



EVROPSKÁ UNIE
Evropské strukturální a investiční fondy
Operační program Výzkum, vývoj a vzdělávání



MINISTERSTVO ŠKOLSTVÍ,
MLÁDEŽE A TĚLOVÝCHOVY

Geochemistry on the Earth's surface for analytical geochemists

2c.

Geochemistry of the hydrosphere

Tento učební materiál vznikl v rámci projektu Rozvoj doktorského studia chemie
č. CZ.02.2.69/0.0/0.0/16_018/0002593

Geochemistry of the hydrosphere

A. Hydrogeochemistry

- Properties of water
- Acid-base reactions – pH, alkalinity, acidity
- Redox reaction
- Complexation , colloids

B. Hydrosphere

- **Water cycle, reservoirs, flows**
- **Ocean**
- **Development of the hydrosphere in the geological past**

HYDROSPHERE

A wide-angle photograph of a calm, deep blue ocean stretching to the horizon. The sky is a clear, pale blue, and the water's surface is covered in gentle, rhythmic ripples. The word "HYDROSPHERE" is printed in a large, bold, black, sans-serif font across the middle of the image, centered horizontally.

Distribution of mass and heat



Oběh vody

Zásoby vody ve sněhu a ledu

Srážky

Odtok z tání sněhu

Vsakování

Pramen

Odtok z podzemních vod

Zásoby podzemních vod

Zásoby vody v atmosféře

Sublimace

Evapotranspirace

Povrchový odtok

Říční odtok

Výpar z volné hladiny

Zásoby sladké vody

Vytváření oblaků

Výpar z volné hladiny

Zásoby vody v mořích

Hydrosphere

- Water on the Earth's surface (and near it) – liquid, gaseous and frozen
- **Reservoirs:**
- ocean 97.5%
- freshwater 2.5%
 - 1.85% (74% of freshwater) permanent polar ice cap
 - 0.64% (98.5% of the rest) groundwater
- atmosphere, surface water (streams, lakes)
0.01%

Reservoirs

Ground water

- less than 1% of the total amount of water
- 40× more than in freshwater lakes
- more than 98% of unfrozen water in the hydrological cycle
- Most in altitude up to 750 m
- a volume equivalent to a layer of 55 m of water on the continents

Ocean

- 71% of the surface, average depth 3.8 km
- 97.5% of water on Earth
- $1370 \times 10^6 \text{ km}^3$ of water



OCEAN

Composition of ocean water

- Very homogeneous
- Main components: Na^+ , Ca^{2+} , Mg^{2+} , K^+ , Cl^- , SO_4^{2-} , HCO_3^-
 - 99% of dissolved substances in most waters (ocean and river)
- Concentrations vary by up to 10%, but ion ratios by only 1%
- Total ocean water salinity between 33 and 38‰
- Minori and trace elements more variable
 - Especially nutrients

