Economic Geology: Lecture Notes

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<u>Volcanogenic ore deposits</u>

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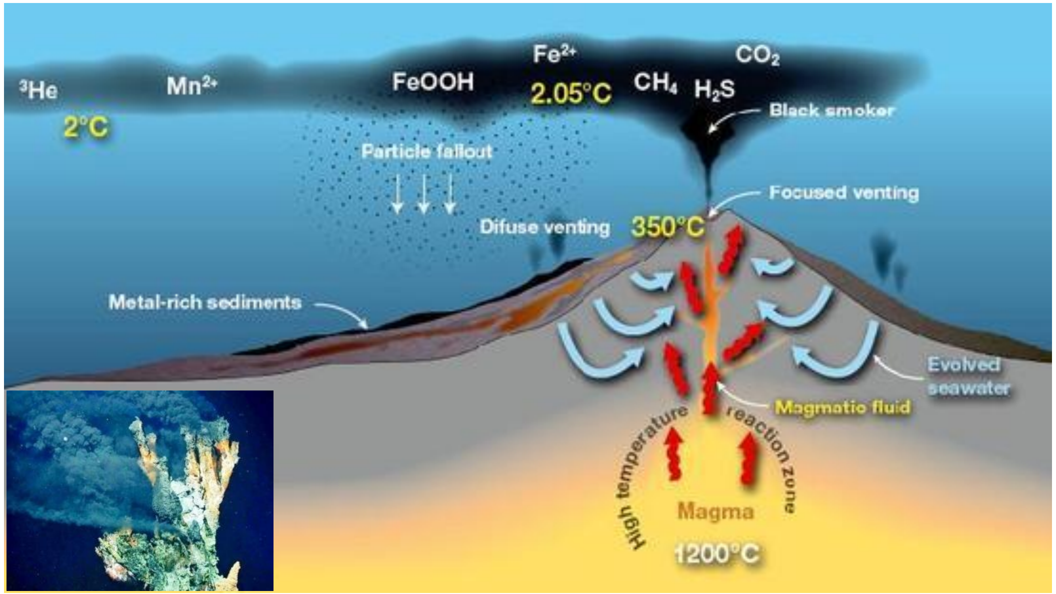
10. Volcanogenic ore deposits (VMS)

I. What are the volcanogenic ore deposits?

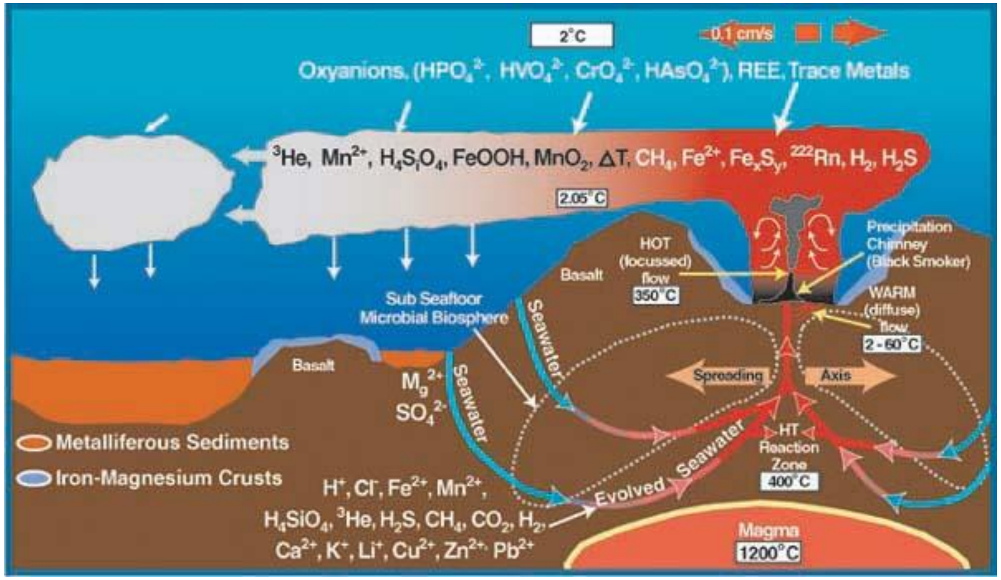
The formation of a large number of important ore deposits is closely related to submarine and terrestrial volcanism. The subvolcanic porphyry ore deposits and the mineralization related to the volcanic section of ophiolites (Cu-Zn-Au ore of Cyprus type) are types of volcanic ores.



Here, other economically significant classes of volcanogenic ore deposits are introduced:

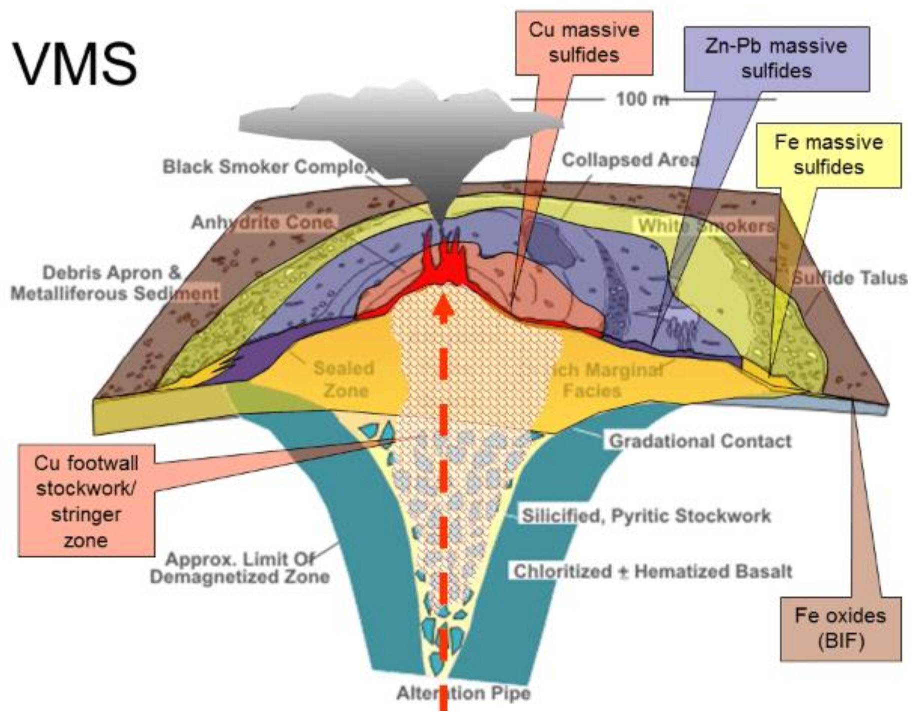
i) the submarine volcanogenic massive sulphide (VMS) deposits;

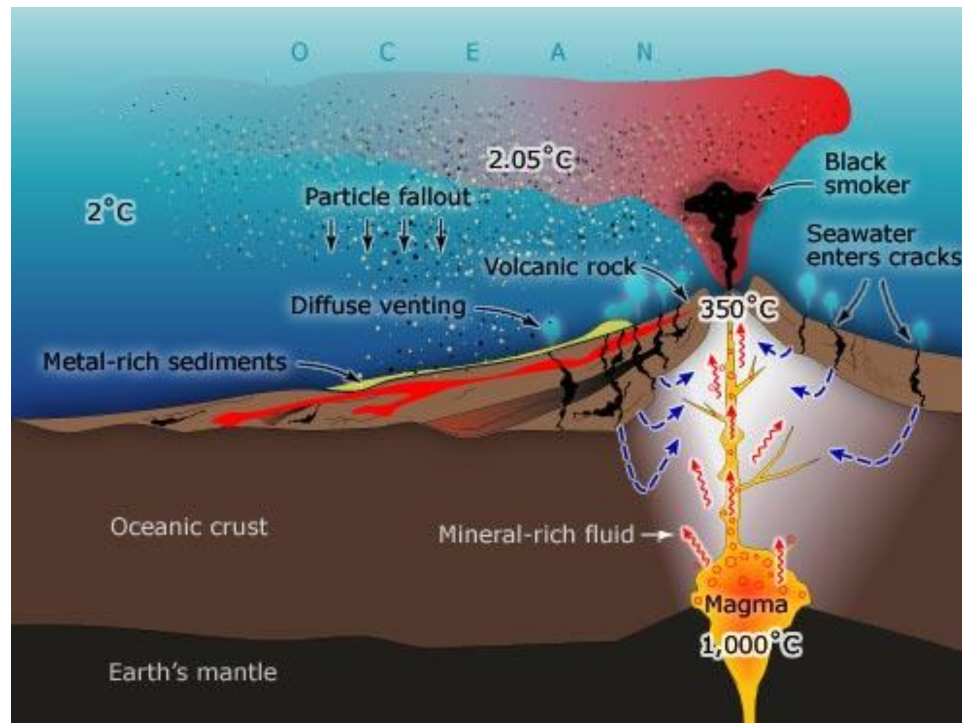
ii) the terrestrial epithermal gold-silver-base metal deposits.



All volcanogenic deposits were formed near active volcanoes or subvolcanic centres, and occur in a “proximal=near” position.

Generally, ores that were formed by hydrothermal solutions venting on the ocean floor are called "submarine exhalative" or "submarine hydrothermal". "Submarine volcanic-exhalative deposits" (volcanic massive sulphides VMS are examples) are discerned/different from "Sedimentary-exhalative type" (SedEx). The first are clearly localized in volcanic centers (host rocks are magmatic), the second occur in sedimentation-dominated basins (host rocks are sedimentary rocks). In both cases, the rocks are called "exhalites" or "hydrothermal sediments".

