

7 Targeted interventions in marine chemistry

> Complex processes allow the ocean to absorb carbon dioxide from the atmosphere, chemically bind much of the carbon it contains, and store this carbon in its water masses. However, the more carbon dioxide the sea absorbs, the more acidified its waters become. This process could be reversed through a targeted boost of its natural acid-binding capacity. As yet, however, little is known about the impacts that could result.



Alkalinity enhancement – an approach in its infancy

> The amount of carbon dioxide the ocean can absorb without substantially acidifying depends on the alkalinity of its surface waters. This term refers to the amount of acid-binding mineral components that were previously dissolved by the weathering of rocks and discharged into the sea. This then raises the question: Could a deliberate input of minerals help to increase the ocean's carbon dioxide uptake without disrupting its chemistry and life in the ocean?

The laws of marine chemistry

The ocean is a gigantic carbon repository. Today, its water masses already contain more than 50 times as much carbon as the Earth's atmosphere, and in recent years it has absorbed one-fourth of the carbon dioxide emissions produced by humans, thus significantly retarding the progress of global warming.

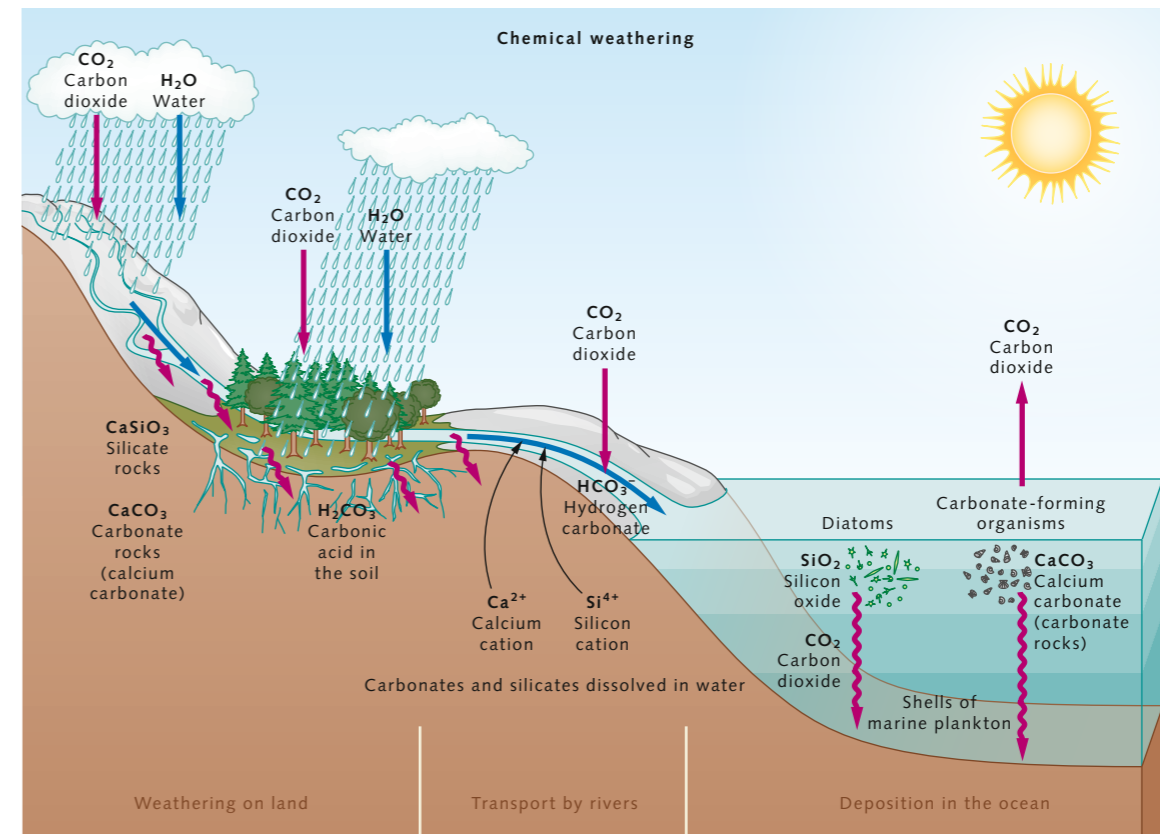
Carbon dioxide uptake by the ocean occurs at the sea surface, and is made possible by the constant exchange of gases between the surface waters and the atmosphere. The exchange balances out pressure differences that exist between the carbon dioxide dissolved in seawater and that in the atmosphere. When the concentration of carbon dioxide in the atmosphere increases, the ocean responds by absorbing more carbon dioxide.

When carbon dioxide dissolves in seawater, a large proportion of the gas undergoes a series of chemical reactions. The dissolved gas, which could otherwise escape back into the atmosphere at any time, is chemically bound rather quickly in the seawater in the form of hydrogen carbonates and carbonates. When this has occurred, outgassing back into the atmosphere is no longer possible. At the same time, as a result of the reactions, the concentration of dissolved carbon dioxide in the surface waters decreases and the ocean is able, to some degree, to take up more carbon dioxide from the atmosphere.

