OPINION

Microbial production of recalcitrant dissolved organic matter: long-term carbon storage in the global ocean

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Abstract | The biological pump is a process whereby CO_2 in the upper ocean is fixed by primary producers and transported to the deep ocean as sinking biogenic particles or as dissolved organic matter. The fate of most of this exported material is remineralization to CO_2, which accumulates in deep waters until it is eventually ventilated again at the sea surface. However, a proportion of the fixed carbon is not mineralized but is instead stored for millennia as recalcitrant dissolved organic matter. The processes and mechanisms involved in the generation of this large carbon reservoir are poorly understood. Here, we propose the microbial carbon pump as a conceptual framework to address this important, multifaceted biogeochemical problem.

The biogeochemical fate of organic matter in the ocean is an important issue that must be considered in order to understand the role of the ocean in climate change. The biological pump involves a series of processes through which CO_2 is fixed as organic matter by photosynthesis and then transferred to the ocean interior, resulting in the temporary or permanent storage of carbon[1–3]. The known mechanisms involved in the biological pump include the sedimentation of particulate organic matter (POM) from surface waters towards the seabed[1] and the export of dissolved organic matter (DOM) from the euphotic zone to deeper waters[2,3] by mixing and downwelling of water parcels. Both POM and DOM are subject to microbial mineralization, and most of the organic carbon will be returned to dissolved inorganic carbon (DIC) within a few decades[4]. Together, these processes remove organic-form carbon from the surface waters and convert it to DIC at greater depths, maintaining the surface-to-deep-ocean gradient of DIC and resulting in the temporary storage of carbon until it is ventilated to the surface again by the thermohaline circulation[2]. A small fraction of POM escapes mineralization and reaches the sediment, where organic carbon can be buried and stored for thousands and even millions of years[1–3]. The long-term storage of carbon by the biological pump is the primary concern regarding the role of the ocean in climate change. The efficiency of the biological pump is currently regarded as a basic measure of the ocean's ability to store biologically fixed carbon. However, in our opinion the production and fate of the large pool of recalcitrant DOM (RDOM) in the oceanic water column has not been adequately considered in the biological pump concept.

Marine bacteria and archaea are responsible for the respiration of most of the carbon that sinks into the ocean's depths[5]. Consequently, these microorganisms and their interactions with organic matter have received much attention recently, and several excellent reviews have been published on this topic[6–9]. One fundamental aspect of the interaction between these bacterial and archaeal species and organic matter sets them apart from other ocean biota: as the dominant heterotrophic osmotrophs, they essentially monopolize the utilization of DOM. The diverse adaptive strategies of microorganisms for using newly fixed carbon are well known. However, there are large gaps in our knowledge of how these microorganisms interact with the large pool of DOM that seems to be recalcitrant. The relationship of microorganisms with this RDOM pool is not well explored, despite great progress in our understanding of the genomic diversity of marine microorganisms and their *in situ* processes. The interaction between this RDOM pool and microorganisms is important, as DOM molecules that are not degraded for extended periods of time constitute carbon storage. In this Opinion article, we propose the microbial carbon pump as a conceptual framework to address the role of microbial generation of RDOM and relevant carbon storage, with the aim of improving our understanding of oceanic carbon cycling and global climate change.

Marine organic matter

Although organic matter in marine environments occupies a molecular-size continuum[10,11], in research practice it is operationally divided into POM and DOM. POM is initially formed as autotrophic biomass and is then transformed through multiple trophic pathways at each level of the marine food web[12,13]. There are many mechanisms of DOM production in the upper ocean, and they vary spatially and temporally. It is difficult to specify or predict the dominant sources of DOM in a given ecological scenario. Phytoplankton release a highly variable, but at times substantial, fraction of primary production into seawater as DOM[14–16]. Another notable mechanism is the release of DOM resulting from viral lysis[8]. 'Sloppy feeding' by metazoan grazers might also release phytoplankton cytosol as DOM, and the egesta of protists and metazoa can contain DOM. Further, a major mechanism of DOM production is POM solubilization by bacterial and archaeal ectohydrolases[17].

