

EARTH 471

Mineral Deposits

Geochemistry of hydrothermal ore deposits

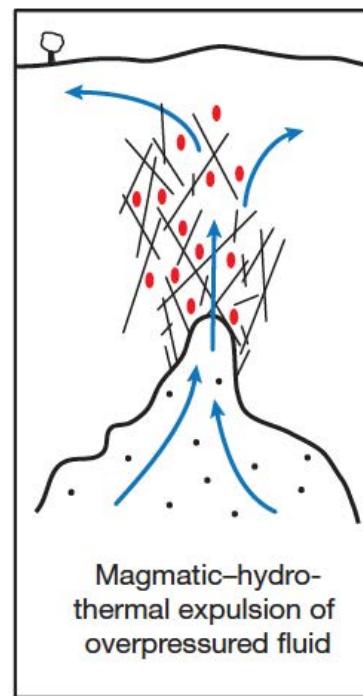
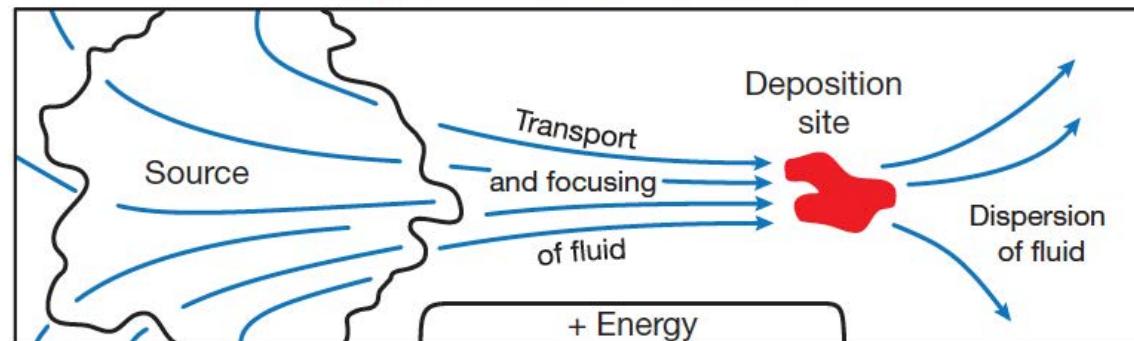
Hydrothermal ore deposits

Hydro: water +
Thermal: heat
= Hot water!

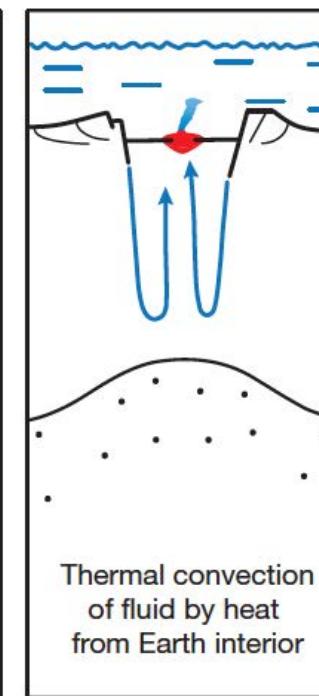
Driving force can
be thermal or
mechanical

Fluid: both liquids
and vapors

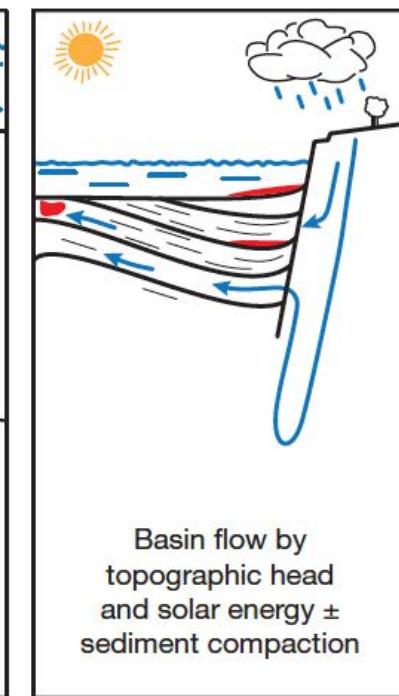
Hydrothermal ore formation



Magmatic-hydro-
thermal expulsion of
overpressured fluid



Thermal convection
of fluid by heat
from Earth interior



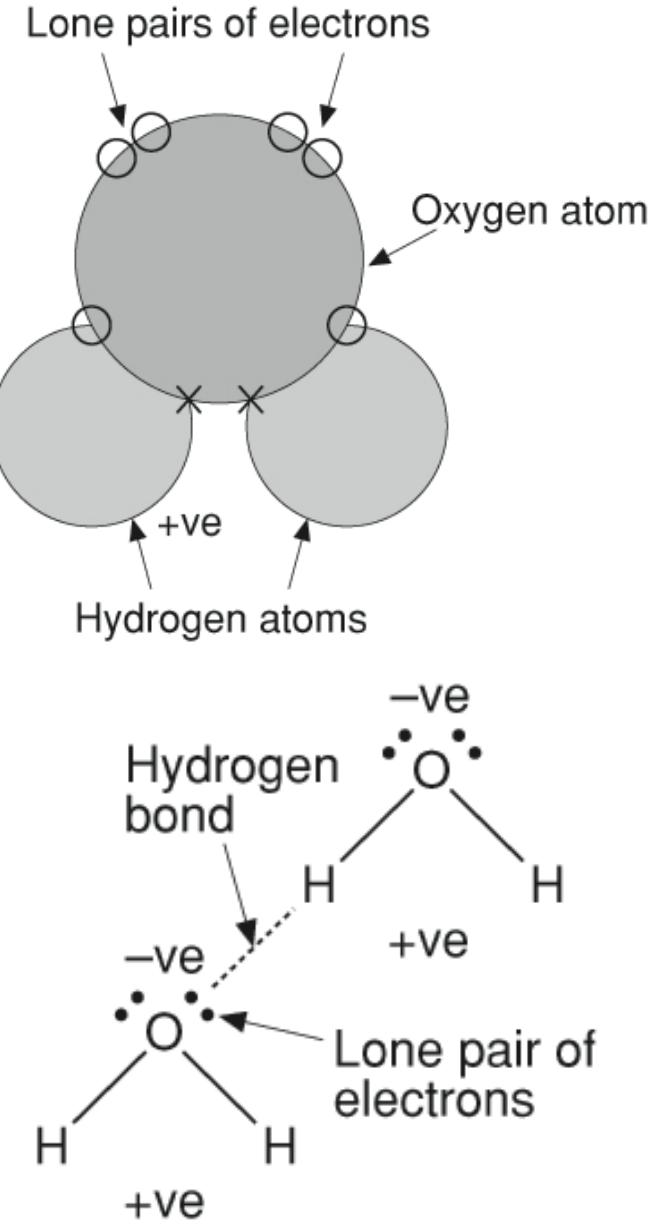
Basin flow by
topographic head
and solar energy ±
sediment compaction

Heinrich & Candela (2014)

Why water?

- High heat capacity (conducts heat more readily than other liquids)
- High surface tension (can easily ‘wet’ mineral surfaces)
- High dielectric constant (can easily dissolve ionic substances)

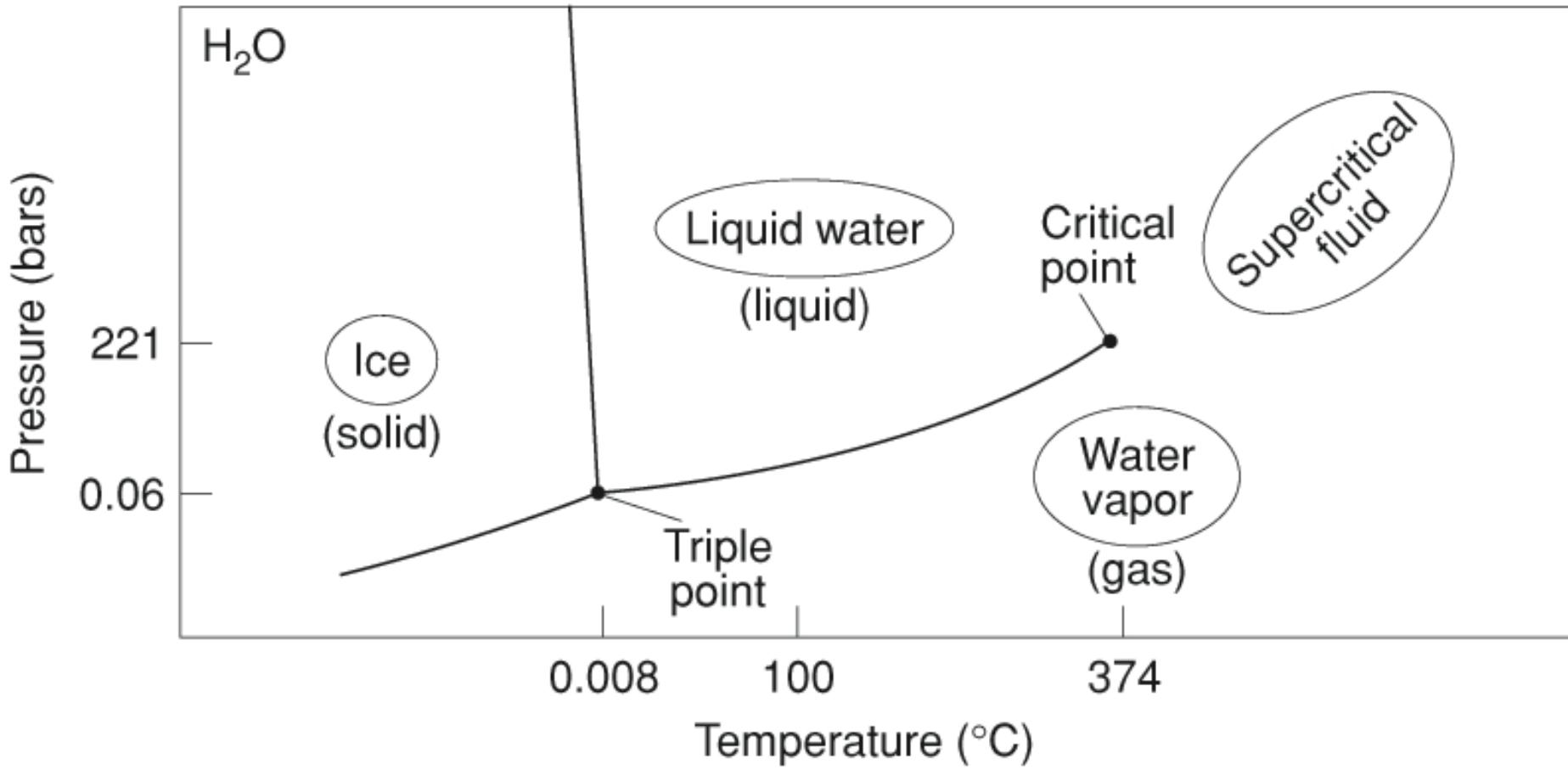
Water is the main transport agent for elements of economic interest due mainly to the high dielectric constant



Water

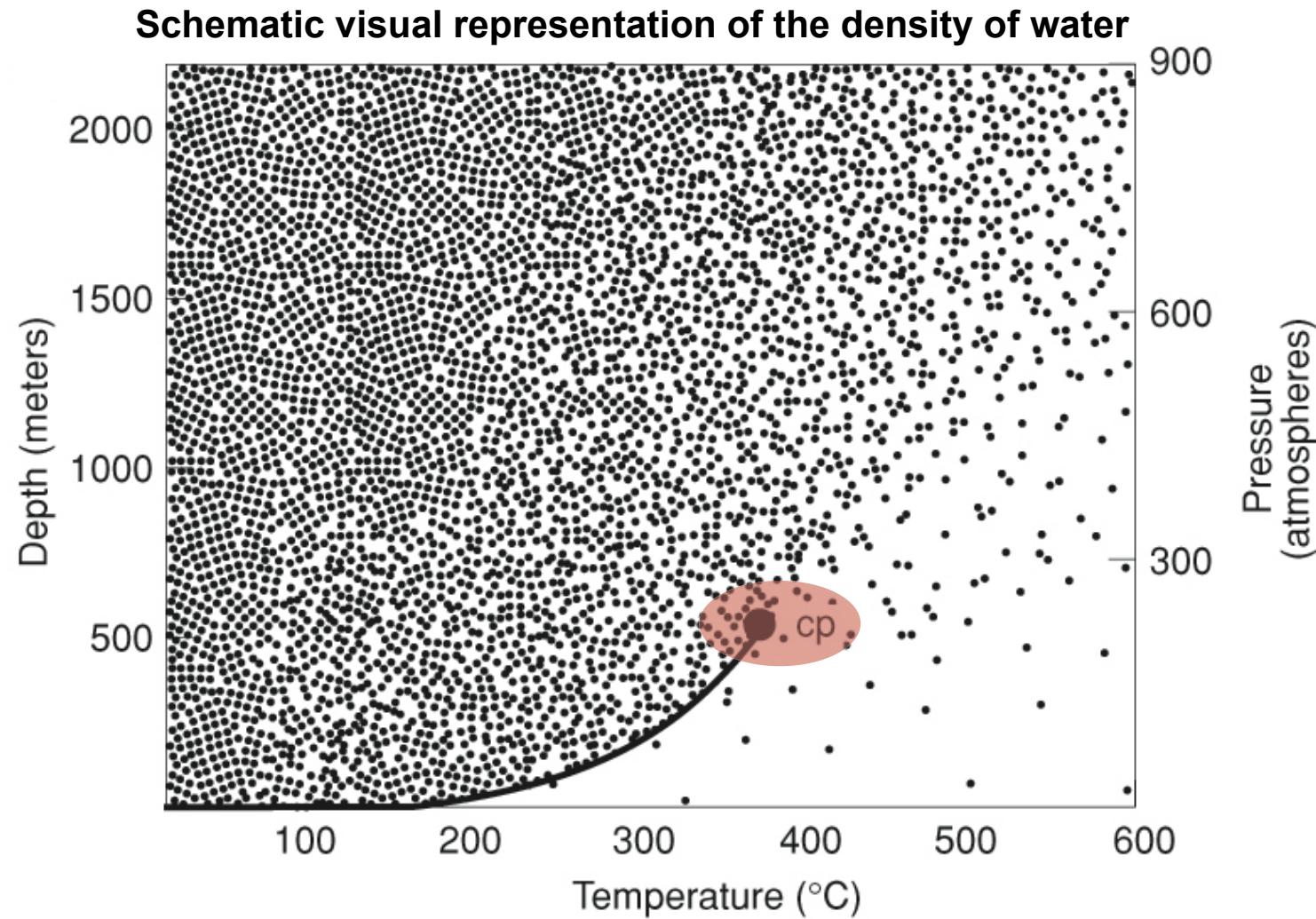
- (1) Ice
- (2) Liquid water

- (3) Water vapour
- (4) Supercritical fluid...



