

Università di Trieste LAUREA MAGISTRALE IN GEOSCIENZE Curriculum Geofisico Curriculum Geologico Ambientale

Anno accademico 2016 – 2017

Geologia Marina

Parte I

Modulo 1.1 Introduzione ai fondali oceanici oceani: Acqua oceanica, sedimento, e fluidi interstiziali

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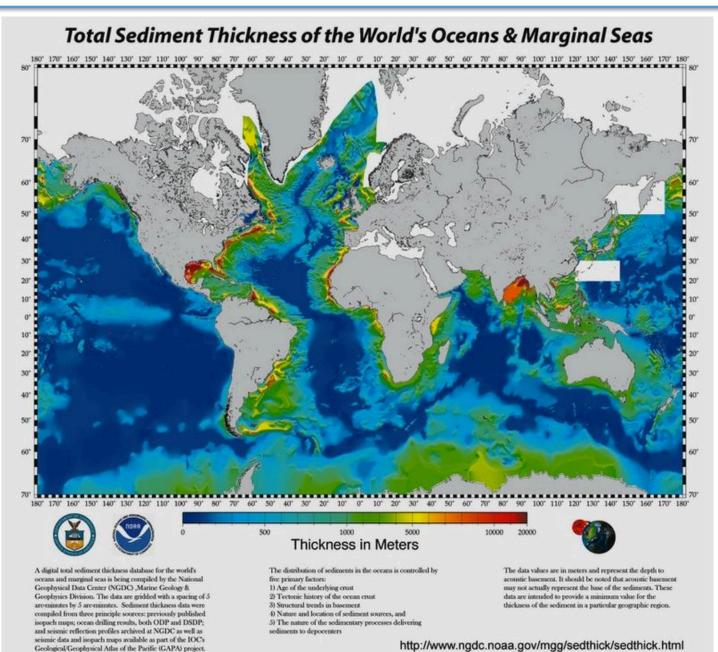


MARINE SEDIMENTS

Composition

- Terrigenous (derived from land)
- Biogenic (derived from plants and animals)
- Authigenic (formed on or in the sediments on the sea floor)
- Volcanogenic (particles from volcanic eruptions)
- Cosmogenous (particles from outer space)

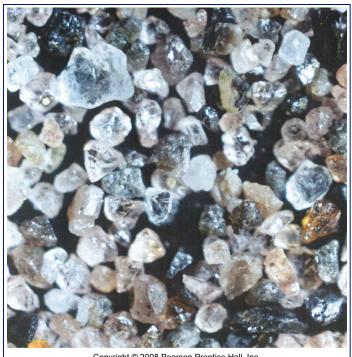






Terrigenous Sediments (also: *lithogenous*)

- Eroded rock fragments from land
- Transported from land by
 - Water (e.g., river-transported sediment)
 - Wind (e.g., windblown dust) aeolian transport
 - Ice (e.g., ice-rafted rocks)
 - Gravity (e.g., turbidity currents)



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Terrigenous Sediments (also: *lithogenous*)

CLAYS (hydrates alumosilicate mineral)

- Kaolinite
- Chlorite
- Illite
- Montmorillonite
- Particles are generally < 2 μm

Also generated by dissolution of calcareous plankton and benthos (red clays, or pelagic clays) below the Carbonate Compensation Depth (CCD) in the open ocean.



Terrigenous Sediments (also: *lithogenous*)

SILTS and SANDS Silts (2 - 63 µm) Sands (>63 µm)

Mainly transported by turbidity currents, debris flows, icebergs Reflect composition of surrounding land masses



Biogenic Sediments (also: *biogenous*)

Hard remains of dead organisms

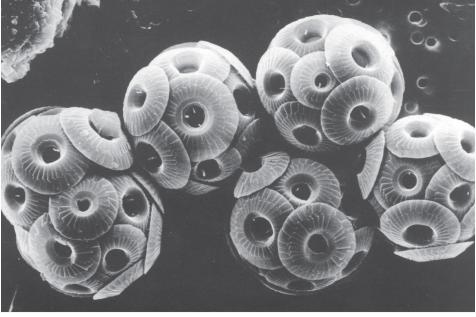
- Macroscopic (large remains)
 - Shells, bones, teeth
- Microscopic (small remains)
 - Tiny shells or tests settle through water column
 - Biogenic ooze (30% or more tests)
 - Mainly algae and protozoans
- Calcium carbonate (CaCO3)
- Silica (SiO2 or SiO2 nH2O)



Calcium carbonate in biogenous sediments

Coccolithophores (algae)

- Photosynthetic
- Coccoliths (nano-plankton)



(a)

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Calcium carbonate in biogenous sediments

Foraminifera

(Benthic and Planktonic Protozoans)

Calcite

30µm - 1 mm



(c)

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Pteropods (planktonic gastropods molluscs)

