

## 2. Structure and Composition of the Atmosphere and Ocean

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### 2.1 OVERVIEW

This chapter summarizes the origins, thermodynamic structure, and composition of the atmosphere and ocean.

### 2.2 THE ATMOSPHERE

The Earth was formed approximately 4.6 billion years ago, with extensive bombardment by meteorites for almost the first billion years of its existence (until at least 3.8 billion years ago). The atmosphere of early Earth, which was very different from that of the present day, was lost during this bombardment process. The current atmosphere formed as the result of degassing from the Earth's interior. Much of this degassing occurred (and continues to occur) in volcanic eruptions.

The present-day atmosphere is made up of a few highly concentrated gases (primarily molecular nitrogen and molecular oxygen) and a large number of trace gases (such as water vapor, carbon dioxide, and ozone). The atmosphere also contains water in the liquid and solid states in the form of clouds, as well as aerosols (solid, liquid, or mixed-phase particles suspended in air). The thermodynamic state of the atmosphere is described by pressure, density, and temperature, which are related by the equation of state

$$p = \rho R_d T \tag{2.1}$$

where  $R_d = 287 \text{ J kg}^{-1} \text{ K}^{-1}$  is the gas constant for dry air. This equation is derived from the equation of state for an ideal gas (see, e.g., derivation in sections 1.6–1.7 by *Curry and Webster, 1999*), and is based on the observation that air as a mixture behaves like an ideal gas (i.e., that

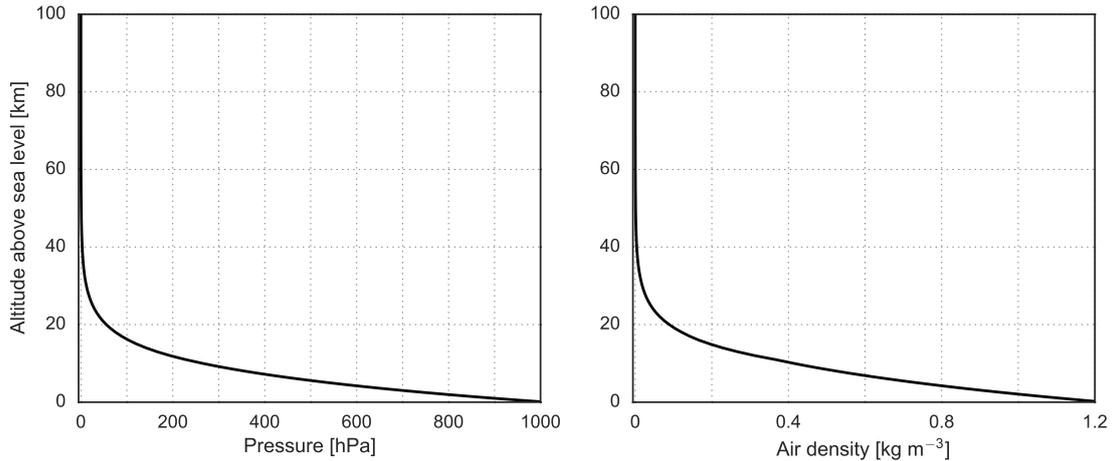


Figure 2.1: The variation of pressure and density with altitude (data from the [1976 U.S. Standard Atmosphere](#)).

the motion of air molecules is random and individual molecules interact only rarely). The concentration of water vapor is also an important contributor to the thermodynamic state of air. We will examine the contributions of water vapor in greater detail in Chapter 2.

### 2.2.1 PRESSURE AND DENSITY: HYDROSTATIC BALANCE

Figure 2.1 shows the variation of pressure and density with altitude in the lowest 100 km of the atmosphere. Both quantities decrease exponentially with altitude. Pressure is defined as force per unit area, and can be thought of as the weight of atmosphere directly above a horizontal plane divided by the area of that plane. Its vertical variation may therefore be understood in terms of a balance of forces between the gravitational force (which pulls air toward the center of the Earth) and the pressure gradient force (which pushes air toward space). Consider a layer of atmosphere with thickness  $\delta z$  and cross-sectional area  $\delta A$ . Assuming no horizontal variations in pressure, the pressure gradient force across the layer is equal to the vertical difference in pressure times the cross-sectional area:

$$\left[ p - \left( \frac{dp}{dz} \right) \delta z \right] \delta A - p \delta A = - \left( \frac{dp}{dz} \right) \delta z \delta A \quad (2.2)$$

The gravitational force acting on the layer is  $\rho \delta A \delta z g$ , where  $g$  is the gravitational constant for Earth ( $\sim 9.81 \text{ m s}^{-2}$ ). Setting the two forces equal and cleaning up the terms yields the hydrostatic balance:

$$g = - \frac{1}{\rho} \frac{dp}{dz} \quad (2.3)$$

The hydrostatic balance is only valid when air is not accelerating vertically. The assumption of hydrostatic balance in the atmosphere is generally reasonable when discussing average

conditions over sufficiently large areas ( $> 2 - 3$  km in diameter), as upward and downward vertical accelerations tend to average out. Vertical accelerations can be large over small areas or within a storm system. In these cases, hydrostatic balance does not hold.

