Hashemite University
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Economic Geology (111201491)
Part3: Sedimentary Ore-Forming Processes

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A. Surficial Processes

Once metals have been concentrated in the Earth's crust and then exposed at its surface, they are commonly subjected to further concentration by chemical weathering.

There are several deposit types where the final enrichment stage is related to surficial weathering processes. Some of these deposit types are economically very important and contain ores, such as **bauxite**, that do not occur in any other form.

Ore–forming processes in the surficial environment are intimately associated with pedogenesis, or soil formation

Many different metals are enriched in the surficial environment, include Al, Ni, Mn, Fe, Cu, Au, PGE, and U in laterite soil.

In addition, **clay deposits**, **calcretes**, and associated **uranium** mineralization, as well as the supergene enrichment of **Cu** in porphyry–type deposits

Principles Of Chemical Weathering

Weathering can be subdivided into three processes:

1. **Dissolution** of rock material and the transport/ removal of soluble ions and molecules by aqueous solutions.
2. **Production** of new minerals, in particular clays, oxides and hydroxides, and carbonates.
3. **Accumulation** of unaltered (low solubility) residual material such as silica, alumina, and gold.

The main chemical processes that contribute to weathering include **dissolution, oxidation, hydrolysis, and acid hydrolysis**.

Chemical Weathering

when rocks arrive near the surface as a result of uplift and erosion, they encounter conditions very different from those under which they originally formed:

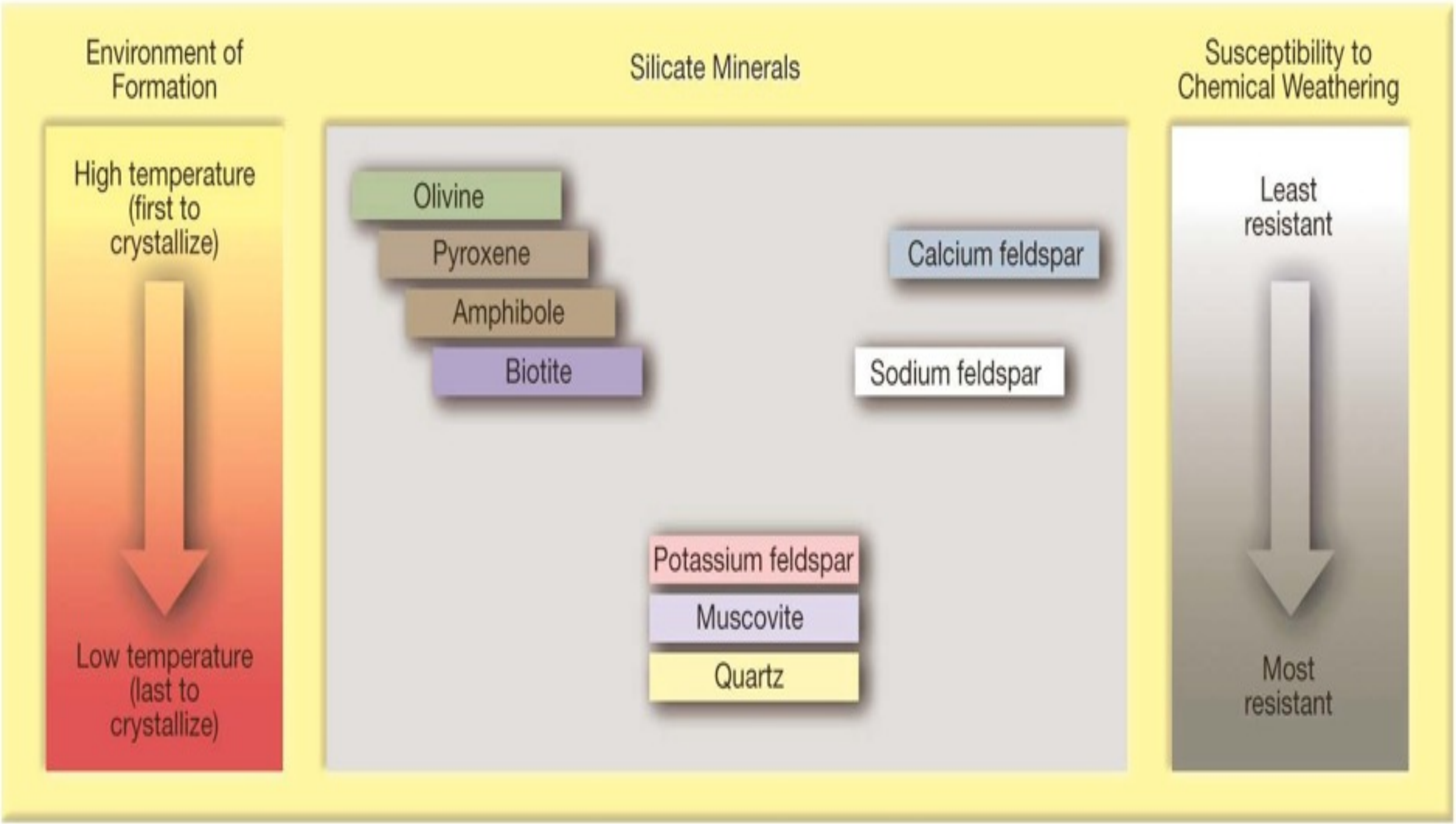
- Lower Temperature (Near the surface T = –20 to 50°C)
- Lower Pressure (Near the surface P = 1 to several hundred atmospheres)
- Higher free water (there is a lot of liquid water near the surface, compared with deep in the Earth)
- Higher free oxygen (although O_2 is the most abundant element in the crust, most of it is tied up in silicate and oxide minerals – at the surface there is much more free oxygen, particularly in the atmosphere).

Because of these differing conditions, minerals in **rocks react with their new environment to produce new minerals that are stable under conditions near the surface**.

Minerals that are stable under P, T, H_2O, and O_2 conditions near the surface are, in order of most stable to:

- Iron oxides, Aluminum oxides – such as hematite Fe_2O_3, and gibbsite $Al(OH)_3$.
- Quartz*
- Clay Minerals
- Muscovite*
- Alkali Feldspar*
- Biotite*
- Amphiboles*
- Pyroxenes*
  Ca–rich plagioclase*
- Olivine*

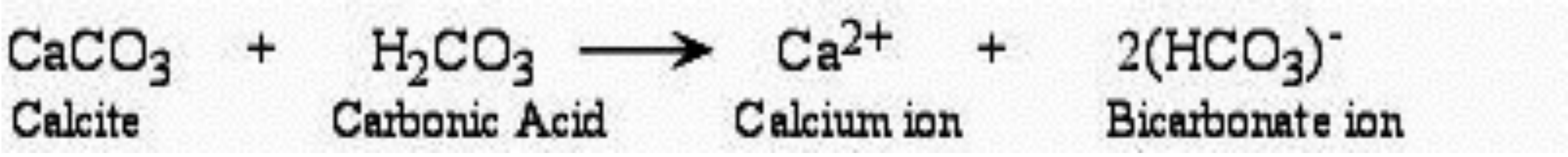
Controls on rates of weathering



The main agent responsible for chemical weathering reactions is water and weak acids that has abundant free H^+ ions in water (carbonic acid H2CO3).

1. Dissolution and hydration

Certain natural materials such as halite (NaCl) and other evaporitic minerals, as well as the carbonate minerals (calcite, siderite, dolomite, etc.), tend to dissolve relatively easily and completely in normal to acidic groundwaters.



$$CaCO_3 + H_2CO_3 \longrightarrow Ca^{2+} + 2(HCO_3)^-$$

The relative solubilities of different elements in surface waters depends on ionic potential (the ratio of ionic charge to ionic radius).

Cations with low ionic potentials (<3) are easily hydrated and are mobile under a range of conditions, although they will precipitate under alkaline conditions and are readily adsorbed by clay particles.

Anions with high ionic potentials (>10) form soluble complexes and dissolve easily, but will precipitate together with alkali elements.

Intermediate values (ionic potentials between 3 and 10) tend to be relatively insoluble and precipitate readily as hydroxides.

Over the **pH** range at which most groundwaters exist (5-9), silicon is more soluble than aluminum

chemical weathering will tend to leach Si, leaving behind a residual concentration of immobile Al and ferric oxides / hydroxides.

This is typical of formation **<u>lateritic</u>** soil profiles, contain concentrations of **bauxite** (aluminum ore) and **Ni**.

Hydration of minerals can also occur directly

Once In aqueous solutions water molecules cluster around ionic species as a result of their charge polarity and this contributes to the efficacy of water as a solvent of ionic compounds.

good examples of which include the formation of gypsum ($CaSO_4 . 2H_2O$) from anhydrite ($CaSO_4$) and the incorporation of water into the structure of clays such as montmorillonite.

2. **Hydrolysis and acid hydrolysis**: chemical reaction in which one or both of the **O-H bonds** in the water molecule is broken

$$Si^{4+} + 4H_2O \Leftrightarrow H_4SiO_4 + 4H^+$$

aluminosilicate minerals such as feldspar, and also the liberation of silicon as <u>silicic acid</u> into solution

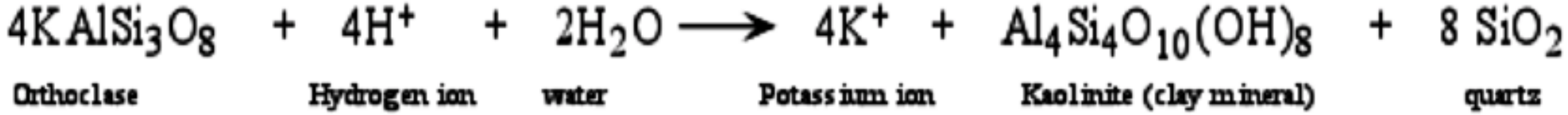
The hydrolysis of aluminum, yielding an aluminum hydroxide precipitate,

$$Al^{3+} + 3H_2O \Leftrightarrow Al(OH)_3 + 3H^+$$

results concentration of aluminum (as **gibbsite** $Al(OH)_3$) and ferric iron (as **goethite** $FeO(OH)$) in lateritic soils.

acid hydrolysis: refers to the processes whereby silicate minerals break down in the weathering zone

activated mineral surfaces react with acids (H+ ions) in solution.



$$\underset{\text{Orthoclase}}{4KAlSi_3O_8} + \underset{\text{Hydrogen ion}}{4H^+} + \underset{\text{water}}{2H_2O} \longrightarrow \underset{\text{Potassium ion}}{4K^+} + \underset{\text{Kaolinite (clay mineral)}}{Al_4Si_4O_{10}(OH)_8} + \underset{\text{quartz}}{8\,SiO_2}$$

This process displaces metallic cations from the crystal lattice, which then either go into solution or precipitate.

3. Oxidation

chemical processes that involve the transfer of electrons.

The element most commonly oxidized in the surficial environment is probably **iron**, which is converted from the ferrous (Fe^{2+}) to the ferric (Fe^{3+}) valence state by oxidation (loss of electrons).

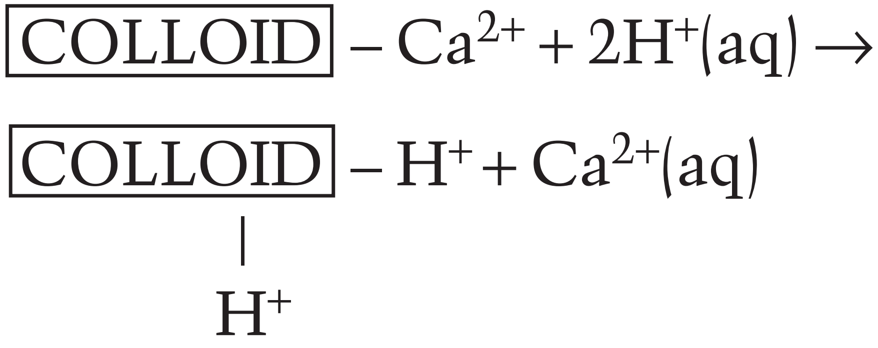
$$\underset{\text{Pyroxene}}{3Fe^{+2}SiO_3} + \underset{\text{Oxygen}}{1/2O_2} \longrightarrow \underset{\text{Magnetite}}{Fe_3O_4} + \underset{\text{Quartz}}{3SiO_2}$$

The presence of iron in minerals such as olivine and the orthopyroxenes is one of the main reasons why they are so unstable in the weathering zone.

