



Economic Geology: Lecture Notes

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Hydrothermal and Skarn Ore Formation

Lecture Contents



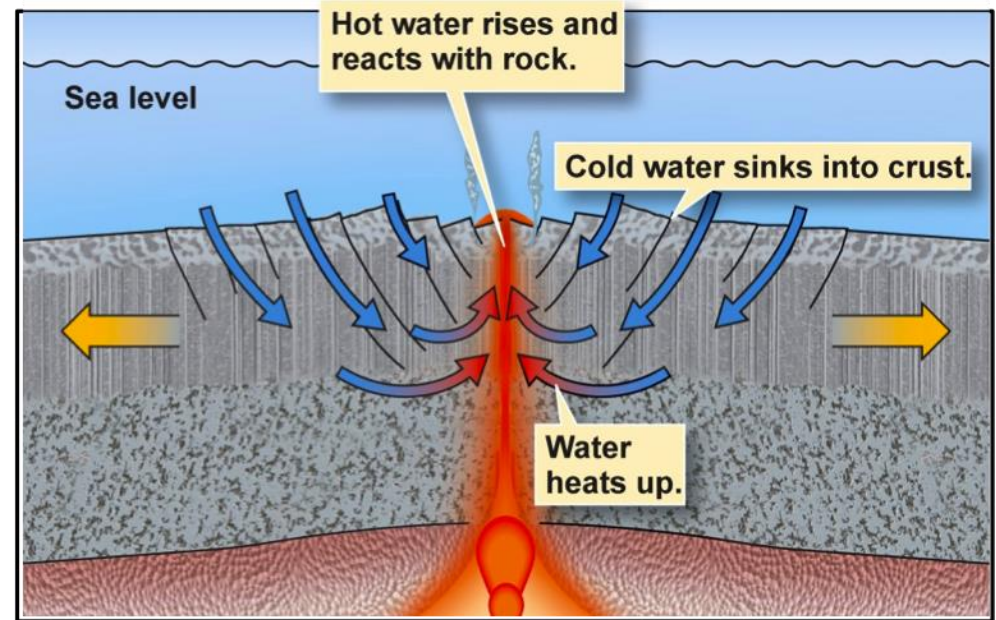
- I. What are hydrothermal solutions?
- II. Hydrothermal convection
- III. Chemical composition of hydrothermal solutions
- IV. How could ore and gangue minerals precipitate from hydrothermal solutions?
- V. Source and origin of hydrothermal fluids and solutions
- VI. Classification of hydrothermal solutions/ore deposits
- VII. What is “Skarn”?
- VIII. How would ore bodies be formed in/around the Skarn?
- IX. Hydrothermal-metasomatic ore deposits

6. Hydrothermal ore formation

The term **“hydrothermal water”** applies to subsurface water with a temperature that makes it an agent of geological processes, including hydrothermal ore formation.

“Geothermal water” is a subgroup of hydrothermal solutions that occur near the Earth’s surface and is mainly used as an geothermal energy source.

Thermal springs are common indicators of **geothermal reservoirs at depth**. Many **hot springs** and **geysers** currently display precipitation of minerals and ore.



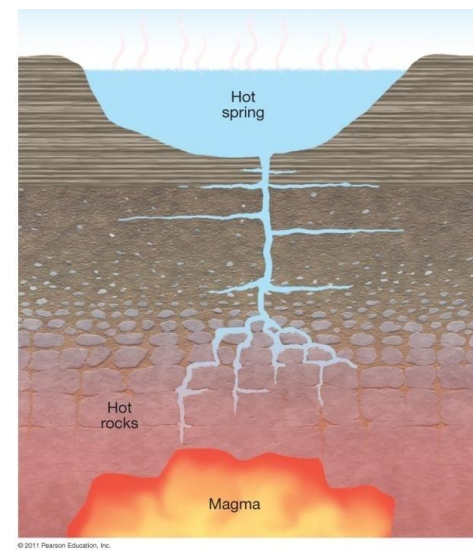
Hydrothermal water



Thermal springs

- **Hot springs**

- **Water heated by magma**
- **Forced upward from pressure resulting from heating**
- **Resulting topographically in hot springs**
- **Algae growth**



- **Geysers**

- **Intermittent hot spring**
- **Accumulation of superheated water and steam builds pressure**
- **Tremendous heat is required for geyser formation**
- **Variable eruption times**
- **Variable deposits, most are sheets of deposits scattered irregularly over ground**



- **Fumaroles**

- **Surface crack connected to a deep-seated heat source**
- Little water drainage
- Water that is drained is converted to steam
- Steam issuing vent, either continuously or sporadically



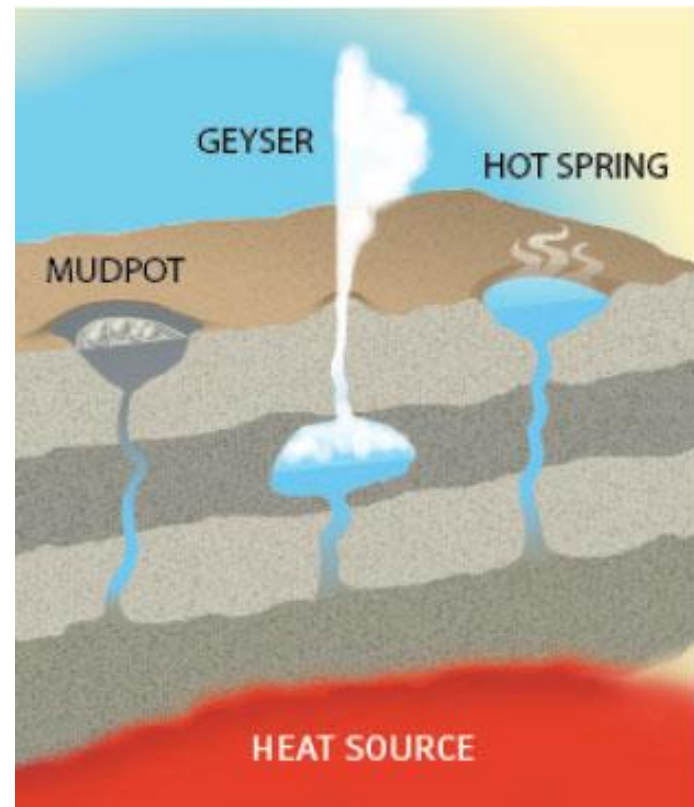
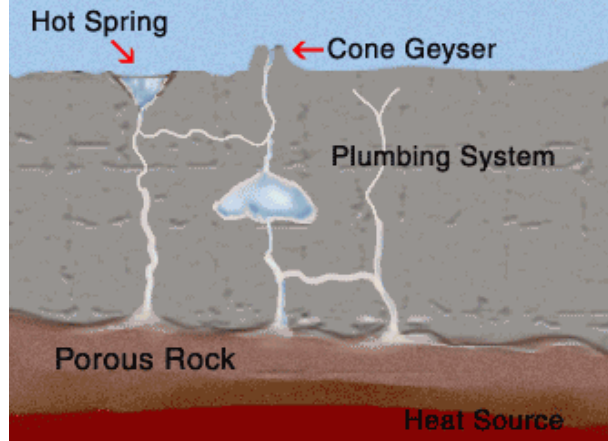
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Similarly, hot water in **mud volcanoes** of oilfields **is not magmatic but formation or connate water** (diagenetically altered seawater enclosed in sediments).

Many other observations confirm that **“hydrothermal water”** has no unique but many possible sources.



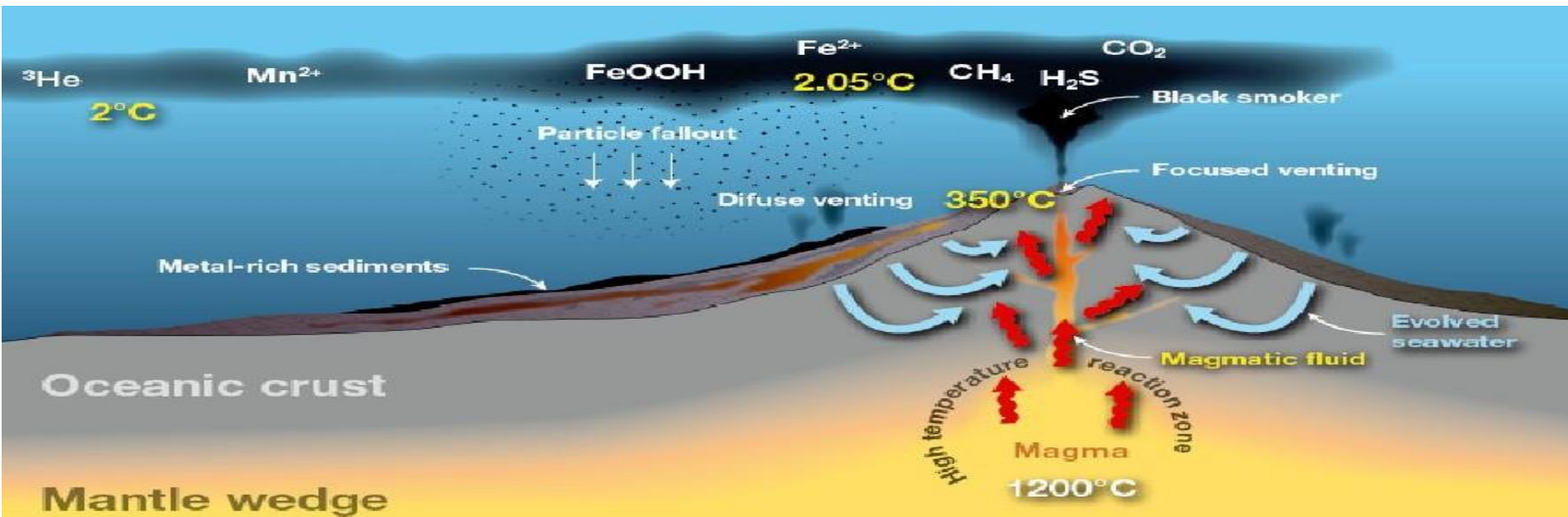
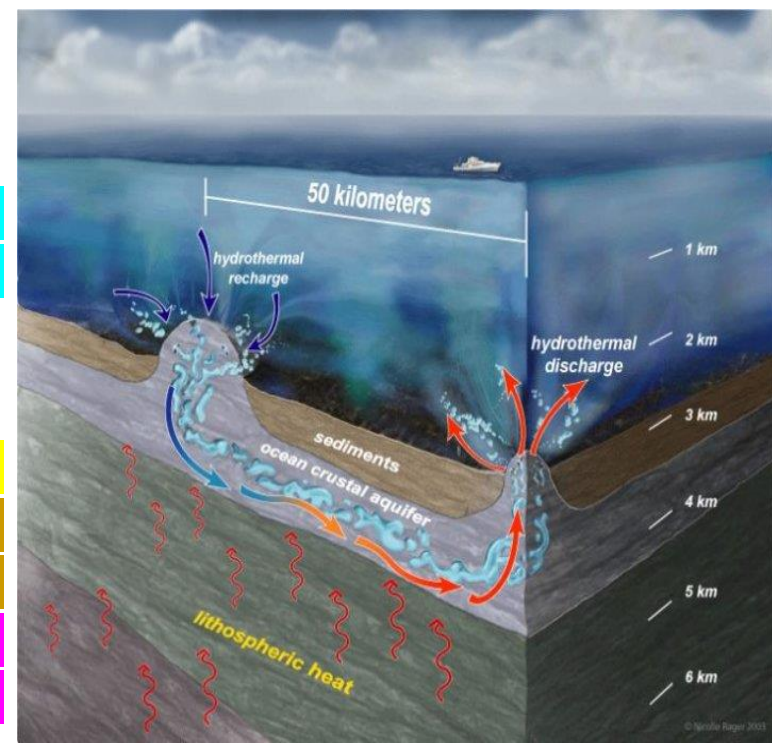
How Geysers Work



I. What are hydrothermal solutions?

Isotopic investigations revealed that many geothermal and hydrothermal waters are not of magmatic but of meteoric derivation (i.e. from local precipitation).

