



Economic Geology: Lecture Notes

Assembled by:

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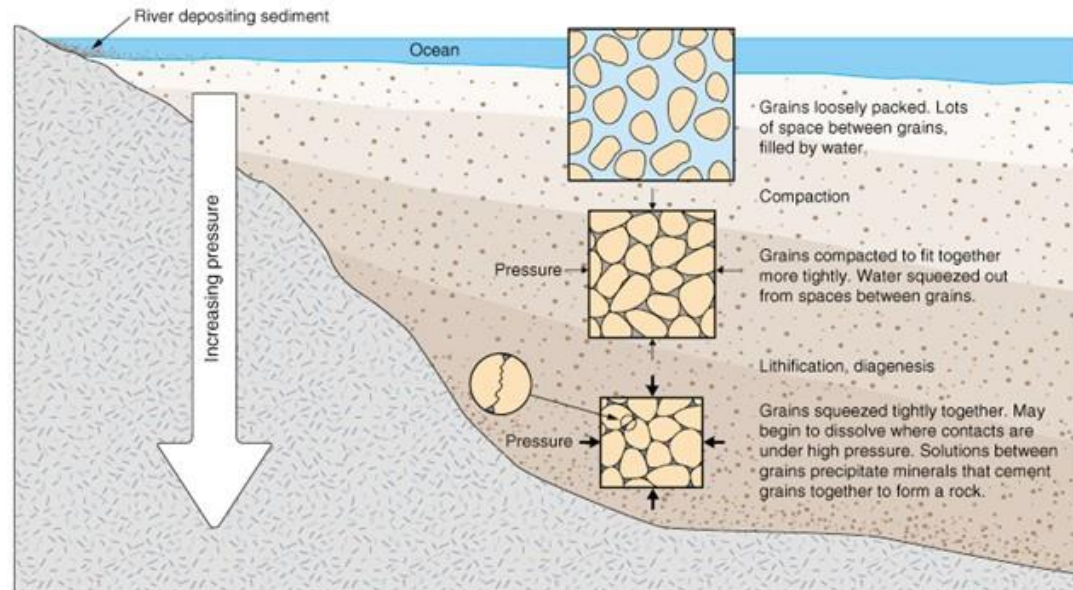
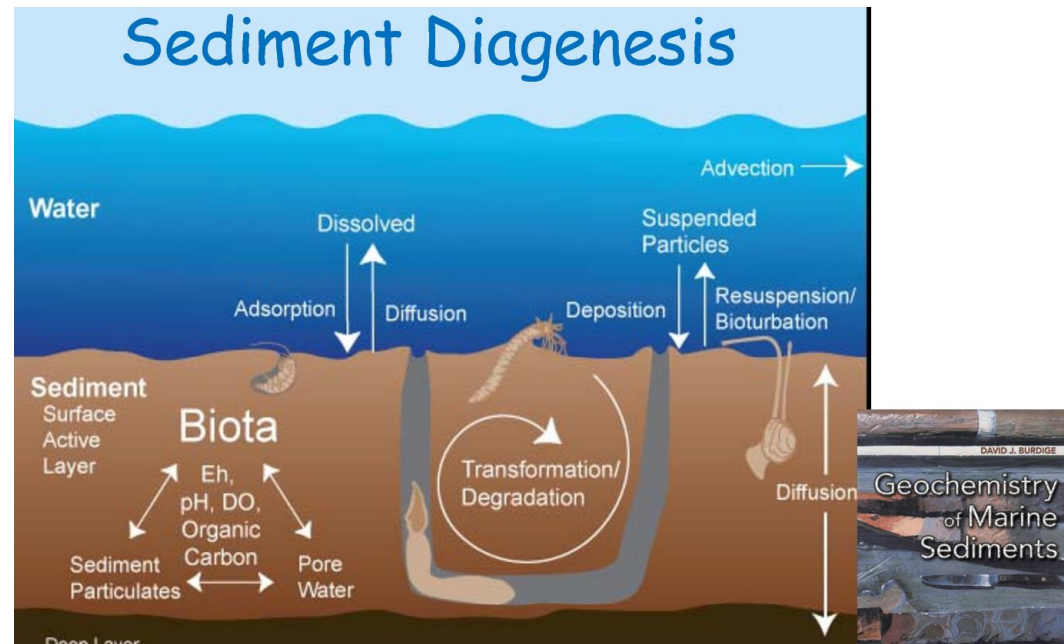
Ain Shams University

Diagenetic ore deposits

Diagenesis is “the sum of all chemical, physical and biologic changes undergone by sediment after its initial deposition, and during and after its lithification, exclusive of surficial alteration (weathering) and metamorphism”.

Examples of ore deposit types that illustrate the **diagenetic realm** include:

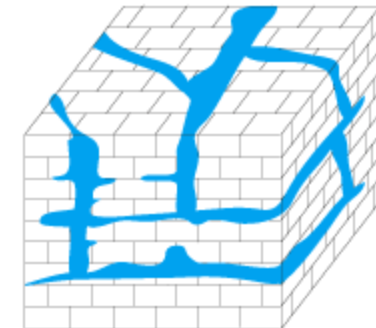
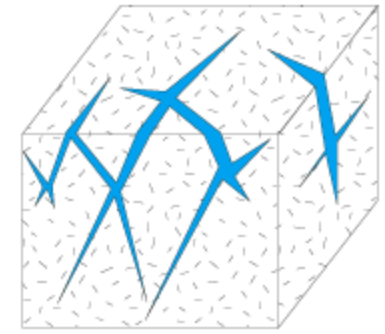
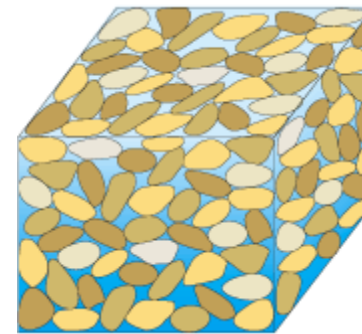
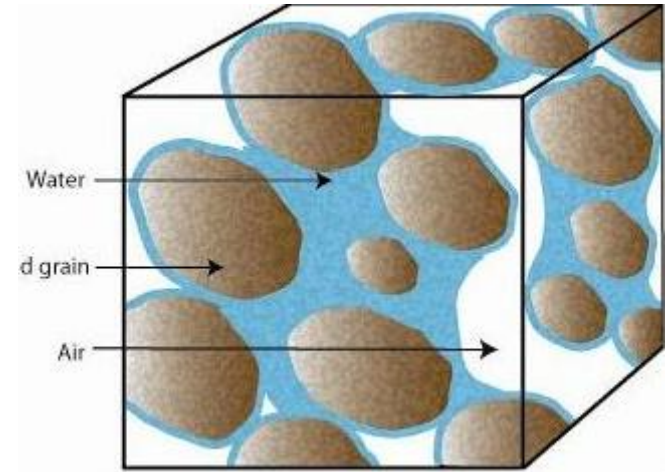
1. the European Copper Shale,
2. many deposits of the Central African Copper-Cobalt Belt,
3. Mississippi Valley Type (MVT) lead-zinc (barite-fluorite-celestite) deposits, and
4. orebodies that originate from brines derived by interaction with salt rocks (e.g. lead zinc and siderite in Northern Africa).



The core of a **diagenetic ore formation model** is the argument that most sediment includes a large mass of water at the time of deposition **“connate/formation water”**. During diagenesis, most of this initial water is expelled by mechanical compaction.

When newly deposited, sand may contain 40 vol. % of water (connate/formation), clay 90%, and carbonates 50%. By diagenesis, the pore space occupied by water is reduced to < 1 vol.%. All this connate/formation water must leave the system by flowing upwards and to the margin of sedimentary basins.

Connate/formation water in sediments frequently attains temperatures of more than $100\text{ }^{\circ}\text{C}$ and reaches a maximum of about $300\text{ }^{\circ}\text{C}$. By reacting with rocks, the connate/formation water acquires a high content of dissolved matter. Where large masses of such fluids pass through geochemical or physical “traps”, minerals may be precipitated (epigenetic) which concentrate useful elements.



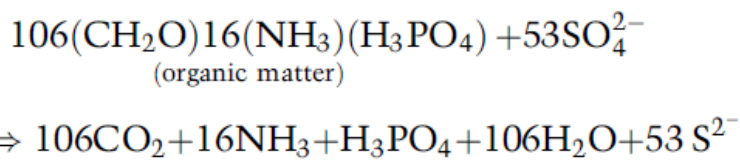
Typical (as example) **connate/formation waters** are **brines** dominated by **Na-Ca-Cl** and elevated traces of **HCO₃, K, I and Br.** (NB. **brine sensu stricto** is defined by a **salt content of more than 10%.**)

Compared with seawater, **iron, manganese, copper, zinc and many other elements** are enriched in the **connate/formation water.** **Magnesium** and **sulphate** are depleted; the first by neogenesis of dolomite and chlorite (minerals containing Mg), the second by (bacterial) or thermochemical sulphate reduction to H₂S.

Table 1.5 What exactly is a brine? Terms for water with different salinities (Davies & DeWiest 1966)