However, as a consequence of this reaction chain, protons, or hydrogen cations, are released, a result that contributes to the acidification of the ocean. The amount of these that are released depends upon the acid-binding capacity of the water, which is also known as its alkalinity. The alkalinity of seawater is primarily determined by the abundance of acid-binding components of mineral origin in the water (hydrogen carbonate, carbonate and others), which were previously dissolved over many millions of years by the weathering of rocks on land, and transported by rainwater through brooks and rivers into the seas. Some rocks are also weathered directly at or in the sea. The slowly eroding chalk cliffs on the coast of Germany's island of Rügen in the Baltic Sea provide a striking example. With a bit of luck visitors to this site can directly observe how rain, wind and waves wash chalk residues (friable limestone) from the cliff walls and disperse the highly reactive minerals within the coastal waters.

When the amount of such acid-binding dissolution products of rock weathering in the water is high, a large proportion of the acidifying protons are not even released in the first place, but are immediately bound by the introduced minerals as part of the chain reaction. In this case,

7.1 > In September 2009, hundreds of fishers participated in a protest against the increasing acidification of the ocean off the southern coast of Alaska. The cold Alaskan waters absorb particularly large amounts of carbon dioxide from the atmosphere and are thus severely affected by acidification.



7.2 > The alkalinity of seawater is determined by two fundamental processes: first, by the introduction of dissolved, acid-binding dissolution products of rock weathering; and secondly, by the natural uptake and further processing of these dissolution products by marine creatures such as calcareous organisms (carbonates) or diatoms (silicates). In the formation of carbonate minerals (CaCO_3) a portion of the bound carbon dioxide (CO_2) is released again.

the acidification of the water is buffered. If the water contains a lesser amount of minerals, however, its acid-binding capacity is limited. The number of free protons increases and the water becomes increasingly acidified, which causes deterioration of the conditions for many marine organisms (as set out in detail in Chapter 2).

The idea – to accelerate natural weathering

The weathering of rocks and the resulting dissolution of the minerals they contain in the sea are natural processes that proceed comparatively slowly, and that influence the Earth's climate over time periods of thousands of years or more. It is estimated that they remove 1.1 billion tonnes of carbon dioxide from the atmosphere annually. As a long-term average, this is roughly the same as the amount of carbon dioxide that is introduced into the atmosphere through volcanic activity and through mineralization pro-

cesses in the Earth's mantle and in the ocean. In order to increase the removal of carbon dioxide to offset unavoidable residual carbon dioxide emissions by human societies, the natural weathering processes would have to be accelerated by a factor of around five. An example calculation: If humans could increase the alkalinity of the upper 50 metres of the world ocean by 0.25 per cent, or five millimoles per cubic metre of water, the change in marine chemistry would result in an uptake of one billion tonnes of carbon. That corresponds to around 3.7 billion tonnes of carbon dioxide, which is one-tenth of the carbon dioxide that was emitted globally from fossil sources in the year 2022.

According to modelling studies, a targeted increase of ocean alkalinity through accelerated natural-rock weathering would indeed be possible. It would require the introduction of additional acid-binding minerals into the ocean. This approach is known as ocean alkalinity enhancement.

Limestone

Limestone is a sedimentary rock comprised primarily of the minerals calcite and aragonite, which are both forms of calcium carbonate (CaCO_3). The overwhelming majority of limestones are of biogenic origin, which means that they were formed and deposited by living creatures such as mussels or corals. Limestone can also, however, be precipitated directly out of the water by chemical processes.

The shellfish trick of the native North Americans

Native peoples on the west coast of North America have been using a natural form of alkalinity enhancement for thousands of years to boost their shellfish production. They have developed a special technique for breeding called clam gardening. The shellfish breeders construct walls in marine bays from debris and rocks along the low-water line. When surf water flows over this wall at high tide, silt, sand and gravel sediments are trapped behind it, settle to the bottom, and over time form a kind of terrace. Native clams then colonize the sediments on the terrace.

To encourage growth, the indigenous people have been scattering broken shells on the terraces and working them into the sediment for generations. The shells are composed of calcium carbonate, an acid-binding mineral. This raises the pH value of the pore waters, which especially benefits the acid-sensitive juvenile clams. Furthermore, the calcareous shell remains serve the young clams as a kind of storehouse for building material.

The results are impressive. Four times as many native butter clams (*Saxidomus gigantea*) and more than twice as many clams of the species *Leukoma staminea* grow on the terraces that have been spiked with clam shells than on a natural stretch of coastline. In addition, the shellfish grow faster, which is due not only to the addition of calcium carbonate, but also to other effects related to the terraced gardens.

Shellfish harvesters in other parts of North America are now also using alkalinity-enhancing methods to prevent production losses related to acidification. The amount of additional carbon dioxide that the clam gardens of the natives remove from the atmosphere, however, has not yet been measured.



7.3 > Native shellfish species grow faster and with greater densities in west-coast native clam gardens than on other stretches of coast without the artificial terracing and additional limestone input.

An intervention of this kind into the marine chemistry would have the advantage of enabling the ocean to absorb more carbon dioxide without additional acidification. At the same time, high acidification, which already affects a number of marine regions and which is harmful to many marine organisms, could be reversed, facilitating a recovery for many coral reefs and shellfish beds. Field experiments for testing the reduction of ocean acidification have already been carried out in the Australian Great Barrier Reef as well as on the coast of Florida. In these studies, researchers were able to demonstrate that calcite formation increased in both mussels and stony corals when the acidification level of the surrounding water was reduced by a targeted boost in alkalinity.