Cation exchange

The Clay particles are often colloidal in nature, characterized by a net negative surface charge brought about by the replacement of Si^{4+} by Al^{3+} in the clay lattice.

The negative charge is neutralized by adsorption of cations onto the surface of the colloids.



$$\boxed{\text{COLLOID}} - \text{Ca}^{2+} + 2\text{H}^{+}(\text{aq}) \rightarrow \underset{\text{H}^{+}}{\underset{|}{\boxed{\text{COLLOID}}}} - \text{H}^{+} + \text{Ca}^{2+}(\text{aq})$$

The adsorbed cations may be exchanged for others when water passes through weathered material containing clay colloids and this has an effect on mineral stabilities as well as the nature of leaching and precipitation in regolith profiles.

Type Of Surficial Ore Deposits

1. Lateritic Deposits

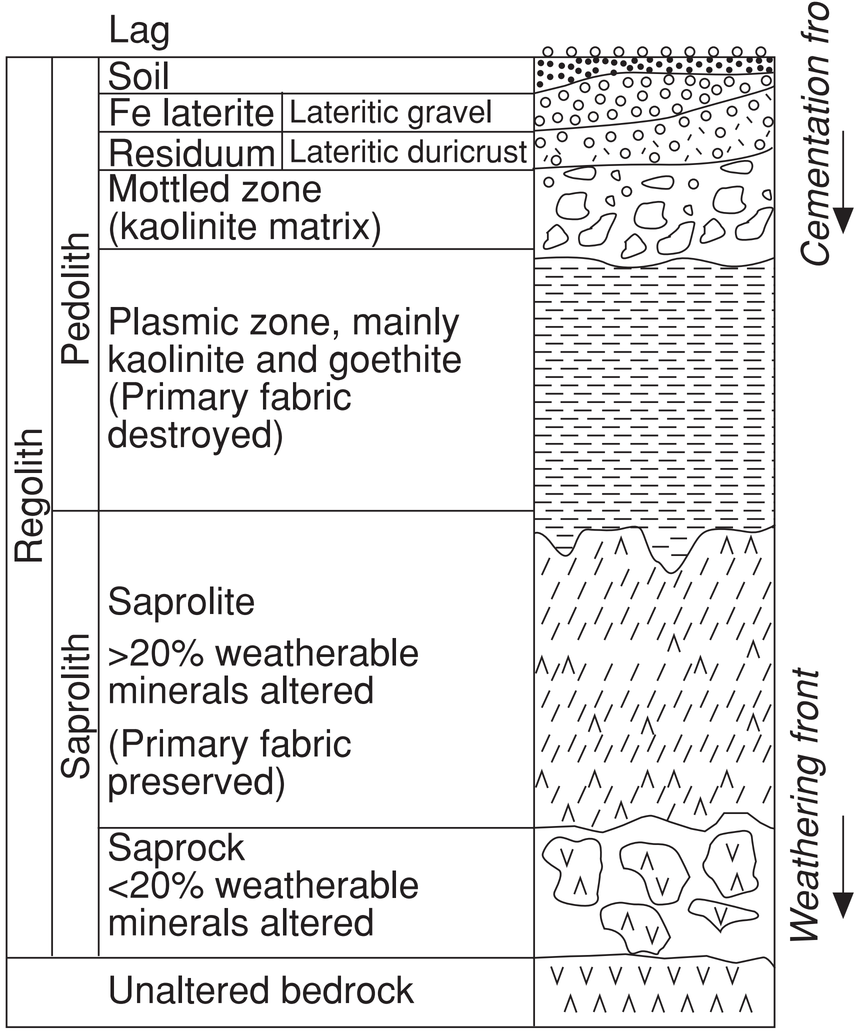
- 6 – 20 m thick on top of mafic and ultramafic rocks.
- Nodular, red to yellow or brown hematite and goethite with as much as 20% Al_2O_3.
- Examples: Guinea, Guyana, Indonesia, Cuba and the Philippines.

Product of intense weathering in humid, warm, intertropical regions of the world, and is typically rich in kaolinitic clay as well as Fe– and Al–oxides oxyhydroxides.

Laterites are economically important as they represent the principal environment within which **aluminum ores** (**bauxite**) occur.

They can also contain significant concentrations of other metals such as **Ni, Mn, and Au, as well as Cu and PGE**.

(a) Generalized lateritic regolith profile



(b) Element mobility in typical lateritic profiles

Host minerals	Leached	Partly retained (in secondary minerals)
Released in the mottled and ferruginous zones		
Aluminosilicates (muscovite, kaolinite) iron oxides; gold	K, Rb, Cs Trace elements; Au	Si, Al (kaolinite)
Released in upper saprolite		
Aluminosilicates (muscovite)	Cs, K, Rb	Si, Al (kaolinite)
Ferromagnesians (chlorite, talc, amphibole)	Mg, Li	Fe, Ni, Co, Cr, Ga, Mn, Ti, V (Fe and Mn oxides)
Smectite clays	Ca, Mg, Na	Si, Al (kaolinite)
Released in the lower saprolite		
Aluminosilicates	Ca, Cs, K, Na, Rb	Si, Al (kaolinite); Ba (barite)
Ferromagnesians (pyroxene, olivine amphiboles, chlorite, biotite)	Ca, Mg	Fe, Ni, Co, Cr, Ga, Mn, Ti, V (Fe and Mn oxides)
Released at weathering front		
Sulfides	As, Au, Cd, Co, Cu, Mo, Ni, Zn, S	As, Cu, Ni, Pb, Sb, Zn, (Fe oxides; sulfates, arsenates, carbonates, alunite-jarosite)
Carbonates	Ca, Mg, Fe, Mn, Sr	

Figure 4.3 (a) A generalized lateritic regolith profile showing the different horizons and the terminology used in their description. (b) Generalized pattern of element mobility in lateritic regoliths (after Butt *et al.*, 2000).

Bauxite ore formation

Bauxitic ore, in the form of the minerals gibbsite/ boehmite and diaspore, is the principal source of aluminum metal.

The accumulation of an alumina–rich due to relatively high Si mobility compared to Al this results in incongruent dissolution of minerals such as felspar and kaolinite, where Si is leached in preference to Al, yielding a gibbsite–like residue.

$$\begin{aligned}&\text{feldspar} - (\text{loss of Si}) \rightarrow \text{kaolinite} - (\text{loss of Si})\\&\rightarrow \text{gibbsite}\ (\mathrm{Al(OH)_3})\end{aligned}$$

Seasonal climatic variations are considered important to the formation of bauxitic ores as the alternation of wet and dry promotes fluctuations in groundwater levels and, hence, dissolution and mass transfer.

High quality bauxitic ores require that both Fe and Si remove

The huge bauxite deposits of **Jamaica** represent a good example of the controls involved in the formation of aluminum ores.

Nickel laterites

Laterites that are developed on ultramafic rocks containing abundant olivine and orthopyroxene and, hence, with high Ni contents e. g. New **Caledonia**.

The alteration of olivine is by hydration to amorphous silica, serpentine, and limonite, with the serpentine able to accommodate as much or more of the Ni as the original olivine.

$$\underset{\text{olivine}}{4(Fe_2,Mg_2)SiO_4} + 8H^+ + 4O_2 \Leftrightarrow$$

$$\underset{\text{smectite}}{(Fe_2,Mg_3)Si_4O_{10}(OH)_2} + \underset{\text{goethite}}{6FeO(OH)} + 5Mg^{2+}$$

Gold in laterites

Gold occurs in the upper pedolithic portions of laterite weathering zones in many parts of the world, including **Brazil, west Africa and Western Australia**

This gold takes many forms, ranging from large, rounded **nugget-like particles** and gold **dendrites** in cracks and joints, to **small crystals** in pore spaces.

At low pH and high Eh, and in the presence of Cl^- ions, gold in the surficial environment can go into solution as an $AuCl_4^-$ complex

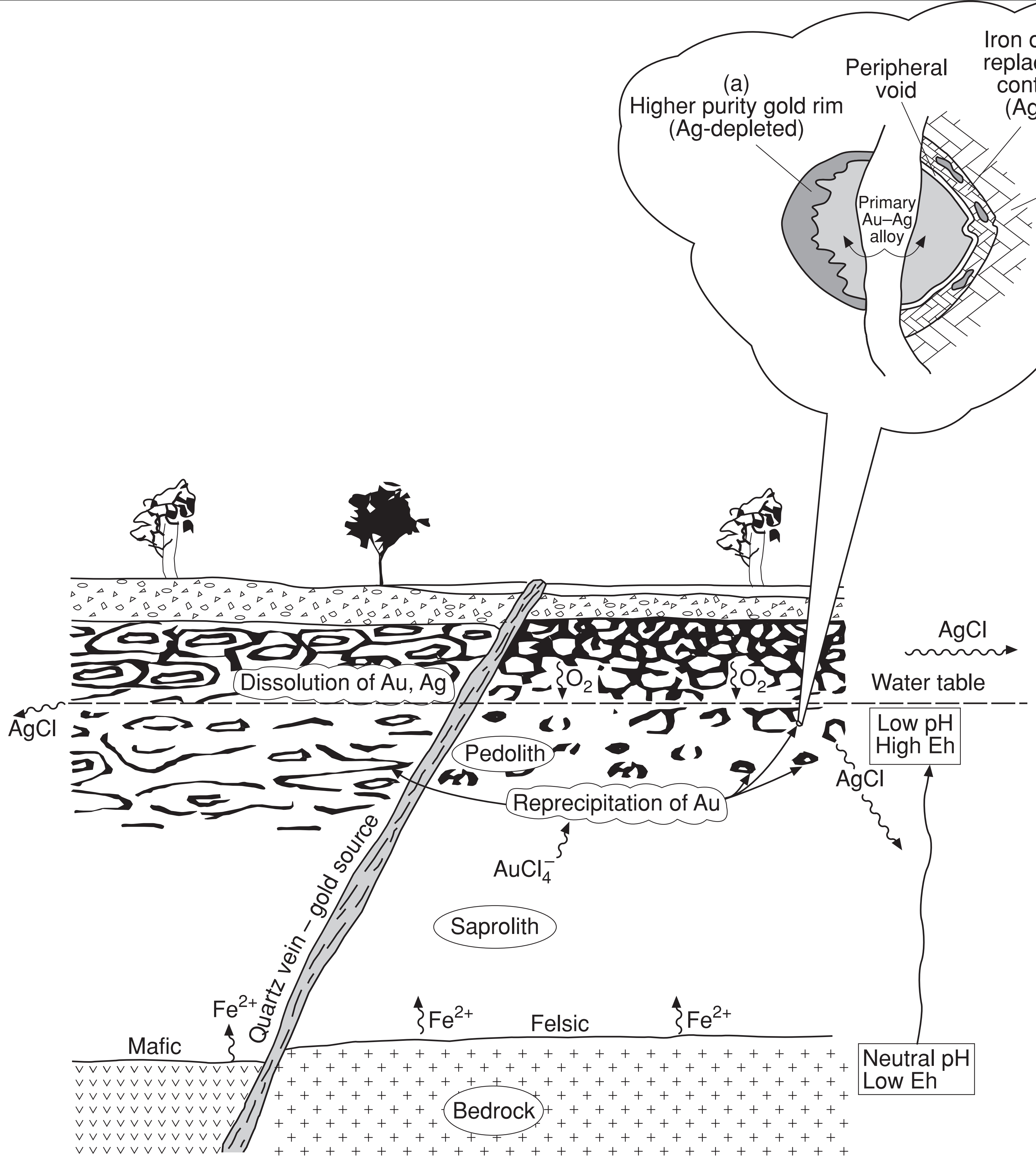


Figure 4.6 The nature and characteristics of gold and silver redistribution in a typical lateritic profile. The inset diagram shows two mechanisms whereby a primary Au–Ag alloy particle could be broken down during lateritization and silver preferentially removed (modified after Mann, 1984; Nahon *et al.*, 1992).

Gold will precipitate with only a slight decrease in Eh under mildly reducing conditions

$$\begin{aligned}&AuCl_4^- + 3Fe^{2+} + 6H_2O \Leftrightarrow \\ &Au + 3FeOOH + 4Cl^- + 9H^+\end{aligned}$$

Type Of Surficial Ore Deposits

2. CLay Deposits

Clay minerals are volumetrically the most abundant product of weathering and either occur in situ or have been transported to a site of deposition.

They are also economically important and used for a variety of industrial applications including paper, ceramics, filtration, and lubricants.