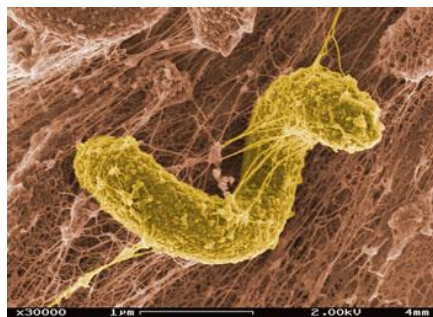
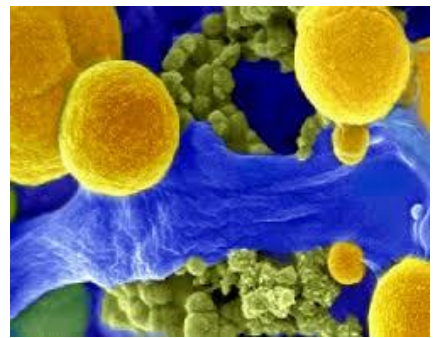
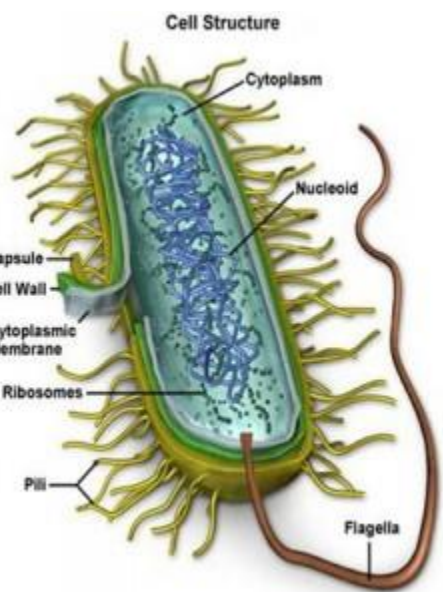
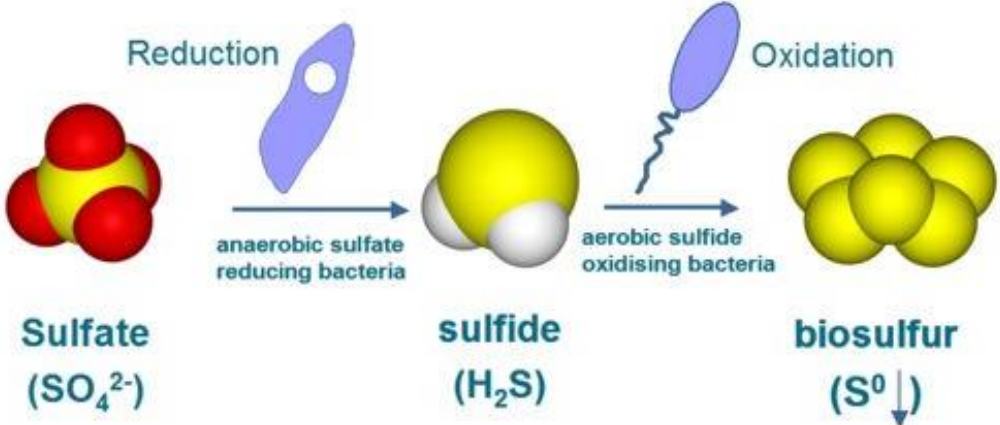
Term	Concentration of total dissolved solids (TDS) in ppm (parts per million) and weight percent	
Fresh water	0–1000	<0.1%
Brackish water	1000–10,000	<1%
Seawater	31,000–38,000	3.1–3.8%
Saline, or salty water	10,000–100,000	<10%
Brine	>100,000	>10%

Anaerobic microbial (bacterial) sulphate reduction:

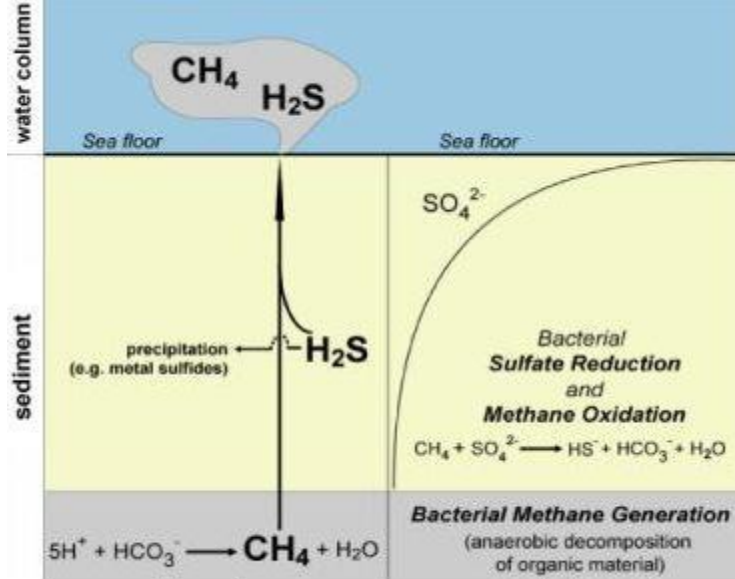
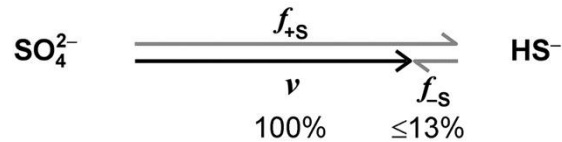
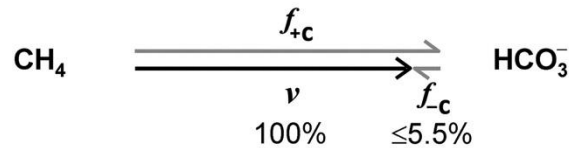
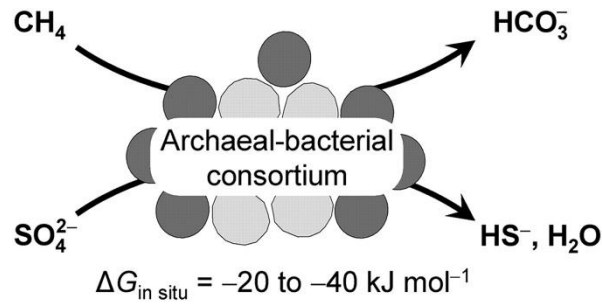
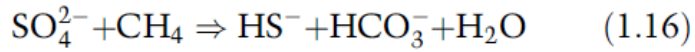


Reduction

Oxidation

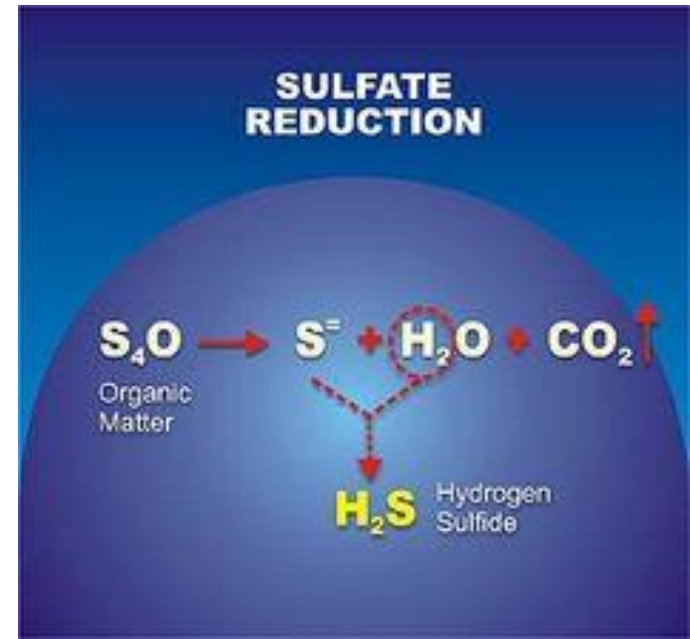
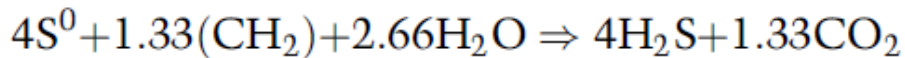
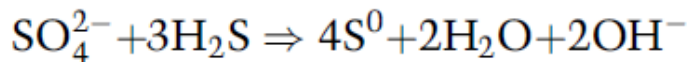
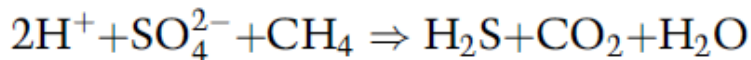


Anaerobic microbial sulphate reduction and concurrent methane oxidation:

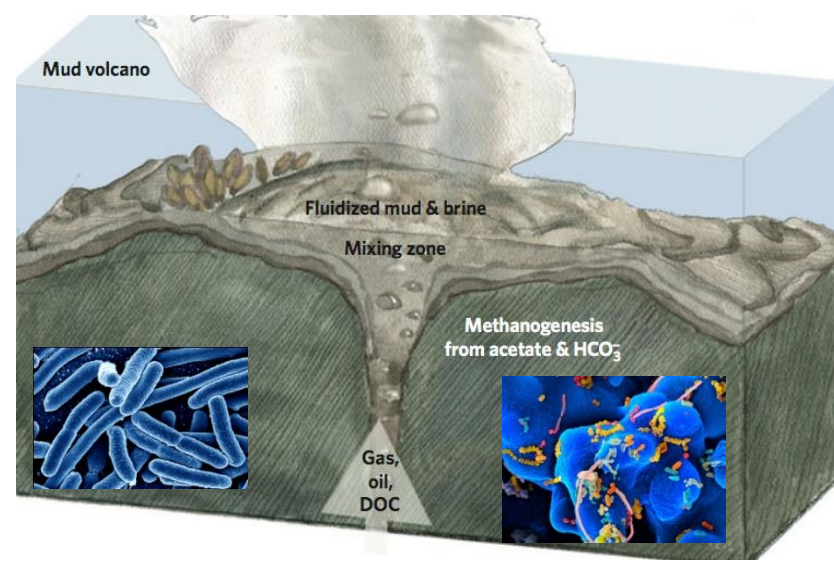


Scheme of methane production and degradation

Thermochemical sulphate reduction (TSR):

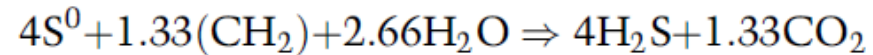
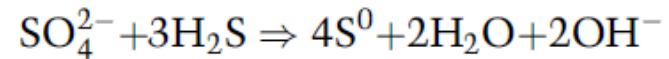
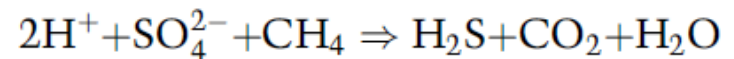


Live microbes exist to a depth of several kilometres below the surface and to temperatures of 140 °C. **Microbes** convert **organic matter to CH₄ and CO₂** and produce the methane of biogenic gas deposits. In the near-surface realm of early diagenesis, **methanogenesis** and **sediment dewatering** combine to cause **methane rich cold seeps (cold enough formation/connate water)** that are sites of submarine barite deposit formation.



Many **microbes** have a role in diagenesis. ***Geobacter metallireducens***, for example, **catalyses Fe(III) reduction and decomposition of organic substance to CO₂**. In the absence of **microbes**, at higher temperature (>80 °C) and greater depth, **abiotic sulphate reduction** based on destruction of organic matter (here represented by CH₄ and CH₂) is possible. By disintegrating anhydrite (**SO₄**), this process can cause a relative enrichment of **CaCl₂** in the fluids.