The lability of DOM

It has been difficult to elucidate the biochemical interactions between

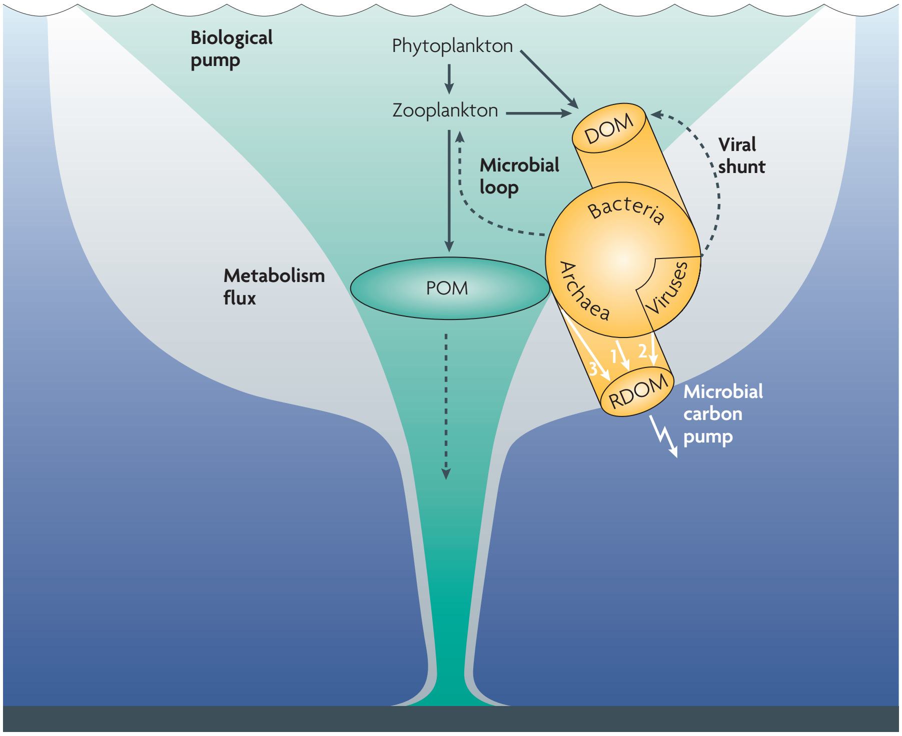

Figure 1 | **Major biological processes involved in carbon cycling in the ocean.** The main biological processes are shown. The biological pump is a process whereby CO_2 in the upper ocean is fixed by primary producers and transported to the deep ocean as sinking biogenic particles (particulate organic matter; POM) or as dissolved organic matter (DOM). The microbial loop is a pathway in the aquatic food web whereby DOM is taken up by bacteria and archaea, which are consumed by protists, which are in turn consumed by metazoans (not shown). The viral shunt reflects virus-mediated lysis of microorganisms, which returns the POM to the DOM pool. The proposed microbial carbon pump is a conceptual framework for understanding the role of microbial processes in the production of recalcitrant DOM (RDOM). RDOM can persist in the ocean for millennia and is therefore a reservoir for carbon storage in the ocean. Three major pathways have been identified in the microbial carbon pump: direct exudation of microbial cells during production and proliferation (path 1); viral lysis of microbial cells to release microbial cell wall and cell surface macromolecules (path 2); and POM degradation (path 3). The grey shading roughly indicates the total flux of carbon metabolism in the water column.

microorganisms and DOM. For the present discussion, it is useful to recognize the operational classification of DOM into three categories according to biological availability: labile DOM (LDOM), semi-labile DOM (SLDOM) and recalcitrant DOM (RDOM)[18–20]. LDOM can be used by heterotrophic microorganisms within days or even hours[21,22], whereas SLDOM can persist for months to years and accounts for most of the DOM that is exported from the euphotic zone to greater depths. RDOM, being resistant to biological decomposition, is the most persistent carbon pool, with the potential to be stored for millennia in the ocean's interior[21,23].

