



#### Università di Trieste Corso di Laurea in Geologia

Anno accademico 2016 - 2017

# **Geologia Marina**

Parte IV

#### Modulo 4.1 Cause e modalità del movimento di fluidi nei sedimenti

Docente A. Camerlenghi





In an ideal sedimentary column where the pore pressure field is hydrostatic, the temperature distribution is controlled by conduction of heat (no advection) and there are no chemical gradients (e.g. salinity, osmosis), the pore fluids do not move. Better: they do move upwards as the porosity decreases with time, but they remain in the sedimentary column.





Net pore fluid movement from the subsurface to through the seafloor is triggered by the establishment of pore **pressure**, **thermal**, **chemical** gradients that depend on the **sedimentary**, **tectonic** and **diagenetic** histories of the sedimentary basin





During the process of consolidation, pore fluids are expelled, initially into the pores of the surrounding sediments

**In homogeneous sedimentary columns** fluids move up-wards, towards strata with higher porosity >>>> higher permeability.

**In inhomogeneous sedimentary columns** sands and oozes experience little compaction (they retain more fluids during compaction). Clays undergo a much larger porosity reduction during compaction (e.g. From 80% to 40 % porosity reduction). Fluids may move from clay-rich strata to sandy strata by moving laterally, upwards, and downwards. Alternatively fluids may move using fractures and faults.



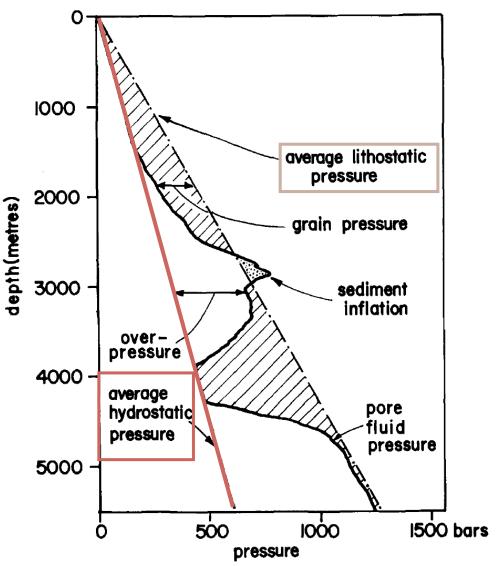


# **Compaction Disequilibriu**

Rapid loading by a huge thickness of the same clay/silt sediment may tip the dewatering balance temporarily in favour of overpressure. In fact the dewatering process is rarely perfectly "normal".

This lack of dewatering conspires to cause the matrix stress between the grains to become "locked" as burial continues, and causes the pore fluids to be responsible for carrying the remaining overburden.

#### SEDIMENT COMPACTION AND INFLATION GRAIN PRESSURE AND OVERPRESSURE



Hydrostatic Gradient (not counting seawater Compressibility) 9.81  $\sim$  10 kPa m  $^{-1}$ 





# **Compaction Disequilibrium**

# The process will continue until the fluid pressure finds relief by rupturing the seal.

This rupture can occur at pressures below the overburden if the rock is brittle or even as much as 40% above the overburden if the rocks have enough tensile strength.

Since **compaction disequilibrium** is common in younger clays, a frequent result of this effect is a suite of **mud diapirs**, **mud lumps**, and **sand volcanoes**.





# **Pore pressure gradients**

### Basic concepts:

A soil (marine sediment in our case) is a compressible skeleton of particles.

- particles are not compressible
- the interstitial fluid (water, gas, or both) is compressible
- the skeleton is compressible

*Volume changes (deformations) do not depend on the total stress applied. They depend on the DIFFERENCE between TOTAL STRESS and PORE FLUID PRESSURE.* 





$$\Delta V/V = -C_c \left( \Delta \sigma - \Delta u \right)$$

 $\Delta V$  = volume change (being V the original volume)  $\Delta \sigma$  = change in total stress  $\Delta u$  = change in pore fluid pressure  $C_c$  = compressibility of the soil skeleton

A volumetric change can be obtained by an increase in  $\Delta\sigma$  as well as by a decrease in  $\Delta u$ 





### Sediment consolidation state

Consolidation is the volumetric change induced by a change of total stress (sedimentary burial, tectonic burial).

When a sediment is buried, it undergoes a process of natural consolidation due to the progressive increase of the overburden (total stress).

#### NORMALLY CONSOLIDATED

The overburden is the maximum stress ever experienced.

#### **OVER-CONSOLIDATED**

The overburden is the less than the maximum stress ever experienced.

#### UNDER-CONSOLIDATED

The overburden is more than the maximum stress ever experienced.





# Factors that determine excess pore water pressure and influence the consolidation state

### The most common factors are:

#### Stress-related factors

- Rapid sedimentation rate
- Tectonic stress

### Fluid volume increase mechanisms

- Temperature increase
- Mineral transformation
- Hydrocarbon Generation

## Fluid movement mechanisms

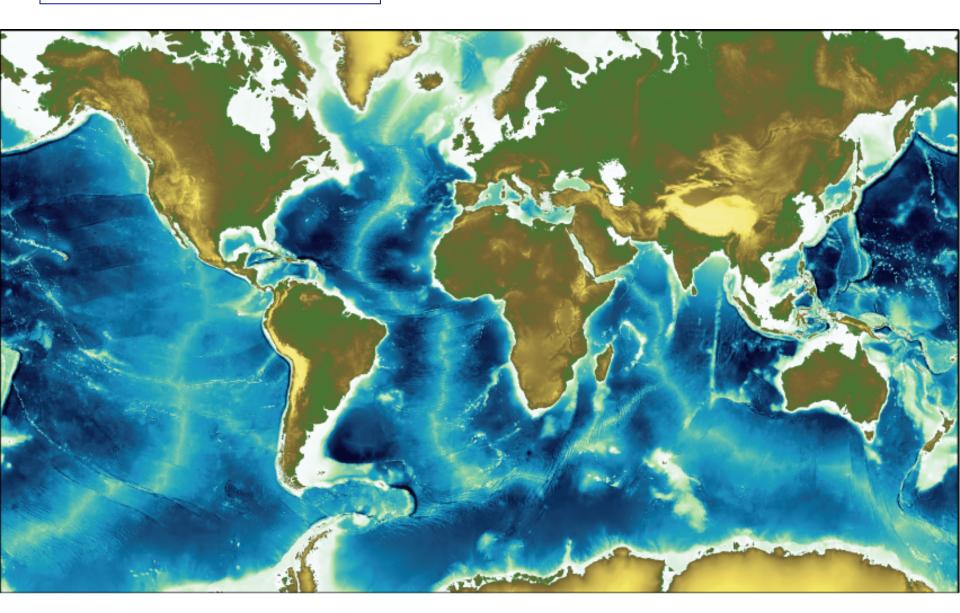
- Osmosis
- Hydraulic head
- Hydrocarbon buoyancy

(**Swarbrick and Osborne, 1998**. Bryant et al., 1974; Sangrey, 1977; Arthur et al., 1980; Demaison & Moore, 1980; Bryant et al., 1981).



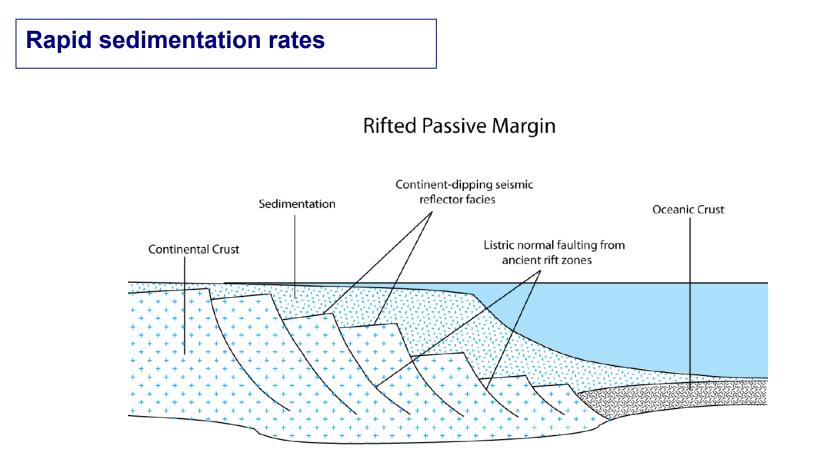


#### **Rapid sedimentation rates**







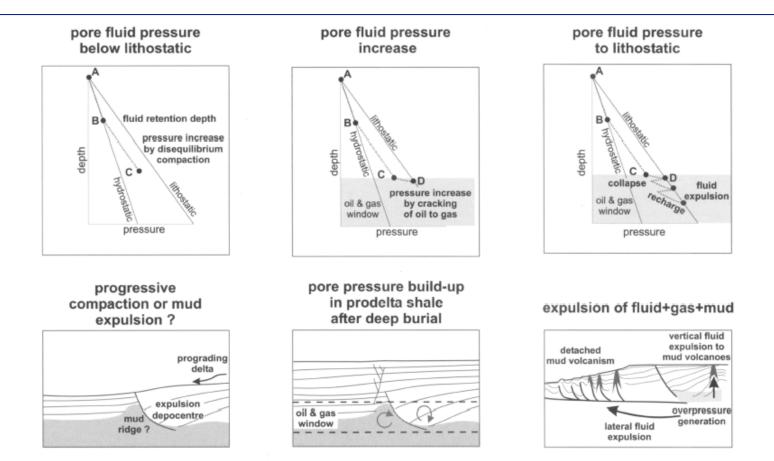


Rapid sedimentation can be produced by:

- River-dominated sedimentary systems (low and medium latitudes)
- Glacial-dominated sedimentary systems (high latitudes)







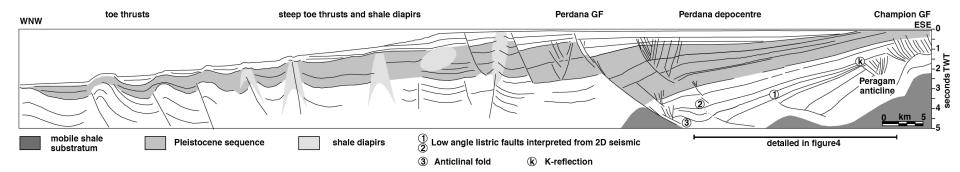
Overview of the styles of shale mobility in relation in relation with pore fluid overpressure; early syndepositional structures can be distinguished from later post-depositional injections of mobilized sediment that occur after large overpressure increase.

