# Part I

### Introduction

### Chapter I

### Why is the ocean important?

The ocean is vast, covering more than two thirds of the Earth's surface (Fig. 1.1). This reservoir of liquid water has helped determine the Earth's climate, storing and transporting heat, making the atmosphere warm and moist, and enabling life to flourish in the sea and on land. In turn, the emergence of life has altered the composition of the atmosphere, increasing the amount of oxygen and ozone, which shields harmful radiation from the Earth's surface.

The anthropogenic release of carbon dioxide is currently perturbing the climate system. The ocean is taking up typically a third of the extra carbon dioxide emitted to the atmosphere, as well as storing and redistributing much of the extra heat supplied to the climate system. To understand this ocean uptake and warming, one needs to understand how the ocean circulates, redistributing heat and carbon, how gases are transferred across the air–sea interface, how carbon dioxide reacts in seawater and the relationship between living plants and carbon.

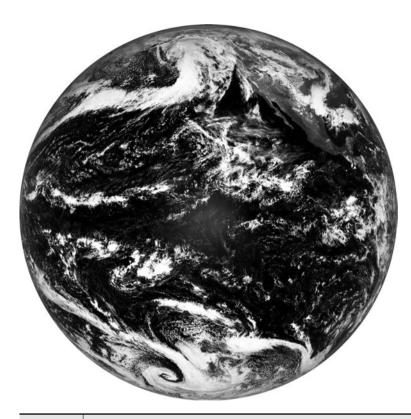
Our aim in this book is to consider the dynamics of the ocean and effect on the carbon cycle, presenting relevant observations, and discussing the fundamental principles and mechanisms at work. In this chapter, we provide a broad context for the book, addressing how the ocean and the carbon cycle have been important in the climate system throughout Earth's history.

### 1.1 What is special about water?

Many important characteristics of the ocean originate from the special properties of water (Table 1.1). A water molecule consists of two hydrogen atoms joined to an oxygen atom: the hydrogen atoms lying on one side of the molecule and the oxygen atom on the other, which leads to a positive charge on the hydrogen side and a negative charge on the oxygen side. At low temperatures, this charge contrast leads to water molecules preferentially orientating themselves in an ordered structure, such that the positive side of a water molecule is opposite the negative side of another water molecule; these inter-molecular bonds are referred to as hydrogen bonds. Extra energy is needed to disrupt this ordered structure in order to make water molecules vibrate more and increase their temperature, as well as to change their phase from ice to a liquid and then to a vapour. Hence, water has a high heat capacity and, combined with its large volume, makes the ocean the largest heat store in the climate system.

Water is a good solvent and dissolves many compounds relatively easily, so that the ocean contains all the natural elements in dissolved form, including dissolved salts making seawater characteristically salty, as well as dissolved gases, oxygen and carbon dioxide, and dissolved nutrients that support life. Water strongly absorbs

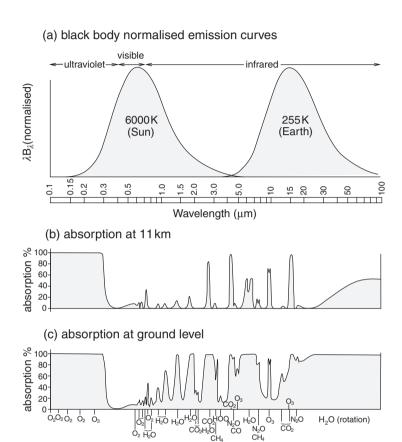
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**Figure 1.1** The ocean covers the majority of the Earth's surface, as emphasised by this visible satellite picture of the Pacific sector of the globe for 6 March 2008 at 2100 UTC. The ocean absorbs much of the incident sunlight and has low reflectance (dark), while there is higher reflectance from land (grey showing the west coast of America) and cloud (white). From GOES West along 135°W; courtesy of NERC Satellite Receiving Station, University of Dundee.

Table I.I Properties of water and their implications for the ocean.
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Property	Definition	How water compares with other substances	Implications for the ocean and climate system
Specific heat capacity	Heat required to raise temperature of a unit mass by 1 K.	Highest for all liquids and solids (except NH <sub>3</sub> ).	Limits temperature range over the Earth.
Latent heat of evaporation	Heat required to evaporate a unit mass.	Highest.	Phase changes are important for the storage and release of heat.
Solvent power	Ability to dissolve substances.	Highest.	Ocean has a high storage of dissolved elements, including nutrients.
Surface tension	Attraction of liquid surface to itself.	Highest.	Bubbles and drops form, which enhance the air-sea transfer of water and gases.
Conduction of heat	Transfer of heat between molecules.	Highest of all liquids.	Heat easily transferred, although turbulence usually dominates.
Molecular viscosity	Resistance to flow.	Less than most liquids.	Ocean easily circulates over the Earth.



