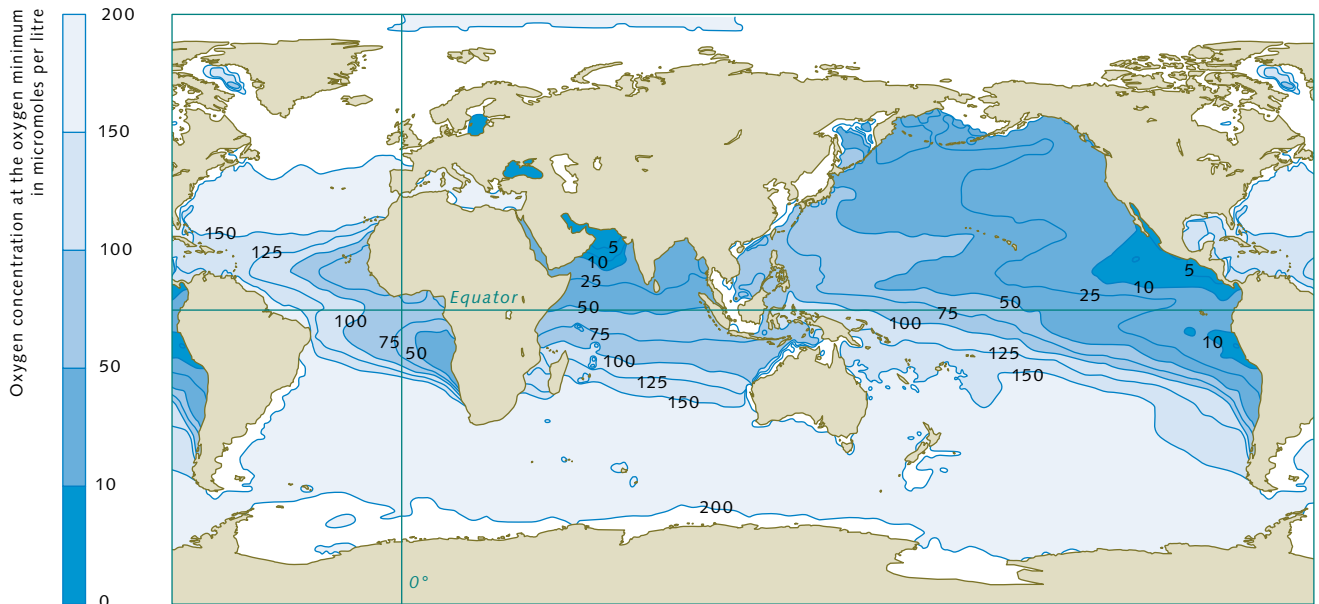
other hand, there is no source of oxygen. Oxygen enters the ocean in the surface water through contact with the atmosphere. From there the oxygen is then brought to greater depths through the sinking and circulation of water masses. These, in turn, are dynamic processes that are strongly affected by climatic conditions. Three factors ultimately determine how high the concentration of dissolved oxygen is at any given point within the ocean:

1. The initial oxygen concentration that this water possessed at its last contact with the atmosphere.
2. The amount of time that has passed since the last contact with the atmosphere. This can, in fact, be decades or centuries.
3. Biological oxygen consumption that results during this time due to the respiration of all the consumers. These range from miniscule bacteria to the zooplankton, and up to the higher organisms such as fish.

The present-day distribution of oxygen in the internal deep ocean is thus determined by a complicated and not

fully understood interplay of water circulation and biological productivity, which leads to oxygen consumption in the ocean's interior. Extensive measurements have shown that the highest oxygen concentrations are found at high latitudes, where the ocean is cold, especially well-mixed and ventilated. The mid-latitudes, by contrast, especially on the western coasts of the continents, are characterized by marked oxygen-deficient zones. The oxygen supply here is very weak due to the sluggish water circulation, and this is further compounded by elevated oxygen consumption due to high biological productivity. This leads to a situation where the oxygen is almost completely depleted in the depth range between 100 and 1000 metres. This situation is also observed in the northern Indian Ocean in the area of the Arabian Sea and the Bay of Bengal.

