Lecture 12: Ocean Acidity & Light

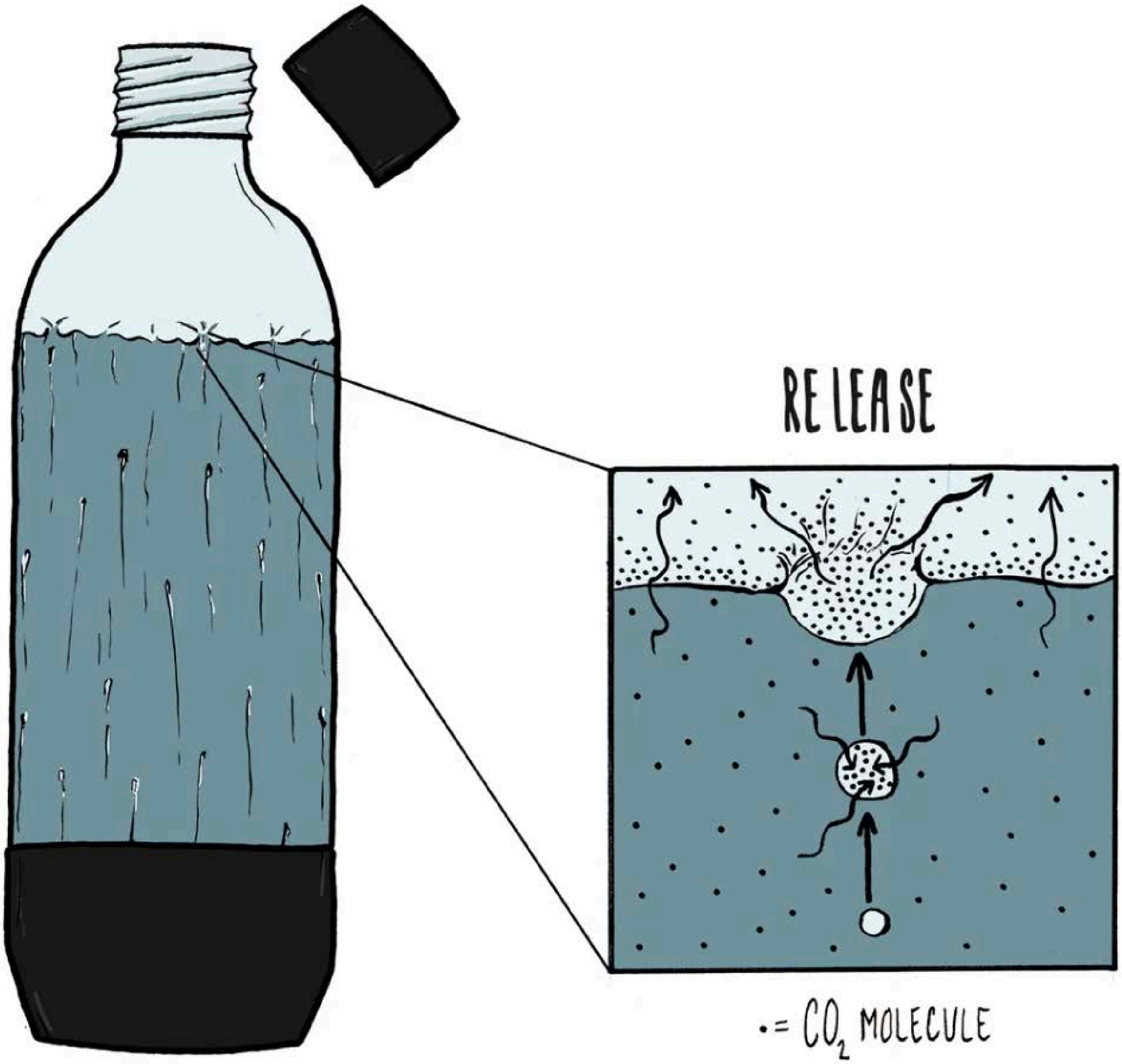
Ocean Acidity & Light

Dissolved Chemistry, With a Special Nod to Carbon

A key concept to understand is that material is continually cycling into and out of the ocean. Material cycles between the ocean and lithosphere (very slow process taking 10's of thousands to millions of years), it cycles between the atmosphere and the ocean (a quick processes, taking decades), it cycles throughout the oceans (a medium scale process taking thousands of years). The residence time is the average length of time that a substance resides in a particular medium. The length varies with the element (remember Na and Cl residence time from earlier lectures) and the location (ocean vs atmosphere).

Quick review of dissolved gas and the oceans & atmosphere. In the ocean there are many dissolved gases in the water. Depending on the gas, it might enter from the atmosphere to the ocean, or it can be produced within the ocean. Wind mixing can dramatically increase the amount of gas that is injected into the ocean. During the extreme storms, the wind mixing can increase the gas concentrations in the ocean. Some of the gases in the ocean can be released from the Earth's interior, a good example of this is Helium.

There is a net uptake (or loss) of a gas between seawater and the atmosphere until it reaches what is called saturation. At the saturation point, the gas is in equilibrium between the atmosphere and the ocean. At equilibrium the rates of gas in and out of the atmosphere and the ocean is equal. The equilibrium values settle at the most favorable conditions chemically (this means that if given infinite time the natural system would reach the equilibrium). Since some gases are more soluble than others, the proportion of gases dissolved in saturated sea water is different from the proportion in the atmosphere. This process is evident when you open a carbonated beverage of your choice. When first opened, there is more CO_2 in the bottle than in the atmosphere, so bubbles of CO_2 move out of the water and into the atmosphere. Eventually, when the beverage of choice becomes saturated (in equilibrium with the atmosphere), the rates of exchange between air and drink will be equal. The ocean surface is the same as your beverage.