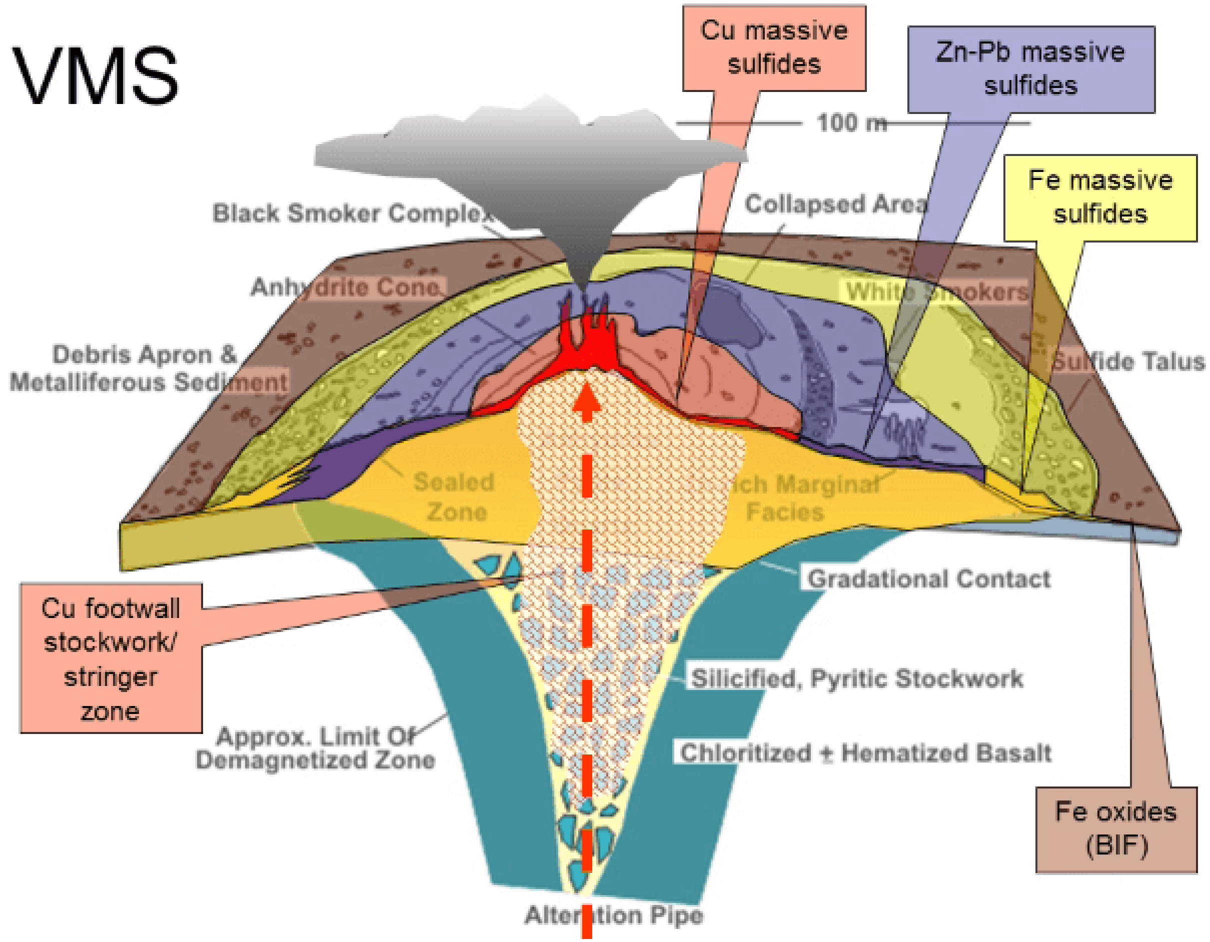




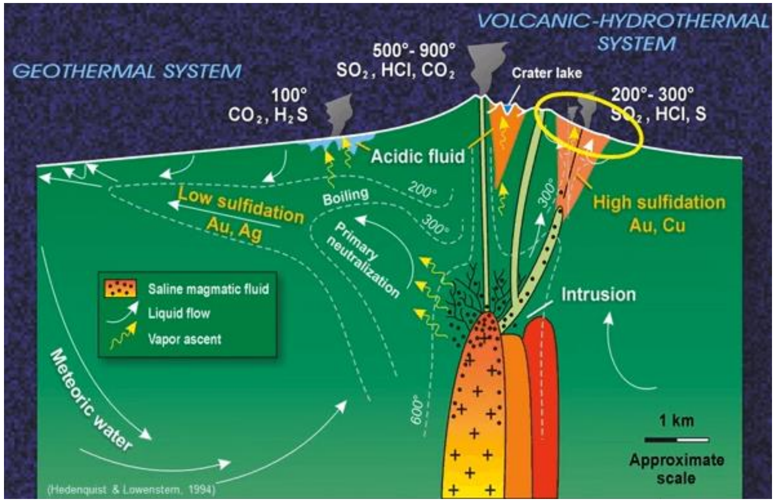
II. Genesis of VMS deposits

VMS deposits have been forming throughout geological history and they still are forming on the seafloor today (from black smokers). VMS are formed by submarine volcanic activity, or more precisely, sub-seafloor hydrothermal activity on the seafloor. VMS-deposits with copper and zinc are hosted by sequences dominated by mafic volcanic rocks. VMS-deposits with zinc-lead-copper occur in sequences dominated by felsic volcanic rocks sourced from continental crust and are best exemplified by the Kuroko deposits of the Miocene Green Tuff Belt of Japan.

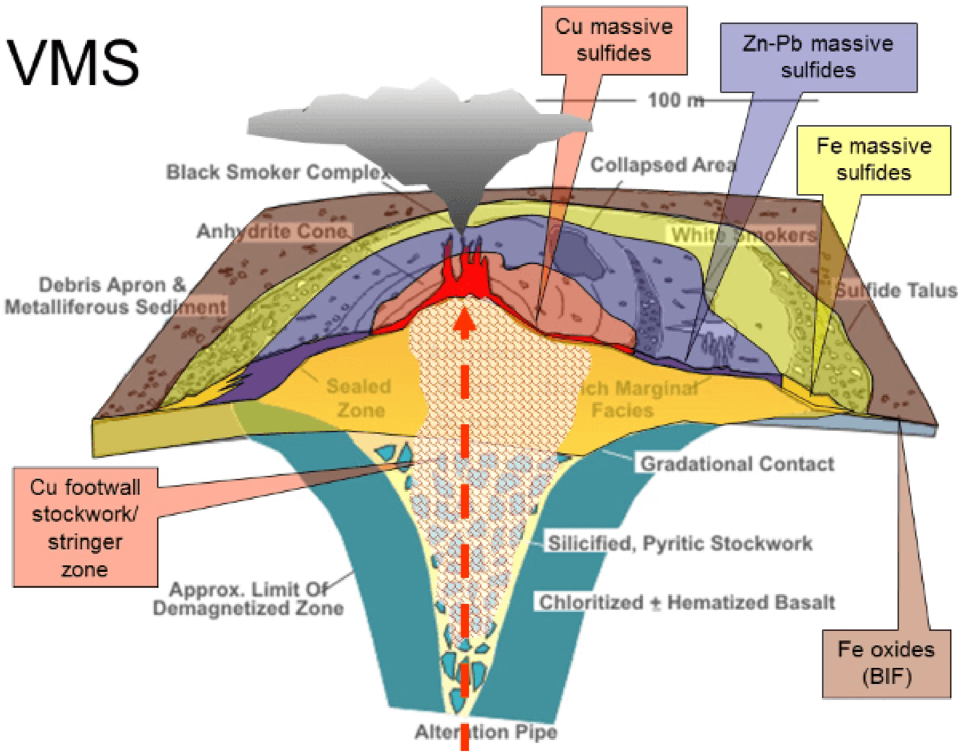
VMS ore deposits are thought to result from seawater convection and hydrothermal dissolution of metals from pervaded volcanic rocks. It is believed that a link with the magmatic evolution and degassing of the volcanic magmas may complement the convection hypothesis.



The VMS deposit form sulphide chimneys like those of the black smokers (old black smokers). Black plumes – hot hydrothermal waters - are emitted from volcanic vents/chimneys into the sea. VMS deposits are basically mushroom shaped tends to be copper rather than zinc rich. VMS deposits often form as clusters/zones over a large intrusive heat source. If the heat chamber is long-lived, flat lenses of massive sulphide are formed.



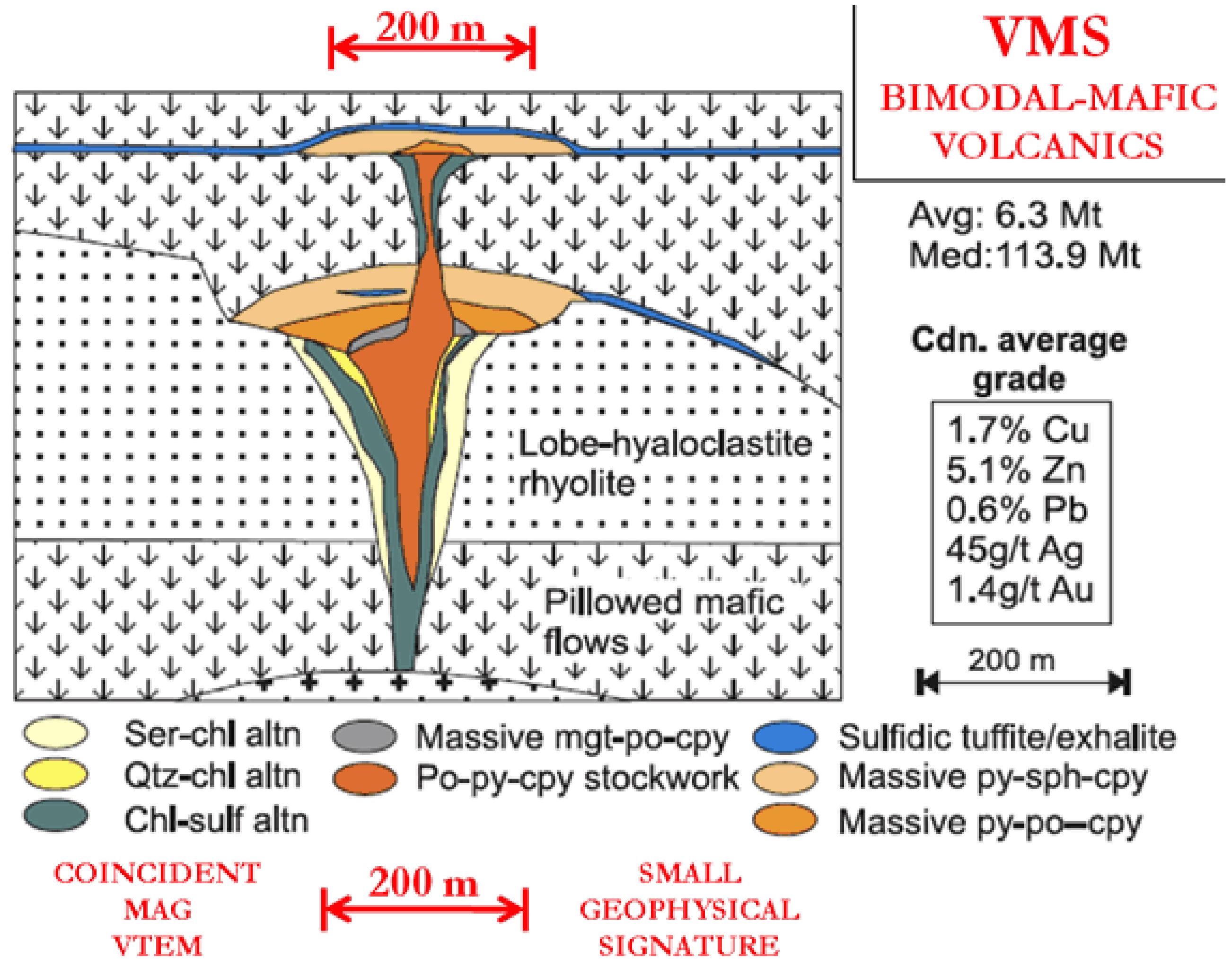
As the hydrothermal fluids reach the cold seawater, the temperature drops within seconds from 300 °C down to 100 °C and less. The fine clouds of sulphide cool and settles on the seafloor, building up a finely banded layers of pure sulphate (anhydrite) which are closest to the vent followed by copper, galena PbS and sphalerite ZnS. Beyond that the sulphur is exhausted and iron-sulphide/oxide and silica is all that's left to precipitate.



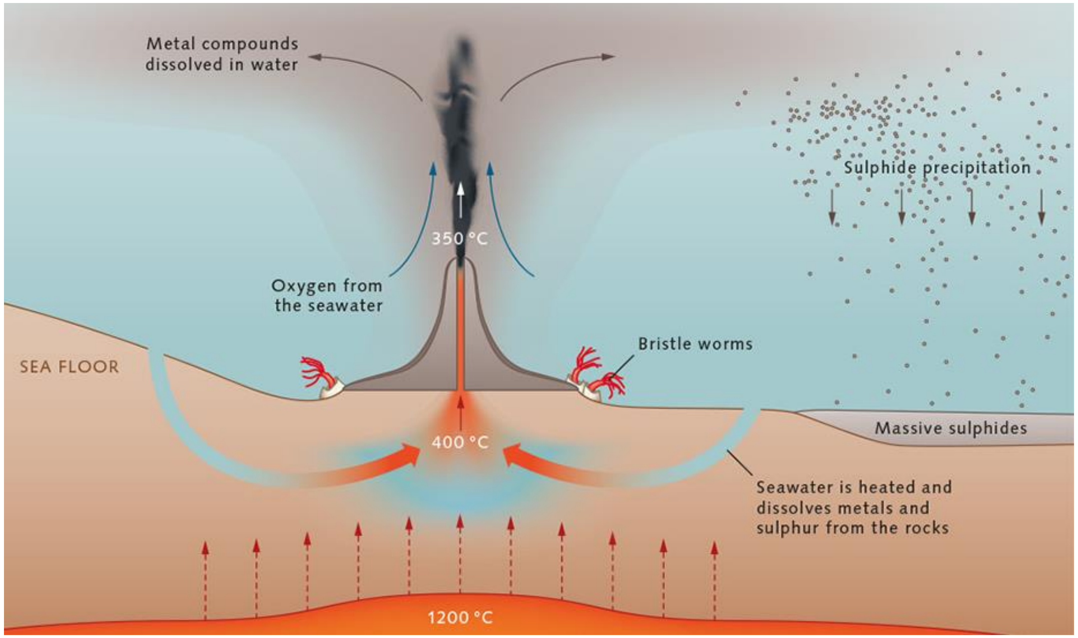
The most important metals in VMS are Fe-Cu-Pb-Zn, with elevated trace contents of Cd-As-Sb-Bi, more rarely including gold and silver. Polymetallic ore deposits are commonly zoned with Fe-Cu at the base, followed upwards by Zn and Pb, and capped by barite, anhydrite or dense SiO_2 exhalites (chert, jasper).