Origin: clay mineral assemblages ultimately form from both felsic and mafic rocks

The more important clay minerals considered here include

- Kaolinite,
- Illite and
- Smectite group (including montmorillonite).

Kaolinite is formed under humid conditions by acid hydrolysis of feldspar– bearing rocks.

e.g., kaolinite(china clay) deposits of Cornwall in south england

Illite forms under more alkaline conditions by weathering of feldspars and micas.

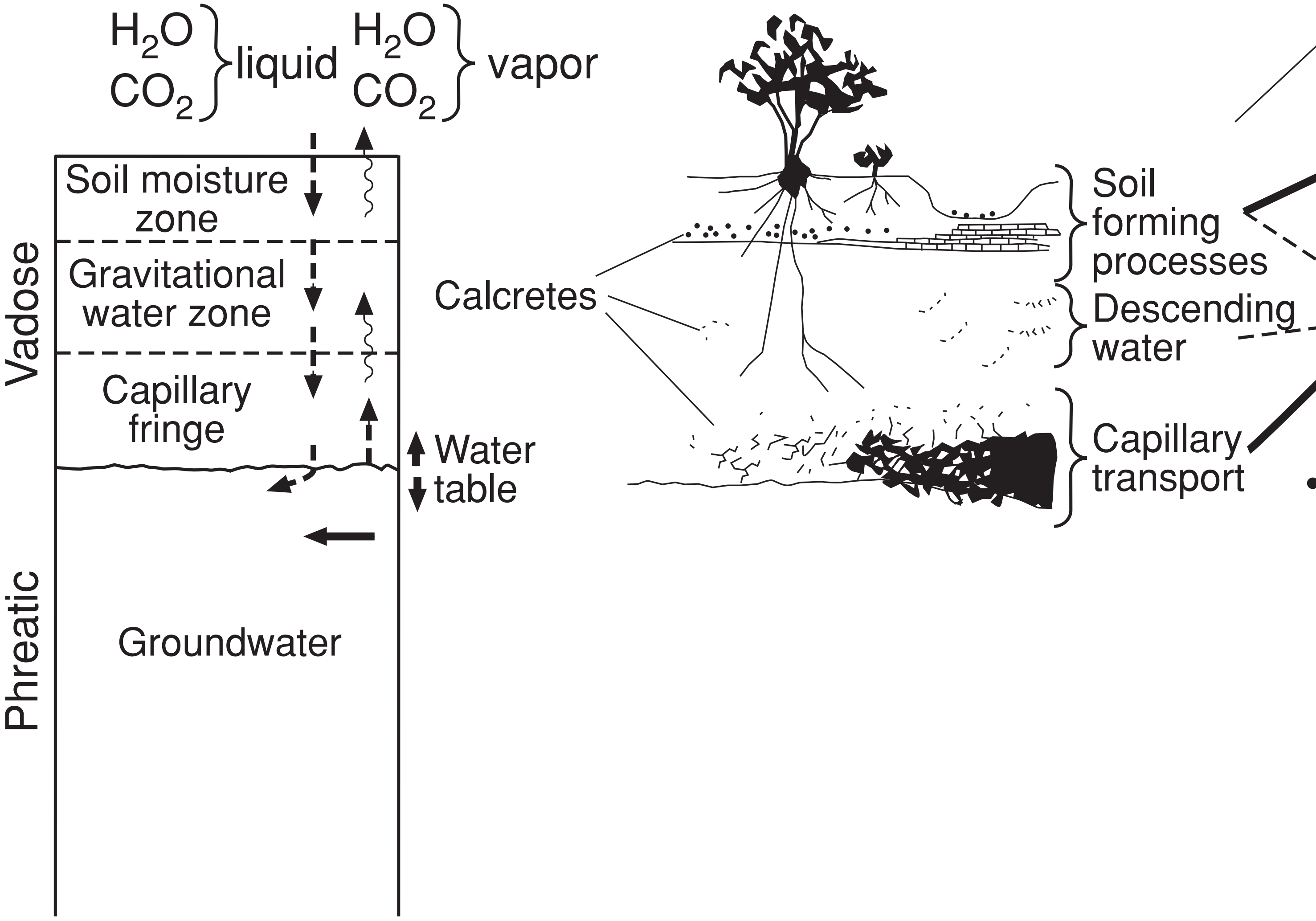
Smectite clays commonly weather from intermediate to basic rocks under alkaline conditions containing intracrystalline layers of water and exchangeable cations.

Calcrete Hosted Deposits

Calcrete (or caliche) is an accumulation of fine grained calcite ($CaCO_3$) in the vadose zone (i.e. above the water table) during a combination of pedogenic (soil forming) and diagenetic (lithification) processes.

Most calcrete layers that typify arid environments around the world.

$$Ca^{2+} + 2HCO_3^- \Leftrightarrow CaCO_3 + CO_2 + H_2O$$



Calcrete classification	*Predominant transport in solution*
Non-pedogenic superficial calcrete	Surficial transport (Essentially no uranium)
Pedogenic calcrete	Vertical redistribution (Minor uranium)
Non-pedogenic groundwater calcrete • Valley (channel) calcrete • Deltaic calcrete • Lake margin calcrete	Lateral transport (Largest uranium potential)

Calcrete-hosted or surficial uranium deposits

Calcrete, also occurs. It is the latter variety that is particularly important as the host rock for surficial uranium deposits.

The formation of this type of uranium deposit is related to high rates of groundwater evaporation and the resultant decrease of aqueous carbonate, vanadium, and uranium solubilities within a few meters of the surface.

Important uranium resources have been discovered in channelized calcretes from arid regions in Australia.

Calcretized channels represent the remnants of rivers from a previous higher rainfall interval. Such channels occasionally drained a uranium fertile source region and preserved.

and then,

Uranium and other components are required to remain in solution until they reach a zone where carnotite can be precipitated by evaporation of the groundwater.

Carnotite is a potassium uranium vanadate radioactive mineral with chemical formula: $K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O$. often found near petrified trees.

The main ingredients of carnotite, U, K, and V, are derived locally from weathered granites (for the uranium and potassium) and possibly more mafic rocks for the vanadium.

In relatively carbonated groundwaters under near neutral conditions, U^{6+} would be transported as a carbonate complex, whereas vanadium was probably in solution as V^{4+}, Focused ground-water flow introduced the ore-forming ingredients into the channel with the combination of high evaporation rates and calcite precipitation ensuring that the solution evolved toward higher salinities and pH along the flow path

A general equation for the precipitation of carnotite can be written as follows (after Carlisle, 1983):

$$2UO_2^{+} + 2H_2VO_4^{-} + 2K^{+} + 3H_2O \Leftrightarrow K_2(UO_2)_2(V_2O_8)\cdot 3H_2O + 4H^{+} \quad [4.13]$$

carnotite

Supergene Enrichment Of Cu And Other Metals In Near Surface Deposits

The processes of weathering can be responsible for the in situ enrichment of Cu, as well as other metals such as Zn, Ag, and Au, in many deposits that occur at or near the surface.

it is a product of oxidation and hydrolysis of sulfide minerals in the upper portions of weathering profiles.

It is an extremely important process in the formation of **low-grade porphyry copper deposits because the presence of an enriched, easily extractable that makes them economically viable**.

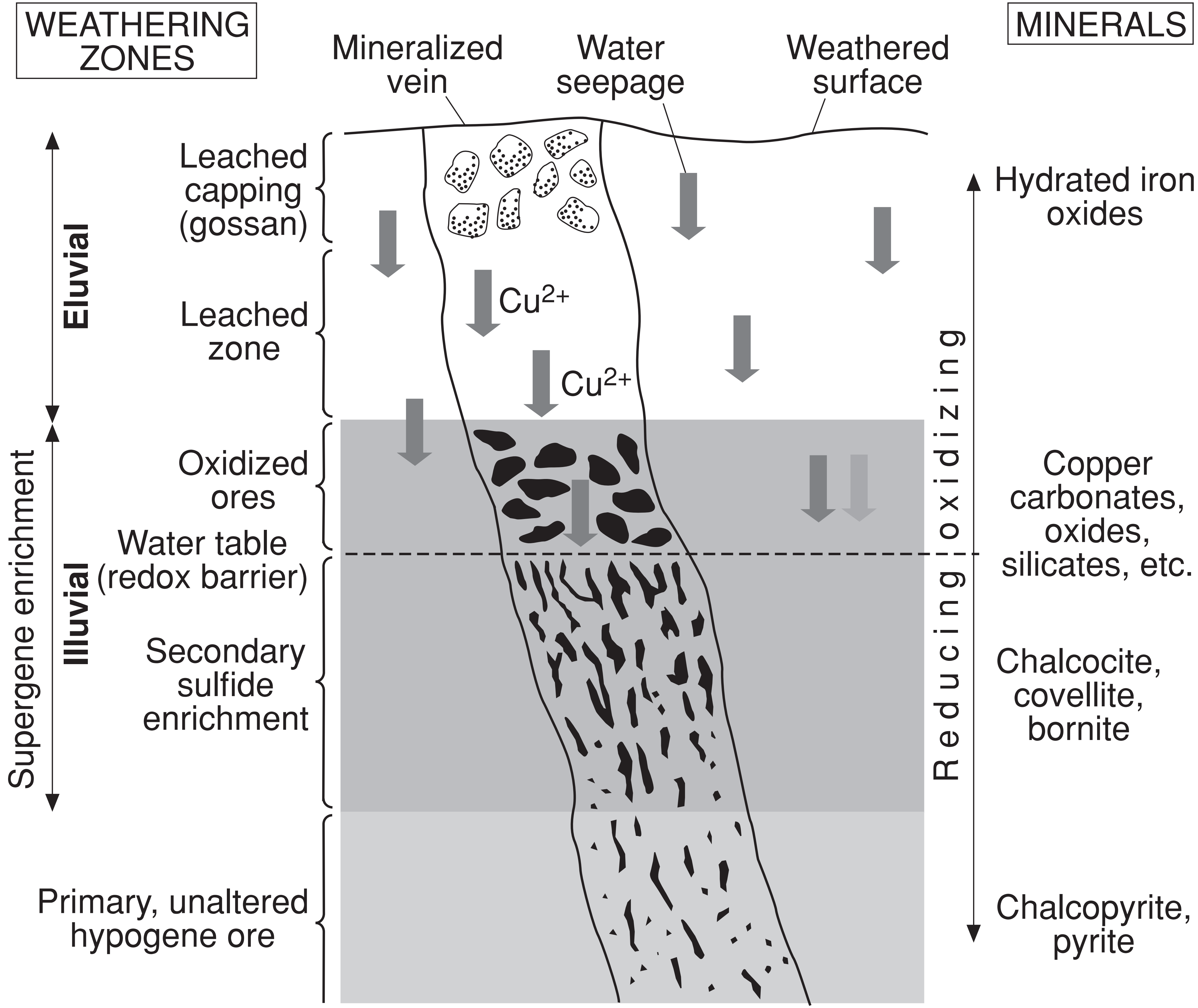
acidic groundwaters are able to destabilize sulfide minerals and leach copper.

$$4CuFeS_2 + 17O_2 + 10H_2O \Rightarrow 4Fe(OH)_3 + 4Cu^{2+} + 8SO4^{2-} + 8H^+$$

chalcopyrite goethite

In most porphyry copper environments **pyrite** is the dominant sulfide mineral and its hydrolysis and oxidation dictates the production of hydrogen ions (i.e. the decrease in pH) in the weathering zone.

Pyrite breakdown is also accompanied by the formation of goethite in the regolith and the liberation of SO24−.


WEATHERING ZONES
MINERALS
Mineralized vein
Water seepage
Weathered surface
Eluvial
Leached capping (gossan)
Leached zone
Cu2+
Cu2+
Hydrated iron oxides
Supergene enrichment
Illuvial
Oxidized ores
Water table (redox barrier)
Secondary sulfide enrichment
Reducing
oxidizing
Copper carbonates, oxides, silicates, etc.
Chalcocite, covellite, bornite
Primary, unaltered hypogene ore
Chalcopyrite, pyrite

B. Sedimentary ore-forming processes

Sedimentary rocks host a significant proportion of mineral deposits and also contain the world's fossil fuel resources.

sedimentary ores concentrate on processes that are **syngenetic** with respect to the host sediments and where the ores are themselves sediments or part of the sedimentary sequence.