Van Rensbergen and Morley, 2003

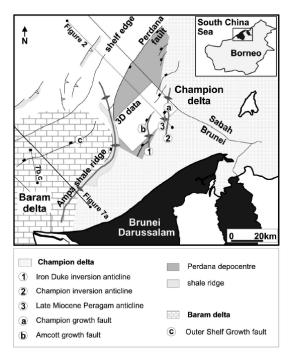




#### **Shale tectonics, Offshore Brunei**



Schematic cross-section of the Champion delta based on 2D regional seismic line.

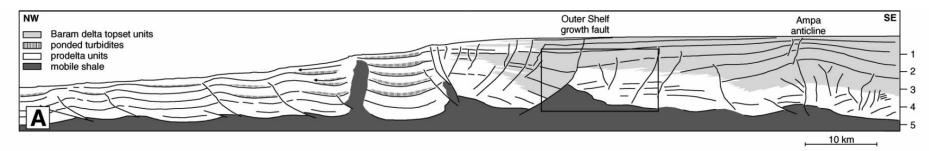


Van Rensbergen and Morley, 2000

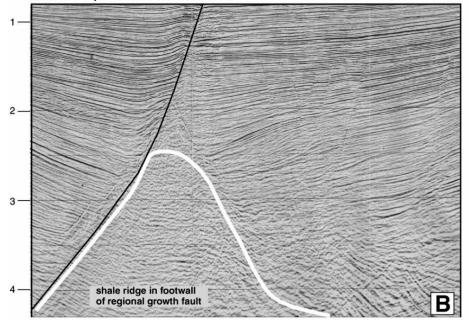




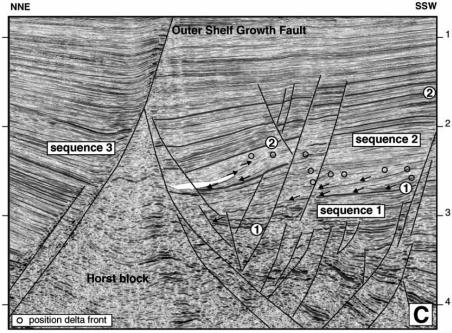
#### Shale tectonics, Offshore Brunei



#### classical interpretation based on 2D seismic



new interpretation basedon 3D seismic

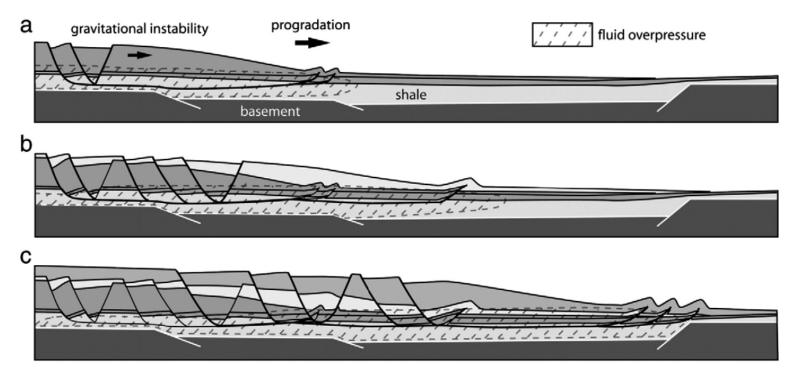


#### Van Rensbergen and Morley, 2000

sec TWT







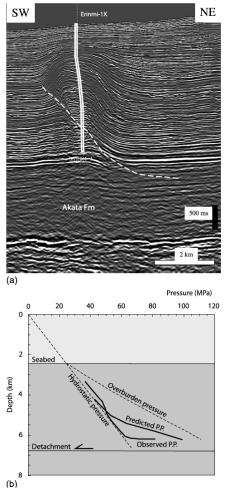
Evolutionary model of fluid overpressure and gravitational deformation in a prograding delta. Whatever the generating mechanism may be (compaction or hydrocarbon generation), the front of the overpressured domain may advance basinward as sediments prograde seaward.

R. Mourgues a,\*, E. Lecomte b, B. Vendeville b, S. Raillard, 2009. An experimental investigation of gravity-driven shale tectonics in progradational delta, Tectoophysics, 474, 643–656.

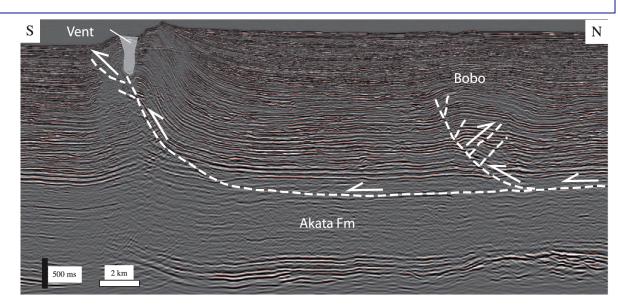


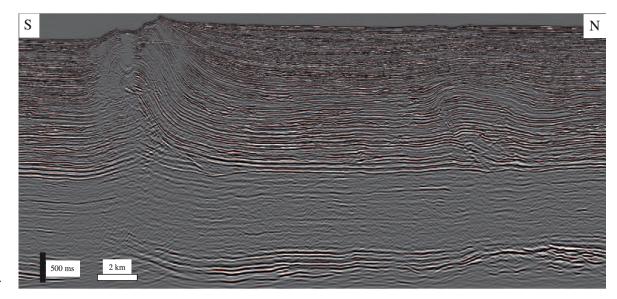


# Shale tectonics in the Niger Delta



Cobbold&al, 2009. Petroleum Geosciences, 15, 3-15.





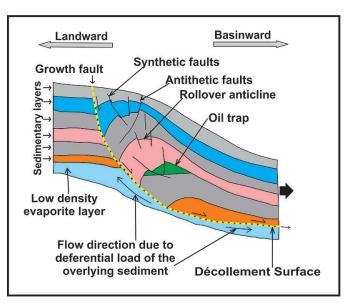




## **Compaction Disequilibrium**

#### **Growth Faults**

Growth faults are syndepositional or synsedimentary extensional faults that initiate and evolve at the margins of continental plates.



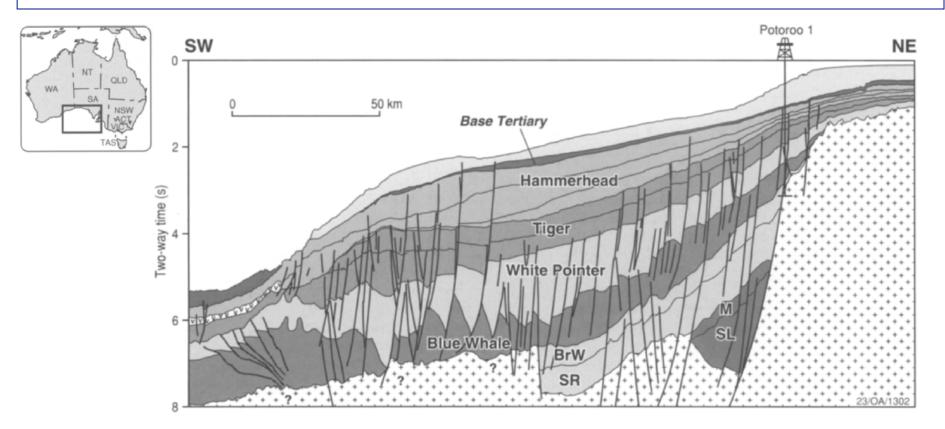
The pressures can sometimes be relieved by systems of **sub-vertical faults** or by **growth fault systems**.

The high pressures in these shale masses are a major contributing factor in the formation of massive "**growth faults**" that cut across the delta, trapping the rollover anticlines (which often form traps for oil and gas in the hanging- wall).

The faults may also trap oil on the foot-wall side where the movement has brought sands against shales to seal them.