The entire ocean as a carbon reservoir

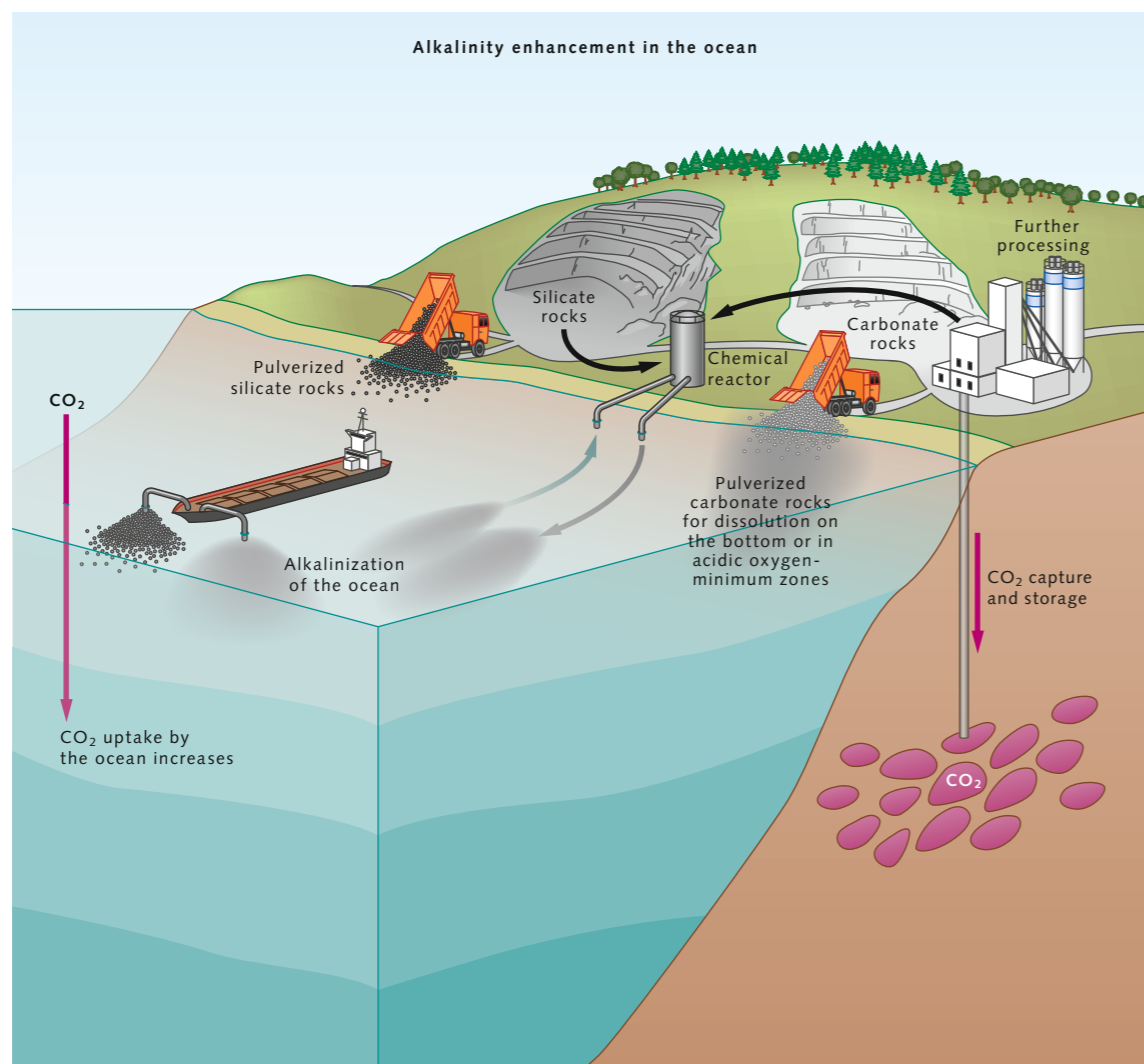
As a result of increased alkalinity, the surface waters are able to absorb more carbon dioxide, which is chemically bound and eventually stored, primarily in the form of hydrogen carbonate. The hydrogen carbonates, along with the weathering products dissolved in the surface waters, are dispersed throughout the ocean by marine currents (physical carbon pump), and are transported to very great water depths. The result is that the entire ocean becomes an immense reservoir for the carbon introduced at the surface. Depending on the water depths and current directions, decades, or even centuries will pass before the carbon-rich water returns to the sea surface through natural pathways.

In the upwelling areas of the world ocean, there is still water rising to the sea surface whose alkalinity has not yet been elevated by human activity. It therefore still possesses the full uptake potential for a targeted increase in alkalinity and the resulting carbon dioxide absorption. And even when water masses return to the surface that already contain stored carbon dioxide released by humans, in the form of dissolved carbon dioxide or hydrogen carbonate, the hydrogen carbonates will still remain in the water for as long as 100,000 years. This means that the carbon bound up in them could not be emitted back into the atmosphere in the form of carbon dioxide.



7.4 > Discoloured seawater enriched in carbon dioxide spreads over corals growing in a shallow-water area on Australia's Great Barrier Reef. In this initial field experiment on ocean acidification, researchers were able to demonstrate that acidification inhibits coral growth.

7.5 > For two of the promising methods for enhancing the alkalinity of the ocean, limestones or silicate rocks must be mined on land and ground into rock powder. The carbon dioxide emissions from these processes would have to be captured and stored. Otherwise, the methods would not have a meaningful positive impact on climate.



Only the dissolved carbon dioxide would be able to escape.

The offsetting effect of lime formation

How long the additional hydrogen carbonates remain dissolved in the ocean depends on a number of chemical and biological processes: The elevated alkalinity reduces the acidity of the water, which inhibits the dissolution of calcareous sediments on the seabed and therefore improves conditions for calcareous species to secrete their calcite shells. Thus, fewer calcareous sediments

are dissolved and more calcareous shells tend to be produced.