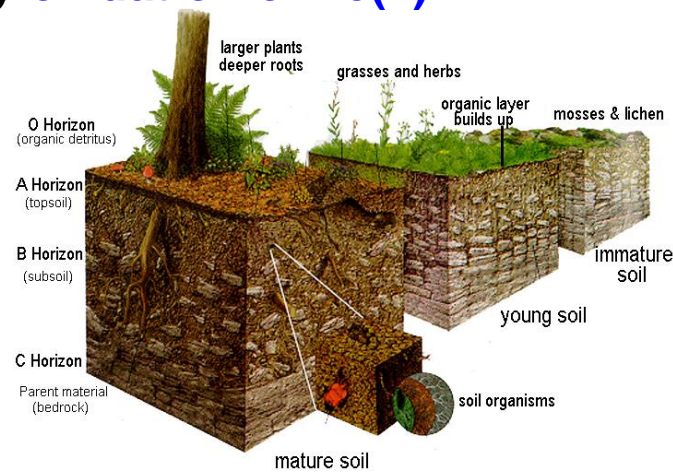
Thermochemical sulphate reduction (TSR):



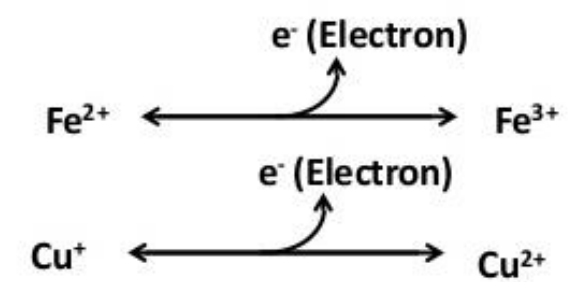
NaCl may be retained and concentrated by clay beds (acting as a semi-permeable membrane). Probably more often, **NaCl brines** originate by evaporation at the surface or by dissolution of salt rocks in the basal sediments. Mature, commonly **deep connate/formation waters** are mostly **concentrated NaCl brines**.

Maturation and decomposition of **organic matter** in sediments results in **dissolved CH₄, CO₂, H₂, N₂** and higher hydrocarbons (e.g. petroleum). **Organic matter** is oxidized by **oxygen induced by infiltrating seawater and meteoric water, and oxygen produced by disproportionation of formation waters.** The **connate/formation water oxygen** is also consumed by **oxidation of Fe(II).**

Therefore, most **connate/formation waters** display a low redox state, **favouring high solubility of many metals.** In solution, some metals may occur in the form of **organo metallic complexes (Ni, V, part of Zn and Cu),** while others such as **Pb, Fe and most Cu and Zn** are dissolved as simple ions.



Oxidation is defined as the removal of electrons



Reduction as the gain of electrons

Oxidation is always accompanied by reduction of an electron acceptor



WATER	O_2 Fe^{3+}	Energy Yield	
sediment column	NO_3^- SO_4^{2-}		
	O_2 - SO_4^{2-}	aerobic resp. 686	
MUD	NO_3^- Fe^{3+} SO_4^{2-}	$\text{O}_2 \rightarrow \text{CO}_2$	
	Fe^{3+} SO_4^{2-}	$\text{NO}_3^- + \text{H}^+ \rightarrow \text{N}_2$	dissimilatory nitrate red. 649
	Fe^{3+} SO_4^{2-}	$\text{Fe}_2(\text{OH})_3 + 2\text{H}^+ \rightarrow \text{Fe}^{2+}$	iron red. 300
	SO_4^{2-}	$\text{SO}_4^{2-} + 2\text{H}^+ \rightarrow \text{HS}^-$	sulfate red. 190
	CO_2	$\text{H}_2 + \text{CO}_2 \rightarrow \text{CH}_4$	methanogenesis 8.3
		due to reduction of organic matter	

Not all **basinal fluids/connate/formation waters** are reduced, **oxidized connate/formation waters** are commonly enriched in **SO₄**. This is possible when the connate water source rock includes predominantly **haematitic sandstone and mudrock, limestone, anhydrite and halite**. **Oxidized fluids** are able to **dissolve Cu, Pb and Zn**, to transport the metals over wide distances and to precipitate ore at suitable traps such as redox fronts established by **organic-rich shale** (e.g. the **European Copper Shale**). **Barium and iron**, in contrast, are **insoluble in oxidized fluids**.

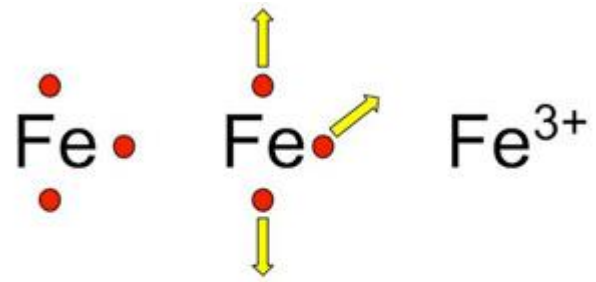
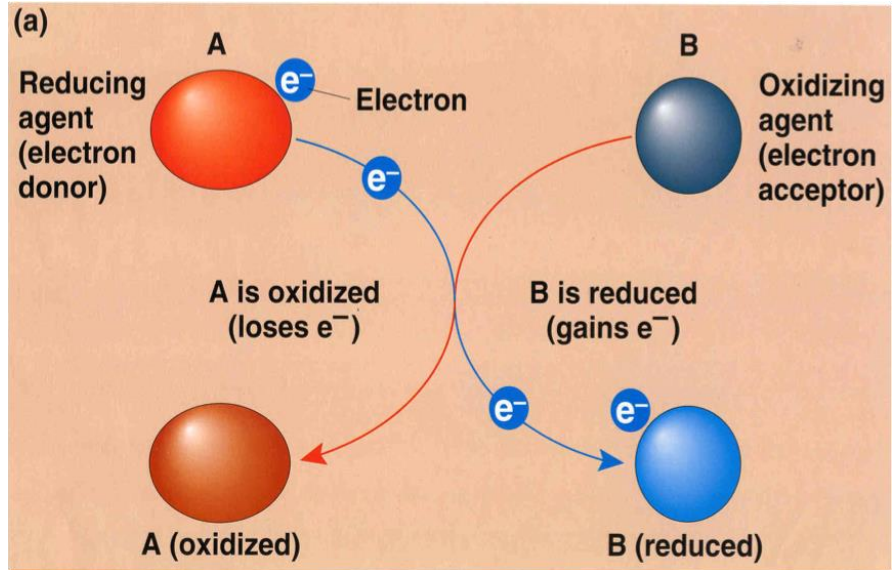
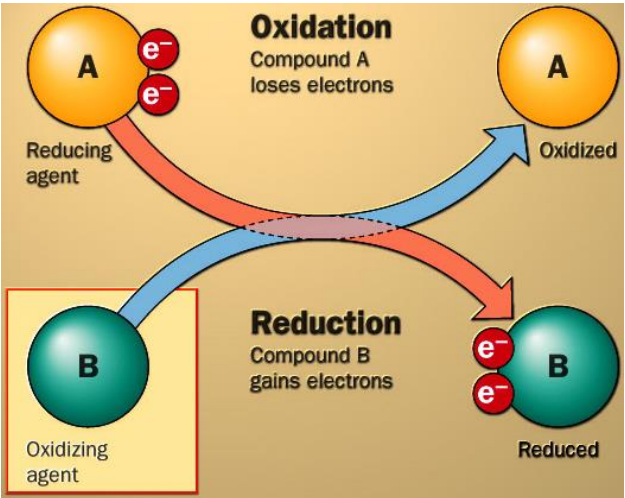
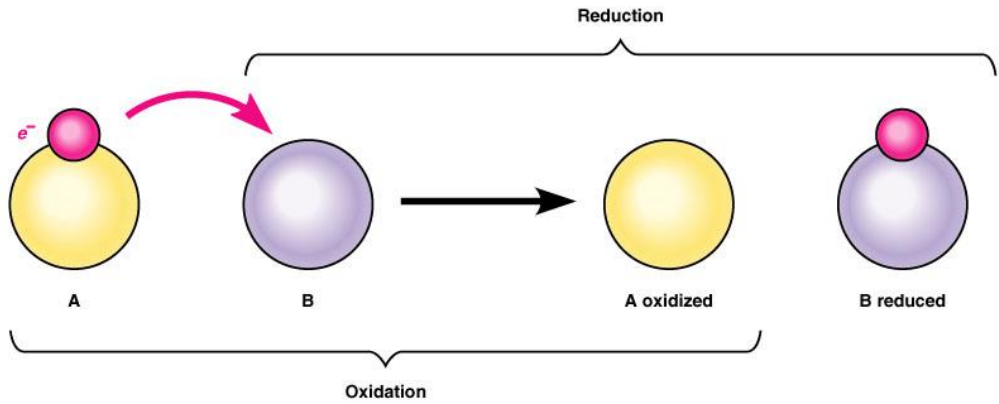


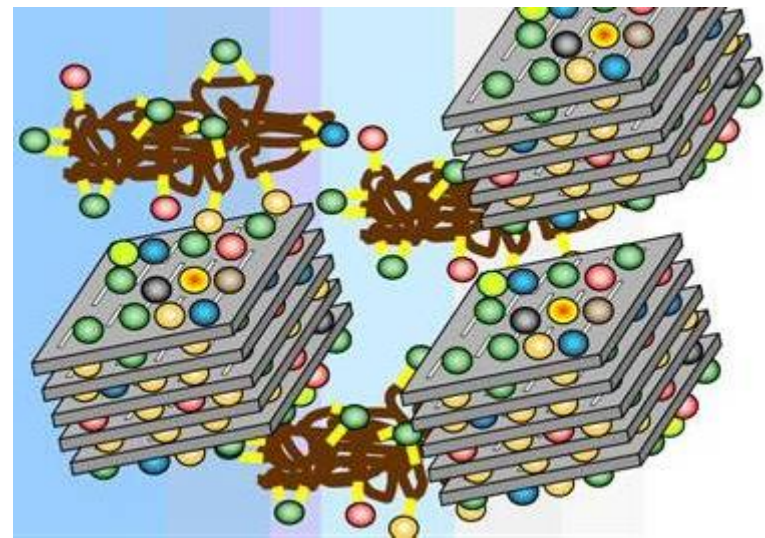
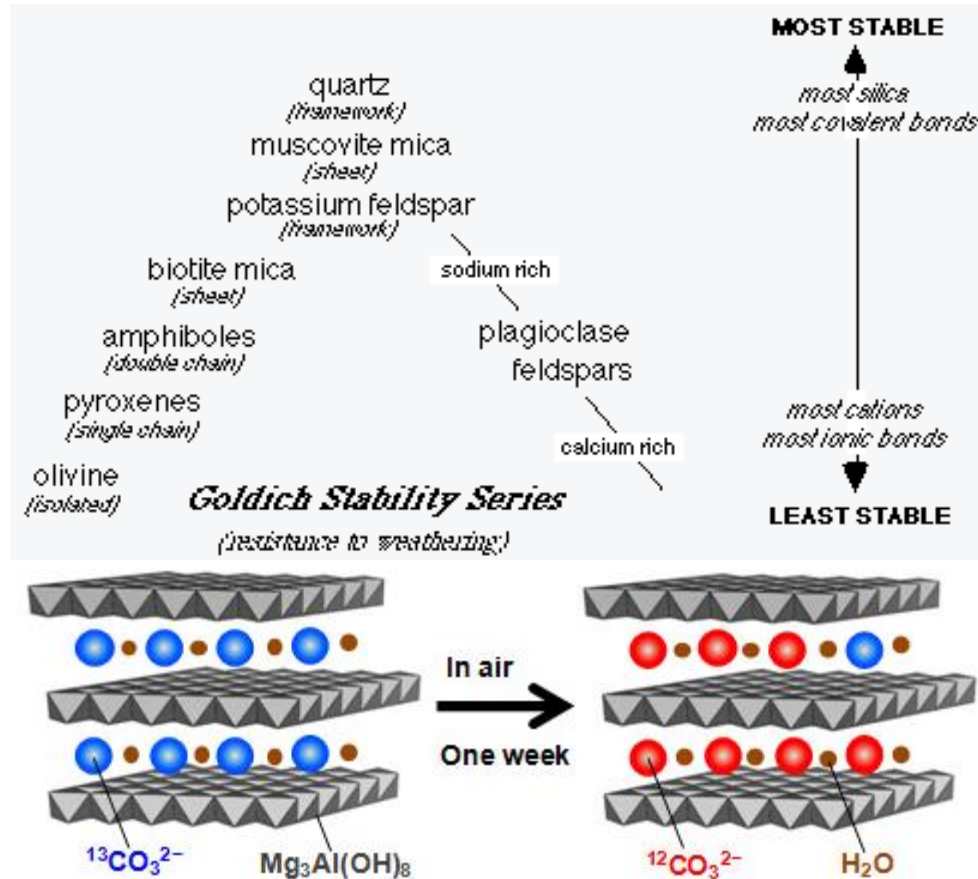
Figure 1: Pure, unoxidized iron has three electrons that can be easily removed.
 Figure 2: When iron undergoes oxidation, it loses the three electrons that are easy to remove.
 Figure 3: After it has undergone oxidation, iron has lost three electrons. The oxidized form of iron is represented with a number and a charge (3+).