Sedimentary processes include the accumulation of:

- Clastic Sedimentation And Heavy Mineral Concentration – **Placer Deposits**
- Chemical Sedimentation – Banded Iron_ Formations,
- Phosphorites
- Bedded Manganese Deposits
- Black Shales
- Ocean Floor Manganese Nodules
- Evaporites
- Fossil Fuels – Oil / Gas Formation And Coalification

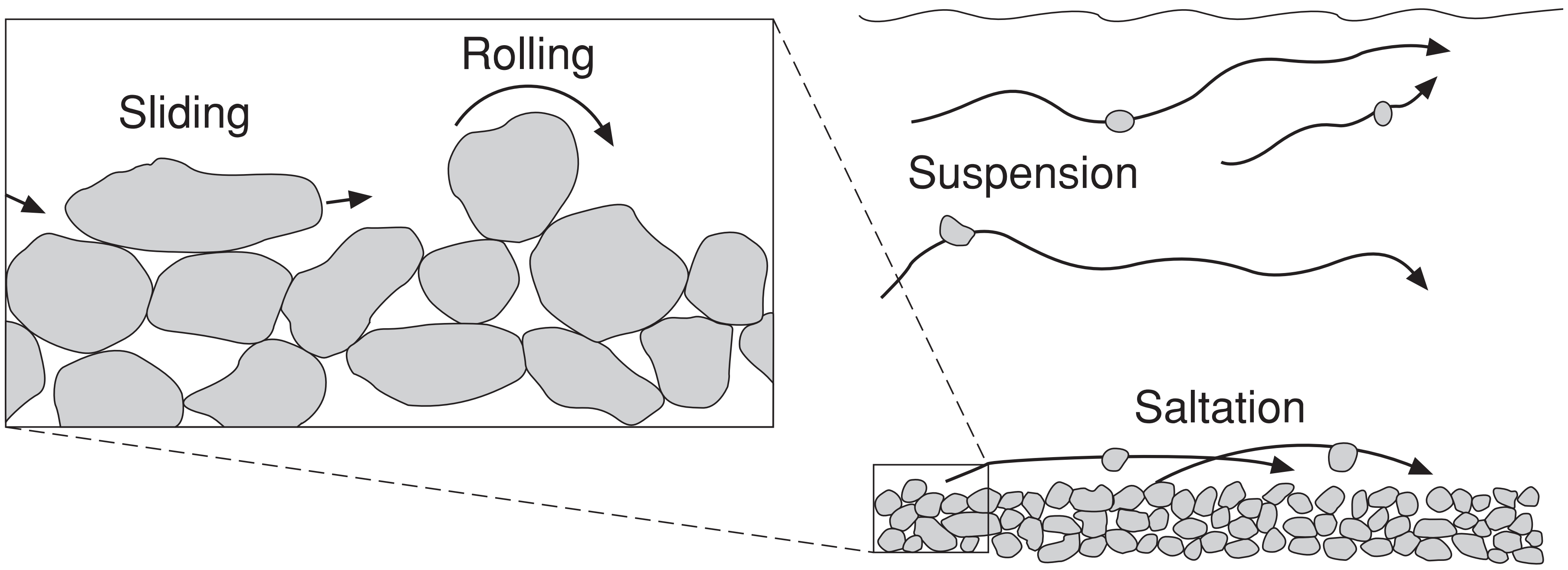
1. Placer Deposits

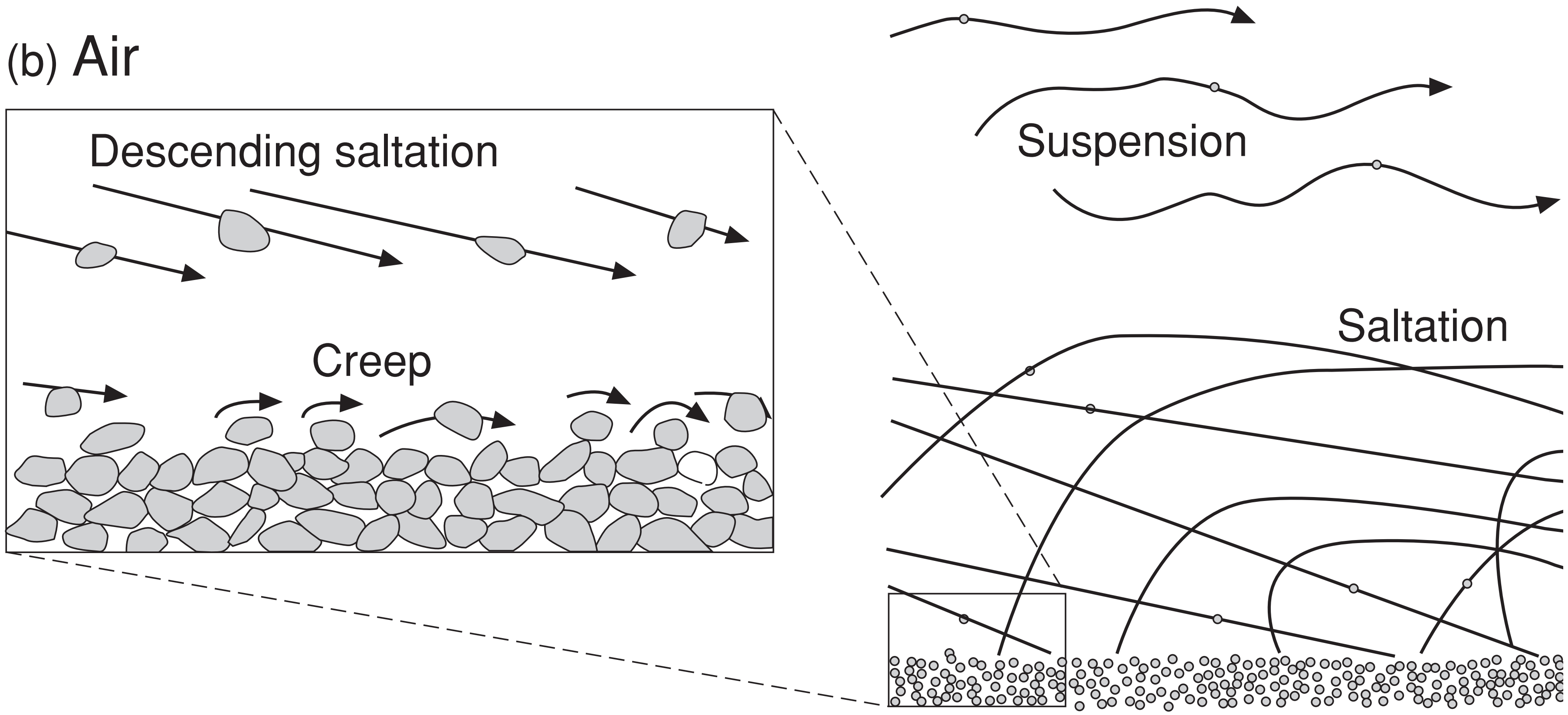
A placer deposit is heavy detrital minerals are concentrated during sediment deposition.

Mechanical processes of sedimentation where the clastic sediment is <u>sorted</u> and <u>deposited</u> by **water** and **wind**,

Contain a wide variety of minerals and metals, including **gold, uraninite, diamond, cassiterite, ilmenite, rutile, and zircon**.

Heavy mineral concentration occurs at a variety of scales, ranging from regional systems (**alluvial fans**, **beaches**, etc.), through intermediate features (the inner bank of a **river** bend or a point bar), to small–scale features (bedding laminae or cross–bed foresets).


(a) Water


(b) Air

igure 5.3 Illustration of the ifferent mechanisms of sediment ransport in water (a) and air (b) after Allen, 1994).

2. ChemiCal Sedimentation

Chemical sedimentation refers to the precipitation of dissolved components from solution, essentially out of sea water or brine.

A wide variety of rocks are formed by the compaction and lithification of chemical precipitates and these include

a. **carbonate** sediments (limestone and dolomite),

b. **siliceous** sediments (chert)

c. **iron**–rich sediments (ironstones and banded iron–formations),

as well as d. less volume of **manganese oxides, phosphates, and barite**.

Places of chemical sediments:

- Marine
- Marginal Marine Environments.
- Continental Shelves, Together With Intratidal And Lagoonal Settings.

Ore concentrations form are complex and controlled by parameters such as

- Oxidation- reduction,
- pH,
- Climate,
- Paleolatitude, and
- Biological-atmospheric evolution.

A. **Iron stones and banded iron–formations**

There are three main types of iron ores based on of morphology, texture and mineralogy

1. **Bog iron deposits,**
2. **Ironstone deposits, and**
3. **Banded iron–formations**

1. Bog iron ores

Place: Form in **lakes** and **swamps** of the glaciated tundra regions of the northern hemisphere, such as northern Canada and Scandanavia.

Form and components: **small and thin,** and comprise concentrations of **goethite** and **limonite** (Fe-oxyhydroxides) associated with organic-rich shale.

Mechanism: the metal occurs in two valence states:

– Fe^{2+} (the ferrous ion) which is generally soluble in surface waters, and

– Fe^{3+} (the ferric ion) which is insoluble and precipitates out of surface solutions.

Interface ferrous iron in solution is oxidized to ferric iron which precipitates as limonite or goethite.

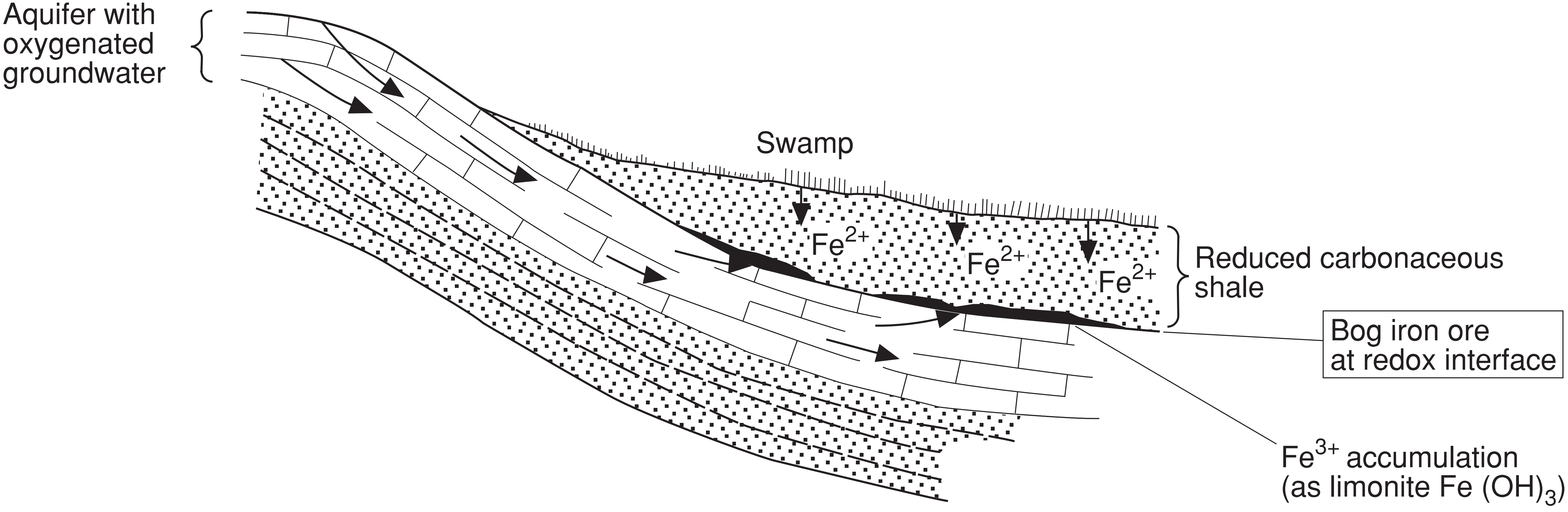


Figure 5.14 The development of limonitic concentrations in the formation of a bog iron ore where a reduced solution transporting ferrous iron interacts with oxidized groundwater flowing along an aquifer (after Stanton, 1972).

2. Banded iron–formations (BIFs)

The most important global source of iron ore

Banded iron–formations are chemical sediments in which the major components, **Fe and Si**, appear to have been derived from the **ocean** itself, rather than from a continental source

formed in essentially three periods of **Archean** and **Proterozoic** Earth history, namely 3500–3000 Ma, 2500–2000 Ma, and 1000 –500 Ma

BIFs phase

- oxide (hematite or magnetite),
- carbonate (siderite),
- silicate (greenalite and minnesotaite),
- sulfide (pyrite)
- together with chert or carbonaceous shale.