The capacity to use various DOM components varies among types of ocean-dwelling microorganisms[24]. The lability of DOM can also be specific to the utilizing microbial species or group[24]. For example, a functional group of bacteria, the aerobic anoxygenic photoheterotrophic bacteria (AAPB), which mainly inhabit the euphotic zone, were found to be less versatile in utilizing diverse organic matter[25] than most other bacterial groups. By contrast, microorganisms in the bathypelagic zone have developed metabolic strategies to adapt to the low reactivity of deep-sea DOM[19]. For instance, high ectoenzymatic activity in deep waters[26] has been suggested to enable deep-sea microorganisms to utilize organic moieties from resistant polymers[27]. Analyses of archaeal cell walls suggest that isotopically heavy carbon sources such as algal carbohydrates and proteins (which are enriched by 4–5 parts per thousand ^{13}C compared with algal lipids) are preferentially used by heterotrophic archaea[28]. Spatio-temporal variation in RDOM production and utilization (even at slow rates) will affect long-term carbon storage in RDOM and, hence, the ocean carbon cycle and global climate.

Generation of RDOM

Determining the sources, mechanisms and rates of RDOM generation are intriguing problems. Empirical tests of RDOM generation from a particular source (for example, a pool of LDOM or SLDOM) become logistically impractical if RDOM is defined only in terms of its extremely long half-life. In fact, the half-life of RDOM varies over a continuum; carbon storage in RDOM molecules with a half-life of 50–100 years is a shorter storage period than average but is still relevant to climate models, and measuring the production of such molecules in experimental systems would be more tractable than for molecules with a half-life of 1,000 years. A promising approach is to experimentally demonstrate the production of molecular species that are known to persist as DOM for long periods[29]. In a 36-day incubation, *Pseudomonas chlororaphis* depleted the sole carbon source, D-glucose, within 2 days and generated >100 DOM compounds that contained carbon from this glucose. Approximately 3–5% of the glucose-derived carbon persisted until the end of the experiment[30]. Year-long experiments exposing DOM to natural assemblages of pelagic bacteria might minimize the LDOM and SLDOM 'noise' sufficiently to allow identification of the sources and mechanisms of RDOM production. In a 1-year incubation with pelagic marine bacteria assemblages and either D-glucose or L-glutamate, ~37% and ~50%, respectively, of the generated DOM persisted until the end of the incubation[31], indicating that bacteria can generate long-lived DOM efficiently. In the deep sea, the fact that microbial RDOM generation occurs can be inferred from the increase in fluorescent DOM as a function of increasing oxygen consumption[32].

Although <10% of marine DOM has been chemically characterized to date, thousands of organic molecules (that is, their mass formulas) have been identified[33,34]. Several molecular species derived from bacteria, such as porins[35], D-amino acids (specifically, D-alanine, D-serine, D-aspartate and D-glutamate[36,37]), muramic acid[36,38] and lipopolysaccharides[39], are detectable in RDOM and might be released by direct exudation during bacterial production (FIG. 1). Viral lysis of microorganisms is another potential source of RDOM (FIG. 1), although some of the products released by lysis are labile[8,40,41]. Microorganisms account for most of the biotic surface area in the ocean, and there is incredible molecular diversity of cell surface layers owing to the great genetic diversity of bacteria and archaea in the ocean. Microbial cell wall and cell surface macromolecules might be important sources of RDOM, as they may be released into the water after the cells have been lysed by viruses. This possibility should be tested, as ~50% of bacterial production flows through the viral shunt[8,42,43]. RDOM can also be released during bacterial degradation of POM, as microorganisms express ectoenzymes to convert POM to DOM at rates exceeding their uptake of LDOM[17,44,45]. The selective action of ectoenzymes could generate RDOM (FIG. 1). Further, high microenvironmental concentrations of hydrolysis products could create conditions conducive to chemical reactions that do not occur in the bulk seawater and that, potentially, produce RDOM. For example, the oxygen demand of attached microorganisms could lead to microspatial anoxia and fermentation and, consequently, microenvironmental acidification. Grazing and egestion by protists might contribute to the production of RDOM[46]. In addition, RDOM could be formed from biomolecules that are altered by photochemical and thermal transformation[47–49], or from geobiomolecules that arise through liposome encapsulation, geopolymerization, sorption–aggregation and selective preservation processes[50].

The microbial carbon pump

As discussed above, many microbial activities can be identified that might be involved in RDOM generation. In addition, the microenvironmental conditions (such as chemical gradients and oxygen depletion) around microbial cells could be conducive to RDOM formation from altered biomolecules. We propose the microbial carbon pump (MCP) (FIG. 1) as a conceptual framework for understanding the role of microbial processes in RDOM generation and relevant carbon storage in the ocean. The MCP provides a framework to explicitly assimilate environmental, trophic, physiological, molecular and genomic data that are relevant to the *in situ* microbial activities which regulate RDOM production and dynamics.