Metal uptake (leaching by connate/formation water) in the source region (reaction zone=interface between connate/formation water and rock) or along **connate/formation water flow paths** is a function of kinetic and thermodynamic factors, including **rock and water chemistry, T, P, Eh and pH.**

In contact with formation waters, several common minerals are unstable, including amphibole, pyroxene, olivine and epidote. Their alteration releases trace metals into the aqueous phase.

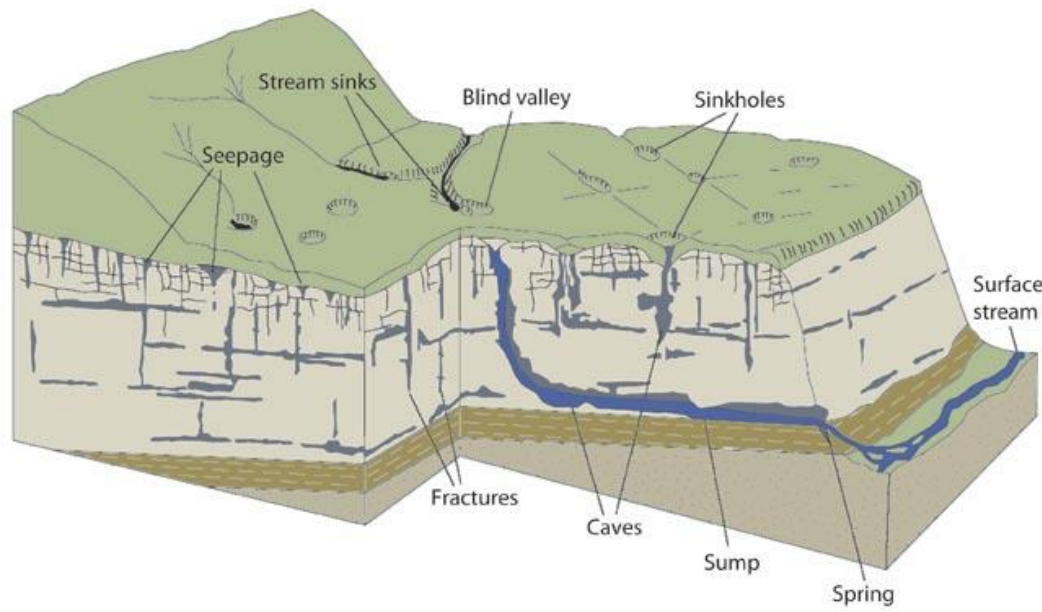
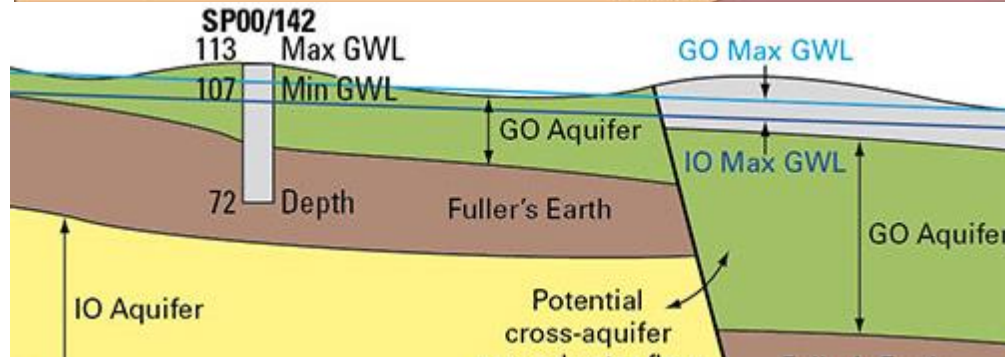
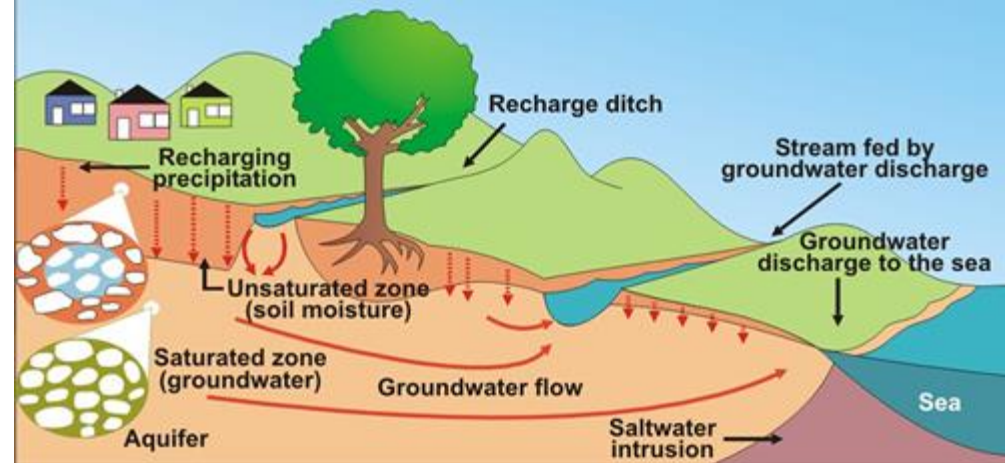
Other mechanisms of liberating metals include **ion exchange with clay minerals** and **simple diagenetic transformation of clays.** An example is **lead** that is often **adsorbed on kaolinite**, but is **released into solution (leached by solution)** during/when illite replaces kaolinite.



The flow paths of expelled deep fluids/connate/formation water are determined by hydrogeological parameters such as permeable rock units, tectonic disaggregation and the general pressure gradient.

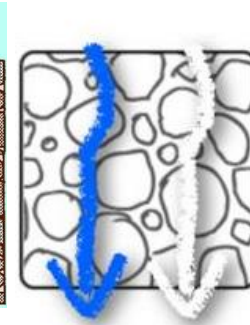
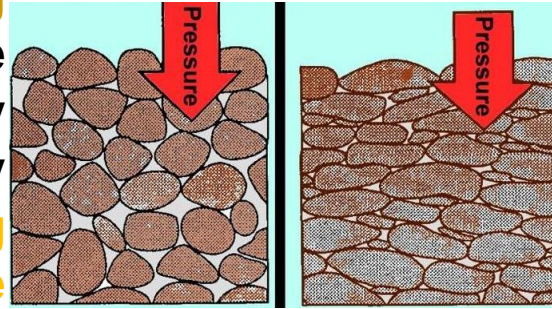
Ore formation will only occur where a large mass of hot brine/connate water is focused into preferential flow paths, which may be envisaged as streams within permeable rocks or tectonic structures.

In these channels, a rapid drop of temperature or pressure, reaction with host rocks, and mixing with chemically different water may precipitate solutes (ore minerals) in a small rock volume. Near-surface faults, reefs or karst cavities at the margins of sedimentary basins or basement islands often locate ore deposit formation.



Some of the more frequent **geological driving agents** of **basinal/fluid/connate/formation water migration paths** are the following:

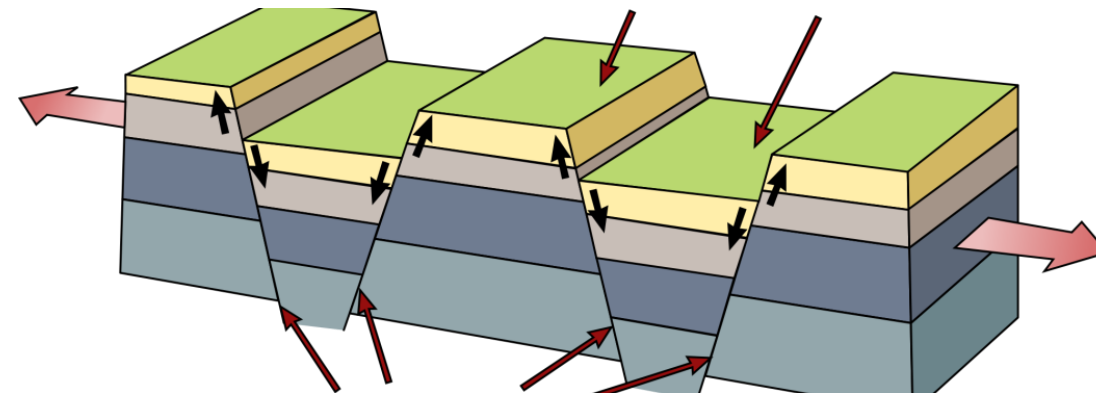
1. **standard diagenetic dewatering by compaction** of pore space (consolidation), in a slowly progressive process, mainly caused by **continuing sedimentation and subsidence** in the basin;