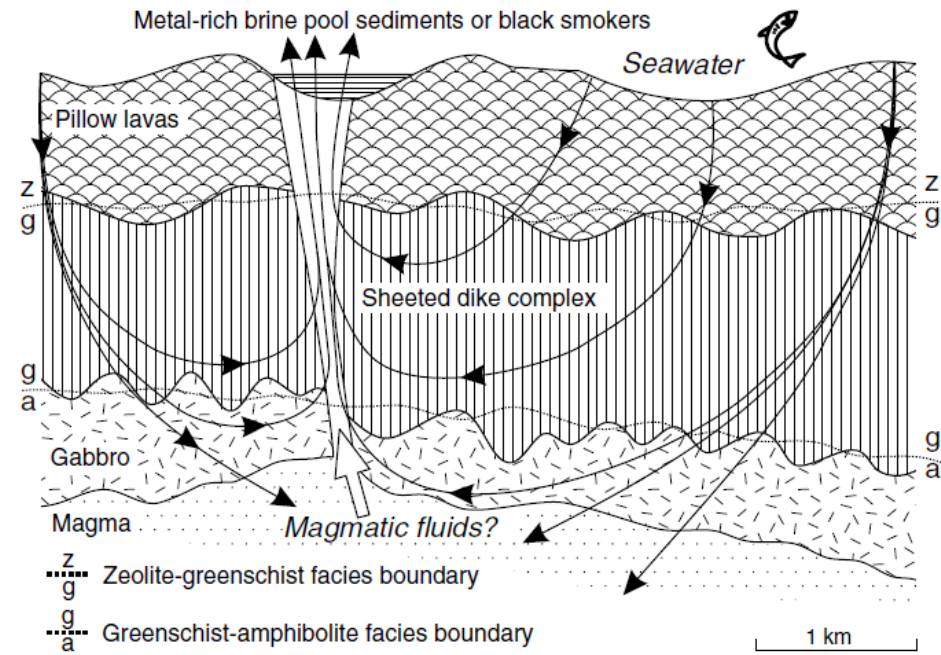
Hydrothermal activity in undersea volcanoes is largely the result of sea water descending into the crust, being heated up and then chemically breaking down the surrounding rocks to be mineral-rich fluids then re-enter the water column either diffusely over a wide area, or out of one of many vents in a hydrothermal field.



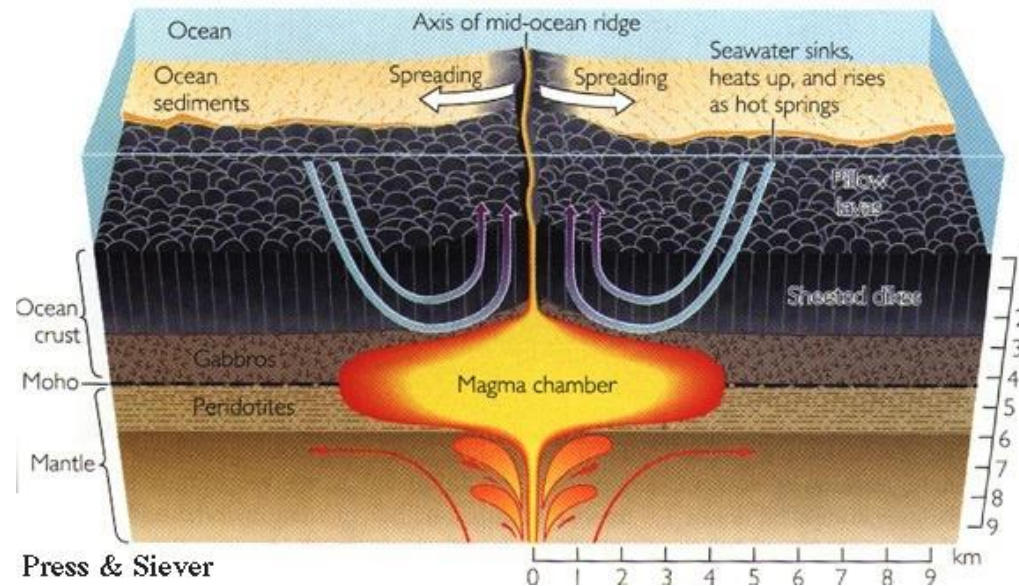
Most hot waters are **dilute solutions** of chloride, carbonate and sulphate, with higher concentration of dissolved silica, boron and sulphides.

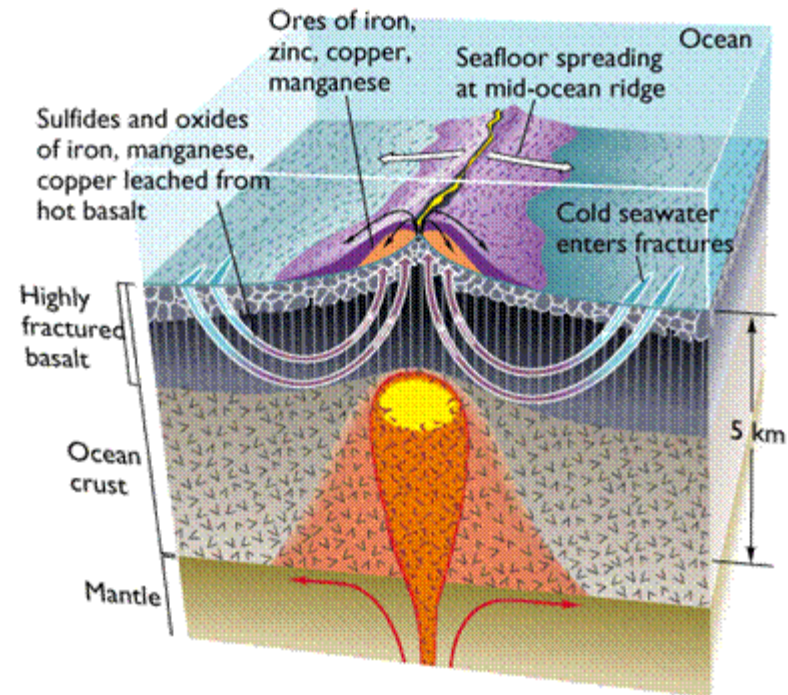
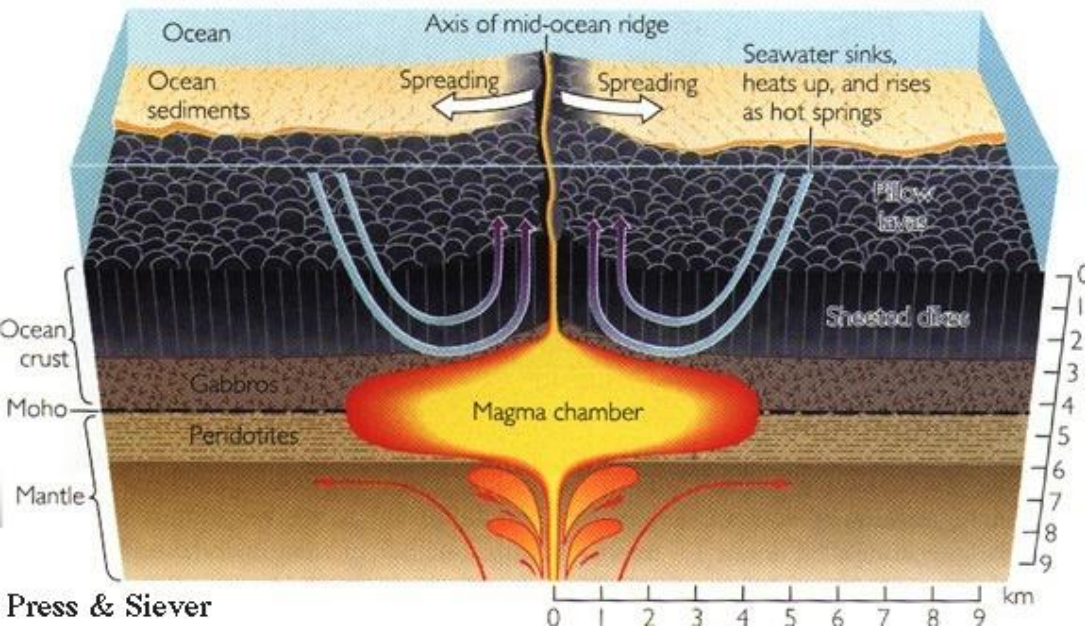
II. Hydrothermal convection

Hydrothermal convection cells are established where heat sources below the surface coincide with permeable flow paths, often provided by extensional tectonic deformation. Cold infiltrating surface and groundwater is drawn to the “heat exchanger” at depth. The lower density hot water, compared to cold water, causes ascent of hydrothermal solutions and establishes hydrothermal convection.

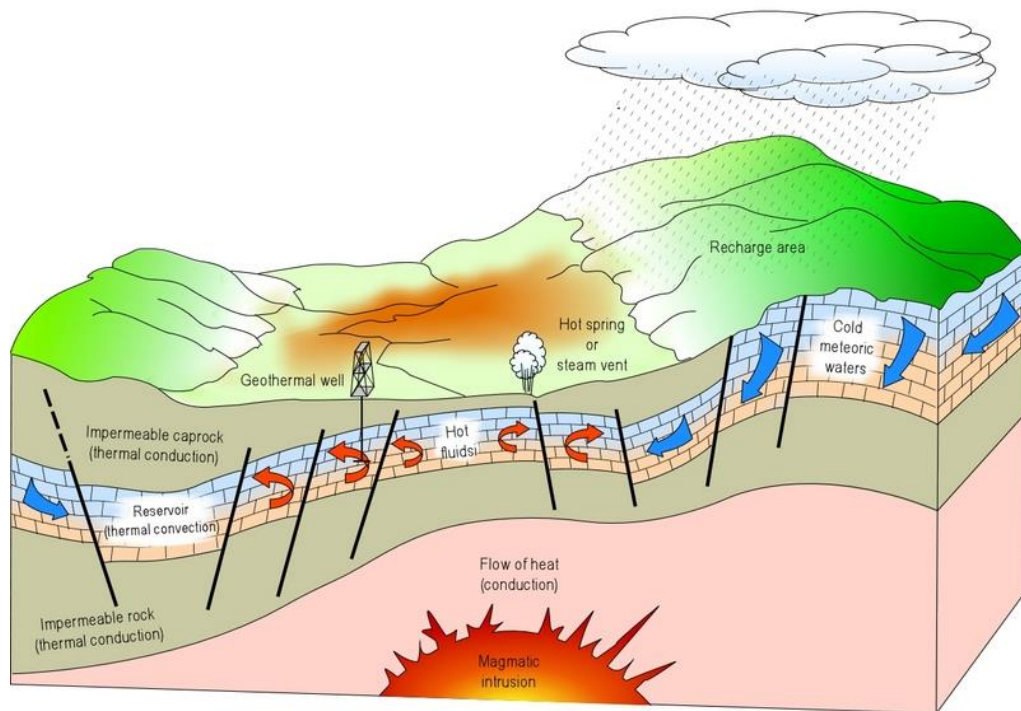


Seawater convection, ocean floor metamorphism and focusing of rising hot fluids by apical parts of a mid-ocean magma chamber and by faulting.





Schematic representation of an ideal geothermal system.