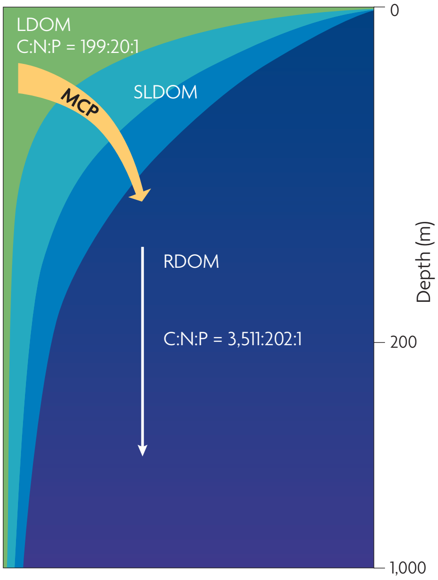

Figure 2 | **The effects of the microbial carbon pump.** Successive transformation of labile dissolved organic matter (LDOM) and semi-labile DOM (SLDOM) through the microbial carbon pump (MCP) results in the accumulation of recalcitrant DOM (RDOM) and an increase in the carbon to nitrogen and carbon to phosphorus ratios in RDOM, thus storing carbon in the ocean.

There are several reasons to propose the MCP concept and to add important emphasis to the role of microbial heterotrophic processes in the more general context of the biological pump. Currently, long-term storage of carbon as RDOM is not explicitly addressed in the biological pump. Further, the conventional interpretation of the biological pump emphasizes the vertical transport of carbon (either POM or DOM) from the euphotic zone to the deep sea, whereas the MCP stresses the formation of RDOM, which can persist at any depth in the water column, including the euphotic zone. The fundamental driver of the conventional biological pump is primary production, whereas that of the MCP is microbial heterotrophic activity; thus, the conventional biological pump mostly concerns new

Glossary

Aerobic anoxygenic photoheterotrophic bacteria
(AAPB). A group of bacteria that are primarily heterotrophic but can utilize light energy through bacterial chlorophyll *a*.

Bathypelagic zone
The water layer that extends from 1,000 metres to 4,000 metres below the ocean surface. Sunlight does not reach this zone.

Dissolved organic matter
(DOM). Marine organic matter that is less than 0.22 μm in diameter (or, sometimes, 0.7 μm, depending on the filter used). DOM can be further classified on the basis of biological availability.

Downwelling
The sinking of higher-density water beneath lower-density water, such as colder or more saline water sinking below warmer or fresher surface water.

Euphotic zone
The surface water layer of the ocean that is exposed to sufficient sunlight for photosynthesis to occur. This layer extends from the atmosphere–water interface to a depth at which the light intensity falls to 0.1% of that at the surface.

f-ratio
The fraction of total primary production that is fuelled by new nitrogen (such as nitrate and N_2) supplied from outside the euphotic zone, as opposed to that fuelled by regenerated nitrogen (such as ammonium) within the euphotic zone.

Geobiomolecule
A long-lived biologically produced molecule.

Heterotrophic osmotroph
An organism requiring DOM for its carbon and energy sources.

Labile DOM
(LDOM). A small fraction of DOM that is present mainly in surface waters and is ready for biological utilization.

Mesopelagic zone
Typically between 200 metres and 1,000 metres below the ocean surface. Although some light penetrates this deep, it is insufficient for photosynthesis.

Microbial loop
A pathway in the aquatic food web, whereby DOM is taken up by bacteria and archaea, which are in turn eaten by protists, and so on up the food chain.

Ocean acidification
The ongoing decrease in seawater pH that is caused by the uptake of anthropogenic CO_2 by the ocean; CO_2 uptake from the atmosphere is controlled by the difference in partial pressure of CO_2 between the air and the sea, as well as by the thermohaline circulation.

Particulate organic matter
(POM). Operationally defined as the material that is retained by a filter with a pore size of 0.22 μm (or, sometimes, 0.7 μm).