2. **episodic expulsion of brine by increasing overpressure** in sand lenses that are enveloped by clay beds of low permeability; this can be observed as **mud-eruptions**;



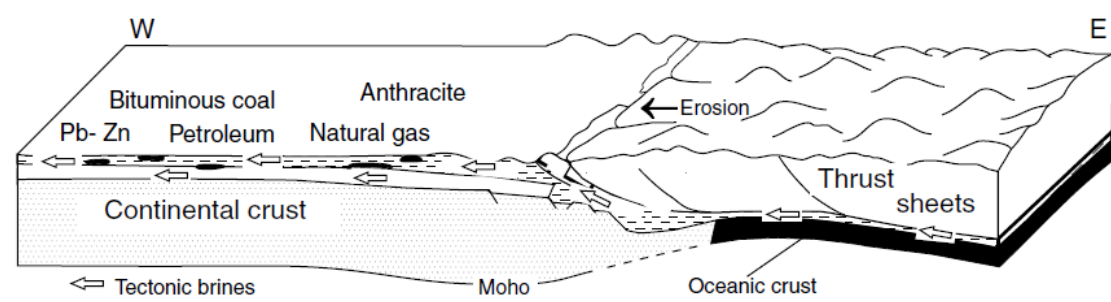
3. **displacement of deep, hot and therefore relatively light brines** by cold, heavy groundwater infiltrating from topographically elevated basin margins; this hypothesis assumes that permeable rocks or active extensional faults provide linkedup flow paths;



4. **tectonic expulsion of formation fluids by a moving nappe pile, causing flow of diagenetic and metamorphic fluids towards the foreland, where transported heat and dissolved matter result in mineral deposit formation; a present day analogue are methane-rich hot fluids ejected from the accretion wedge at many subduction fronts;**

5. **fluid overpressures can also be induced by pulses of hydrocarbon generation caused by a rapid thickness increase of cover sediments and consequently of rock temperature; or by a rapid fall of sea levels;**

6. **expulsion of formation waters by deep heatflow (e.g. cryptic intrusions, underplating).**



Many **diagenetic mineral deposits** display strikingly banded textures of newly-formed precipitates that have been called “**diagenetic crystallization rhythmites**” (DCR) or “**zebra textures**”.

The thickness of the bands varies between millimetres and decimetres. They occur in dolomite, evaporite, in sparry magnesite, in siderite and most typically, in stratabound Pb-Zn-Ba-F deposits hosted by platform carbonates.

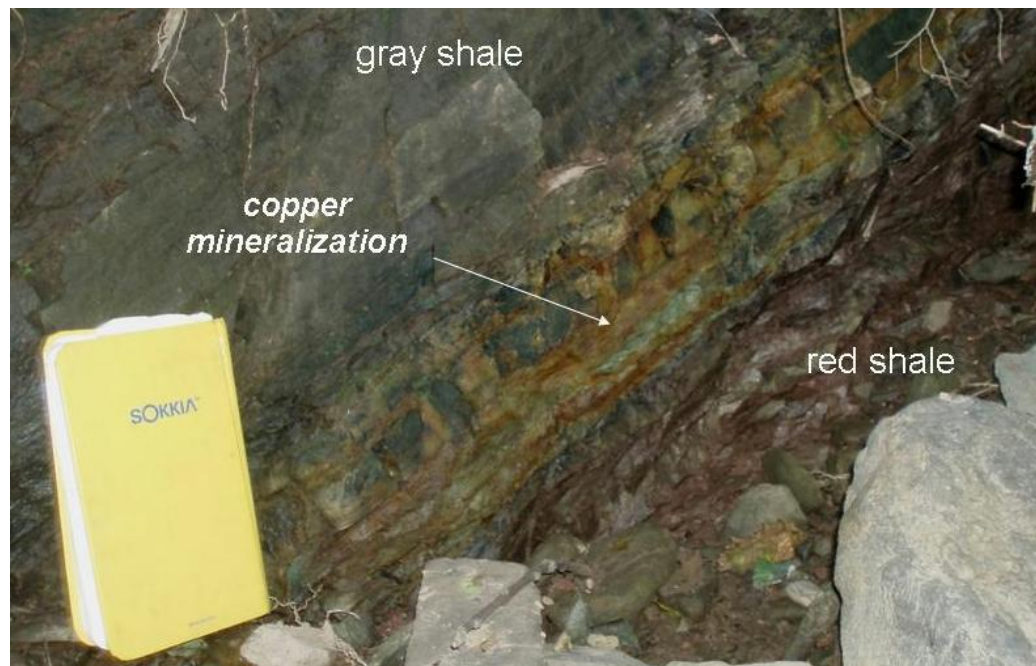


1- The European Copper Shale

The European Copper Shale is a euxinic sediment deposited in a shallow sea of only a few hundred metres water depth.

The European Copper Shale is a black laminated marly claystone formed from clay minerals, dolomite, organic matter, sulphides, anhydrite or gypsum, phosphates and little quartz. It rests on red sand/conglomerate, but in some marginal exposures Copper Shale rests directly on folded basement. The European Copper Shale is overlain by carbonates, anhydrite and salt rock.

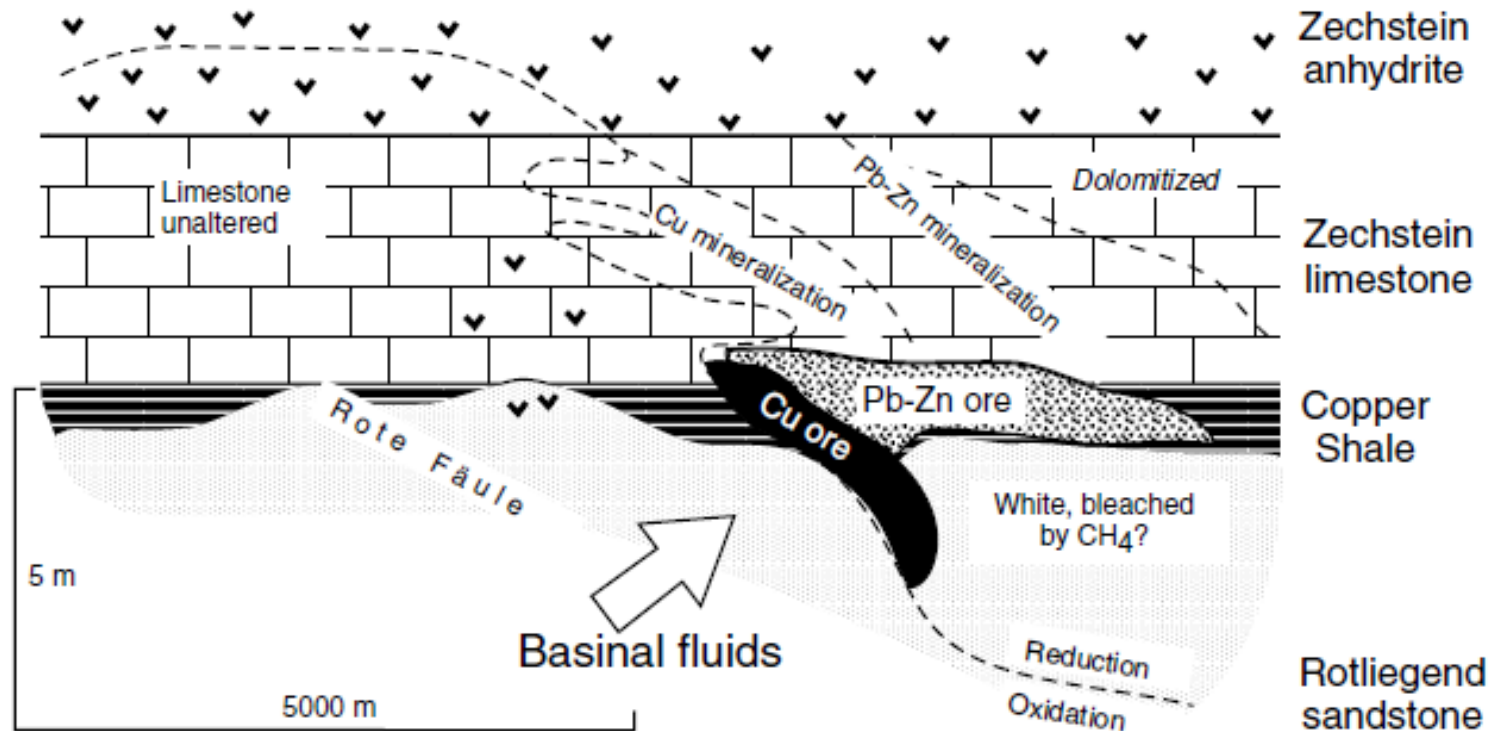
Genetic interpretations of Copper Shale ore formation have always been dominated by the controversy between syn- and epigenetic models.



The diagenetic model of **Copper Shale** ore formation include **hot, oxidized** (e.g. sulphate-bearing) **Ca-Mg-K-Cl connate/formation waters** flowing up from **deeply buried red bed sediments and volcanics** where they acquired their metal contents. Increasing compaction and the low permeability of the hanging evaporites, acting as a seal, **focused the flow towards basin margins** where the metals were **precipitated**. Possible agents of ore precipitation from the hot connate/formation waters are:

- I. **decreasing T and P;**
- II. **mixing with cool, alkaline, meteoric (or sea-) water and**
- III. **reduction by contact with organic matter and sulphides of the shale; and methane in the sandstone.**

Schematic section of a Copper Shale deposit in Northern Germany and Poland (modified from Jowett 1992 with permission from Elsevier).



The Copper Shale is dissected by **faults/fissures**. It is believed that they were the pathways for the hot connate/formation water fluids. The bulk of the extracted ore, however, is stratiform bodies within the shale containing the ore minerals **chalcopyrite, bornite, chalcocite and marcasite**.

However, some copper orebodies extend from bleached footwall sandstone through shale to hanging wall carbonate.

The copper province of White Pine, Michigan, USA and the African Copper Belt of the Democratic Republic Congo and Zambia are comparable but not identical to the European Copper Shale.