This chemical stratification can in some cases be explained by changes in the composition of the hydrothermal solutions.

In other cases, a secondary mobilization of more easily soluble components (e.g. zinc) of early precipitates results in this pattern, caused by continuous flow of hydrothermal solutions upward through the earlier metalliferous hydrothermal sediments ("zone refining").



Some of the metals are contributed by the underlying magma chamber, through the hydrothermal fluids. It is the seawater circulation through the host volcanic that provides the remainder of the metal inputs. The secret of the high grade of the ore lies in rapid cooling of the hydrothermal fluid when it reaches the full seafloor.

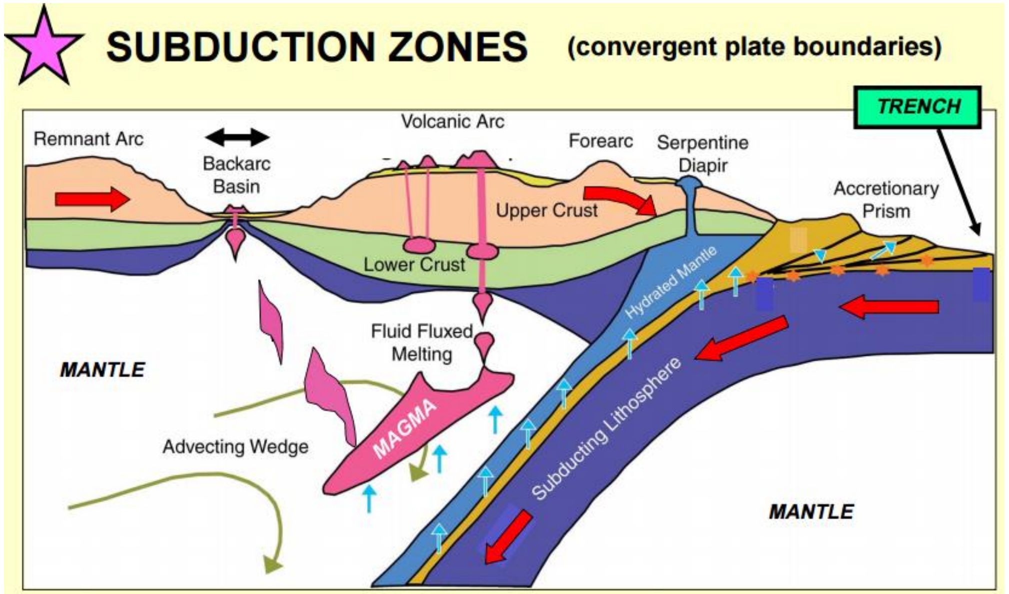


Colloidal textures prevailed initially, before zone refining, diagenesis and metamorphism caused coarsening and recrystallization. Banding, synsedimentary soft-sediment deformation and graded bedding of sulphides are often observed in VMS deposits. Ooids and pisoids form where outpouring solutions caused both ore precipitation and agitation of hydrothermal seafloor sediment.

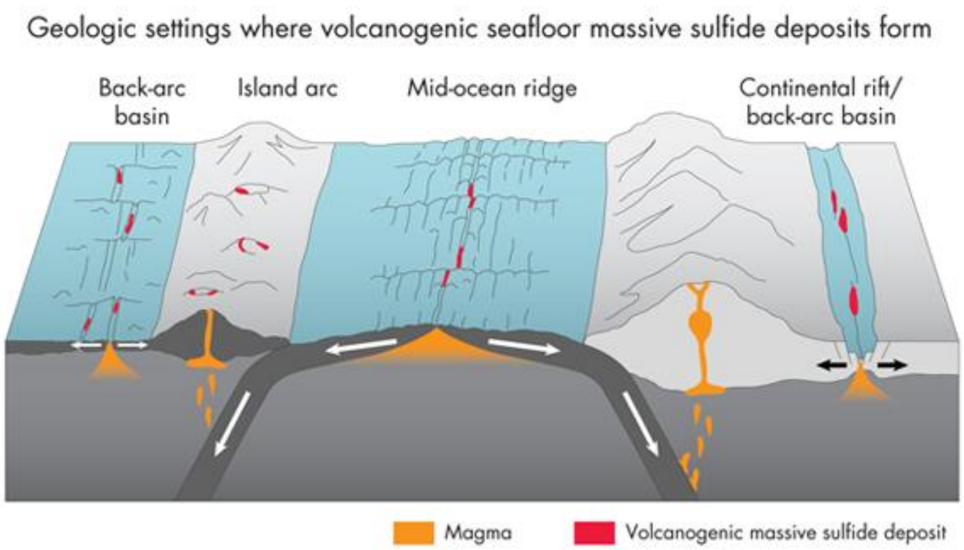
III. Forms and tectonic environment of VMS

VMS deposits show a great variety of forms, including lenses and blankets (the most common), but also mounds, pipes and stringer deposits.

Iron-rich sulphides occur predominantly with basalts, whereas Fe-Cu-Zn appear in volcanic terranes of andesite-dacites and Fe-Pb-Zn with rhyolites. The scarcity of Ti, V, Cr, Co and Ni in VMS deposits may be due to early precipitation / settling / crystallization of magnetite from mafic melt which extracts these metals at early magmatic stage.



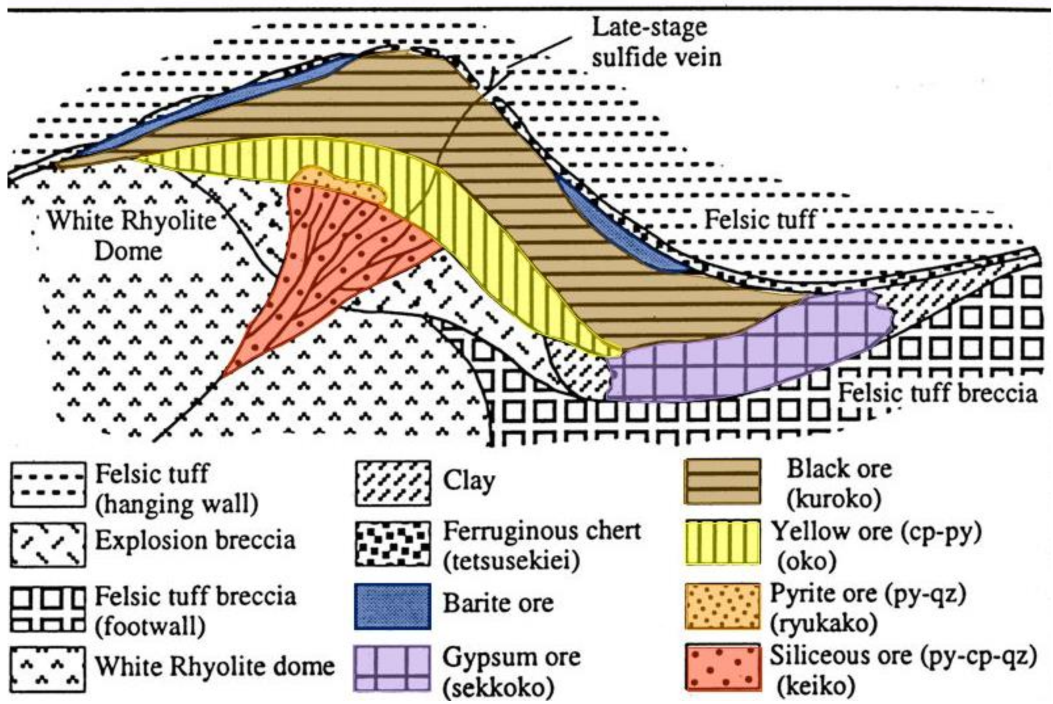
Generally, VMS occur in convergent plate boundary settings. However, the prevailing nature of the volcanic rocks and geochemical indices imply that most VMS were generated during phases of major crustal extension, resulting in rifting (divergent environment), subsidence and deep marine conditions.



IV. Kuroko VMS deposits

"Kuroko"' ore deposits are an economically significant. The term "kuroko" is derived from the black lead zinc ore that was exploited in Japan for centuries. Many mines had also stockwork orebodies of yellow ore ("oko") consisting of pyrite and chalcopyrite (gold). Fine-grained ores of ZnS, PbS, copper, pyrite and barite were formed during extrusion of rhyolite domes by hydrothermal exhalation through submarine vents and mound-building on the seafloor. The temperature of the hydrothermal fluids rose during ore formation from 150 to 350 °C. Stable water isotopes indicate a seawater origin of the solutions with a low salinity of <5% NaCl (equivalent). Seawater contributed sulphur, but part of sulphide sulphur was leached from the magmatic rocks.

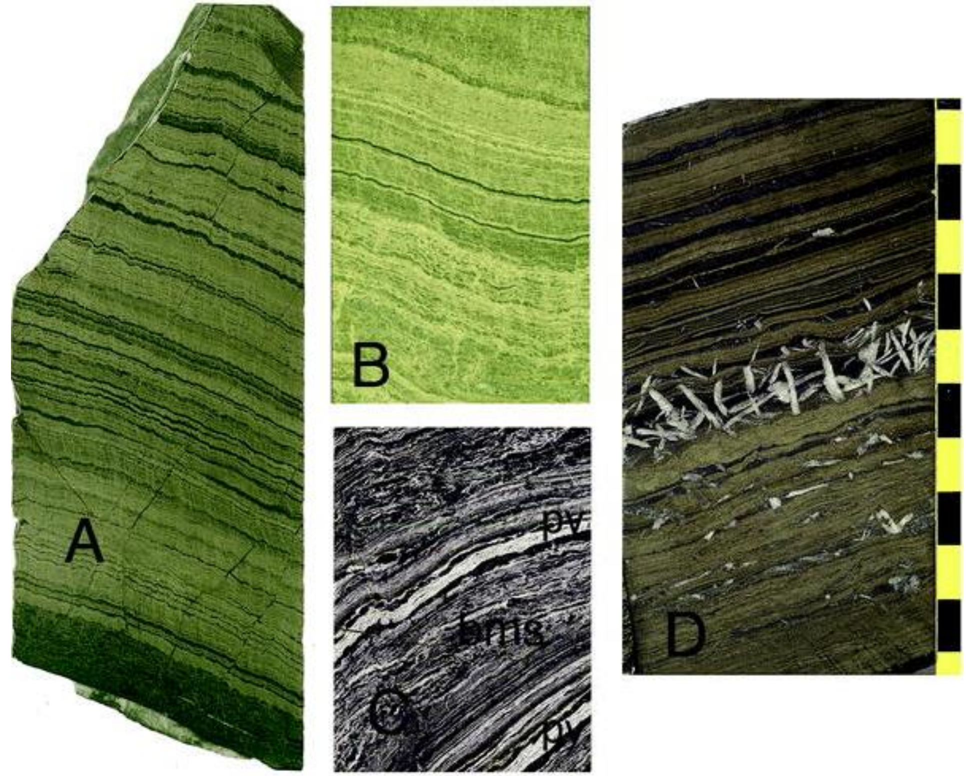
Kuroko Type VMS deposits



The hydrothermal alteration in the footwall of the massive sulphide ores is concentrically zoned around the stockwork, from innermost K-feldspar and illite to distal montmorillonite and zeolites.