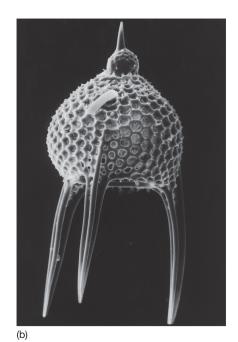
Aragonite (a variety of calcite, more soluble)



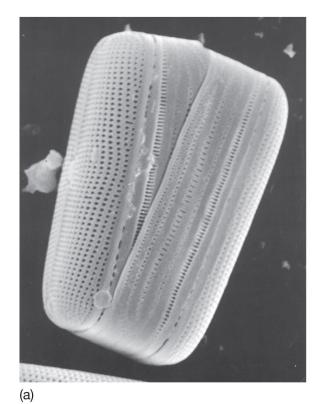


Silica in biogenic sediments

Diatoms (algae) $< 200 \mu$ m Radiolarians (protozoans) 50-300 μ m



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Authigenic Sediments (also: *Hydrogenous*)

- Minerals precipitate directly from seawater
 - Manganese nodules
 - Phosphates (beneath areas in surface ocean of ver high biological productivity)
 - Carbonates (Aragonite and calcite)
 - Metal sulfides (Associated with hydrothermal vents)
 - Evaporites (Minerals that form when seawater evaporates)
- Small proportion of marine sediments

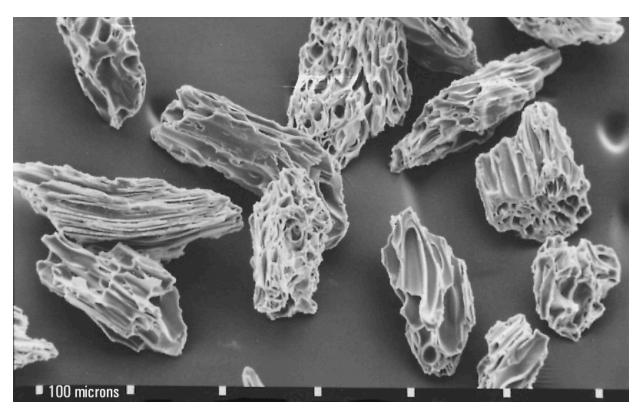


(a)



Volcanogenic Sediments (also: *Hydrogenous*)

- Ash layers
- Lava basalts



Glass shards



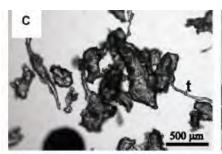
Cosmogenous Sediments

- Macroscopic meteor debris
- Microscopic iron-nickel and silicate spherules
- Tektites
- Space dust
- Overall, insignificant proportion of marine sediments

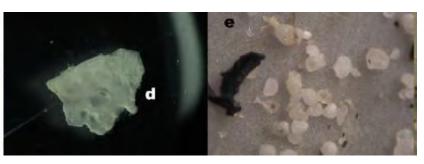


Plastics

- "New and emerging issue" GESAMP (Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection (GESAMP) is an advisory body, established in 1969, that advises the United Nations (UN) system on the scientific aspects of marine environmental protection.
- Plastic particles < 5mm
- Primary microplastics are deliberately manufactured
- Secondary microplastics are break-down products of larger debris
- Most plastic derives from land-based sources
 - Household and industrial waste + wastewater
 - Fishing, aquaculture, shipping, tourism, etc.









MARINE SEDIMENTS

Distribution

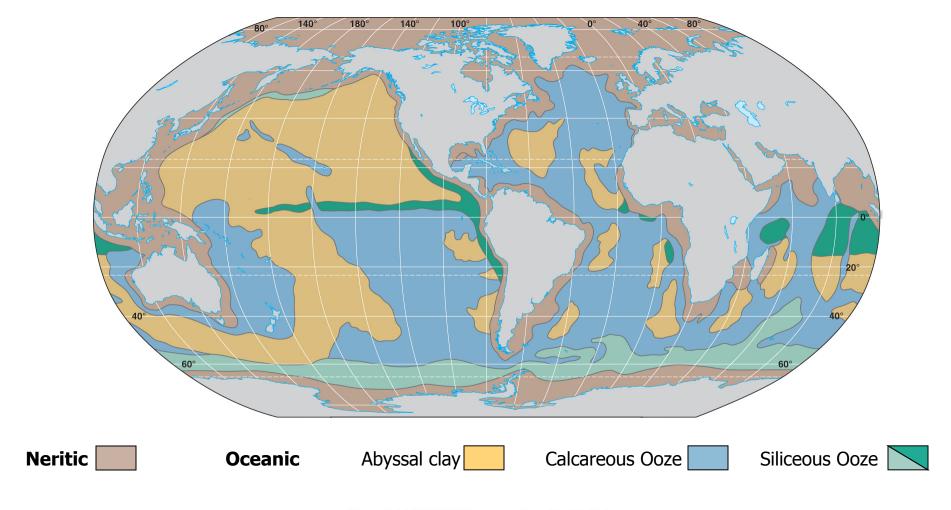
Neritic

- Shallow water deposits
- Close to land
- Dominantly lithogenous
- Typically deposited quickly