Recalcitrant DOM
(RDOM). DOM that is resistant to microbial utilization and that can persist in the ocean interior for up to thousands of years. This is the major fraction of DOM found throughout the entire water column, with an inventory of 624 Gt C, accounting for more than 95% of the total dissolved organic carbon in the ocean.

Semi-labile DOM
(SLDOM). DOM that can be used gradually, over months to years. SLDOM is a small fraction of the total ocean DOM (~50 Gt C) and is mainly present in surface waters.

Sloppy feeding
Metazoan grazing on phytoplankton, entailing organic matter spill in the form of DOM.

Solubility pump
(SP). A physicochemical process that transports dissolved inorganic carbon from the ocean's surface to its interior. The SP is primarily driven by the solubility of CO_2 and the thermohaline circulation.

Thermohaline circulation
Also called the ocean conveyor belt, this is the part of the large-scale overturning circulation that is thought to be driven by the global density gradients caused by temperature and salinity.

Viral shunt
Viral lysis of microorganisms, which returns organic carbon from the POM form to the DOM form.

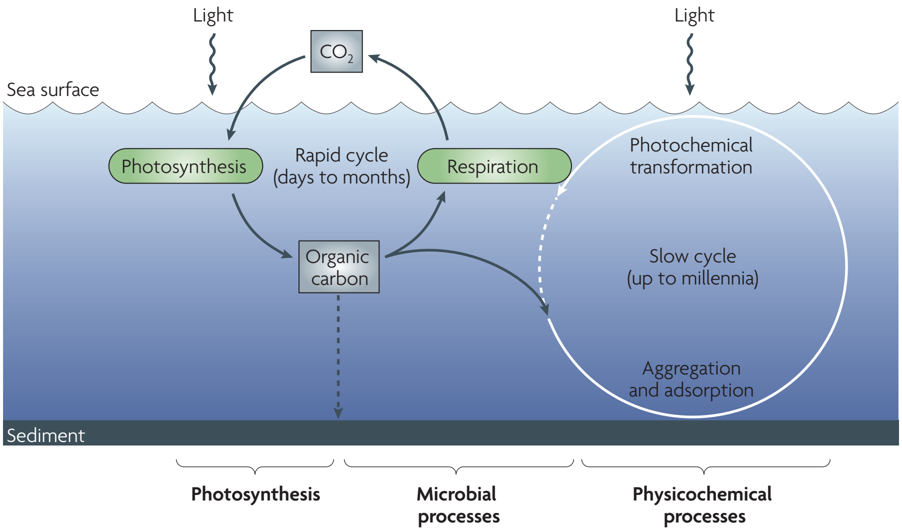

Figure 3 | **Dynamic interactions between rapid and slow cycles of organic carbon in the ocean.** Organic carbon undergoes either rapid cycling or slow cycling in the ocean. Rapid cycling is driven mainly by photosynthesis and subsequent particulate organic matter sedimentation through the biological pump, whereas the slow cycle is mediated by the microbial carbon pump, prolonging the residence time of carbon in the ocean.

production, whereas the MCP mostly concerns regenerated production. Furthermore, the MCP can be very strong where the conventional biological pump is very weak (for example, in oligotrophic oceanic waters with strong stratification).

In the MCP model, the successive — and perhaps repetitive — processing of DOM by the MCP transforms some organic carbon from the reactive DOM pools to a recalcitrant carbon reservoir in the form of RDOM (FIG. 2). Two important consequences of the MCP must be highlighted. First, it 'pumps' organic carbon from low concentrations of reactive carbon to high concentrations of recalcitrant carbon, building up a huge reservoir for carbon storage. Second, it alters the chemical composition of DOM, resulting in changing ratios of carbon to nitrogen, phosphorus and other elements. Field studies have clearly demonstrated the selective remineralization of phosphorus from DOM with increasing depth in the ocean[51]. Stoichiometric analyses show that the carbon:nitrogen:phosphorus ratios of RDOM (~3,511:202:1) are very different from LDOM (199:20:1) and POM (106:16:1)[23]. This difference indicates that the MCP transfers more carbon, relative to nitrogen and phosphorus, from the reactive organic matter pool into RDOM (FIG. 2). Thus, the MCP keeps relatively more carbon in the RDOM pool than organic nitrogen and phosphorus, and it releases more inorganic nitrogen and phosphorus into the water, providing essential nutrients for primary production.