Components of ocean water

A. **Conservative** (Br^- , Cl^- , Na^+ , Mg^{2+})

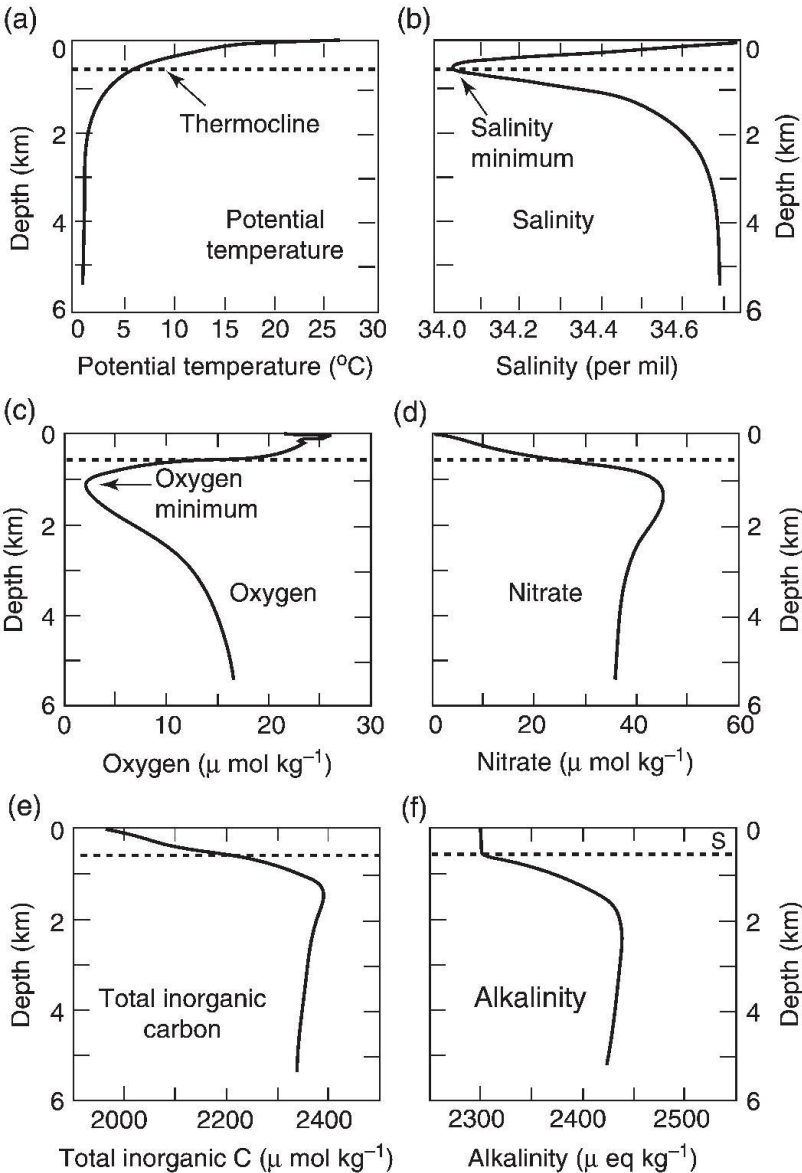
- The concentration relative to other conservative components is constant
- Constant concentration with depth
- Long residence times ($> 10^6$ years)

B. **Non-conservative** (recycled...)

- Variable concentration
- Recycled by activities of organisms
 - Organic C, H_4SiO_4 , Ca^{2+} , NO_3^- and PO_4^{3-}
- Adsorption on surfaces of solid particles
 - Sn, Mn, Pb
- Division sometimes based on use by living organisms (biolimiting, etc.)