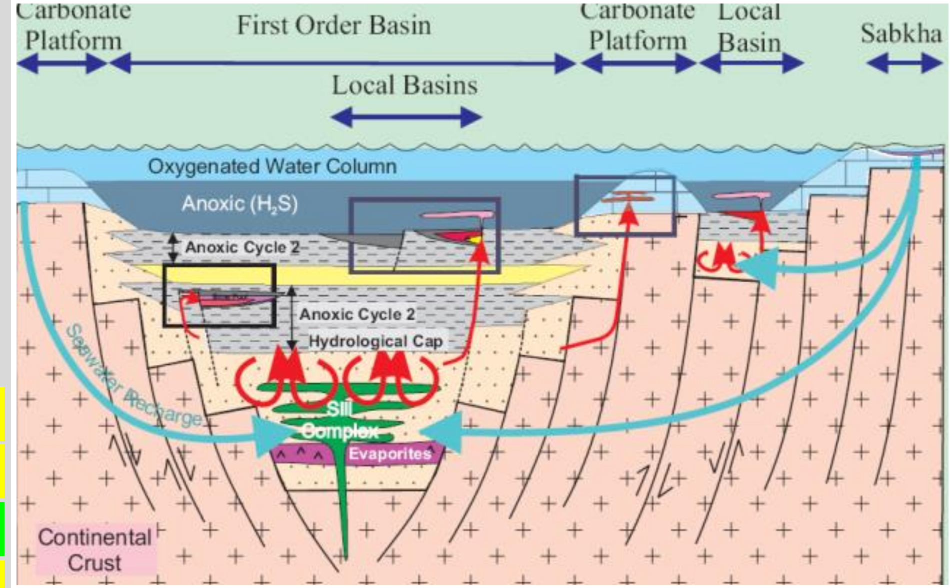
V. VMS and SedEx

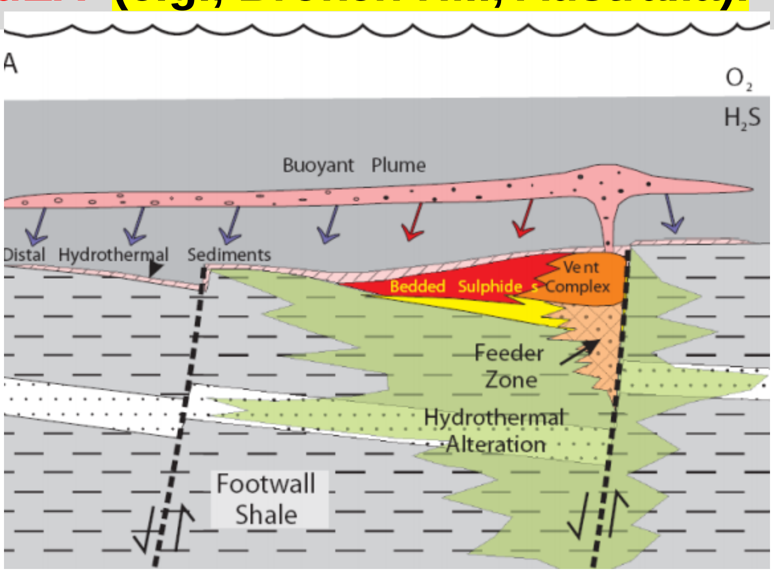
SedEx are very familiar in genesis to the VMS deposits except they are not primarily driven by intrusions below but are instead products of dewatering and metamorphism of thick piles of accumulated sediments in ocean basins hence the "Sed" part of the name, the "exhalative" portion of the name (EX) refers to the geological process of venting hydrothermal solutions into submarine environment.

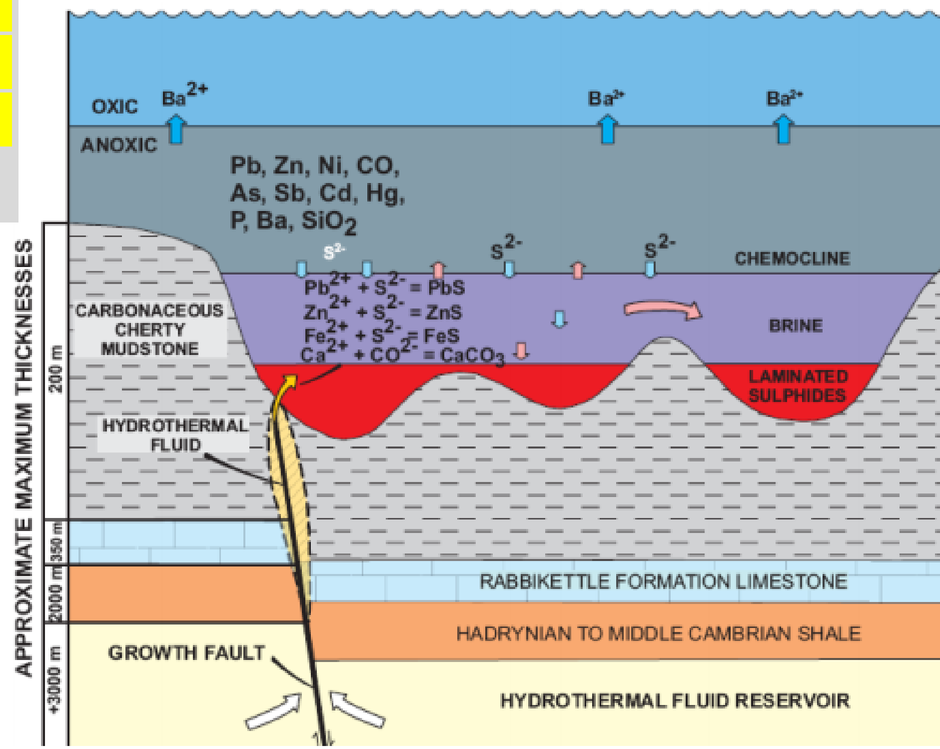


Both SedEx and VMS are syngeneic, that is they drop deposit at the same time as hosting rocks. The majority of metal in SedEx deposits is in the form of bedded exhalative massive sulphides, with an underlying feeder zone, they too often occur in clusters. The massive sulphide lenses are usually highly deformed (Why?).

SedEX deposits are generally formed in **fault-bounded sedimentary basins** on continental crust rather than in volcanic piles on oceanic crust. To achieve **SedEX** deposits, **the basin needs to accumulate kilometres or tens of kilometres of oxygen lacking sediment, usually shales.** **The heat derived from the hydrothermal solutions together with the heat from the sediment burial leach the metals; lead, zinc and silver from the sediments and concentrate them with those in the hydrothermal solutions forming the SedEX (e.g., Broken Hill, Australia).**

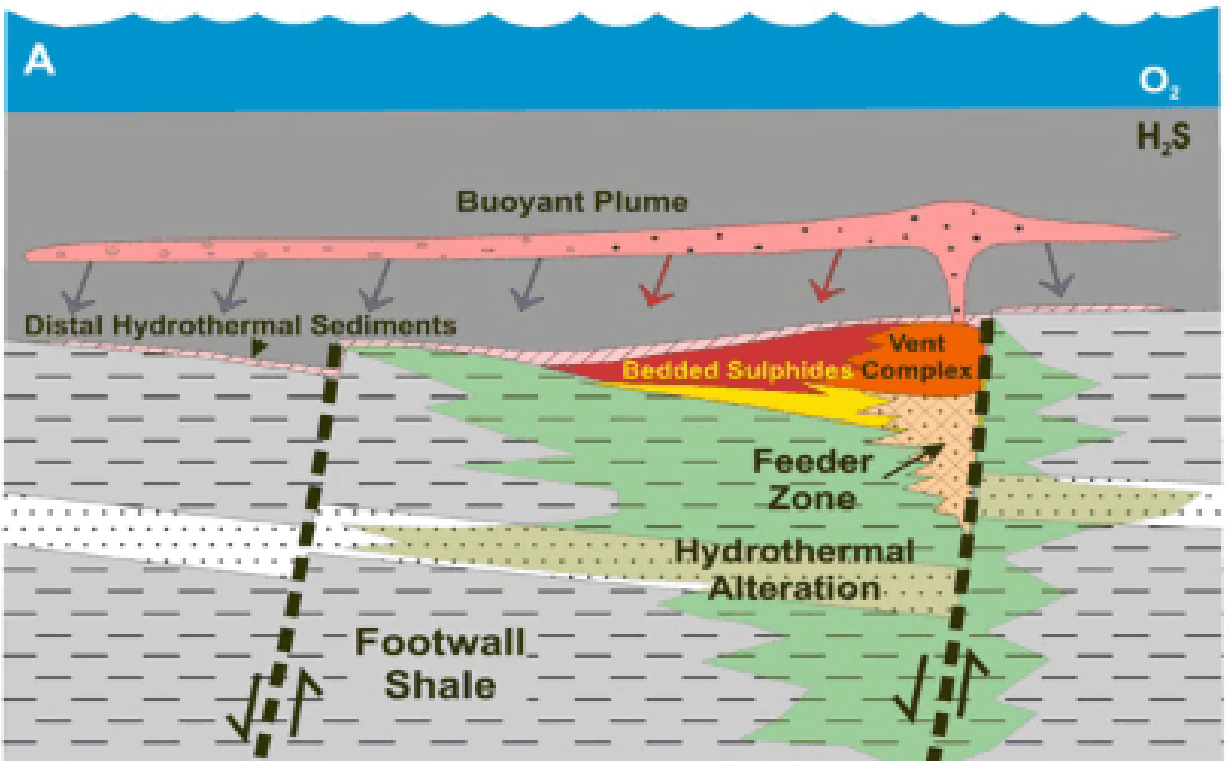




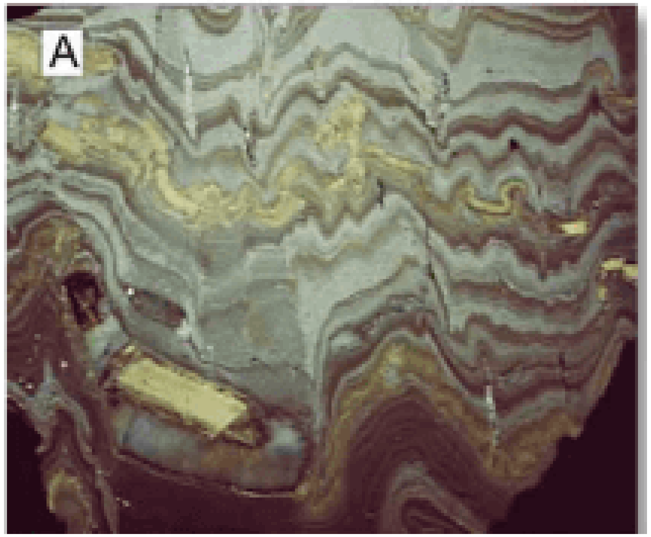


SedEx – Similarities to VMS

- Deposited on the **seafloor** at the same time as the host rocks
- Massive sulfide lenses with underlying feeder zones
- Often form in **clusters** or **stacked lenses**
- Metal transported as chloride complexes in brines.



- Often deformed

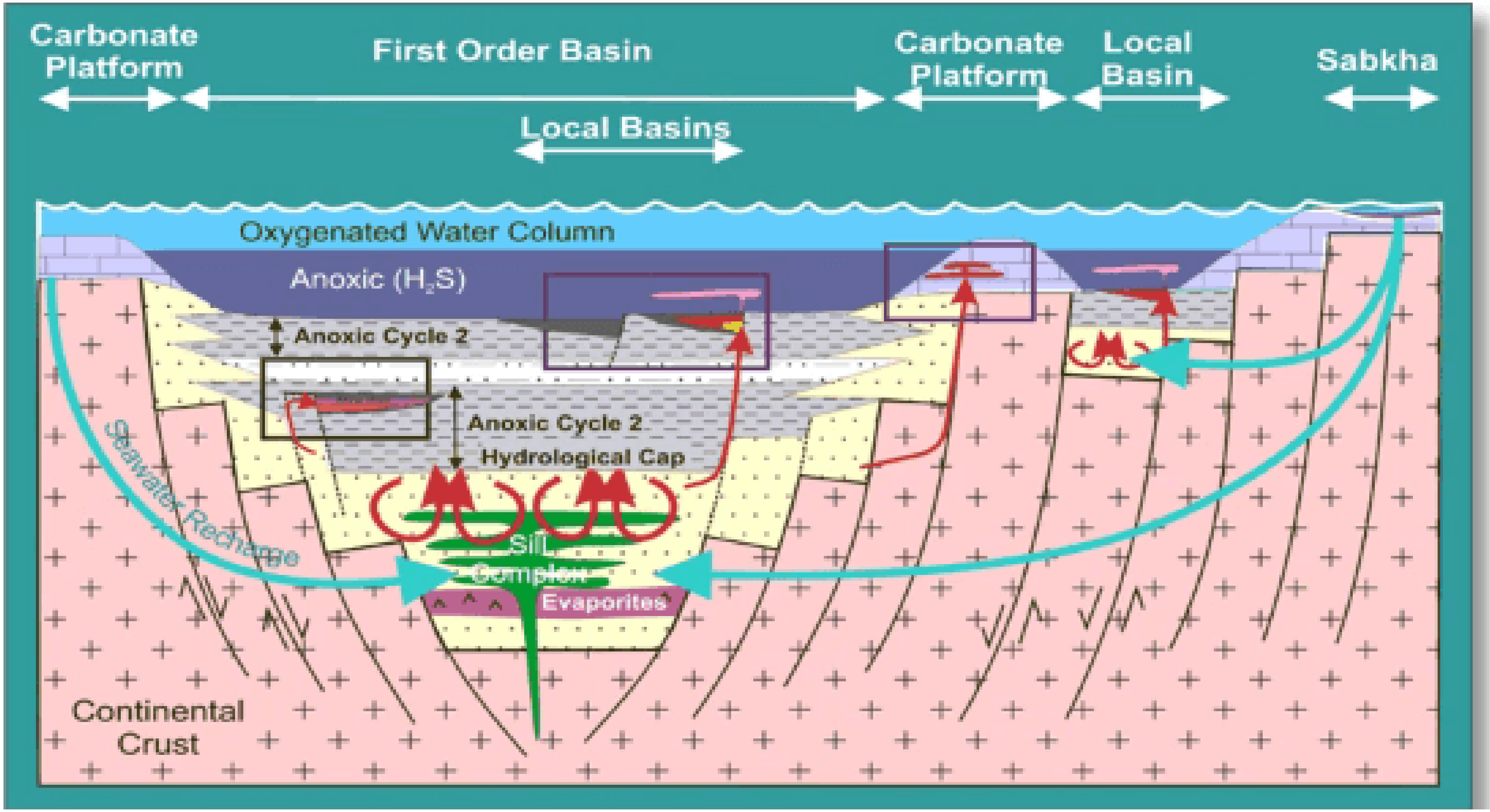


SedEx – Differences from VMS

Form in fault-bounded **sedimentary** basins on **continental crust**, not oceanic crust. **Host rocks** are usually shales - volcanics are rare