Pelagic (Also Oceanic)

- Deeper water deposits
- Finer-grained sediments
- Deposited slowly







Distribution of pelagic sediment

Dominant component	Composition	Atlantic	Pacific	Indian	Total %
Foraminiferal and nannofossil ooze	Calcium carbonate	65	36	54	47
Pteropod ooze	Calcium carbonate	2	0.1	-	0.5
Diatom ooze	Silica (opal)	7	10	20	12
Radiolarian ooze	Silica (opal)	_	5	0.5	3
Red (actually brown) clay K, Fe	Al silicate	26	49	25	38

Source P.Pinet Invitation to Oceanography, 2000 2nd Edition, Jones and Barlett Publishers, Massachusetts



Take-home messages

Marine sediments are very heterogeneous material, whose solid component is made by a mixture of particles with different composition, shape and size

All of the inorganic solid components of marine sediments undergo some kind of chemical alteration through time essentially in consequence of the exposure to salt water



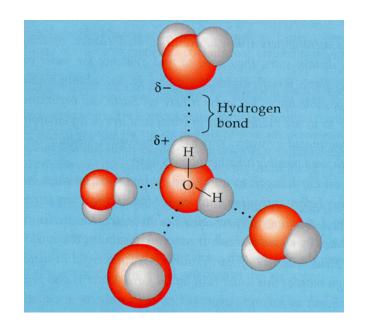


SEAWATER

Water has unique and unusual properties both in pure form and as a solvent. These properties influence many of the chemical reactions taking place in the oceans.

"Distorted" tetrahedral arrangement, with 2 electrons in each lobe. Two lobes are used for O-H bonds and two lobes have free lone pairs of electrons.

The H-O-H tetrahedral angle of 105°, results in dipole moments, which means that this is a polar molecule.



Propensity to form hydrogen bonds. "Cooperative Bonding" in which the water molecules link together to form regions with structure.



SEAWATER

- SALINITY: dissolved ion content by weight.
- Average 3.5 % or 35 parts per thousands
- Varying between 3.1% and 3.8%
- Not uniform distribution (horizontal and vertical)





Seawater composition (by mass)

Element	%	
Oxygen	85.84	
<u>Hydrogen</u>	10.82	
<u>Chlorine</u>	<u>1.94</u>	because salinity is directly proportional
<u>Sodium</u>	1.08	to the amount of chlorine in sea water,
<u>Magnesium</u>	0.1292	and because chlorine can be measured
<u>Sulfur</u>	0.091	accurately by a simple chemical analysis
Calcium	0.04	salinity S is defined using chlorinity
<u>Potassium</u>	0.04	$S(o/o_0) = 1.80655 \times Cl(o/o_0)$
<u>Bromine</u>	0.0067	
Carbon	0.0028	

Now Salinity is measured by Electroconductivity in Practical Salintiy Units (PSU)



Seawater composition

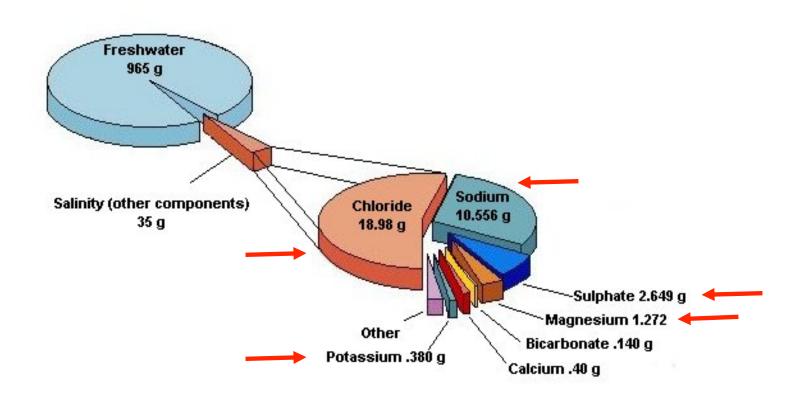
Marcet's Principle (constancy of composition):

- True for *conservative* elements, which include most of the major ions in seawater (Na⁺, K⁺, SO₄⁻², and Cl⁻).
- The concentration of this elements, normalized to salinity, is constant with depth and in the different oceans.
- The ratio of one conservative element to another will also be constant.



Seawater composition

Conservative elements





What does and what does not affect the constancy of composition of salt in seawater?