Gradient

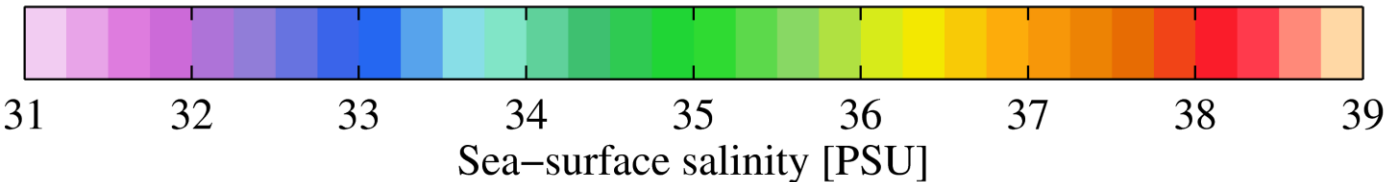
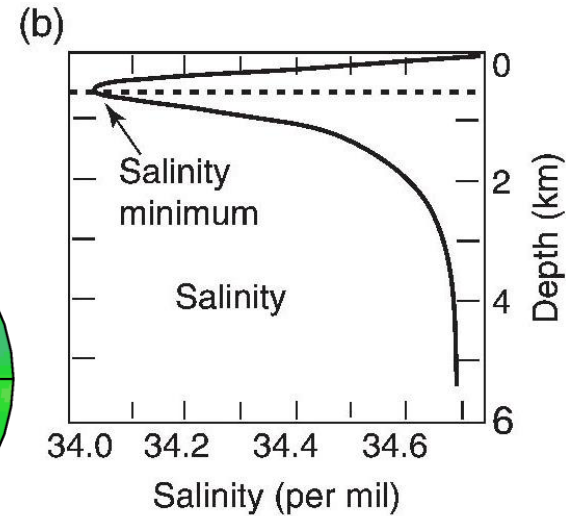
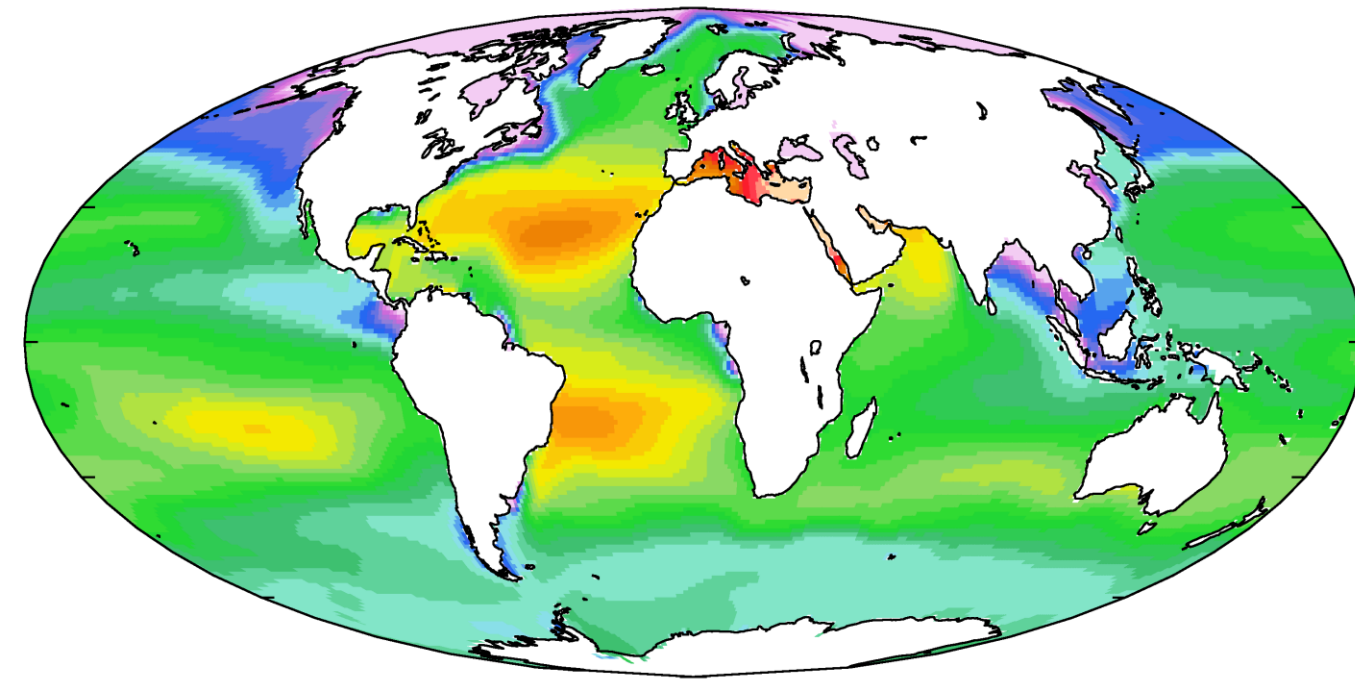
Adapted from Misra (2012)



- Main gradient controlled by biological processes
- Biota consume elements and produce organics near the surface
- Decomposition of organic matter descending to depth
- With the exception of oxygen, abundance of most substances increases with depth
- Surface water warm
- Deep water cold
- Transition zone = thermocline
 - Influenced by latitude and season
 - Determines the use of substances by biota

Salinity

- Highest at the surface – evaporation
- 30‰ (estuary) to 40‰ (shallow waters in arid regions)