Using equation 2.1, we can rewrite the hydrostatic balance as

$$\frac{dp}{p} = -\frac{dz}{H} \quad (2.4)$$

where  $H = \frac{R_d T}{g}$  has units of length and is called the scale height of the atmosphere. If we assume that the temperature is constant (i.e., that the atmosphere is isothermal), then the scale height is also constant and equation 2.4 can be integrated from the surface ( $p = p_s$ ) to an arbitrary height  $z$ :

$$p = p_s e^{-z/H} \quad (2.5)$$

This relationship shows that pressure decreases exponentially with height from the surface.

Density is defined as the mass of air per unit volume, and is typically expressed in units of  $\text{kg m}^{-3}$ . Again assuming an isothermal atmosphere, the relationship between pressure and density in equation 2.1 indicates that, like pressure, density decreases exponentially with altitude (as shown in Fig. 2.1).

The hydrostatic balance (equation 2.3) can be rearranged to relate the mass between two altitudes to the pressure change between those altitudes:

$$dm \equiv \rho dz = -\frac{dp}{g} \quad (2.6)$$

The total mass of the atmosphere per unit area is therefore equal to the pressure difference between the surface and the top of the atmosphere ( $dp = p_s - 0 = p_s$ ):

$$M = \frac{p_s}{g} \quad (2.7)$$

Substituting  $M = 10.328 \times 10^3 \text{ kg m}^{-2}$  and  $g = 9.81 \text{ m s}^{-2}$ , we find a mean surface pressure of 101325 Pa, where 1 pascal (Pa) =  $1 \text{ N m}^{-2}$ . Atmospheric pressure is generally expressed in hectopascals (hPa) or millibars (mb), where 1 hPa = 1 mb = 100 Pa. Other commonly used units of pressure include bars (1 bar =  $10^5$  Pa), atmospheres (1 atm =  $1.01325 \times 10^5$  Pa), and torricelli (1 torr = 133.322 Pa). Ocean pressure may be expressed in bars, decibars (1 dbar = 0.1 bar), or atmospheres. Torricelli are used in atmospheric chemistry and chemical oceanography.

## 2.2.2 TEMPERATURE STRUCTURE

Temperature, which is a measure of thermal energy (molecular motion), is typically expressed using the Kelvin scale (K), although temperatures are also often expressed in degrees Celsius ( $^{\circ}\text{C}$ ) in meteorology and oceanography. A one Kelvin difference in temperature is equal to a one degree difference in the Celsius scale, with  $0^{\circ}\text{C} = 273.16 \text{ K}$ . The temperature 273.16 K corresponds to the freezing point of pure water (as we shall see, the freezing point of seawater is slightly colder), while a temperature of 0 K indicates the absolute absence of thermal energy.

