Session 14 – Evolution of the Oceans

Where did all this water come from?

Hydrogen: ~75% of the known mass of the Universe – the most abundant element.
Oxygen: ~0.04% of the known mass of the Universe – 3rd most abundant element! *(After hydrogen and helium)*
Water (as water vapour) therefore must be the commonest chemical compound in the Universe.

So how did water arrive on Earth?

Lot of water trapped in the accumulating ball of material forming the early Earth, from where it has been slowly escaping ever since. Still the main component of volcanic gases (>70%)

Water in the oceans probably came mainly from the interior of the Earth, in 50-100 million years from the formation of the Earth. But comets (dirty ice-balls) colliding with Earth have been another source, and continue to add more water. Ongoing debate as which source is more important.

Estimated that there is twice as much water within the Earth's crust and mantle as there is in the present oceans.

Water has been found on almost all planets in the Solar System, as well as many of their satellites.

So why is Earth so different from the other planets?

Earth's surface temperature lies mainly in the 0-50°C range. Only at the poles does it drop below 0°C. Only planet where the temperature range matches the liquid range for water.

Why does Earth have ocean basins?

Continental plates are less dense and thicker than oceanic plates, so 'float higher' than the oceanic plates (their surfaces are further from the centre of the Earth)

Not enough continental plate material to cover the entire surface – only ~30%, so 70% is occupied by denser oceanic plates.

Result: a very uneven surface to our planet, where water fills the gaps between the continental plates, and erodes away the continental margins, encroaching on the continental shelves.

So now let's fill these basins with water – create the hydrosphere...

Some estimated figures (many different estimates!)….
Total mass of water on Earth's surface = 1.463 x 10^{18} tonnes

- 95.7% of this is in the oceans = 1.400 x 10^{18} tonnes
- 4.1% in rocks and soil = 0.060 x 10^{18} tonnes
- 0.2 % as ice, lakes, rivers… = 0.003 x 10^{18} tonnes
- 0.001% in the atmosphere = 0.000014 x 10^{18} tonnes

The total mass of the oceans is about 1000 times the total mass of the atmosphere.

...which under a blazing sun sets off the water cycle!

Every year, ~300,000 km^3 of water evaporate from the oceans
Every year, ~100,000 km^3 of water are precipitated on the continents, which washes to the oceans...
... matter as solids in suspension to become sediments.
... matter in solution in the water, which essentially means as ions.

The water cycle transports from the continents to the oceans each year...
...about 8 x 10^{12} tonnes of weathered and eroded material
...of which about 2.5 x 10^{12} tonnes is as ions in solution.

Solutes in the ocean

A crude calculation: The ocean now contains 3.5% dissolved ions by mass **= 0.05 x 10^{18} tonnes**

If the water cycle has transported 2.5 x 10^{12} tonnes of solutes per year for the past 4000 million years, the total mass of solutes transported to the oceans in that time would be **= 10 000 x 10^{18} tonnes!**

So on this basis dissolved ions stay in the oceans for a relatively short time - the average residence time for a dissolved ion may only be a few tens of thousands of years!

Chemical weathering causes...

...Group 1 and 2 metal cations to go into solution (Na^+, K^+, Mg^{2+}, Ca^{2+})
...iron cations (Fe^{3+})mainly to form colloidal suspensions or insoluble minerals
...carbonate anions (CO_3^{2-}) to go into solution as hydrogencarbonate anions (HCO_3^-)
...silicate and aluminosilicate anions to form complex insoluble hydroxysilicates (clay minerals)...
which are all transported to the ocean in solution and suspension with other minor components.

The twelve main component ions

Element	mg dm^{-3}	% by mass	mol dm^{-3}
chloride	19 000	55.04 %	0.535
sodium	10 500	30.42 %	0.457
magnesium	1350	3.91 %	0.056
sulphate	2655	7.69 %	0.028
calcium	400	1.16 %	0.010
potassium	380	1.10 %	0.0097
carbonate	140	0.41 %	0.0023
bromide	65	0.19 %	0.00081
borate	20	0.06 %	0.00034
silicate	8	0.02 %	0.00011
strontium	8	0.02 %	0.00009
fluoride	1	0.003 %	0

cations	concentration /mol dm^{-3}	anions	concentration /mol dm^{-3}
sodium	0.457	chloride	0.535
magnesium	0.056	sulphate	0.028
calcium	0.010	carbonate	0.0023
potassium	0.0097	bromide	0.00081
strontium	0.00009	borate	0.00034
		silicate	0.00011
		fluoride	0.00005

The puzzle of the anions.

The Earth's crust does **not** contain significant amounts of fluoride, chloride, bromide, sulphate, and borate anions. ***So*** these anions in the ocean have to come from a different source or sources.

Volcanic outgassing indicates where these elements are coming from, but cannot account for all the accumulated anions in the oceans.

Seawater trapped in subducting sediments is eventually recycled, but this only recycles the solutes.

Water circulating at mid-ocean ridges brings up more dissolved matter than it takes down. This dissolved matter derives from the basaltic magma at depth, which contains trapped gases. It is estimated that seawater circulates through the rocks of the mid-ocean ridges at a rate equivalent to the whole of the oceans every 8 million years.

So two major routes by which these anions can be transferred from deep lithosphere and mantle:

– basalt lavas extruded onto the continents

– deep circulation of water at mid-ocean ridges

NB These anions are of course accompanied by metal cations such as iron, magnesium, aluminium and many others. But these cations mainly react with other anions in seawater and precipitate out in the ocean-floor sediments, especially as clay minerals

So we reach a surprising conclusion:

- The **sodium** cations come mainly from weathered minerals transported from the continents.
- The **chloride** anions come mainly from gases released from the interior of the Earth.