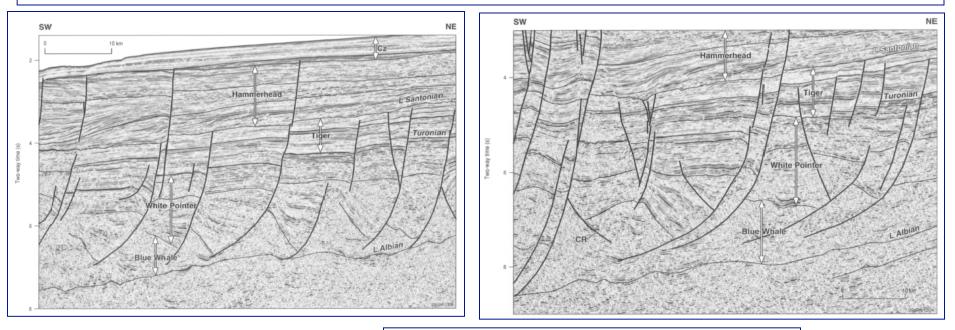


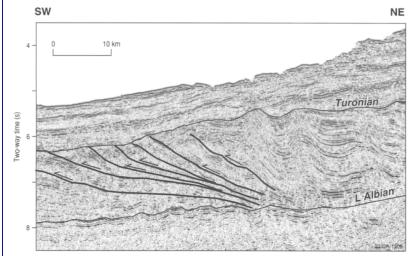
Geoseismic profile across the northern Ceduna Sub-basin. Jumssic-E~ly Cretaceous supersequences abbreviated as follows: SL Sea Lion; M Minke; SR Southern Right; BrW Bronze Whaler

Totterdell and Krassay, 2003









Totterdell and Krassay , 2003

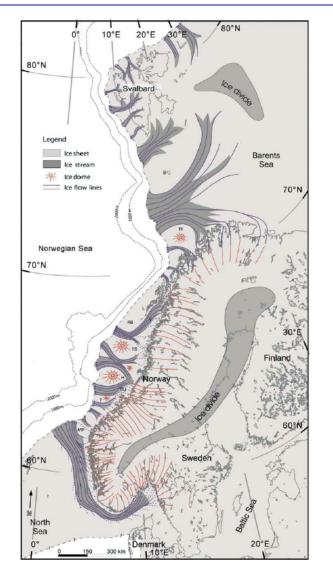


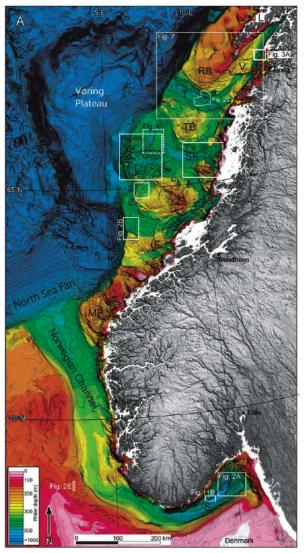
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#### **Rapid sedimentation rates in glacial environments**

#### **North Sea Fan**



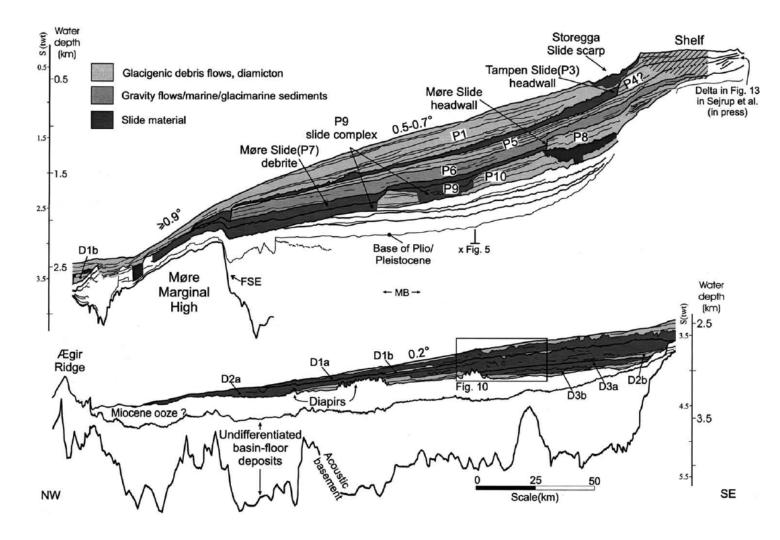


Ottesen et al., 2005





#### **Rapid sedimentation rates in glacial environments**

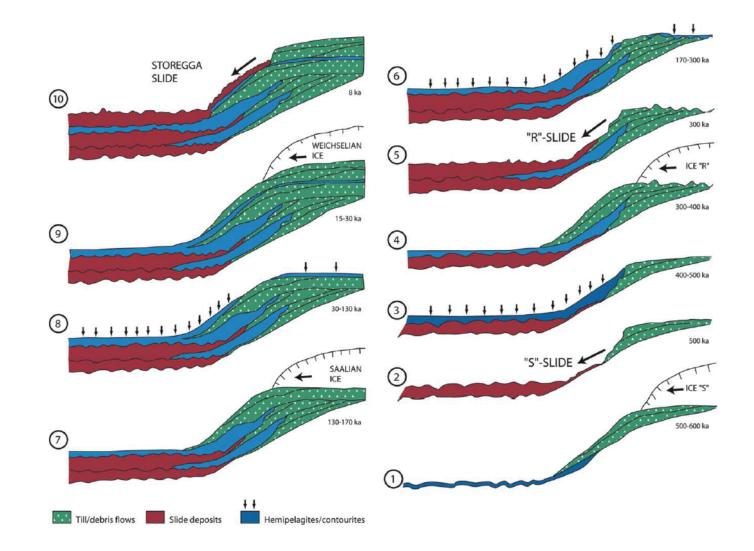


Nygård et al., 2005





#### **Rapid sedimentation rates in glacial environments**



Rise et al., 2005

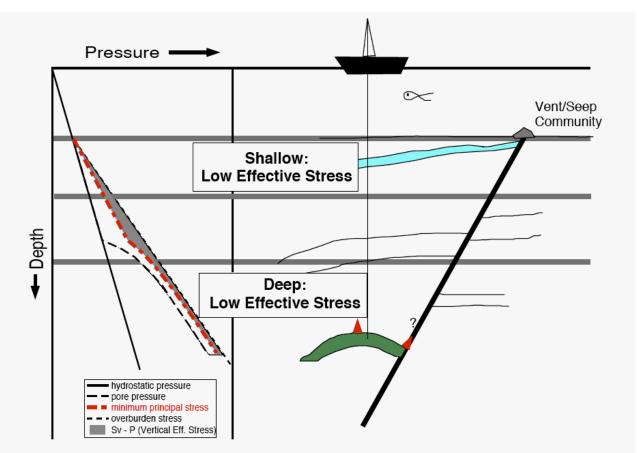


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#### **Rapid sedimentation rates**

Rapid sediment loading (>1 mm  $a^{-1}$ ) is documented as a source of overpressure ( $P^*$ , pressure in excess of hydrostatic) in basins around the world. When low-permeability sediments are rapidly loaded, pore fluids cannot escape, and the fluids bear some of the overlying sediment load. In this situation a pore pressure exceeding the hydrostatic pressure develops.



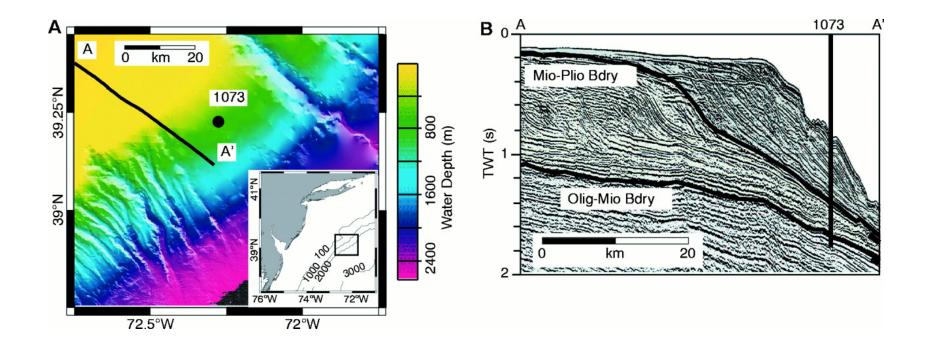


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#### **Rapid sedimentation rates**

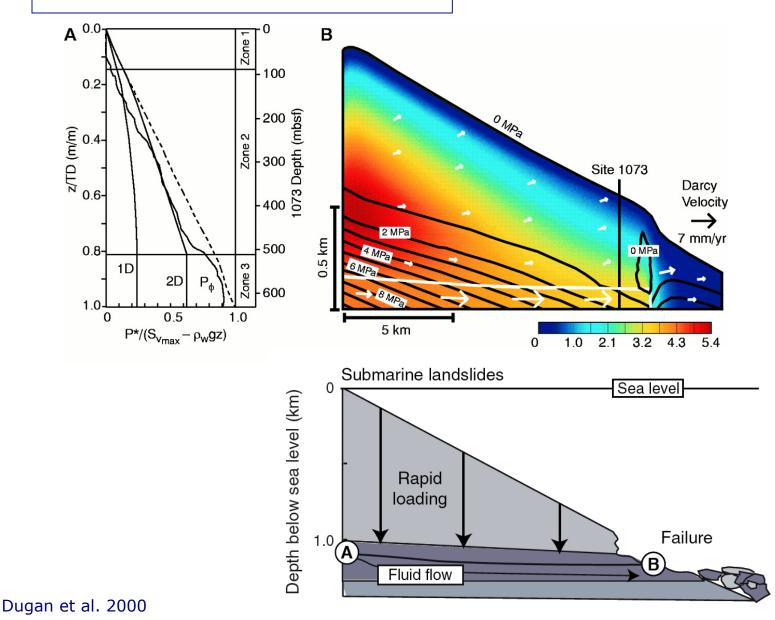
#### New Jersey Margin. Rapid sedimentation of clays over a high permeability sand layer