Mechanism:

Ferrous iron from deep, reduced ocean levels is introduced to shallower shelf environments by upwelling currents.

These currents interact with the shallower waters and Fe^{2+} is oxidized, with subsequent hydrolysis and precipitation of ferric hydroxide ($Fe(OH)_3$).

In marine environments where CO_3 activities are sufficiently high, $FeCO_3$ would precipitate.

3. **Iron stone ores**

typically **Phanerozoic** in age and are widespread in occurrence, representing an important source of iron in the **eastern USA and western Europe**

Ironstones form in **shallow marine and deltaic environments** and typically consist of **goethite and hematite** that has been rolled into oolites or pellets, suggesting the action of mechanical abrasion.

The environment of deposition suggests that the iron was introduced from a continental source via a fluvial system in which the metal was either in solution as Fe^{2+} or transported as a colloid.

B. Bedded manganese deposits

Manganese deposits are located in sediments of variable age, from the **Paleoproterozoic** to **recent**.

the world’s largest exploited Mn deposits in the **Kalahari manganese field of South Africa**.

Precipitation controlled by oxidation potential and it exists as Mn^{2+}, which is soluble under reducing and acidic conditions, as well as Mn^{3+} and Mn^{4+},

which are less soluble and stabilize as manganese oxides under relatively oxidizing and alkaline conditions

Pyrolusite, or MnO_2 , is the dominant oxide phase at high Eh and over a range of pH.

C. Phosphorites

Phosphorus as element is essential for the **growth** and development of most **living organisms**.

It is a building block for the **bones and teeth, shells and exoskeletons** of many invertebrates.

Plants also require it for growth and it is for this reason that phosphate is such an important ingredient of **fertilizer**.

50 million tons of phosphate per year consumed for manufacture of artificial fertilizers.

the raw material for which comes predominantly from phosphorus–rich sediments (i.e. a sediment containing more than 15–20% P_2O_5).

Places: Phosphorites generally form along **continental shelves and in shallow marginal marine settings such as lagoons and deltas**.

Mechanism: The processes of formation involve the **upwelling** of cold ocean water containing above–normal concentrations of metals, and their subsequent precipitation onto the continental shelves.

Phosphorus dissolves in sea water as 3 states

- $PO4^{3-}$ (stable under very alkaline conditions),
- $HPO4^{2-}$ (the dominant anionic complex), or
- $H2PO_4^{-}$ (stable under acidic conditions) complexes.

These anionic complexes are absorbed by the organisms living in shallow marine environments to form their shells, bones, and teeth.

The organism dies and settles to the ocean floor.

Phosphorus is released from the decaying organism to form a calcium phosphate compound, which then converts to an impure, cryptocrystalline form of **apatite** ($Ca5(PO4)3[F,OH]$) or **collophane** (a carbonate – apatite).

$$3Ca^{2+} + H2PO4 \Leftrightarrow Ca3(PO4)2 + 2H^{+}$$

Deeper, colder and more acidic waters will promote phosphate solubility.

Apatite formation is more likely to occur **under alkaline, warm-water conditions**

Ages: Phosphate concentrations in the **Precambrian oceans** might have been higher than at present because the lower O_2, higher CO_2 atmospheric conditions prevailing at that time would have meant a more acidic sea-water composition and higher phosphate solubility.

D. Black shales

Shales that are rich in **organic matter** are economically important because they are often **enriched in a large variety of metals, including V, Cr, Co, Ni, Ti, Cu, Pb, Zn, Mo, U, Ag, Sb, Ti, Se, and Cd**.

Black shales are characterized by significant quantities of **organic carbon** which is preserved from degradation/oxidation by the almost total lack of **free oxygen in the immediate environment of deposition**.

Since the higher the content of **sulfate**–reducing bacteria, the more sulfide is produced and the greater the degree of extraction of metal from the sea water column would be.

$$R(CH2O)2 + SO2_4^- \Rightarrow R + 2HCO^{-3} + H2S$$

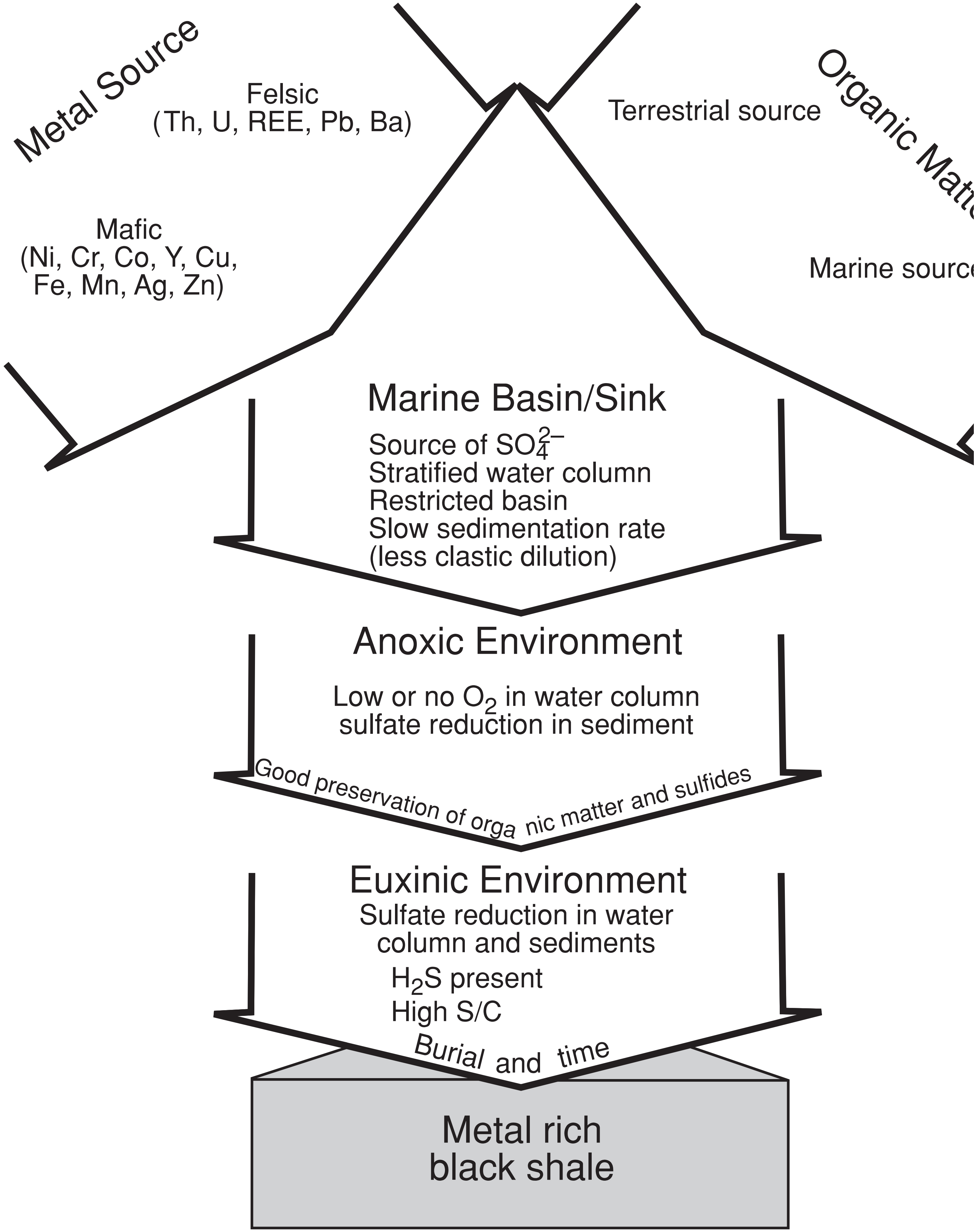
where R(CH2O)2 is an abbreviated representation of a complex (organic) carbohydrate molecule.

$$HS^- + Me^{2+} \Rightarrow MeS + H^+$$

where Me is a metal.

Many black shales are spatially associated with **ironstones**.

Well known examples of **metalliferous** black shales include the **Cambro – Ordovician** of Scandanavia, which is particularly enriched in uranium, and the Devonian New Albany shale of Indiana, USA, which has significant concentrations of Pb as well as V, Cu, Mo, and Ni.



Metal Source

Felsic
(Th, U, REE, Pb, Ba)

Mafic
(Ni, Cr, Co, Y, Cu,
Fe, Mn, Ag, Zn)

Organic Matt

Terrestrial source

Marine sourc

Marine Basin/Sink

Source of SO_4^{2-}
Stratified water column
Restricted basin
Slow sedimentation rate
(less clastic dilution)

Anoxic Environment

Low or no O_2 in water column
sulfate reduction in sediment

Good preservation of organic matter and sulfides

Euxinic Environment

Sulfate reduction in water
column and sediments
H_2S present
High S/C

Burial and time

Metal rich
black shale

E. Ocean floor manganese nodules

Manganese nodules typically occur in parts of the **ocean basins** where ;

a. sediment accumulation **rates are very low** and are absent from areas of rapid sedimentation

b. **high biological productivity** and chemical sedimentation.

They appear to be best developed in the **Pacific** Ocean, where exploration has identified large areas of nodule formation

Nodules are resources of Mn, Fe, Cu, and Ni (as well as lesser amounts of Co, Zn, and other metals)

The formation of the nodules attributed to the following mechanisms:

- Settling of clay and biogenic debris that contained either absorbed or ingested metals obtained from the sea water.
- Direct precipitation of metals from sea water onto a suitable substrate which forms the nucleus around which concretionary growth takes place.

- Upward diffusion of metals in ocean bottom sediment pore waters.
- Authigenic reactions in ocean bottom sediments during alteration and compaction.
- Bacterial activity and the oxidation of transition metals.

F. Evaporites

the world's production of rock salt (halite), as well as of potash, borates, and nitrates for agricultural fertilizers, comes from rocks known as evaporites.

These are chemical precipitates that form as a result of evaporation of a brine, usually derived from sea water.

There are two main environments in which evaporites form.

1. <u>Saline giants</u>

Marginal marine in setting and represented by large lagoons. This type of deposit may be both laterally extensive and thick, but is characterized by a relatively limited range of mineral precipitants derived from sea water.

2. Intracontinental and lacustrine and results in much smaller, thinner deposits which are characterized by a more diverse range of mineral precipitants .

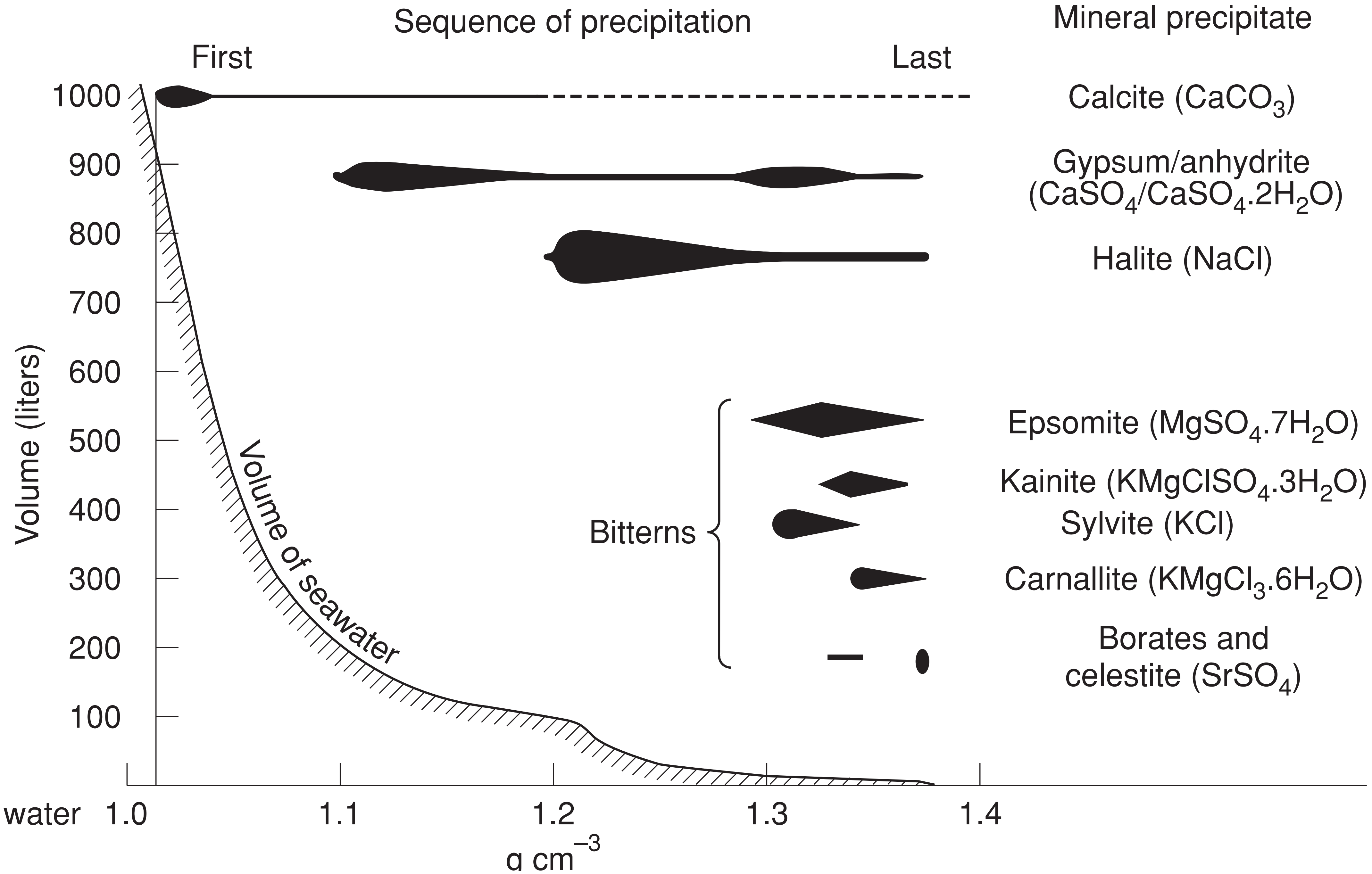
As sea water or brine evaporates and water vapor is removed into the atmosphere, the salinity (i.e. the total content of dissolved salts in solution) of the residual solution increases and individual salts precipitate as their respective solubility limits are reached.