The formation of calcium carbonate is the reverse process of weathering. This chemical reaction consumes hydrogen carbonates dissolved in the water, thus reducing the alkalinity of the seawater. But at the same time, the process of limestone formation releases carbon dioxide, which again increases its concentration in the surrounding water. This dissolved carbon dioxide could escape into the atmosphere again if it comes into proximity with the sea surface. This means that through the formation of calcium carbonates, the carbon formerly

stored in the ocean water is again transformed into a greenhouse gas and becomes relevant with regard to the climate.

In the ocean, however, calcite is produced not only by clams, corals and calcareous algae. It can also be precipitated directly from the water as a secondary mineral through a chemical reaction. If water masses are alkalinized too often, or if too many acid-binding minerals are introduced at once into a water body, it can lead to an oversaturation of the seawater. As a result, depending on the initial material, secondary minerals such as carbonates or silicates can precipitate. Solid limestone or silicate particles thus form spontaneously. When carbonate minerals precipitate, carbon dioxide is released. Experts thus assume that the precipitation of secondary minerals promoted by mineral supersaturation can limit the effectiveness of alkalinity enhancement as a carbon dioxide removal method, and may even completely cancel it out in some conditions.

They therefore draw two important lessons from the laws of marine chemistry: For one, in proposals for the targeted enhancement of seawater alkalinity, careful consideration would have to be given to deciding which minerals could be introduced at what locations in the sea, at what quantities, and in what form (as rock powder or alkaline solution), in order to avoid exceeding critical threshold values and to prevent supersaturation and the resulting carbonate precipitation. It is known, for example, that in marine regions where winds, waves and currents thoroughly mix the surface waters, critical oversaturation is less likely to occur than in regions where the introduced mineral remains near the surface for an extended time at high concentrations. Good mixing conditions would be found in coastal areas or in the open ocean.

Secondly, alkalinity enhancement measures cannot be repeated indefinitely as a way to increase natural carbon dioxide uptake by the sea. Presumably they would “only” be effective for several decades to a few centuries. Nevertheless, experts say, application over this time frame could be quite sufficient to offset residual emissions, and thus stabilize the climate.

Methods of alkalinity enhancement

A variety of approaches by which the alkalinity of seawater could be increased are presently being developed. These include possibilities such as the mining on land of naturally occurring minerals like limestone and chalk, or siliceous rocks such as basalts and olivine, then crushing them to increase their total surface area to enhance weathering (chemical reactions), and then spreading the rock powder on beaches or directly on the sea. Residual materials rich in calcium or magnesium, or waste products from cement production could also be used for the same purpose. These may include synthetically produced minerals such as quicklime (calcium oxide), slaked lime (calcium hydroxide), periclase (magnesium oxide), brucite (magnesium hydroxide) and sodium hydroxide. Brucite and sodium hydroxide, for example, are produced during

7.6 > Basalt is formed from cooling lava and is generally dark in colour. This basalt rock comes from the Cascade Mountain Range in the US state of Washington.



Electrochemical procedures to accelerate marine chemistry using electricity

The dissolution of minerals in seawater takes time. It can require as long as several months for alkalized seawater to exert its chemical effect and absorb additional carbon dioxide from the atmosphere. Some experts are developing electrochemical procedures to accelerate this process. They employ an electrochemical cell through which seawater is passed. The cell contains two electrodes. When an electric current is applied to the cell, the electrodes become a positively charged anode and a negatively charged cathode. The anode attracts bases, while the cathode attracts acids, resulting in an “acid current” and a “base current”. Both of these currents can be used to influence the carbon dioxide concentration in seawater. Depending on the approach, the objective is either to increase the alkalinity of the seawater or to remove carbon dioxide directly from the seawater.

Two examples – how electrochemical methods can be applied

Scientists at the University of California have developed an electrochemical cell method by which the dissolved carbon dioxide in seawater reacts with and ultimately mineralizes the calcium and magnesium cations present in the water. The result is that carbon dioxide is chemically fixed through the formation of new rock material. The total carbon content of the water is thereby reduced, allowing it to absorb additional carbon dioxide from the atmosphere when it is reintroduced into the sea.