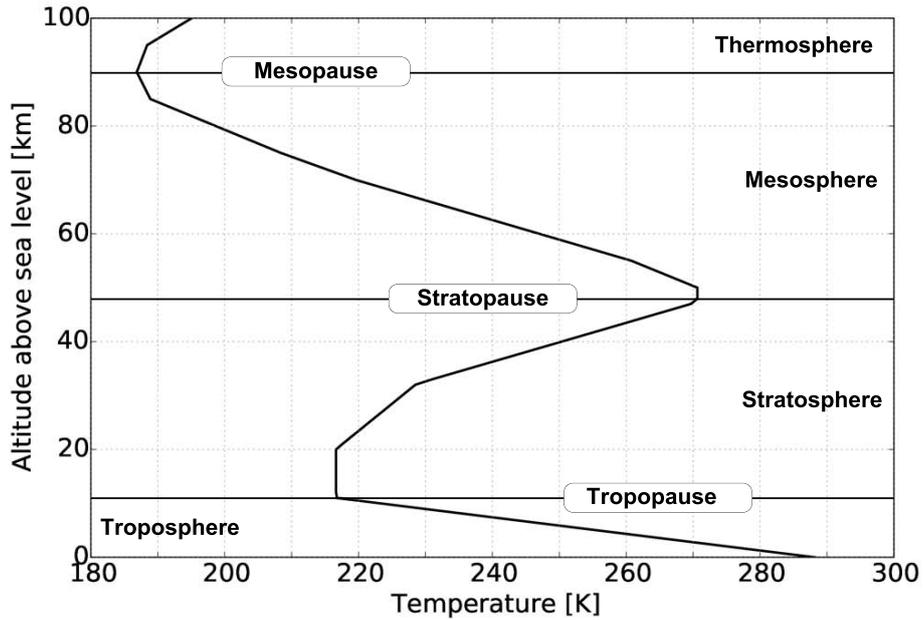


Figure 2.2: The temperature structure of the atmosphere (data from the [1976 U.S. Standard Atmosphere](#)).

Figure 2.2 shows the vertical variation of temperature with altitude in the lowest 100 km of the atmosphere. Temperature decreases sharply with height in the lowest part of the atmosphere, which is called the troposphere. The decrease in temperature with height in the troposphere can be understood in the context of the simple energy balance models introduced in section 1.3. Solar radiation warms the surface every day, while the atmosphere is constantly radiating energy to space. Absorption and re-emission of infrared radiation by greenhouse gases in the atmosphere reduces the availability of long-wave radiation with altitude, leading to warmer temperatures at lower levels (more absorption of long-wave radiation from both above and below) and cooler temperatures at higher levels (consider, e.g., a version of Fig. 1.11 with multiple atmospheric layers).

The temperature change with height is described by the lapse rate:

$$\Gamma = -\frac{\partial T}{\partial z} \quad (2.8)$$

An increase of temperature with height ( $\Gamma < 0$ ) is called a temperature inversion, while a layer of zero change in temperature with height ( $\Gamma = 0$ ) is called isothermal. The average lapse rate in the troposphere is  $6.5 \text{ K km}^{-1}$ .

The upper boundary of the troposphere is called the tropopause. Figure 2.2 indicates a shallow isothermal layer above the tropopause, with a strong increase of temperature with height (temperature inversion) above. This layer of the atmosphere is called the stratosphere. The increase of temperature with height in the stratosphere is caused primarily by the absorption

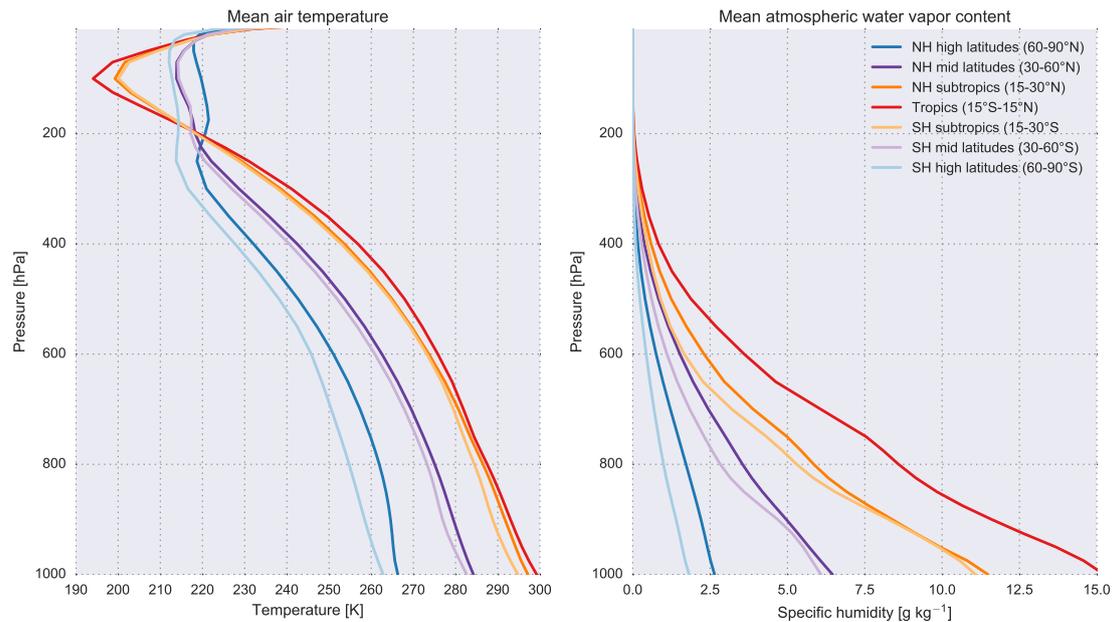


Figure 2.3: Profiles of temperature (left) and water vapor (right) averaged over various latitude bands, as indicated in the legend. Data from the [Climate Forecast System Reanalysis](#).