Typical products mined from these deposits include **halite, potash, and sulfates**.

The largest known evaporite sequence occurs in **late Miocene strata beneath the floor of the Mediterranean Sea,** where deposits extend laterally for over 2000 km and may be up to 2 km thick.

Sea water g kg^{-1}

$CaCO_3$	0.11
$CaSO_4$	1.20
NaCl	26.90
NaBr $MgBr_2$	0.03 0.09
$MgSO_4$	2.25
KCl	0.70
$MgCl_2$	3.18
borates, sulfates	0.01 0.02
Total	34.48



3. Fossil Fuels – Oil / Gas Formation And Coalification

A fossil fuel is formed from the **altered remains of organic matter (plant and animal) trapped in sedimentary rock**.

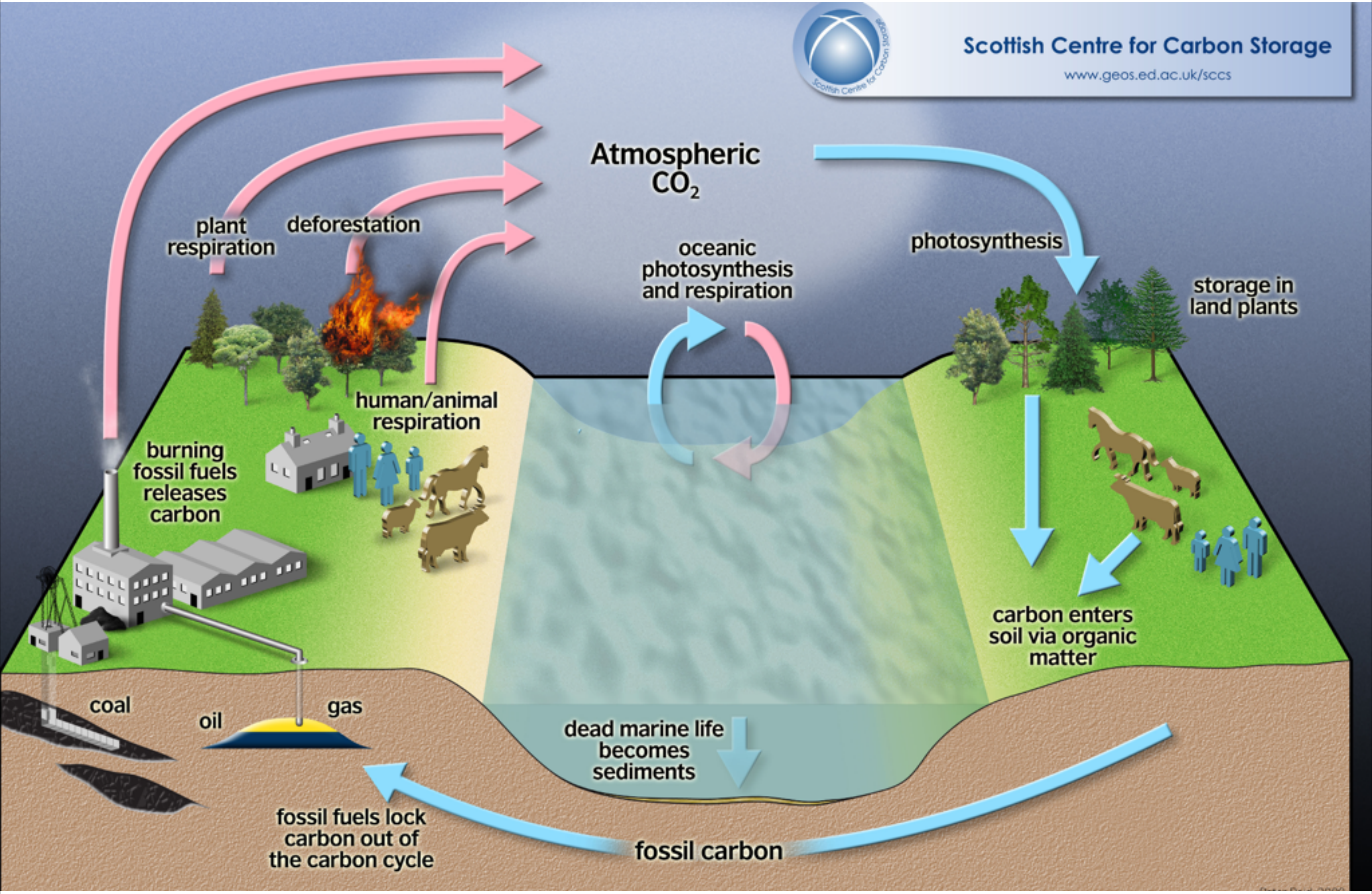
The **hydrocarbon compounds** that form during the burial and degradation of organic material retain a significant proportion of the chemical energy imparted into the original living organism by the sun.

The main fossil fuels are

- **Coal**
- **Petroleum**
- **Crude oil**
- **Natural gas**

The global carbon cycle is complex, involving both circulation, mainly in the form of gaseous CO_2 and CH_4, and storage, as reduced carbon or carbonate minerals, in different reservoirs such as the deep ocean and sedimentary rocks.

The areas of greatest organic productivity on Earth are represented on the continents by tropical vegetative zones, and in the oceans by areas of cold current upwelling.


Scottish Centre for Carbon Storage
www.geos.ed.ac.uk/sccs
Atmospheric CO_2
plant respiration
deforestation
human/animal respiration
burning fossil fuels releases carbon
oceanic photosynthesis and respiration
photosynthesis
storage in land plants
carbon enters soil via organic matter
coal
oil
gas
dead marine life becomes sediments
fossil fuels lock carbon out of the carbon cycle
fossil carbon

Oil and gas deposits develop mainly from the accumulation of **phyto-plankton** in marine settings.

When organisms die they decompose by bacterial decay and/or oxidation, and rapidly break down to relatively simple molecular constituents such as CO_2 and CH_4.

Such a process would not be conducive to the formation of fossil fuels, which requires preservation of much of the complex organic hydrocarbon material.

Suitable source rocks from which fossil fuels accumulate must, therefore, have formed in reducing sedimentation environments.

Coals develop mainly in continental settings, from accumulation of **vegetation** in either humid, tropical swamp environments.

The vegetation is buried, little or no oil is formed, although significant volumes of gas.

The solid residue that remains in this case is more voluminous and compacts to form coal.

The nature of the solid coal residue changes with depth, from **peat and lignite** at shallow burial depths (less than about 500 m), to **bituminous coal** and subsequently **anthracitic coal** (at depths of around 5000 m).

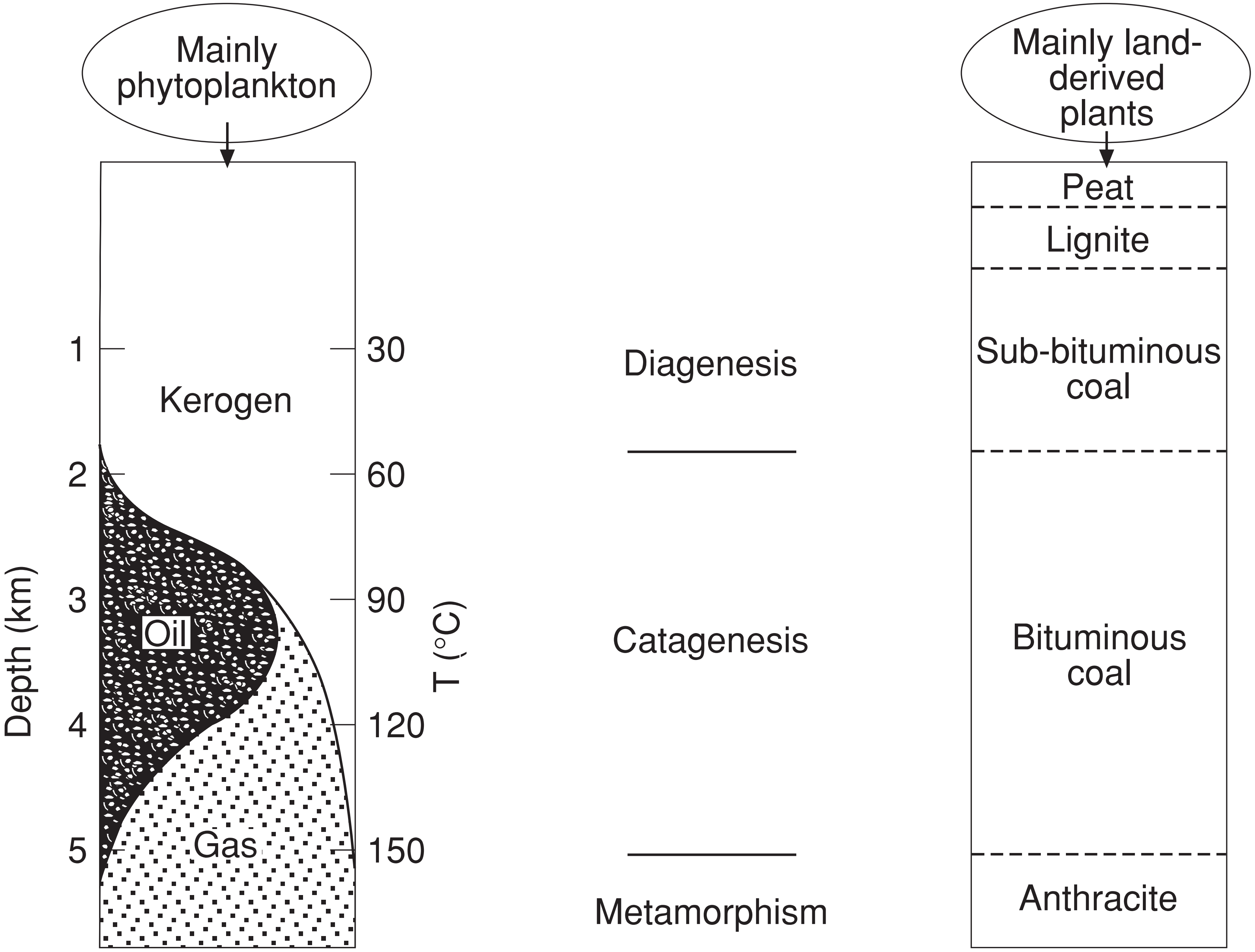


Figure 5.26 Simplified scheme illustrating the formation of oil, gas, and coal by the progressive burial of different types of mainly vegetative matter (after Hunt, 1979).