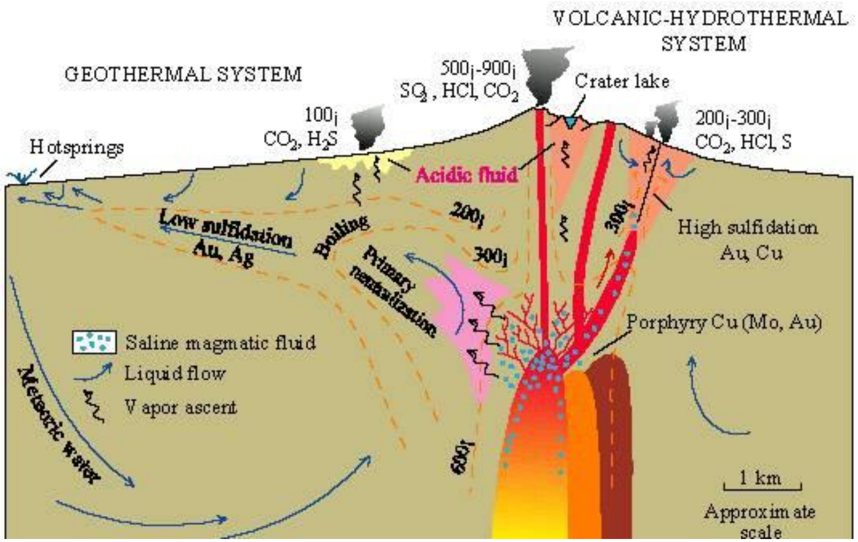
Metals derived ~100% from host sediments/basement, not intrusives

Insignificant Cu and Au; more Pb and Ag; Zn in both.

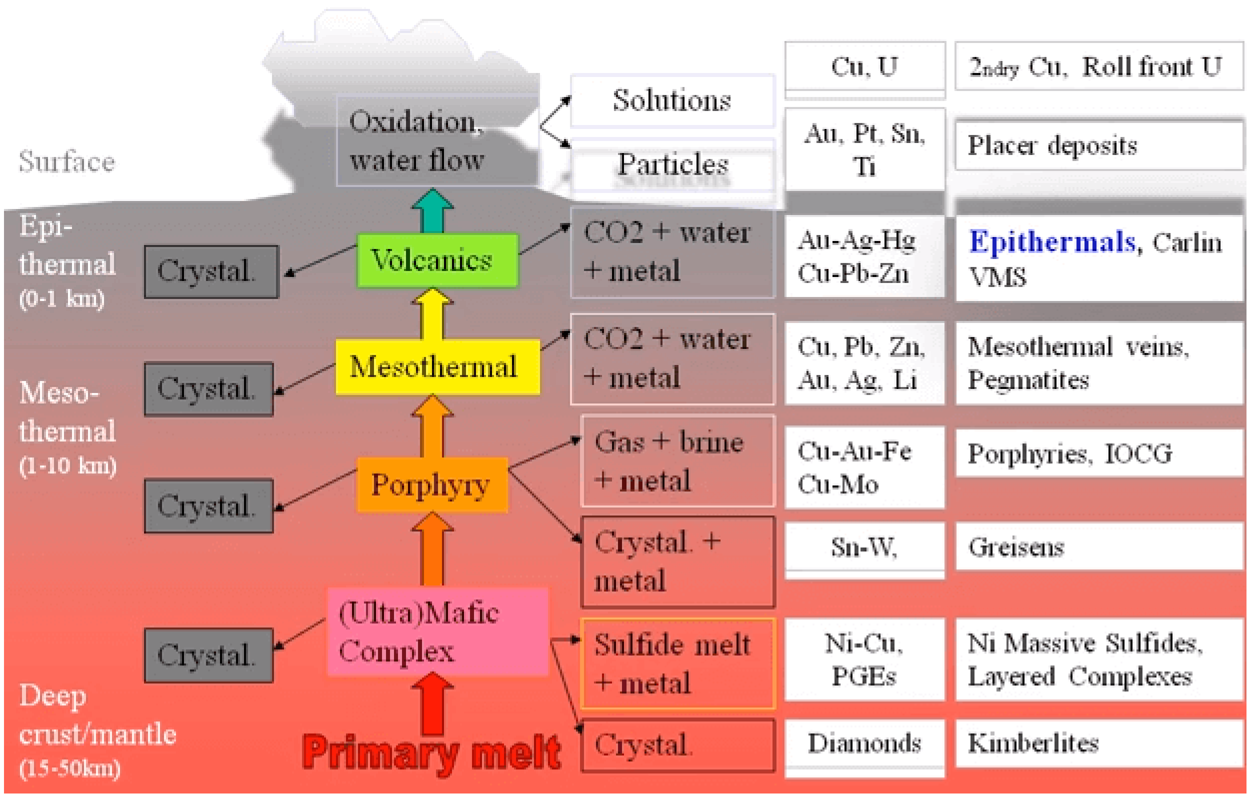


VI. Terrestrial epithermal gold, silver and base metal ore deposits

Many important ore deposits are connected with terrestrial volcanism. In previous sections, iron oxide lavas and tuffs, and the subvolcanic porphyry copper ore deposits were mentioned. Here, we focus on a deposit class that is commonly called "epithermal". These deposits formed by near surface hydrothermal processes (they occur at shallow epizonal depth (0 to 1 km) "100-300°C"; "hot springs").



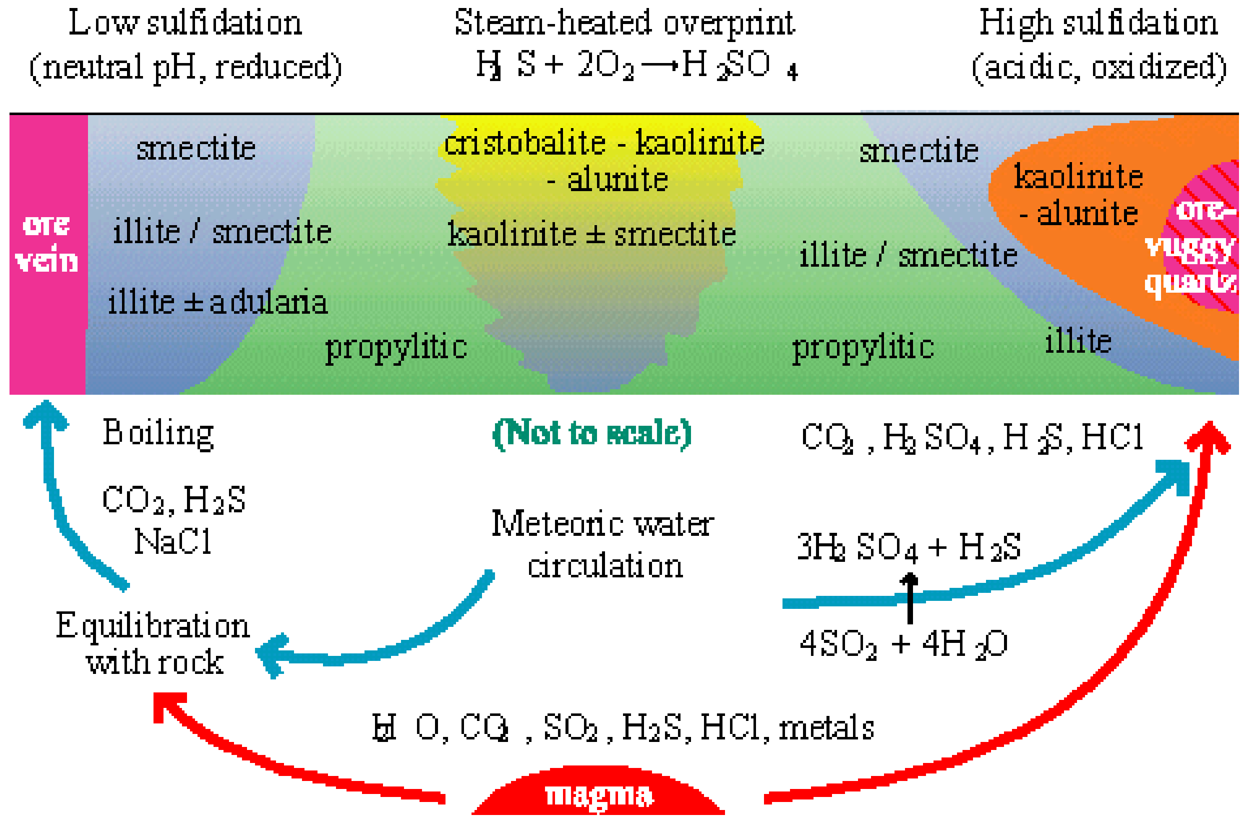
Epithermal ore deposits are remarkable as a major source of gold, silver, zinc, lead, bismuth and the minerals alunite, barite and fluorite. Active epithermal systems of today's volcanic regions are mainly investigated in view of their role as an energy source.



Epithermal ore bodies take the shape of veins, breccias, metasomatic masses and impregnations within hydrothermally altered host rocks. They are closely related to metalliferous sinter mounds that occur on the land surface ("hot springs deposits").

Epithermal ore is formed in the aureole of near-surface subvolcanic magma bodies that induce a high heat flow and a steep geothermal gradient.