of solar radiation by ozone. The peak temperatures occur at the top of the stratosphere, where ozone absorbs the shortest (highest energy) ultraviolet wavelengths (see Fig. 1.10). These short wavelengths do not penetrate to the lower stratosphere, so temperatures are lower than in the upper stratosphere. The upper boundary of the stratosphere, called the stratopause, occurs where ozone densities become too small to exert a strong influence on temperature. Temperature decreases with altitude above the stratopause. This layer of temperature decrease with height is called the mesosphere, and is capped by the mesopause. Above the mesopause, solar absorption by molecular oxygen and nitrogen leads to another increase of temperature with height in the thermosphere.

Interactions between the atmosphere and ocean are generally limited to the lowest levels of the atmosphere, particularly the troposphere, although recent research indicates that interactions between the stratosphere and ocean may also be relevant for understanding climate variability ([Reichler et al., 2012](#)).

The left panel of Fig. 2.3 shows mean vertical profiles of temperature with pressure at low latitudes (20°S–20°N), middle latitudes (between 30° and 60° in both hemispheres) and high latitudes (poleward of 75° in both hemispheres). The vertical profile of temperature varies significantly with latitude in both structure and magnitude. Temperatures from the surface to approximately 200 hPa are warmer in the tropics than in the mid-latitudes, and warmer in the mid-latitudes than near the poles. Above 200 hPa, the tropical profile is colder than the others, with a sharp minimum in temperature at the tropopause. The tropopause is also much higher

Table 2.1: Major gaseous atmospheric constituents (updated from *Jacobson, 2005*).

gas	percent by volume
Nitrogen (N <sub>2</sub> )	78.08%
Oxygen (O <sub>2</sub> )	20.95%
Argon (Ar)	0.93%
Water Vapor (H <sub>2</sub> O)	0.00001–4.0%
Carbon Dioxide (CO <sub>2</sub> )	0.040%
Neon (Ne)	0.0015%
Helium (He)	0.0005%
Methane (CH <sub>4</sub> )	0.00018%
Ozone (O <sub>3</sub> )	0.000003–0.001%
Krypton (Kr)	0.0001%

in the tropics than in the mid-latitudes, and slightly higher in the mid-latitudes than near the poles. We will discuss the reasons for these differences later in the course.

The right panel of Fig. 2.3 shows mean vertical profiles of water vapor with pressure for the same latitude ranges. The saturation vapor pressure (maximum possible amount) of water vapor is dependent on temperature via the Clausius–Clapeyron equation, which determines the leading order variations of water vapor with both latitude and altitude. The sharp minimum of temperature at the tropical tropopause is crucially important for climate as we know it, because it limits the amount of water vapor that can pass through the tropopause into the upper levels of the atmosphere. Solar radiation can dissociate water vapor at very high altitudes, breaking it up into very light constituent parts that can then escape to space. If the cold temperatures at the tropopause did not limit the amount of water vapor entering the upper atmosphere, the removal of water from the Earth system would be much more effective. This process would deplete the oceans over time, fundamentally changing Earth’s climate and its ability to support life.

In section 2.2.1, we used the assumption of an isothermal atmosphere to derive the exponential decrease of pressure and density with height. In reality, temperature varies with both height and latitude (Figs. 2.2 and 2.3); however, changes in temperature in the lower atmosphere are small ( $\sim 100$  K) relative to the magnitude of temperature (e.g.,  $T_e = 255$  K). This is particularly true over shallow vertical ranges, where changes in temperature are on the order of ones to tens of Kelvins. The assumption of an approximately isothermal atmosphere is therefore generally reasonable for global mean conditions, although like any assumption it should be applied with caution.

### 2.2.3 ATMOSPHERIC COMPOSITION

Table 2.1 lists the typical composition of the lowest 100 km of the atmosphere. The primary constituents are molecular nitrogen (N<sub>2</sub>) and molecular oxygen (O<sub>2</sub>), which together make up approximately 99% of the atmosphere by volume. Most of the remaining 1% is made up

of argon (Ar), a chemically inert noble gas. The concentrations of these gases are well-mixed, in that they do not vary significantly within the lowest 100 km of the atmosphere. Other well-mixed, chemically inert gases present in the atmosphere include Neon (Ne), helium (He), krypton (Kr), and xenon (Xe). Table 2.1 also lists water vapor ( $\text{H}_2\text{O}$ ), carbon dioxide ( $\text{CO}_2$ ), methane ( $\text{CH}_4$ ), and ozone ( $\text{O}_3$ ) as major gaseous constituents in the atmosphere. The concentrations of these gases vary significantly in either time or space, and often both.