Supercritical water

Above the critical point, there is no physical distinction between liquid and vapour

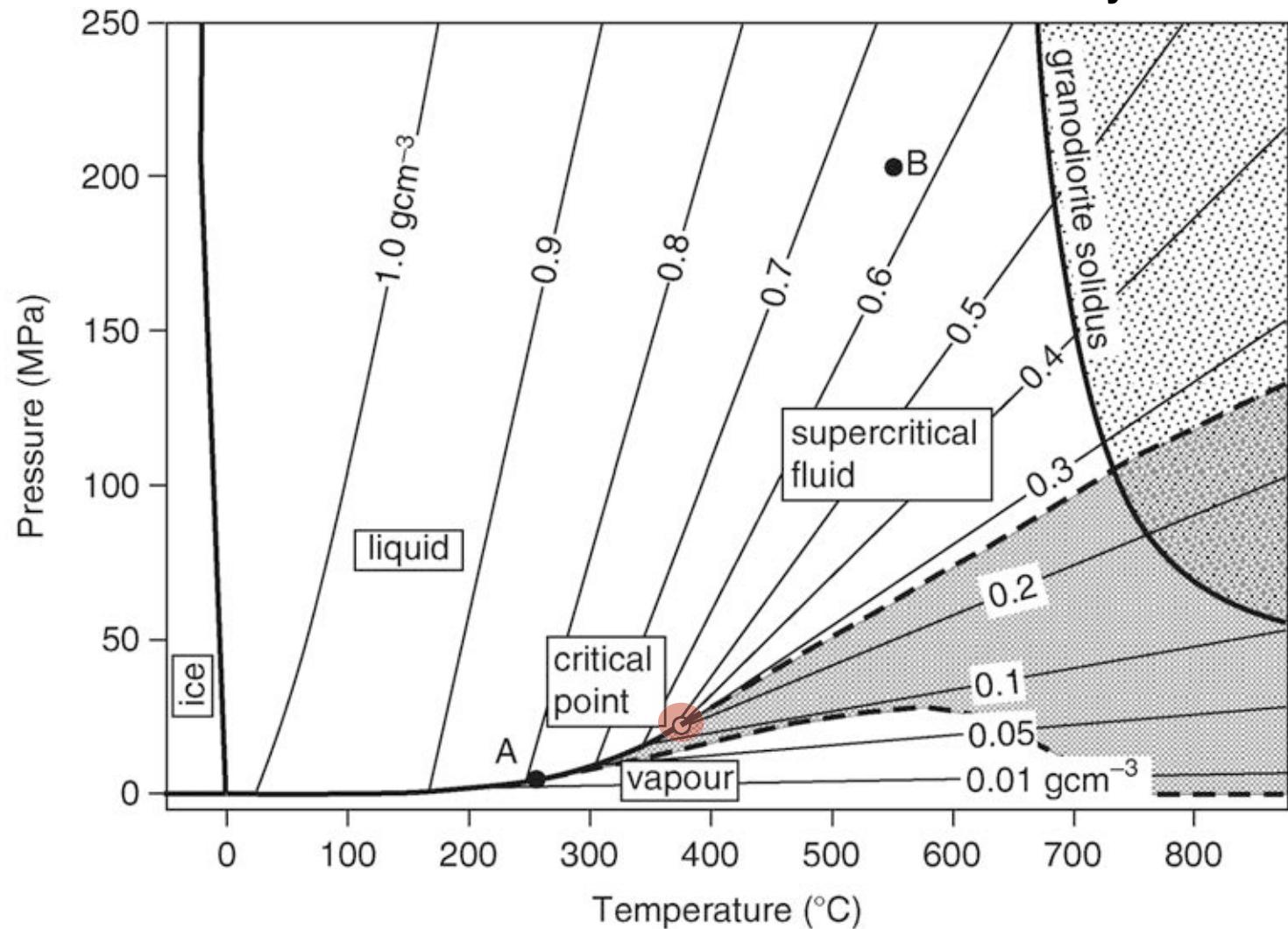


Supercritical water

Above the critical point, there is no physical distinction between liquid and vapour

...which can sometimes lead to weird behavior...

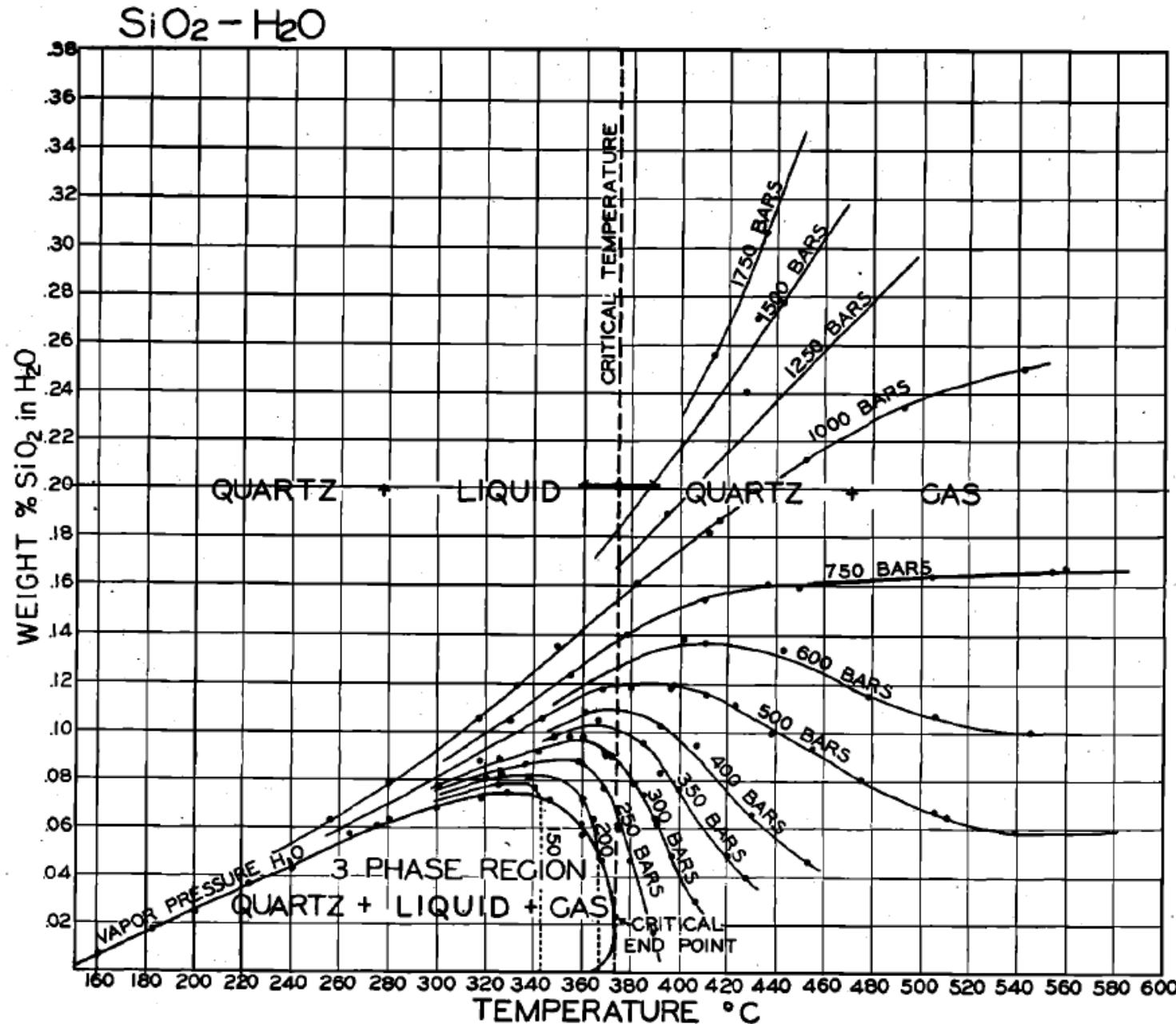
contours are density of water





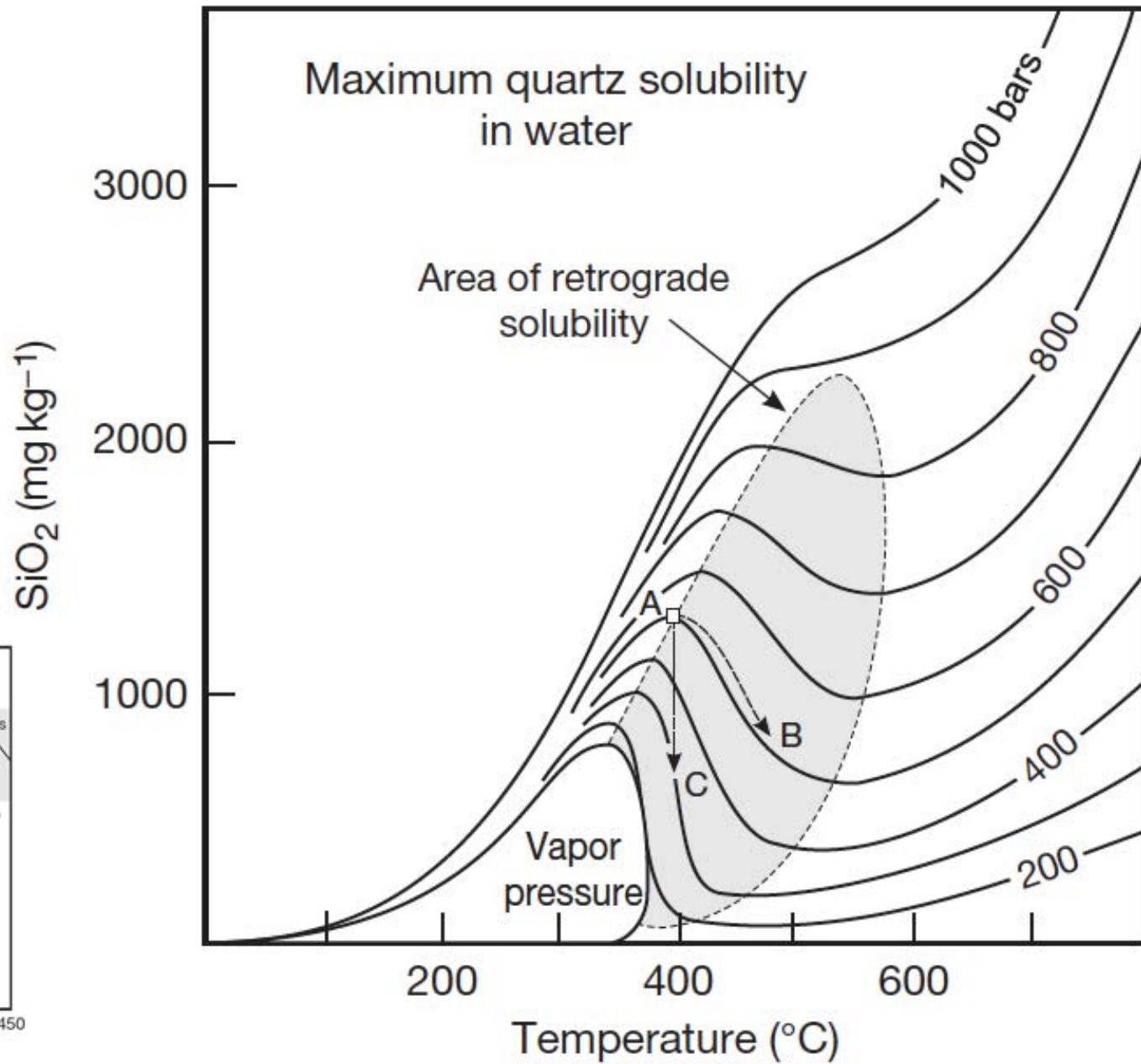
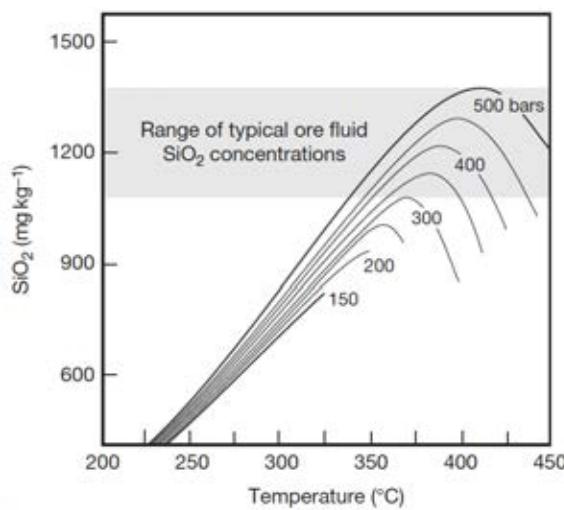
Quartz solubility in H₂O

Figure 2
Kennedy (1950,
Econ. Geol.)



Quartz solubility in H_2O

Figure 7
Hannigan (2014,
Treatise on
Geochemistry 2nd
ed.)

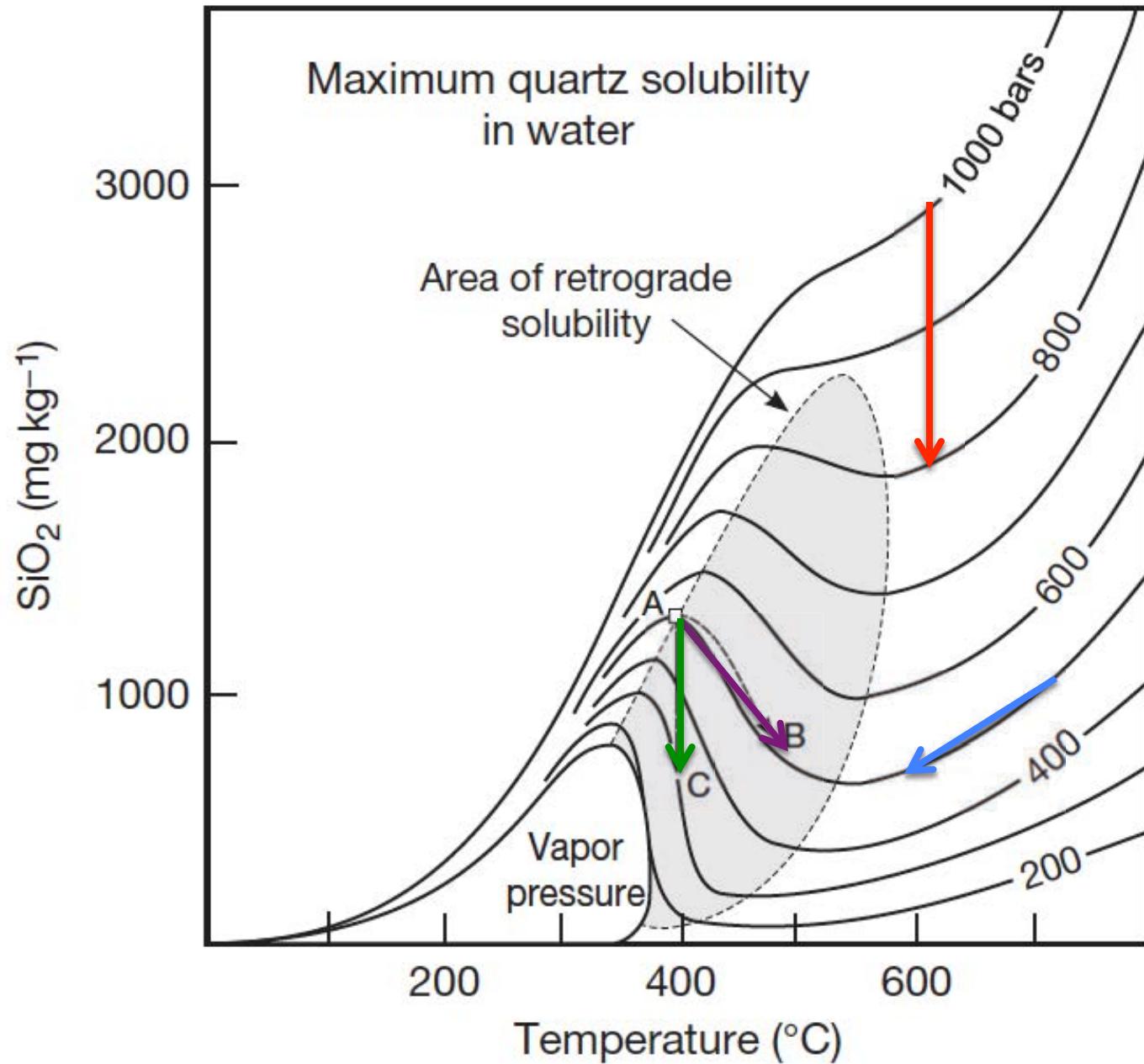


Decrease P from
1000 to 800 bars (at
600°C) = precipitate
quartz

Decrease T from 700
to 600°C (at 500 bar)
= precipitate quartz

Increase T from 400
to 500°C (at 500 bar)
= precipitate quartz

Decrease P from
1300 to 800 bar (at
400°C) = precipitate
quartz

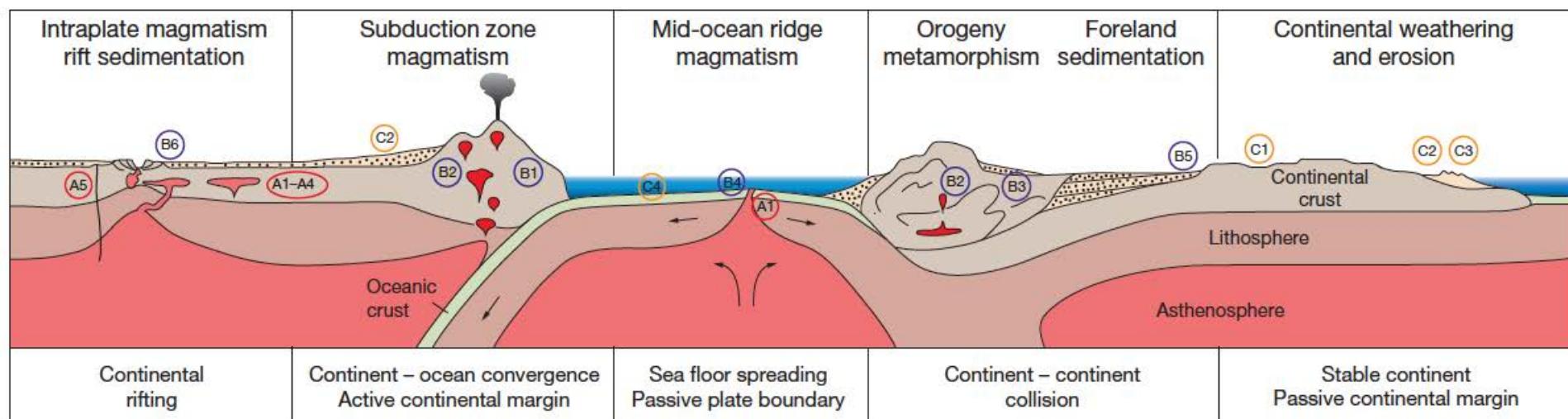


Hydrothermal ore deposits – a huge subject

B. Hydrothermal ore deposits: Enrichment by selective dissolution, transport, and precipitation from aqueous fluids of different sources