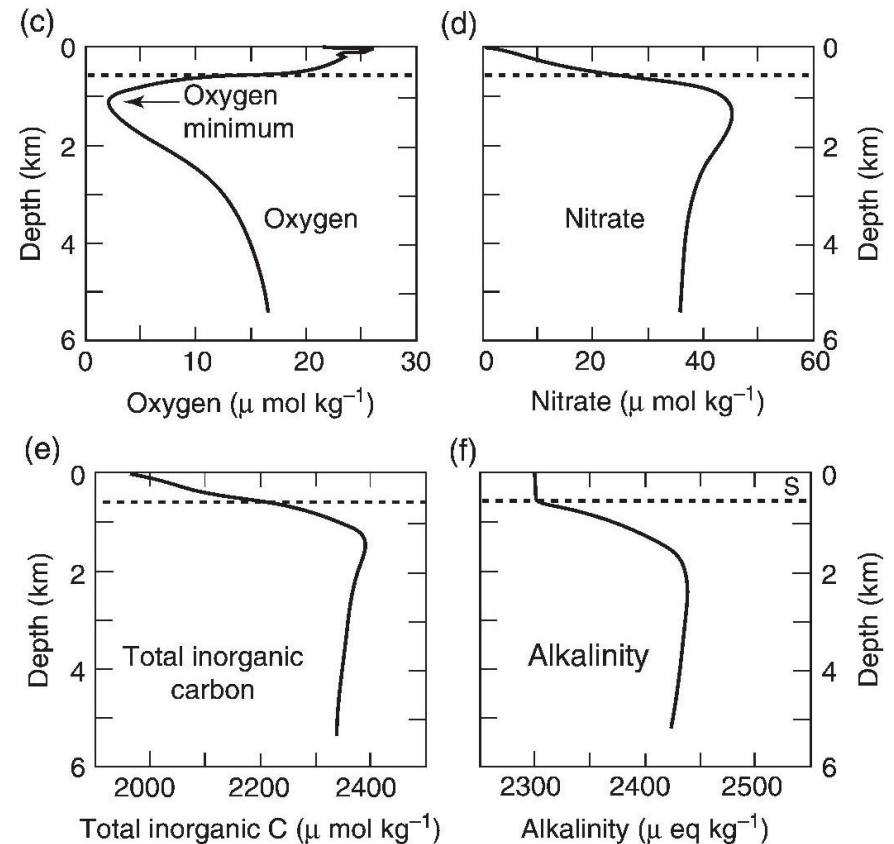


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Adapted from Misra (2012)

Gases in water

- Concentration of gases
 - A. Given by solubility
 - B. Controlled by metabolic processes of organisms
- More than the equilibrium oxygen concentration at the water surface
 - Produced by photosynthesis
- Oxygen minimum given by decomposition of org. matter sinking from the surface zone
- O_2 increase in depth via the oxygenated water input by ocean currents
- There is not enough organic matter to consume all the oxygen
- Carbon is consumed by photosynthesis and the production of $CaCO_3$ shells
 - These dissolve again in the depth due to high concentration of CO_2
- Ocean pH buffered in the 7.8–8.4 range



Adapted from Misra (2012)

Ocean mass balance

- Previously, rivers were considered a source of dissolved salts in the ocean
 - Sediments show stable composition of oceans since Cambrium
 - At the present input, the composition would be reached in several tens of millions of years

Table 13.7 Influx of dissolved constituents by rivers into the oceans and the time required for these constituents to reach oceanic accounts.

Dissolved constituent	Concentration		Mass in the oceans ^c ($\times 10^{20}$ g)	Annual flux from rivers ^d ($\times 10^{14}$ g)	Time for river fluxes to attain oceanic amounts ($\times 10^6$ yr)
	Average river water ^a (ppm)	Average seawater ^b (ppm)			
Cl ⁻	7.8	19,000	260.3	2.53	102.9
Na ⁺	6.3	10,500	143.8	2.05	70.2
Mg ²⁺	4.1	1300	17.8	1.33	13.4
SO ₄ ²⁻	11.2	2650	36.3	3.64	10.0
Ca ²⁺	15.0	400	5.5	4.87	1.1
K ⁺	2.3	380	5.2	0.75	6.9
HCO ₃ ⁻	58.4	140	1.9	18.98	0.1
Br ⁻	–	65	0.9	–	–
CO ₃ ²⁻	–	18	0.2	–	–
Sr ²⁺	–	8	0.1	–	–
SiO ₂	13.1	6	0.1	4.26	0.02
Organic C	9.6	0.5	0.01	3.12	0.002

^aLivingstone (1963); ^bGoldberg (1957).

^cTotal mass of ocean water used in the calculation = 1.37×10^{21} kg.

^dTotal river discharge into the oceans per year used in the calculation = 374×10^{14} kg.