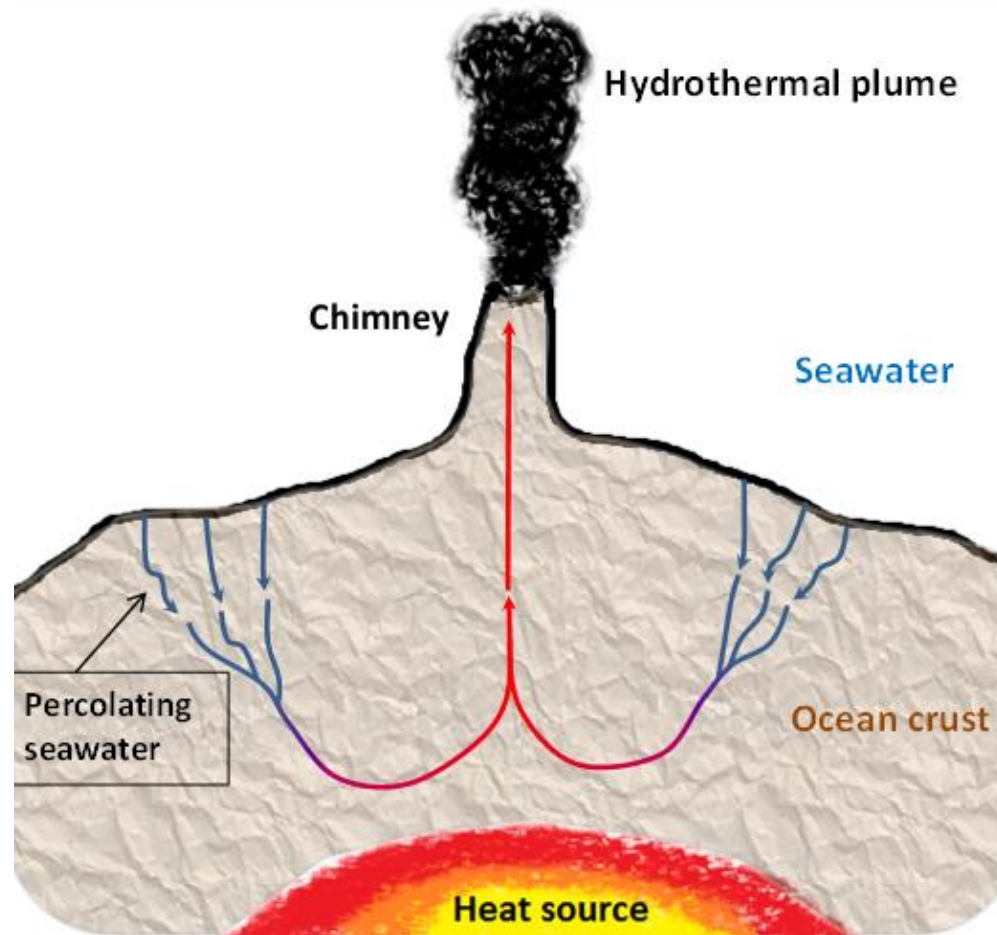
III. Chemical composition of hydrothermal solutions

The chemistry of hydrothermal solutions is variable and a result of interaction between rocks and hot water.

Factors like initial state of rock and water, the water/rock mass ratio, temperature, chloride concentration, pressure and redox state control the chemistry of hydrothermal solutions.

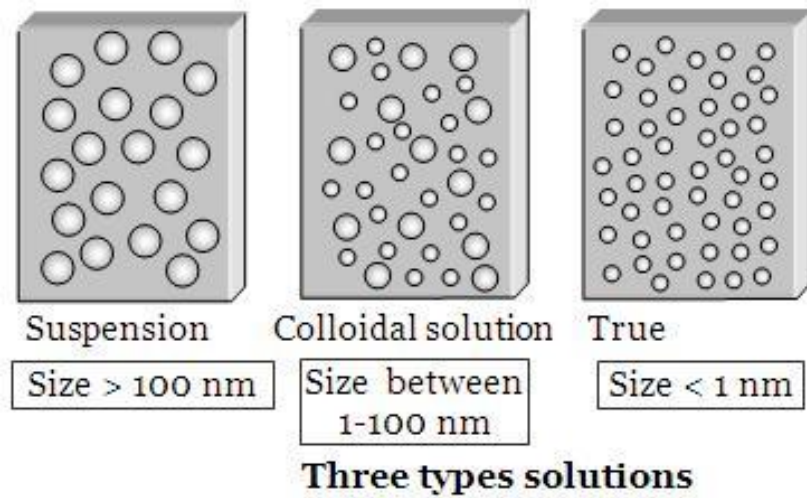
The fraction of dissolved matter in hydrothermal solutions varies from less than 1 to over 50wt.% of its weight.

Chlorine and sulphur are the most important anions. Salinity ranges from very low to more than 50% and the source of salinity (e.g. halite dissolution, evaporation of seawater, etc.) is detectable by determination of halogens and electrolytes.

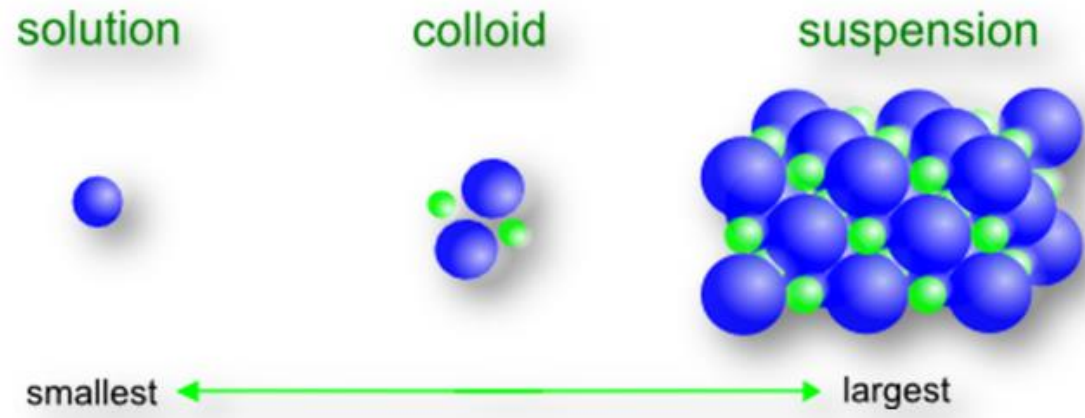


Seawater percolates down through the ocean crust, becomes super-heated by magma (Heat source) and reacts with the surrounding rock then rises rapidly and is expelled from the vent forming a plume of precipitating particles (Hydrothermal plume)

Metals are to some extent **dissolved as simple ions or ion pairs**, but more commonly in the form of **complex ions**, which combine **chlorine, dissociated OH groups and bi-sulphides**, as well as **NH₃, H₂S and CO₃**.



Metal concentrations in hydrothermal solutions range from <1 to several 1000 ppm (parts per million, equal to gram/tonne). Even higher concentrations in solution are possible when metals are part of complex ions. **Hydrothermal solutions carry metals not only in dissolved form but also as colloidal particles.**

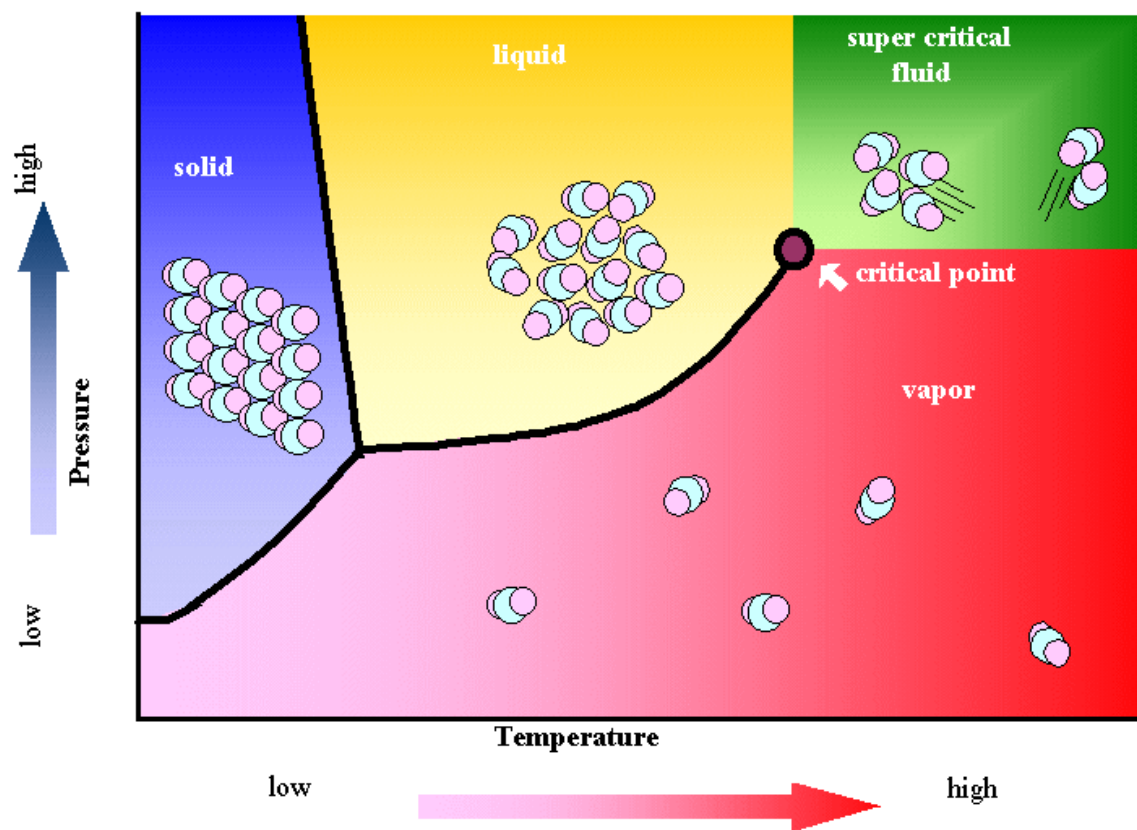


Colloids are tiny particles (1–1000 nm), which are quite common in many natural waters, usually at low concentrations. High concentrations of dispersed colloids in water are called hydrosols. In many cases, **hydrosols** are the precursors of gels. Hydrosols and gels may form by local super-saturation of a substance, because of a **sudden change of pH, T, P or Eh.**

Possible phase states of hydrothermal waters are liquid, gaseous (vapour) and fluid (fluid= supercritical “gas” or “liquid”).

Many hydrothermal deposits were formed by supercritical fluids (water reaches its supercritical state at $T > 374\text{ }^{\circ}\text{C}$ and $P > 225\text{ bar}$) (increasing salinity moves the critical point to higher T and P).

Similar to gas, supercritical fluids have a smaller viscosity, higher diffusivity and mobility.



Supercritical fluid has high thermal motion, and it is possible to change the density widely (from low like a gas to high like a liquid), therefore we can control many properties whose function is expressed by density.

