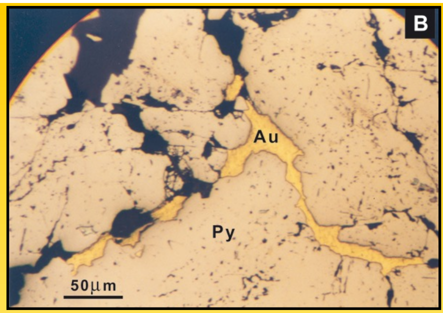
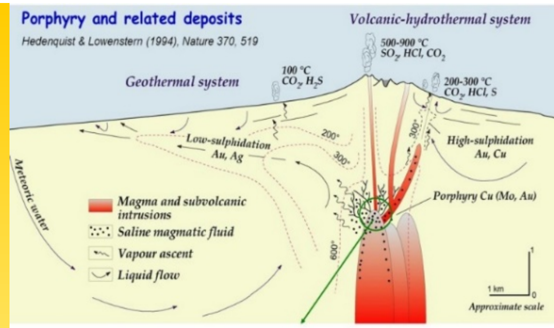
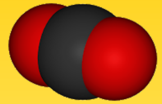






Comment le soufre et le carbon forment-ils les gisements hydrothermaux des métaux?

Maria Kokh[1], Anastassia Borisova[1], Pascal Gisquet[1], Jean-Louis Hazemann[2], Eric Lahera[2], William Delnet[2], Olivier Proux[2], Denis Testemale[2], Volker Haigis[3,4], Romain Jonchière[4,5], Ari Seitsonen[3], Guillaume Ferlat[4], Rodolphe Vuilleumier[3], Marco Saitta[4], Marie-Christine Boiron[5], Jean Dubessy[5], Nikolai Akinfiev[6], Stéfano Salvi[1], Didier Béziat [1], and Gleb S. Pokrovski[1]

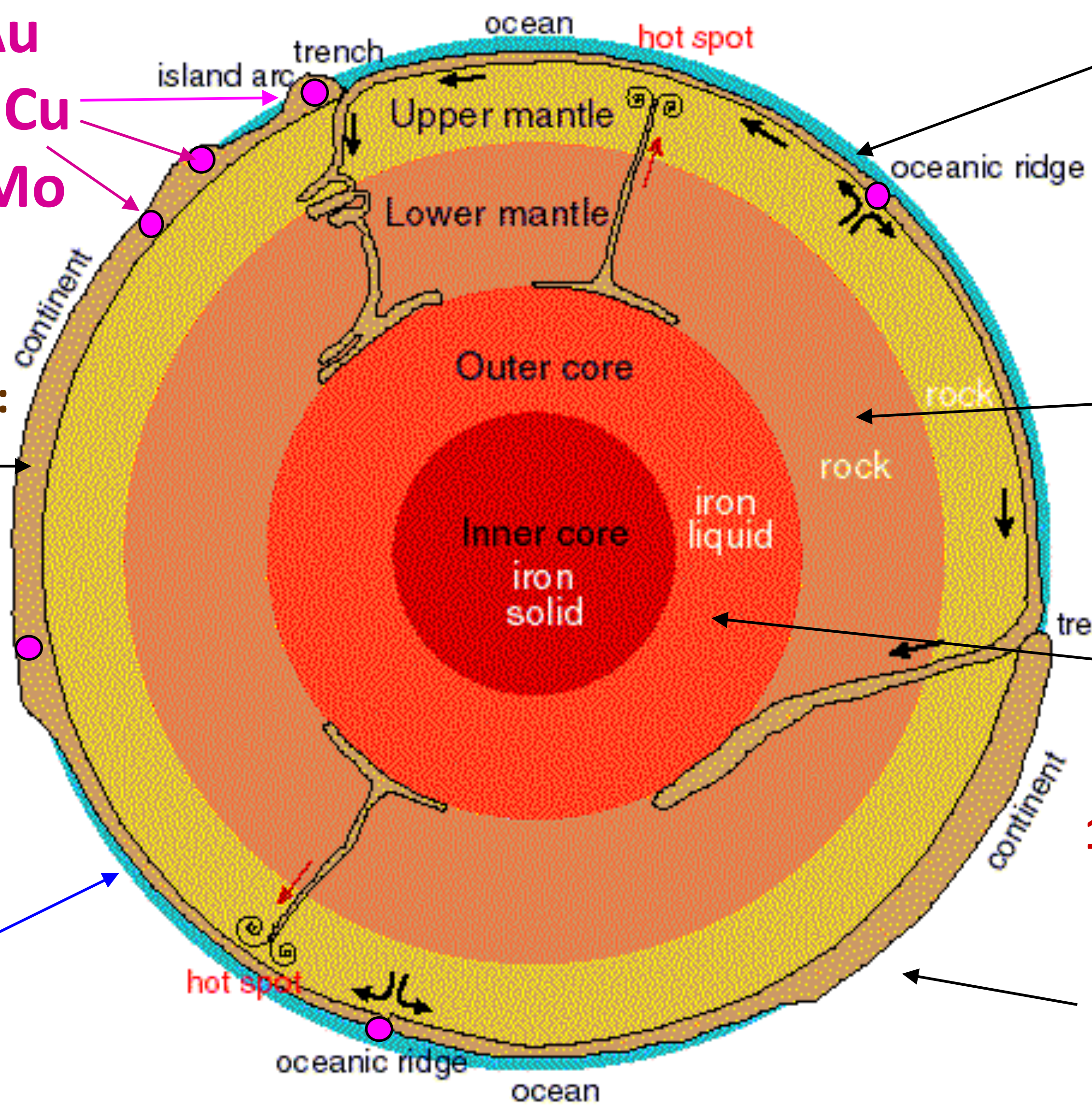
(1) GET, Toulouse; (2) INEEL-ESRF, Grenoble; (3) ENS-UPMC, Paris; (4) IMPMC, Paris; (5) GeoRessources, Nancy, (6) IGEM, Moscow