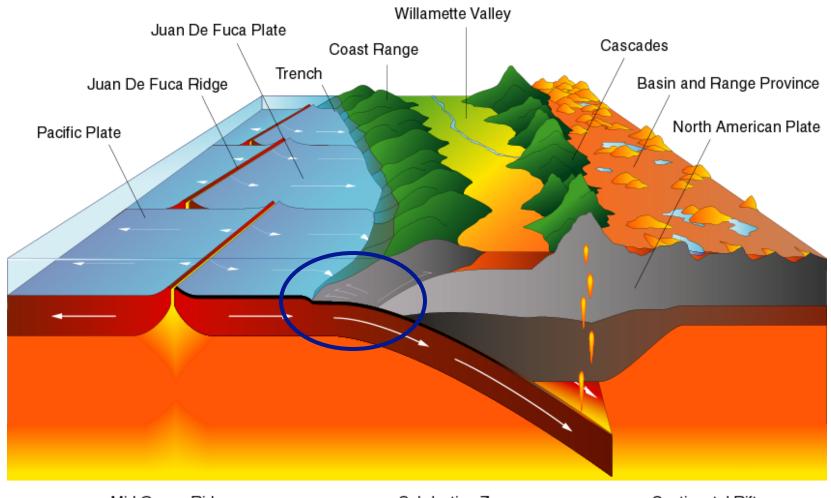


#### **Rapid sedimentation rates**









Mid-Ocean Ridge

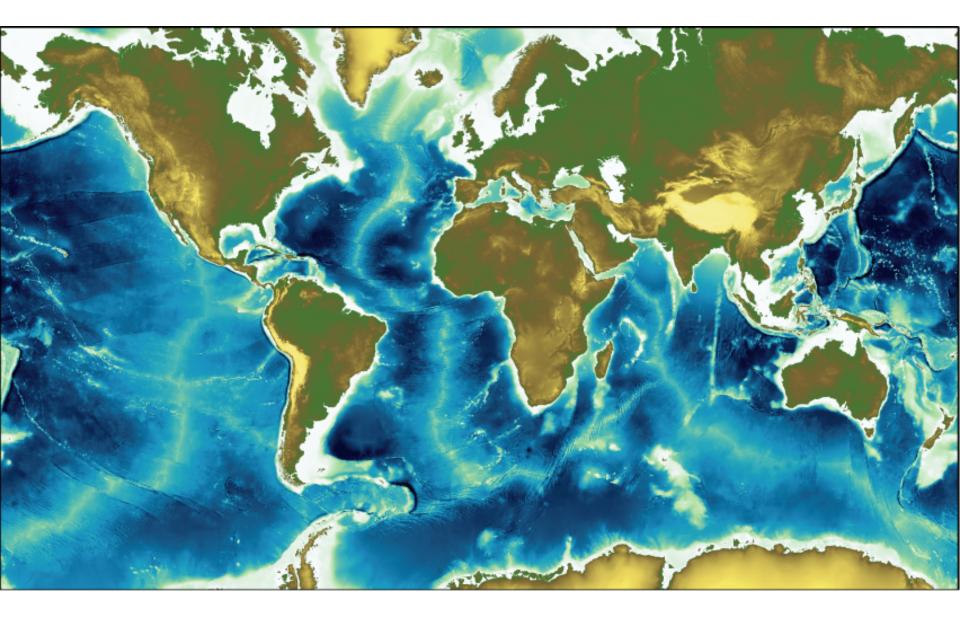
Subduction Zone

Continental Rift

#### Subduction zones are most prevalent in the Pacific Ocean





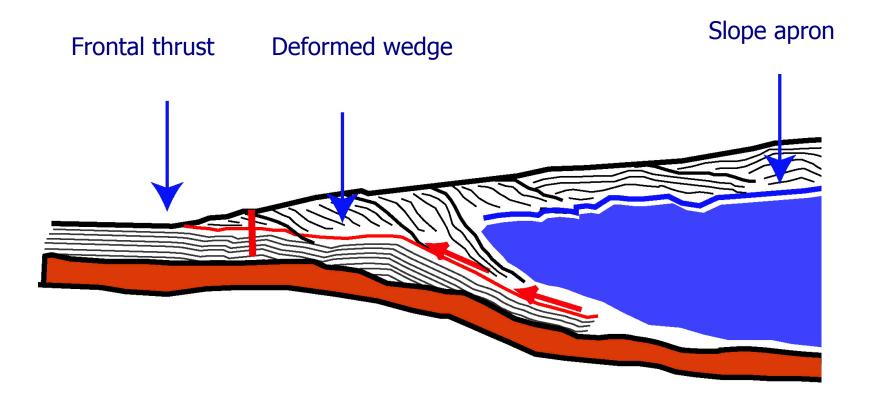




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#### **Tectonic stress**







# **DISPERSED FLOW**

If the rate of pore fluid flow is sufficiently low that advection can be accommodated by intergranular permeability, fluids might be expected to leak out of the prism over large areas, as "dispersed flow," driven by some regional sublithostatic pressure gradient.

### **FOCUSSED FLOW**

In contrast, observations establish that flow is often focused at vent sites, confined to fault zones , or expelled from mud volcanoes.

Fluid loss evolves from dispersed to focused flow over time. Observations indicate **episodic flow**, which may be coupled to episodic fault displacement and ultimately to the earthquake cycle.





At the deformation front the incoming sediments above the decollement are folded and/or faulted, usually into elongated ridges that rise 200-700 m above the adjacent deep-sea floor (**proto-thrust zone**)

Sequential faulting thickens the accreting sediment section and causes the deformation front to step seaward periodically, widening the lower continental slope. The **thrust faults** rise from the decollement, and controls the amount of sediment that is initially subducted.

The initial **frontal thrust fault** and others that originate after uplift and folding ("**out-of-sequence**" **thrusts**) rapidly emplace older, compacted sediments above younger, less consolidated deposits.

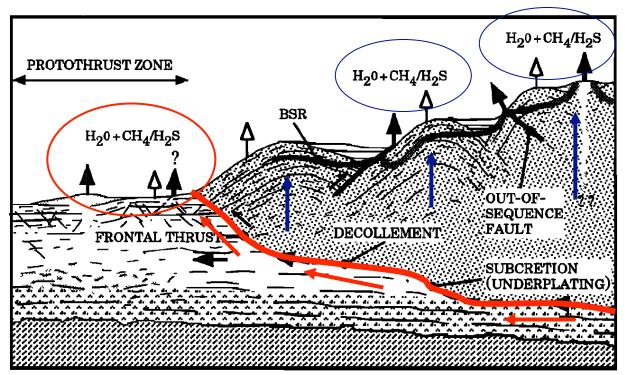
This tectonic burial creates overpressures that lead to fluid expulsion.





The fluids, are expelled along the decollement are primarily sourced from the underthrust sediments,

The fluids derived from compaction within the prism generally move upsection to the seafloor.



Fluid pressures at the decollement can be approximately lithostatic



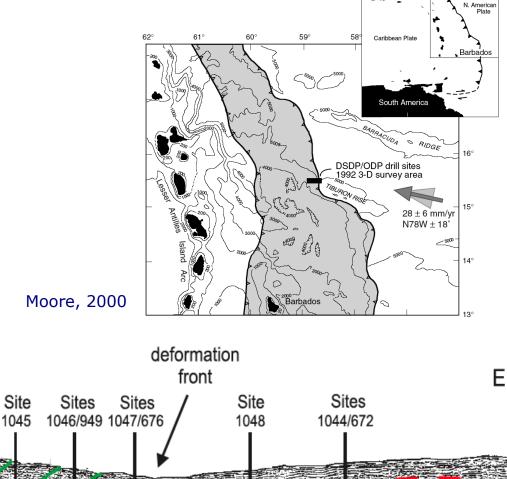
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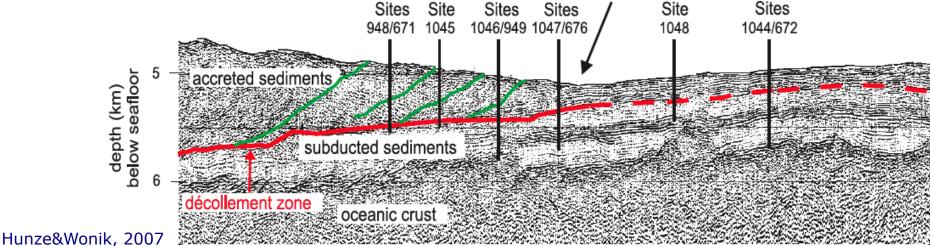


#### **Tectonic stress**

### **ODP Leg 171A. Barbados Accretionary Prism**

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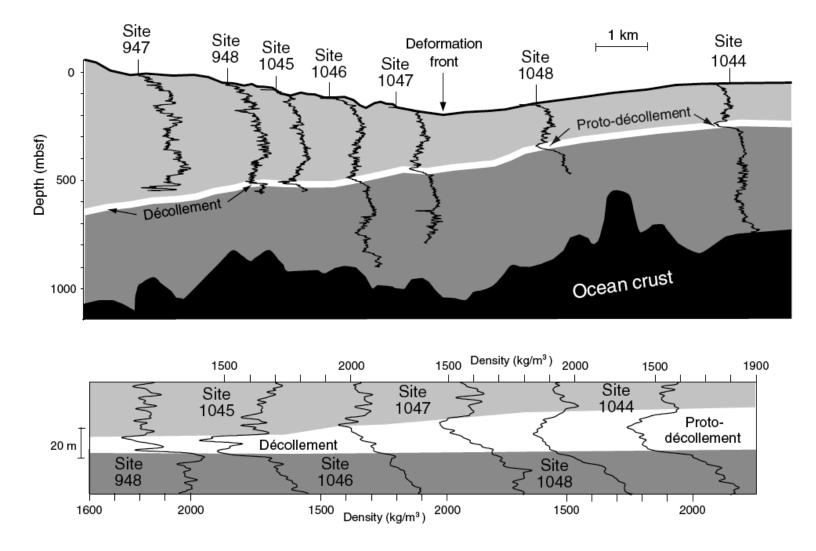