The main molecular building blocks involved in petroleum formation include:

- **Harbohydrates** are mono– and polysaccharide polymers and include the sugars, chitin and lignin.
- **Proteins** these are high molecular weight amino acid polymers and represent one of the most important constituents of life processes.
- **Lipids**, which are represented in animal fats and vegetable oils and are abundant in crude oils.
- **Other** substances such as **resins** and **pigments** are of lesser importance but also occur variably in both plant and animal matter.

Table 5.1 Average chemical compositions (in wt%) of the main organic building blocks compared to those of petroleum and a typical coal

	C	H	O	N	S
Carbohydrates	44	6	50	–	–
Lignin	63	5	31.6	0.3	0.1
Proteins	53	7	22	17	1
Lipids	76	12	12	–	–
Petroleum	85	13	0.5	0.5	1
Coal	70	5	23	1	1

As the original organic constituents are buried, they are subjected to **increases in pressure and temperature**, resulting in systematic changes which are divided into three stages, termed

- Diagenesis,
- Catagenesis, and
- Metamorphism.

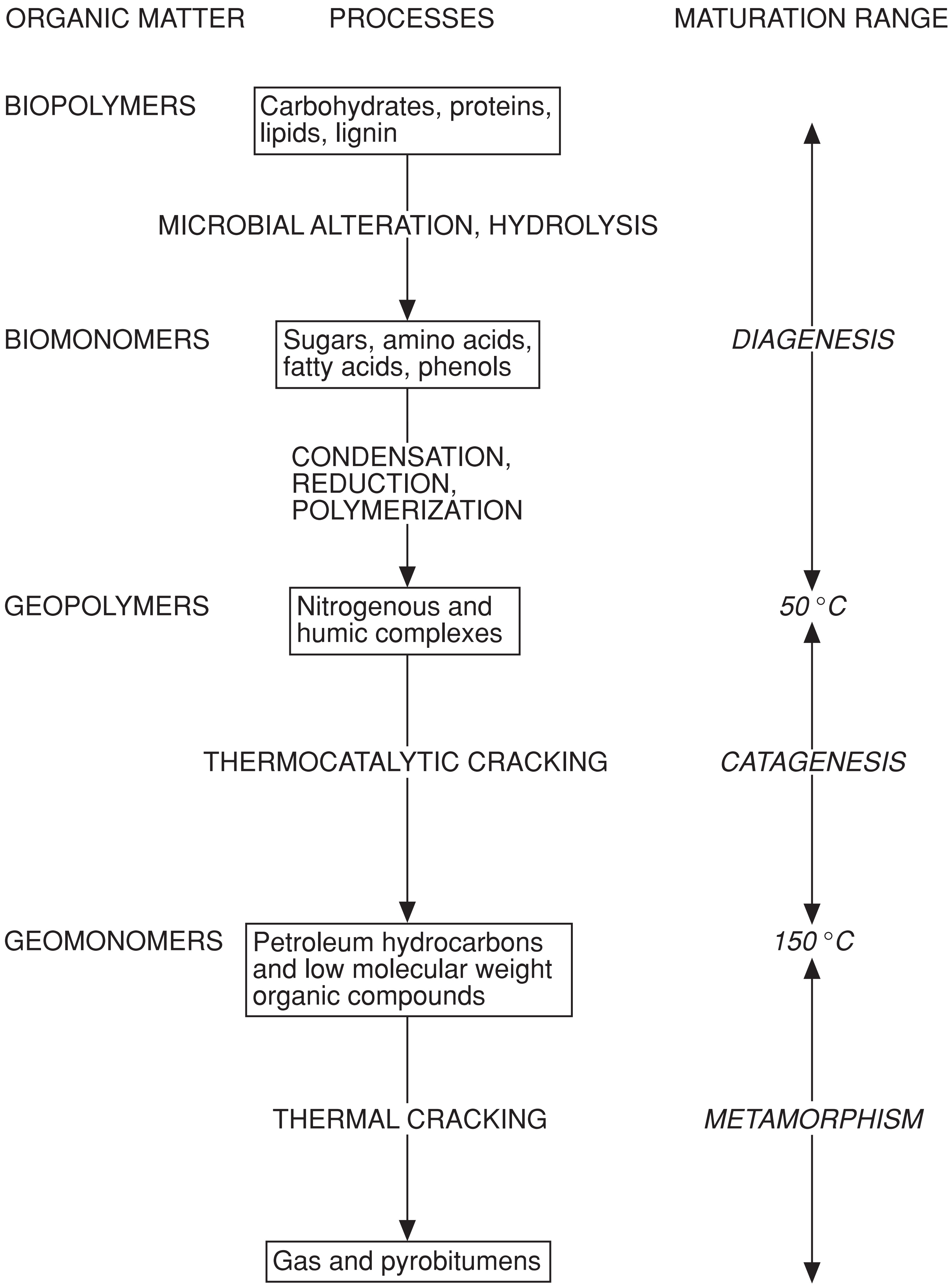


Figure 5.27 Summary of the stages and processes involved in the transformation of organic matter during burial to form oil and gas (after Hunt, 1979).

Diagenesis refers to the early biological and chemical changes that occur in organic–rich sediments prior to the pronounced temperature–dependent effects of later reactions (i.e. less than about 50 °C).

During this stage the biopolymers of living organisms converted into less complex molecules which may, in turn, react and condense to form more complex, high molecular weight geopolymers that are the precursors to kerogen.

A significant amounts of gas produced which typically escapes into the atmosphere or water column and is not retained in the sediment.

Catagenesis occurs between about 50 and 150 °C and is the most important stage as far as petroleum generation is concerned.

The majority of which result in the formation of light hydro–carbons from high molecular weight kerogen by the breaking of carbon-carbon bonds.

Temperature and time are inversely related in terms of petroleum productivity so that, for example, a given quantity of oil formed at 110 °C over 25 million years would require 100 million years to form at 90 °C .

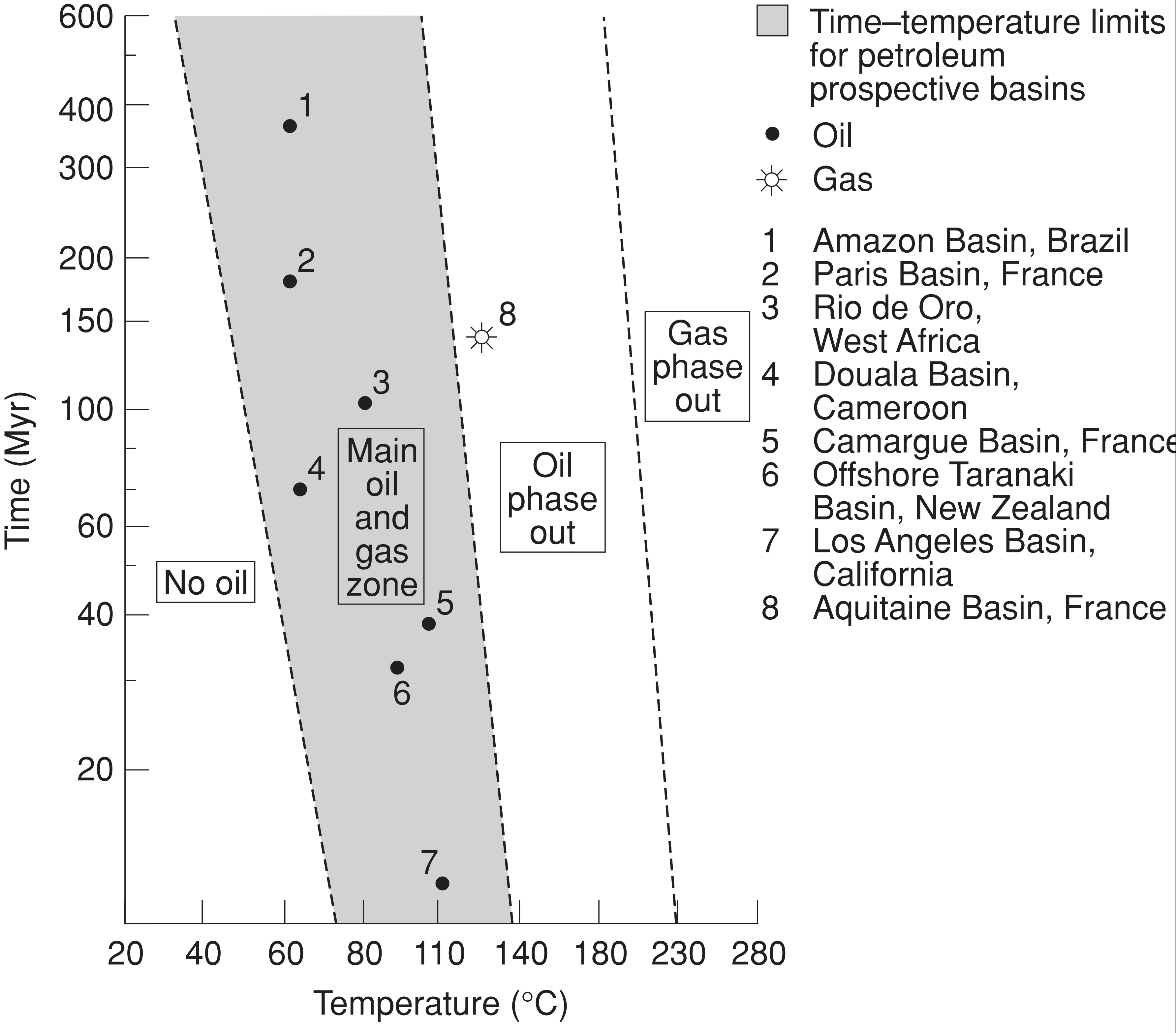


Figure 5.28 Graph showing the relationships between temperature and time with respect to the generation of oil and gas in sedimentary basins. The shaded area refers to the optimum range of conditions for petroleum generation and the points are actual examples of petroleum-bearing basins from several locations around the world (after Connan, 1974).

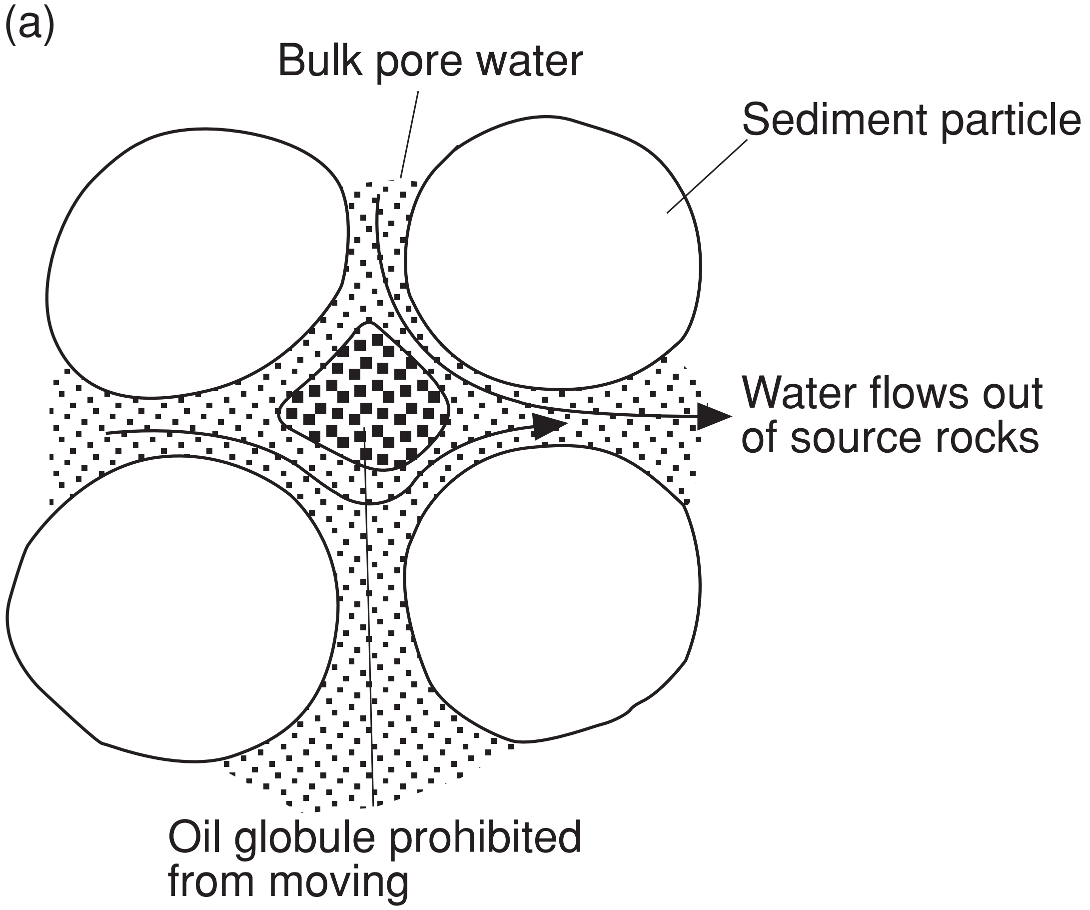
Petroleum migration and reservoir considerations