Water vapor is important not only as a greenhouse gas, but also for atmospheric chemistry and energy transfer to the atmosphere via latent heat. The primary source of water vapor in the atmosphere is evaporation from the oceans (~85%). Evaporation from land water reservoirs (lakes, rivers, streams, and soil water), sublimation from ice reservoirs (glaciers, snow, and sea ice), and transpiration from plants also provide water vapor to the atmosphere. Water vapor can be removed from the atmosphere via cloud formation and precipitation, transfer to the ocean or other surface reservoirs, or chemical reactions. As mentioned in the previous section, the saturation vapor pressure of water vapor is dependent on temperature. When temperatures are cold, excess water vapor condenses to the liquid or solid phase and mixing ratios are low. When temperatures are warm, water in liquid or solid form readily evaporates and mixing ratios are generally high. Strictly speaking, only the maximum amount of water vapor depends on temperature: water vapor concentrations may be low when temperatures are warm, but water vapor concentrations may not be high when temperatures are cold. We will examine water vapor and its importance in more detail in two weeks.

Carbon dioxide is another important greenhouse gas. Carbon dioxide is added to the atmosphere by cellular respiration in plants, decomposition of organic matter, ocean and volcanic outgassing, and combustion of fossil fuels. It is removed by photosynthesis in plants, dissolution in ocean water or raindrops, and chemical weathering of rocks. Carbon dioxide is not chemically active in the atmosphere and its lifetime in the atmosphere is long (30–200 years), so that it is generally well-mixed within the atmosphere. Observations of carbon dioxide over the past fifty years show a strong seasonal cycle (related to seasonal variations in photosynthesis and decomposition of organic material) and a clear increase in concentration from approximately 0.031% by volume in the 1950s to approximately 0.040% today. Isotopic analysis of carbon dioxide in the atmosphere shows that this increase is related to human activity, specifically fossil fuel combustion.

Methane has also increased in recent decades due to human activity, such as agriculture and landfills. Methane is formed by bacteria in anaerobic environments, such as wetlands, rice paddies, landfills, and the digestive tracts of livestock animals. It can also be produced by forest fires and chemical reactions in the atmosphere. Like water vapor and carbon dioxide, methane is an important greenhouse gas. The lifetime of methane (~12 years) is shorter than that of carbon dioxide; however, the major removal process is reaction with the hydroxyl radical resulting in carbon dioxide and water. The greenhouse impacts of methane emissions are therefore much longer-lived than the methane itself. Oxidation of methane also plays key roles in atmospheric chemistry, notably the chemical production of water vapor in the stratosphere.

Ozone is an important absorber of both solar and infrared radiation, and plays a key role in atmospheric chemistry (particularly in the stratosphere). Atmospheric ozone is produced by photochemical reactions, including photolysis of molecular oxygen in the stratosphere

and photolysis of nitrogen dioxide ( $\text{NO}_2$ ) near the surface. Stratospheric ozone absorbs high-energy ultraviolet radiation from the sun. Ultraviolet radiation damages the tissues that make up plants and animals; without stratospheric ozone, the Earth would be much less hospitable to life as we know it. By contrast, ozone near the surface is considered a pollutant and is harmful to human health. Automotive exhaust contains high concentrations of  $\text{NO}_2$ , so that near-surface concentrations of ozone are often high near major roads in urban areas.

## 2.3 THE OCEAN

The ocean is thought to have formed from the precipitation of a steam atmosphere as early Earth cooled. The existence of a liquid ocean presents upper and lower limits on global mean temperatures, as the oceans have neither evaporated completely nor frozen completely. The stability of climate on geologic timescales was crucial for the evolution of life on Earth. The crust at the ocean floor is relatively young, with new crust constantly being formed along the mid-ocean ridges at rates of a few centimeters per year. The creation of new crust adds water to the oceans from the Earth's interior. This newly formed water is in an approximate steady-state equilibrium with the loss of water to space in the upper atmosphere, so that the total amount of water in the Earth system is approximately stable.