Different groups of marine organisms react to the oxygen deficiency in completely different ways, because of the wide range of tolerance levels of different marine



2.15 > Marine regions with oxygen deficiencies are completely natural. These zones are mainly located in the mid-latitudes on the west sides of the continents. There is very little mixing here of the warm surface waters with the cold deep waters,

so not much oxygen penetrates to greater depths. In addition, high bioproductivity and the resulting large amounts of sinking biomass here lead to strong oxygen consumption at depth, especially between 100 and 1000 metres.

animals to oxygen-poor conditions. For instance, crustaceans and fish generally require higher oxygen concentrations than mussels or snails. The largest oceanic oxygen minimum zones, however, because of their extremely low concentrations, should be viewed primarily as natural dead zones for the higher organisms, and by no means as caused by humans.

Oxygen – the renaissance of a hydrographic parameter

Oxygen distribution in the ocean depends on both biological processes, like the respiration of organisms, and on physical processes such as current flow. Changes in either of these processes should therefore lead to changes in the oxygen distribution. In fact, dissolved oxygen can be viewed as a kind of sensitive early warning system for global (climate) change in the ocean. Scientific studies show that this early warning system can detect the

expected decrease in oxygen transport from the atmosphere into the ocean that is driven by global current and mixing processes, as well as possible changes in the marine biotic communities. In recent years, this knowledge has led to a renaissance of oxygen in the field of global marine research.

In oceanography, dissolved oxygen has been an important measurement parameter for over a hundred years. A method for determining dissolved oxygen was developed as early as the end of the 19th century, and it is still applied in an only slightly modified form today as a precise method. This allowed for the development of an early fundamental understanding of the oxygen distribution in the world ocean, with the help of the famous German Atlantic Expedition of the “Meteor” in the 1920s.

Research efforts in recent years have recorded decreasing oxygen concentrations for almost all the ocean basins. These trends are, in part, fairly weak and mainly limited to water masses in the upper 2000 metres of the ocean.

Therefore, no fully consistent picture can yet be drawn from the individual studies. Most of the studies do, however, show a trend of decreasing oxygen concentrations. This trend agrees well with an already verified expansion and intensification of the natural oxygen minimum zones, those areas that are deadly for higher organisms. If the oxygen falls below certain (low) threshold values, the water becomes unsuitable for higher organisms. Sessile, attached organisms die. Furthermore, the oxygen deficiency leads to major changes in biogeochemical reactions and elemental cycles in the ocean – for instance, of the plant nutrients nitrate and phosphate.

Oxygen levels affect geochemical processes in the sediment but also, above all, bacterial metabolism processes, which, under altered oxygen conditions, can be changed dramatically. It is not fully possible today to predict what consequences these changes will ultimately have. In some cases it is not even possible to say with certainty whether climate change will cause continued warming, or perhaps even local cooling. But it is probable that the resulting noticeable effects will continue over a long time period of hundreds or thousands of years.

Even today, however, climate change is starting to cause alterations in the oxygen content of the ocean that can have negative effects. For the first time in recent years, an extreme low-oxygen situation developed off the coast of Oregon in the United States that led to mass mortality in crabs and fish. This new death zone off Oregon originated in the open ocean and presumably can be attributed to changes in climate. The prevailing winds off the west coast of the USA apparently changed direction and intensity and, as a result, probably altered the ocean currents. Researchers believe that the change caused oxygen-poor water from greater depths to flow to surface waters above the shelf.

The death zone off Oregon is therefore different than the more than 400 near-coastal death zones known worldwide, which are mainly attributed to eutrophication, the excessive input of plant nutrients. Eutrophication normally occurs in coastal waters near densely populated regions with intensive agricultural activity.