Fluid saturation of H ₂ O-bearing magmas: magmatic–hydrothermal	Porphyry deposits ('Cu, Mo porphyries') (13.14) Sn–W veins and replacement deposits Skarn and Cordilleran deposits replacing carbonates	Cu; Mo Au Sn, W (Cu, Pb, Ag) W, Cu, Au	Circumpacific GUS, China, Aus China W
Continental geothermal systems (\pm shallow magmatic fluids)	Epithermal veins and breccias (13.15; 13.16)	Au, Hg (Ag, Pb, Zn)	Circumpacific, CIS
Continental magmatic fluids interacting with evaporitic brines	Iron oxide hosted Cu–Au–U–REE ('IOCG') deposits (13.20)	Cu, Au, U, Fe, REE	Aus, Brazil, Chile
Seawater convection through oceanic crust	Volcanic-hosted massive sulfide deposits (13.18) Mid-ocean ridges ~ 'black smokers' Arc-related basins and submarine volcanoes	Cu, Zn (Pb, Au, Sn)	Can, Iberia, Aus Cyprus; TAG Kuroko; Kermadec
Metamorphic dehydration \pm deep magmatic fluids	Orogenic ('mesothermal') gold-quartz-veins (13.15) Archean greenstone belts, younger continental orogens	Au	Can, Aus, CIS
Basin brines: connate or meteoric water + evaporites	Sediment-hosted Cu \pm Co deposits (13.10) Stratiform Pb–Zn–Ag deposits (13.9) ('sedex' = sedimentary-exhalative, early diagenetic)	Cu, Co, Ag Pb, Zn, Ag	USA, C. Africa, Poland Can, Aus, Ireland
Deep infiltration of oxygenated surface waters	Mississippi Valley-type Pb–Zn = epigenetic replacement in carbonates \pm sandstones (13.9) Uranium in sandstones ('roll-front U deposits') Vein- and 'unconformity-related U deposits' (13.19)	Pb, Zn, Cd; F U, V U (Au, Pd, Pt)	USA, Can USA Can, Aus

Heinrich & Candela (2014)



A: Magmatic ore deposits

- A1. Chromitites as (ultra-)mafic cumulates in layered intrusions and ophiolites
- A2. V-magnetite in mafic intrusions (V, Ti)
- A3. Pegmatites (Li, Cs, Be, Nb, Ta)
- A4. Ni- und PGE-sulfide deposits in mafic intrusions und flood basalts
- A5. Carbonatite (REE) and kimberlite (diamond) deposits

B: Hydrothermal ore deposits

- B1. Porphyry Cu (Mo, Au) and epithermal Au, Ag (Hg, ...) deposits
- B2. Sn-W veins and greisens in granites
- B3. Orogenic ('metamorphogenic') Au-quartz vein deposits
- B4. Volcanogenic massive sulfides (Cu, Zn)
- B5. Sediment-hosted (MVT, 'sedex') Pb, Zn, Cd, Cu, Co deposits

C: Surface-related ore deposits

- C1. Residual ore deposits: bauxite (Al), Ni-laterite deposits
- C2. Alluvial placer deposits (Sn, Ta, Au; U)
- C3. Beach-sand placers (Ti, Zr, REE)
- C4. Manganese nodules and crusts on the ocean floor (Mn, Co, Ni, Cu...)
- B6. Sandstone-hosted and unconformity-related U (V, F, Mo, Au, PGE) deposits

Figure 3 Schematic illustration of the recurrent association of ore deposit types with global tectonic settings, including active and passive continental margins, oceanic spreading centers including back-arc basins, as well as land surfaces, sedimentary basins and hot spots in the interior of lithospheric plates. Labels A, B, C refer to major metal-transporting media and ore deposit types in Table 3.

Ridley (2013)

What you need:

1. Fluid
 2. Ligands
 3. Source of metals
 4. Transport conduit(s)
 5. Trap
 - Acts as a filter
 - If all fluid stopped, no increase in concentration
 - Need to precipitate ore minerals and allow the (depleted) fluid to pass through
-
- ```
graph TD; MS((metal source)) -- leaching --> FLS((fluid ± ligand source)); FLS -- fluid focussing --> OD((ore deposit)); FLS -- "changing P-T-X" --> OD; OD -- precipitation --> MS;
```



# Source of fluids I

## (1) Sea Water

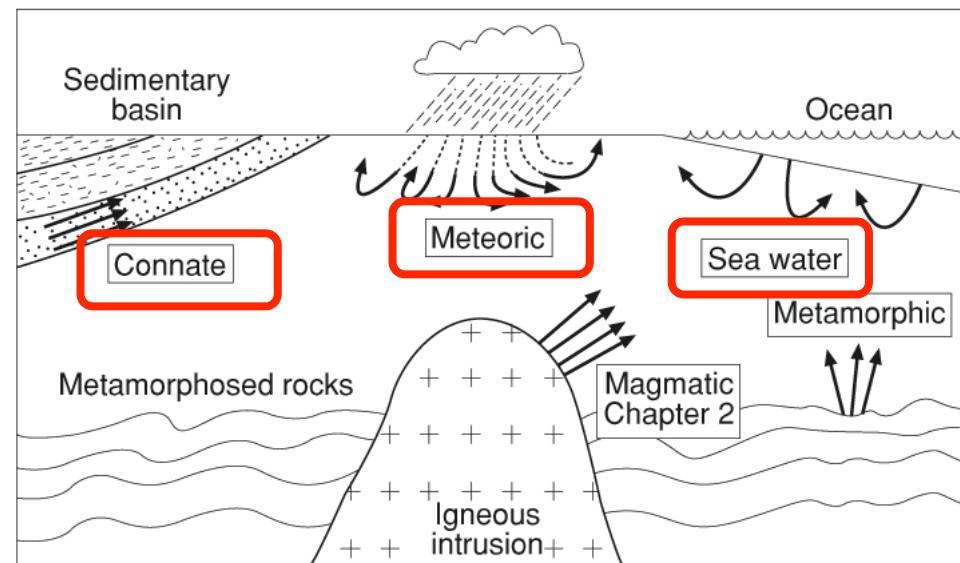
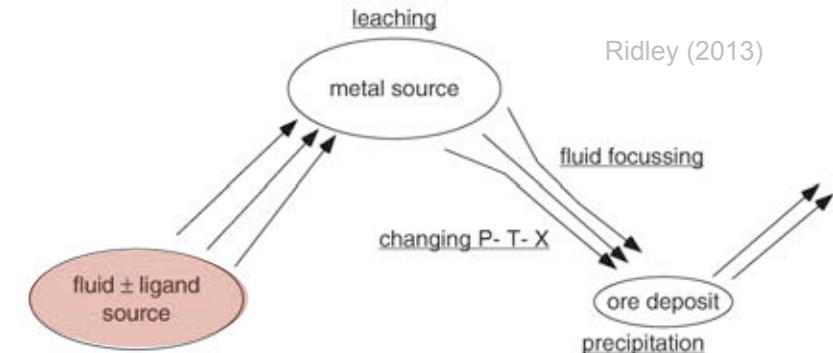
- Contains significant amounts of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$
- Seawater  $\sim 35$  g of solid per kg water ( $\sim 3.5$  wt%)

## (2) Meteoric (fresh) water

- Geologically speaking, it is groundwater that has infiltrated the upper crust through rainfall or standing/flowing surface water

## (3) Connate

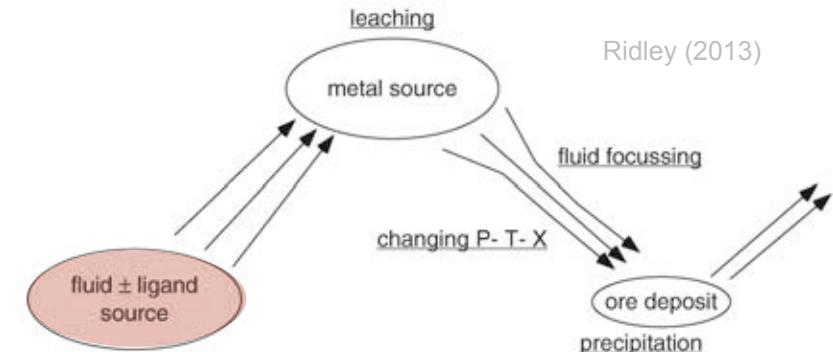
- Trapped in pore spaces of sediment during deposition
- Modified during diagenesis (become more saline with depth)



# Source of fluids II

## (4) Metamorphic

- Reactions produce less hydrous minerals, which releases H<sub>2</sub>O

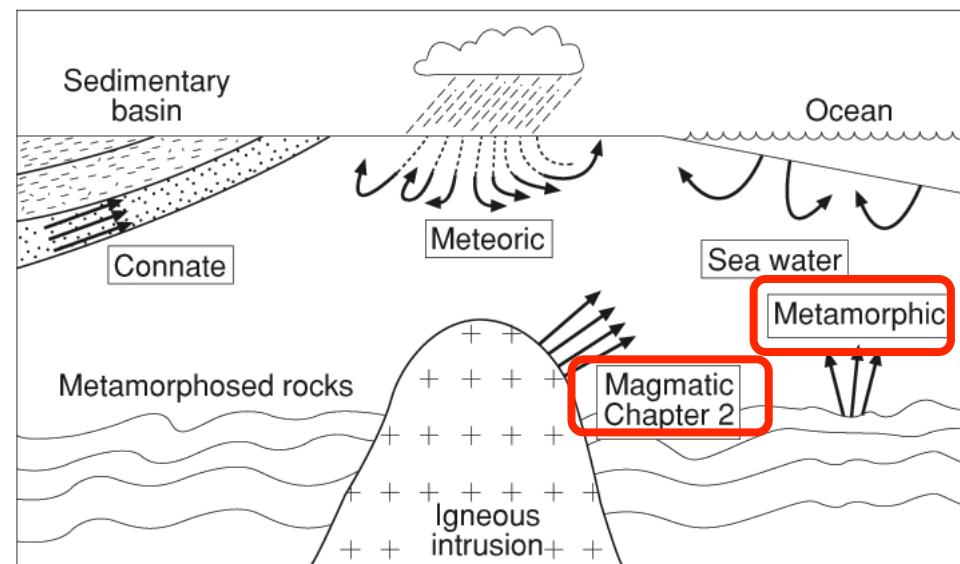


## (5) Magmatic

- Exsolved from a magma

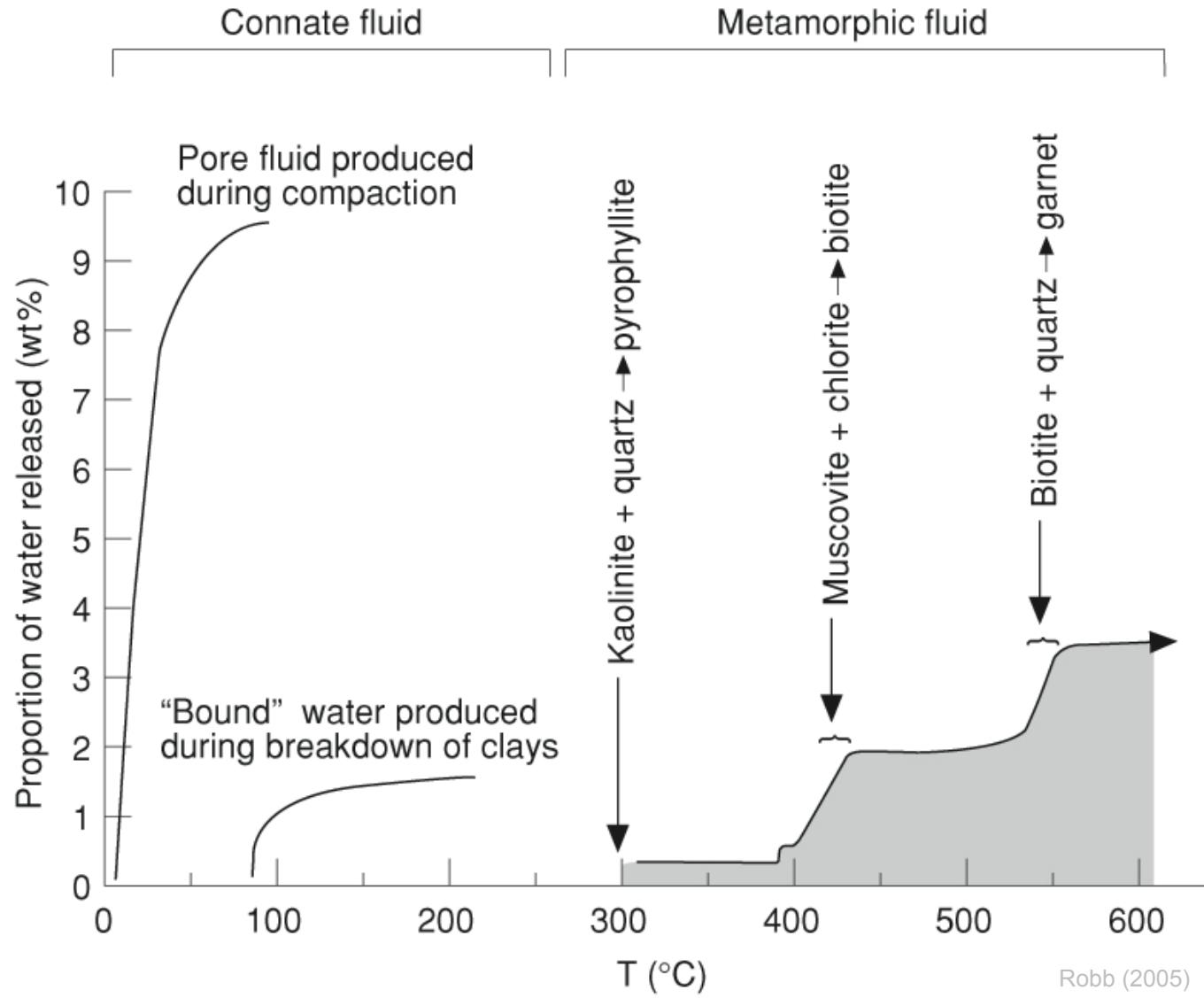
## (6) Mixed

- Of course, you can mix waters from different sources



Robb (2005)