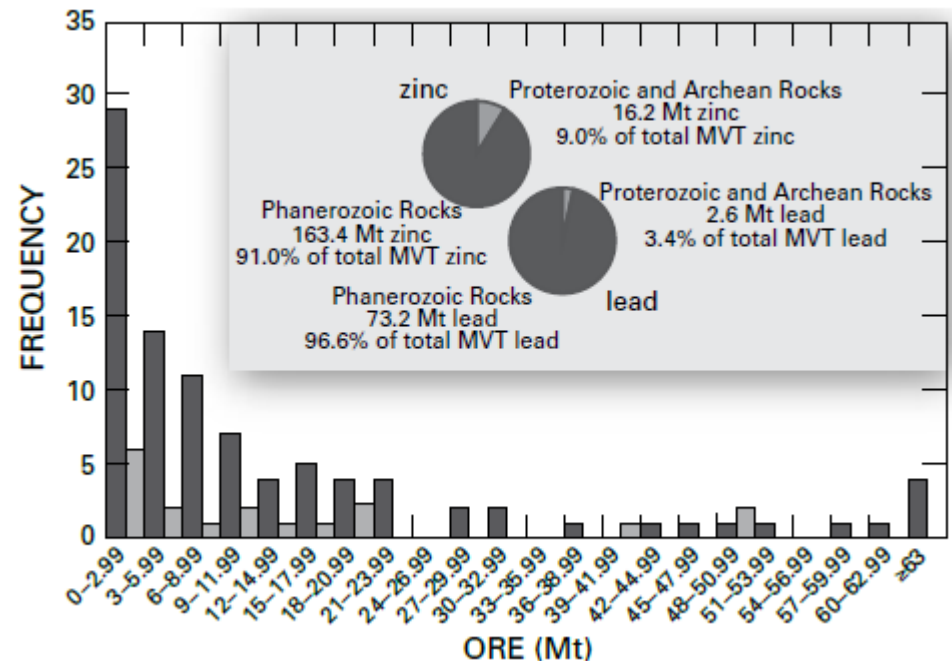


2- Diagenetic-hydrothermal carbonate hosted Pb-Zn (F-Ba) deposits (Mississippi Valley type - MVT)

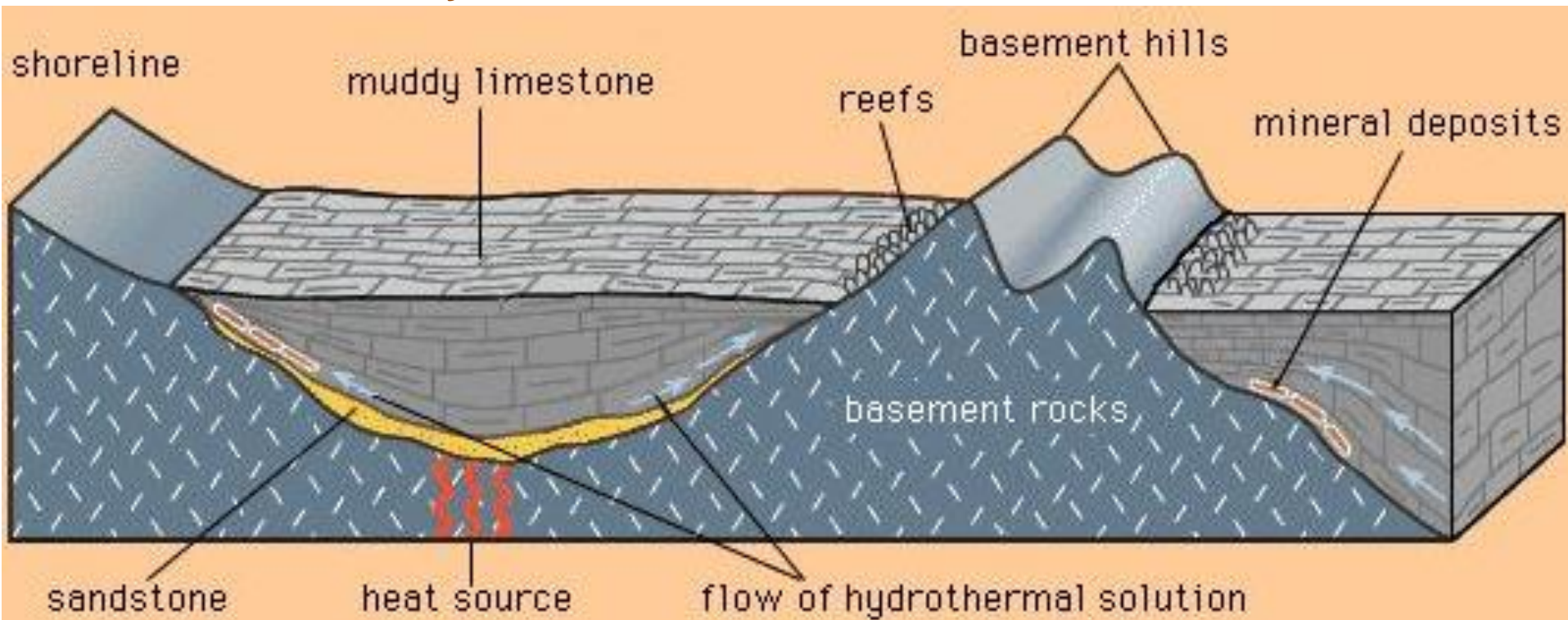
Lead-zinc ore deposits hosted by marine carbonate rocks are a large and heterogeneous group. They are formed by diagenetic processes.

Provinces with more homogeneous characteristics are commonly designated as “types”. Mississippi Valley type (MVT) province, hosts the most intensively investigated lead-zinc deposits.

The paragenesis of diagenetic hydrothermal carbonate-hosted deposits comprises galena and sphalerite, with a gangue of barite, fluorite, pyrite, marcasite, calcite, dolomite, aragonite, ankerite, siderite, quartz, colloform silica (chert) and occasionally, bitumen.



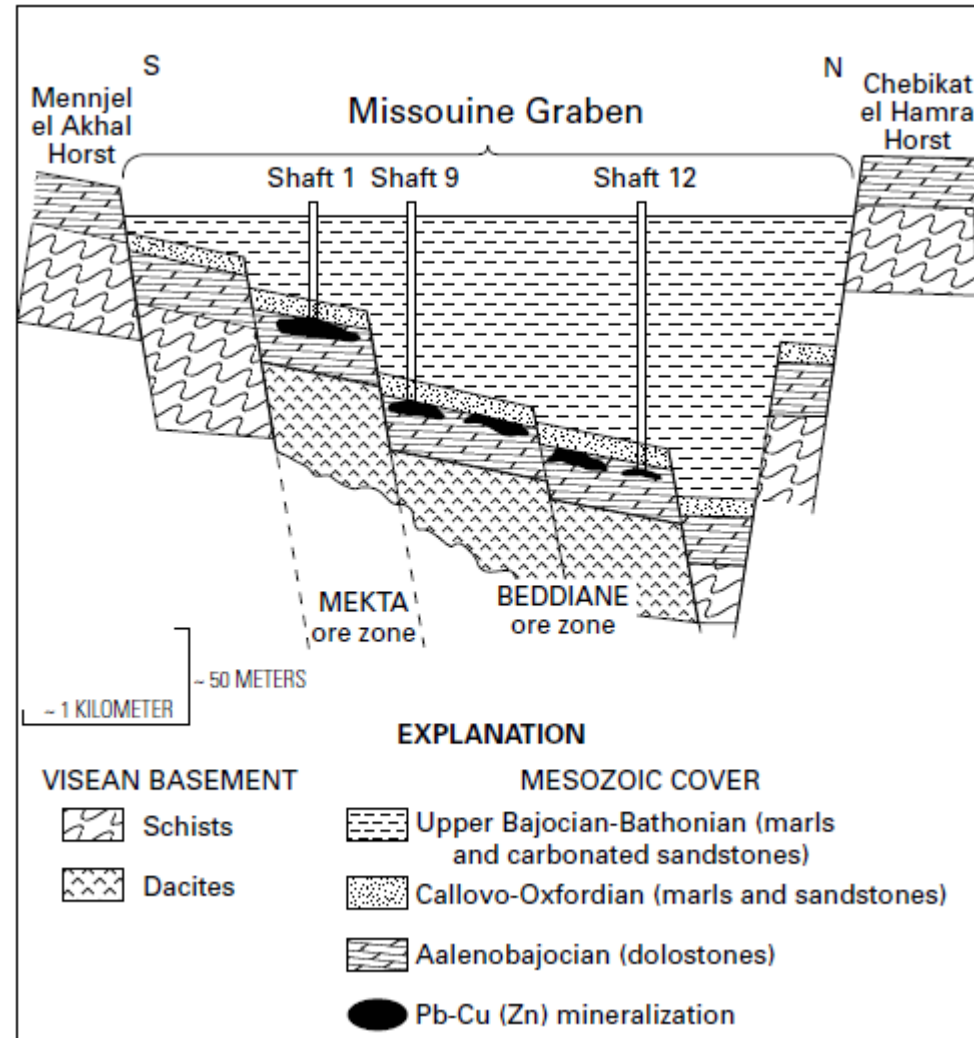
Pb-Zn originate diagenetically by mixing hydrothermal diagenetic water with near surface waters that contained reduced sulphur during diagenesis. The diagenetic process was encouraged by bacterial sulphate reduction and consumption of organic matter of the carbonate rocks. Diagenetic ore fluids were derived mainly from evaporated seawater and were driven within platform carbonates by large-scale tectonic events. In addition, magmatic fluids rich in fluorine were mixed into the diagenetic fluids. Diagenetic-hydrothermal carbonate hosted Pb-Zn mineralization is closely related to basinal evolution.