Ocean mass balance

- Steady state
- Why are there differences in ocean water and sea water?
- Other processes changing the composition of ocean water:
 1. Biological processes
 - Effect on recycled components (Organic C, CO_2 , O_2 , H_4SiO_4 , Ca^{2+} , NO_3^- and PO_4^{3-})
 - Bodies, boxes, decomposition of organics
 2. Interaction of underwater volcanism and seawater
 3. Reaction of water with particles from the continent (silicates, especially clay minerals)
 - Transformation of minerals, sorption
 4. Transfer of particles to the atmosphere (e.g. droplets from surf)
 5. Precipitation of evaporites
 - Na^+ , Ca^{2+} , Cl^- and SO_4^{2-}
 6. Element-specific processes (e.g. nitrification/denitrification)

Table 13.8 Major processes affecting the concentration of specific dissolved constituents in seawater numbered in the order of approximate decreasing importance, and the status of their mass balance. (Modified from Berner and Berner, 1996.)

Constituent	Input processes	Output processes	Mass balance	
			Long-term budget	Present-day budget
Chloride (Cl ⁻)	1. Rivers (including pollution)	1. Evaporative NaCl deposition 2. Net ocean-air transfer 3. Porewater burial	B	NB
Sodium (Na ⁺)	1. Rivers (including pollution)	1. Evaporative NaCl deposition 2. Net ocean-air transfer 3. Cation exchange 4. Volcanics-seawater reaction 5. Porewater burial	B	NB
Sulfate (SO ₄ ²⁻)	1. Rivers (including pollution) 2. Polluted rain and dry deposition	1. Evaporative CaSO ₄ deposition 2. Biogenic pyrite formation 3. Net ocean-air transfer	B	NB
Magnesium (Mg ²⁺)	1. Rivers	1. Volcanics-seawater reaction 2. Biogenic Mg-calcite deposition 3. Net ocean-air transfer	B	?
Potassium (K ⁺)	1. Rivers 2. High-temperature volcanics-seawater reaction	1. Low-temperature volcanics-seawater reaction 2. Fixation on clay minerals near river mouths 3. Net ocean-air transfer	B	?
Calcium (Ca ²⁺)	1. Rivers 2. Volcanics-seawater reaction 3. Cation exchange	1. Biogenic CaCO ₃ deposition 2. Evaporitic CaSO ₄ deposition	NB	NB
Bicarbonate (HCO ₃ ⁻)	1. Rivers (including pollution) 2. Biogenic pyrite formation	1. CaCO ₃ deposition	NB	NB
Silica (H ₄ SiO ₄)	1. Rivers 2. Volcanics-seawater reaction	1. Biogenic silica precipitation	?	NB
Phosphorus (PO ₄ ³⁻ , HPO ₄ ²⁻ , H ₂ PO ₄ ⁻ , organic P)	1. Rivers (including pollution) 2. Rain and dry fallout	1. Burial of organic P 2. CaCO ₃ deposition 3. Adsorption on volcanogenic ferric oxides 4. Phosphorite formation	B	NB
Nitrogen (NO ₃ ⁻ , NO ₂ , organic N)	1. N ₂ fixation 2. Rivers 3. Rain and dry deposition	1. Denitrification 2. Burial of organic N	NB	?

B = balanced; NB = not balanced.