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Figure 1.2 (a) Normalised curves for the emission of radiation versus wavelength  $(\mu m = 10^{-6} \text{ m})$  from the Sun with a temperature of 6000 K and the Earth with a temperature of 255 K assuming blackbody emission spectra, which span the ultraviolet, visible (0.4 to 0.7 µm) and infrared wavelengths. The radiation from the Sun and Earth is referred to as solar and long wave, respectively; (b) percentage absorption of radiation at a height of 11 km versus wavelength; and (c) at the ground. The absorption of radiation depends on the chemical composition of the atmosphere: oxygen and ozone molecules in the ultraviolet band; oxygen, ozone and water vapour, carbon dioxide, methane and nitrous oxide for the infrared band. Redrawn from Goody and Yung (1989).

electromagnetic radiation and sunlight only penetrates a few tens of metres in the ocean, leading to the surface ocean being sunlit and warm, while the vast bulk of the ocean is dark and cold. Water has a low viscosity and moves more freely than many liquids, so that the ocean easily circulates and redistributes heat, carbon and other properties over the globe.

## I.2 How does the ocean store and transfer heat?

The ocean affects the properties of the overlying atmosphere, modifying the radiation balance, as well as the storage and transport of heat.

# 1.2.1 How does atmospheric composition affect radiative heating?

The chemical composition of the atmosphere determines the radiative heating of the Earth, as

the molecular structure of each gas affects which wavelengths of radiation are absorbed and emitted (Fig. 1.2):

- Oxygen accounts for about one fifth of the gas molecules in the atmosphere and is formed by biological activity in the oceans and on land. Ultraviolet radiation from the Sun splits oxygen molecules forming ozone, a molecule of three oxygen atoms. Ozone effectively absorbs much of the incoming ultraviolet radiation high in the atmosphere, acting as a 'sunscreen' for the living creatures at the surface of the Earth.
- Water vapour is an important minor constituent of the atmosphere, supplied by evaporation from the ocean and land surface, and returned in the form of rain and snow when the atmosphere becomes saturated. Water vapour primarily absorbs infrared radiation emitted from the Earth, as well as some infrared radiation emitted from the Sun. The atmosphere absorbs and emits infrared radiation both out to space and back down to the surface, which then warms

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the Earth's surface; this process is referred to as the 'greenhouse effect'.

• Carbon dioxide and other minor atmospheric constituents including methane and nitrous oxide absorb strongly in the infrared, and so collectively contribute to the greenhouse effect.

At first sight, radiative heating of the planet might appear only to depend on the atmosphere. However, the ocean plays an important modulating role. Firstly, the ocean has a low albedo compared with most land surfaces and ice, so absorbs a large proportion of the incident sunlight. Secondly, the ocean affects the properties of the overlying atmosphere by releasing moisture and affecting the concentration of trace gases. For example, a warmer ocean leads to more water vapour and carbon dioxide being held in the atmosphere, which increases the atmospheric absorption and emission of infrared radiation. In turn, this increase in radiative heating warms the ocean, which further increases the amount of water vapour and carbon dioxide in the atmosphere. This feedback process plays an important role in the climate system, since the ocean store of carbon dwarfs that of the atmosphere; typically more than fifty times as much carbon is stored in the ocean as in the atmosphere. Hence, small fractional changes in the ocean store of carbon can drive much larger changes in atmospheric carbon dioxide, which then alters the radiative heating.

### 1.2.2 How does the ocean storage of heat affect the planet?

The oceans provide a stabilising effect on the Earth since the presence of water limits temperature changes over the globe. Energy supplied to water molecules is used to break hydrogen bonds, as well as increase the temperature of the molecules.