### **ODP Leg 171A. Barbados Accretionary Prism**

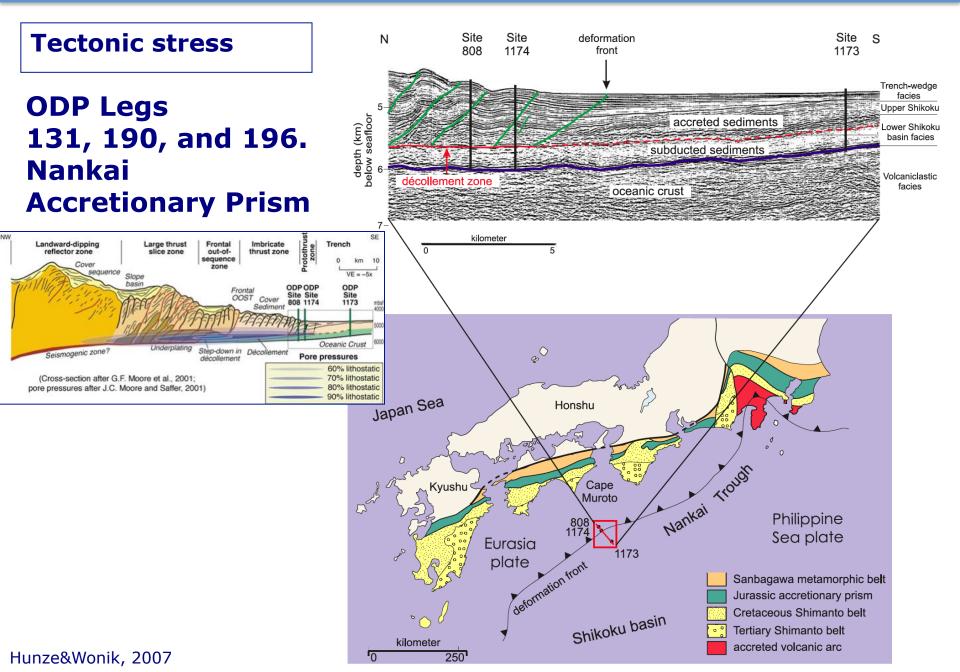


Moore, 2000.



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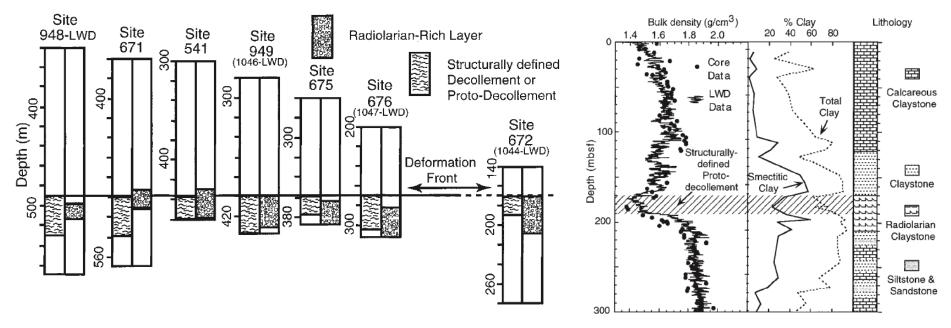








## ODP Leg 171A. Barbados Accretionary Prism



The decollement zone initiates in a low-density smectitic radiolarian claystone.

During underthrusting, the decollement zone consolidates heterogeneously due to shear-induced collapse of the radiolarian tests and clay fabric. This consolidation locally increases the pore pressure and facilitates underthrusting.

More et al., 1998





# Factors that determine excess pore water pressure and influence the consolidation state

### The most common factors are:

### Stress-related factors

- Rapid sedimentation rate
- Tectonic stress

### Fluid volume increase mechanisms

- Temperature increase
- Mineral transformation
- Hydrocarbon Generation

### Fluid movement mechanisms

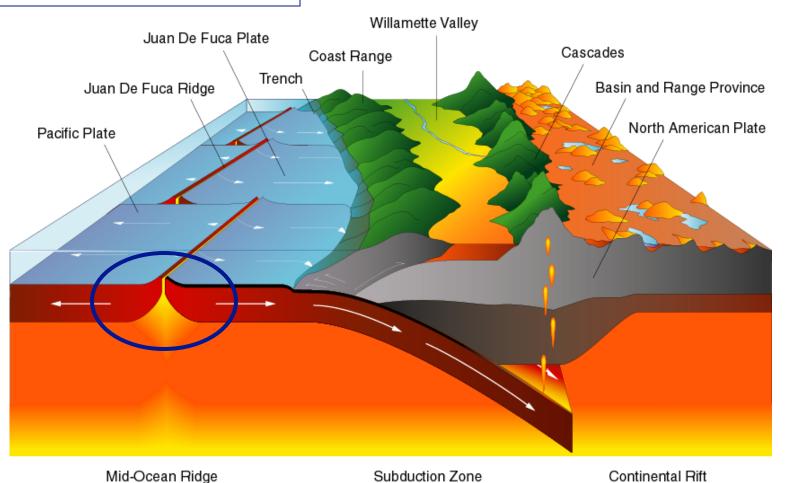
- Osmosis
- Hydraulic head
- Hydrocarbon buoyancy

(**Swarbrick and Osborne, 1998**. Bryant et al., 1974; Sangrey, 1977; Arthur et al., 1980; Demaison & Moore, 1980; Bryant et al., 1981).





### Heat transfer at mid-ocean ridges



# Mid ocean ridges (spreading centres) are present in all oceans. The spreading rate is fast in the Pacific, and slow in the Atlantic

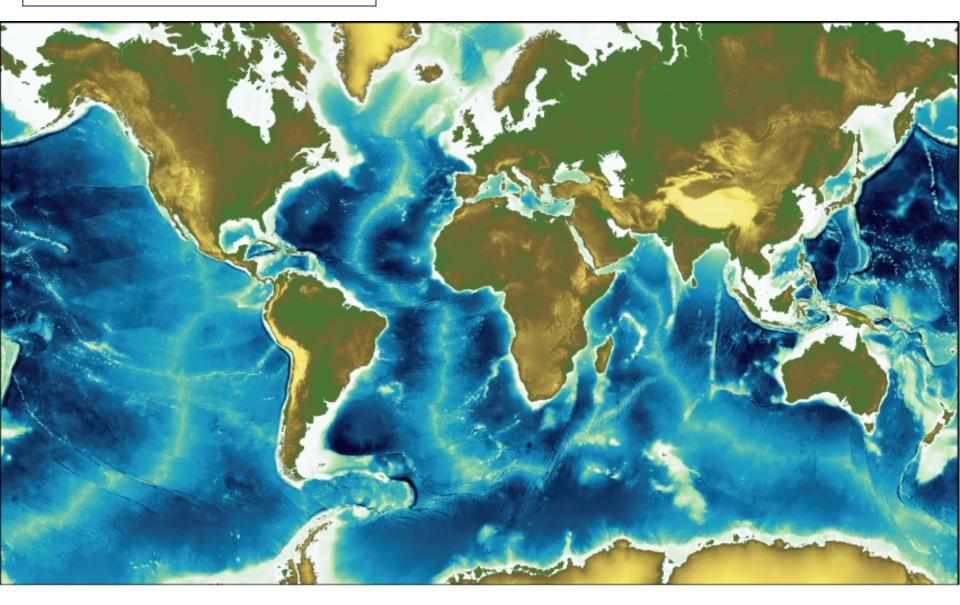


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#### **Temperature increase**

### Heat transfer at mid-ocean ridges







### **Aquathermal Expansion of water**

Compressibility: is a measure of the relative volume change of a fluid or solid as a response to a pressure (or mean stress) change.

Compressibility: 
$$\beta = -\frac{1}{V} \frac{\partial V}{\partial p}$$

where *V* is volume and *p* is pressure

At 0 °C the compressibility is 5.1 · 10<sup>-5</sup> bar<sup>-1</sup> As the pressure is increased the compressibility decreases, being 3.9 · 10<sup>-5</sup> bar <sup>-1</sup> at 0 °C and 1000 bar.

The low compressibility of water leads to them often being assumed as **incompressible**. The low compressibility of water means that even in the deep oceans at 4000 m depth, where pressures are  $4 \cdot 10^7$  Pa, there is only a 1.8% decrease in volume.