Does Not:

- Precipitation evaporation
- Freezing thawing
- Turbulent mixing between water masses

Does:

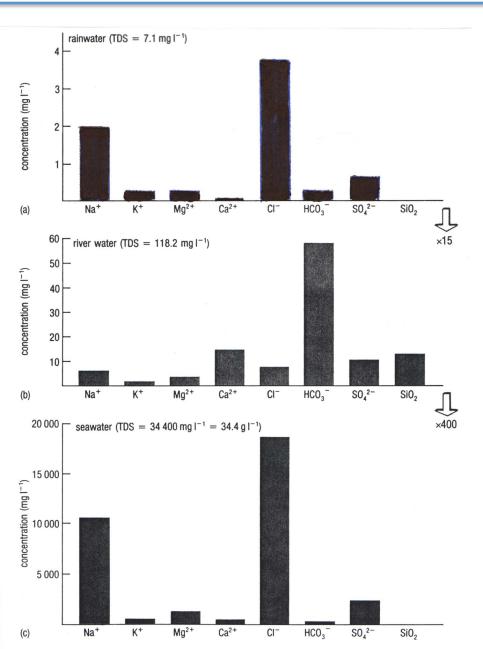
- Marginal seas receiving significant river runoff, e.g Baltic Sea
- Anoxic basins where sulfate reduction occurs, e.g. Black Sea
- Shallow water environments where significant inorganic aragonite (a form of CaCO₃)
 precipitation occurs oolites
- Hydrothermal vents where seawater influx through hydrogeological processes causes low and high temperature alteration of basalts
- Evaporite basins, e.g. Dead Sea
- Interstitial waters of sediments



Origin of dissolved ions

rain water does not look like river water

seawater doesn't look like river water





Origin of dissolved ions

IGNEOUS ROCK + RAIN WATER >>>> SEDIMENTARY ROCK + RIVER WATER

Order of loss of cations during weathering of igneous rocks:

$$Ca^{++} > Na^{+} > Mg^{++} > K^{+} > Si^{++++} > Fe^{+++} > Al^{+++}$$

 $Ca^{++} > Na^{+} > Mg^{++}$ are the most abundant cations in river water K^{+} is retained in clay minerals and is not abundant in river water

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

carbonic acid





Origin of dissolved ions

Product of alteration of igneous rocks:

LIMESTONES 5 - 15%

SANDSTONES 11 - 30%

SHALES 65 - 80%

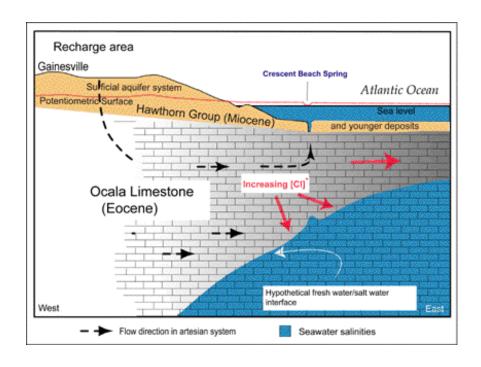
MINOR COMPONENTS (evaporites, cements...)





Other input of ions to the oceans

Groundwaters



Around the world groundwater discharge was observed at several coastal regions

Considerable flow rates of more than 1000 liters per minute were measured for submarine springs in the northeastern Gulf of Mexico.

Using the enrichment of ²²⁶Ra, Moore (1995) estimated that the groundwater flux to the coastal waters of South Atlantic Bay must be ~40% of the river-water flux (LOCAL).





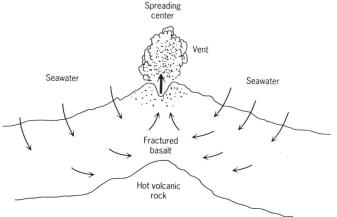


FIGURE 19.2. Hydrothermal convection cells.

Hydrothermal Systems

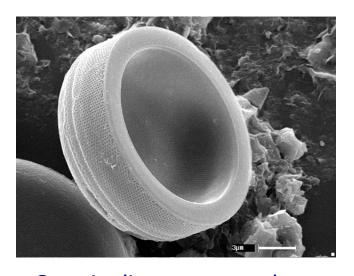
- Seawater is entrained at spreading centers and contributes to hydrothermal circulation.
- Rate of hydrothermal circulation 0.3 to 3% of river input.
- Reactions between seawater and basalt modify composition of the circulating fluids.