The MCP and carbon storage

The current carbon inventory of RDOM (624 Gigatonnes (Gt) C[52]) is comparable to the atmospheric CO_2 reservoir (~750 Gt C[50,53,54]), but the average apparent radiocarbon age of RDOM is high, at 4,000–6,000 years[21]. This age is higher than the turnover time of the thermohaline circulation (550–2,000 years)[55,56], indicating that RDOM generation by the MCP might be an important mechanism for long-term storage of fixed atmospheric carbon by the ocean.

Potential evidence for the sequestration of atmospheric CO_2 by the MCP can be found in Earth's history. The carbon isotope record for the post-2.0 Gyr (billion years) ago Proterozoic indicates that there was a decrease in the size of the marine DIC reservoir[57]. By the Neoproterozoic (1.0–0.543 Gyr ago), the dissolved organic carbon (DOC) reservoir (3.2×10^{19} mol C) reached at least ten times the DIC pool of the modern ocean; the turnover time of the Neoproterozoic DOC reservoir is estimated to be at least 10,000 years[58]. However, the biological pump-mediated POM flux was probably not efficient until the evolution of planktonic animals producing faecal pellets that formed rapidly sinking POM[58], which occurred after the Ediacaran (0.631–0.542 Gyr ago)[59]. By contrast, the MCP may have been very effective under the anoxic conditions at that time and, thus, responsible for the inflated DOC reservoir and storage of atmospheric CO_2. It is not known whether the oceanic RDOM carbon inventory is currently changing as a function of a changing ocean[52], but the formation of RDOM plays an important part in the storage of atmospheric carbon because it cycles very slowly. As indicated in FIG. 3, organic carbon can undergo rapid cycling or slow cycling in the ocean. Rapid cycling currently transports 0.1–0.16 Gt C per year as POM that sinks to the sea floor[60,61] through the biological pump (FIG. 4). The slow cycle prolongs the residence time of carbon in the ocean. Non-sinking RDOM could adsorb to sinking particles or form aggregates with, for example, transparent exopolymer particles[7,62] and marine snow[63]. An unknown amount of RDOM is deposited in sediments through absorption and aggregation (FIG. 4). The RDOM is transported to deep waters during downwelling and convective deepwater formation[52,64]. The RDOM production rate could be equivalent to its removal rate[52] or even higher under certain conditions (6-month incubation experiments have suggested an RDOM production rate of 0.5–0.6 Gt C per year[65], but further studies are needed for accurate estimates). Thus, the MCP-mediated slow cycling of organic carbon could play a hitherto unrecognized role in atmospheric carbon storage, in particular over millennial timescales.

The solubility pump is another mechanism for ocean carbon storage that could have a large impact on marine organisms and biogeochemical cycles owing to ocean acidification[66] (FIG. 4). By contrast, MCP-driven RDOM storage does not appreciably alter the buffering capacity of seawater and has no known negative impact on marine organisms.

Connecting the two pumps

The concept of the MCP highlights the mechanistic contrasts to, and seeks biogeochemical connections with, the conventional biological pump. We envision that carbon storage mediated by POM export through the biological pump and by the MCP are connected by the microbial loop, whereby DOM is taken up by heterotrophic microorganisms and transported to the grazing food web (FIG. 1). Our current understanding of microbial processing of organic matter leads to some general predictions. The relative importance of the two mechanisms is expected to vary both spatially and temporally (for example, seasonally). In eutrophic waters, carbon storage mediated by POM export through the biological pump probably exceeds that mediated by the MCP owing to high primary production in this zone. However, the