Fine and Millero, 1973

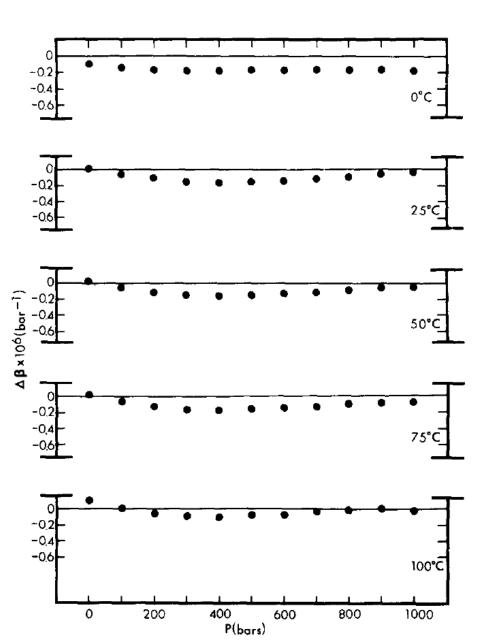


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#### **Temperature increase**

### **Compressibility of water**



Fine and Millero, 1973

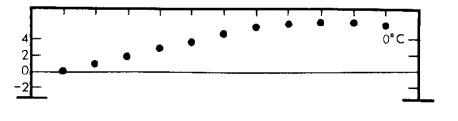


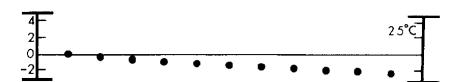
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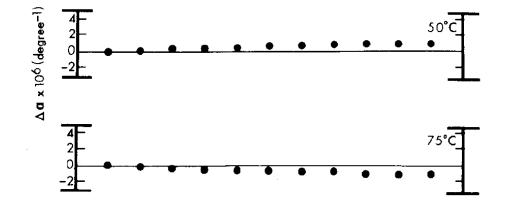


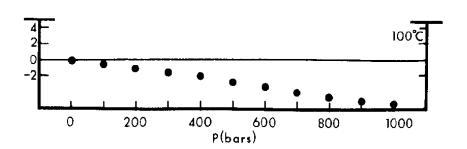
#### **Temperature increase**

### **Aquathermal Expansion of water**









### Thermal expansion:

 $\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)$ 

where V is volume and T is temperature

Typical value 5  $\cdot$  10<sup>-4</sup>  $^{\rm o}C^{\rm -1}$ 

Fine and Millero, 1973





If a body of water is **SEALED** in a vessel, the pressure will increase rapidly if temperature rises above +4°C.

E.g. Pressure increase of 55MPa from heating sealed water from 54 to 93°C (caused by a volume increase of 1.65%!)

The problem is that in nature, **absolute sealing of water in geological formations is practically impossible**. In addition, the reduction of viscosity of water during heating, facilitates its escape through pores and fractures even at low permeability.

Numerical modelling shows little overpressure in muds with extremely low permeability  $(3 \cdot 10^{-14} \text{ mD})$ 

**Only cementation** can provide a seal that is nearly absolute.





#### Sub-surface boiling and supercritical water

In deep sedimentary basins with total depths beyond 10 km, it is conceivable that pore waters can locally (and perhaps temporarily) achieve temperatures of **400** °C or more.

(assume an average geothermal gradient of 40°C km<sup>-1</sup>)

When the pressure is too great for water to boil (>221 bar for pure water, and >300 bar for normal seawater), it attains the supercritical phase, which is neither steam nor liquid, but something in between. (assume an hydrostatic gradient of 100 bar km<sup>-1</sup>)

Near the critical point on the boiling curve, the density of water changes rapidly, and is intermediate between that of liquid water (1 g cm<sup>-3</sup>) and low-pressure water vapour (<0.001 g cm<sup>-3</sup>).

At typical supercritical conditions, the density is approximately **0.3 g cm<sup>-3</sup>** 





### Sub-surface boiling and supercritical water

Hydrogen bonding is reduced in supercritical water (non-polar fluid)

Supercritcal water can be regarded as a non-polar fluid that is able to dissolve organic liquids (oils), but unable to dissolve common sea salts.

Supercritcal water is also highly **corrosive to silicate rocks**, a property that is of particular importance when studying deep hydrothermal systems and alteration of rocks and sediments.

Martin Hovland proposes that many deeply rooted piercement structures, like mud volcano, mud diapirs, asphalt volcanoes, can be triggered by supercritical water movement in rocks.

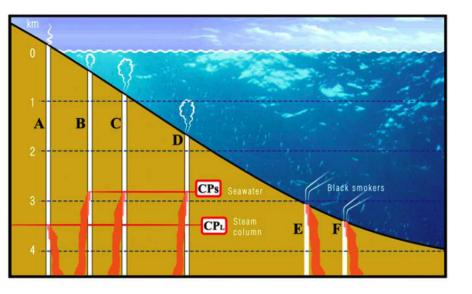
Hovland et al., 2006





#### Geological conditions for supercritical water flow:

- 1) A deep sedimentary basin >10 km deep.
- 2) An underlying crust, which is either relatively thin (hot), or which contains fault intersections with high heat-flow.
- 3) Excess water either within the crust or the sediments, which becomes exposed to the anomalous heat sources (at fault intersections).
- 4) Local anomalously high or increasing temperature gradients with depth.



CP = Critical Point

Column A shows the association between boiling fresh water and depth on land. The steam column forms above a deep-lying heat source (>374°C) and the CP occurs deeper than 3 km, because the density of the steam column is low.

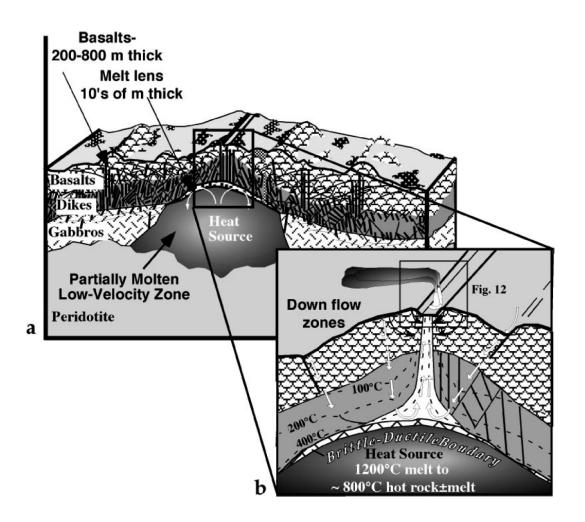
In the ocean, beneath a cold seawater column, above a deep-lying heat source (>405°C), the CP lies at around 2800m (pressure of about 300 bar). Colums B, C, D have a CP lying at this depth, even though the seafloor depth varies.

The two hot vents E, F have CPs at different depths, as they are both deeper than 2800m and the CP is defined by temperature (cooling by seawater) rather than by depth. These 'black smokers' invariably construct sulphide and silicate chimney structures formed by mineral precipitation as supercritical fluids are instantly cooled by seawater.









## Mantle-crust relationships beneath ridge crests.

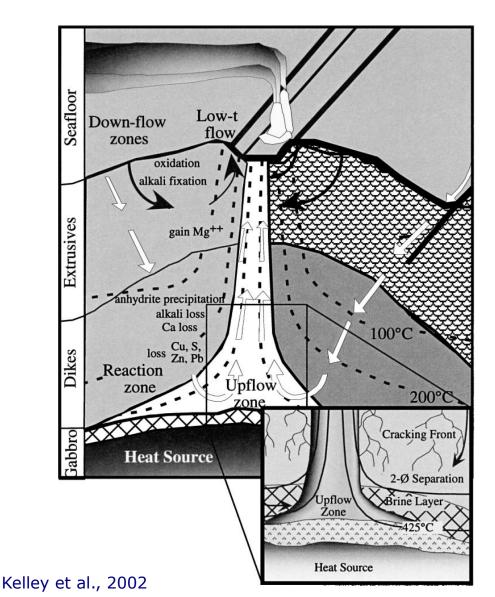
- (a) Crustal magma chambers, fed from melt percolating through the underlying mantle section, typically form at depths of 1–4 km below the seafloor.
- (b) Steep thermal gradients resulting from intrusion of 1200±C basaltic melt into cool, water-saturated and porous crustal rocks drive hydrothermal circulation beneath the spreading centers. Hightemperature limbs of the resultant hydrothermal cells focus metal-rich, acidic fluids onto the seafloor, which form sulfide deposits upon mixing with cold, oxygenated seawater.



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#### **Temperature increase**



#### Heat transfer at mid-ocean ridges

Schematic showing chemical reactions and mineral precipitation associated with downwelling recharge systems, low-temperature shallow circulation, and deep penetration by hydrothermal fluids into the reaction zone.

At the base of many mid-ocean ridge hot springs, the seawater-derived fluids undergo either boiling or condensation. If condensation occurs for prolonged time periods, a brine layer may develop deep within the crust. These fluids may be expelled during waning of hightemperature hydrothermal flow.

Fluid penetration is believed to occur during downward migration of small fracture networks and cooling of the crust along a cracking front, which allows fluids to have continual access to hot, fresh rock.





- Smectite dehydratation
- Smectite to Illite Transformation
- Gypsum to Anhydrite Dehydratation



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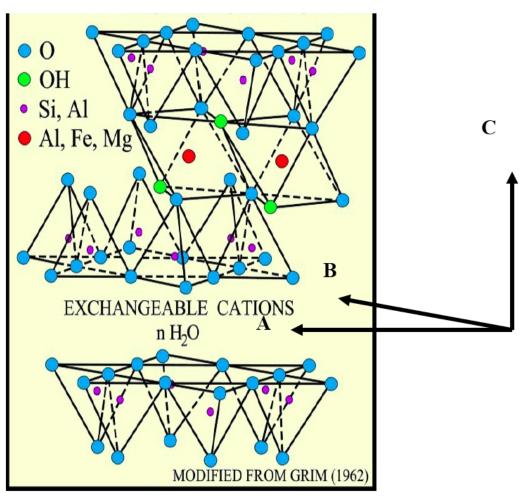


#### **Mineral transformation**

### Smectite dehydratation

A significant feature of the smectite group is its very high surface area. These clay platelets are held together by a weak electromagnetic force (Van der Waal's bonds), and there is a considerable amount of area to which up to ten layers of water can bond. The result is a low density "swelling clay".