The present-day ocean is 4000 m deep on average, and contains 97% of the world's water. More than 75% of the ocean is between 3000 and 6000 m deep. Of the remainder, approximately 8% is continental shelf less than 200 m deep and approximately 15% is continental slope (a transitional region between the continental shelf and the deep ocean). Only about 1% of the ocean is deeper than 6000 m., with the maximum depth of 11 500 m occurring in the Mindanao Trench east of the Philippines.

### 2.3.1 OCEAN STRUCTURE

Like the equation of state for the atmosphere (equation 2.1), the equation of state for seawater is a function of pressure, temperature, and density. Unlike the atmosphere, there is no general theory for liquids to match that for ideal gases. The equation of state must be determined empirically based on large numbers of measurements. Furthermore, while density in the atmosphere is a function of only pressure and temperature, density in the ocean is a function of pressure, temperature, and salinity (where salinity is the concentration of dissolved ions, or salts, in the water). The full equation of state is therefore extremely complicated, as it involves the properties of all of the constituent salts. Fortunately, the relative concentrations of the individual salt ions do not vary significantly in the ocean, so that salinity can usually be expressed as one quantity that represents the total concentration of all salt ions in the seawater.

The variation of pressure with depth in the ocean is approximately linear (Fig. 2.4), and varies little with latitude. Pressure typically increases by 1.019716 dbar per meter of seawater. The pressure of the top 10 m of ocean is roughly equivalent to the atmospheric surface pressure. Pressure in the ocean is therefore typically expressed as only the portion of total pressure due to the ocean, with the atmospheric pressure taken to be zero.

Figure 2.5 shows the mean profiles of temperature and salinity in the upper 2000 m of the

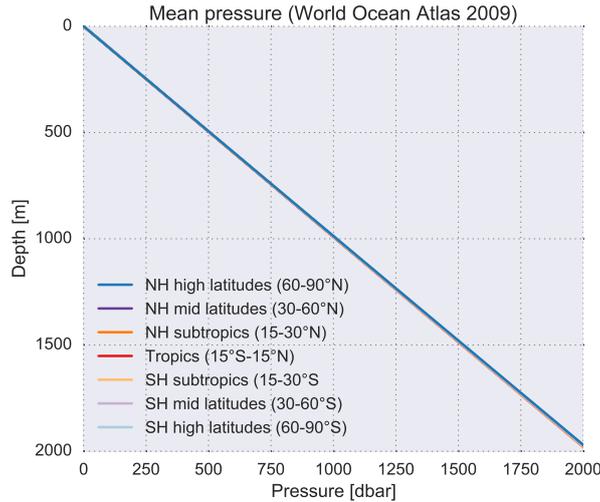


Figure 2.4: The variation of pressure with depth in the upper 2000 m of the ocean.

ocean based on observations made at different latitudes. Spatial variations in temperature and salinity are most pronounced in the upper ocean, particularly in the top 300–500 m. Interaction with surface winds at the ocean–atmosphere interface leads to the development of a shallow mixed layer, where temperature and salinity are nearly constant. Temperature decreases sharply below this mixed layer in the tropics and mid-latitudes. This region of sharp temperature decrease is called the thermocline, and extends down to approximately 1000 m. The temperature gradually decreases to approximately 0–3°C below the thermocline, with very little seasonal variation. No permanent thermocline exists at polar latitudes because the water temperature is very cold and often covered by sea ice. Furthermore, temperatures in the high-latitude oceans may be below 0°C, even in the time mean, reflecting the fact that the presence of salts reduces the freezing temperature of water.

In contrast to temperature, salinity increases sharply from the surface, with the most pronounced increases at polar and high latitudes. Variations in salinity are an important part of variations in density at all latitudes, and especially at high latitudes. These variations drive the deep ocean circulation, which is a critical component of the climate system. Salinity near the ocean surface varies significantly by latitude, with relatively fresh water at polar latitudes and relatively saline water in the tropics and especially in the subtropics. These variations in surface salinity depend on the fluxes of freshwater at the ocean boundaries, including the distribution of precipitation and evaporation, input from rivers, and melting ice.