Oxygen – challenge to marine research

The fact that model calculations examining the effects of climate change almost all predict an oxygen decline in major parts of the ocean, which agrees with the available observations of decreasing oxygen, gives the subject additional weight. Even though the final verdict is not yet in, there are already indications that the gradual loss of oxygen in the world ocean is an issue of great relevance which possibly also has socio-economic repercussions, and which ocean research must urgently address.

Intensified research can provide more robust conclusions about the magnitude of the oxygen decrease. In addition it will contribute significantly to a better understanding of the effects of global climate change on the ocean. In recent years marine research has addressed this topic with increased vigour, and has already established appropriate research programmes and projects. It is difficult, however, to completely measure the temporally and spatially highly variable oceans in their totality. In order to draw reliable conclusions, therefore, the classic instruments of marine research like ships and taking water samples will not suffice. Researchers must begin to apply new observational concepts.

“Deep drifters” are an especially promising tool: these are submersible measuring robots that drift completely autonomously in the ocean for 3 to 4 years, and typically measure the upper 2000 metres of the water column every 10 days. After surfacing, the data are transferred to a data centre by satellite. There are presently around 3200 of these measuring robots deployed for the international research programme ARGO, named after a ship from Greek mythology. Together they form a worldwide autonomous observatory that is operated by almost 30 countries.

So far this observatory is only used on a small scale for oxygen measurements. But there has been developed a new sensor technology for oxygen measurements in the recent past that can be deployed on these drifters. This new technology would give fresh impetus to the collection of data on the variability of the oceanic oxygen distribution.

The Atlantic Expedition

For the first time, during the German Atlantic Expedition (1925 to 1927) with the research vessel “Meteor”, an entire ocean was systematically sampled, both in the atmosphere and in the water column. Using an echosounder system that was highly modern for its time, depth profiles were taken across 13 transits of the entire ocean basin.

Climate change impacts on methane hydrates

> Huge amounts of methane are stored around the world in the sea floor in the form of solid methane hydrates. These hydrates represent a large energy reserve for humanity. Climate warming, however, could cause the hydrates to destabilize. The methane, a potent greenhouse gas, would escape unused into the atmosphere and could even accelerate climate change.

How methane ends up in the ocean

People have been burning coal, oil and natural gas for more than a hundred years. Methane hydrates, on the other hand, have only recently come under controversial discussion as a potential future energy source from the ocean. They represent a new and completely untapped reservoir of fossil fuel, because they contain, as their name suggests, immense amounts of methane, which is the main component of natural gas. Methane hydrates belong to a group of substances called clathrates – substances in which one molecule type forms a crystal-like cage structure and encloses another type of molecule. If the cage-forming molecule is water, it is called a hydrate. If the molecule trapped in the water cage is a gas, it is a gas hydrate, in this case methane hydrate.