Sulphur is an important component of magmatic volatiles. Near the surface, oxidation of sulphur produces strong acids that **react with host rocks.** The resulting **hydrothermal alteration** is very conspicuous because of bleaching and formation of alunite. **Alunite can also be formed when oxic magmatic exhalations that are enriched in HCl and SO_2 dissolve in groundwater and react with host rocks.** This is the environment of the formation of **epithermal gold deposits of the alunite, or high sulphidation type.**

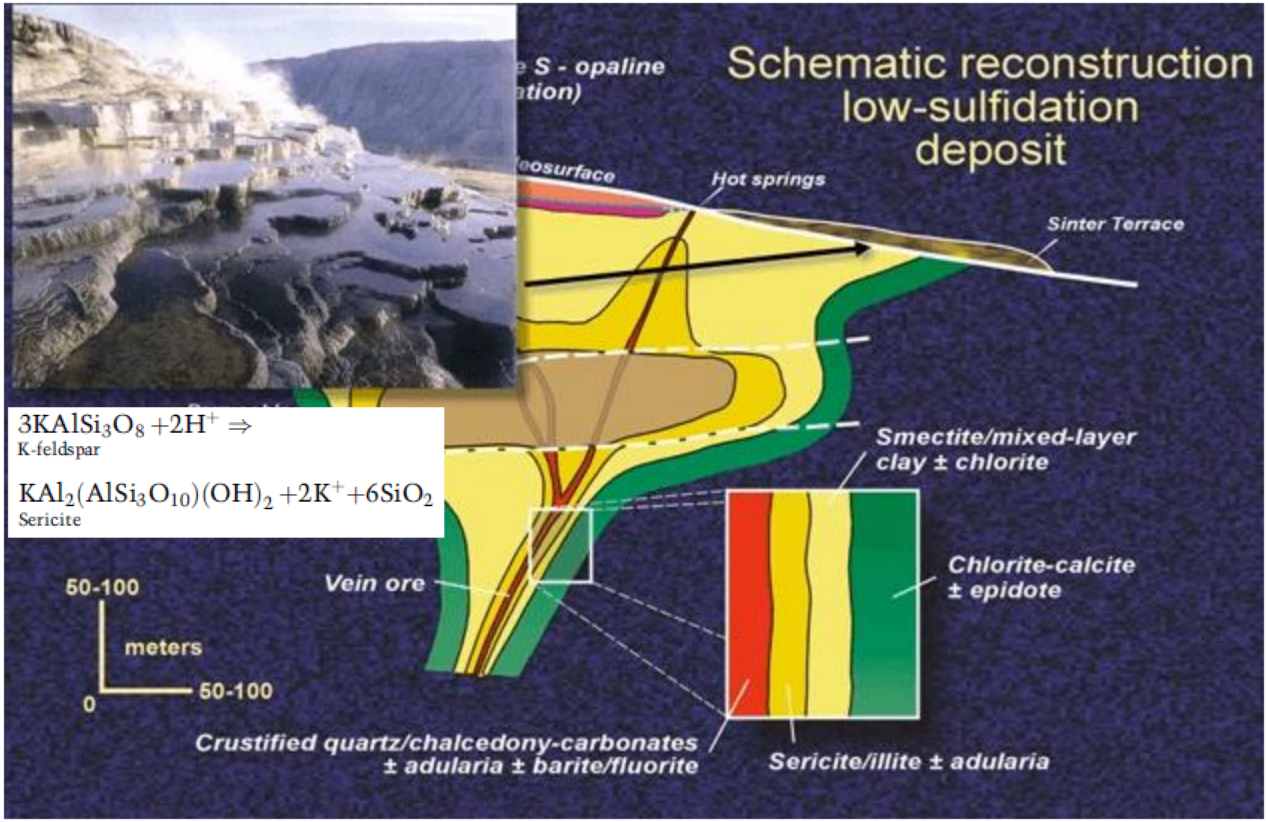


$$\underset{\text{K-feldspar}}{KAlSi_3O_8} + 2Al^{+3} + 2H_2SO_4 + 4H_2O$$

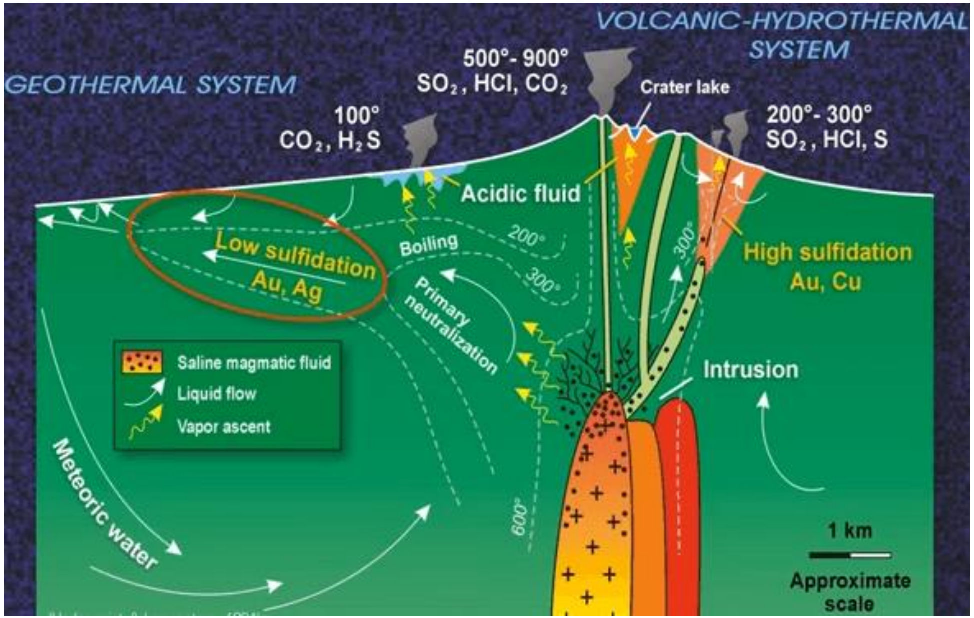
$$\rightarrow \underset{\text{Alunite}}{KAl_3(SO_4)_2(OH)_6} + 3SiO_2 + 6H^+$$

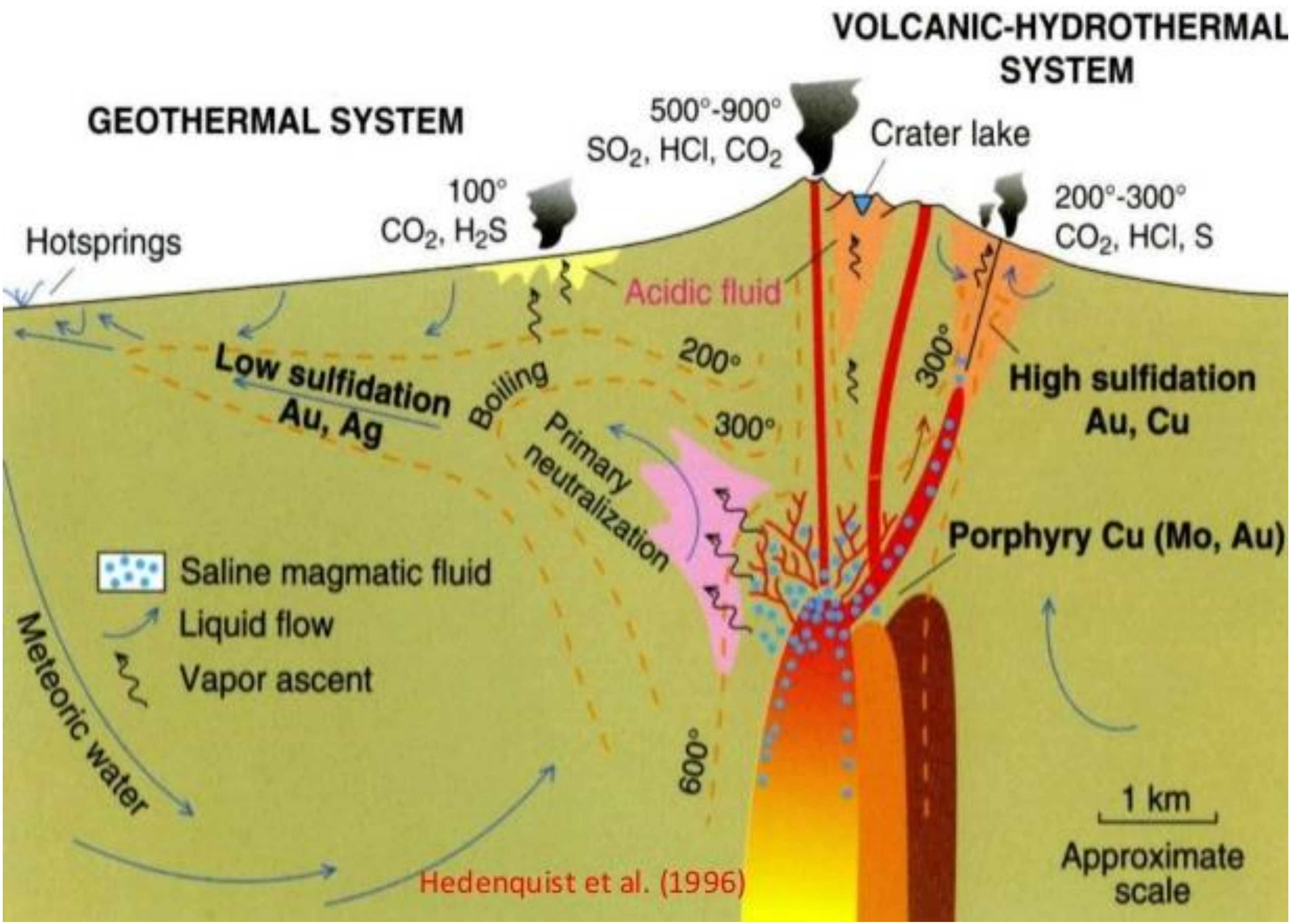
High sulphidation (high fS2 in oxic conditions) is indicated by **ore minerals such as enargite, tennantite and covellite,** and by advanced **argillic alteration gangue minerals including alunite, pyrophyllite, dickite and kaolinite. High sulphidation epithermal deposits are often in close spatial association with copper-gold porphyries.**

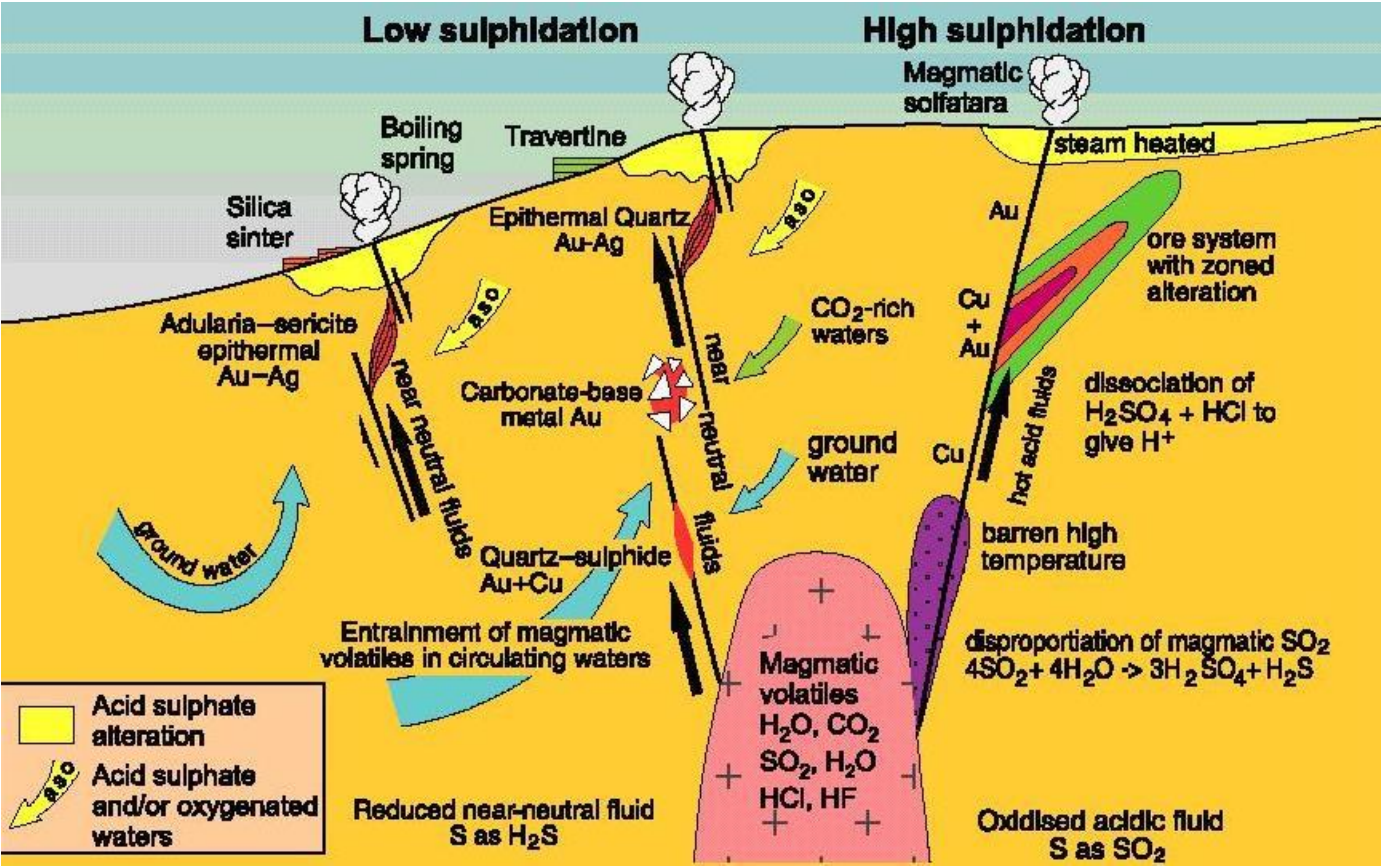
Epithermal deposits of the adularia-sericite, or low sulphidation type are produced by **reduced and neutral to mildly alkaline fluids that carry H_2S and other reduced sulphur species.** In the **low sulphidation type** deposits, **silver, gold and base metals** dominate and typical gangue minerals are calcite, adularia and illite.