Let's compare some of the gases in the atmosphere and in the oceans. For the ocean conditions, we are looking here at the ocean at 15°C and a salinity of 35‰ (temperature and salinity can affect the amount of gases that ocean water can hold). The table below provides the proportion of different gases

Table 5.5 Abundances of major gases in the atmosphere and in seawater

Gas	Percentage by volume in the atmosphere	Percentage of total gas dissolved in surface seawater[a]	Average concentration in parts per million by mass in the ocean as a whole
Nitrogen (N_2)	78.1	63	33
Oxygen (O_2)	20.9	34	6
Carbon dioxide (CO_2)	0.04	1.4	99[b]

[a] Data based on the mole fraction of these gases in seawater at equilibrium, after Millero, *Chemical Oceanography*, 4th edition, 2013.
[b] Measured as total inorganic carbon ΣCO_2, after Broecker, *Chemical Oceanography*, 1974.

The table above shows the proportions of Nitrogen, Oxygen, and Carbon Dioxide in the atmosphere and in the surface of the ocean, and their concentration in ppm (parts per million). You can see from comparing the amount of Oxygen in the atmosphere to that in the surface ocean, that the ocean has more. This is because there are phytoplankton in the ocean surface producing O_2 and thereby increasing the concentration. You will also notice that there is a log more CO_2 in the ocean surface than in the atmosphere. This is because CO_2 is highly soluble, meaning it will react with water and other compounds in the seawater. Solubility is the tendency of a substance to dissolve in water. Many substances become more soluble as water temperature increases (think of dissolving sugar in your hot coffee, versus trying to dissolve sugar in cold water). CO_2 and other gasses are the opposite – they become less soluble as water temperature increases.

Again, saturation and solubility in the ocean depend on temperature and saility. Here are some examples:

Conditions	*Saturation concentration for O_2 (oxygen) gas*
Freshwater (25°C)	258
Seawater (25°C)	206
Freshwater (5°C)	398
Seawater (5°C)	308

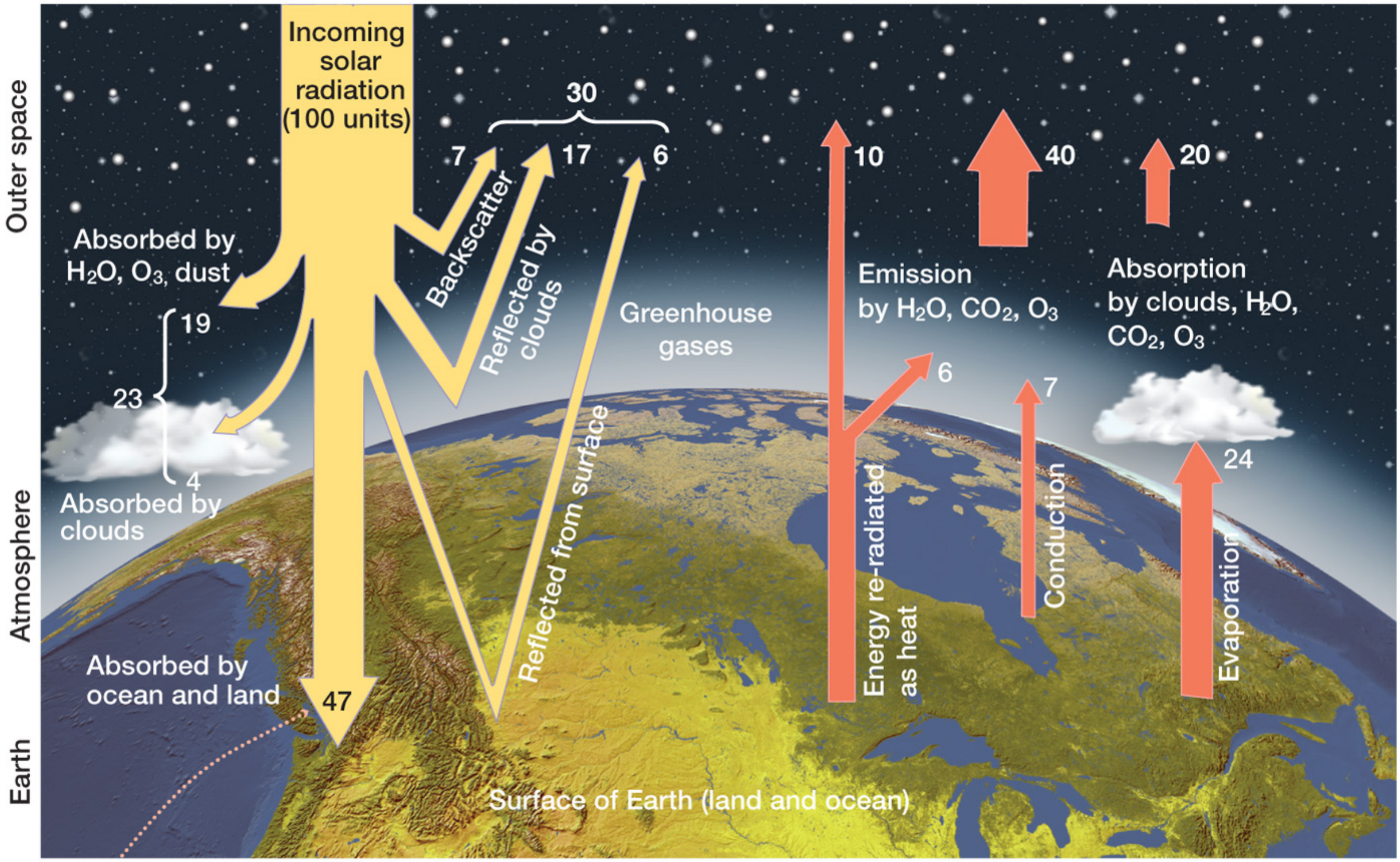
OK, you now are totally an excellent gas chemist. We are going to switch gears to carbon. But let me explain why this is a key concept.

Many of you have heard about the greenhouse effect. The greenhouse effect describes the physical chemistry of the CO_2 in the atmosphere. The sun radiates light into the Earth system. Most of the light is absorbed into the earth's surface and the solar radiation warms the surface. This is a good thing. Some of the energy bounces off the atmosphere and the Earth surface. Of the radiation that has been reflected from the Earth's surface, some gets out of the atmosphere to outer space (a heat loss for Earth) and some of the radiation is trapped. The energy that does not get out of the atmosphere warms the planet. The radiation that is reflected to the atmosphere is infrared radiation. Carbon dioxide (CO_2) is a gas, which absorbs infrared radiation.