By **HIGH** and **LOW** temperature geochemistry



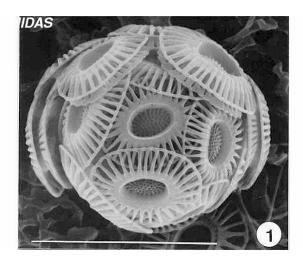


Biological factors



Centric diatoms – an alga

Make a skeleton based on the element Si – 'biogenic silica' or SiO₂



Emiliania huxleyi, a coccolithorophorid

Make skeletal material from **calcium carbonate**CaCO₃



Microbiology: Sulfate reduction in anoxic basins

$$SO_4^{--} + 2 CH_2O \longleftrightarrow H_2S + 2 HCO_3^{--}$$

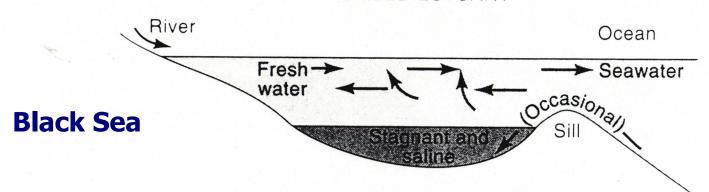
Organic matter

Increase in alkalinity

2 FeO · OH + 3
$$H_2S \leftarrow \rightarrow$$
 2 FeS + S^{--} + 4 H_2O Pyrite

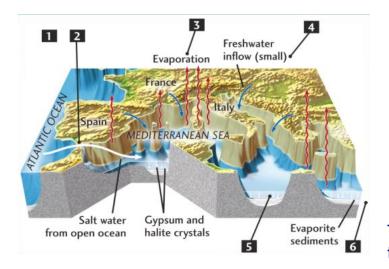
$$Ca^{++} + 2 HCO_3^- \longleftrightarrow 2 CaCO_3 + 2 H^+$$
Calcite

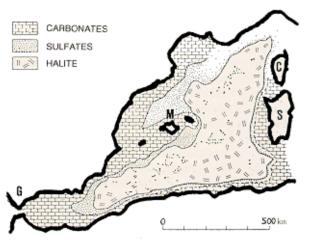
SILLED ESTUARY

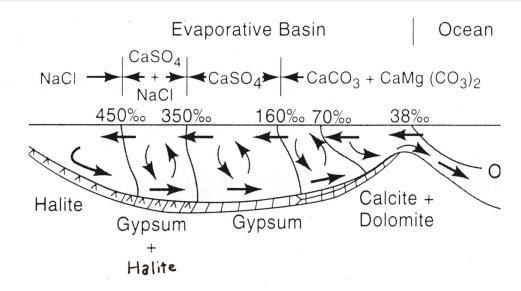




Evaporation







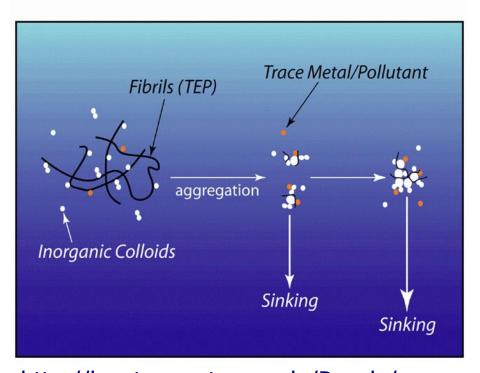
The minerals precipitate out of solution in the reverse order of their solubilities, such that the order of precipitation from sea water is:

- 1 Calcite (CaCO₃) and dolomite (CaMg(CO₃)₂)
- 2 Gypsum (CaSO₄ · 2H₂O) and anhydrite (CaSO₄)
- 3 Halite (i.e. common salt, NaCl)
- 4 Potassium and magnesium salts

Limestone (calcite) and dolomite are more common than gypsum, which is more common than halite, which is more common than potassium and magnesium salts.



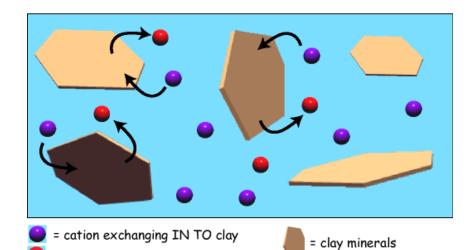
Extra-cellular polysaccharides may play a role in the formation of aggregates and transport of trace metals and pollutants in aquatic systems



http://loer.tamug.tamu.edu/People/ Santschi/santschi_research.htm

= cation exchanging OUT OF clay





Salt sinks

Ion Exchange on Sedimentary Particles

Ca introduced in rivers is removed from clays at the expense of Na and K uptake

TABLE 12-4 CHANGE IN EXCHANGEABLE CATIONS WHEN RIVER-BORNE CLAYS ENTER SEAWATER® (after Sayles and Mangelsdorf, 1977).

	Average equivalent fraction ^b		Change in equiv.	Net removal from ocean	Percent of river	
	in river water	in seawater	fraction	$(g/yr)^c$	input	
Na ⁺	0.04	0.47	+0.43	0.45×10^{14}	20.5 (30) ^d	
K+	0.01	0.06	+0.05	0.09×10^{14}	13	
Ca ²⁺	0.06	0.16	-0.44	-0.4×10^{14}	-8	
Mg^{2+}	0.25	0.32	+0.07	0.04×10^{14}	3	
H ⁺	0.10	0	-0.10			

^a A + sign indicates uptake by the clay.

^b Equivalent fraction is the fraction of the total exchange sites occupied by that cation.

 $^{^{\}circ}$ Assuming a suspended sediment input of 183 \times 10¹⁴ g/yr and a CEC of 25 meq/100 g.

^d Value in parentheses is corrected for cyclic salts.