# Connate $\rightarrow$ metamorphic fluids



# How do we know where fluids come from?

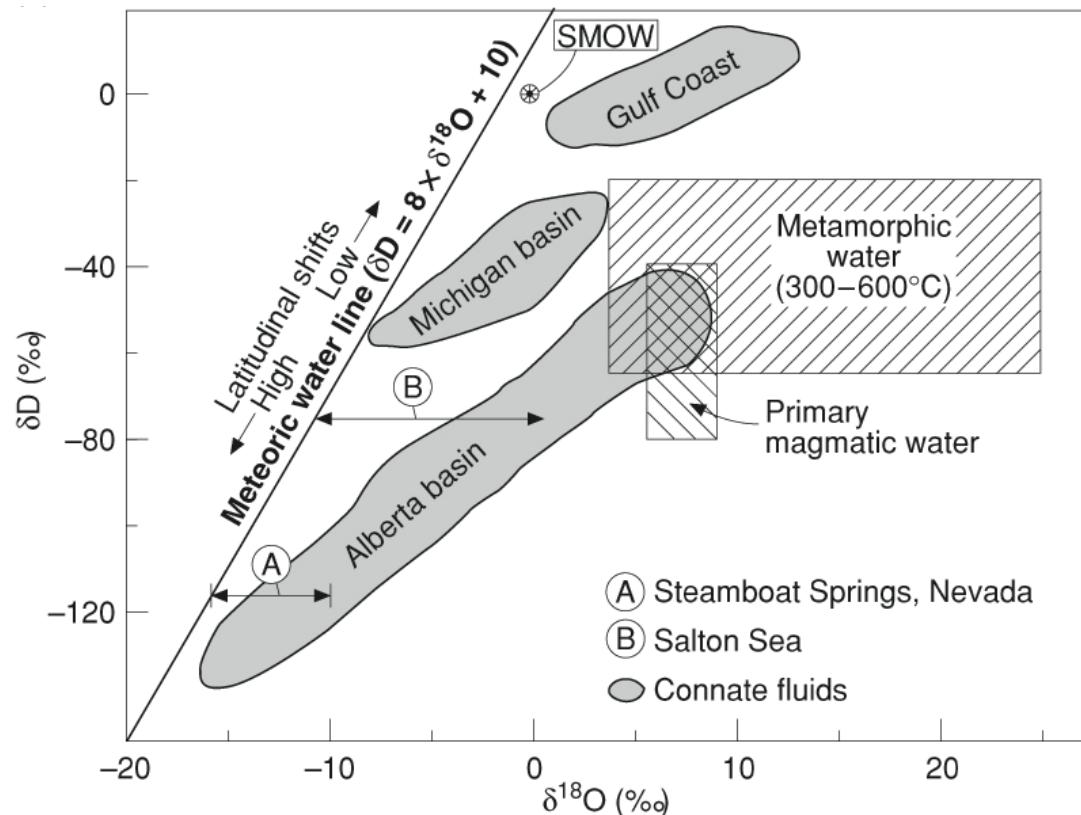
## Stable isotope analysis:

- Oxygen
- Hydrogen
- Chlorine/Bromine

TABLE 1. Natural abundances and reference standards for light stable isotopes

| Element  | Isotope             | Atomic Abundance+ | Ratio                            | International Standards                          |
|----------|---------------------|-------------------|----------------------------------|--------------------------------------------------|
| Oxygen   | <sup>16</sup> O     | 99.763%           | <sup>18</sup> O/ <sup>16</sup> O | Vienna Standard Mean Ocean Water (VSMOW)         |
|          | <sup>17</sup> O     | 0.0375%           |                                  | Vienna Pee Dee Belemnite (VPDB) (for carbonates) |
|          | <sup>18</sup> O     | 0.1995%           |                                  |                                                  |
| Hydrogen | <sup>1</sup> H      | 99.9844%          | D/H                              | VSMOW                                            |
|          | <sup>2</sup> H (D)* | 0.0156%           |                                  |                                                  |
| Sulfur   | <sup>32</sup> S     | 95.02%            | <sup>34</sup> S/ <sup>32</sup> S | Cañon Diablo Troilite (CDT)                      |
|          | <sup>33</sup> S     | 0.75%             |                                  |                                                  |
|          | <sup>34</sup> S     | 4.21%             |                                  |                                                  |
|          | <sup>36</sup> S     | 0.02%             |                                  |                                                  |
| Carbon   | <sup>12</sup> C     | 98.89%            | <sup>13</sup> C/ <sup>12</sup> C | VPDB                                             |
|          | <sup>13</sup> C     | 1.11%             |                                  |                                                  |

\*The mass 2 isotope of hydrogen is named deuterium (D)



$$\delta^{18}\text{O} = [ (\text{$_{18}$O}/\text{$_{16}$O})_{\text{sample}} / (\text{$_{18}$O}/\text{$_{16}$O})_{\text{standard}} ] - 1] * 1000$$

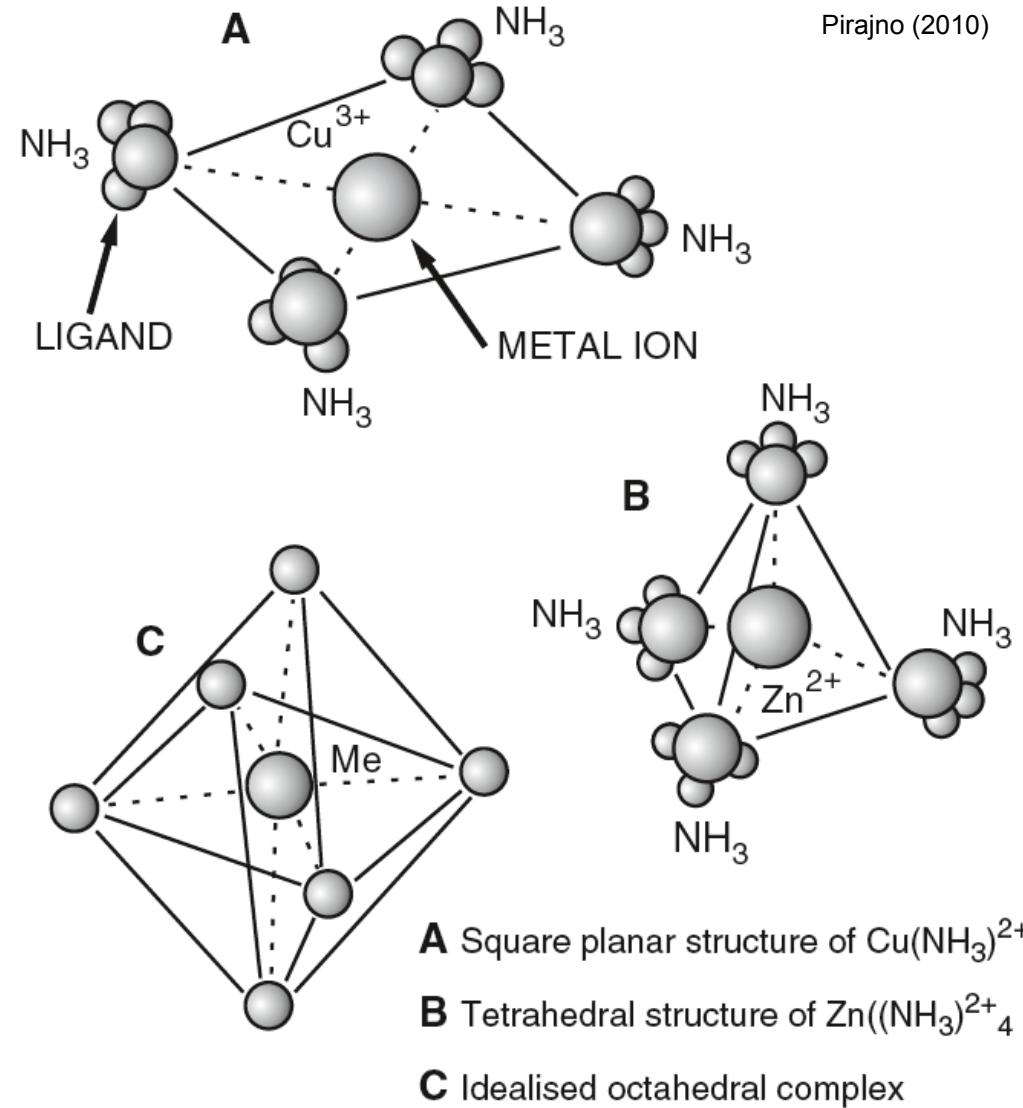
$$\delta\text{D} = [ (\text{$_{2}$H}/\text{$_{1}$H})_{\text{sample}} / (\text{$_{2}$H}/\text{$_{1}$H})_{\text{standard}} ] - 1] * 1000$$

‰ = parts per thousand

Robb (2005)

# Ligands

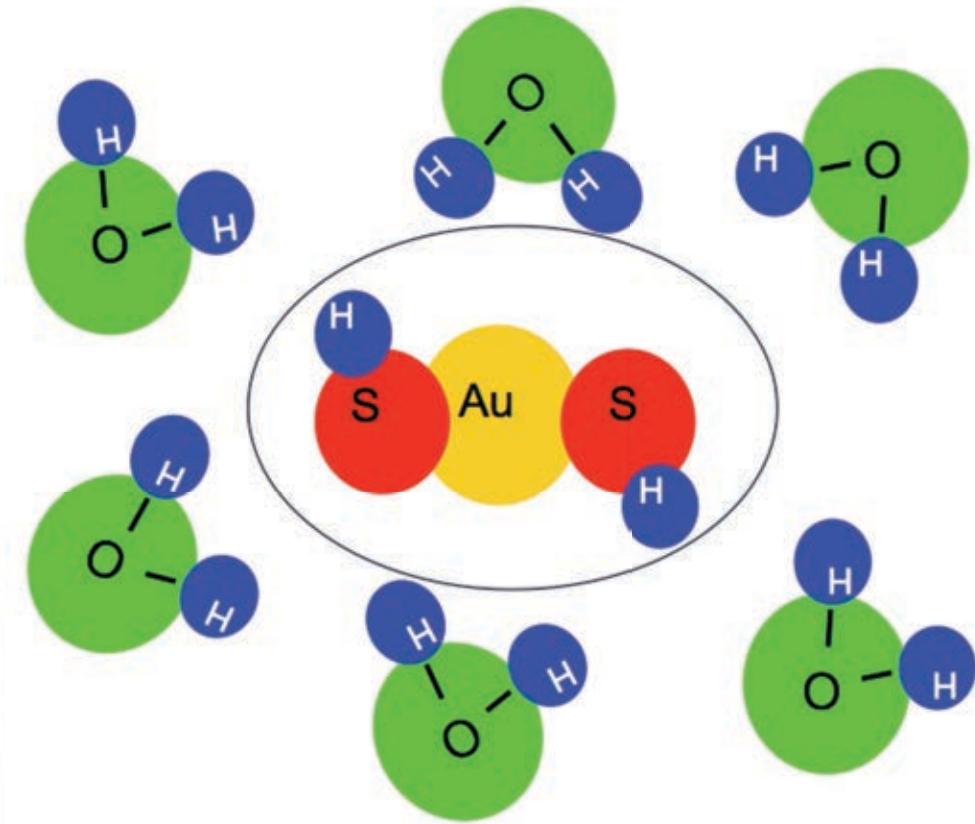
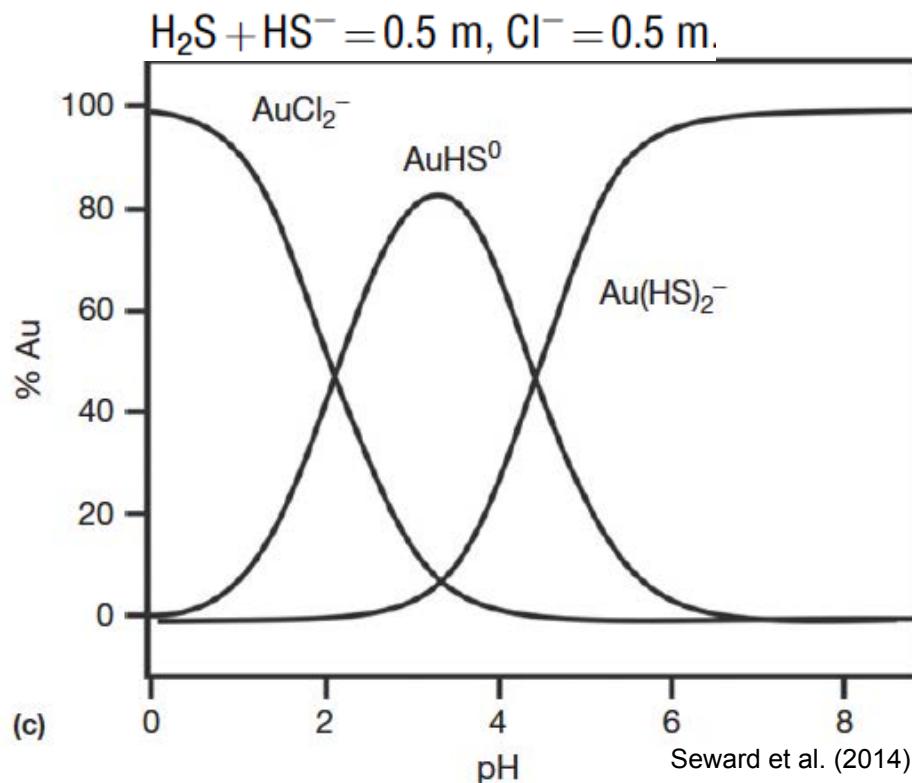
- Ion or molecule that binds to a central metal atom to form a coordination complex
- Complex ions dissolve easier into hydrothermal fluids
- Increase the “ore carrying potential” of the hydrothermal fluid



Prajno (2010)

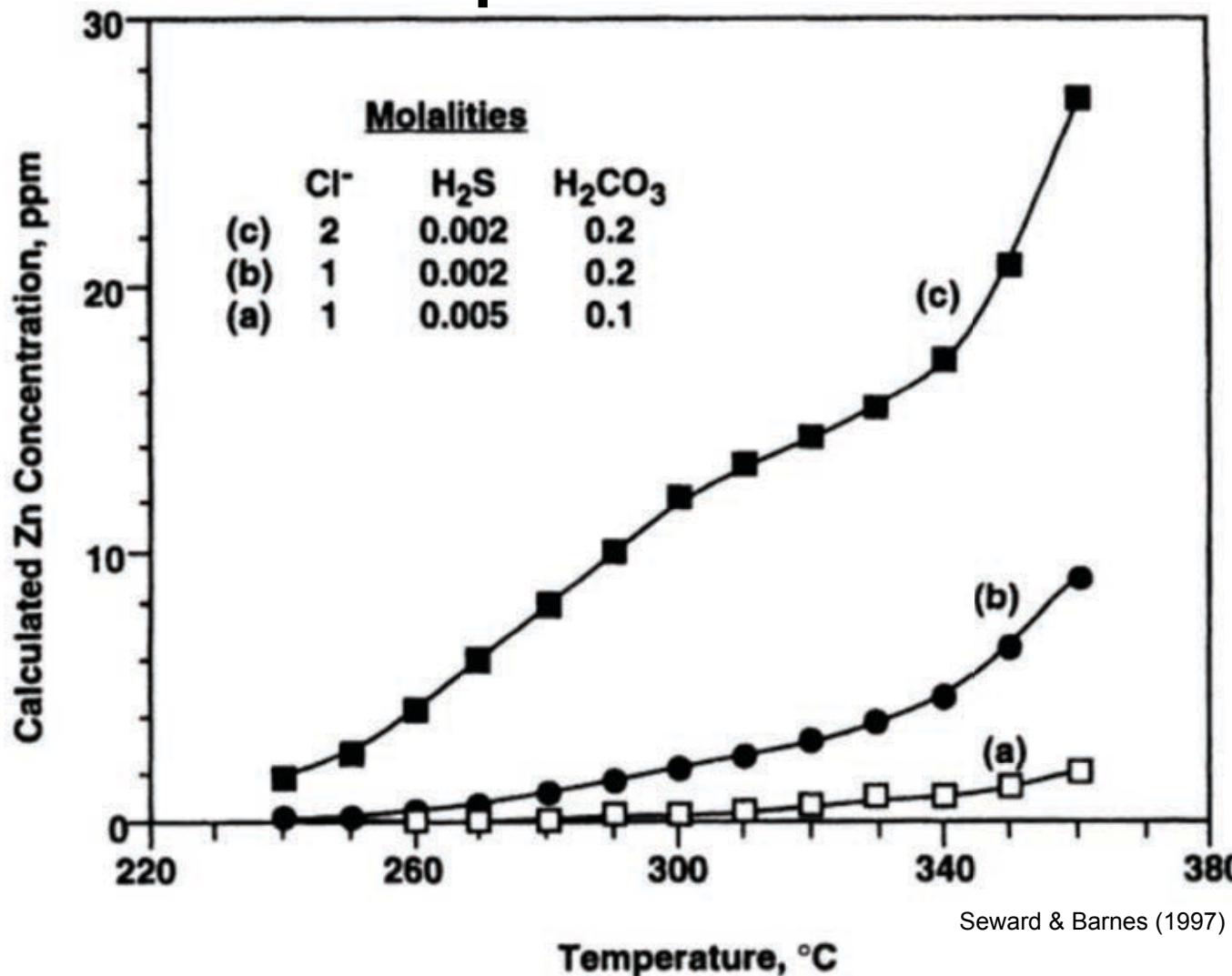
# Ligands

Au can be transported as soluble  $\text{Au}(\text{HS})_2^-$



From A.E. Williams-Jones

# Effect of complex ions on Zn solubility



**FIGURE 9.13** Calculated zinc concentration in solutions of the three compositions shown and saturated with calcite and sphalerite at equilibrium at each temperature (adapted from Gould, 1989).