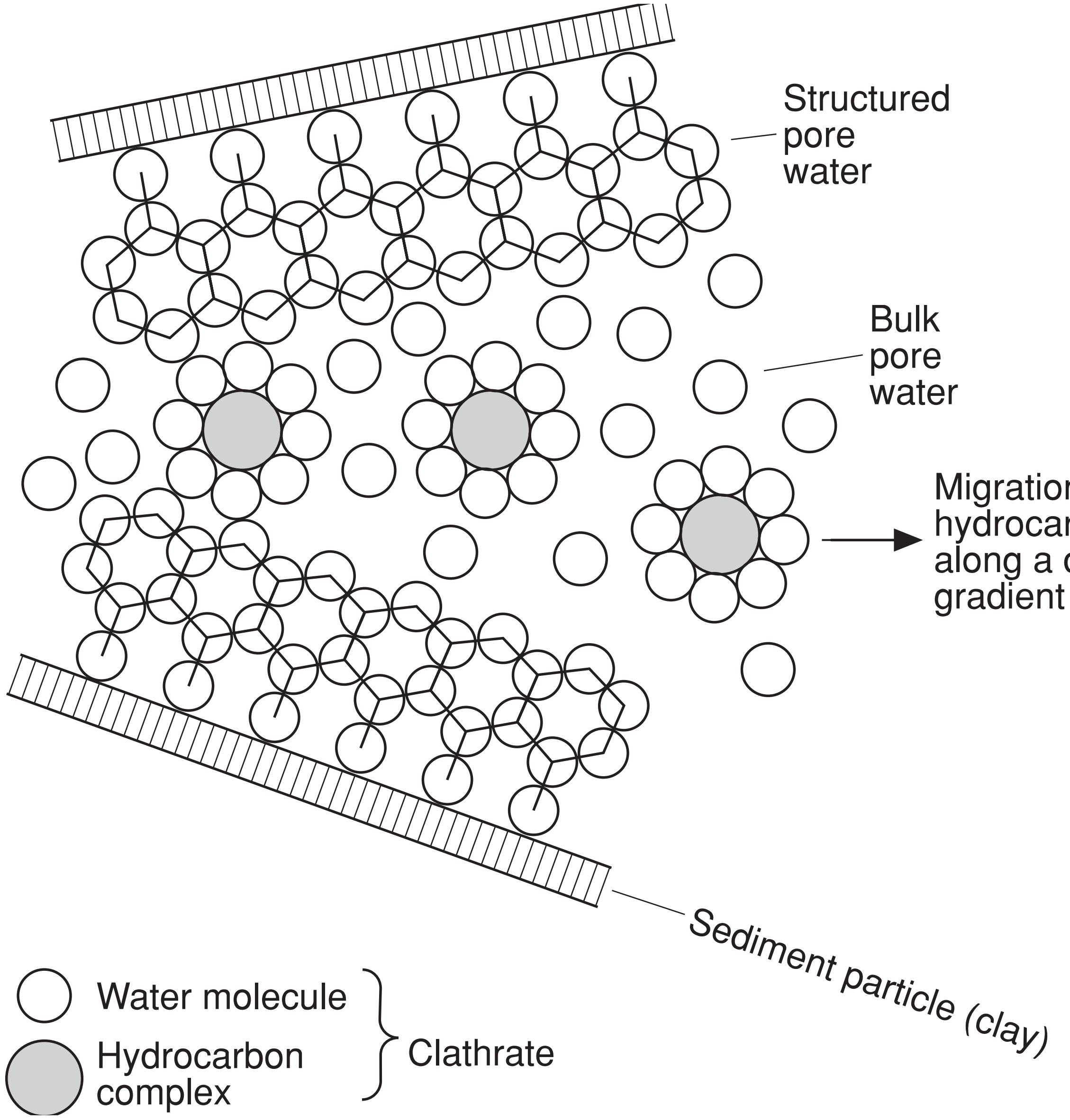
petroleum originates in a fine grained source rock and then migrates into more **permeable, coarser grained, reservoir sediments**.

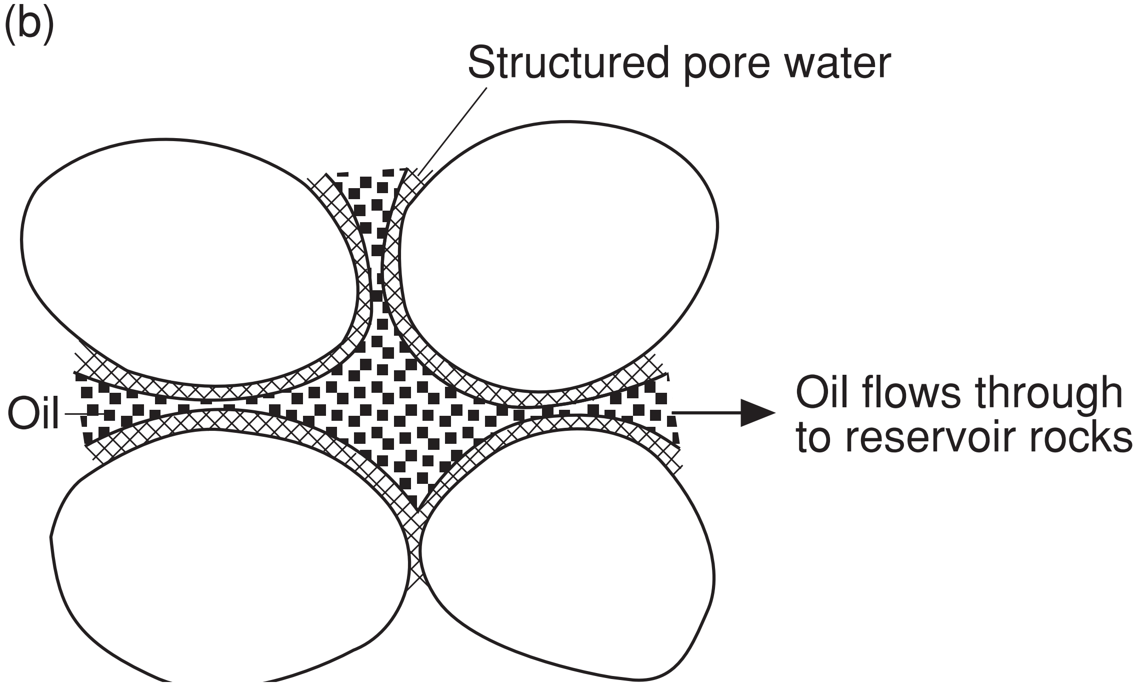
As the organic source rock is lithified during diagenesis, water (usually a low to moderate salinity brine) is expelled from the sediment to form a connate fluid.

Oil and gas migrate in the presence of water over tens to hundreds of kilometers.

The main factor that controls hydrocarbon migration pathways is the existence of a **pressure** differential in the host rock.







(a) “Water saturated” pore spaces in a sedimentary source rock in which little or no oil migration takes place because oil capillarity is impeded by the presence of water-wet pores which block the pore throats.
(b) “Oil saturated” pore spaces formed after compaction of the sediment has driven off much of the bulk pore water, which facilitates capillary-related oil migration by removing pore throat blocking
free water (c) diffusional migration of hydrocarbons takes place away from structural water-bound mineral grains

Entrapment of oil and gas

trap any geological feature that either **reduces permeability** of the reservoir or provides a physical **barrier** that impedes the further migration of fluid.

A trap prevents the petroleum from further flow and allows it to accumulate.

Evaporite a good hydrocarbon traps as they are laterally extensive and have zero permeability.

Many of the giant oil fields of the Arabian Gulf are capped by evaporite sequences

Structural features such as **faults** and **anticlines** tend to be the dominant hydrocarbon traps

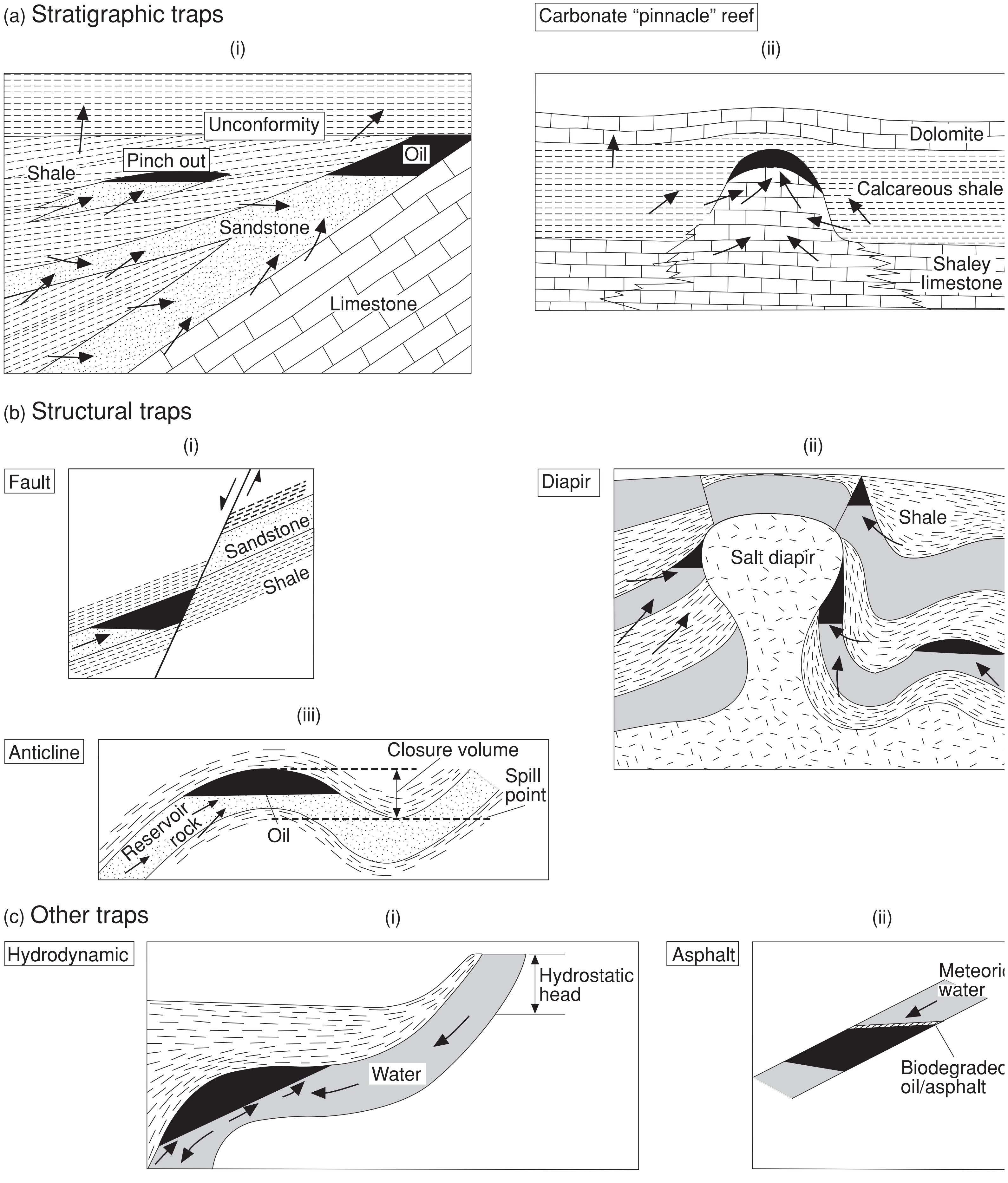


Figure 5.33 Geological scenarios for hydrocarbon trap sites. (a) Stratigraphic traps represented by unconformities, pinch-outs, and carbonate "pinnacle" reefs. (b) Structural traps represented by faults, diapiric features, and anticlinal or dome like structures. (c) Other features, such as hydrodynamic and asphalt traps (after Hunt, 1979; Bjørlykke, 1989).