Salt sinks

Hydrothermal systems

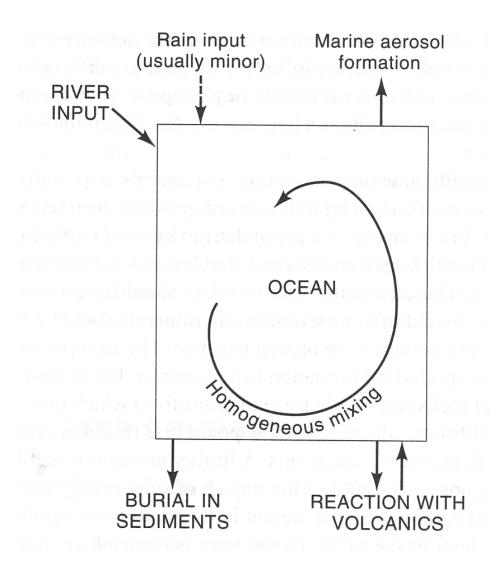
Basalt alteration at 200 °C

Source for Ca, sink for Mg, SO₄

Fresh Basalt + Mg^{++} + $2HCO_3^-$ = altered basalt + Ca-Silicate + $2CO_2$



Mass balance: Simple box models



From Berner and Berner. Box model appropriate for conservative elements in seawater.



Physical properties of sea water

In oceanography, the calculation of water movement requires measurements of density with an accuracy of a few parts per million. This is not easy.

Absolute Density of water can only be measured in special laboratories, and only with difficulty. The best accuracy is $1:2.5\cdot 10^5=4$ parts per million.

To avoid the difficulty of working with absolute density, oceanographers use **density relative to density of pure water**. Density ρ (S, t, p) is now defined using Standard Mean Ocean Water of known isotopic composition, assuming saturation of dissolved atmospheric gasses.

S, t, p refer to salinity, temperature, and pressure.

In practice, **density is not measured**, **it is calculated** from in situ measurements of pressure, temperature, and conductivity using the **equation of state for sea water***. This can be done with an accuracy of two parts per million.

The International Equation of State (1980) published by the Joint Panel on Oceanographic Tables and Standards (1981) is now used. See also Millero and Poisson (1981) and Millero et al (1980).

T₀C



Physical properties of sea water

Density of water at the sea surface is typically 1027 kg m⁻³.

For simplification, physical oceanographers often quote only the last 2 digits of the density, a quantity they call density anomaly or Sigma (S, t, p):

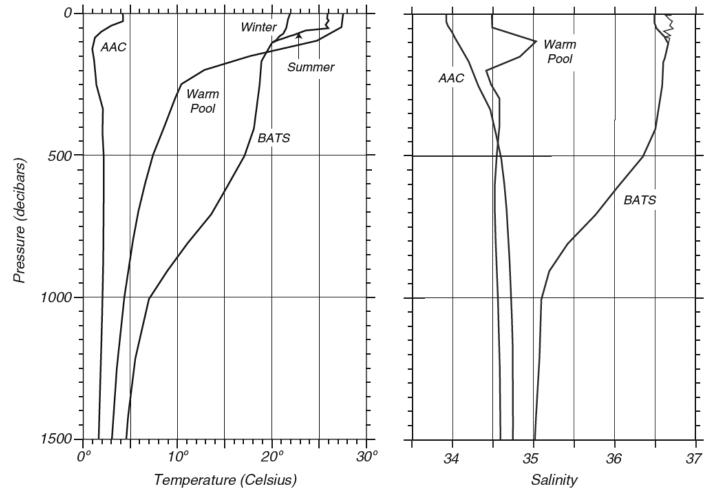
$$\sigma(S, t, p) = \rho(S, t, p) - 1000 \text{ kg m}^{-3}$$

1 0			Saminey (g kg)								
		20	25	30	35	40					
	0	16.0)4	20.0)6	24.08	2	28.10		32.14	
	5	15.8	34	19.7	78	23.73	2	27.68		31.64	
	10	15.3	31	19.1	.8	23.07	2	26.96		30.86	
	15	14.4	48	18.3	30	22.13	2	25.97		29.82	
	20	13.3	39	17.1	7	20.96	2	24.75		28.56	
	25	12.0	07	15.8	32	19.57	2	23.34		27.12	

Salinity (g kg ⁻¹)



Vertical variability of seawater temperature and salinity



Typical temperature and salinity profiles in the open ocean. **AAC**: At 62.0. S, 170.0. E in the Antarctic Circumpolar Current on 16 January 1969 as measured by the R/V Hakuho Maru. **Warm Pool**: At 9.5. N 176.3. E in the tropical west Pacific **warm pool** on 12 March 1989 as measured by Bryden and Hall on the R/V Moana Wave. **BATS**: At 31.8. N 64.1. W near Bermuda on 17 April and 10 September 1990 as measured by the Bermuda Biological Station for Research, Inc.