TABLE 2. Representative ranges of ligand concentrations in natural hydrothermal fluids

| Ligand                    | Concentration range (moles/kg H <sub>2</sub> O) | Source                |
|---------------------------|-------------------------------------------------|-----------------------|
| $\Sigma\text{Cl}^-$       | <0.03 to >7                                     | Barnes (1979)         |
| $\Sigma\text{SO}_4^{2-}$  | $10^{-10}$ to 0.3                               | Barnes (1979)         |
| $\Sigma\text{S}^{2-}$     | $10^{-4}$ to 0.1                                | Barnes (1979)         |
| $\Sigma\text{NH}_3^{2-}$  | $10^{-3.9}$ to $10^{-1.5}$                      | Barnes (1979)         |
| $\Sigma\text{CO}_3$       | $10^{-3.4}$ to 1                                | Barnes (1979)         |
| $\Sigma\text{acetate}$    | 0 to 0.17                                       | Kharaka et al. (1998) |
| $\Sigma\text{propionate}$ | 0 to 0.059                                      | Kharaka et al. (1998) |
| $\Sigma\text{oxalate}$    | 0 to 0.005                                      | Kharaka et al. (1998) |
| $\Sigma\text{malonate}$   | 0 to 0.025                                      | Kharaka et al. (1998) |

Seward & Barnes (1997)

# Hard v. soft ligands

Hard = mostly ionic behavior

Soft = mostly covalent behavior

Metals with preferentially complex with ligands of similar ‘hardness’

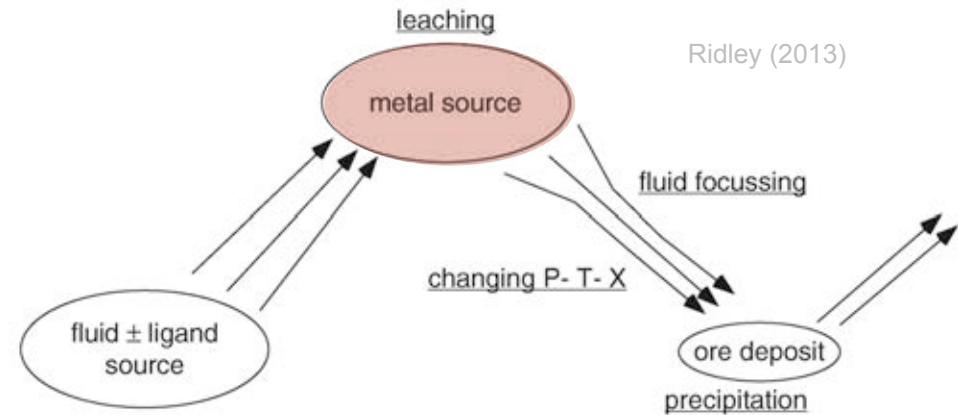
| Hard metals                                                                                                                                                                                 | Intermediate (borderline)                                                  | Soft metals                                                                          |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------|--------------------------------------------------------------------------------------|
| $H^+$ , $Li^+$ , $Na^+$ , $K^+$ , $Be^{2+}$ , $Ca^{2+}$ , $Mg^{2+}$ , $Sr^{2+}$ ,<br>$Al^{3+}$ , $Fe^{3+}$ , $Cr^{3+}$ , $La^{3+}$                                                          | Divalent transition metals,<br>including $Zn^{2+}$ , $Pb^{2+}$ , $Bi^{3+}$ | $Cu^+$ , $Ag^+$ , $Au^+$ , $Hg^{2+}$ ,<br>$Sn^{2+}$ , $Tl^+$ , $Ti^{3+}$ , $Au^{3+}$ |
| Hard ligands                                                                                                                                                                                |                                                                            | Soft ligands                                                                         |
| $F^-$ , $OH^-$ , $NH_3$ , $NO_3^-$ , <b><math>HCO_3^-</math></b> , <b><math>CO_3^{2-}</math></b> , $HSO_4^-$ ,<br><b><math>SO_4^{2-}</math></b> , $H_2PO_4^-$ , $HPO_4^{2-}$ , $H_3SiO_4^-$ | $Cl^-$ , $Br^-$                                                            | $I^-$ , <b><math>HS^-</math></b> , $S_2O_3^{2-}$ , $SCN^-$ ,<br>$CN^-$               |

Classification of metals and ligands with respect to hard–soft behaviour (as a measure of ionic vs. covalent behaviour). A metal will form a complex preferentially with a ligand of similar hardness (after Crerar *et al.*, 1985). Ligands in bold are typically the most abundant in geological environments, and are hence generally the most important complex formers.

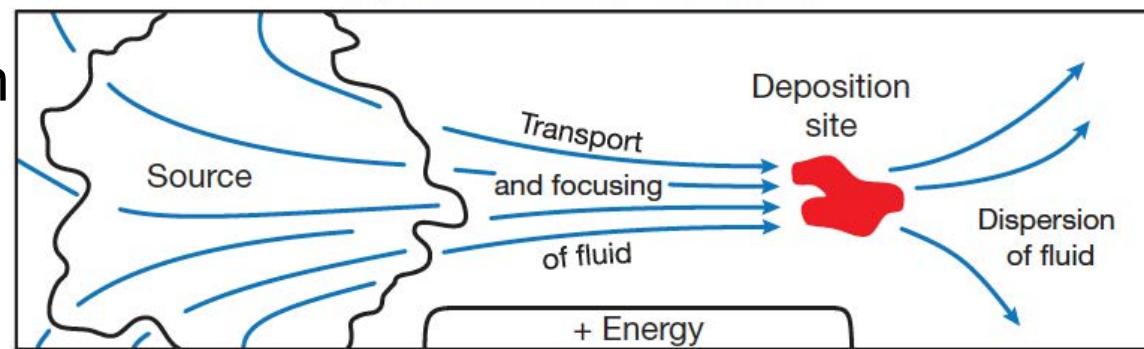
Ridley (2013)

# Source of metals

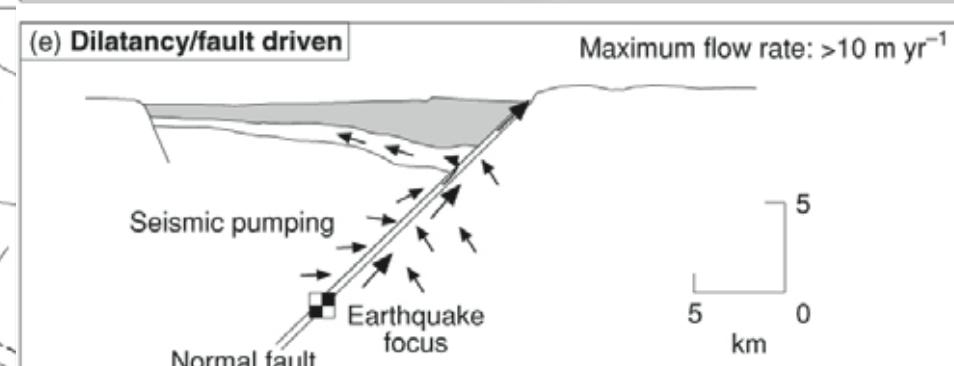
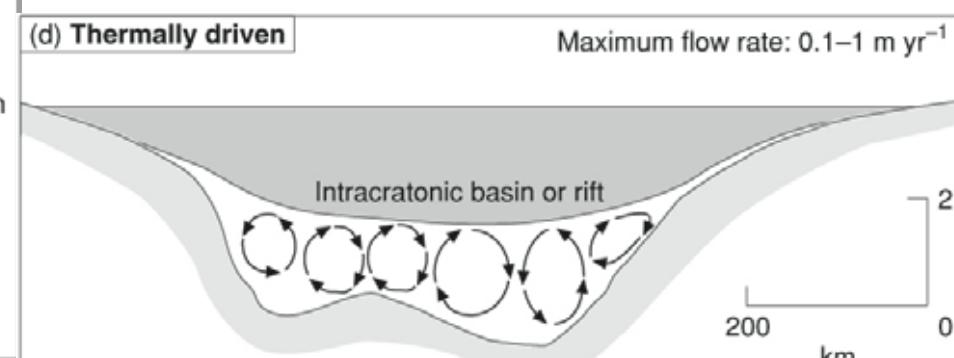
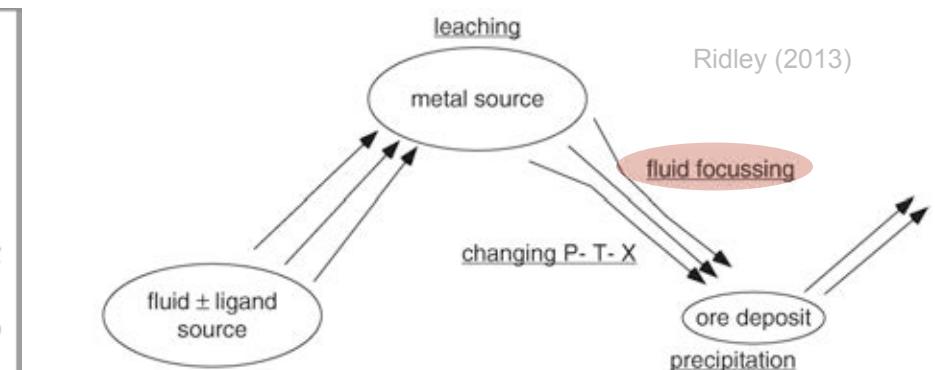
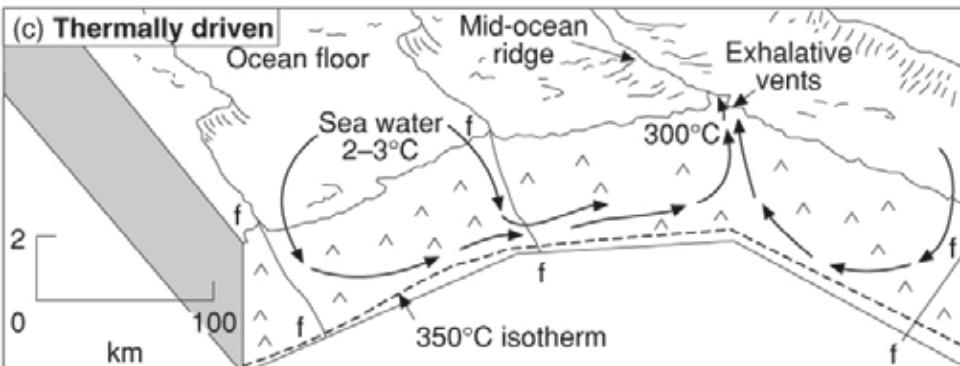
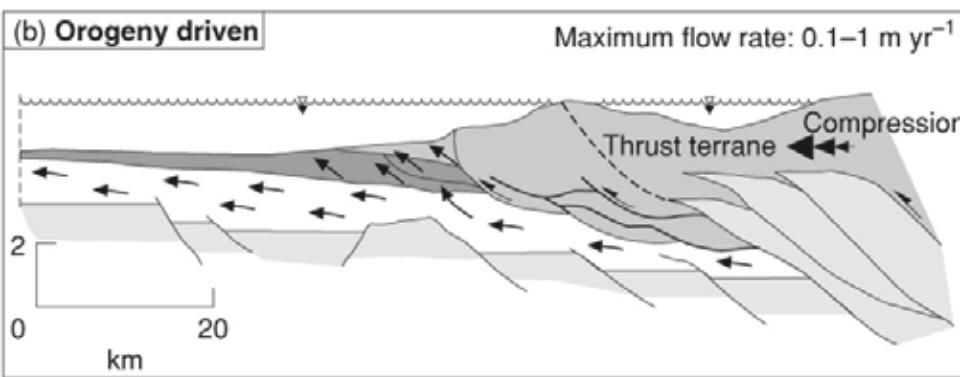
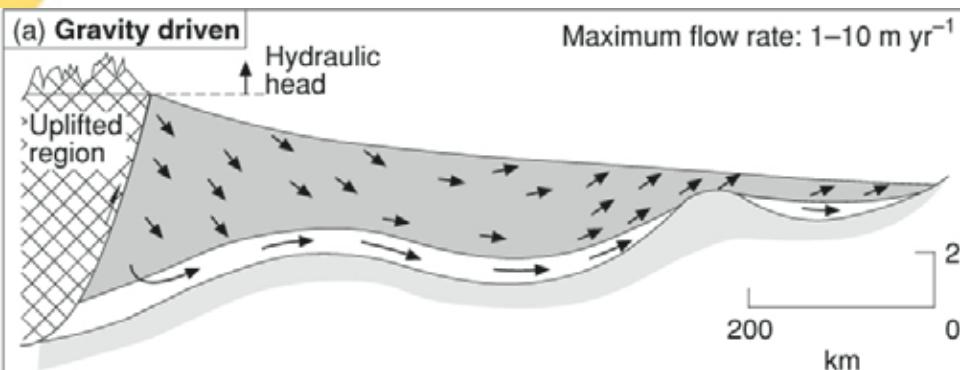
- Enrichment needs to be 100–10,000 times average crustal concentrations
- Therefore, metals need to be leached from a large volume of material, which may include:
  - Fluid source rocks and/or
  - Rock interacting with migrating fluid



Considering mass balance, a small amount of the crust affected by hydrothermal systems contains enough material to produce very large ore deposits