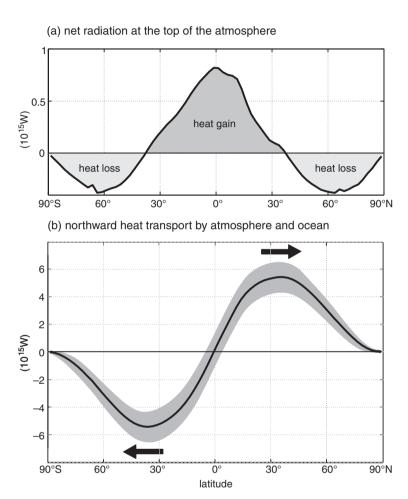
The ocean store of heat far exceeds that of the atmosphere or the surface land due to two factors. Firstly, the ocean storage of heat is much larger than that of the atmosphere due to the greater density of water and the greater heat capacity per unit mass (Table 1.1); the upper 2.5 m of ocean holds as much heat as the entire overlying atmosphere. Secondly, the ocean holds more heat than the surface land (defined by the upper few metres

of soil) because heat is transferred more effectively in a convecting fluid than within a solid. Seasonal temperature changes extend to depths of several hundreds of metres in the upper ocean, but only penetrate a few metres in soil. Thus, seasonal heat storage is spread over a larger mass in the ocean than in the surface land. Hence, seasonal temperature changes are much smaller in the air over the surface ocean than the land surface, defining the contrasting marine and continental climates over the Earth.

### 1.2.3 How does the ocean affect the redistribution of heat?

Rather than only acting as a local reservoir of heat, the ocean assists the atmosphere in redistributing heat over the globe. To understand this process, one needs to consider how the Earth is heated. The Earth is warmed by the incident radiation from the Sun, with about 70% of sunlight absorbed by the ocean, land and the atmosphere, and the remainder reflected back to space. In return, thermal energy is emitted back to space as infrared radiation from the atmosphere, ocean and land. Averaged over the globe and over several years, the net incoming solar radiation (incident sunlight minus reflected sunlight) balances the amount of outgoing infrared radiation at the top of the Earth's atmosphere.

However, this overall balance does not apply locally. There is a greater intensity of sunlight in the tropics than at the poles due to the angle between the incident sunlight and the Earth's surface. Outgoing infrared radiation instead only weakly decreases with latitude due to relatively small changes in absolute temperature in the upper atmosphere. Consequently, there is a net radiative heating over the tropics and cooling over the poles (Fig. 1.3a). In response to this latitudinal contrast, the atmosphere and ocean together transfer heat poleward (Fig. 1.3b), reaching 5 PW at mid latitudes (1 PW  $\equiv 10^{15}$  watt; 1 watt  $\equiv$  joule s<sup>-1</sup>). This heat transfer prevents the tropics becoming even warmer and the poles even cooler. Indeed, if there was not this heat transfer, the latitudinal temperature contrast would increase across the globe, probably becoming twice as large as in the present day, until a local radiative heat balance was reached.



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Figure 1.3 (a) The net radiation at the top of the atmosphere averaged over latitude bands (PW  $\equiv 10^{15}$  watts) revealing heat gain in the tropics (dark grey) and loss over the mid and high latitudes (light grey). (b) The implied northward transfer of heat (PW) with shading denoting the error range and arrow denoting the direction. Data from the Earth Radiation Budget Experiment from 1987–1989; redrawn from Wunsch (2005).

We next consider how the ocean affects the climate system through the carbon cycle.

# 1.3 What is the role of the ocean in the global carbon cycle?

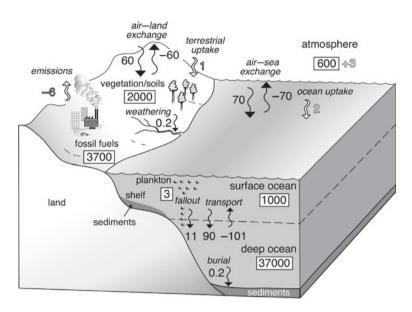
The amount of carbon dioxide residing in the atmosphere is important in affecting the Earth's radiative heating. However, this atmospheric store of carbon is dwarfed by the amount of carbon stored in the land and the oceans (Table 1.2). The carbon reservoir in terrestrial plants and soil is also several times larger than that in the atmosphere. Since all of these reservoirs are connected, minor changes in the ocean or geological reserves of carbon can lead to large changes in atmospheric carbon dioxide.

Table 1.2	Carbon budget for the Earth in the			
pre-industrial era (Sarmiento and Gruber, 2002;				
Tyrell and V	Wright, 2001).			