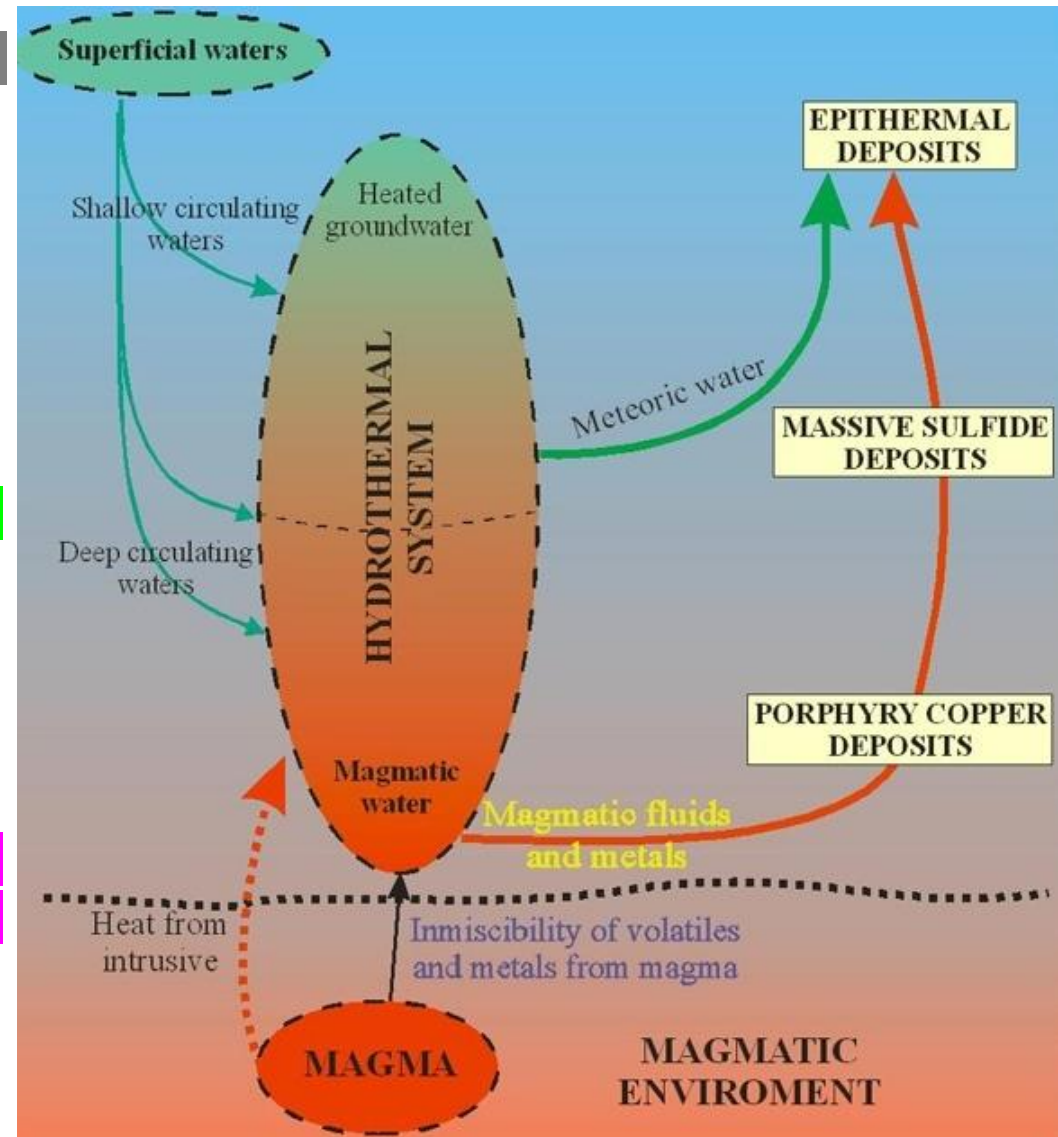
A supercritical fluid is any substance at a temperature and pressure above its critical point, where distinct liquid and gas phases do not exist. It can effuse through solids like a gas, and dissolve materials like a liquid. In addition, close to the critical point, small changes in pressure or temperature result in large changes in density.

A fluid comprising CO_2 or CH_4 in addition to water has a high carrying capacity that depends on pressure and density variations. Very small variations cause either dissolution or precipitation of solids.

Hydrogen ion activity (pH) of hydrothermal solutions varies from moderately acidic to moderately Alkalic (exceptions could occur, acidic conditions, for example, cause formation of kaolinite, alunite or topaz from feldspar).

Deep hydrothermal water is normally reduced (low oxygen); however, oxygen content may increase near the surface by mixing with fresh meteoric water.

Bituminous substances are a common accessory in hydrothermal deposits. This can be a sign that the hydrothermal solutions were sourced in basinal sediments (e.g. diagenetic formation water mixed with hydrocarbon fluids).



Magmatic, metamorphic and groundwater fluids may interact in hydrothermal systems to different degrees

IV. How could ore and gangue minerals precipitate from hydrothermal solutions?

1- Changing temperature and pressure reduces solubility of metals in hydrothermal solutions.

Precipitation is a function of the relative stability of metal complexes and decreasing temperature often results in the common sulphide precipitation sequence from early Cu to Zn, Pb, Ag and finally Hg.

Pressure drops may cause fluid immiscibility such as the formation of two fluids (e.g. aqueous and carbonic) from an originally homogeneous fluid (aqueous-carbonic).

Pressure drop can change pH, fO_2 and temperature, thus inducing mineral deposition. Rapid pressure fluctuations are typically caused by tectonic events.



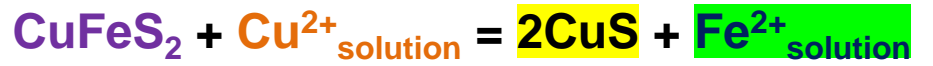
Falling **pressure** associated with **boiling** changes chemical properties of a **hydrothermal solution** (concentration, pH, Eh, stability of complex ions), which **consequently reduces the solubility of dissolved matter.**

The term **“effervescence”** is preferably used in place of **“boiling”** due to the **involvement of gases.**

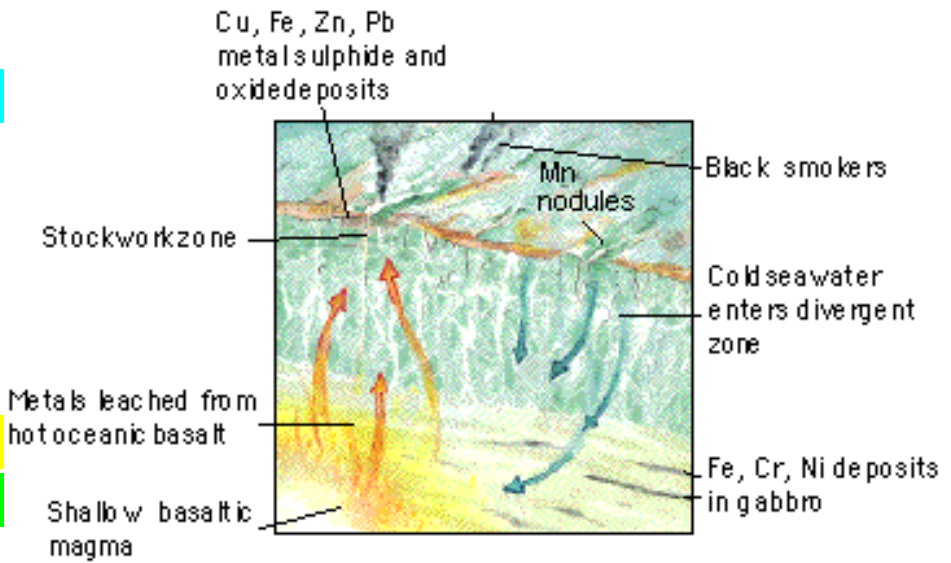


2- Mixing of chemically different waters induces deposition of **ores and minerals**. A common example is the formation of barite. **Barite (BaSO₄)** is precipitated when **ascending chloride solutions with dissolved barium ions** encounter **sulphate-ion bearing water (e.g. seawater)**.

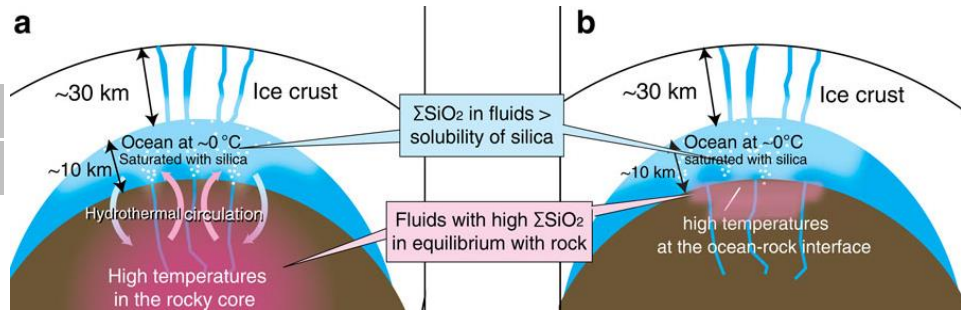
3- The reaction of hydrothermal solutions with host rocks or with previously deposited ore minerals is a very efficient means of mobilizing dissolved elements. When **metal-bearing solutions** encounter **sulphide minerals**, **the more noble metals are precipitated**, whereas **the less noble elements pass into solution**:



This **selective precipitation of more noble metals from solution by exchange with less valuable elements** is a function of **electronegativity, ionization potential, electron affinity, redox potential and the energy of chemical bond formation**.



Circulation of fluids and precipitation of mineral deposits



(a) Deep hydrothermal circulation would have occurred between a warm, and probably porous, rocky core. (b) Hydrothermal reactions would have taken place at the ocean-rock interface.

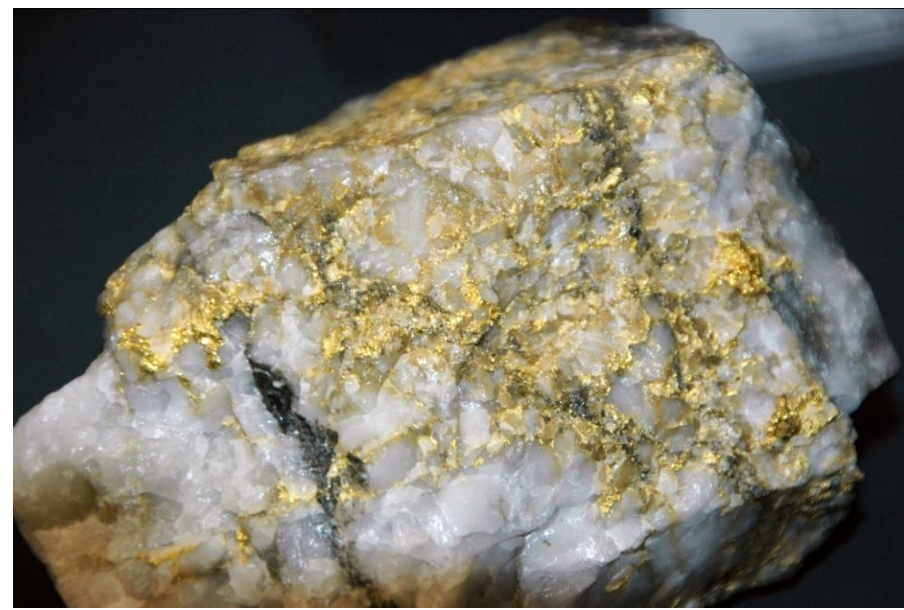
Gold (electronegativity 2.4 Pauling's) **is more noble** than **silver** (1.9), which is followed by **Cu** (1.9) and **Fe** (1.8), explaining common replacement relations. In physical terms, **only copper, silver and gold are noble metals**. In chemistry, the electronegativity of elements is used to define relative nobility.