Physical properties of sea water

Potential Density

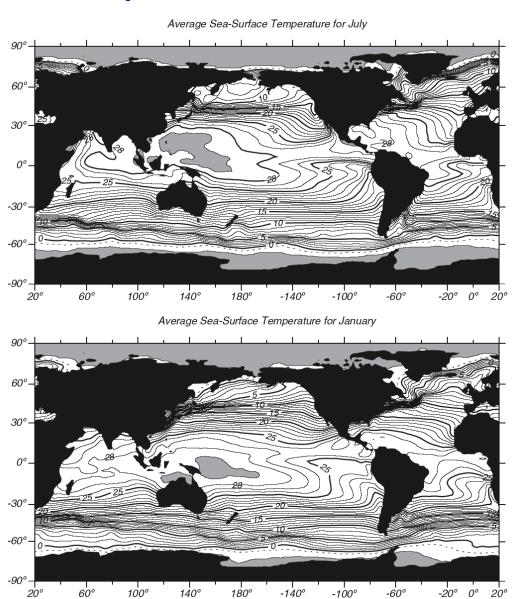
Potential density σ_{τ} is the density a parcel of water would have if it were raised adiabatically to the surface without change in salinity. Written as sigma, $\sigma_{t} = \sigma(S, t, 0)$ Potential Density is especially useful because it is a conservative thermodynamic property.

Potential Temperature

Potential temperature is defined as the temperature of a parcel of water at the sea surface after it has been raised adiabatically from some depth in the ocean. Raising the parcel adiabatically means that it is raised in an insulated container so it does not exchange heat with its surroundings.

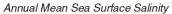


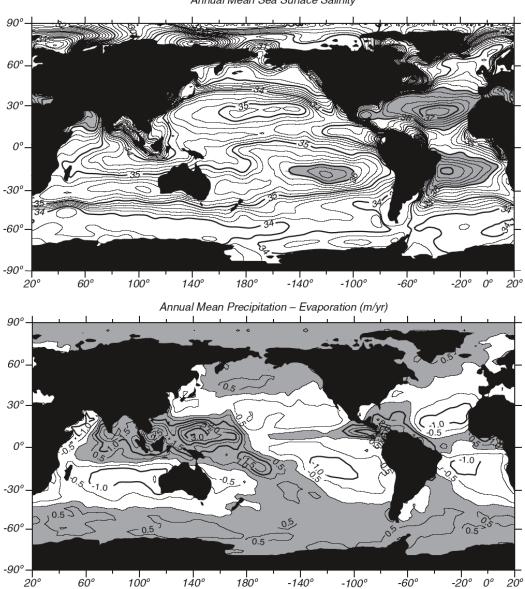
Variability of seawater temperature





Variability of seawater salinity







Variability of seawater density

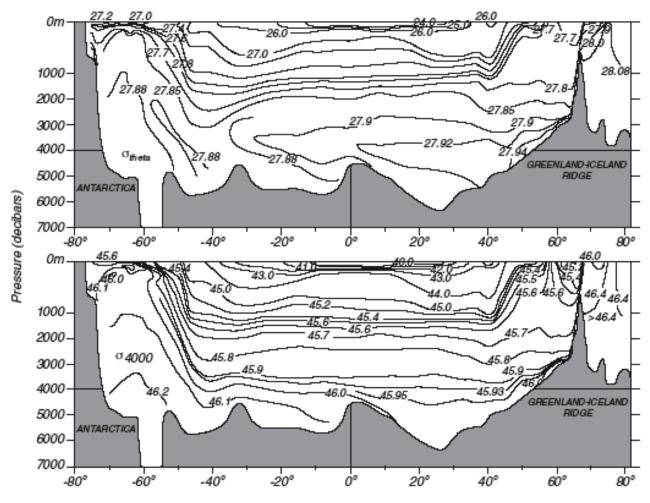


Figure 6.10 Vertical sections of density in the western Atlantic. Note that the depth scale changes at 1000 m depth. Upper: σ_{Θ} , showing an apparent density inversion below 3,000 m. Lower: σ_{4} showing continuous increase in density with depth. After Lynn and Reid (1968).





Physical properties of sea water

(function of temperature, salinity and pressure)

Mechanical and thermal properties of sea water at salinity 35 g ${\rm kg}^{-1}$ and atmospheric pressure (unless otherwise stated)

Property	0 °C	20 °C
Dynamic viscosity	$1.88 \times 10^{-3} \text{Pa s}$	$1.08 \times 10^{-3} \text{ Pa s}$
Kinematic viscosity, v	$1.83 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$	$1.05 \times 10^{-6} \; \text{m}^2 \; \text{s}^{-1}$
Thermal conductivity	$0.563 \text{ W m}^{-1} \text{ K}^{-1}$	$0.596~W~m^{-1}~K^{-1}$
Thermal diffusivity, κ	$1.37 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$	$1.46 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$
Prandtl number, v/κ	13.4	7.2
Specific heat capacity, C_p	3985 J $kg^{-1} K^{-1}$	$3993 \text{ J kg}^{-1} \text{ K}^{-1}$
Thermal expansion coefficient		
Pressure = 0.1 MN m ⁻²	$52 \times 10^{-6} \text{K}^{-1}$	$250 \times 10^{-6} \text{ K}^{-1}$
Pressure = 100 MN m ⁻² $\dots \dots \dots$	$244 \times 10^{-6} K^{-1}$	$325 \times 10^{-6} \text{ K}^{-1}$
Ratio of specific heat capacities, $C_p \ / C_v \ $	1.000 4	1.010 6
Velocity of sound*	1449 m s ⁻¹	1522 m s^{-1}
Compressibility	$4.65 \times 10^{-10} \text{ Pa}^{-1}$	$4.28 \times 10^{-10} \mathrm{Pa^{-1}}$
Freezing point		- 1.910 °C
Boiling point		100.56 °C