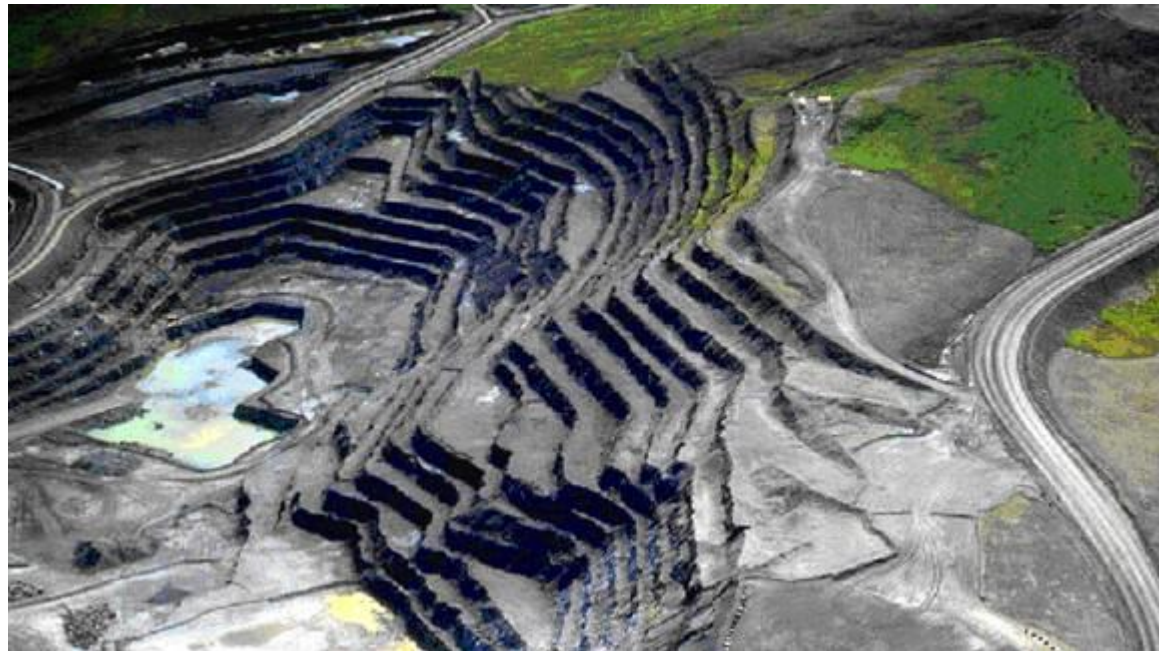
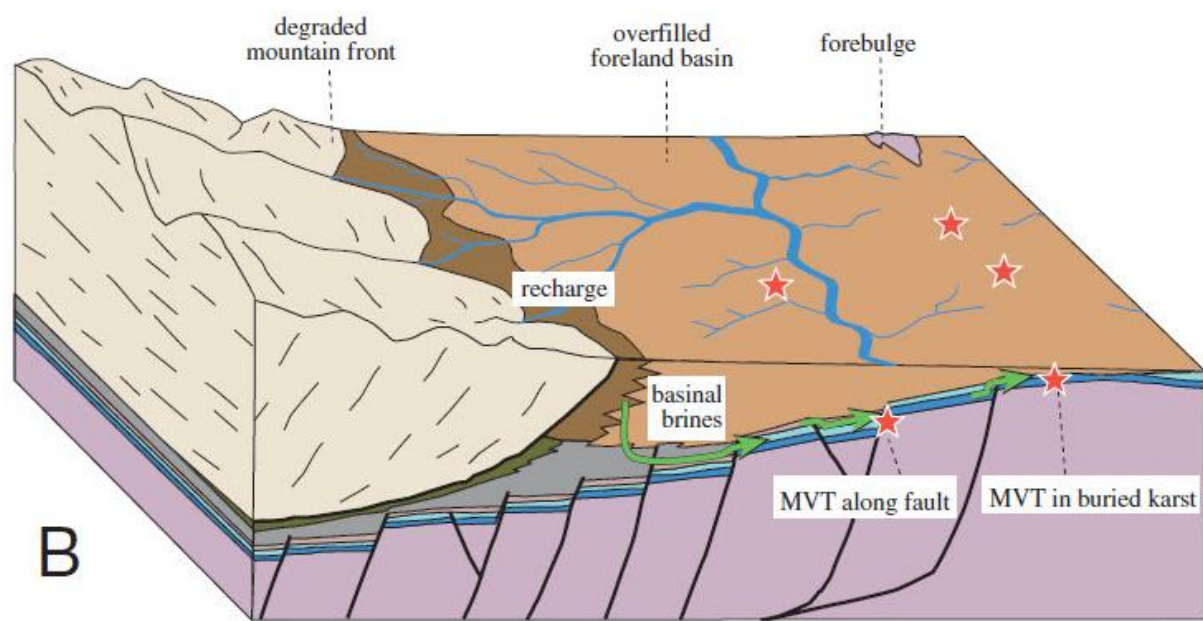
MVT deposits are always in limestones and are generally located near the edges of sedimentary basins. The hydrothermal solutions that introduced the ore minerals (principally the lead mineral [galena](#) and the zinc mineral sphalerite) apparently flowed through the sandstones and conglomerates that commonly underlie the limestones. Where they met a barrier to flow, such as a basement high or a basin edge, the solutions moved and reacted with the limestone, depositing ore minerals.

The most important characteristics of MVT deposits, are:

1. they are epigenetic;
2. they are not associated with igneous activity;
3. they are hosted mainly by dolostone and limestone, in platform carbonate sequences and usually located at flanks of basins rock-dominated passive margin sequences;
4. the dominant gangue minerals are sphalerite, galena, pyrite, marcasite, dolomite, and calcite, whereas barite is typically minor and fluorite is rare;
5. they occur in platform carbonate sequences commonly at flanks of basins or foreland thrust belts;
6. they are commonly stratabound but may be locally stratiform; and include tectonic or karst cavity breccias that were cemented by ore and gangue minerals; replacement bodies and cross-cutting veins.



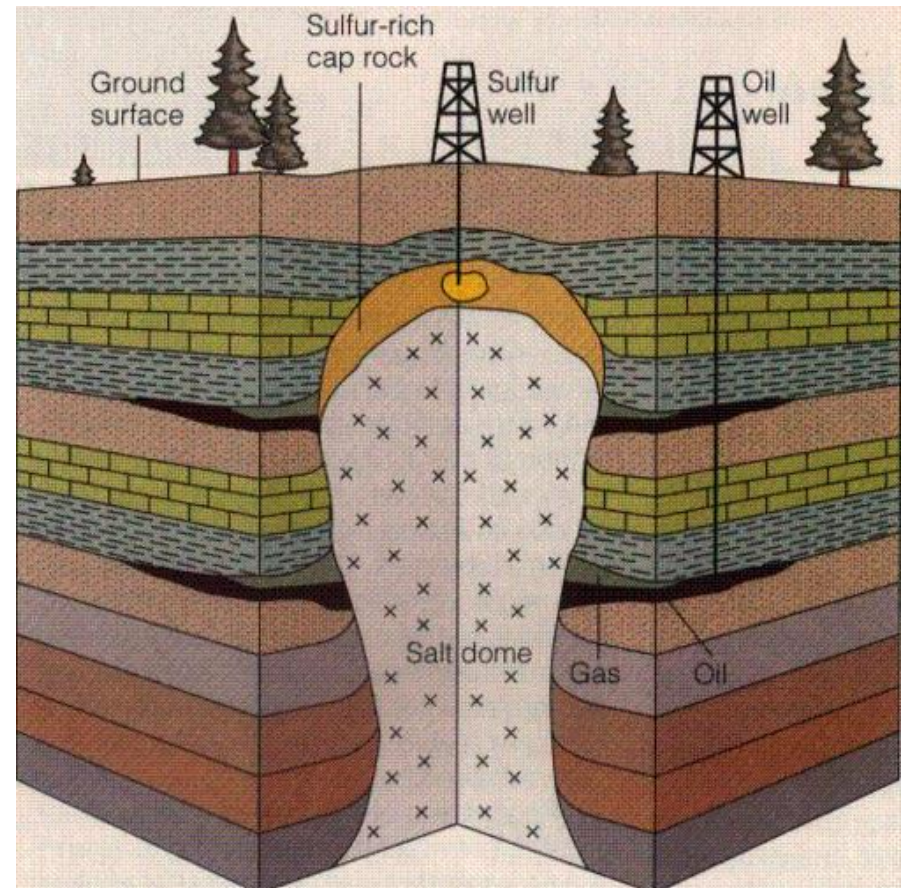
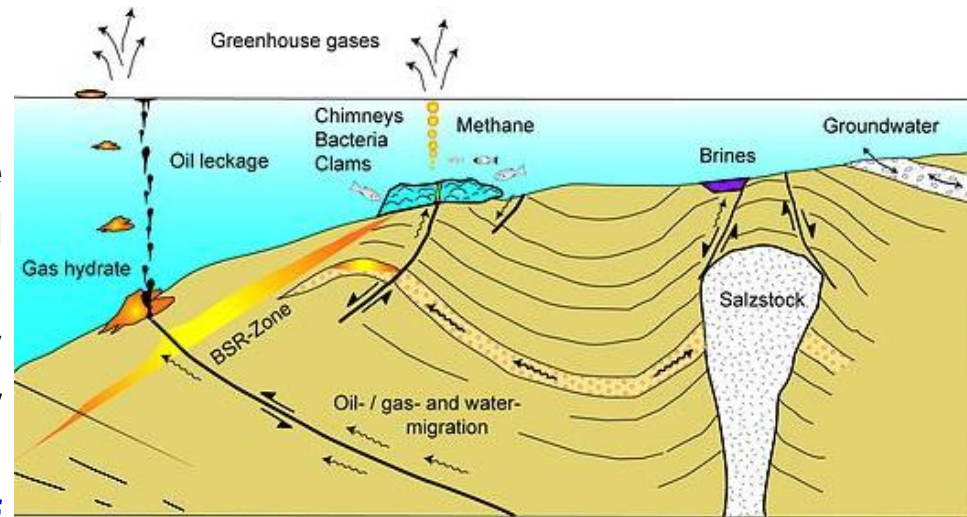
7. the ore fluids were basinal brines with ~10 to 30 wt. percent salts; with metal contents reach several thousand ppm.
8. they have crustal sources for metals and sulfur;
9. the most important ore controls are faults and fractures, dissolution collapse breccias, and lithological transitions;
10. temperatures of ore deposition are typically 75°C to about 200°C;
11. sulfides are coarsely crystalline to fine grained, massive to disseminated;
12. the sulfides occur mainly as replacement of carbonate rocks and to a lesser extent, open-space fill.



3- Diagenetic-hydrothermal ore formation related to salt diapirs

Basinal brines and salt rocks, which are assimilated by magmatic intrusions and consequently leach metals from pervaded rocks, may be the key for understanding the iron oxide-copper gold class of deposits. **Brines** formed by dissolution and/or dehydration of salt rich evaporites within basinal sediments are of specific origin.