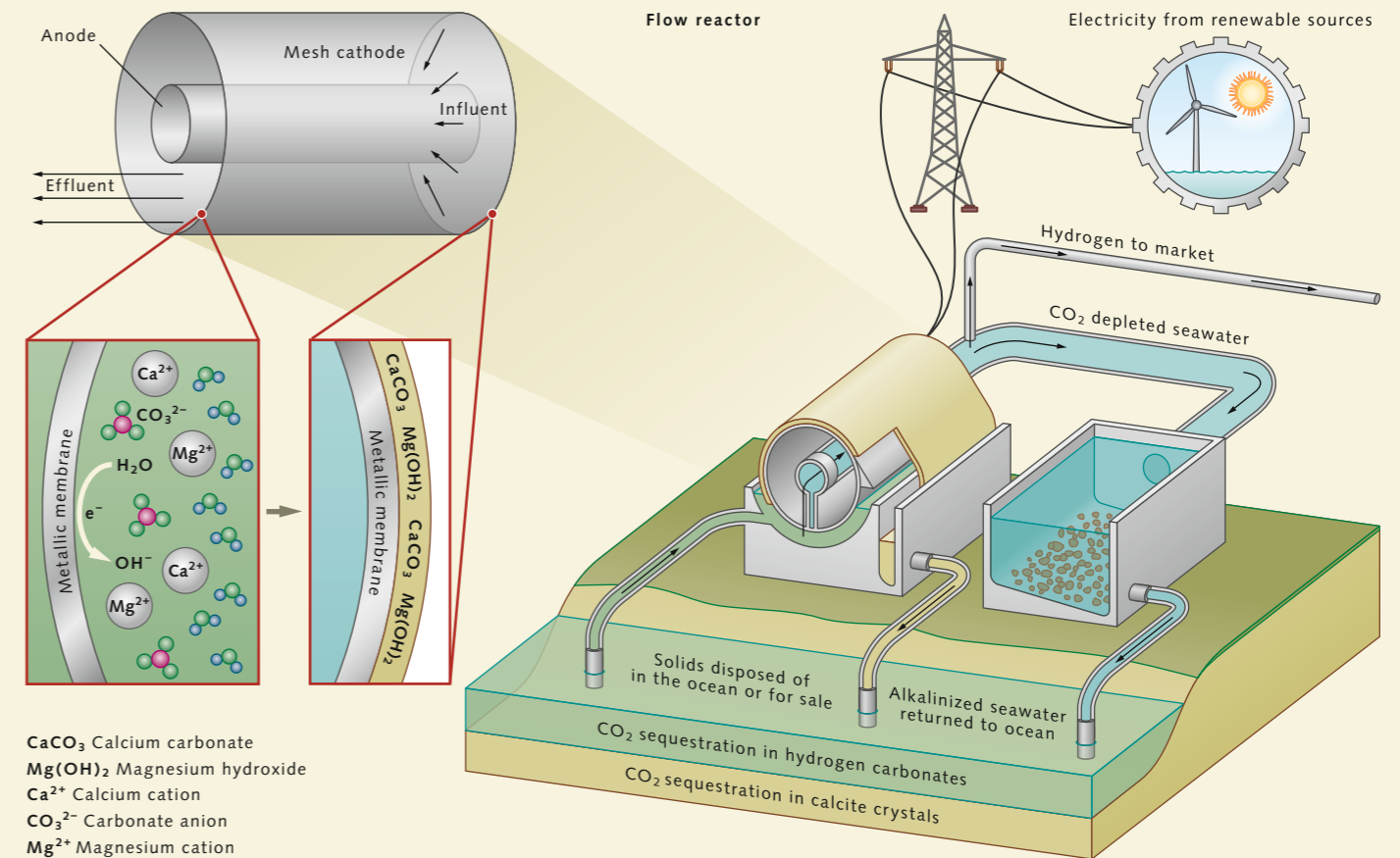
To achieve this chemical bonding, the seawater is passed through a machine called a flow reactor. In the machine the water flows across a network of electrodes that electrically charge it and electrochemically increase its alkalinity. In this state, the dissolved carbon dioxide and mineral components in the water can react instantly with one another. One result of this reaction is the formation of various solid materials such as calcium carbonate – CaCO_3 –, magnesium carbonate – MgCO_3 – and magnesium hydroxide – Mg(OH)_2 –, which can be further processed as mineral raw materials. Another result is water depleted in carbon dioxide,

which is reintroduced into the sea. Hydrogen, which is in demand as a renewable fuel, is also produced in the process.

The researchers have calculated the scale at which this technology would have to be applied if the goal were to remove ten billion tonnes of carbon dioxide per year from the ocean and thus indirectly from the atmosphere. Worldwide, it would require the installation of around 1800 systems. The costs for the construction and operation of these flow reactors would reach several trillion US dollars. The necessary electricity would also have to come from renewable energy sources.

Researchers at the Massachusetts Institute of Technology (MIT) in Cambridge, Massachusetts have discovered a much less expensive solution. They channel seawater into an electrochemical cell where it is strongly acidified by protons from a bismuth electrode. This acidification causes the breakdown of the carbonates and hydrogen carbonates present in the water and frees up the carbon dioxide bound to them. This is then drawn off and collected. However, the acidified water has to be neutralized before it can be pumped back into the sea. This is achieved by passing it through a second cell with a reversed electrical charge, allowing the protons from the first pass to be recovered. This slightly basic water can then take up new carbon dioxide from the atmosphere. Here, the cost per tonne of carbon dioxide removed is 56 US dollars.

In contrast to the former method, however, the carbon dioxide removed is not bound in solid rock, but is gaseous and thus highly volatile. So it still must be further processed or stored in such a way that it does not escape back into the atmosphere. The second process can be conveniently integrated into existing seawater desalination plants where the necessary water intake and outlet installations are already in place. But before the MIT experts can build their first demonstration system there are several issues that need to be addressed. One of these is mineral precipitation that occurs during the process and contaminates the electrical terminals and electrodes of the cells.



7.7 > A flow generator forms the core of an electrochemical approach that has been developed by scientists in the US state of California. In the generator, carbon dioxide dissolved in the seawater reacts with and mineralizes calcium and magnesium cations. This decreases the total carbon content of the water so that it can absorb new carbon dioxide from the atmosphere when it is released back into the sea.

the manufacture of green hydrogen and could subsequently be used for alkalinity enhancement. The minerals would be distributed on the sea surface using ships or aircraft. On beaches, spreading vehicles or even manual efforts would be employed.