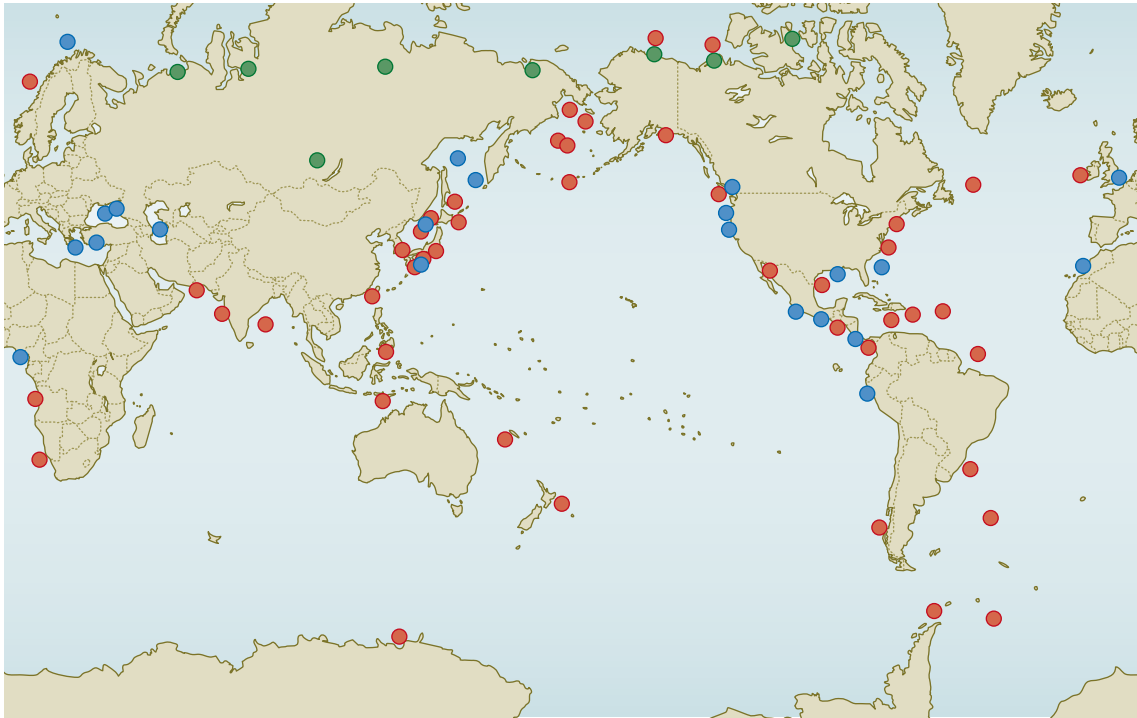
2.16 > Methane hydrate looks like a piece of ice when it is brought up from the sea floor. This lump was retrieved during an expedition to the “hydrate ridge” off the coast of Oregon in the US.



Methane hydrates can only form under very specific physical, chemical and geological conditions. High water pressures and low temperatures provide the best conditions for methane hydrate formation. If the water is warm, however, the water pressure must be very high in order to press the water molecule into a clathrate cage. In this case, the hydrate only forms at great depths. If the water is very cold, the methane hydrates could conceivably form in shallower water depths, or even at atmospheric pressure. In the open ocean, where the average bottom-water temperatures are around 2 to 4 degrees Celsius, methane hydrates occur starting at depths of around 500 metres.

Surprisingly, there is no methane hydrate in the deepest ocean regions, the areas with the highest pressures, because there is very little methane available here. The reason for this is because methane in the ocean is produced by microbes within the sea floor that break down organic matter that sinks down from the sunlit zone near the surface.

Organic matter is composed, for example, of the remains of dead algae and animals, as well as their excrements. In the deepest areas of the ocean, below around 2000 to 3000 metres, only a very small amount of organic remains reach the bottom because most of them are broken down by other organisms on their way down through the water column. As a rule of thumb, it can be said that only around 1 per cent of the organic material produced at the surface actually ends up in the deep sea. The deeper the sea floor is, the less organic matter settles on the bottom. Methane hydrates therefore primarily occur on the continental slopes, those areas where the



2.17 > Methane hydrate occurs in all of the oceans as well as on land. The green dots show occurrences in the northern permafrost regions. Occurrences identified by geophysical methods are indicated by red. The occurrences shown by blue dots were verified by direct sampling.

continental plates meet the deep-sea regions. Here there is sufficient organic matter accumulating on the bottom and the combination of temperature and pressure is favourable. In very cold regions like the Arctic, methane hydrates even occur on the shallow continental shelf (less than 200 metres of water depth) or on the land in permafrost, the deep-frozen Arctic soil that does not even thaw in the summer.

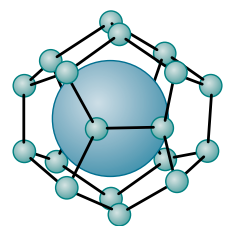
It is estimated that there could be more potential fossil fuel contained in the methane hydrates than in the classic coal, oil and natural gas reserves. Depending on the mathematical model employed, present calculations of their abundance range between 100 and 530,000 gigatons of carbon. Values between 1000 and 5000 gigatons are most likely. That is around 100 to 500 times as much carbon as is released into the atmosphere annually by the burning of coal, oil and gas. Their possible future excavation would presumably only produce a portion of this as actual usable fuel, because many deposits are inaccessible, or the production would be too expensive

or require too much effort. Even so, India, Japan, Korea and other countries are presently engaged in the development of mining techniques in order to be able to use methane hydrates as a source of energy in the future (Chapter 7).