Reservoir	Mass of carbon $(10^{15}g = Pg)$
Atmosphere	600
Ocean	38 000
Vegetation/soils	2 000
Fossil fuels	3 700
Rocks (organic)	14000000
Rocks (as calcium carbonate)	60 000 000

**I.3.1 How does the ocean store carbon**? Carbon dioxide is soluble and reacts with seawater to form bicarbonate and carbonate ions; the sum of the bicarbonate and carbonate ions, and dissolved carbon dioxide is collectively referred to

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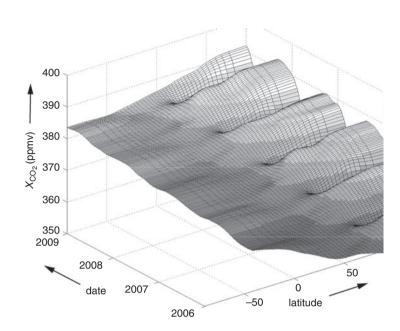
**Figure 1.4** Estimated reservoir sizes (Pg C, boxed numbers) and annual fluxes (Pg C  $y^{-1}$ , associated with arrows) for the global carbon cycle in the immediate pre-industrial era. The emissions from fossil fuels are driving fluxes of anthropogenic carbon dioxide (white arrows). Estimates are for the 1990s taken from Sarmiento and Gruber (2002), where a more detailed evaluation can be found. Drawn by K. Lancaster.

as dissolved inorganic carbon. Due to the particular chemistry of seawater and the influence of dissolved salts, more than 99% of the dissolved inorganic carbon is in the form of bicarbonate and carbonate ions, enhancing the ocean capacity as a carbon reservoir by more than 100-fold to about 38 000 Pg C. Most of the ocean's storage of carbon is due to this chemical reactivity. This store of carbon is not restricted to the surface ocean. Instead, most of the carbon is held in the deep ocean through its greater volume and higher concentrations of dissolved inorganic carbon (Fig. 1.4). The increase in dissolved inorganic carbon concentration in the deep ocean is primarily due to carbon being more soluble in cold waters and the physical transport of cold, carbon-rich waters from the surface to the deep ocean. Biological transfer of organic carbon also leads to an increase in dissolved inorganic carbon in the deep ocean, accounting for perhaps 10% of its increase with depth.

### 1.3.2 How is carbon exchanged between the atmosphere and ocean?

There are large seasonal exchanges of carbon dioxide between the atmosphere, ocean and terrestrial biosphere, leading to the atmospheric reservoir of carbon being replaced every few years. The spring and summer expansion of the terrestrial biosphere is imprinted on atmospheric CO<sub>2</sub>: lowest  $CO_2$  during the autumn and highest  $CO_2$  during spring, with the strongest seasonality in the northern hemisphere due to the greater extent of land masses (Fig. 1.5). The exchange between the atmosphere and ocean is communicated through the surface mixed layer of the ocean, which is on the order of 100 m thick, and holds a comparable amount of carbon as stored in the atmosphere. Over the globe, ocean circulation transfers about 100 Pg C between this surface layer and the deep ocean each year, taking several hundred years for the carbon in the deep ocean to be replaced and flushed through, since its reservoir is so large, reaching 37 000 Pg C.

The available fossil-fuel reservoir is large relative to the atmospheric store of carbon dioxide (Table 1.2). The release of fossil-fuel carbon has increased the atmospheric concentration over the past century (Fig. 1.4); only about half of anthropogenic emissions have remained in the atmosphere since the pre-industrial era, with the remainder going into the terrestrial biosphere and oceans in roughly equal proportions. However, the fluxes of anthropogenic carbon into the terrestrial biosphere and ocean are relatively small compared with the natural, seasonal exchanges; only one to two per cent of the seasonal fluxes (Fig. 1.4, white arrows). Thus, it is difficult to quantify accurately the fate of anthropogenic carbon dioxide in the global system.



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**Figure 1.5** Near-surface mixing ratio of atmospheric carbon dioxide  $X_{CO_2}$  (ppmv) as a function of latitude and time, for years 2006–2008 inclusive, interpolated from observations by the GLOBALVIEW-CO2 network of monitoring stations (GLOBALVIEW-CO2, 2009). Note date increases to the left.

### 1.3.3 How do marine ecosystems cycle carbon?

The Sun's rays not only provide the ultimate source of heat to the Earth, they also provide the fundamental energy source for photosynthesis: the energy from photons in visible wavelengths are utilised to create organic molecules from water, carbon dioxide and other nutrients. The organic molecules form the machinery enabling life to function and provide a store of energy which can be accessed by respiration, ultimately sustaining most of life on land and in the oceans.