Humans have industrialized the planet. This is not wholly negative, as a larger proportion of humanity now has a high standard of living that has never existed in Earth's history. While there is still much need, more people are living longer and living better. The big issue facing your generation is how sustainable this strategy is, and what solutions may be available to help. Industrialization has been powered by the burning of oil and coal. This process has released CO_2 which was stored in the lithosphere and moved it to the atmosphere, where now there is more CO_2 to absorb radiation. This warms the Earth. This has happened in the past (we discuss this later), but humans have had enough of rapid and large impact that the role of humans cannot be ignored.

Shorter-wavelength visible light passes through Earth's atmosphere, where it interacts with gases, clouds, and dust before striking Earth's surface.

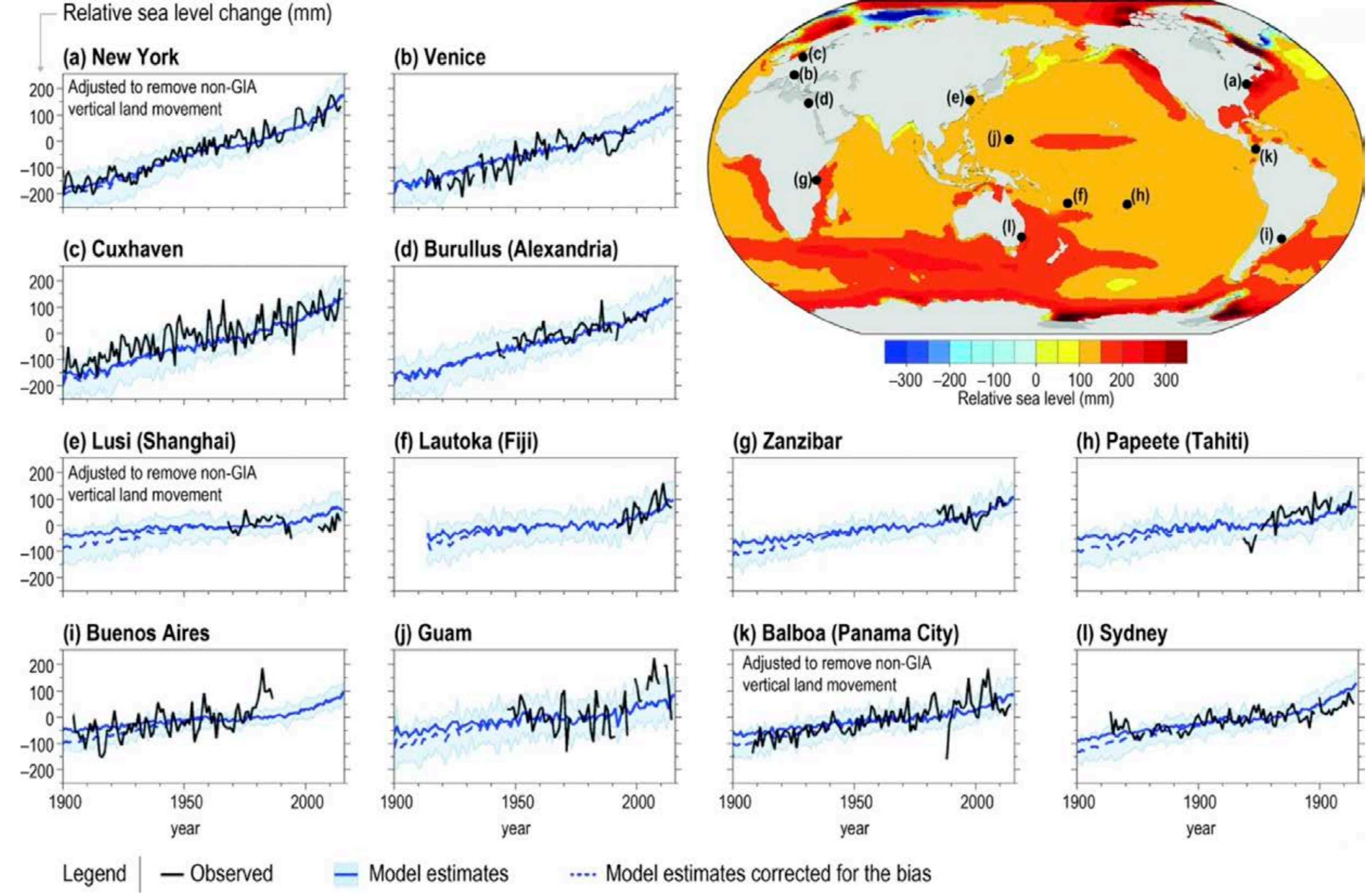
If re-radiated heat does not leave Earth, it causes the planet to warm.