Seawater is approximately 1000 times as dense as air. The boundary between the atmosphere and ocean is therefore very stable. The density of seawater is a function of pressure, temperature, and salinity, and is typically expressed as a deviation from the density of pure water at 4°C ( $1000 \text{ kg m}^{-3}$ ):

$$\sigma(T, P, S) = \rho(T, P, S) - 1000 \text{ kg m}^{-3} \quad (2.9)$$

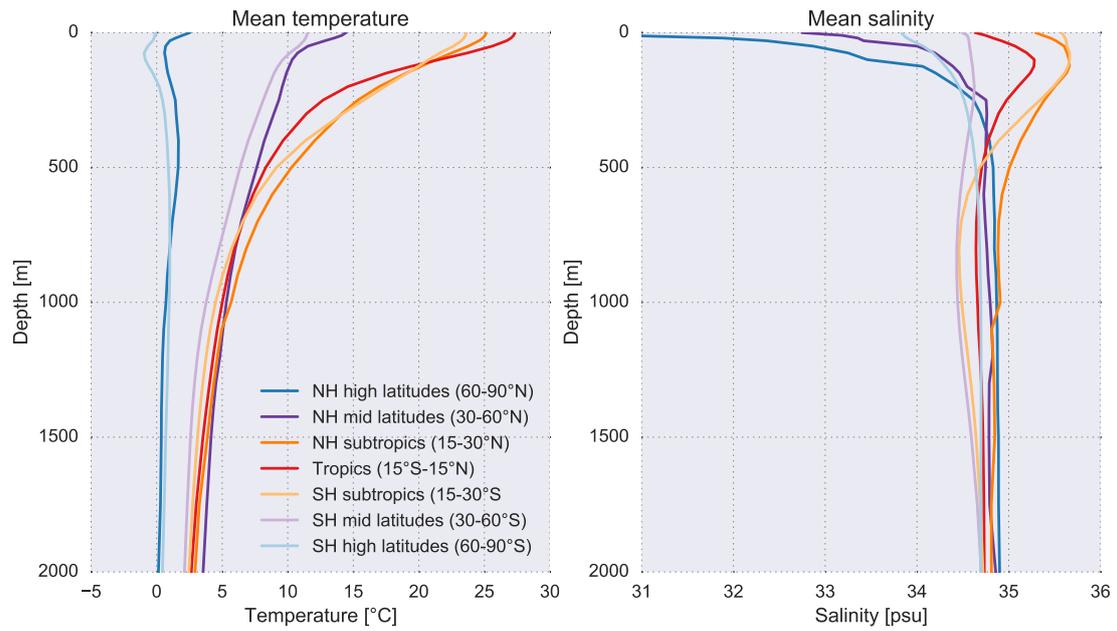


Figure 2.5: Profiles of temperature (left) and salinity (right) in the upper 2000 m of the ocean averaged over various latitude ranges as indicated in the legend. Data from the [World Ocean Atlas 2009](#).

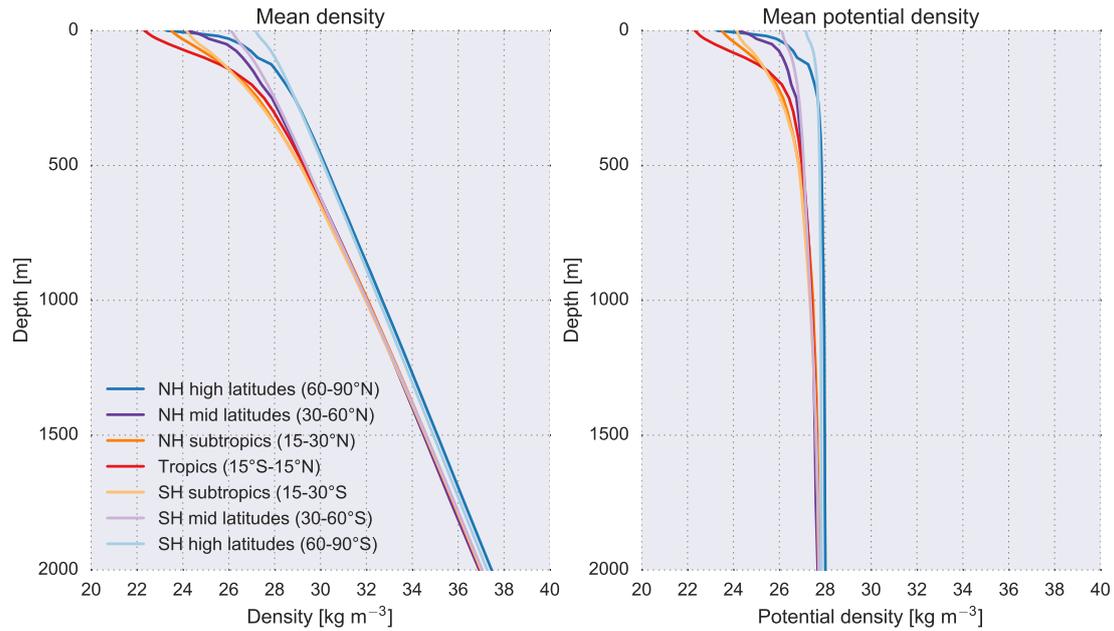


Figure 2.6: Profiles of ocean density (left) and potential density (right) calculated from the profiles of temperature and salinity shown in Fig. 2.5.