ANR project SOUMET; UPS project CO_2MET; INSU-CESSUR projects ORPY and ASORPY

Sulfur and metals on Earth

Ore deposits:
100,000s ppm S
1-10 ppm Au
10,000 ppm Cu
1,000 ppm Mo

Oceanic crust:
1,000 ppm S
1.5 ppb Au
45 ppm Cu
1 ppm Mo



Mantle:
200 ppm S,
1 ppb Au
40 ppm Cu
1 ppm Mo

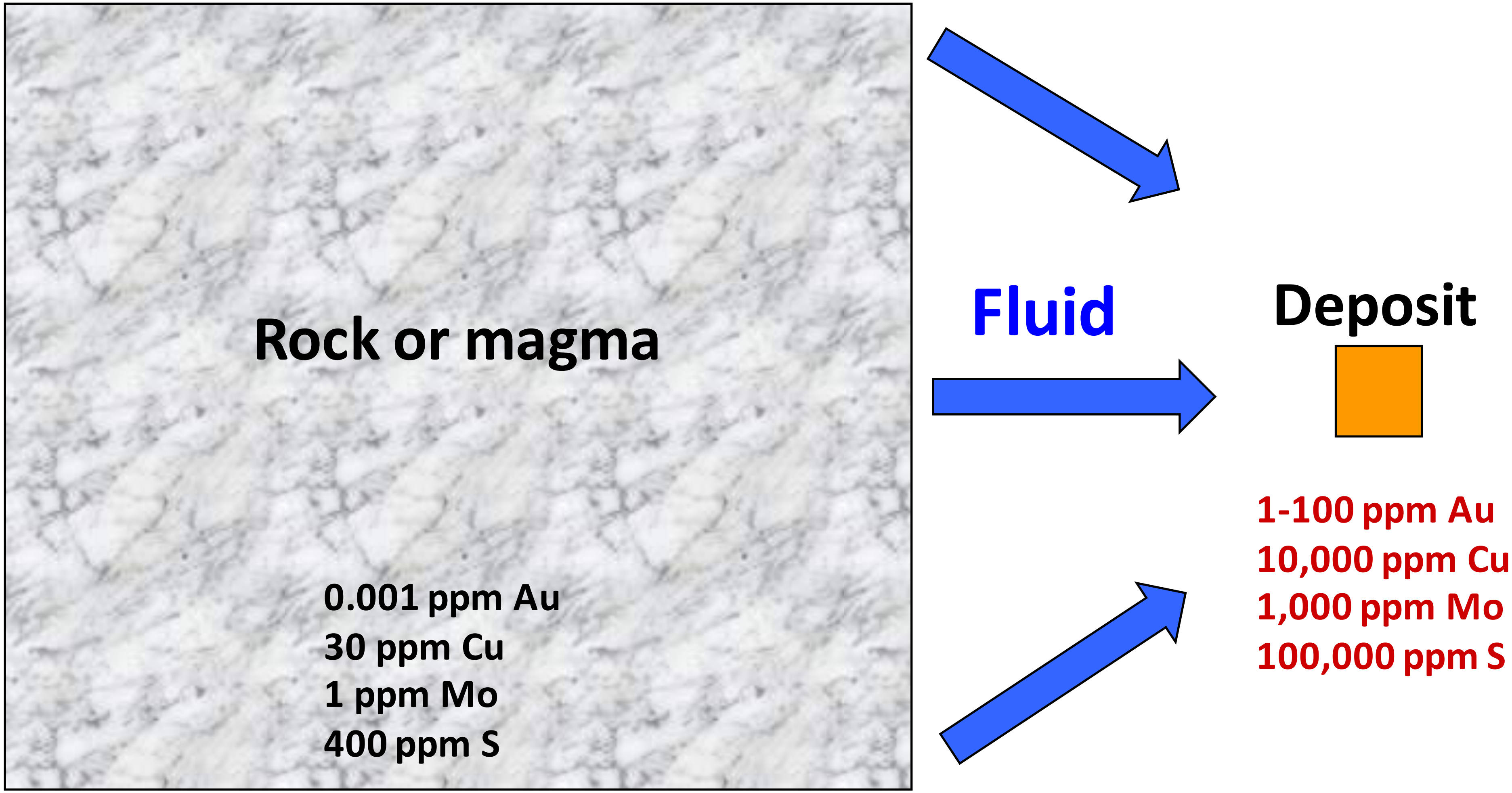
Continental crust:
400 ppm S
1.3 ppb Au
30 ppm Cu
0.8 ppm Mo