A second approach would involve the installation of chemical reactors on the coasts, on ships, or on platforms in the sea. Under the controlled conditions in these reactors, the calcium- or magnesium-rich rock powder would weather very rapidly after adding water rich in carbon dioxide, thus creating an alkalic solution. This would then be fed into the sea or sprayed onto its surface. In this way, the concentration of hydrogen carbonate in particular, as well as the amounts of calcium, magnesium or silicate,

depending on the weathered rocks used, would be increased. These compounds are already present at high concentrations in seawater today, so the changes in these caused by targeted mineral input would be proportionately small. However, the potential impacts of altered mineral concentrations on marine ecosystems still need to be investigated.

But whether additional carbon dioxide can ultimately be removed from the atmosphere through alkalinity enhancement in the ocean, and how much might be removed, also depends on the amount of overall emissions produced by the work involved in the process. It is estimated that the extraction potential of alkalinity-enhancing processes is 100 million to one billion tonnes of carbon

dioxide per year. If these were to be applied ocean-wide – not limited to particularly suitable areas – the removal potential could even exceed one billion tonnes of carbon dioxide per year.

Studies indicate, however, that the effectiveness of the processes also depends on the marine regions and the time of year in which they are applied, because the chemical and physical preconditions differ regionally and are also subject to seasonal changes. Strong surface currents can rapidly transport the injected minerals into regions where the alkalinity of the water is already higher and additional carbon dioxide uptake is hampered. Or strong mixing of the surface waters by winds and waves leads to displacement of the minerals to deeper waters, resulting in a merely minimal change to the alkalinity of the surface water. Specialists are also cognizant of the fact, based on climate simulations, that the effectiveness of alkalinity enhancement declines with increasing global warming. In a world that warms by more than four degrees Celsius by the year 2100, a much greater volume of minerals would have to be input into the ocean to effect the additional uptake of a given amount of carbon dioxide than would be needed if global warming were limited to well below two degrees Celsius.

Mineral requirement – several kilograms of lime per person per day

Estimates to date assume that to increase surface-water alkalinity to a level that would be effective with respect to climate, something between one-half tonne and five tonnes of mineral products would have to be employed for every tonne of carbon dioxide that is fixed. For basalt rocks, for example, the removal proportion would be around three to one. This means that three tonnes of basalt rock would have to be weathered in the sea in order for the ocean to remove an additional tonne of carbon dioxide.

The following calculation illustrates how great the additional mineral requirement could be for a large-scale programme of alkalinity enhancement: If we assume that the Federal Republic of Germany still has residual emis-

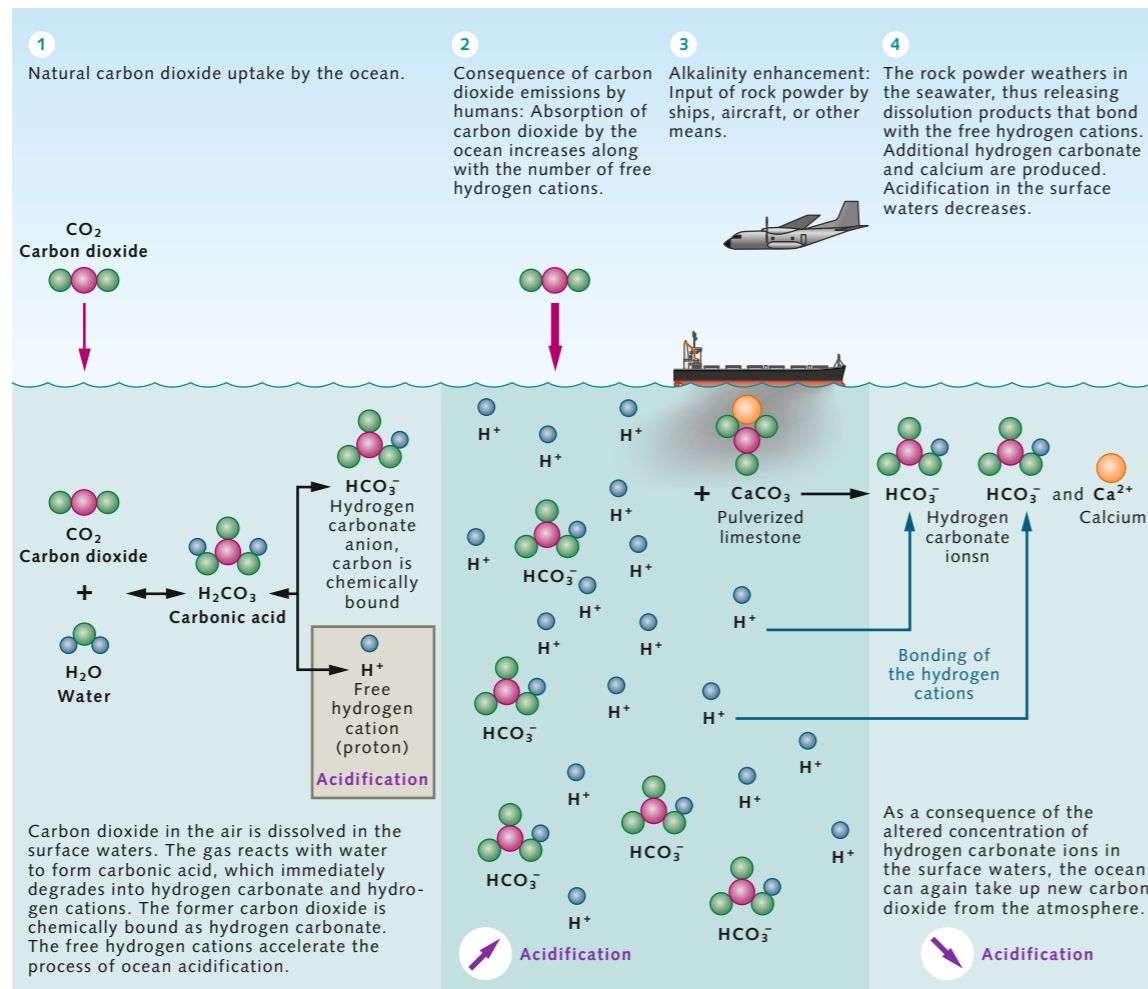
sion levels of 60 to 130 million tonnes of greenhouse gases per year by the year 2045, that would represent 0.7 to 1.5 tonnes for each of its 83.2 million inhabitants. For Germany's population to compensate for these residual emissions solely through ocean alkalinity enhancement, each person would have to dissolve 6.5 to 14 kilograms of basalt, or five to eleven kilograms of limestone in the sea every day. Extrapolated for Germany's total population, this would result in an additional basalt demand of 200 to 416 million tonnes or a limestone demand of 150 to 312 million tonnes per year. If, on the other hand, the compensation process were to be divided among several carbon dioxide removal methods, the mineral demand would be proportionately smaller.