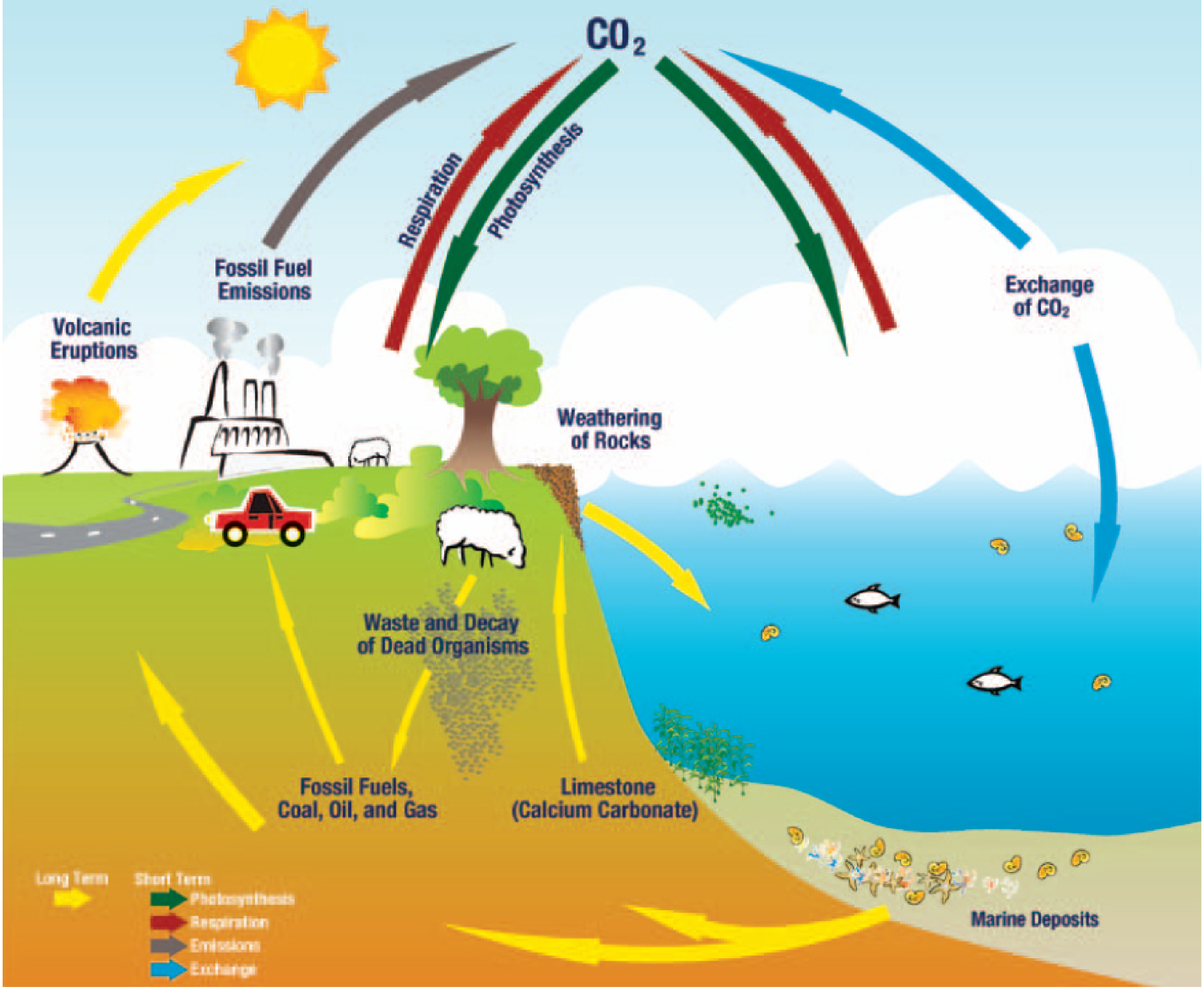
Of all solar radiation able to penetrate Earth's atmosphere, only 47% is absorbed by the ocean and land.

Longer-wavelength infrared radiation either radiates back into space or is trapped in Earth's atmosphere.

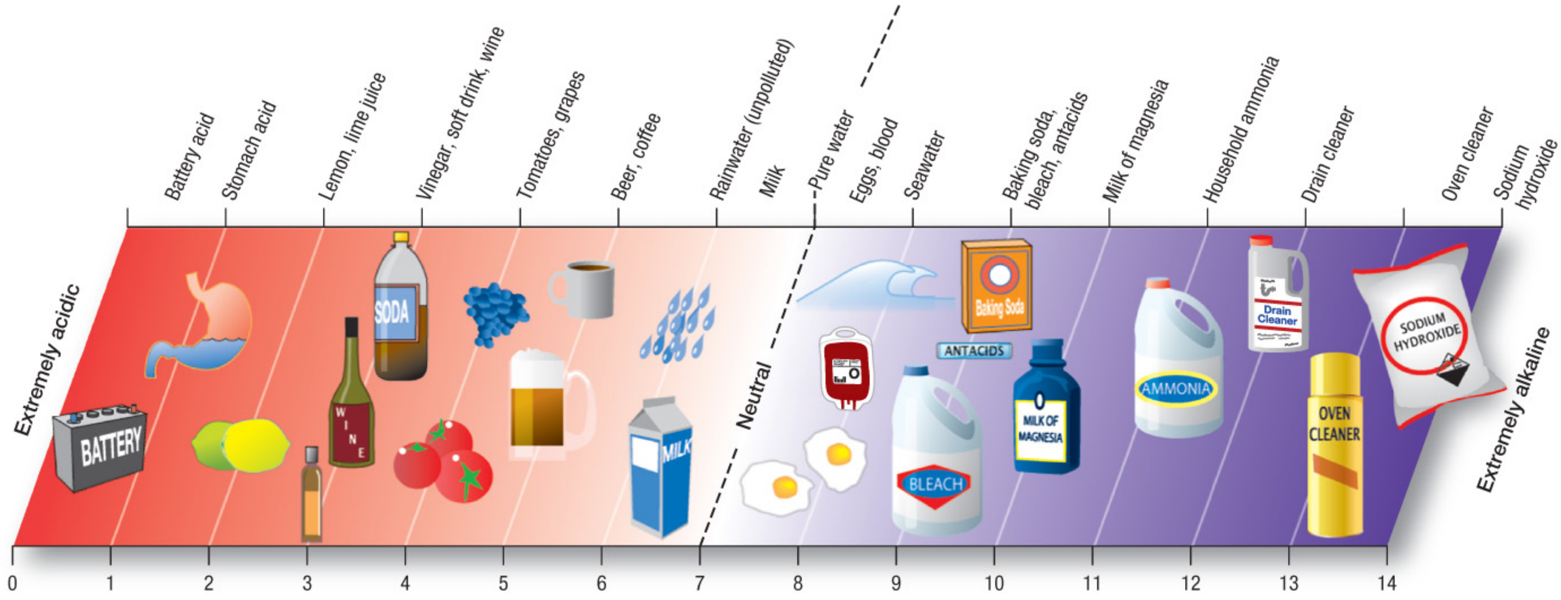
Make no mistake, the policy to deal with warming is a difficult problem as your generation will be required to maintain a standard of living and bring humanity to a better place while reducing environmental impacts. This is one of the great challenges facing YOUR generation. So for CO_2, we know humans release it by burning oil. The amount that has been released in the past century or two is rapidly accelerating, which has warmed the planet at a rapidly increasing rate. The warming has been so rapid that it is causing glaciers and icecaps to melt and measurably increase the amount of water in the ocean at an uprecedented rate – you also know that warmer water takes up more space so increasing temperatures have expanded the ocean at the same time. The figures below (from the IPCC's sixth report) show some data that reflects these concerning trends. The black line shows the data for sea level over time. New York (top left) has seen over 1 foot (~350 mm) higher sea level over the last century. The global map shows estimated sea level rise for the planet - it is enough in some places for **entire nations to be nearly underwater** (https://politheor.net/the-paradise-paradox-maldives-a-sinking-country/). We will discuss sea level rise later in the course - for now, back to carbon!