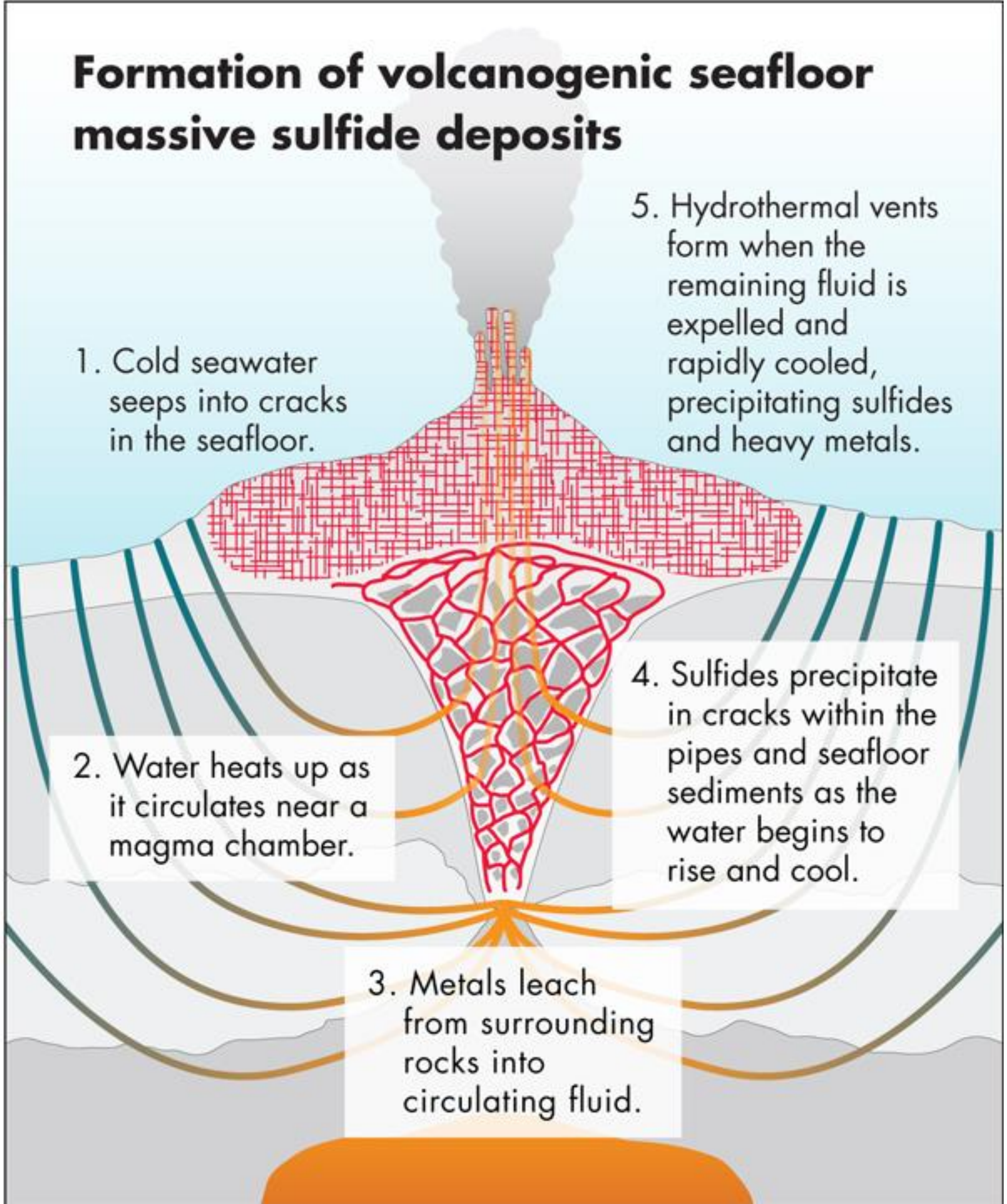
Generally, terrestrial volcanogenic deposits occur in convergent plate boundary and subduction settings. Many of these systems were triggered by tensional events.

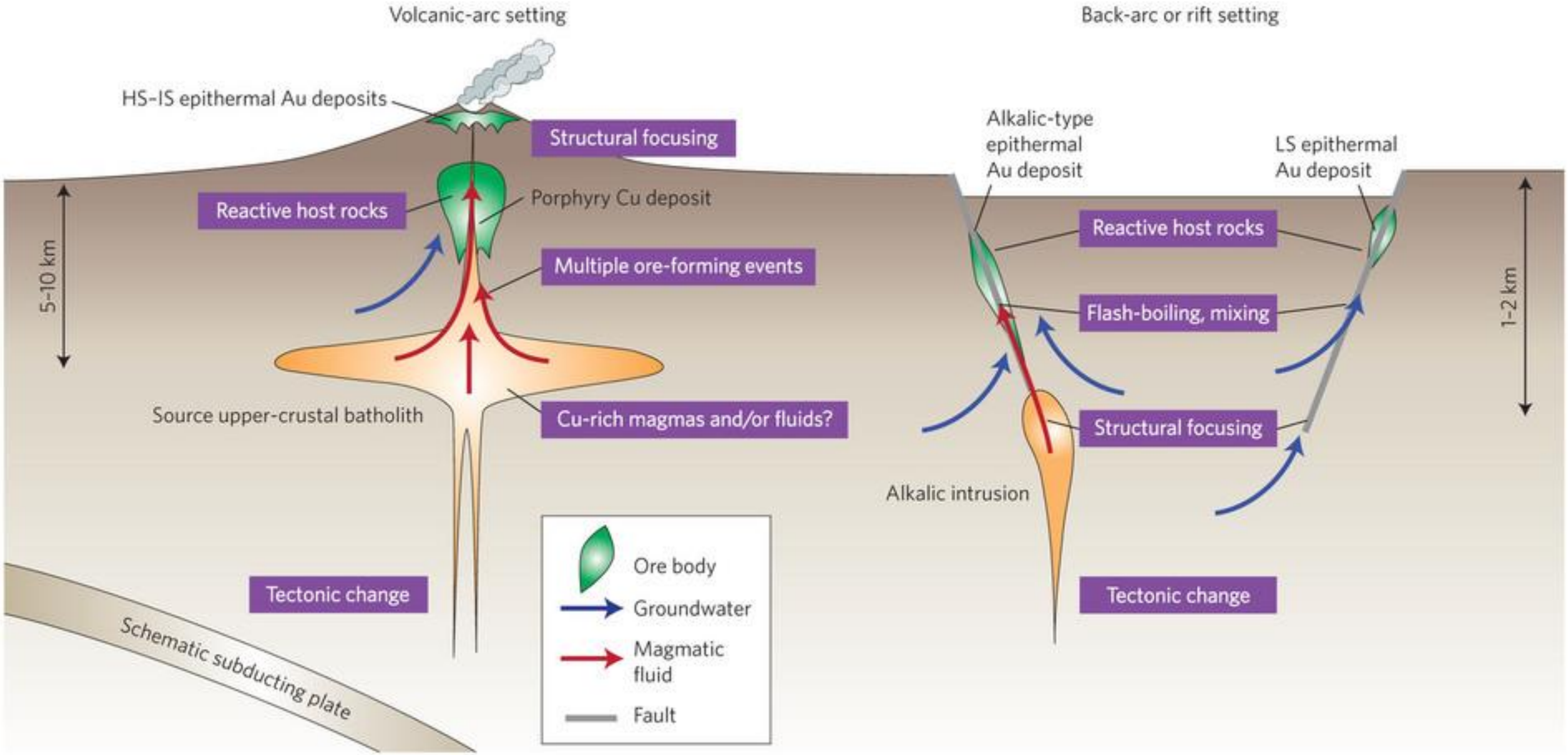



VOLCANIC-HYDROTHERMAL SYSTEM
GEOTHERMAL SYSTEM
500°-900°
SO2, HCl, CO2
Crater lake
100°
CO2, H2S
200°-300°
CO2, HCl, S
Hotsprings
Acidic fluid
200°
300°
300°
600°
Low sulfidation
Au, Ag
Boiling
Primary neutralization
High sulfidation
Au, Cu
Porphyry Cu (Mo, Au)
Saline magmatic fluid
Liquid flow
Vapor ascent
Meteoric water
1 km
Approximate scale
Hedenquist et al. (1996)

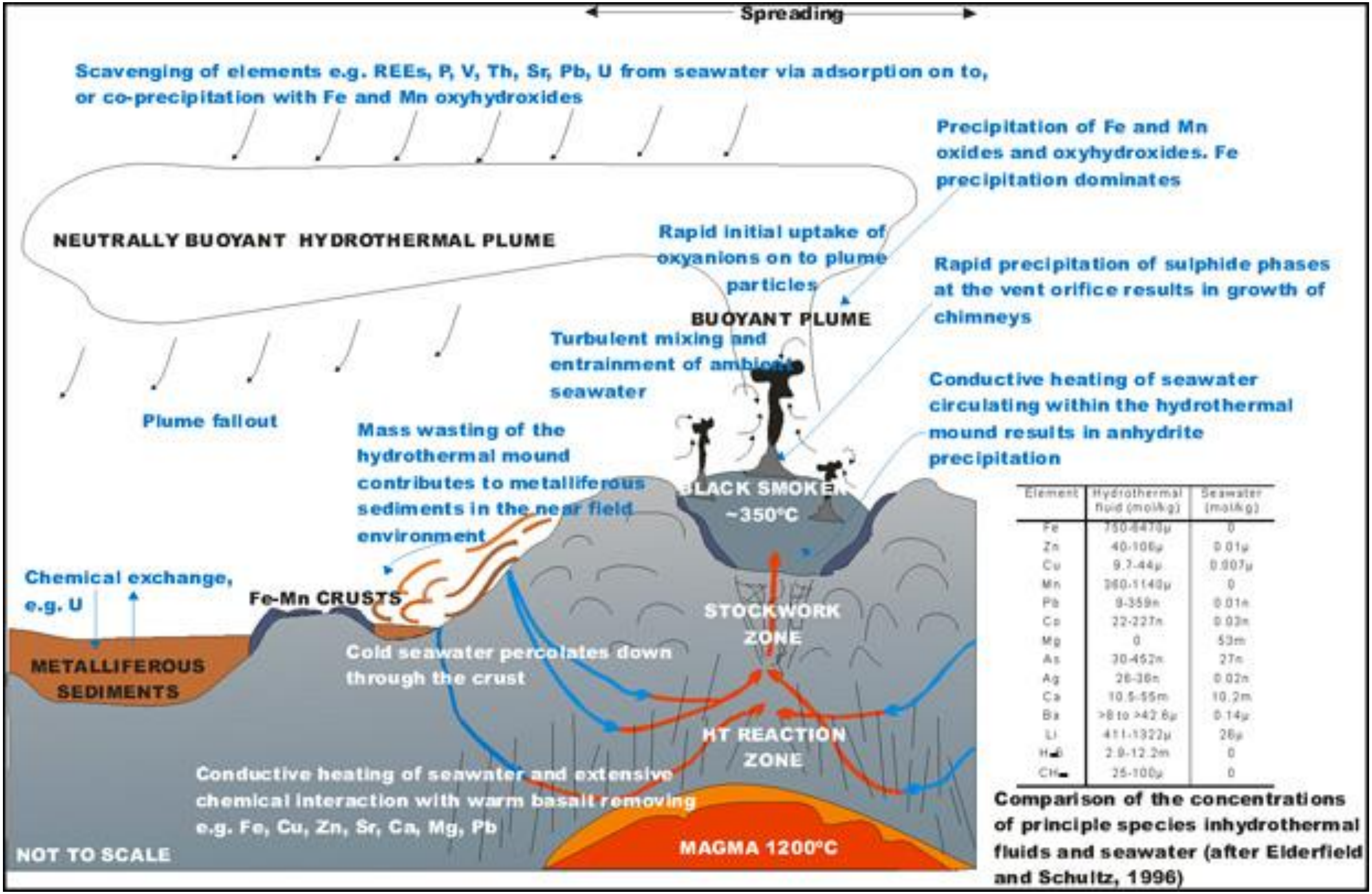


Low sulphidation
High sulphidation
Magmatic solfatara
Boiling spring
Travertine
steam heated
Silica sinter
Epithermal Quartz Au-Ag
Au
aso
ore system with zoned alteration
Cu + Au
CO2-rich waters
Adularia–sericite epithermal Au–Ag
near neutral fluids
near neutral fluids
Carbonate-base metal Au
hot acid fluids
dissociation of H2SO4 + HCl to give H+
ground water
Cu
ground water
barren high temperature
Quartz–sulphide Au+Cu
Entrainment of magmatic volatiles in circulating waters
Magmatic volatiles H2O, CO2 SO2, H2O HCl, HF
disproportiation of magmatic SO2
4SO2+ 4H2O -> 3H2SO4+ H2S
Acid sulphate alteration
Acid sulphate and/or oxygenated waters
Reduced near-neutral fluid S as H2S
Oxidised acidic fluid S as SO2