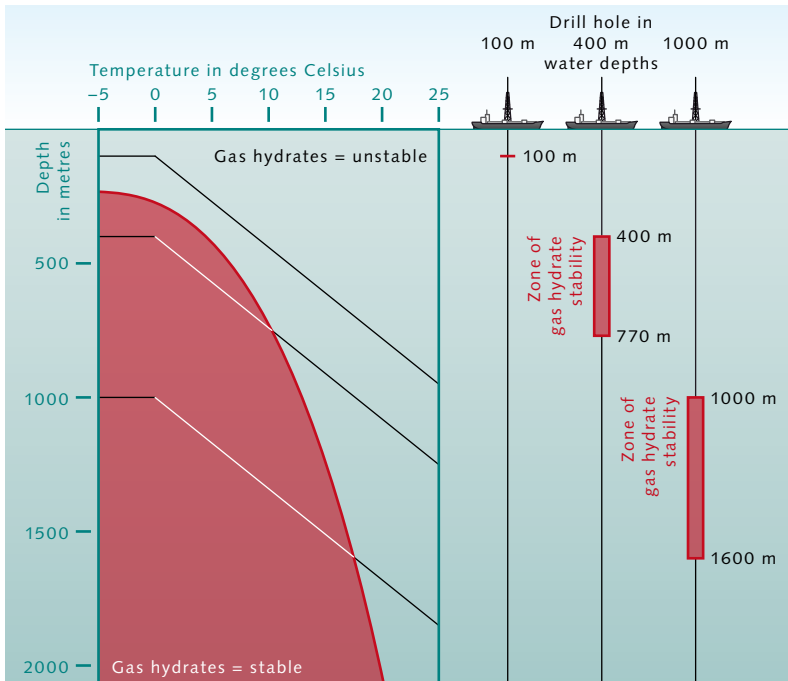
Methane hydrates and global warming

Considering that methane hydrates only form under very specific conditions, it is conceivable that global warming, which as a matter of fact includes warming of the oceans, could affect the stability of gas hydrates.

There are indications in the history of the Earth suggesting that climatic changes in the past could have led to the destabilization of methane hydrates and thus to the release of methane. These indications – including measurements of the methane content in ice cores, for instance – are still controversial. Yet be this as it may, the issue is highly topical and is of particular interest to scientists concerned with predicting the possible impacts



2.18 > In hydrates, the gas (large ball) is enclosed in a cage formed by water molecules. Scientists call this kind of molecular arrangement a clathrate.



2.19 > Gas hydrates occur when sufficient methane is produced by organic matter degradation in the sea floor under low temperature and high pressure conditions. These conditions occur predominantly on the continental margins. The warmer the water, the larger the water depths must be to form the hydrate. Deep inside the sea floor, however, the temperature is too high for the formation of methane hydrates because of the Earth's internal heat.

Oxidation

Many bacteria use methane to provide energy for their metabolism. They take up methane and transform it chemically. In this process the methane releases electrons and is thus oxidized. Some bacteria break the methane down with the help of oxygen. This is called aerobic oxidation. Other bacteria do not need oxygen. This kind of oxidation is called anaerobic.

of a temperature increase on the present deposits of methane hydrate.

Methane is a potent greenhouse gas, around 20 times more effective per molecule than carbon dioxide. An increased release from the ocean into the atmosphere could further intensify the greenhouse effect. Investigations of methane hydrates stability in dependence of temperature fluctuations, as well as of methane behaviour after it is released, are therefore urgently needed.