### Under normal hydrostatic conditions smectite contains 2 or 3 layers of water.



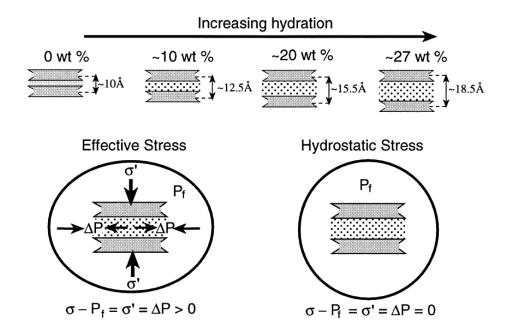




Smectite dehydratation

### Smectite changes with burial. Effect of lithostatic stress.

1) Increasing pressure will drive out the loosely bound water



Smectites can partially dehydrate from 18.5 Å to 15.4 Å hydrates when they are subjected to effective mineral framework stresses above 1.3±0.3 MPa (sort of squeezing of interlayer water out of the mineral structure)

Fitts and Brown et al., 1999





### Smectite dehydratation

### **Role of temperature**

- 1) Under stress (burial) at temperature of about 60°C, smectite molecules will lose interlayer water except the last two layers.
- 2) With temperature of about 100°C one the penultimate layer will be displaced.
- 3) A further rise in temperature to 172° 192° C is required to drive off the last layer, which is very closely bound between the clay plates.

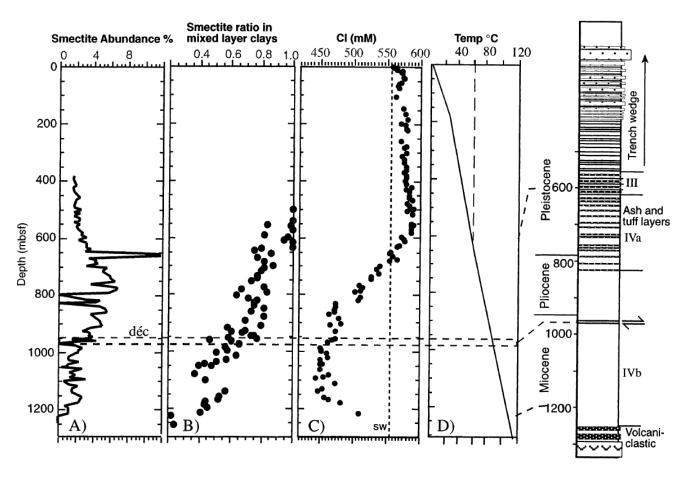
Although the initial dewatering may actually cause some overpressures, the resulting extra hydraulic pressure will also tend to inhibit further dewatering. Therefore, under most conditions the simple dewatering process will not lead to excessive overpressure (**volume increase of about 4%**), since there is a negative feedback loop at work.

Iain Hillier, Baker Hughes INTEQ





### Smectite dehydratation



Possibility that the observed low-Cl anomaly is a compound effect of both lateral flow and in situ smectite dehydration.

Brown et al., 2001

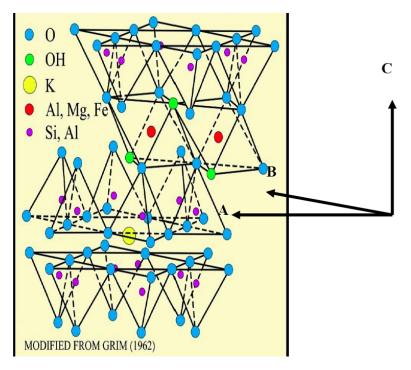




• Smectite to Illite Transformation

During Burial, smectite alters chemically to produce illite

Smectite + (Al, K) - (Na, Ca, Mg, Fe, Si, water) >>>> illite







- Smectite to Illite Transformation
- The reaction is kinetically controlled.
- It usually happens at temperature range of 70°C 150°C
- It often accompanies the loss of the penultimate water layer of smectites.
- It has been shown that in order for the transformation to occur Potassium **(K) ions are required** in the interstitial fluids. These come from K-Feldspars
- Illites do not have the same capacity to adsorb water as smectities.
- The **threshold temperature** for the loss of the penultimate water layer is roughly the same at which **hydrocarbons are generated**.





• Smectite to Illite Transformation

The volumetric change of Smectite to Illite is unknown.

Some models say  $\Delta V = + 23-25 \%$ 

It is a fact that overpressure is often detected in wells in correspondence with such diagenetic transformation.

Consequences during the transformation :

- Compressibility increases
- Overpressure
- Disequilibrium compaction
- Perhaps reduction of permeability by silica cementation





Gypsum to Anhydrite Dehydratation

Heating gypsum to between 100 °C and 150 °C partially dehydrates the mineral by driving off approximately 75% of the water contained in its chemical structure.

The temperature and time needed depend on ambient partial pressure of  $H_2O$ .

The reaction for the partial dehydration is:

```
CaSO_4 \cdot 2H_2O + heat >>> CaSO_4 \cdot nH_2O + nH_2O
```

Anhydrite:  $CaSO_4 \cdot nH_2O$ , where n is in the range 0.5 to 0.8.

The temperature of the reaction depends on the physical and geochemical environments





Gypsum to Anhydrite Dehydration

Geological factors:

- Thermal conductivity of the overlying rock
- Basal heat flow
- Porosity
- Sedimentation rate

Geochemical factors:

- Activity of pore water
- Pore fluid pressure

Jowett et al., 1993





**Hydrocarbon** is an organic compound consisting entirely of hydrogen and carbon.

"**Impure**" hydrocarbons include bonded compounds or impurities of sulphur or nitrogen

• 1 **Saturated hydrocarbons** (**alkanes**) are the most simple of the hydrocarbon species and are composed entirely of single bonds and are saturated with hydrogen; they are the basis of petroleum fuels and are either found as linear or branched species of unlimited number. The general formula for saturated hydrocarbons is  $C_n H_{2n+2}$ .

• 2 **Unsaturated hydrocarbons** have one or more double or triple bonds between carbon atoms. Those with one double bond are called alkenes, with the formula  $C_nH_{2n}$  (assuming non-cyclic structures). Those containing triple bonds are called alkynes.

• 3 **Cycloalkanes** are hydrocarbons containing one or more carbon rings to which hydrogen atoms are attached. The general formula for a saturated hydrocarbon containing one ring is  $C_n H_{2n}$ 

• 4 **Aromatic hydrocarbons**, also known as arenes which have at least one aromatic ring





### Natural gases (alkanes gases )

METHANE  $CH_4$ ETHANE  $C_2H_6$ PROPANE  $C_3H_8$ BUTANE  $C_4H_{10}$ 

**METHANE**: OXYDATION OF ORGANIC MATTER BY ANAEROBIC BACTERIA (BIOGENIC)

C<sub>2+</sub> GASES: THERMAL MATURATION OF ORGANIC MATTER (THERMOGENIC)





# IN NATURAL GAS THERE ARE TWO TYPES OF METHANE:

# Biogenic Methane

Biogenic methane is produced as an end product of the metabolism of a diverse group of obligate **anaerobic archaea** (killed by even traces of oxygen), generally known as **methanogens**.

Methanogens live in the shallow geosphere such as **marine and lacustrine sediments** (sub-bottom depth less than 1 km, temperature less than 80°C).



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#### **Hydrocarbon Generation**

In the absence of light, photosynthesis cannot occur. Respiration makes use oxygen of dissolved in water with microbial mediation.

Organic matter (preferably proteins and carbo-hydrates) is decomposed trough hydrolysis by micro-organisms, that produce sugars and aminoacids that more evolved organisms can use.

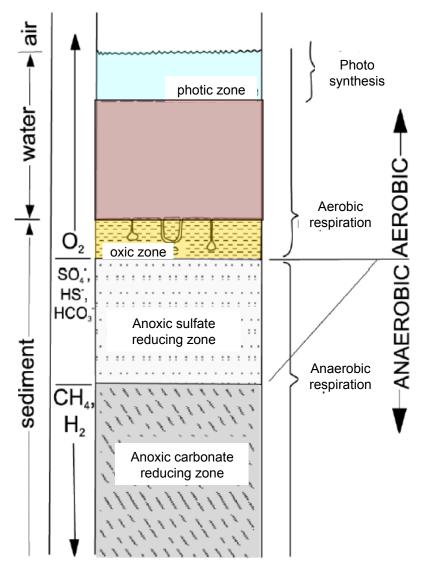
Aerobic respiration in the interstitial fluids of the uppermost sediments can cause **oxygen depletion** in pore water (usually the exchange of fluids between pores and water column is negligible due to low permeability).

Respiration then uses oxygen from Mn-Oxides, Nitrates and Iron-Oxides (**sub oxic Zone**)

Aerobic respiration is then replaced by **anaerobic fermentation**, that is the microbial reduction of the sulfate ion (SO<sub>4</sub>) with release of S<sup>-</sup> ions and production of  $H_2S$ , and  $CO_2$ .

When all the Sulfate ion has been used, the Archea begin to produce methane  $(CH_4)$  from the remaining organic matter.

The biogenic production of methane continues until the temperature of 75-80°C is reached.