Formation of volcanogenic seafloor massive sulfide deposits
1. Cold seawater seeps into cracks in the seafloor.
2. Water heats up as it circulates near a magma chamber.
3. Metals leach from surrounding rocks into circulating fluid.
4. Sulfides precipitate in cracks within the pipes and seafloor sediments as the water begins to rise and cool.
5. Hydrothermal vents form when the remaining fluid is expelled and rapidly cooled, precipitating sulfides and heavy metals.



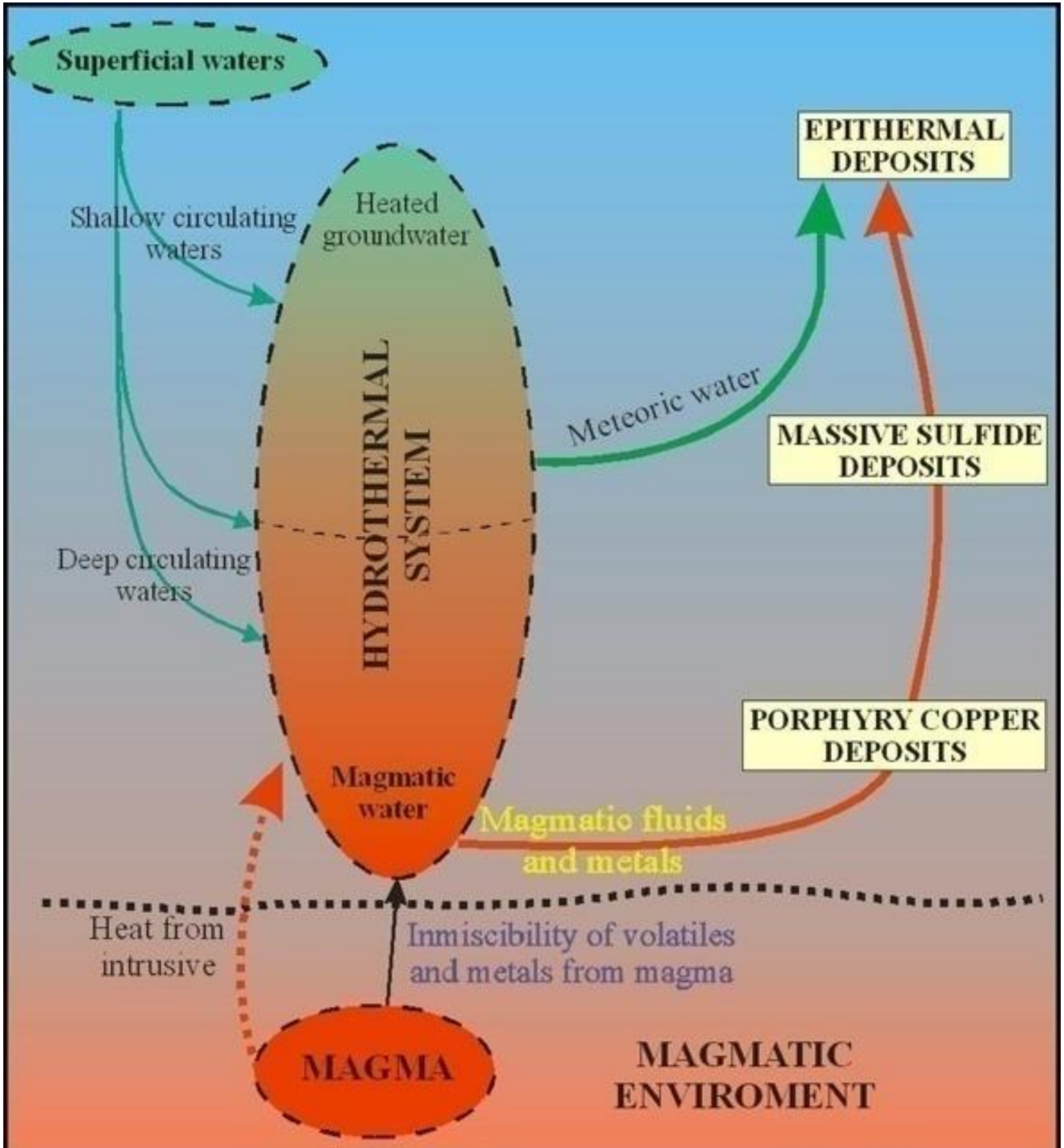
The figure schematically illustrates the general modes of formation of porphyry Cu and epithermal Au deposits. (LS, low sulphidation). Purple boxes highlight features or processes that may result in supercharging these systems to form giant deposits.



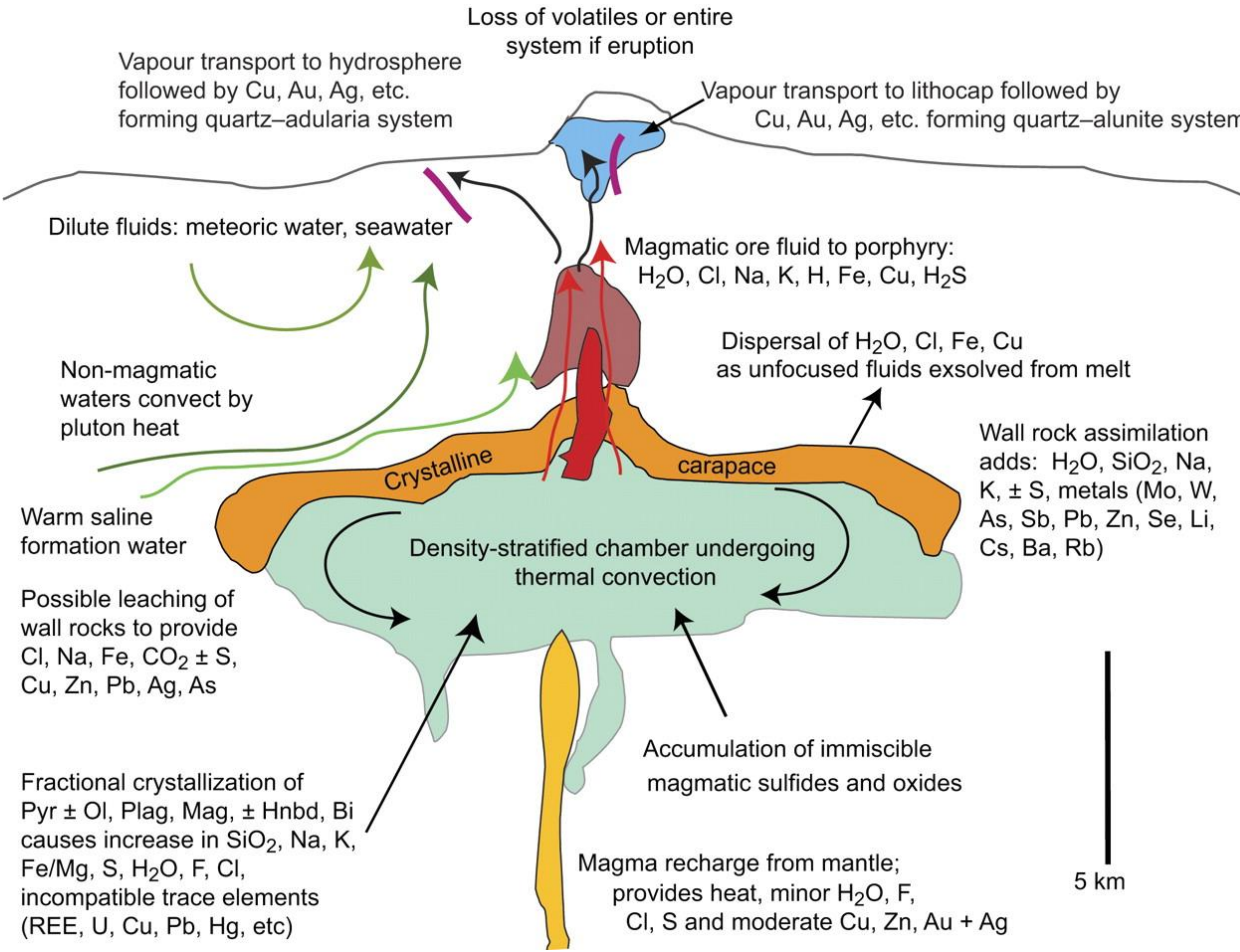
Element	Hydrothermal fluid (mol/kg)	Seawater (mol/kg)
Fe	750-6470µ	0
Zn	40-106µ	0.01µ
Cu	9.7-44µ	0.007µ
Mn	360-1140µ	0
Pb	9-359n	0.01n
Co	22-227n	0.03n
Mg	0	53m
As	30-452n	27n
Ag	26-38n	0.02n
Ca	10.5-55m	10.2m
Ba	>8 to >42.6µ	0.14µ
Li	411-1322µ	26µ
H[illegible]	2.9-12.2m	0
CH[illegible]	25-100µ	0

Comparison of the concentrations of principle species inhydrothermal fluids and seawater (after Elderfield and Schultz, 1996)

A Schematic diagram of hydrothermal circulation.



Superficial waters
EPITHERMAL DEPOSITS
Shallow circulating waters
Heated groundwater
HYDROTHERMAL SYSTEM
Meteoric water
MASSIVE SULFIDE DEPOSITS
Deep circulating waters
PORPHYRY COPPER DEPOSITS
Magmatic water
Magmatic fluids and metals
Heat from intrusive
Inmiscibility of volatiles and metals from magma
MAGMA
MAGMATIC ENVIROMENT


Loss of volatiles or entire system if eruption
Vapour transport to hydrosphere followed by Cu, Au, Ag, etc. forming quartz–adularia system
Vapour transport to lithocap followed by Cu, Au, Ag, etc. forming quartz–alunite system
Dilute fluids: meteoric water, seawater
Magmatic ore fluid to porphyry: H_2O, Cl, Na, K, H, Fe, Cu, H_2S
Dispersal of H_2O, Cl, Fe, Cu as unfocused fluids exsolved from melt
Non-magmatic waters convect by pluton heat
Wall rock assimilation adds: H_2O, SiO_2, Na, K, ± S, metals (Mo, W, As, Sb, Pb, Zn, Se, Li, Cs, Ba, Rb)
Crystalline
carapace
Warm saline formation water
Density-stratified chamber undergoing thermal convection
Possible leaching of wall rocks to provide Cl, Na, Fe, CO_2 ± S, Cu, Zn, Pb, Ag, As
Accumulation of immiscible magmatic sulfides and oxides
Fractional crystallization of Pyr ± Ol, Plag, Mag, ± Hnbd, Bi causes increase in SiO_2, Na, K, Fe/Mg, S, H_2O, F, Cl, incompatible trace elements (REE, U, Cu, Pb, Hg, etc)
Magma recharge from mantle; provides heat, minor H_2O, F, Cl, S and moderate Cu, Zn, Au + Ag
5 km

End of Lecture