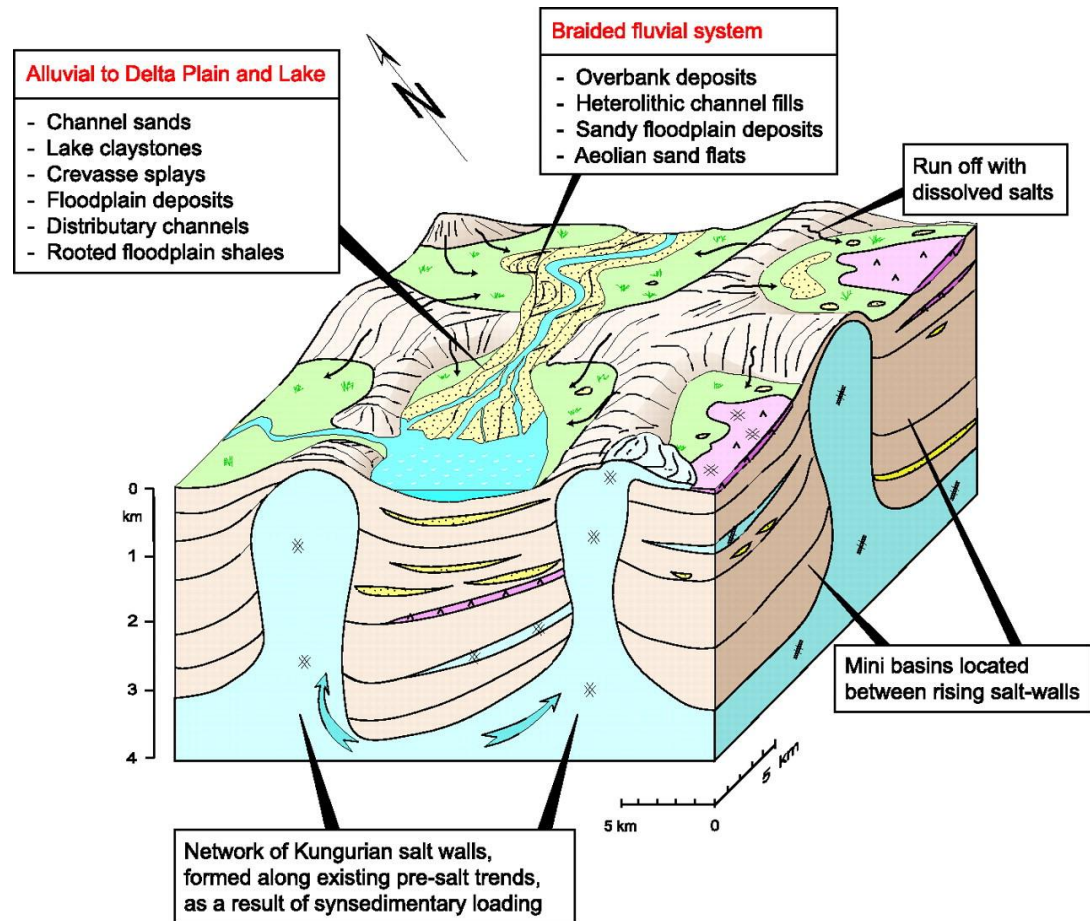
Most sedimentary basins contain common **evaporitic rocks** such as anhydrite and rock salt. **Dehydration water** from evaporites and formation water in contact with these rocks must acquire the character of a saline brine. Other sources of **brines** in sedimentary basins include **evaporated seawater**, **terrestrial saline lakes** and **mature formation water**. The source of salinity is discerned by determination of halogen and electrolyte ratios.



Metallogenetic action of brines is especially obvious when salt and epigenetic hydrothermal ore deposits are closely related, in space and time. The best sites for studying this relationship are salt diapir related ore deposits. In addition to oil, some salt diapirs are intimately related to ore deposits (Pb, Ag, Zn and Fe in North Africa), and to non-metallic mineral deposits (barite, fluorite, strontianite; emerald in Colombia).

Several large metasomatic diapir-related ore deposits represented by siderite and numerous small lead-silver-zinc deposits are found in Early Cretaceous limestones where these are in contact with apical parts of the diapirs in Morocco.

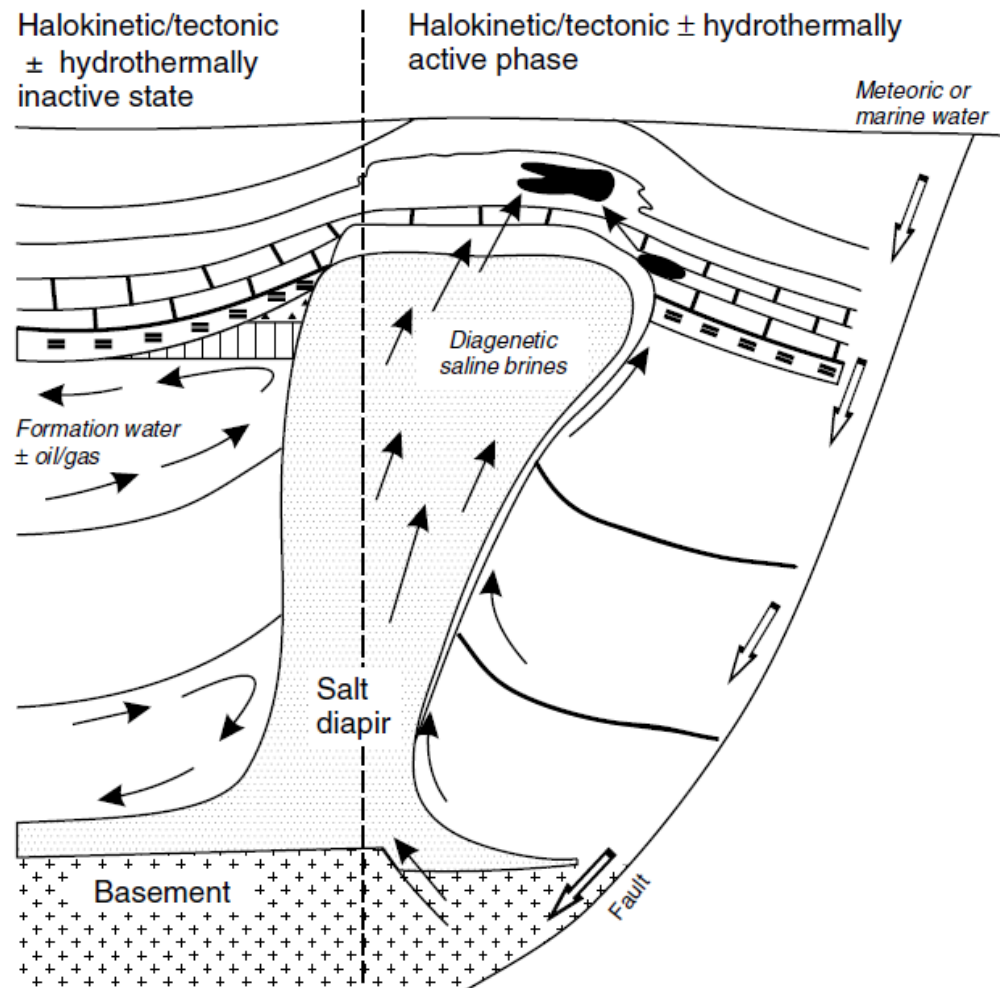
The siderite replaces Aptian limestone that is in direct contact with salt rock. Orebodies are stratabound. Siderite near the boundaries faithfully preserves bedding, stylolites and fossils of metasomatized limestone and contains large druses of coarse calcite, quartz and tetrahedrite.



The origin of these ores is believed to represent a complex interplay of **halokinesis (the movement of salt bodies)** with **fluid generation by diagenesis of evaporites and host rocks**.

Partial admixture of **meteoric or seawater** and **brines sourced from the diapir** are all possible. At elevated temperature, iron is extremely soluble in reduced, acidic and highly concentrated brines. Precipitation of siderite is induced by drastic pH-change in contact with the carbonates and by sudden lowering of pressure and temperature.

In this model, the **diapirs and their solution breccia envelope** are preferred channels for upflowing deep diagenetic brines. In active halokinetic phases diapir salt is permeable.



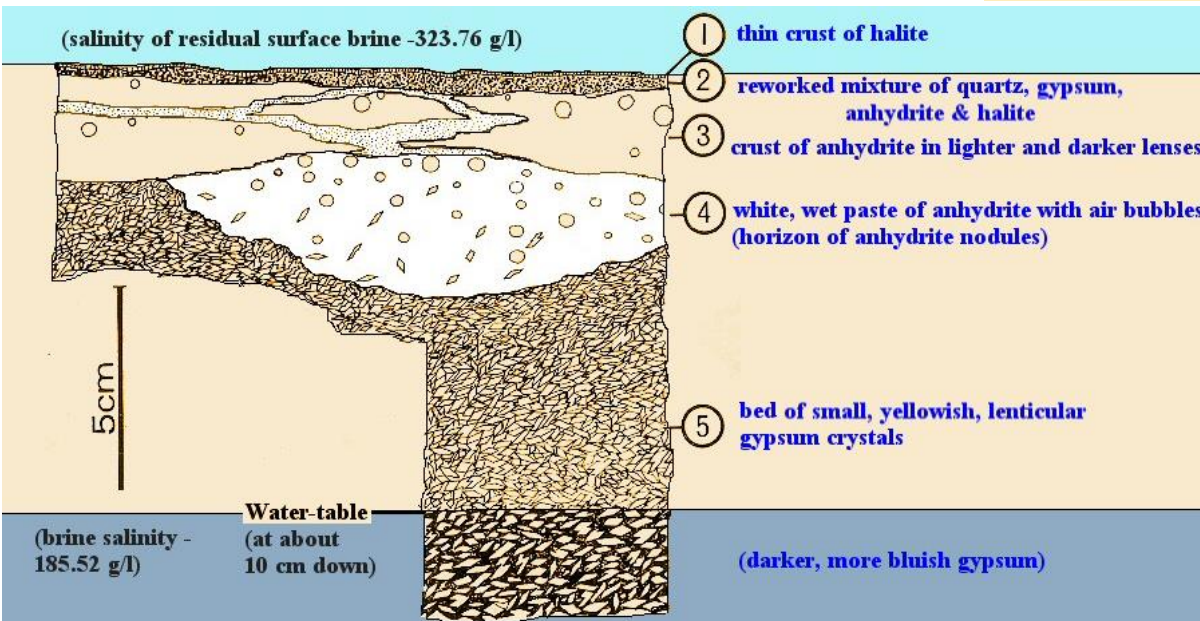
Diagenetic metallogenesis related to brines released from salt diapirs, based on observations in the Maghreb region in North Africa.

Occasionally, a **pre-enrichment of metals in evaporites is possible**. Many **terrestrial salt lake brines contain anomalous and in part exploitable metal concentrations**, for example of **lithium, tungsten and magnesium**.

Sabkhas are believed to trap metals and elements such as **fluorine and barium** that are delivered by **inflowing groundwater**.



Pit into sabkha of the First Depression about halfway between Alexandria and El Alamein on Mediterranean coast of Egypt. Gypsum is precipitated a few cm beneath the surface in the form of displacive nodules and incipient enterolithic veins. Shovel gives an approx scale. Sulphate-saturated groundwater can be seen about half a metre down. Ian West & Yehia Ali (c) 2008.



Profile through uppermost part of sabkha sediments about 50 metres from the margin of the salt crust (salt lake) in the northern part of Dukhan Sabkha. Modified after Perthuisot (1977). Compare with later photograph of pit in the sabkha where the nodules occur. Ian West & Tonya West (c) 2006.

End of Lecture