Various methods are employed to predict the future development. These include, in particular, mathematic modelling. Computer models first calculate the hypothetical amount of methane hydrates in the sea floor using background data (organic content, pressure, temperature). Then the computer simulates the warming of the seawater, for instance, by 3 or 5 degrees Celsius per 100 years. In this way it is possible to determine how the

methane hydrate will behave in different regions. Calculations of methane hydrate deposits can then be coupled with complex mathematical climate and ocean models. With these computer models we get a broad idea of how strongly the methane hydrates would break down under the various scenarios of temperature increase. Today it is assumed that in the worst case, with a steady warming of the ocean of 3 degrees Celsius, around 85 per cent of the methane trapped in the sea floor could be released into the water column.

Other, more sensitive models predict that methane hydrates at great water depths are not threatened by warming. According to these models, only the methane hydrates that are located directly at the boundaries of the stability zones would be primarily affected. At these locations, a temperature increase of only 1 degree Celsius would be sufficient to release large amounts of methane from the hydrates. The methane hydrates in the open ocean at around 500 metres of water depth, and deposits in the shallow regions of the Arctic would mainly be affected.

In the course of the Earth's warming, it is also expected that sea level will rise due to melting of the polar ice caps and glacial ice. This inevitably results in greater pressure at the sea floor. The increase in pressure, however, would not be sufficient to counteract the effect of increasing temperature to dissolve the methane hydrates. According to the latest calculations, a sea-level rise of ten metres could slow down the methane-hydrate dissolution caused by a warming of one degree Celsius only by a few decades.

A wide variety of mathematical models are used to predict the consequences of global warming. The results of the simulations are likewise very variable. It is therefore difficult to precisely evaluate the consequences of global warming for the gas hydrate deposits, not least of all because of the large differences in the calculations of the size of the present-day gas hydrate deposits. One major goal of the current gas hydrate research is to optimize these models by using ever more precise input parameters. In order to achieve this, further measurements, expeditions, drilling and analyses are essential.

What happens when methane hydrate melts?

Not all the methane that is released from unstable methane hydrates ends up in the atmosphere. The greatest portion is likely to be broken down during its rise through the sediments and in the water column. This decomposition is mediated by two biological processes:

- anaerobic oxidation of methane by bacteria and archaea (formerly called archaebacteria) within the sea floor;
- aerobic oxidation of methane by bacteria in the water column.

During anaerobic oxidation of methane in the sediment the microbes use sulphate (SO_4^{2-}), the salt of sulphuric acid that is present in large quantities in sea water, for the methane decomposition. In this process methane is converted to bicarbonate (HCO_3^-). If the bicarbonate reacts further with calcium ions (Ca^{2+}) in the seawater, calcium carbonate (CaCO_3) precipitates, which remains stored in the sea floor over long periods of time. That would be the ideal situation, because it would make the potent greenhouse gas methane (CH_4) harmless. At the same time, hydrogen sulphide (H_2S) is produced from the sulphate, which provides energy to chemosynthetic communities, including symbiotic clams and tube-worms. During aerobic oxidation in the water column, however, bacteria break down methane with the help of oxygen (O_2). In this process, carbon dioxide is produced, which dissolves in the water. Carbon dioxide contributes to ocean acidification. Furthermore, aerobic oxidation of methane consumes oxygen. The depletion of oxygen in the water column could create or expand oxygen minimum zones in the ocean, which are a threat for fishes and other sensitive organisms. Rough estimates suggest that anaerobic and aerobic oxidation of methane together currently convert around 90 per cent of the methane produced in the sea floor before it can reach the atmosphere. The more slowly methane migrates through the sea floor or through the water column, the more effective the microbes are in converting it.