Relative Electronegativities of the Elements

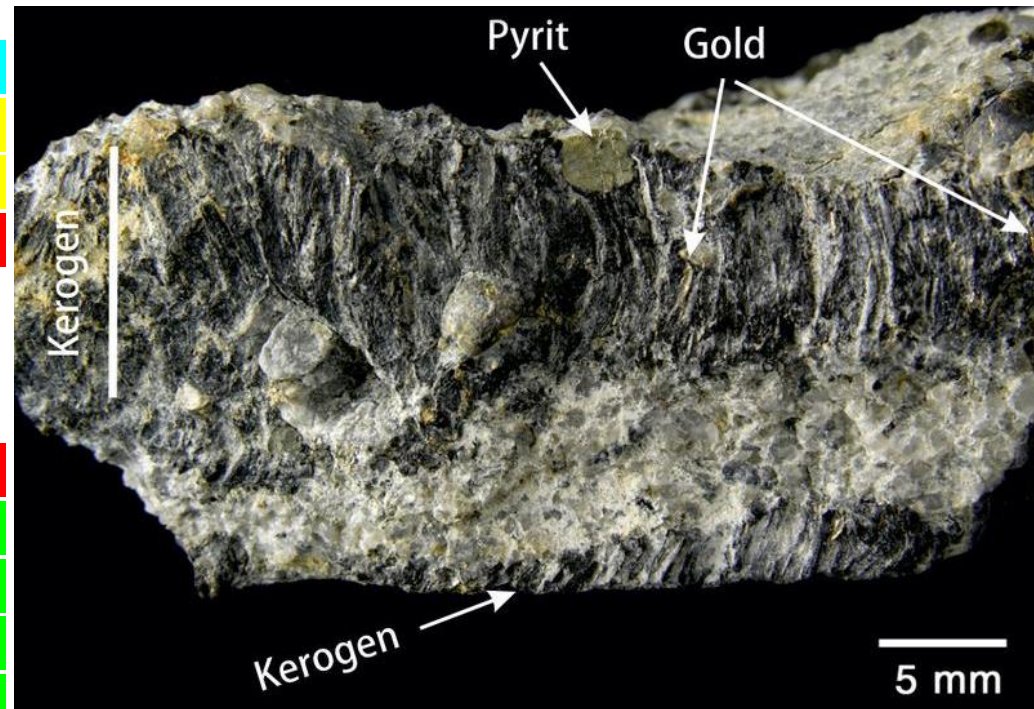
1												13	14	15	16	17		
H 2.1												B 2.0	C 2.5	N 3.0	O 3.5	F 4.0		
2	Li 1.0	Be 1.5												Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
3	Na 0.9	Mg 1.2	3	4	5	6	7	8	9	10	11	12						
	K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	
	Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	
	Cs 0.8	Ba 0.9	La* 1.1	Hf 1.3	Ta 1.5	W 2.4	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	
	Fr 0.7	Ra 0.9	Ac† 1.1	* Lanthanides: 1.1–1.3 † Actinides: 1.3–1.5														

Electronegativity is a **chemical property** that describes the tendency of an **atom** or a **functional group** to attract **electrons** towards itself. An atom's electronegativity is affected by both its **atomic number** and the distance at which its **valence electrons** reside from the charged nucleus. **The higher the associated electronegativity number, the more an element or compound attracts electrons towards it.** The opposite of electronegativity is electropositivity: a measure of an element's ability to donate electrons. **Caesium** is the least electronegative element in the periodic table (=0.8), while **fluorine** is most electronegative (=4).

Host rocks exert a strong control on noble metal enrichment. Deposition of gold is explained by reaction of sulphide solutions with reduced iron (Fe^{2+}) of doleritic host rocks, forming pyrite “sulphidation”. When sulphidation happens, a pronouncing decrease of Sulphur occurs in the hydrothermal solutions causing gold precipitation.



4- Organic substances (coal, kerogen, oil, gas) also motivate immobilization of many metals by adsorption or reduction. Gold ore veins and the metasomatic gold orebodies of Carlin, USA are enriched where host rocks contain kerogen-rich layers. Sulphide precipitation in Mississippi Valley Type deposits is often caused by reaction between solutions and the organic substance of host rock carbonates.



Carbonaceous layer of sediment rocks, essentially consisting of kerogen, gold and pyrite

Incompletely oxidized sulphur

(e.g. thiosulphate, $S_2O_3^{2-}$, polysulphides, colloidal sulphur)

supports high metal content in solution.

These compounds, however, are easily reduced by contact with organic matter so that metals are instantly immobilized as sulphides.

An indirect consequence is the precipitation of gangue, such as barite $BaSO_4$ and fluorite CaF_2 .

5- Although reduction is a frequent means of ore mineral deposition, oxidation

can have a similar role, most often concerning iron and manganese. Hydrothermal solutions transport these metals in reduced form (Fe^{2+} , Mn^{2+}) and precipitation of haematite, magnetite or pyrolusite requires oxidation to Fe^{3+} or Mn^{4+} .



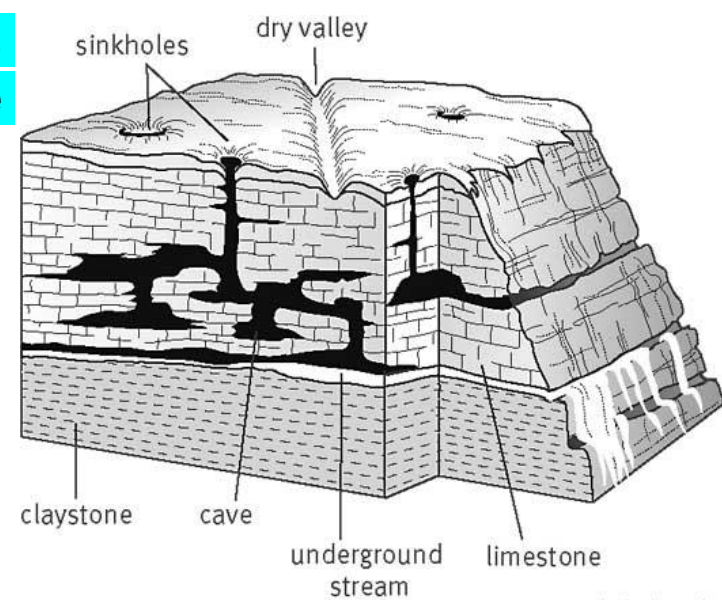
Haematite



Pyrolusite

6- Contact of hydrothermal metal-bearing solutions with carbonate rocks is a frequent factor of ore precipitation. Individual agents include:

- A. the “pH shock”** upon contact with alkaline rocks (carbonates) and formation fluids;
- B. a larger permeability** compared with pelitic country rocks;
- C. a higher solubility of carbonates** in acidic or CO₂-rich solutions (which may result in the formation of “hydrothermal karst”) and
- D. mixing with formation water** in carbonate rocks.



Elizabeth Morales

Orebodies in carbonates - due to hydrothermal solutions - take the form of veins, breccia, karst pipes and stratiform orebodies with irregular outlines (“mantos”). When the replacing masses consist of sulphides, dissolution of the original carbonate rock and replacement (“metasomatism”) by ore take place. **“Metasomatism”** is used for cases where only cations are exchanged (e.g. siderite in limestone).

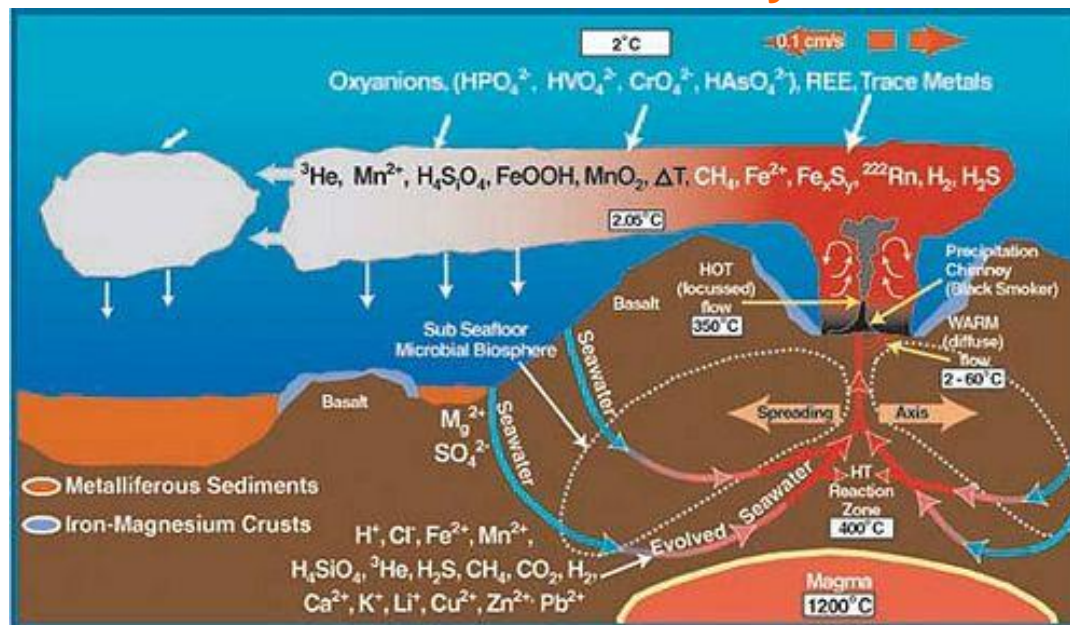


stratiform Zn-Pb-Ag-rich, generally Fe and Cu sulfide-poor, massive and semi-massive sulphide.

V. Source and origin of hydrothermal fluids and solutions

Source and origin of **hydrothermal fluids and solutions** may be related to quite different geological process systems:

1. **magmatism** (exsolution of an aqueous fluid phase from silicate magma);
2. **heating of meteoric, oceanic or formation water by convection** within or near cooling intrusions, including large faults or uplifted hot metamorphic complexes;
3. **diagenesis** (mainly **physical dehydration of sediments** by increasing pressure and temperature because of increasing overburden, thrust sheet superposition, or accretion on active continental margins);
4. **metamorphism** (mainly **chemical dehydration** of minerals that include OH-groups in their crystal lattice, caused by prograde metamorphic reactions);
5. **mixing of two or more of the mentioned source systems.**

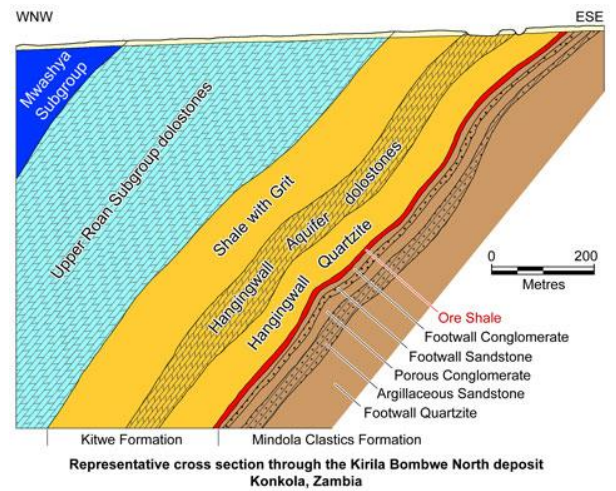
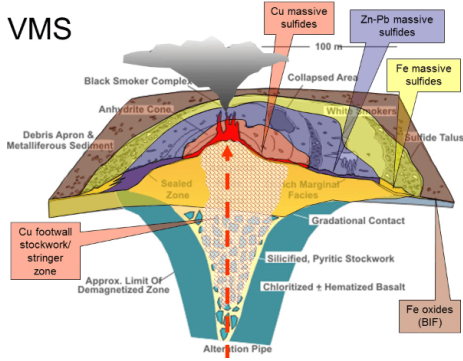
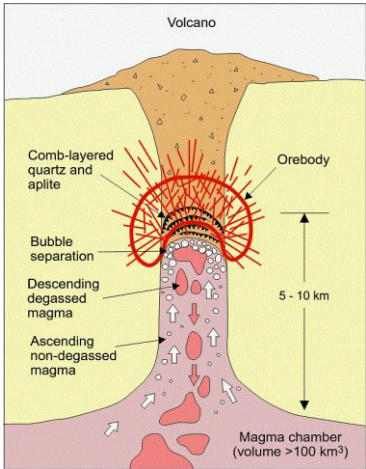
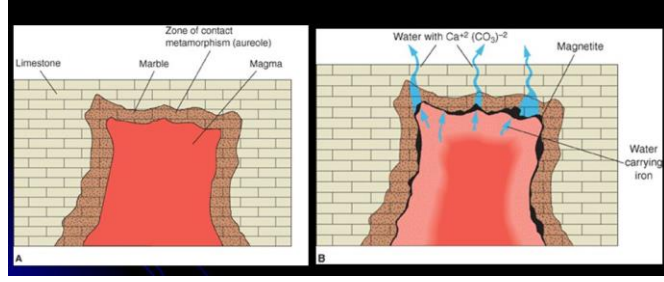