There are two great biochemical reactions that fuel our planet. Photosynthesis is the biological process that takes solar radiation, and its associated energy, and converts it into chemical energy that supports the majority of life on the planet. This is a most AWESOME chemical reaction! The reaction *reduces* carbon dioxide into organic carbon molecules. This reaction is fueled by the splitting of water molecules that results in the release of oxygen. The net effect is that CO_2 is consumed and oxygen is released. The universe has a yin and yang. If photosynthesis is the yin, then the yang is the biochemical process by which the organic molecules are used by organisms. The organic molecules are "burned" to provide energy to do work, but the process consumes oxygen and releases CO_2. So the balance of carbon dioxide and oxygen on the Earth is a delicate balance between these processes. Now remember from before the concept of residence time, humans have decreased the residence time of organic carbon in the lithosphere, and much of the released carbon goes to the atmosphere initially. Over longer periods of time, some of it moves into biology on land and the ocean via photosynthesis. Some of it is absorbed into the ocean via physical processes.



Given this, let's think about the carbon cycle in the ocean as it relates to the gas exchange. The ocean has a vast reserve of carbon. The carbon system in the ocean is often referred to as the carbonate system. CO_2 is a soluble gas in sea water. The gas reacts chemically with the water and is present in the sea water as one of two dissolved anions—bicarbonate and carbonate—and as carbonic acid The major forms of carbon dioxide in seawaters are carbon dioxide (CO_2, the one dissolved gas), carbonic acid (H_2CO_3), bicarbonate (HCO_3^-), and carbonate ion (CO_3^{2-}). The form of the carbon is determined by the pH (a measure of the concentration of hydrogen ions) in the seawater. If pH drops, a solution becomes acidic. If the pH increases, the solution is becomes basic. A pH of a value 7 is considered neutral.



pH Values of Common Substances

Reactions 2 and 3 (below) are acid-base reactions. Bicarbonate ion which is one of the major ions in sea water can act as both an acid and a base.

1). CO_2 H_2O « H_2CO_3

2). H_2CO_3 H_2O « H_3O **HCO_3^-**

acid base acid base

3). **HCO_3^-** **H_2O** « H_3O CO_3^{2-}

acid base acid base

The carbonate system is largely responsible for maintaining seawater pH close to a value of 8.1 i.e., slightly basic (also called alkaline). This is largely because in the ocean, sea water is also in contact with sediments that contain carbonate minerals, the most important of which is calcite ($CaCO_3$). If excess acid is added to the deep ocean (say for example via hydrothermal vent emissions) the acid is neutralized by reacting with carbonate ions in solution, and these are replaced by dissolution of carbonates in the sediments. If excess base is added more carbonate minerals precipitate and are removed to the sediments. Thus the reactions are constantly going back and forth.

Over time humans through the combustion of oil have increased the CO_2 in the atmosphere. Some of that excess CO_2 diffuses into the ocean. The increase in CO_2 results in decreasing pH, which means overtime the ocean has been becoming more acidic. There is concern this shift in pH will impact the biology. We will talk about this process, called Ocean Acidification, later in the course.

Photosynthesis uses up CO_2 and releases oxygen. The bulk of the photosynthesis in the ocean is carried out by the phytoplankton. Phytoplankton are the dominant plant in the ocean. The average ocean plant is around

50 microns in size. Ocean plants are small, but remember, they produce ~50% of Earth's oxygen. For phytoplankton to grow, you need a few things. You need light to power photosynthesis. You need building blocks to construct a cell. These building blocks include, carbon, nitrogen, phosphorus, and metals.

Photosynthesis is represented very simply . It can be represented more completely, if we think of it as a process that generates the organic matter in phytoplankton cells. Phytoplankton organic matter is made up of a large number of organic compounds (e.g. proteins, lipids, carbohydrates), but on average it has atomic ratios of C to N to P of 106 to 16 to 1. This ratio is often referred to as the Redfield ratio.

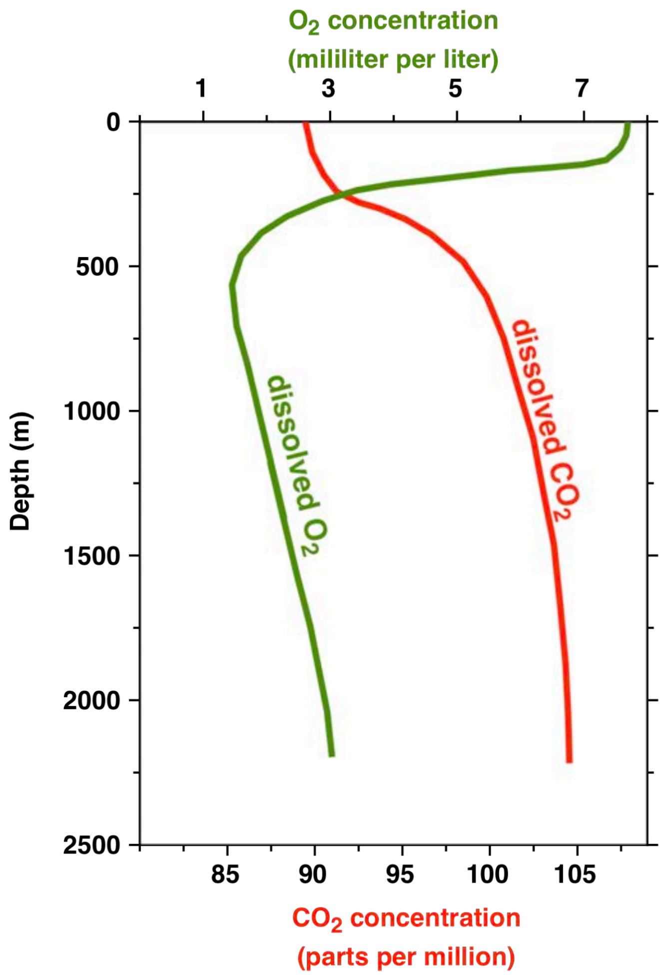
Thus, the process of photosynthesis can be represented as:

$$106CO_2\ 122H_2O\ 16HNO_3\ H_3PO_4 \xrightarrow{\text{LIGHT}} (CH_2O)_{106}(NH_3)_{16}H_3PO_4\ 138O_2$$

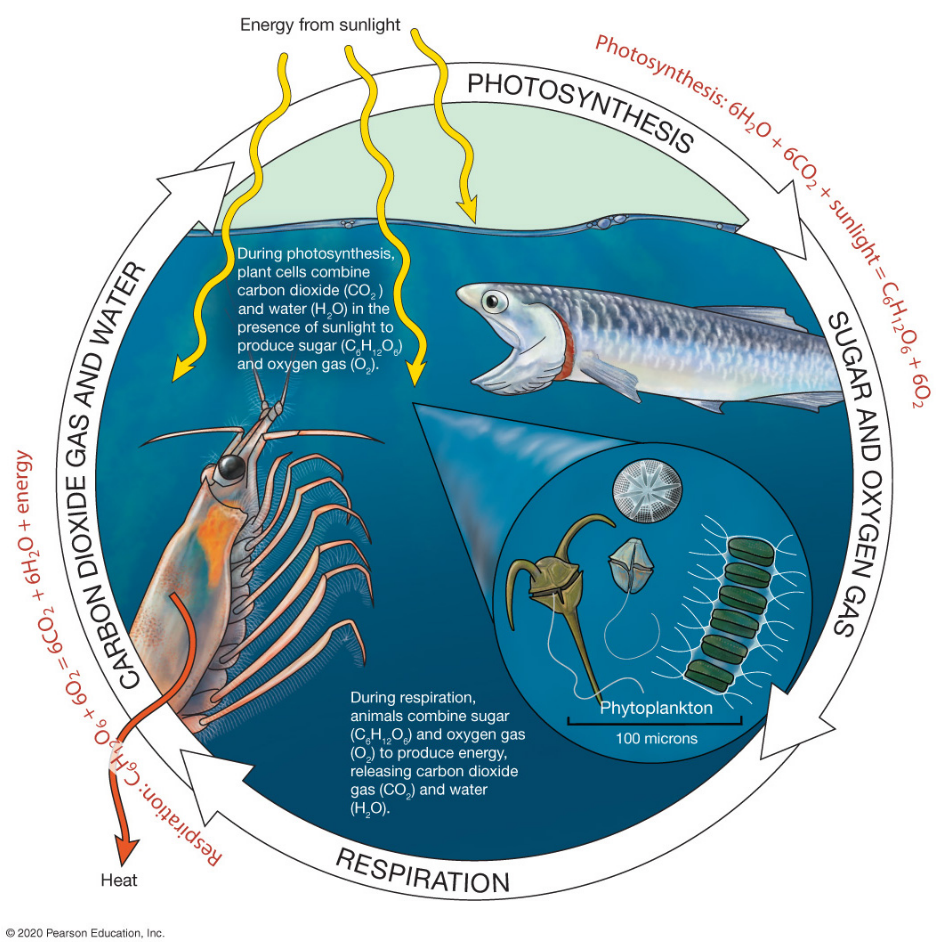
This reaction illustrates the need for the nutrients: nitrate and phosphate. It also shows that for every 106 CO_2 molecules taken up, approximately 138 O_2 molecules are liberated. Marine bacteria, fungi, protozoans and animals that can not get energy from photosynthesis, decompose organic matter. This process is called *respiration.* It can be represented as the reverse of photosynthesis.

$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4\ 138O_2 \longrightarrow 106CO_2\ 122H_2O\ 16HNO_3\ H_3PO_4$$

Respiration puts CO_2 and nutrients back into the water. Respiration depletes O_2, making deep waters *undersaturated* with respect to the oxygen in the atmosphere (i.e. less oxygen then the atmosphere). Respiration occurs throughout the entire water column and in sediments, but its effect on the distributions of oxygen and total-CO_2 are usually not seen until depths below the euphotic zone. The net effect is for surface water to be close to pH of 8.1, but the pH decreases as you move deeper because there are animals there who are respiring, which releases even more CO_2, thereby shifting that acid-base balance. When you get even deeper still, to depths below where marine animals are respiring, the pH tends to increase again slightly. Generally, deeper water is more acidic (lower in pH) than surface water because CO_2 from respiration increases, and this acidity affects the Calcium Carbonate Compensation Depth (CCD) that we learned about in previous lectures, which controls the accumulation of calcareous sediments. What about O_2? What pattern would that follow with depth? Plants at the surface perform photosynthesis which releases O_2, but then as you go deeper in the ocean the ability to photosynthesize decreases because light becomes limited – which takes us to the next section of the lecture.



When you think about it, it is pretty amazing that photosynthesis and respiration are cyclic and complimentary reactions that are fundamental to life on the planet.



Light in the Sea

Light from the sun is the source of energy that fuels life on Earth. The light energy fueling the ecosystems of this planet is provided by the fusion reactions that are occurring in our sun (you learned about that in a previous lecture). The fusion reactions that produce the light originate in the center of the sun, and the energy from these fusion reactions diffuses out of the edge of the sun from which it travels and reaches our planet. This process is slow given the large size of the sun and the distances involved. The sun you experienced today as you walked around originated from fusion reactions that occurred when the pyramids were being built!