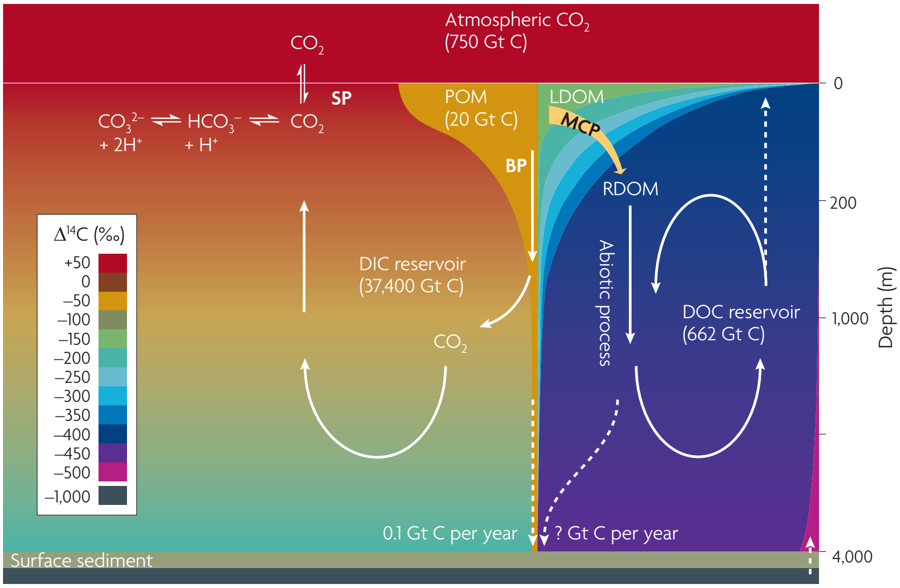

Figure 4 | **The major mechanisms for formation of oceanic carbon reservoirs.** The major oceanic carbon reservoirs and the mechanisms that control carbon cycling and storage in the ocean are shown. The dissolved organic carbon (DOC) reservoir is comparable to the atmospheric CO_2 inventory and is formed by recalcitrant dissolved organic matter (RDOM) accumulation, driven mainly by the microbial carbon pump (MCP). The biggest oceanic carbon reservoir is the dissolved inorganic carbon (DIC) pool, which is formed by biological pump (BP)-mediated transportation of organic carbon (in the form of particulate organic matter; POM) into the ocean interior and its subsequent remineralization, as well as by the solubility pump (SP) (which is driven by differences in CO_2 partial pressure). The SP has an impact on marine organisms and biogeochemical cycles, as it can lead to ocean acidification. MCP-driven carbon storage does not appreciably alter the buffering capacity of seawater and has no known negative impact on marine organisms. Background colours indicate the rough radiocarbon ages, according to the change in ^{14}C parts per thousand ($\Delta^{14}C$‰) values[85]. Gt, gigatonne; LDOM, labile dissolved organic matter.

efficiency of POM export by the biological pump is low in oligotrophic waters, which is reflected in the low f-ratios and the picoplankton dominance of the phytoplankton communities in these systems[1,67–69]. The ecosystem-level metabolism in these nutrient-depleted systems is dominated by cyanobacteria, heterotrophic bacteria and archaea, and a high proportion of primary production is channelled to DOM[70], part of which can be subsequently transformed to RDOM. Therefore, the importance of the MCP is expected to be high in oligotrophic systems. The relative importance of the MCP versus the export of POM by the biological pump is also expected to change if a system shifts from high to low productivity. For example, negligible primary productivity in Antarctic waters during the austral winter is associated with substantial microbial-loop activity, which varies over time according to DOM drawdown before[71] or well into[72] the winter. This shows that variation in the degradability of different DOM components has important implications for the functioning of the ecosystem[72]. In the Southern Drake Passage[72] in the Antarctic, the over-wintering populations of bacteria and archaea presumably carry metabolic attributes that allow them to utilize SLDOM, but such processing might also lead to the generation of RDOM.

Moving down into the mesopelagic zone and bathypelagic zone, the conventional biological pump and the MCP are probably coupled, and the strength of coupling might influence RDOM formation at the expense of POM-derived DOM that is supplied by biological pump-mediated particle flux. A reverse scenario might arise when sinking particles adsorb DOM, including RDOM, thus connecting RDOM with POM export[52,73]. A further hypothetical connection between the MCP and POM export in the ocean's interior is that the input of LDOM from sinking particles creates microscale bursts of microbial activity accompanied by co-metabolism of SLDOM in the surrounding water. In this scenario, high POM export activity will tend to reduce SLDOM levels but might stimulate the production of RDOM.

These considerations are relevant for the consequences of climate change: ocean warming is likely to strengthen ocean stratification and decrease nutrient supply to the euphotic zone, making the surface layer more oligotrophic[74]. In such a scenario, the partitioning of biogenic carbon flow will change, with the flow to POM diminishing and that to DOM increasing[75]. This outcome will probably enhance the role of the MCP in carbon storage. These examples show that POM export by the biological pump and RDOM generation by the MCP — as carbon storage mechanisms — should be studied as parts of an integrated system. Neither can be understood without the other.