The most abundant photosynthesising organisms in the sea are the phytoplankton, tiny unicellular organisms ranging between 1 and 100 microns in size, often forming chains or colonies constituting many cells, and extremely diverse in both form and function, as depicted in the microscope images in Fig. 1.6.

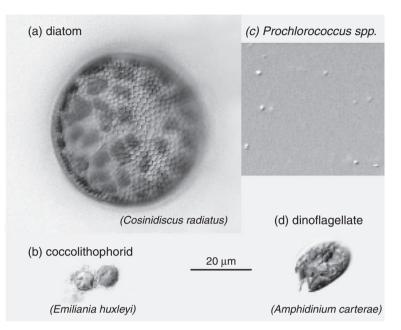
Due to the efficient absorption of electromagnetic radiation by seawater, phytoplankton are only able to grow in the upper, sunlit layer of the ocean, typically above the upper 100 m or so. The organic matter created by phytoplankton and their detritus is respired by other organisms, including submicron size bacteria and archaea (both single-celled micro-organisms without a nucleus). Larger organisms, including zooplankton graze upon living phytoplankton and are, in turn, eaten by fish. Phytoplankton cells and faecal pellets from the larger organisms sink into the deeper, dark waters where, even though photosynthesis cannot occur, there is a rich and diverse ecosystem. The surface ocean ecosystem produces about 11 Pg C of sinking organic particles each year, but maintains a biomass of only 3 Pg C at any time, reflecting a rapid cycle of production and loss.

Almost all of the sinking organic matter is respired back to dissolved inorganic form before reaching the sea floor. In this way, dissolved inorganic carbon is biologically transferred to organic carbon in the surface, sunlit ocean, the organic carbon sinks, and then is respired and returned to dissolved inorganic carbon at depth (Fig. 1.4). This biologically mediated transfer of carbon enhances the deep ocean's store of dissolved inorganic carbon by about 10%.

### 1.3.4 How does ocean circulation affect the ecosystem?

Phytoplankton use chlorophyll *a*, a pigment which absorbs sunlight at red and blue wavelengths while scattering green wavelengths. Remotely sensed images of the Gulf Stream reveal a ribbon

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**Figure 1.6** Light microscope images of representatives of several 'functional groups' of phytoplankton at the same magnification scale (horizontal line represents  $20 \ \mu m = 20 \times 10^{-6} \ m$ ). The phytoplankton population is extremely diverse in terms of function and genetic make-up, as well as spanning many orders of magnitude in cell volume. Cell size places some important restrictions on their ability to acquire resources and their interaction with predators. (a) Diatoms form silica-based cell structures (here seen as a beautiful honeycomb pattern in *Coscinodiscus radiatus*, which may provide an energy saving relative to a cellulose structure. (b) Coccolithophorids, like *Emiliania huxleyi* form calcium carbonate mineral structures, providing defence against grazing. (c) *Prochlorococcus* are the smallest photosynthesising cells on the planet. Their small size makes them highly suited to nutrient starved situations. (d) Dinoflagellates combine both photosynthesis and predation as energy sources. In coastal waters, some dinoflagellates, such as *Amphidinium carterae*, produce toxins, possibly as a defence strategy, which lead to harmful algal blooms and can affect shell fisheries. Images M. Follows with help from R. Andersen.

of warm water running along the western boundary of the North Atlantic, separating from the North Carolina coast and extending into the open ocean (Fig. 1.7a, light shading). As is common in the ocean, there are higher chlorophyll concentrations in the cooler waters to the north of the Gulf Stream (Fig. 1.7b, light shading) than in the warmer waters within the current or to the south.

Biochemical reactions proceed faster at warmer temperatures, so more biomass might be expected in warmer waters. However, the opposite situation occurs, reflecting how photosynthesis is more strongly controlled by the availability of nutrients than by temperature. The organic molecules of living organisms require elements, including nitrogen, phosphorus, silica and other trace metals, in addition to carbon, hydrogen and oxygen. These nutrients are often in scarce supply in the surface ocean and, thus, their availability controls the production of new organic matter. In the open ocean, nutrients are primarily supplied to surface waters by the physical circulation transferring nutrient-enriched deep waters to the surface. In turn, the consumption and sinking of organic matter, as well as the sinking of cold waters, returns nutrients back to the deep waters.

# I.4 How have climate and life evolved on the planet?

Stepping back in time, the ocean has played a central role in the evolution of the planet by assisting in the burial of carbon in sedimentary rocks and providing the habitat for the first living creatures.