	Seawater (35‰)	Pure Water
Temperature of maximum density:	3.25°C	3.98°C
Freezing point	-1.91°C	0.00°C



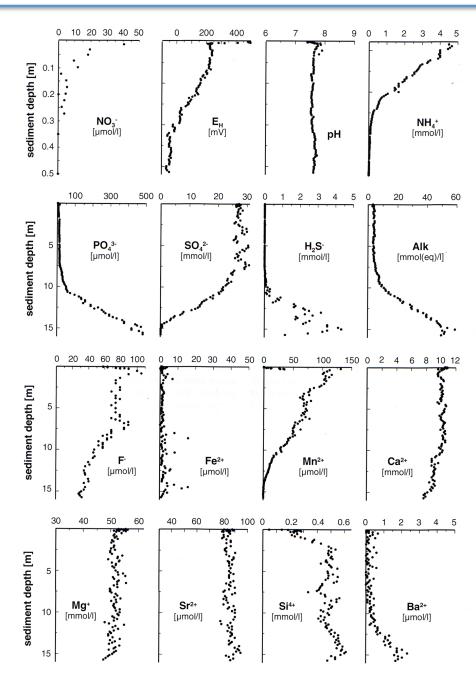
Pore water in marine sediments

Chemically unstable sediment particles:

Igneous rock fragments
Amorphous material (e.g. opal)
Organic matter
Remnants of Organisms (bones, teeths)
Clay minerals
Aragonite and Mg Calcite

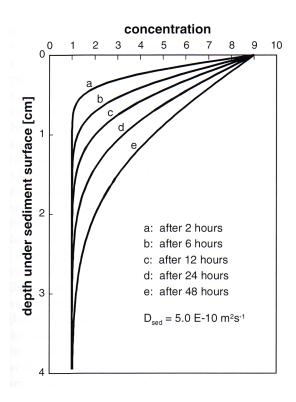
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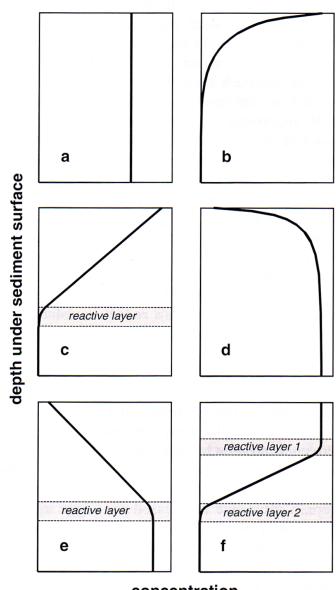
Pore water in marine sediments





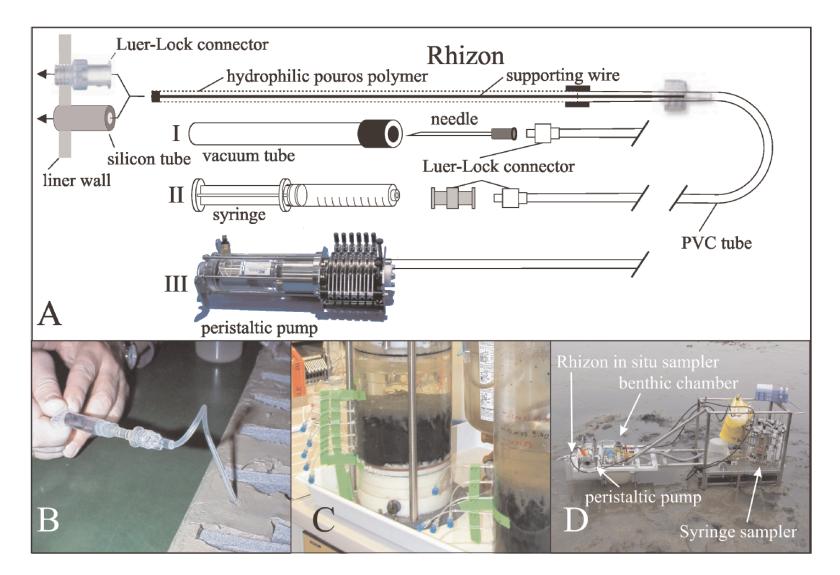
Pore water in marine sediments





concentration



















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