In the Earth's crust, the **hydrothermal ore deposits** occur in a fascinating diversity:

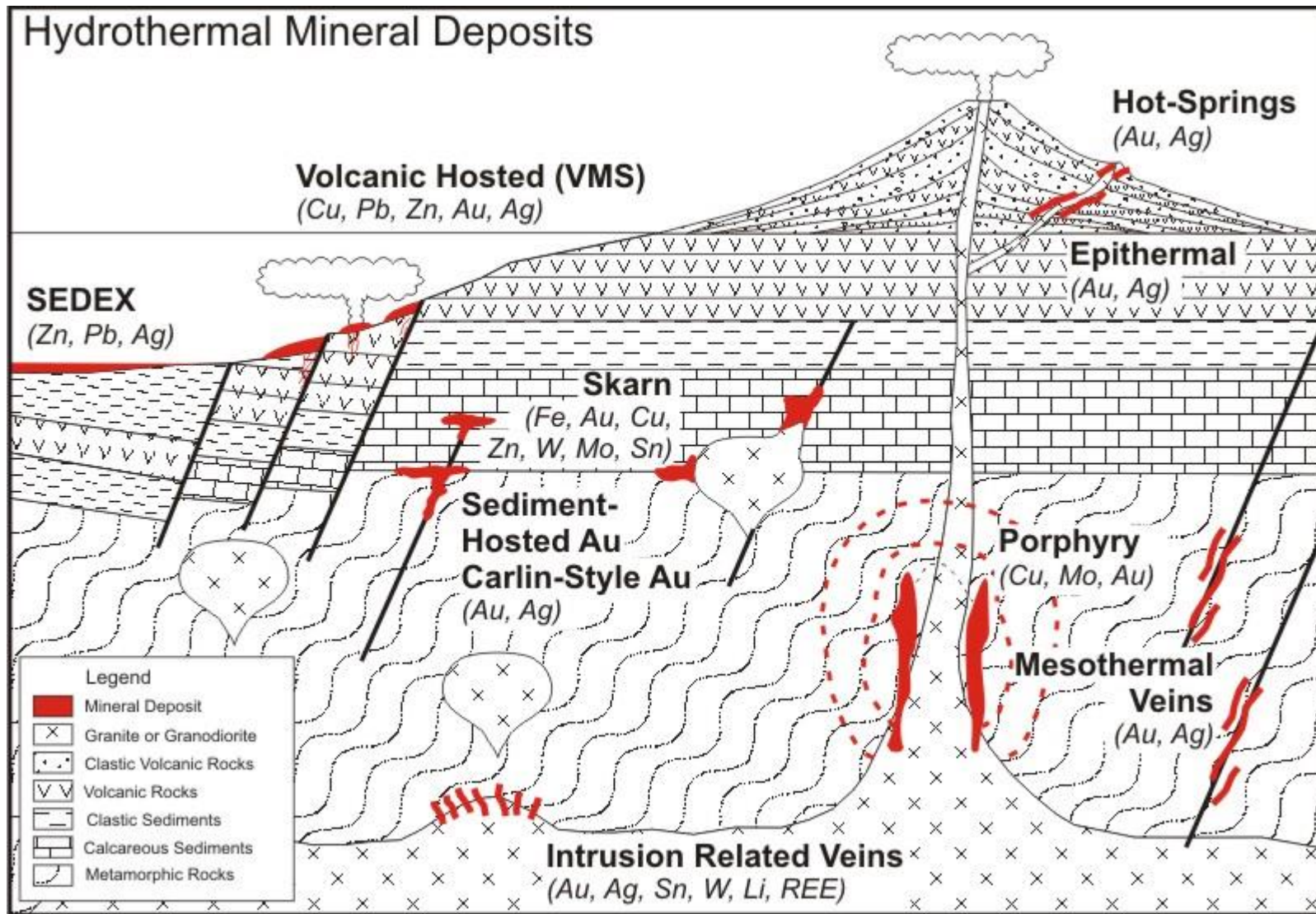
1. **Veins;**
2. **metasomatic bodies in carbonates;**
3. **breccia ores in magmatic rocks ("porphyry deposits");**
4. **ore stockworks and pipes;**
5. **volcanogenic terrestrial and submarine exhalations;**
6. **stratiform base metal ore beds in marine sediments (sedimentary-exhalative ore SEDEX) and**
7. **stratabound diagenetic Pb-Zn-Ba-F deposits in marine carbonates.**



Metasomatism: Water brings in ions from outside rocks that are exchanged with ions inside the metamorphosing rock. New minerals then replace old ones as the water both dissolves the rock and brings in new ions.



Hydrothermal Mineral Deposits



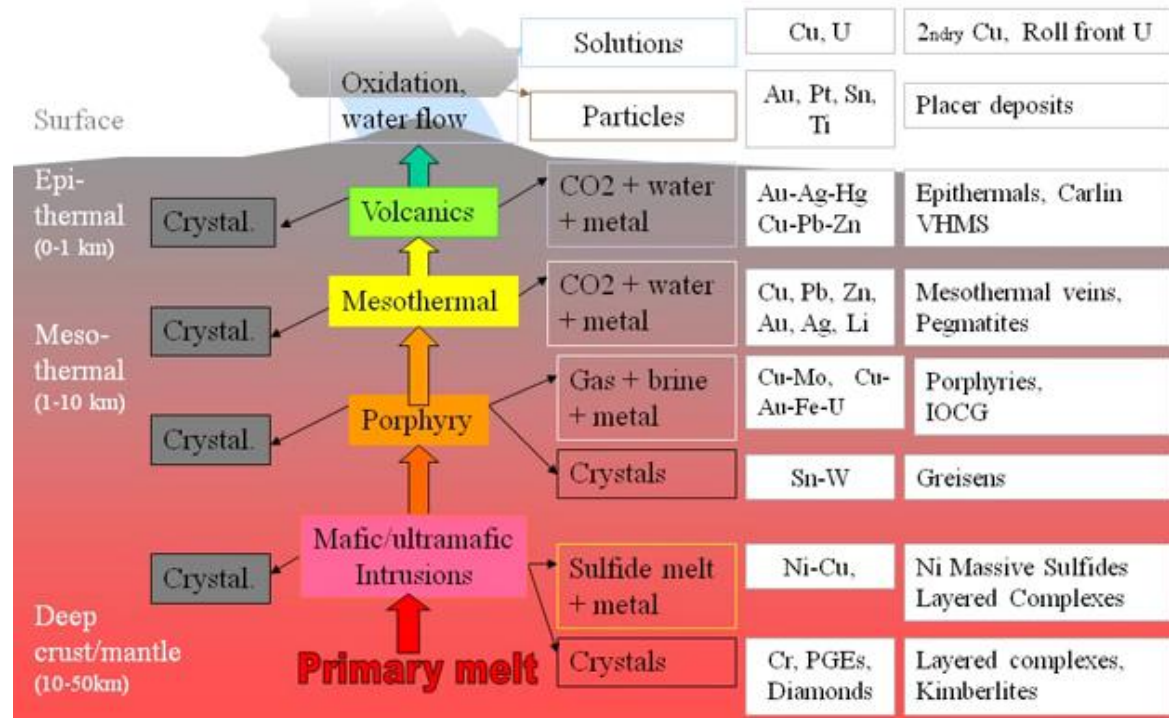
Hydrothermal mineral deposits, are formed by a process involving the dissolution, transportation, and precipitation of metals in “hot” hydrothermal fluids. These deposits can form at or near the earth’s surface or they can form deep in the crust and show distinct characteristics based on the depth of formation. Each mineral deposit shows distinct characteristics which are controlled by the characteristics of the mineralizing fluids, the characteristics of the host rocks and the solubility of the elements of interest.

VI. Classification of hydrothermal solutions/ore deposits

Traditionally, hydrothermal ore deposits were grouped according to the **formation temperatures** into:

1. **hypo- or katathermal (500–300 °C);**
2. **mesothermal (300–200 °C) and**
3. **epithermal (below 200 °C).**

This classification was quietly abandoned because temperatures vary within one single hydrothermal system. The above terms are used in a wide sense, indicating depth rather than temperature.



Depth-zone classification of hydrothermal mineral deposits

Epizonal	150–300°C	0.5–1.5 kbar	<6 km depth
Mesozonal	300–475°C	1.5–3.5 kbar	6–12 km
Hypozonal	475–700°C	3–6 kbar	>12 km

Clearly, depth (or pressure) is a much more useful criterion to describe related groups of hydrothermal deposits. Therefore, the terms “epi-, meso- and hypozonal” similar to the notations referring to metamorphism or the intrusion depths of granites.

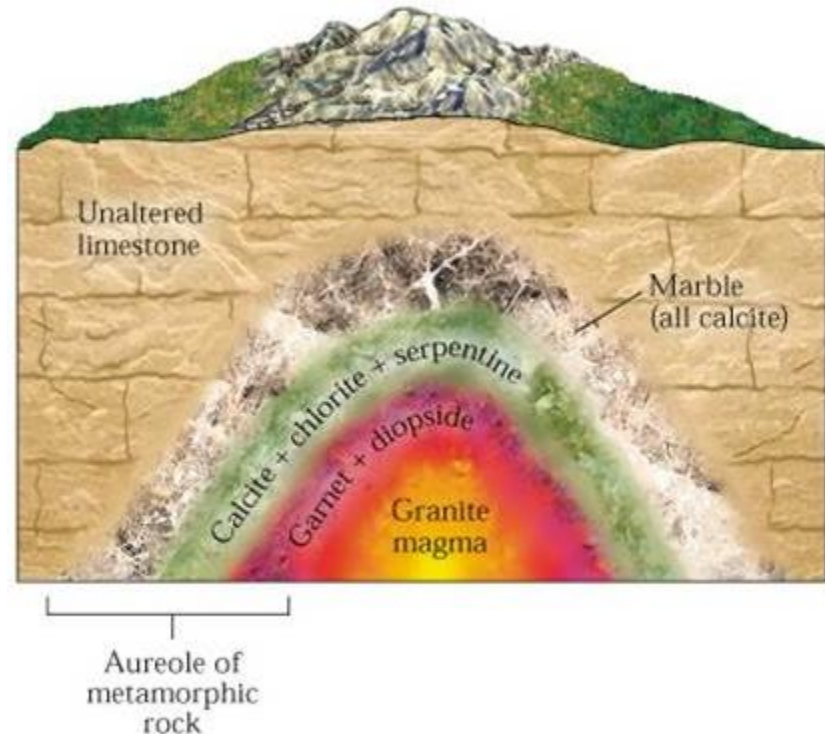
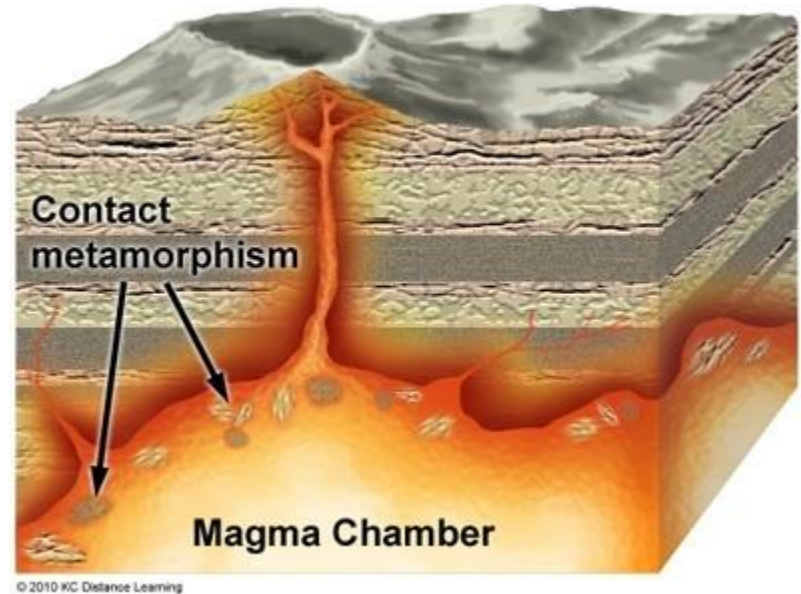
7. Skarn- and contact-metasomatic ore deposits