At this point, the good news is that both limestone and silicate rocks like basalt and olivine are present in sufficient amounts underground. The latter, in fact, are the most abundant rocks in the Earth's crust. It is not yet clear, however, how much energy and other investments would be required to extract the rocks on an industrial scale, process them and transport them to the coast or subsequently out to sea – and what greenhouse-gas emissions would be produced by each of the individual steps. A study in 2013 concluded that 100 universal bulk carriers with capacities of 300,000 dry-weight tonnes each would be needed, and that they would have to be in practically constant operation in order to distribute one billion tonnes of rock powder onto the ocean annually. At the time of the study, this demand would have corresponded to around four per cent of the total global shipping capacity.

Old and new input materials

It is known that limestone does not dissolve in seawater because the surface water of the ocean, as a rule, is chemically supersaturated with carbonates. Acidic and oxygen-deficient water masses, which occur, for example, in some deep areas of the Baltic Sea, are an exception to this rule. Often, the water within surface sediments is also very acidic, so that limestone can also be dissolved there. By contrast, seawater everywhere is undersaturated with

7.8 > Complex ocean chemistry: The chemical reactions through which the input of limestone powder and its subsequent weathering contribute to reduce ocean acidification are illustrated schematically here. The reactions shown would occur in carbonate-undersaturated waters such as oxygen-depleted regions just below the sea surface.



Green hydrogen
For the production of green hydrogen, water is split into its molecular components hydrogen and oxygen using electric power from renewable energy sources (electrolysis). This ensures that the hydrogen production is climate neutral.

silicates, which means that silicate rocks would generally dissolve. In order to increase the alkalinity of the ocean as rapidly as possible, the silicate rocks would have to be very finely pulverized and distributed in shallow coastal waters, or dissolved in seawater in chemical reactors at high energy input.

Naturally occurring calcareous and silicate rocks or artificially produced minerals (quicklime, slaked lime, etc.), however, are not the only options. Researchers are now also testing synthetically produced ikaite for its suitability and its weathering properties. Ikaite is a very rare form of hydrated calcium carbonate that only forms in nature at temperatures below 15 degrees Celsius in seawater. If it should prove to be feasible, therefore, it could only be applied in marine regions with correspondingly cool water masses.

Laboratory and field studies of risks and side effects are lacking

To date, the greatest part of our knowledge about the chemical and biological consequences of alkalinity enhancement comes from modelling studies (computer simulations). Robust laboratory or field studies on the local, regional and global impacts of industrial-scale mineral input are lacking. For this reason, very little is known as yet about the possible risks and side effects of large-scale mineral input.

It is a well-known fact that the mining of minerals in quarries often leads to land-use conflicts and impacts on local ecosystems, as well as increased volumes of traffic accompanied by increased noise and dust pollution. Furthermore, it is also known that silicate rocks contain certain nutrients (silicon, iron) and heavy metals (nickel, chromium, zinc). The former would influence the growth of diatoms and thus impact the marine nutrient cycle, while some experts are optimistic that a boost in algal growth could stimulate the biological carbon pump, allowing the ocean to absorb additional carbon dioxide. Heavy metals, for their part, could have a toxic effect and thus cause damage to the ocean's ecosystems. There is some optimism, however, that the potentially

harmful side effects of alkalinity enhancement could be avoided through the production of purely synthetic minerals.

As part of a German research mission that comprises various laboratory and mesocosm experiments, scientists are currently studying the extent to which the input of mineral materials or the weathering of rocks on the seafloor would impact coastal ecosystems in the North and Baltic Seas, and the threshold values to which the negative effects of alkalinity enhancement on marine communities could be avoided. This involves analyses of how phytoplankton, zooplankton, and other selected organisms that live on or in the seafloor react to the increased mineral input. Is there a risk, for example, that copepods or fish larvae might mistake the mineral particles for food, eat them, and then starve to death with a full stomach? This cannot presently be ruled out.