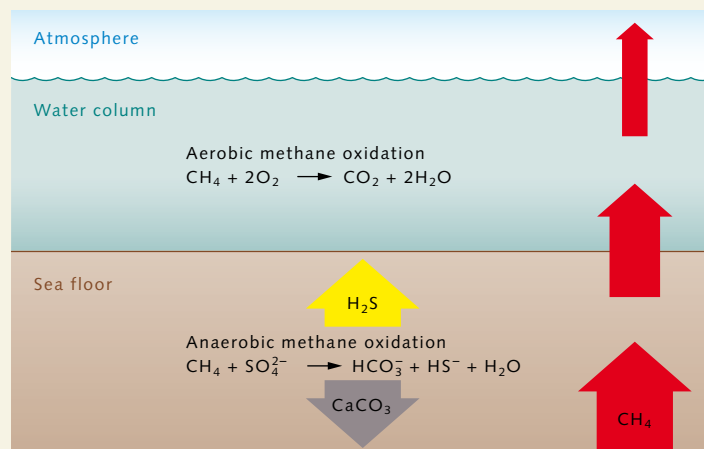
A prerequisite for this kind of degradation is that the methane molecules are dissolved in water. Methane can

only be degraded by the bacteria in this form. If the methane is released rapidly from the hydrates, it could rise in the form of gas bubbles that are not accessible by microorganisms. The microbial methane filter would thus fail, at least in part, if the methane hydrates break down very rapidly and large quantities of methane are released at once.

There is also a problem at shallow water depths, where the methane bubbles cannot completely dissolve in the water over the short distance from the sea floor to the atmosphere. In order to better understand such processes and to be able to make predictions about the functions of the microbial filters, researchers are currently investigating natural methane sources on the sea floor, so-called

Bacteria convert methane

Methane (CH_4) in the ocean is to a large extent consumed by microorganisms. During anaerobic decay within the sea floor, microbes convert methane with the help of sulphate (SO_4^{2-}). This process produces hydrogen sulphide anions (HS^-) and hydrogen sulphide (H_2S), which are closely related chemically and occur naturally together, as well as bicarbonate (CaCO_3). Bicarbonate can react with calcium ions (Ca^{2+}) to precipitate as calcium carbonate (CaCO_3). During aerobic decay (in the water column) oxygen (O_2) from the water is consumed. Carbon dioxide (CO_2) and water (H_2O) are produced. If large amounts of methane are released in the future from the gas hydrates in the sea floor, aerobic decay could result in the creation of oxygen minimum zones. The carbon dioxide produced could also contribute to ocean acidification.





2.20 > Large quantities of methane hydrate are stored not only in the sea floor, but also on land, especially in the perpetually frozen permafrost ground of the Russian tundra, such as here

in the Russian republic of Komi. Scientists are concerned that the permafrost soils could melt due to global warming and thus release the methane hydrates.

cold seeps, which constantly release larger quantities of methane. These include near-surface gas hydrate deposits, mud volcanoes, and natural-gas seeps in shallow marine regions. These seeps are a kind of natural model where the behaviour of methane in the ocean can be studied. If we understand how nature reacts to these methane seeps at the sea floor, it will help us to estimate the consequences of larger methane releases from gas hydrates. The data obtained at the methane seeps should also help to improve the precision of mathematical methane hydrate simulations.

The disappearance of methane hydrates could have fatal consequences. Gas hydrates act like a cement that fills the pores between the fine sediment particles and stabilizes the sea floor. If the methane hydrates decompose, the stability of the sea floor is reduced due to the

missing cement and the possible generation of excess pore pressure. In the worst case, large parts of continental margins fail. The resulting submarine landslides might cause severe tsunamis.

Massive mass movements occurred during the last ice age and the following deglaciation. The trigger was probably not always warming of the atmosphere, but also the opposite. Because large quantities of water were stored in the ice during the last ice age, sea level was around 120 metres lower than it is today. Especially in the shallow ocean regions, the water pressure was so low that massive amounts of methane hydrate could have been destabilized. Direct evidences for such slope failures caused by decomposing gas hydrates have not yet been found. There are, however, some indications suggesting a process in the past. Signs of seeping fluids are almost

always found in the vicinity of slope failures. These slopes were possibly destabilized by gases released by decomposing gas hydrates and liquids. Researchers also, however, definitely see the possibility of a reverse relationship: it is conceivable that slope failures and the resulting reduction in pressure on underlying sediments caused the dissociation of methane hydrates at the continental margins, thereby releasing large amounts of free gas. The slumps would have been the cause rather than the result of gas escape. These uncertainties highlight the need for further research. It is, however, fairly certain that the disappearance of methane hydrates could lead to serious problems.