VII. What is “Skarn”?

Many **ore deposits** are formed close to **intrusive igneous rock bodies**. The location of the **ore** may be **at the immediate contact between the intrusion and the host rocks**, or **at a certain distance**. In the first case, the host rocks will be affected by **contact metamorphism** due to heating (e.g. the formation of andalusite in slates and schists).

If carbonate rocks are present, **skarn = tactite (a Ca-Mg silicate rock)** is frequently formed by **decarbonation and addition of silica**. This process releases **large quantities of CO₂** that may pass into the magma inducing profound changes.

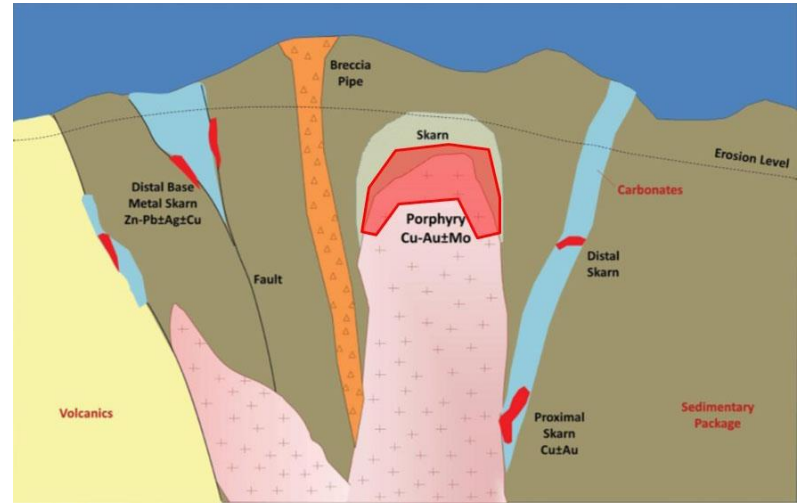
Massive ore bodies may occur in **proximity to the skarn (proximal contact-metasomatic ore)**. **The ore replaces carbonate rocks (or replaces the skarn) by a process called metasomatism.**



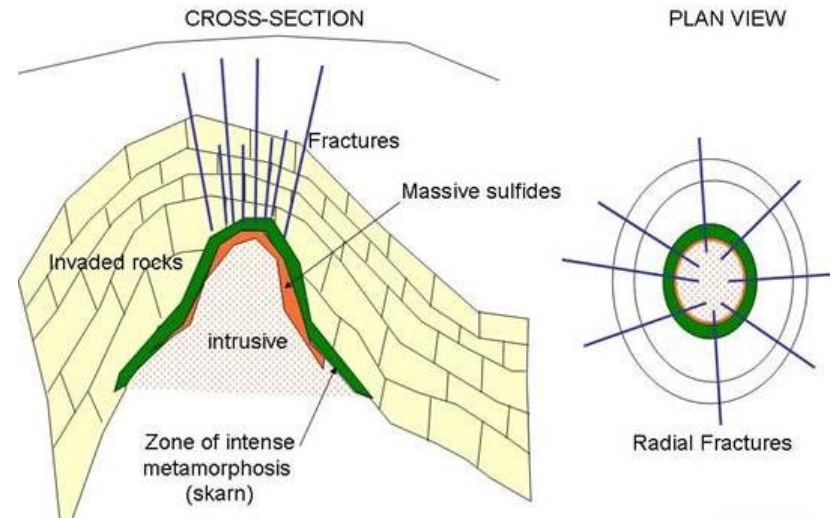
Metasomatism is the chemical alteration of a rock by hydrothermal and other fluids. In the igneous environment, metasomatism creates skarns, greisen, and may affect hornfels in the contact metamorphic aureole adjacent to an intrusive rock mass. In the metamorphic environment, metasomatism is created by *mass transfer* from a volume of metamorphic rock at higher stress and temperature into a zone with lower stress and temperature, with metamorphic hydrothermal solutions acting as a solvent.

The replacement is the result of the **passage of hot aqueous fluids** that are given-off by the **cooling magmatic body** or by **dehydrating country rocks**. If the **metasomatic ore formation** takes place at a distance from the intrusion, the ore will **less likely be associated with skarn rock**.

Skarn is an old Swedish mining term for a tough **calc-silicate gangue** that is associated with iron and sulphide ores. **“Skarn” in USA** commonly describes iron-rich rock bodies of Ca-Mg silicates formed from **limestone or dolostone** by abstraction of CO_2 and **hydrothermal addition** of SiO_2 , Al, Fe and Mg in the contact aureole of intrusions.

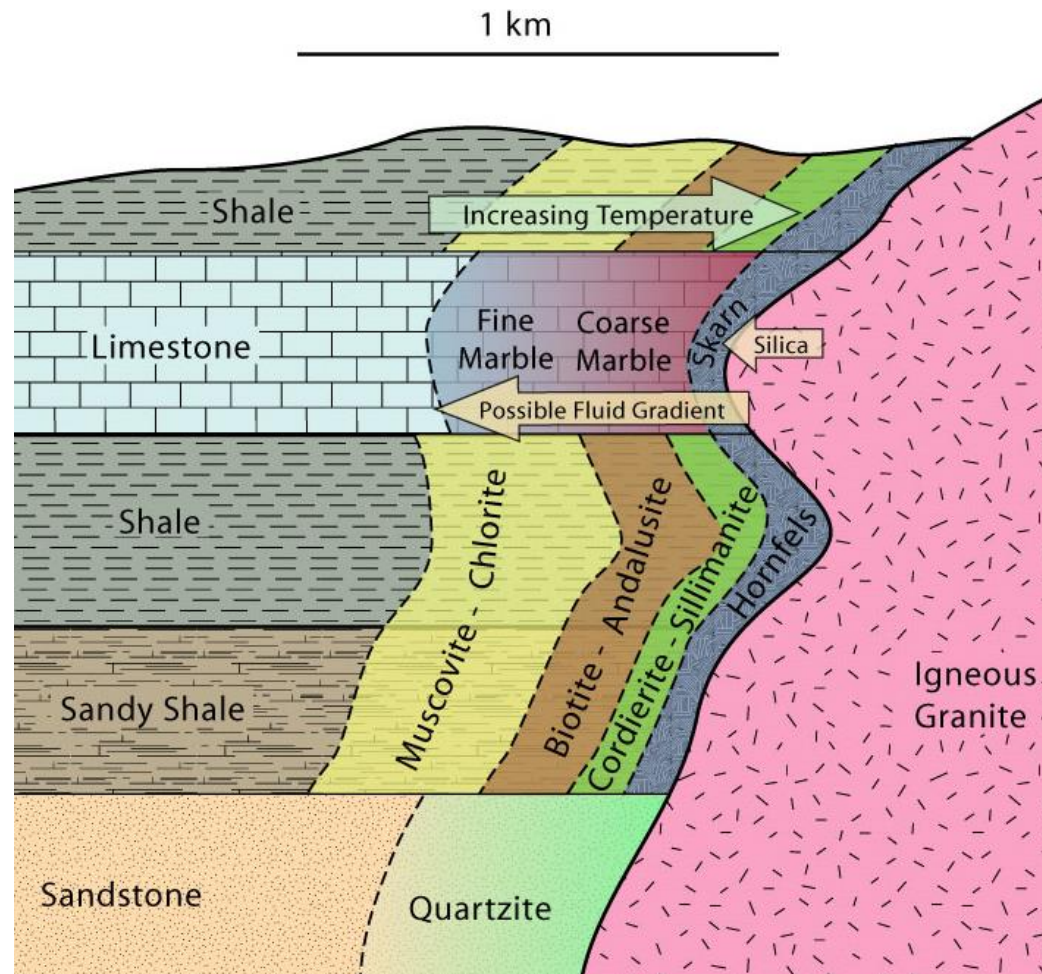


GENERALIZED ACID MAGMA INTRUSIVE IN LIMESTONE



VIII. How would ore bodies be formed in/around the Skarn?

1. Emplacement of a **hot magma** body in **cool country** rocks causes the **build-up of a thermal halo** with **outward migrating isotherms**, driving-off water and other volatiles.
2. During this prograde phase – contact metamorphism – **the skarn area is born**. In the skarn area, **anhydrous minerals are formed** that include grossular-andradite, diopside, forsterite and periclase (MgO, if dolomite was present), and part of the ore.
3. Outward from the intrusion, **skarn is followed by a narrow zone of wollastonite** and a shell of isochemical re-crystallization of the precursor carbonate rock to carbonate marble.



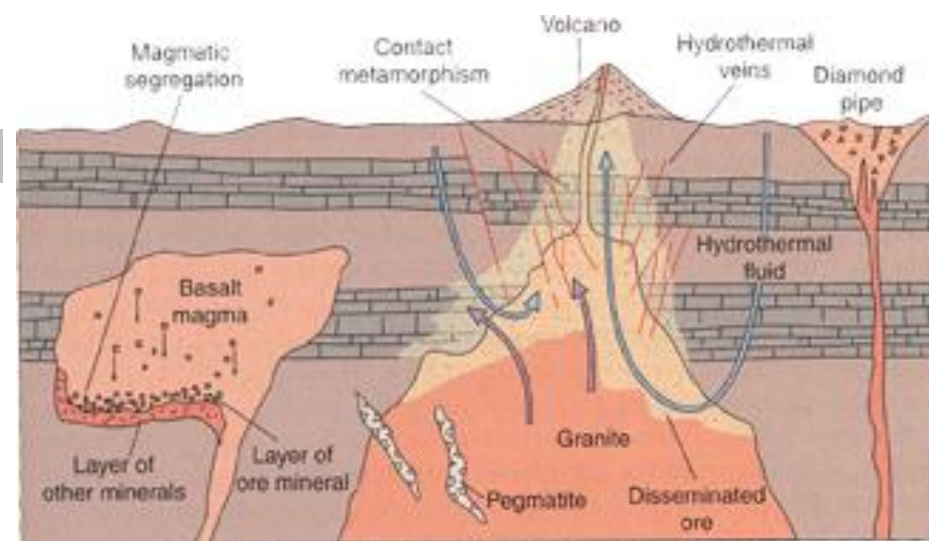
Contact aureole around an igneous pluton

4. The export of matter from the cooling magma into the country rocks is due to hot (maximum >700 °C) hypersaline melt/hydrothermal fluids and gas.