There is also evidence that the mineral type and composition would determine which marine organisms might benefit from an increase in alkalinity and which may tend not to. For example, if minerals rich in calcium are input, it becomes easier for the carbonate-forming organisms to form their skeletons and shells. Under these conditions, they would have a growth advantage, while diatoms would not receive much benefit. If, on the other hand, the material input contains silicates, diatoms would have the upper hand because they need these minerals to build their silicon-rich shells. The advantage of carbonate formation in the first case, however, would bring with it a critical disadvantage. When animals use the introduced minerals to construct their skeletons or shells, carbon dioxide is released into the seawater rather than removed.

The scientists will ultimately use numerical models to project their local research results to regional and global scales, and to simulate the application of measures to increase alkalinity in German territorial waters and other marine areas. With this approach they hope to identify risks, delineate critical threshold values, test concepts for monitoring and control procedures, and derive appropriate possible courses of action at the local, national and international levels.

Mesocosms

The mesocosms used in the experiments are transparent, hose-like tubes that are filled with seawater and float in the surface waters. Organisms in the tubes are thus exposed to the same environmental conditions (temperature, light, etc.) as the organisms in the sea, but can be studied individually because there is no exchange of water between the sea and the tubes.



7.9 > Limestone is mined in large quarries like this one. It is evident that the possibility of environmental damage on land must also be taken into account when considering whether alkalinity enhancement of the ocean would be worthwhile as an approach to combat climate change.

7.10 > Scientists have moored a mesocosm in the ocean off the coast of Gran Canaria. Several years ago, in its hose-like tubes, they studied the reactions of microalgae and zooplankton to increasing ocean acidification. They are now using it to investigate the possible consequences of an alkalinity increase.



Much development work also awaits the researchers regarding the measurement and monitoring of carbon dioxide uptake by the ocean as a result of alkalinity enhancement. The application of this approach only makes sense if the desired effects can be measured and unambiguously attributed to the mineral input. In this context, scientists refer to the verification and attribution of a change – in this case, a change in alkalinity and increase in the carbon content of the ocean. Measuring these, distinguishing them from natural fluctuations, and attributing them to specific interventions is an immense scientific challenge for which no reliable method is yet available.

Further exacerbating matters is the fact that, unlike with projects for the restoration of seagrass beds or mangrove forests, the effects of increasing alkalinity cannot be confined within a specific marine region. The world ocean is a contiguous global system. Changes in one

ocean region lead to interactions with other interconnected areas. That is especially true for the parameters of marine chemistry. For this reason, it is believed that a local input of minerals would result in impacts that not only extend far beyond the boundaries of the marine area originally targeted, but that could also last for very long periods of time. What these effects might be is presently being studied.

Legal framework

From a legal point of view, distributing acid-binding minerals in the form of rock flour or alkaline lye on the ocean would constitute an additional input of substances into the sea. Such activities are regulated internationally, primarily by the London Convention of 1972 – also known as the Convention on the Prevention of Marine Pollution by

Dumping of Wastes and Other Matter – and its 1996 supplement, the London Protocol. However, the Convention on Biological Diversity may also apply.

The scope of the London Protocol was expanded in 2013 such that marine CDR procedures can be regulated under the authority of the treaty. However, these changes will not take effect until they are ratified by a sufficient number of signatory states, which has not yet happened. Presently, an amendment to the London Protocol lists only iron fertilization as a CDR method that can be regulated. According to experts, however, procedures to enhance the alkalinity of the ocean could also be regulated under the Protocol. For this to happen, the Protocol would have to be amended to include them (more on this in Chapter 9).

In Germany, the use of procedures for alkalinity enhancement of the oceans is prohibited under current law. Similarly, the determining factors here are found in the provisions of the German Act on the Prohibition of Dumping Waste and Other Substances and Objects into the High Seas. Accordingly, it is prohibited for scientists at German research institutes to carry out field experiments related to this subject, both in national waters and on the high seas. This legal framework will need to be revised if society decides to increase the carbon dioxide uptake of the ocean through the input of acid-binding minerals. The fact is that comprehensive knowledge about the risks and side effects of such operations cannot be gained without field experiments.

CONCLUSION

Alkalinity enhancement – understood in theory but insufficiently tested in the field

Mineral-rich dissolution products from the natural weathering of rocks enable the chemical bonding of dissolved carbon dioxide in the ocean, and the subsequent absorption of new carbon dioxide from the atmosphere. This natural process of climate regulation could be selectively accelerated if large amounts of limestone and silicate rocks were mined and distributed in the sea in the form of rock flour or alkaline solutions. Such alkalinity-enhancing processes would also have the benefit of reducing acidification in the treated water masses and improving the living conditions for many marine organisms.

The chemical processes involved in a targeted programme of alkalinity enhancement of the ocean are now quite well understood. Its technical feasibility, however, is difficult to assess because most of our knowledge comes from computer simulations and small-scale laboratory experiments. Large-scale field experiments are still lacking.

In the laboratory, researchers are now testing various naturally occurring and artificially produced minerals for their suitability and weathering properties. At the same time, initial studies are being carried out on the possible environmental impacts and risks, about which very little is yet known. Specialists are also working on electrochemical methods of alkalinity enhancement. These require a high input of energy but, in contrast to other methods, could be applied without the massive input of rock material.

The true potential for carbon dioxide removal using alkalinity-enhancement methods is also difficult to quantify. According to calculations, if the presently known methods were to be applied worldwide, an additional 100 million to more than a billion tonnes of carbon dioxide could be removed from the atmosphere. However, this would be countered by new greenhouse gas emissions generated in the activities of quarrying, transporting and processing the rocks. As a consequence, potential methods for targeted alkalinity enhancement in the ocean are still subject to large uncertainties.