The formation of the oceans

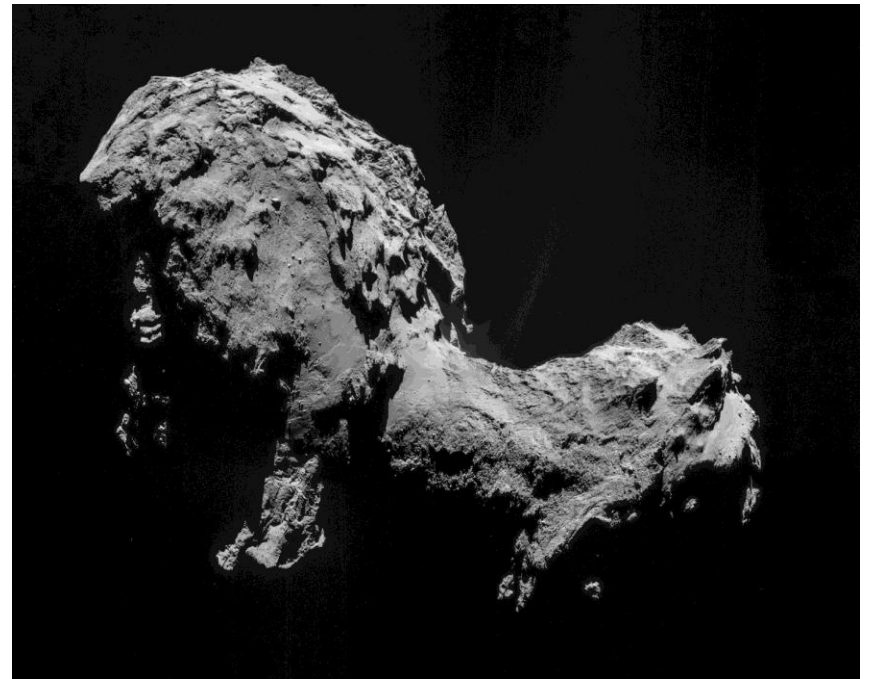
- Based on the isotopic composition (^{18}O)
- Ocean formed about 4.3 ± 0.1 Ga
- Requirement for origin of life
- Essential for the carbon cycle – protection of the planet from overheating (Venus)

The origin of water

- Unlikely to form by synthesis from H and O or oxidation of hydrocarbons
- Most likely sources:
 1. Comets
 2. Watery asteroids
 3. Phyllosilicates
 4. "wet" planetesimals
- Each has its pros and cons

Comets

- For
 - High temperature near the Sun – problem of condensation of volatile components
 - Existence of magma ocean – possible loss of water from accretion
- Against
 - Isotopic composition of water in known comets (but we do not know the composition of Kuiper belt objects)
 - If they are representative, they represent max. 30% of water on Earth



Watery asteroids

- Water a significant component of some chondrites (up to 9%)
- Asteroid bombardment used to be more intense
- Isotopes again show that they are not the main source of water

Phyllosilicates

- Formation of hydrated phyllosilicates in the asteroid belt (thermodynamically stable) and then transport to Earth
- Same problems as watery asteroids

Wet planetesimals

- Water is sorbed onto the surface of cosmic dust
- Cosmic dust forms planetesimals
- Accretion
- Water comes directly from the creation of the Earth
- Problem – there shouldn't be any "dry" asteroids
 - Anhydrous chondrites would have to be the decay product of metamorphosed and dehydrated bodies

Chemical history

- Since the formation of the oxygen atmosphere, the subsurface part of the ocean has been oxygenated
 - Conditions in deeper parts unclear
- Throughout the Phanerozoic, the surface is well oxygenated – there are large fluctuations in depth
 - Sedimentation of black shales in anoxic conditions
 - Links to extinctions?

Chemical history

- Composition evolution can be estimated from the sediments
- Fluid inclusions in evaporites
- Nothing about Hadean
- In the Archean, the composition is not dissimilar to the present one
 - Na^+ , K^+ , Ca^{2+} , Mg^{2+} and Cl^-
 - Carbonate sediments, but no evaporites
 - Enough HCO_3^- , but little SO_4^{2-}
- In the Proterozoic, the content of sulfates slowly increases, the content of CO_2 decreases (concurrently with the atmosphere)
 - An increase in the pH of ocean water
- At the end of the Precambrian, conservative elements composition very similar to today
 - In the Cambrian, an increase in Ca^{2+} , significant changes in recycling elements



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- Images from the following publications are also used:
 - Appelo, C. A. J., & Postma, D. (2005). *Geochemistry, groundwater and pollution* : (2nd ed.). Leiden: AA Balkema publishers.
 - Clark, I. (2015). *Groundwater Geochemistry and Isotopes*. CRC Press. 442 p. ISBN 978-1-4665-9174-5 (eBook - PDF)
 - Misra , K. (2012). *Introduction to geochemistry: principles and applications*. Wiley-Blackwell. 438 p. ISBN 978-1-4443-5095-1.
 - Oki and Kanae 2006: available from http://www.u-tokyo.ac.jp/en/about/publications/tansei/14/science_1.html
 - Ryan, P. (2014). *Environmental and low temperature geochemistry*. John Wiley and Sons. 402 p. ISBN 978-1-4051-8612-4 (pbk.)