Methane emissions from the Arctic – a prime focus of future gas hydrate research

In the field of methane emission research today, the Arctic is one of the most important regions worldwide. It is believed that methane occurs there both in the form of

gas hydrate in the sea and as free gas trapped in the deep-frozen permafrost. Methane deposits in permafrost and hydrates are considered to be very sensitive in the expansive shallow-shelf regions, because with the relatively low pressures it would only take a small temperature change to release large amounts of methane. In addition, new methane is continuously being produced because the Arctic regions are rich in organic material that is decomposed by microbes in the sediment. The activity of these microbes and thus the biological release rates of methane are also stimulated by increases in temperature. Hence methane emissions in the Arctic have multiple sources. International scientific consortia are now being established involving researchers from various disciplines – chemists, biologists, geologists, geophysicists, meteorologists – which are intensively addressing this problem. No one can yet say with certainty how the methane release in the Arctic will develop with global warming, either in the ocean or on the land. This research is still in its infancy.

CONCLUSION

Material fluxes – getting the full picture

The chemical and geochemical processes in the ocean are complex. Explaining them in their entirety will be a challenge for decades. There is clear evidence of global changes, such as the decrease in oxygen levels and acidification in the oceans. So far, however, our knowledge is not sufficient to say with certainty or in detail what impact climate change will have and how it will affect various parameters in the future.

It is certain that disturbances caused by climate change can have very serious consequences, because the chemical and geochemical material fluxes amount to many billions of tons. The amount of methane hydrate bound up in the sea floor alone is gigantic. If it is released and the methane rises

into the atmosphere, it will have a significant impact on the development of future climate. Investigations of the chemical and geochemical processes are therefore of enormous importance if we want to learn what to expect and how humanity can respond to it.

Analyses of the CO₂ cycle reveal how the CO₂ reservoirs of the atmosphere, land biomass and ocean interact. The oceans are buffering increasing concentrations of atmospheric trace gases. But these processes and reaching a new CO₂ equilibrium will take millennia. Natural processes therefore cannot keep up with the speed at which humans continue to discharge CO₂ and other climate-relevant trace gases into the air. The only solution is to save energy and significantly reduce greenhouse gas emissions.

Table of figures chapter 2

pp. 26–27: Steve Gschmeissner/Science Photo Library/Agentur Focus, Fig. 2.1: after IPCC (2007), Fig. 2.2: dpa Picture-Alliance/DB Philipp Assmy/Awi, Fig. 2.3: Stephan Köhler/Zoonar, Fig. 2.4: after Sabine et al. (2004), Fig. 2.5: Nicolai, IFM-GEOMAR, Fig. 2.6: top: Martin Hartley/eyevine/interTOPICS; left: mauritius images; mid: Carmen Jaspersen/picture-alliance/dpa; right: Cliff Leight/Aurora Photos, Fig. 2.7: Fine und Tchernov (2007); Foto: Avinoam Briestien, Fig. 2.8: after Gutowska et al. (2008), Fig. 2.9: Steve Gschmeissner/Science Photo Library/Agentur Focus, Fig. 2.10: Reprinted by permission from Macmillan Publishers Ltd: Nature Publishing Group, U. Riebesell et al., Nature 407, 2000, Fig. 2.11: Mike Watson Images Limited/Getty Images, Fig. 2.12: Hall-Spencer et al. (2008), Fig. 2.13: after Vaquer-Sunyer und Duarte (2008), Fig. 2.14: maribus, Fig. 2.15: after Keeling et al. (2010), Fig. 2.16: dpa Picture-Alliance/MARUM, Fig. 2.17: after Kvenvolden und Lorensen (1993), Fig. 2.18: maribus, Fig. 2.19: after IFM-GEOMAR, Fig. p. 51: after Treude, IFM-GEOMAR, Fig. 2.20: imago/ITAR-TASS

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