The nature of light: Light is truly a cool phenomenon. It has the characteristics both of particles and waves. The particle nature of light means that it can be measured as a discrete event. This is the feature that light detectors measure, where the "light" particle called a photon collides with the detector surface, which then results in a measurable discrete voltage. Much of our understanding of the particulate nature of light was described by a smart dude called Einstein. Light also is an electromagnetic wave. This gives light a characteristic frequency (u), amplitude, and wavelength (λ) (see below). You can relate the frequency of the light to the wavelength of light through the equation:

$$u = c/\lambda$$

where c is the speed of light. We can also relate the energy of the light to the wavelength through the equation:

$$e \text{ (volts)} = hc/\lambda$$

Where h is a constant called Planck's constant. Looking at the second equation, the bigger the wavelength (l) the lower the energy. This is very important in understanding how light works in the ocean. You can divide the electromagnetic spectrum into specific regions, as follows:

<u>Radiowaves</u> (very long wavelengths, tens of meters: size of soccer field or house) energy is so low that it does not interact with molecules.

<u>Microwaves</u> (long wavelengths: size of a baseball) energy is enough to make molecules vibrate, this is how a microwave in your kitchen heats water.

<u>Infrared</u> (moderate wavelengths, size of a cell). It has energy sufficient to carry heat. The absorption of infrared light by carbon dioxide in the atmosphere is what is heating Earth through the Greenhouse effect.

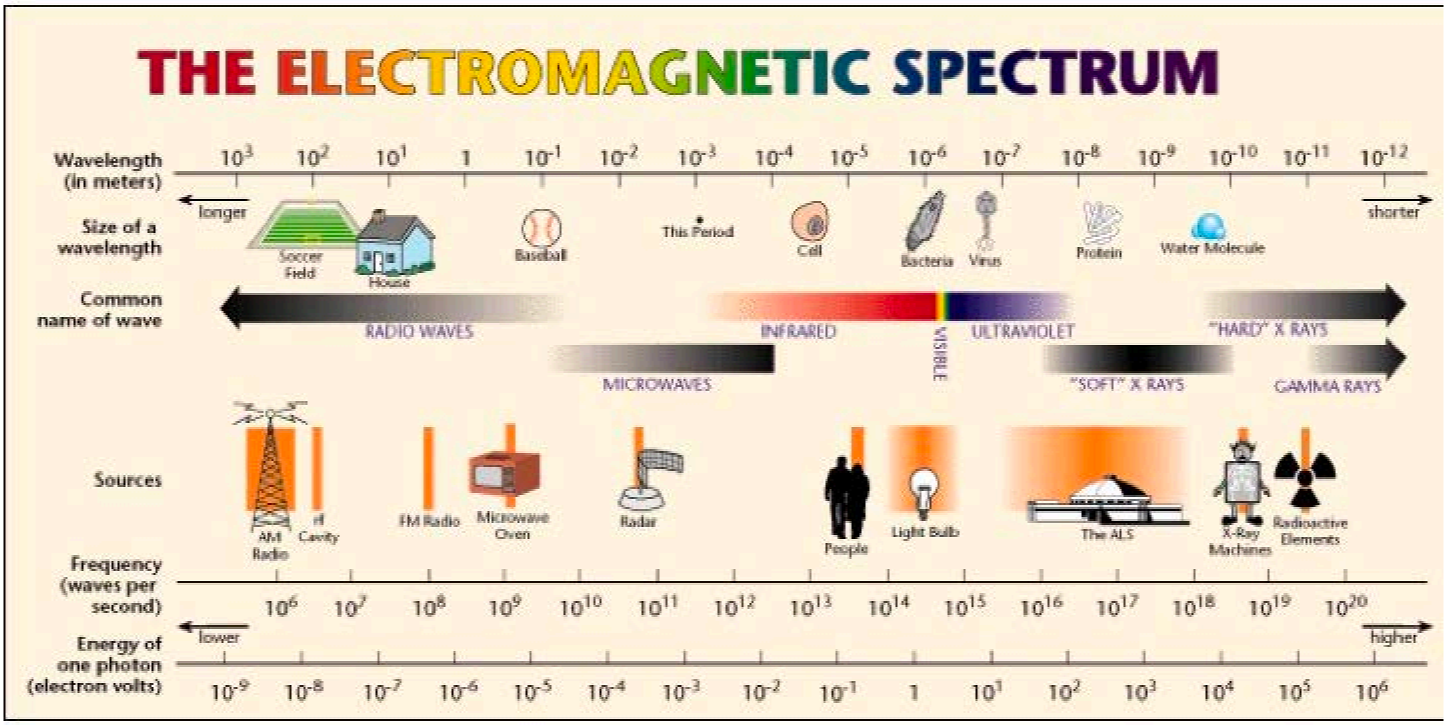
<u>Visible</u> (short wavelengths, size of a bacterium) These are wavelengths of light your eye can detect. The wavelengths range from 400 to 700 nanometers (10^{-9} meters). The lower wavelengths ~400-450 nanometers is the color blue. The high wavelengths 675-700 nano-meters is red. These wavelengths have sufficient energy to excite molecules enough so that electrons can be ejected from a molecule. This is how photosynthesis works. The specialized pigments in plants absorb the light, and some specialized molecules eject an electron. Photosynthesis involves capturing that ejected electron and using it for making biological molecules.

<u>Ultraviolet</u> (shorter wavelengths, size of a virus) These wavelengths have sufficient energy to reorganize molecules. This is problematic for life. Ultraviolet light can disrupt important molecules like DNA, essentially this is the pain you feel during a sunburn. On Earth the ozone layer absorbs much of the UV light produced by

the sun, lucky for us. That is the reason the ozone hole is a big issue, because when ozone levels decrease, then the increased UV light leads to increased skin cancer (due to the damaged DNA).