A number of algorithms are available for calculating the density of seawater (see, e.g., the [gsw](#) and [seawater](#) python modules, which we will use later in the course). Many implementations remove the effect of the pressure profile by using surface pressure as an input instead, resulting in

$$\sigma_t(T, S) = \rho(T, S) - 1000 \text{ kg m}^{-3} \quad (2.10)$$

Figure 2.6 shows profiles of  $\sigma_t$  calculated based on the mean temperature and salinity profiles in the three previously defined latitude zones (Fig. 2.5). Ocean density increases monotonically with depth in the first 2000 m below the surface, with the densest surface waters located in the southern hemisphere high latitudes and the least dense located in the tropics. Subsidence of surface waters occurs when the potential density (Fig. 2.6, right panel) of surface waters become denser than the water underneath. We will learn more about potential density in next week's lecture; for now it is enough to note that the distribution and variability of potential density controls the distribution and variability of mixing between the surface layer and the deep ocean. Hot spots for density-driven mixing are located in the mid-high latitude North Atlantic and high latitude southern ocean, where subsidence of surface waters is both more likely and more vigorous than in the tropics or subtropics. Mixing in these regions results in the formation of North Atlantic Deep Water (NADW) and Antarctic Bottom Water (AABW); we will discuss these water masses in more detail in lecture 8.

Table 2.2: Composition of standard ocean water with a salinity of 34.7 psu (from [Wells, 2012](#)).

constituent ion	mass mixing ratio in seawater [g kg <sup>-1</sup> ]	percentage of global salt
Chloride (Cl <sup>-</sup> )	19.215	54.96%
Sodium (Na <sup>+</sup> )	10.685	30.58%
Sulphate (SO <sub>4</sub> <sup>2-</sup> )	2.693	7.70%
Magnesium (Mg <sup>2+</sup> )	1.287	3.69%
Calcium (Ca <sup>2+</sup> )	0.410	1.17%
Potassium (K <sup>+</sup> )	0.396	1.13%
Bicarbonate (HCO <sub>3</sub> <sup>-</sup> )	0.142	0.41%
Bromide (Br <sup>-</sup> )	0.067	0.19%
Boric acid (H <sub>3</sub> BO <sub>3</sub> )	0.026	0.07%

### 2.3.2 OCEAN COMPOSITION

On average, dissolved salts make up approximately 3.5% of seawater by volume. Seawater contains salts because ionic compounds dissolve readily in water. These salts come from a variety of sources, including the breakdown of continental rocks, volcanic eruptions, geothermal hot springs, and the atmosphere. Salts are lost from the ocean by sedimentation to the ocean floor, as well as transfer to the biosphere and atmosphere. The pH of the ocean must have remained relatively constant for marine life to evolve. The total salinity of the ocean is therefore believed to have been in equilibrium for at least 100 million years, although paleoclimatologists believe that the ratios of the constituent salts have changed considerably over time. These changes are related to changes in the use of various salts by biological organisms (for example, some organisms use calcium ions to build shells).

Table 2.2 lists the major constituents of seawater. The ocean also contains several minor constituents, including strontium, silicon, iron, lithium, phosphorus, iodine, and the dissolved gases oxygen and nitrogen. These minor constituents play important roles in chemical and biological processes in the ocean, but we will not discuss them in detail in this course.

The earliest measurements of salinity in the ocean indicated that, while total salinity varied by location, the ratios of the constituent ions were largely constant regardless of sampling location. This observation led to the definition of a single parameter, salinity, in which the proportions of the major constituents are assumed to be constant. The development of electrical conductivity techniques for measuring salinity in the 1980s improved measurement accuracy considerably. Salinity was then redefined as the ratio of the electrical conductivity of seawater to the electrical conductivity of a standard potassium chloride solution at a standard temperature and pressure. This quantity is designated the practical salinity, and is expressed in practical salinity units (psu). Recent advances in measurement technology led to the adoption of an even more accurate definition of salinity (the absolute salinity) in 2009 (see the [Thermodynamic Equation of Seawater 2010](#) for details). The introduction of absolute salinity has removed the assumption that the proportions of the major constituents

are constant. In this course, we will focus more on the qualitative impacts of salinity, rather than the quantitative impacts, and will therefore typically retain the assumption that the ratios of the constituent ions are approximately constant.

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