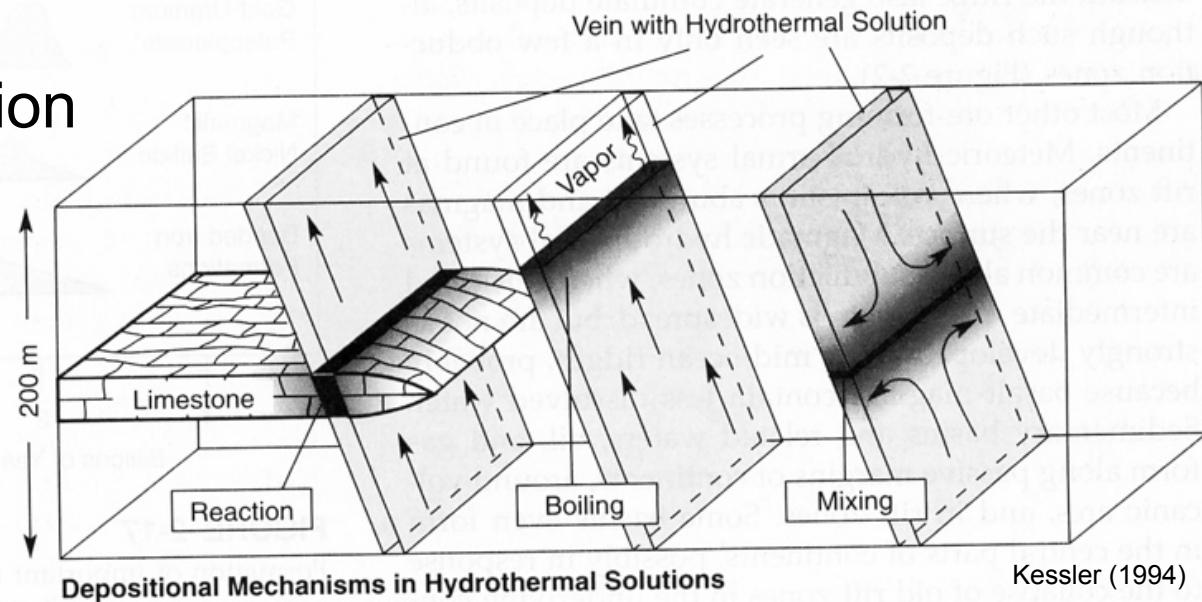
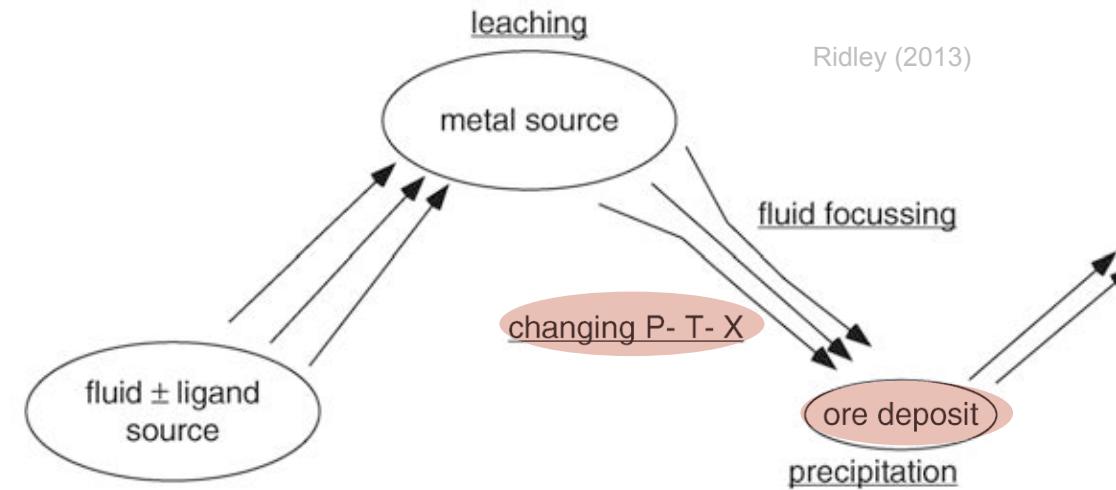


# Transport channels/conduits



# Metal precipitation controlled by:

1. Temperature
2. Pressure
3. Phase separation
4. Fluid mixing
5. Fluid–rock interaction
6. Adsorption
7. Biomineralization



# Simplified precipitation equations:

## Chloride precipitation (Barnes, 1979)



## Sulfide precipitation (Barnes, 1979)



Me = metal (with a +2 charge:  $\text{Me}^{2+}$ )

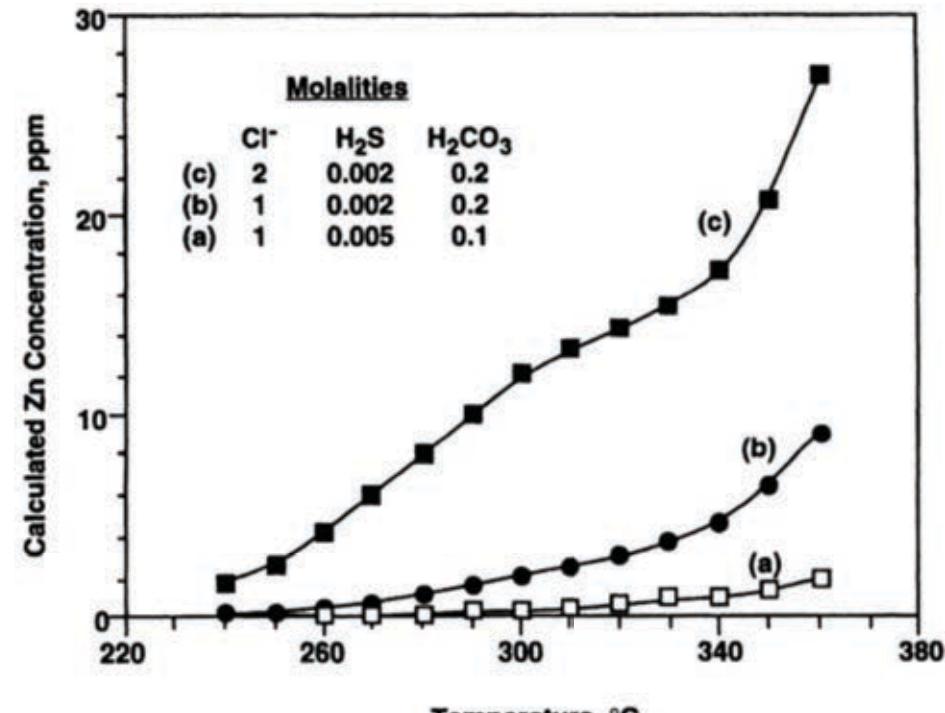
# 1. Temperature

## Temperature changes:

- Impact the formation of solubility products of oxides and sulfides
- Affect the stability of complex ions ( $\text{Cl}^-$  and  $\text{HS}^-$ ) transporting the metals

## Causes of temperature changes:

- Mixing can cooler water (meteoric/ocean)
- Adiabatic (no heat loss/gain) decompression
- Conductive heat loss to wall rocks



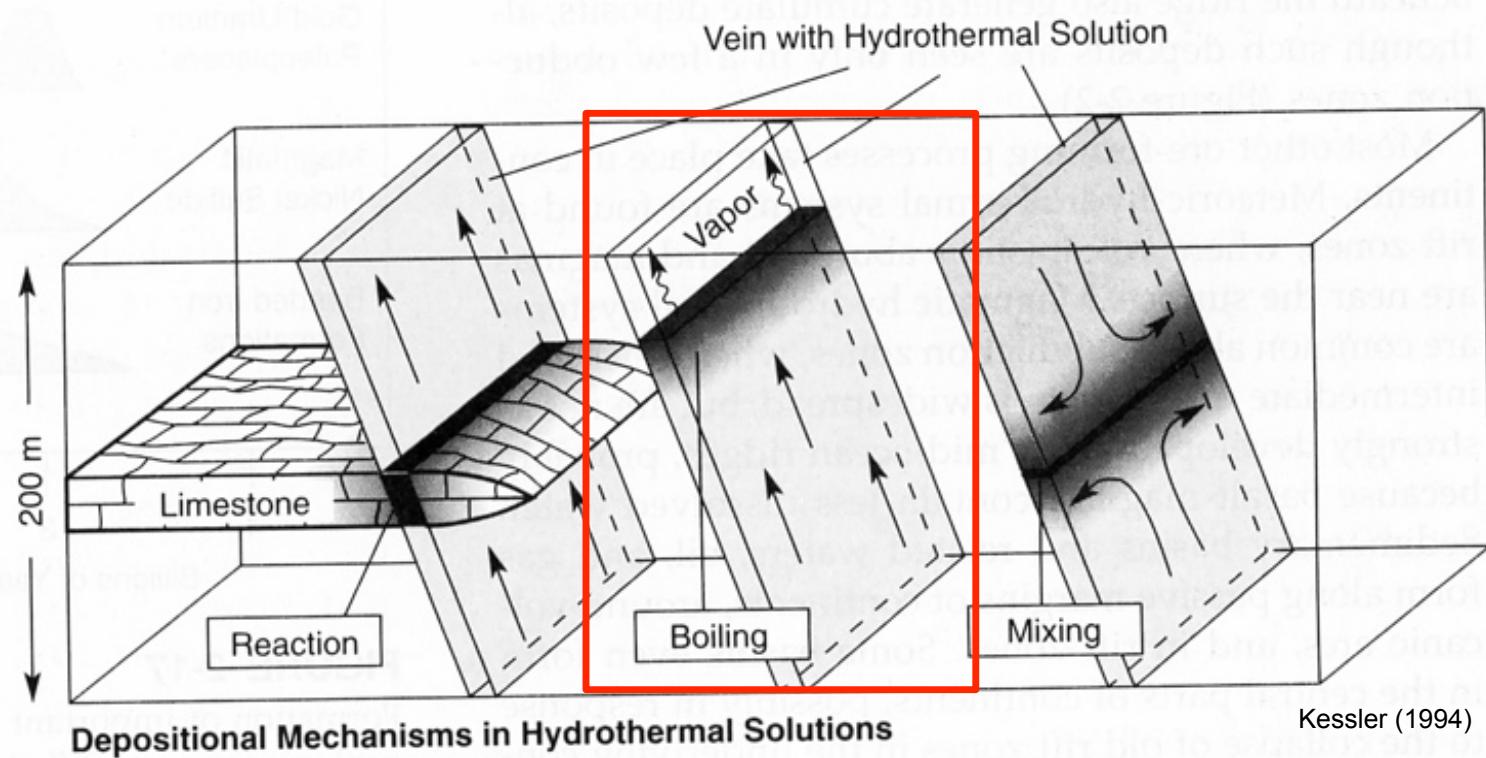
Seward & Barnes (1997)

## 2. Pressure

- Generally, large pressure drops ( $>1$  kbar) are necessary to change solubility
- Some solubilities of Fe–Pb–Zn increase with decreasing pressure
- So, pressure does not play a major role in ore deposition
- However,  $P$  drops can lead to boiling...

### 3. Boiling

- Transition from one to two physically separable phases (e.g. liquid → liquid + vapor)
- Vapor bubbles less dense than magma, so they rise and are enriched in volatile elements (Cl, F) and metals (Cu, Zn)



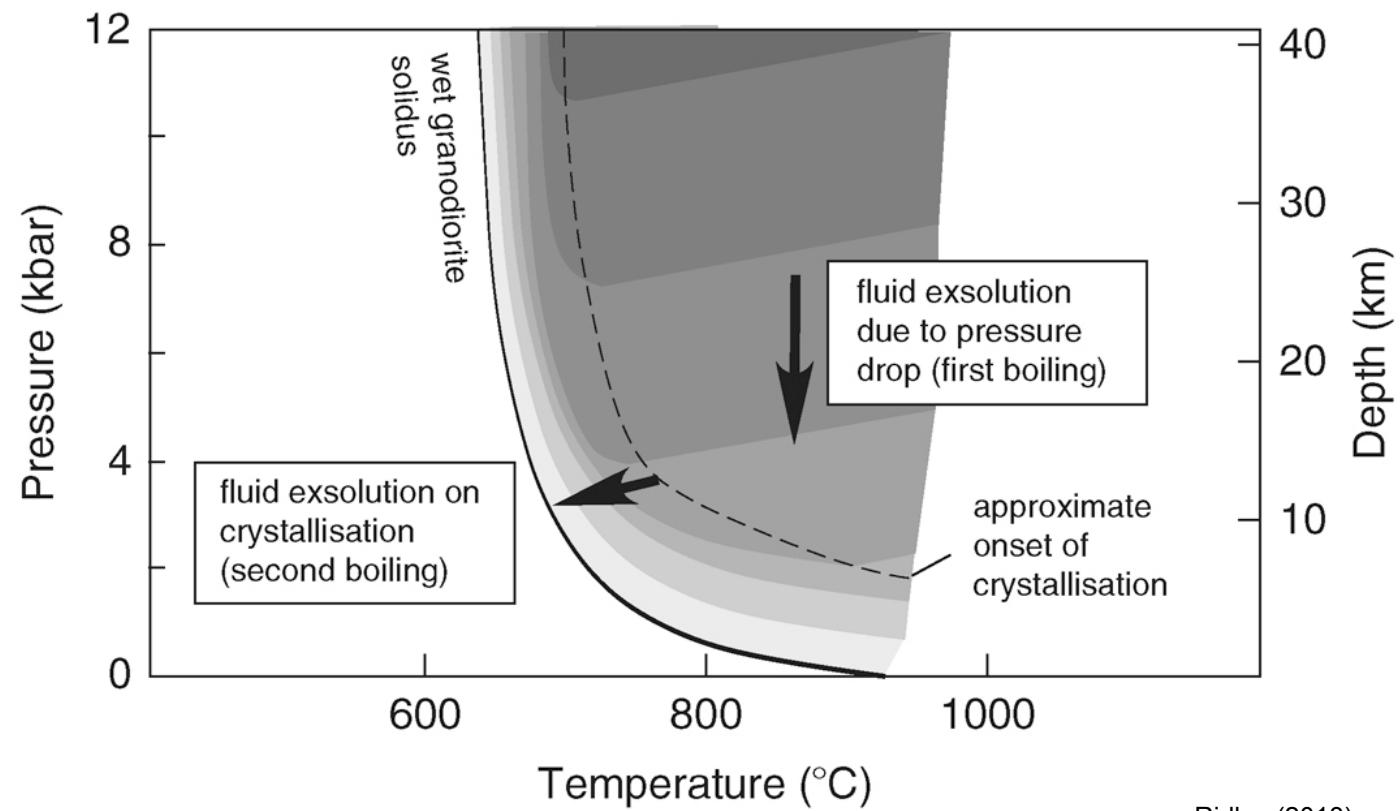
# 3. Boiling

## First boiling:

- Caused by a drop in pressure
- Generally associated with an ascending shallow magma

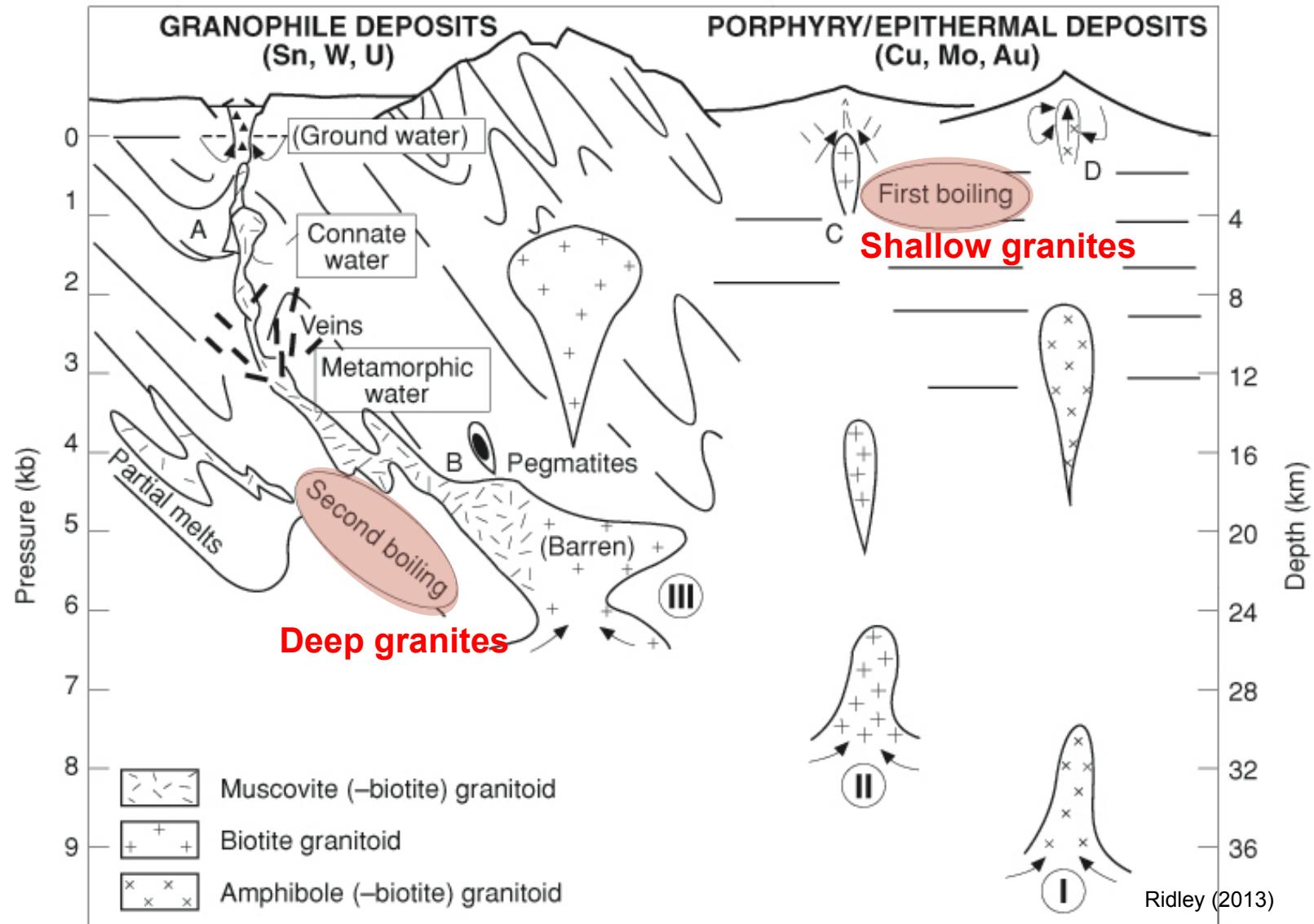
## Second boiling:

- Vapor saturation reached due to progressive crystallization of anhydrous minerals (deep magmas)
- Usually associated with a drop in  $T$  towards the end of magma crystallization



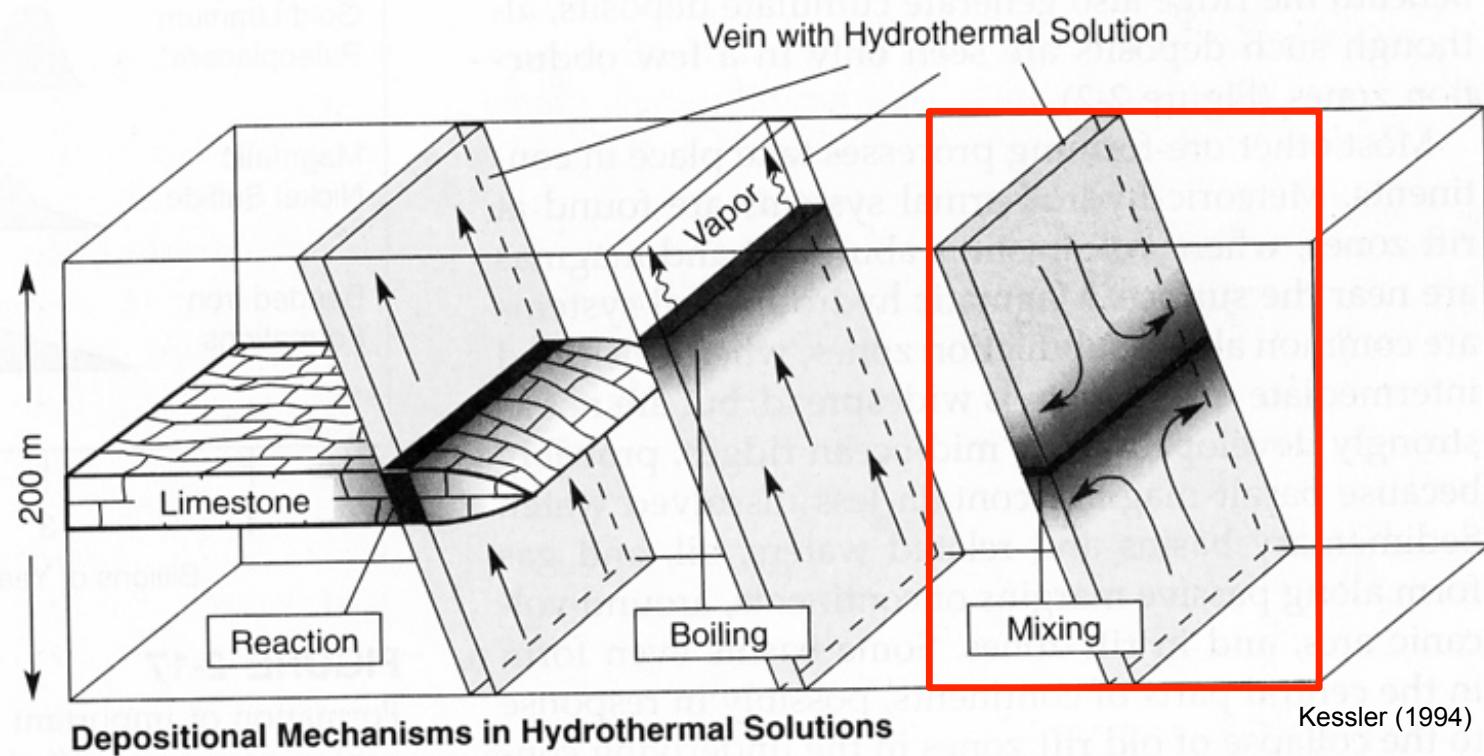
Ridley (2013)

### 3. Boiling



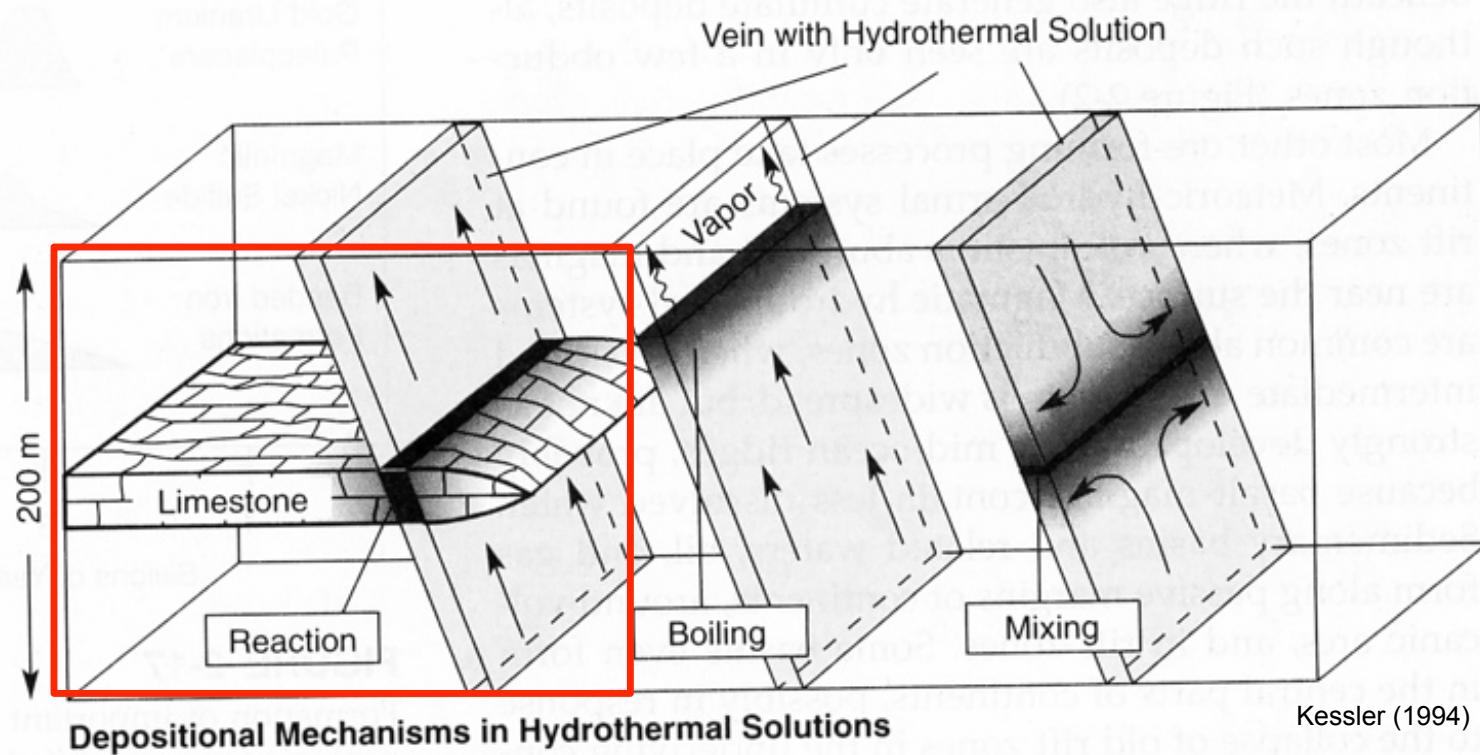
## 4. Fluid mixing

- $T$ : hot and cold fluids mix
- $X$ : fluids with different compositions mix
- $fO_2$ : a reducing fluid mixes with an oxidized one
- $pH$ : an acidic fluid mixes with a neutral fluid



## 5. Fluid–rock interactions

1. Hydrogen exchange can modify the pH of the fluid (e.g. dissolution of carbonates and hydrolysis of feldspars)
2. Addition of components from wall rock pyrite ( $\text{H}_2\text{S}$  or  $\text{S}^{2-}$ )
3. Sulfate reduction which changes the oxygen fugacity of the fluid



## 5. Fluid–rock interactions

Acidic fluid with Zn<sup>2+</sup>-chloride complexes reacts with limestone (calcite):

$$\text{pH} = -\log_{10}(a_{\text{H}^+})$$



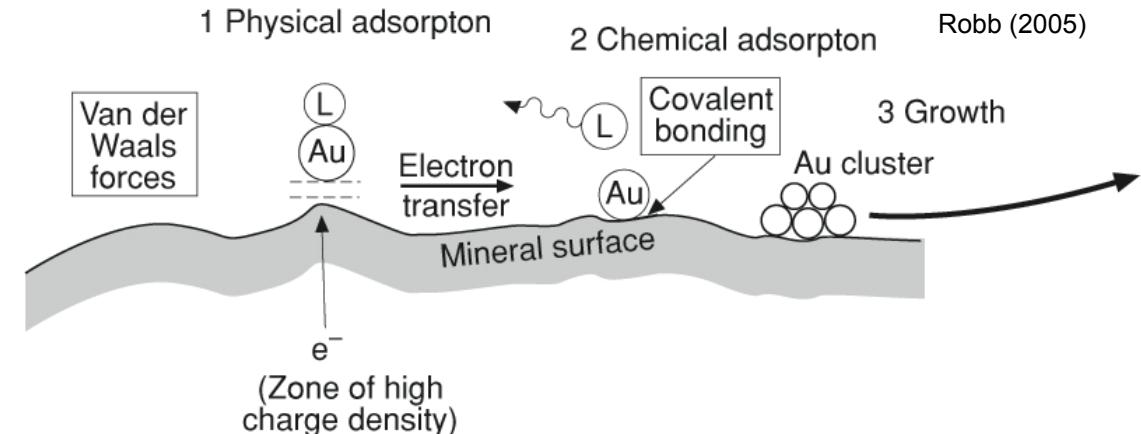
- Calcite dissolves (empty space), hydrogen ions consumed, pH increases



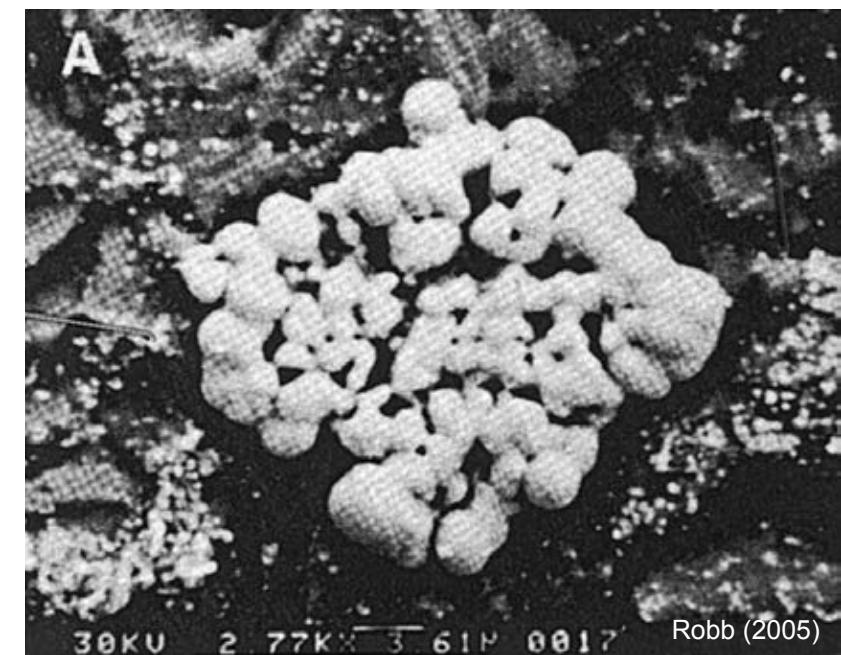
- system wants to produce more H<sup>+</sup> to compensate, which induces sphalerite precipitation

## 6. Adsorption

*Adherence of an ion in solution to the surface of a solid (e.g. mineral) with which it is in contact*



- Mineral surfaces will contain some charge imbalances
- Amount of imbalance usually relates to pH
- Ions with opposite charge to surface with ‘stick’ to surface, even if fluid is undersaturated



Gold particles on surface of a sulfide mineral

Robb (2005)

## 7. Biomineralization

Microrganisms (e.g. bacteria) either actively concentrate elements during growth or minerals form as a consequence of microbial activity

Important for redox sensitive elements (e.g. Fe, Mn)

Bacteria catalyze the oxidation of soluble metals to insoluble oxides.

# Chloride precipitation (Me = metal) (Barnes, 1979)



[Use Le Chatelier's principle]

- Increase H<sub>2</sub>S through (1) sulfate reduction, (2) reaction with organic compounds, (3) mixing with sulfide solutions
- Increase pH by (1) reaction with carbonates or feldspars, (2) boiling off acid gases
- Reduce Cl<sup>-</sup> content: (1) dilution by circulating meteoric waters

# Sulfide precipitation (Me = metal) (Barnes, 1979)



[Use Le Chatelier's principle]

- Decrease H<sub>2</sub>S through boiling H<sub>2</sub>S<sub>(aq)</sub> → H<sub>2</sub>S<sub>(g)</sub>
- Oxidize\*\*: H<sub>2</sub>S<sub>(aq)</sub> + 2O<sub>2</sub><sub>(aq)</sub> → H<sup>+</sup> + HSO<sub>4</sub><sup>2-</sup>

\*\*Note that this is the opposite direction to chlorides:



Therefore, oxidation is not the dominant cause of precipitation in most base and ferrous metal sulfides because these are transported as Cl<sup>-</sup> complexes. But, it can be important in Au deposits.