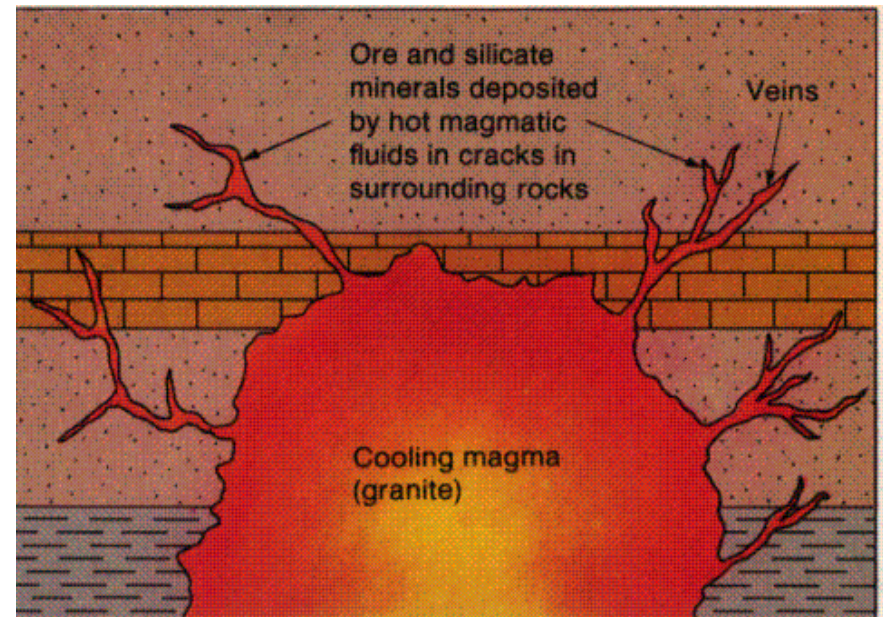
5. The hydrothermal fluid flow in aureole rocks has variable temperature and CO₂ concentrations. Commonly, initial heating will produce high CO₂.

6. Magmatic waters, i.e., hydrothermal fluids continue to exsolve from the intrusive magma during further cooling and deposit ores.

7. The continuous hydrothermal fluids would transform the anhydrous mineral phases, such as MgO to hydrous phases brucite (Mg(OH)₂) and the formation of water-rich silicates (amphibole, epidote, talc, chlorite), concurrently with the main mass of the ore.



Hydrothermal deposits form when water, heated by the cooling magma dissolves heavy metallic elements from the intrusion. These hydrothermal solutions cool as they leave. Slow moving solutions leave disseminated ore. If the solution cools quickly, it can deposit mineral rich veins.

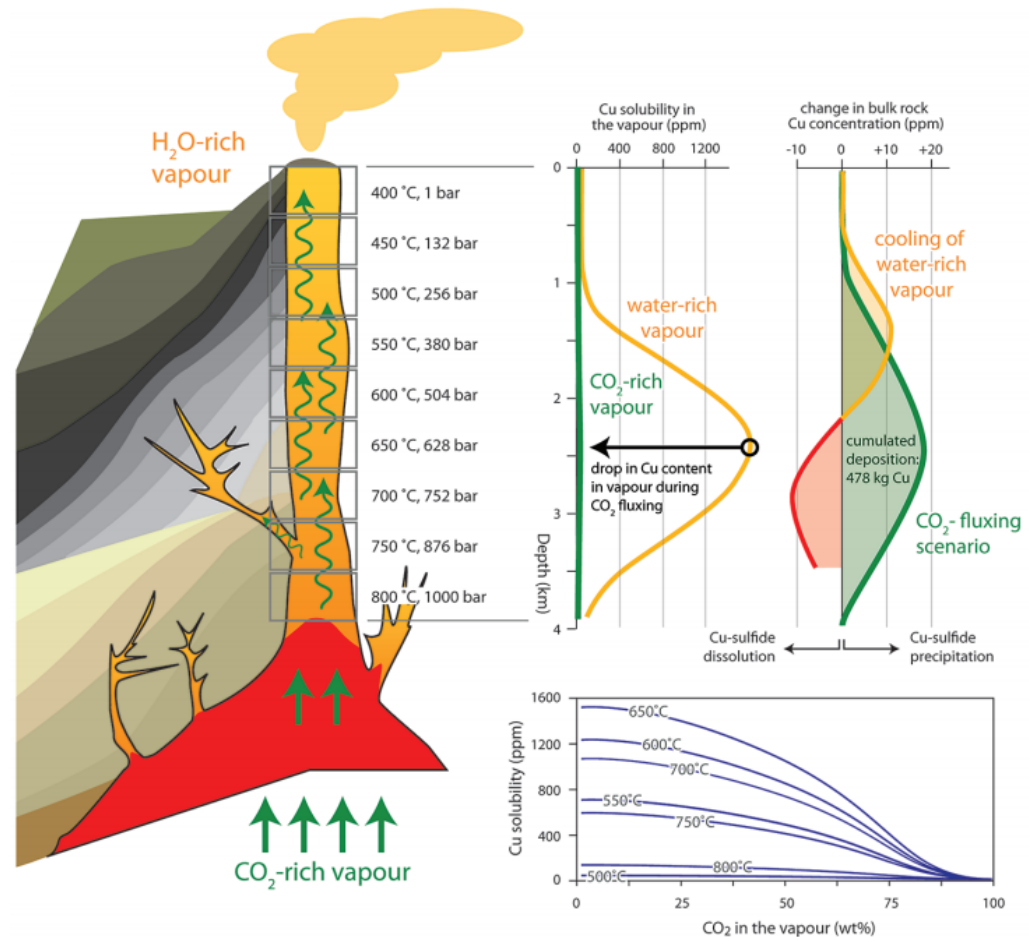


In this way **Gold and Iron skarn** deposits are formed from different hydrothermal solutions.

Skarn orebodies display characteristically irregular outlines that can be explained by the two main factors, **lithology and structures of the replaced host rocks**, which impose **chemical and physical controls on permeability and reactivity**.

Orebodies in skarns are often zoned, for example with copper in a proximal (near position) and lead-zinc in a more distal (far away) position.

Skarn orebodies are a **major source of many metals** but also of **industrial minerals** including wollastonite, graphite, asbestos, magnesite, talc, boron and fluorite.

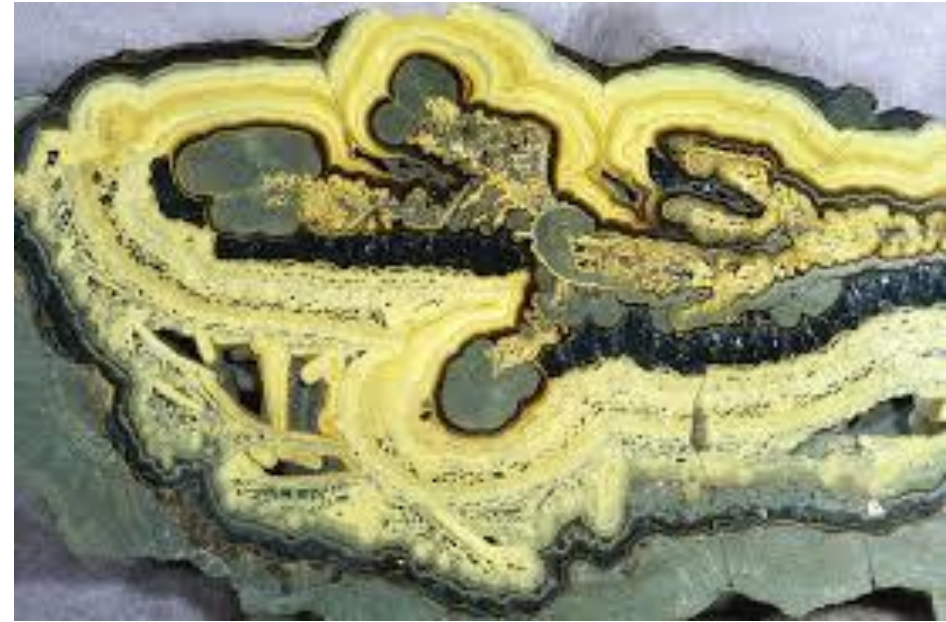


Impact of CO₂-fluxing on Cu solubility in a volcanic conduit filled with vapour. Fluxing deep-sourced CO₂-rich vapour through shallower, water-dominated vapour reduces Cu solubility as the water partial pressure is reduced. Cu contents are significant for the water-dominated vapour. Assuming upward flow, Cu is dissolved from wall rocks to 2.2 km, and subsequently deposited. In contrast, contents in the CO₂-rich vapour are negligible. Therefore, a single pulse of CO₂-rich vapour will deposit essentially all Cu in the water-vapour, with deposition at all depths and all temperatures.

IX. Hydrothermal-metasomatic ore deposits

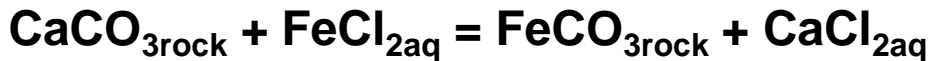
Other types of **metasomatic ore deposits** result from **hydrothermal diagenetic** and **metamorphic fluids** of **evaporative** and **salt-solution brines**. These hydrothermal fluids are Non-magmatic.

Typically, the **metasomatized rocks are marine limestones**. This preference can be demonstrated with numerous examples (e.g. many **lead-zinc orebodies**, gold as at **Carlin, USA**, **magnesite** and **siderite**).



Lead-Zinc Ores

Main controls of the replacement process include the **reactive surface** and permeability of the precursor rock, **pH and Eh of the mineralizing solutions**, and the **relative solubility of the participating minerals**. The equation below describes the metasomatic formation of **siderite rock (an iron ore)** from limestone.

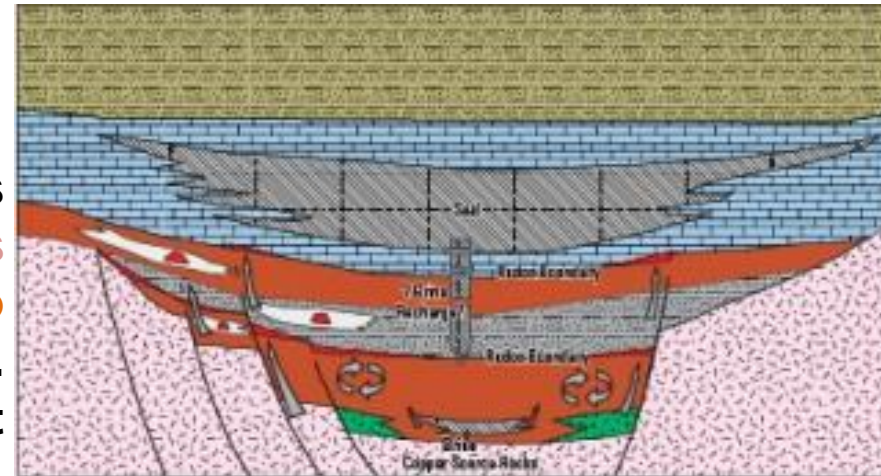


In this case, **cation exchange** is the dominant mechanism, replacing each molecule of calcite with one of siderite.

The emplacement of **metasomatic ore** is favoured by **low-permeability rock horizons** (e.g. shales) that form **a physical barrier to upward flow** (similar to petroleum traps). Focused **hydrothermal solutions** react more intensively with the carbonate host. **Hydrothermal-metasomatic** ore deposits are often **stratabound** and occur in the same stratigraphic level across large regions (**MVT deposits**).



Siderite Ore



sediment-hosted stratabound copper deposits

End of Lecture