So the components of the salts in the ocean come essentially from two different sources.

When sea water is evaporated, only then do the two ions form sodium chloride for the first time!

Variation in salinity

Percentage of dissolved solids by mass:

Open ocean	3.5 ± 0.3 %
Mediterranean	3.9 %
Red Sea (northern end)	4.1%
Dead Sea	27 %

Evaporating the ocean:

Evaporation of a1 km depth of ocean to dryness would leave these layers, with total thickness of 15 m.

Mixed chlorides of sodium, potassium and magnesium
Sodium chloride
Calcium sulphate
Calcium carbonate

In the **open oceans**, the effect of evaporation is simply part of the water cycle

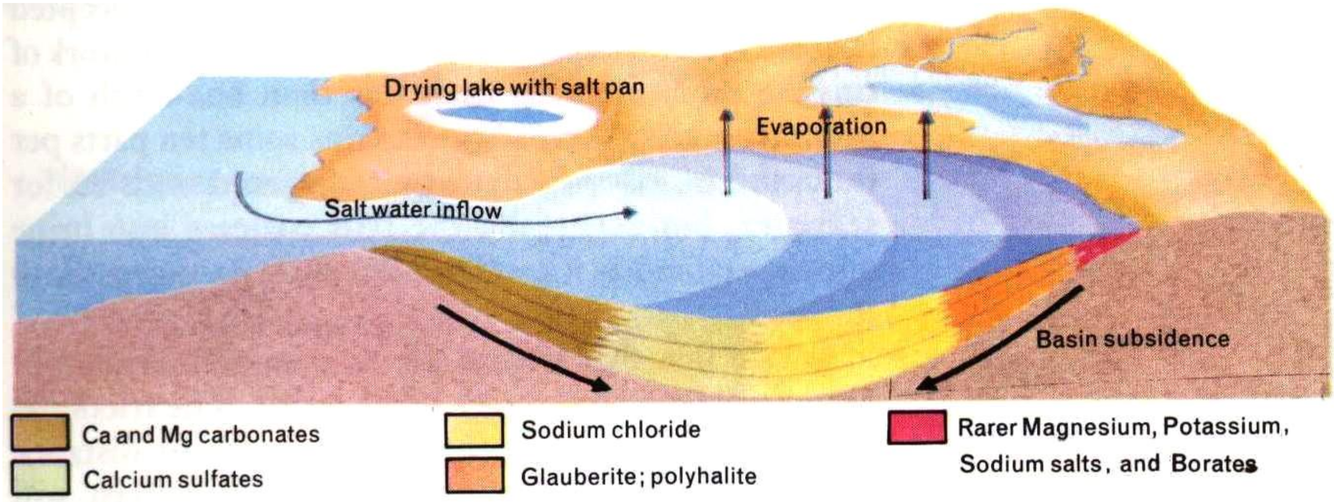
> **concentrations remain roughly constant**.

In **restricted seas** (e.g. Mediterranean), evaporation rates exceed inflow of fresh water from rivers and from the open ocean (e.g. Straits of Gibraltar) > **enhanced concentrations**

In **landlocked seas** (e.g. Dead Sea, Lake Eyre), evaporation rates can far exceed evaporation rates
> **crystallisation of salts from solution**

The result of high evaporation rates is the formation of **evaporite deposits**

The Mediterranean Sea is the last remnant of the ancient Tethys Ocean, remaining as the African and Eurasian plates collided. In the late Miocene (12 - 5 Ma BP) the sea was cut off from the neighbouring oceans. The sea eventually dried up, forming thick beds of evaporite salts that still lie beneath the sea bed. When water from the Atlantic Ocean broke through the Straits of Gibraltar in a major flood ~5.3 Ma BP, the Mediterranean basin was re-filled in less than two years. Water poured in over a gigantic waterfall at 3 times the current flow of the present Amazon River.



Cumbria: anhydrite, gypsum, dolomite
Cheshire, Staffordshire, Worcestershire: halite
Somerset: celestite (strontium sulphate – world's main supply)
Durham, Yorkshire: halite, potash (sylvine), anhydrite, magnesian limestone
Europe: Stassfurt deposits (Germany), Wieliczka Salt Mines (Poland), Halstatt (Austria)

Other mineral deposits involving the oceans:

Vast quantities of seawater circulating through hot, cracked rocks dissolve all sorts of metal ions.

The solutions move on, the pressure reduces, the temperature drops – mineral crystallise out.

Black smokers are a particular example of such deposits.

Some of these solutions reach the open ocean waters, and deposit minerals on the ocean floor – called *manganese nodules*, but contain several metals as carbonates and oxides.

The part played by living organisms

Every element finds its way into seawater in one form or another, mostly in tiny concentrations.

Many marine organisms have evolved the ability to extract some of these elements and make use of them. Some tunicates concentrate **vanadium**, and use it in solution in 10% sulphuric acid as their blood supply! Oysters take in zinc, lobsters copper – molluscs use haemocyanin (a copper compound) as their oxygen carrier. Microbes play a very large role.

Gold – a case study!

Approximately 1 gram of gold in 100 million tonnes of seawater, or 10 g in 1 cubic kilometre. In total this amounts to about 8 times the quantity of gold extracted in all history so far!
At current gold prices (highest ever), the gold in a cubic kilometre of sea water might be worth £300, many orders of magnitude less than the cost of extraction.

An Ocean in the Making

The Red Sea, part of the Great Rift Valley, was once a dried up remnant of the Tethys Ocean – a giant salt pan – but in the last few million years a new spreading centre has started down the median line.

Max. Depth: 2211 metres in the narrow central median trench, where volcanic activity is constant.