Hypotheses and future research directions

The MCP provides a conceptual framework and testable hypotheses for the sources and transformations of DOM, the production of RDOM, the underlying biogeochemical mechanisms and the consequences for the future biogeochemical state of the ocean. The anthropogenic increase in atmospheric CO_2 is a global challenge that will affect seawater chemistry, particle size distributions, and the diversity and function of microbial communities[76]. In one hypothetical scenario, the concurrent elevation of $p\text{CO}_2$ and ocean temperature could increase microbial activity, channelling a greater fraction of the fixed carbon into DOM and its derivative gel phases, consistent with recent studies[7,10,75]. Future studies on the consequences of global change should consider the hypothesis of enhanced microbial activity and increased relevance of the MCP in oceanic carbon flow. In view of our poor mechanistic understanding of carbon flux partitioning and its global consequences, we stress the need for a new emphasis on research that explicitly applies considerations of the microbial loop to the broader and deeper biogeochemical context of the MCP.

Future research on the MCP needs to first address basic questions of RDOM composition, the mechanisms of its formation, the nature of its interface with microbial-loop biochemistry, and the associated community shifts and trophic dynamics. For example, the importance of the viral shunt for RDOM partitioning is unknown. Further, the MCP framework underscores the need to understand the ability of microorganisms to process DOM at various taxonomic and functional-group levels. Bacterial anoxygenic phototrophy can reduce the respiratory consumption of DOM and, thus, could be influential for a marine region becoming a CO_2 sink[77]. Such energy supply-related microbial activities must be taken into account if we are to understand

Box 1 | Questions for future research

- What are the concentrations, compositions and spatiotemporal variations of recalcitrant dissolved organic matter (RDOM) in the ocean?
- Is the RDOM inventory currently changing and, if so, is the rate of change fast enough for RDOM to serve as an evolving reservoir for stored carbon?
- Why do heterotrophic bacteria and archaea not degrade RDOM in 'microbial timeframes'?
- What are the structural and biochemical constraints on degradability?
- What environmental conditions make RDOM more or less degradable?
- Can we predict the chemical composition of the degradation products?
- What is the taxon-specific variation in the degradability of RDOM?
- Is ecosystem energy supply also a constraint on RDOM degradability?
- How does organic-matter flux through the microbial loop affect RDOM lability?

carbon cycling in a changing ocean. Just as the regional characteristics of marine DOM shape the microbial community[78], so global changes could shift the microbial dominance and degradative capabilities and, subsequently, influence the RDOM reservoir in the ocean as a whole.

Studying RDOM as part of a DOM reactivity (or recalcitrance) continuum continues to be a 'recalcitrant' problem owing to the complexity of the underlying biogeochemical interactions and the limitations of the available study methods. Powerful new methods in physical chemistry, analytical chemistry[33,79] and microbial genomics and metabolomics[80–82] provide cause for optimism that we can now test hypotheses regarding the function of the MCP and the carbon flux through RDOM. Although new methods will help, we need novel and innovative, probably multidisciplinary, approaches to directly address the kinetic and mechanistic aspects of the functioning of the MCP in the context of the ocean's biogeochemical dynamics. A few basic questions are shown in BOX 1.

Closing remarks

The biogeochemistry of DOM is complex and intimately connected with microbial processes. Although the magnitude of RDOM as one of the largest pools of organic matter on Earth is appreciated, RDOM is not noted for its dynamic state. Marine geochemists are awed by the molecular complexity of RDOM, and microbial oceanographers are intrigued by the very persistence of RDOM as an apparent stark departure from the principle of microbial infallibility[83]. The MCP provides a formalized focus on the importance of microbial processes in carbon storage in the RDOM pool as well as a framework for testing hypotheses regarding the sources and sinks of DOM and the underlying biogeochemical mechanisms. Our proposal that microbial processes underlie the long-term carbon storage in RDOM underscores the proposition that the part that the ocean plays in structuring the Earth's climate is largely driven by microorganisms[84].

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Competing interests statement

The authors declare no competing financial interests.

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