# How do we know the composition of ore fluids?

**Fluid inclusion:** microscopic bubbles of liquid, gas ± solid

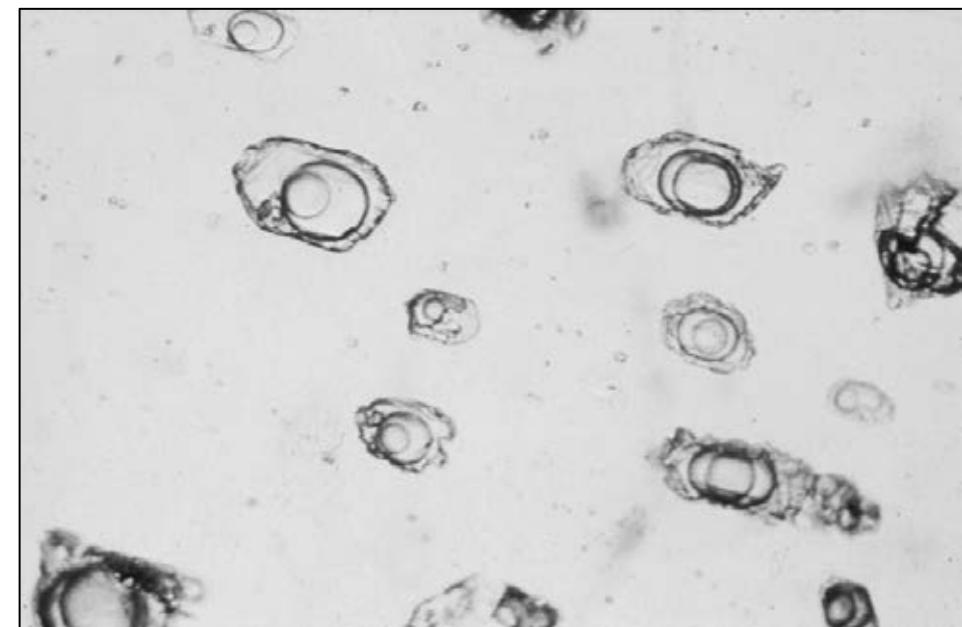
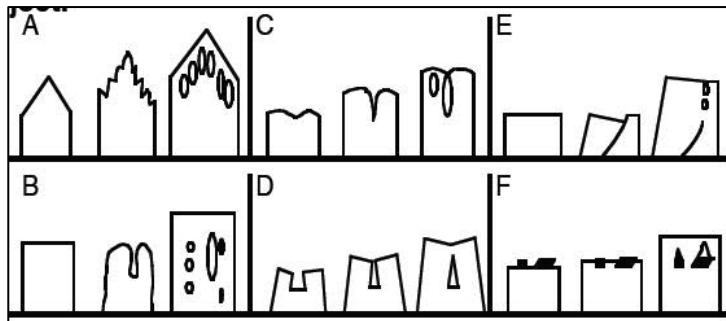
Gas/liquids: H<sub>2</sub>O and CO<sub>2</sub>

Solids: usually salts (NaCl, KCl)

Found in ore forming minerals (most commonly observed in quartz)

**Primary:** Trapped during growth of the host mineral

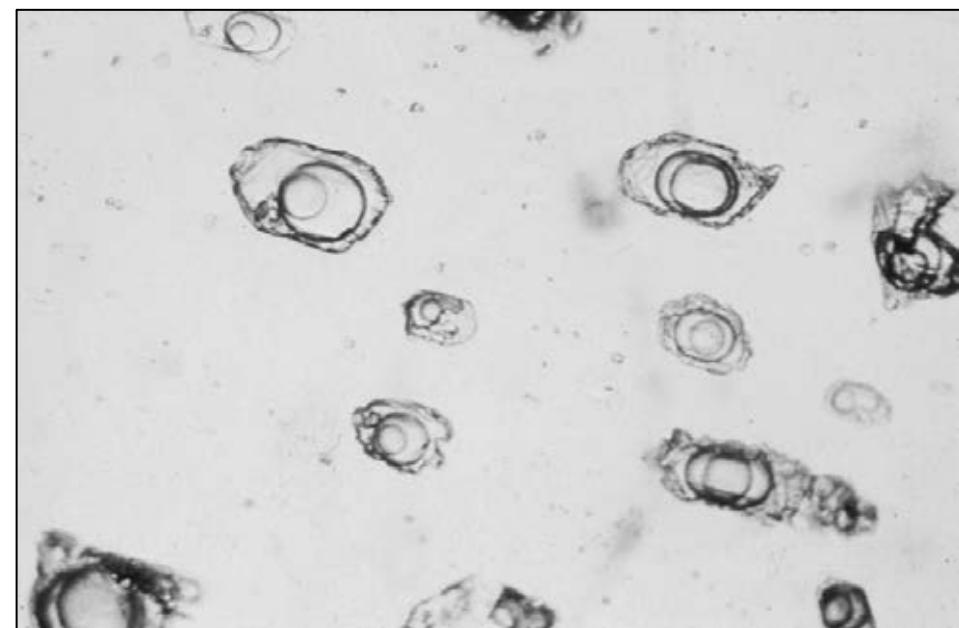
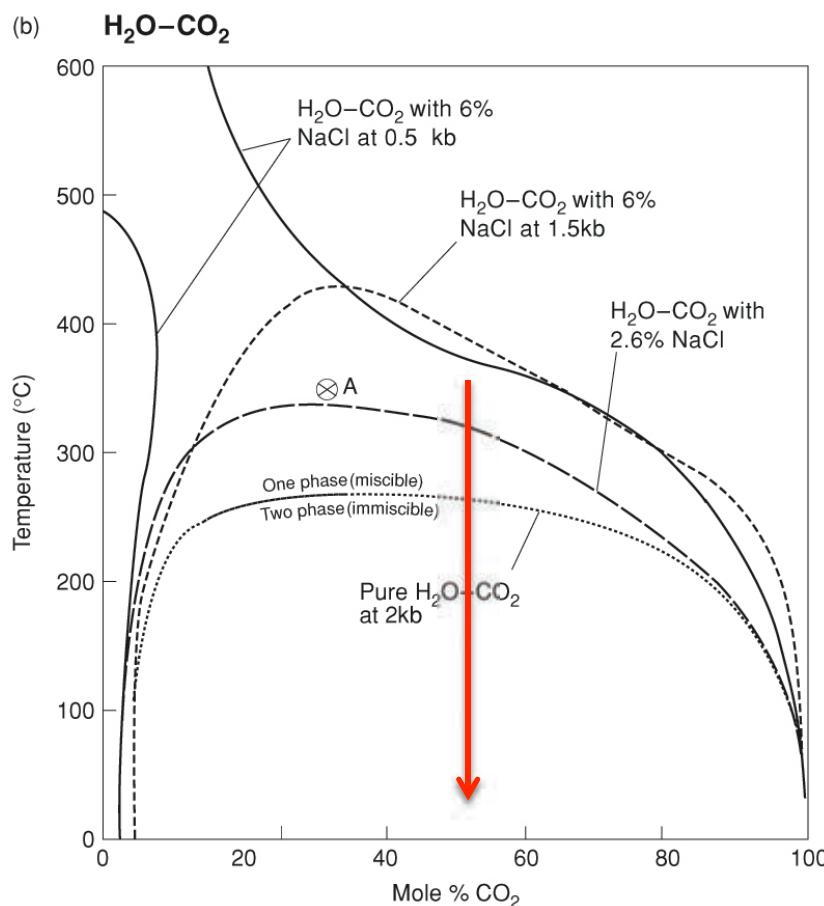
**Secondary:** Developed after crystallization of host



Photomicrograph showing H<sub>2</sub>O–CO<sub>2</sub> fluid inclusions. During entrapment, the fluid was one phase but has now separated into CO<sub>2</sub> (inner bubble) and H<sub>2</sub>O (outer fluid). Each inclusion is ~10–30 µm in length.

# How do we know the composition of ore fluids?

These inclusions were trapped as one miscible phase. During cooling, separated into two immiscible phases



Photomicrograph showing  $\text{H}_2\text{O}-\text{CO}_2$  fluid inclusions. During entrapment, the fluid was one phase but has now separated into  $\text{CO}_2$  (inner bubble) and  $\text{H}_2\text{O}$  (outer fluid). Each inclusion is  $\sim 10\text{--}30 \mu\text{m}$  in length.

# Measuring fluid inclusions

If we assume the inclusion was trapped and has not been modified, we can measure the  $T$  of formation and obtain compositional information:

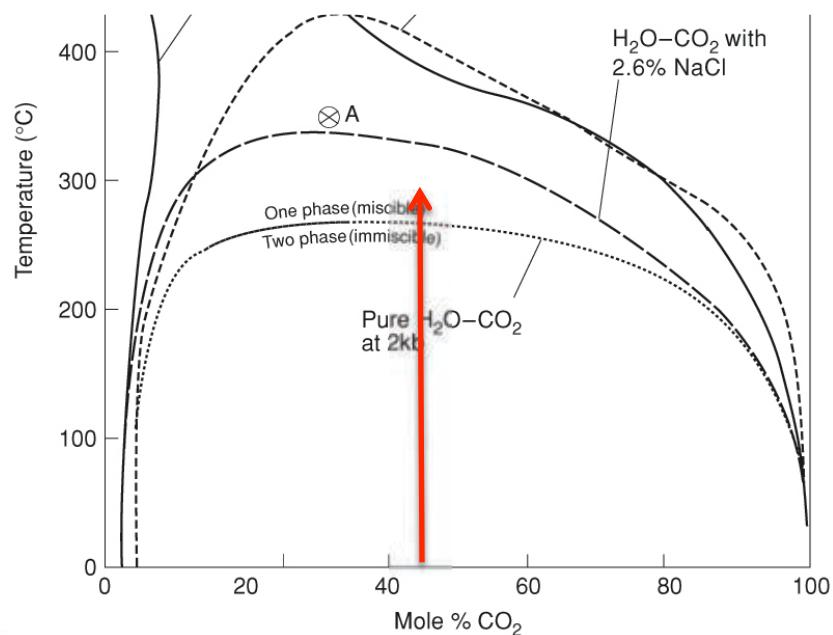
Two methods:

## (1) Heating:

- Heat up stage until no bubbles left (minimum  $T$  of entrapment)

## (2) Freezing:

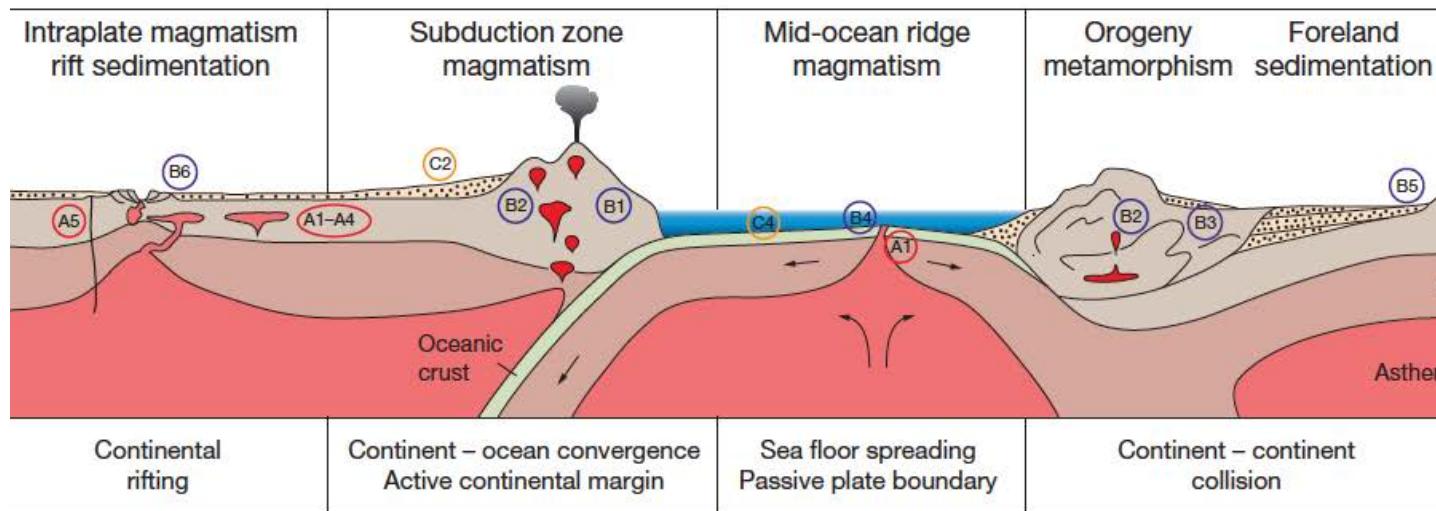
- Cool stage until a solid develops from the fluid(s) (provides information of salt content – think of fresh vs salt water freezing)



# Hydrothermal ore deposit models

## Four associations

- (1) Magmatic
- (2) Oceanic
- (3) Orogenic
- (4) Sedimentary basins



### A: Magmatic ore deposits

- A1. Chromitites as (ultra-)mafic cumulates in layered intrusions and ophiolites
- A2. V-magnetite in mafic intrusions (V, Ti)
- A3. Pegmatites (Li, Cs, Be, Nb, Ta)
- A4. Ni- und PGE-sulfide deposits in mafic intrusions und flood basalts
- A5. Carbonatite (REE) and kimberlite (diamond) deposits

### B: Hydrothermal ore deposits

- B1. Porphyry Cu (Mo, Au) and epithermal Au, Ag (Hg, ...) deposits
- B2. Sn-W veins and greisens in granites
- B3. Orogenic ('metamorphogenic') Au-quartz vein deposits
- B4. Volcanogenic massive sulfides (Cu, Zn)
- B5. Sediment-hosted (MVT, 'sedex') Pb, Zn, Cd, Cu, Co deposits

### C: Surface-related deposits

- C1. Residual bauxite
- C2. Alluvium
- C3. Beaches
- C4. Marine on land
- B6. Sandstone-hosted U (V, F, Mo, Au)

## Genetic model terminology:

**Epithermal:** hydrothermal ore formed at low T (50–200°C) and shallow depths (~0–1.5 km)

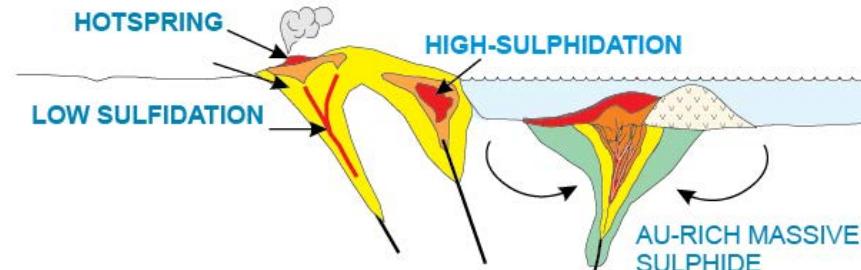
**Mesothermal:** hydrothermal ore formed at intermediate T (200–300°C) and intermediate depths (~1.5–4.5 km)

**Hypothermal:** hydrothermal ore formed at high T (400–600°C) and great depths (>4.5 km)  
**(a.k.a. intrusion related)**

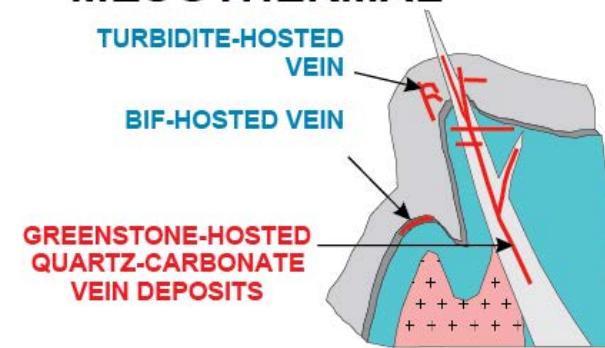
depth ↓

### Au–Ag hydrothermal deposits

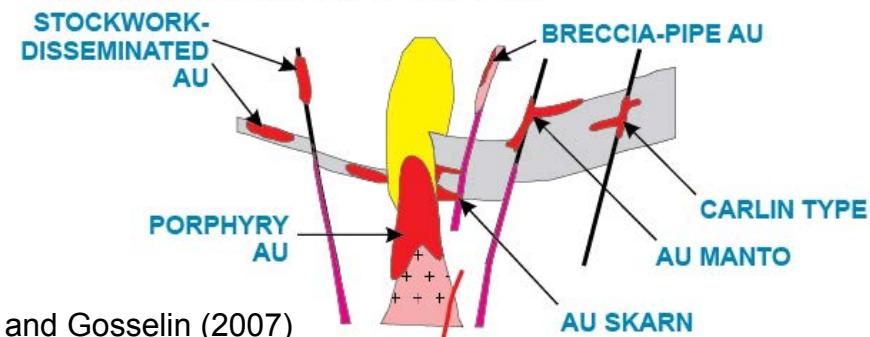
#### EPITHERMAL



#### MESOTHERMAL



#### INTRUSION-RELATED



Modified from Dubé and Gosselin (2007)

## Take home messages

**Chemical properties of water make it an important hydrothermal fluid in ore formation**

**A hydrothermal ore deposit system consists of:**

1. Fluids (seawater, meteoric, connate, metamorphic, magmatic)
2. Ligands (mainly  $\text{Cl}^-$  and  $\text{HS}^-$ )
3. Source of metals
4. Transport conduits and driving force
5. Trap

**Metal precipitation mechanisms include:**

- (1) Temperature, (2) Pressure, (3) Phase separation – boiling, (4) Fluid mixing, (5) Fluid–rock interaction, (6) Adsorption and (7) Biomineralization

**Fluid inclusions** provide information on the composition of mineralizing fluids and the temperature of formation

Hydrothermal deposits are often classified into **epithermal, mesothermal and hypothermal types**