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#### **Hydrocarbon Generation**

seafloor

0

1. Aerobic (respiration):  $CH_2O + O_2 = CO_2 + H_2O$ 

2. Sub-oxic zone

3. Anoxic (sulfate reducing) zone:  $CH_2O + SO_4 = CO_2 + H_2S$ 

4. Methanogenesis:  $CH_2O = CO_2 + CH_4$ 







		Energetically
Oxidation by dissolved Oxygen		
$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138 O_2 \rightarrow$	-3190 kJ/mol	most favorable
106 CO₂ + 16 HNO₃ + 122 H₂O + H₃PO₄		
Oxidation by Manganese-Oxides		
$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 236 \text{ MnO}_2 \rightarrow$	-3090 kJ/mol	
236 Mn <sup>2+</sup> + 106 CO₂ + 8 N₂ + 366 H₂O + H₃PO₄		
Oxidation by Nitrate		
$(\rm CH_2O)_{106}(\rm NH_3)_{16}(\rm H_3PO_4) + 84.4\ \rm HNO_3 \rightarrow$	-2750 kJ/mol	
106 CO <sub>2</sub> + 42.2 N <sub>2</sub> + 16 NH <sub>3</sub> + 148.4 H <sub>2</sub> O + H <sub>3</sub> PO <sub>4</sub>		
Oxidation by Iron-Oxides		
$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 212 \text{ Fe}_2O_3 + 848 \text{ H}^+ \rightarrow$	-1410 kJ/mol	
424 Fe <sup>2+</sup> + 106 CO <sub>2</sub> + 16 NH <sub>3</sub> + 530 H <sub>2</sub> O + H <sub>3</sub> PO <sub>4</sub>		
Oxidation by Sulfate		
$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 53 SO_4^{2-} \rightarrow$	-380 kJ/mol	•
106 CO₂ + 16 NH₃ + 53 S <sup>2-</sup> + 106 H₂O + H₃PO₄		
Methane Fermentation		
$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) \rightarrow$	-350 kJ/mol	♥
53 $CO_2$ + 53 $CH_4$ + 16 $NH_3$ + $H_3PO_4$		
		least favorable



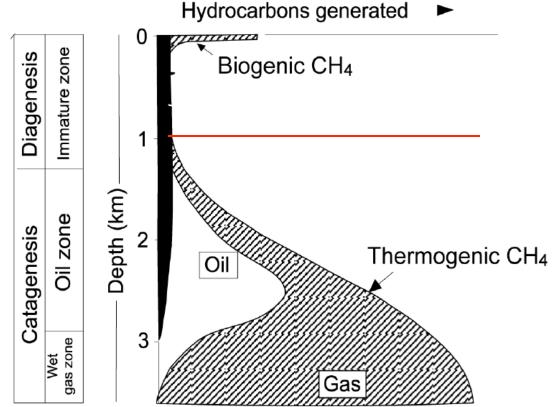


# Thermogenic Methane

#### Deeper in the sediment, thermal alteration of organic matter generates

organic matter generates methane and higher order hydrocarbons by catagenesis.

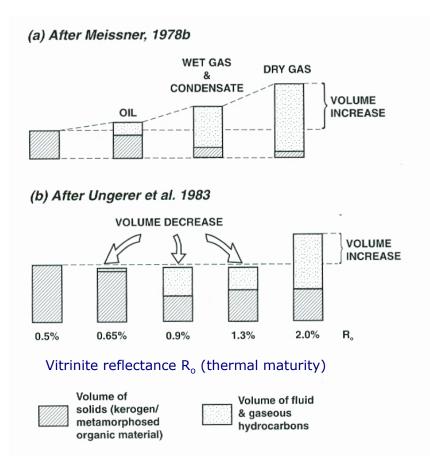
Catagenesis occurs within the temperature range of 50° to 200° C, and gases (methane to butane) are produced at rates that are proportional to temperature.



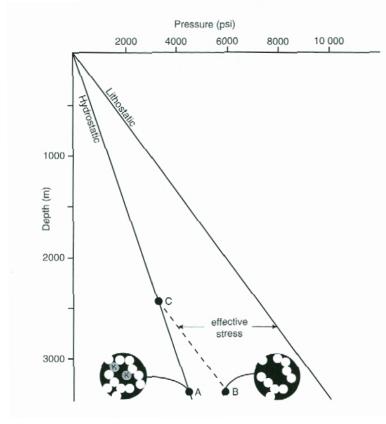
Tissot and Welte, Petroleum Formation and Occurrence, Springer-Verlag, 1992.

#### università degli studi ditrieste Dipartimento di Matematica e Geoscienze





# Estimation of volume change when Type II Kerogene matures to produce oil and gas.



Estimation of the overpressure created by disequilibrium compaction in a maturing source rock. Half of the initial Kerogene (10% by volume) is transformed into liquid products, thereby increasing the porosity from 13 to 18%. The effect is to transfer the part of the overburden supported by the original kerogene onto the pore fluid.

Swarbrick and Osborne, 1998





# Factors that determine excess pore water pressure and influence the consolidation state

### The most common factors are:

### Stress-related factors

- Rapid sedimentation rate
- Tectonic stress

### Fluid volume increase mechanisms

- Temperature increase
- Mineral transformation
- Hydrocarbon Generation

### Fluid movement mechanisms

- Osmosis
- Hydraulic head
- Hydrocarbon buoyancy

(Swarbrick and Osborne, 1998. Bryant et al., 1974; Sangrey, 1977; Arthur et al., 1980; Demaison & Moore, 1980; Bryant et al., 1981).





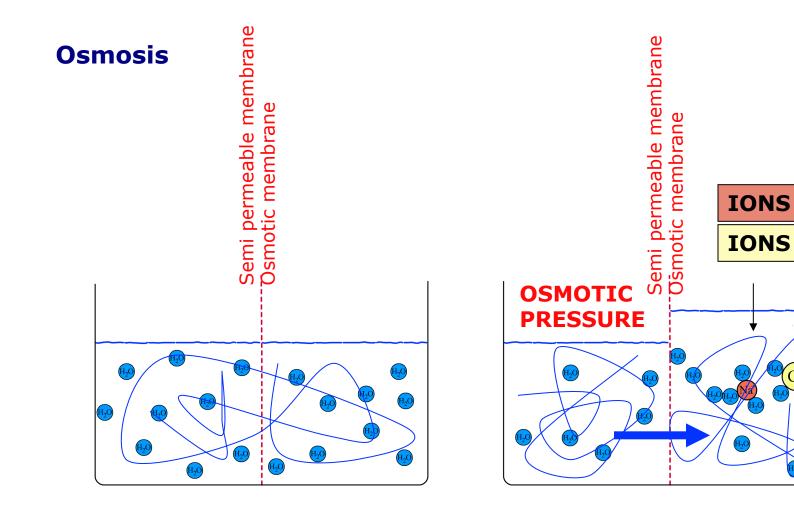
### Osmosis

**Osmosis** is the diffusion of a solvent (e.g. water) through a membrane (osmotic membrane, or semi-permeable membrane) from a solution of low solute concentration to a solution with high solute concentration, up a solute concentration gradient.

A solvent moves without input of energy, across a semi permeable membrane (permeable to the solvent, but not the solute) separating two solutions of different concentrations.











#### Osmosis

As a consequence of pore water expulsion due to consolidation, pore water salinity often increases with subsurface depth in a sedimentary basin due to

#### **REVERSE OSMOSIS**.

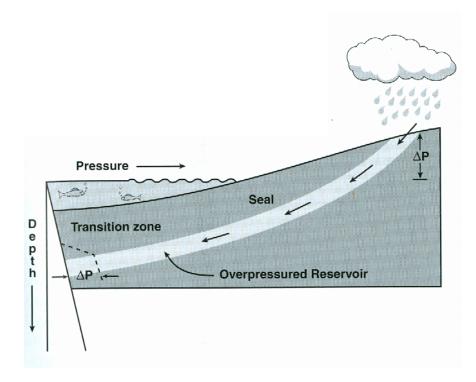
Reverse osmosis occurs when a pressure head forces brines through an osmotic membrane, allowing the solvent to pass and retaining the solute.

Reverse osmosis is therefore considered as a possible sink of Na $^+$  and Cl $^+$  ions from seawater.





### Hydraulic head

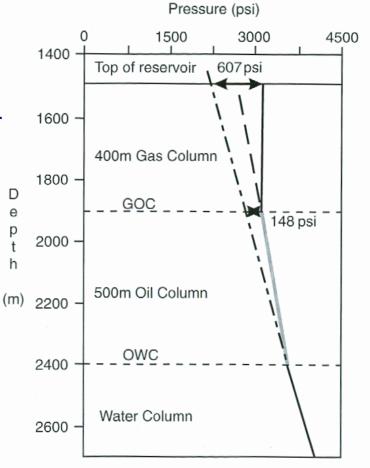






### Hydrocarbon buoyancy

- All gasses and oils have lower density than water
- They have a lower pressure gradient than waterBecause overpressure is an excess pressure
- above hydrostatic for a given depth,
- There is always a certain amount of overpressure ina a reservoir.
- This is a **local** overpressure







### **APPENDIX. PRESSURE UNITS CONVERSION**

- The SI unit for **pressure** is the Pascal (Pa)
- 1 Pa = one Newton per square metre ( $N \cdot m^{-2}$  or kg $\cdot m^{-1} \cdot s^{-2}$ ).

Non-SI measures such as *pound* per square inch (**psi**) and *bar* 

1 Pa =  $10^{-5}$  bar =  $145.04 \cdot 10^{-6}$  psi

1 bar = 100,000 Pa = 14.504 psi

1 psi = 6,894.76 Pa =  $68.948 \cdot 10^{-3}$  Bar

1 bar = 0.98692 atmospheres





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