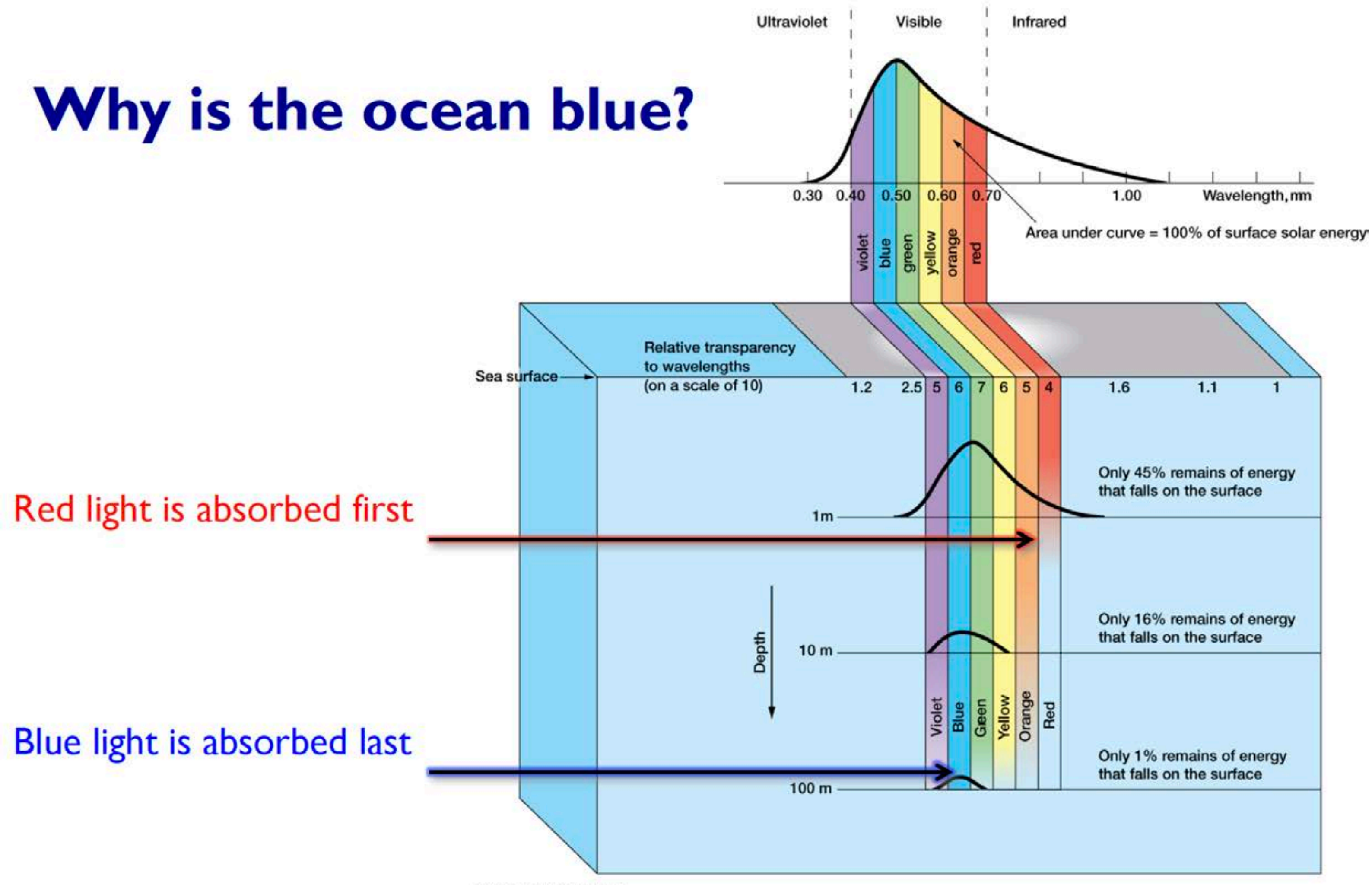
Soft and hard x-rays (short wavelengths, size of a protein). These wavelengths can modify and break molecules.

Gamma rays (shorter wavelengths, smaller than a molecule). So much energy here, it made the incredible Hulk ...... at least according to the movie.



Light in water. On Earth, because of the atmosphere, the most prevalent light at the surface is the infrared, visible, and a little ultraviolet. Once in the atmosphere, light then enters the water. How far does the light penetrate? The depth the light penetrates depends on the molecules that absorb the light. The more molecules present, that can absorb the light, the shallower the light will penetrate. The molecules that absorb the light are water itself, and the plants and chemicals in the water. The specific wavelengths of light that are absorbed by a molecule is a function of the structure of the molecule. Water molecules are very effective at absorbing infrared and red visible light. Water molecules are so effective that infrared light will only penetrate a few centimeters into the water. This leaves the visible blue and green light, which are preferentially absorbed by the plants and the molecules.

The figure below shows the penetration of different wavelengths of light. Looking at the three curves, the red light penetrates to the shallowest depth. It is undetectable in water below 10 meters depth. The blue light is the wavelength of light that penetrates to the deepest water depth. Even in the world's clearest water, light can only penetrate to about 300 feet. Given that the ocean is very deep >30000 feet in some locations, most of the ocean is completely dark with no light present. The attenuation of light (or loss of light as you move deeper in the water) is why many fish are very vibrantly colored – those vibrant colors actually look pretty boring when you are below the depths that red orange and yellow can penetrate. Recall the previous concepts of energy and wave length – which has more energy? Red or blue light? And which penetrates deeper?



Ocean plants (the phytoplankton) require sunlight to grow through photosynthesis they can only grow in that very shallow well-lit surface layer. This shallow well-lit surface layer, called the photic zone, amazingly produces enough plant material to support the entire food web of the ocean. When conditions are right, the phytoplankton can grow to very high concentrations, called a bloom. When a bloom is happening, the plants can dramatically discolor the water. Below is a link to a satellite video of a plankton bloom – amazing! We often use satellites to detect the color of the ocean, and we use the colors to map the plant material in the ocean from space. Want to download satellite chlorophyll data and play around with it yourself – **go for it** (https://oceancolor.gsfc.nasa.gov/atbd/chlor_a/) !

https://youtu.be/BsAUmTPcc7c (https://youtu.be/BsAUmTPcc7c)

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