Core:
≤ 20,000 ppm S (?)
100s ppb Au (?)
1000s ppm Cu & Mo (?)

Sea water:
900 ppm S
10^{-5} ppb Au
0.15 ppb Cu
10 ppb Mo

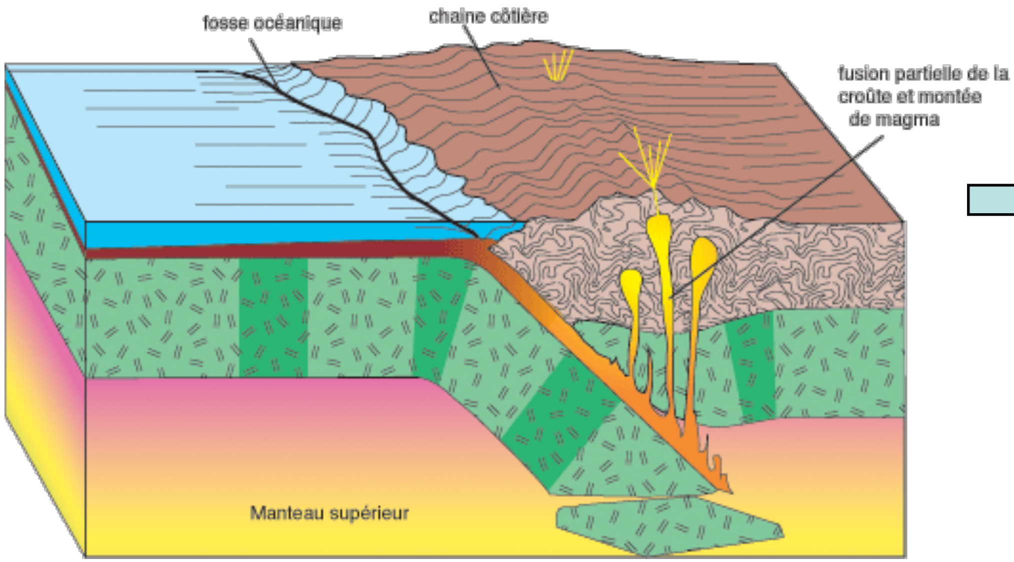
Atmosphere:
< 0.1 ppb S
< 10^{-6} ppb Au
< 10^{-3} ppb Cu
< 10^{-4} ppb Mo

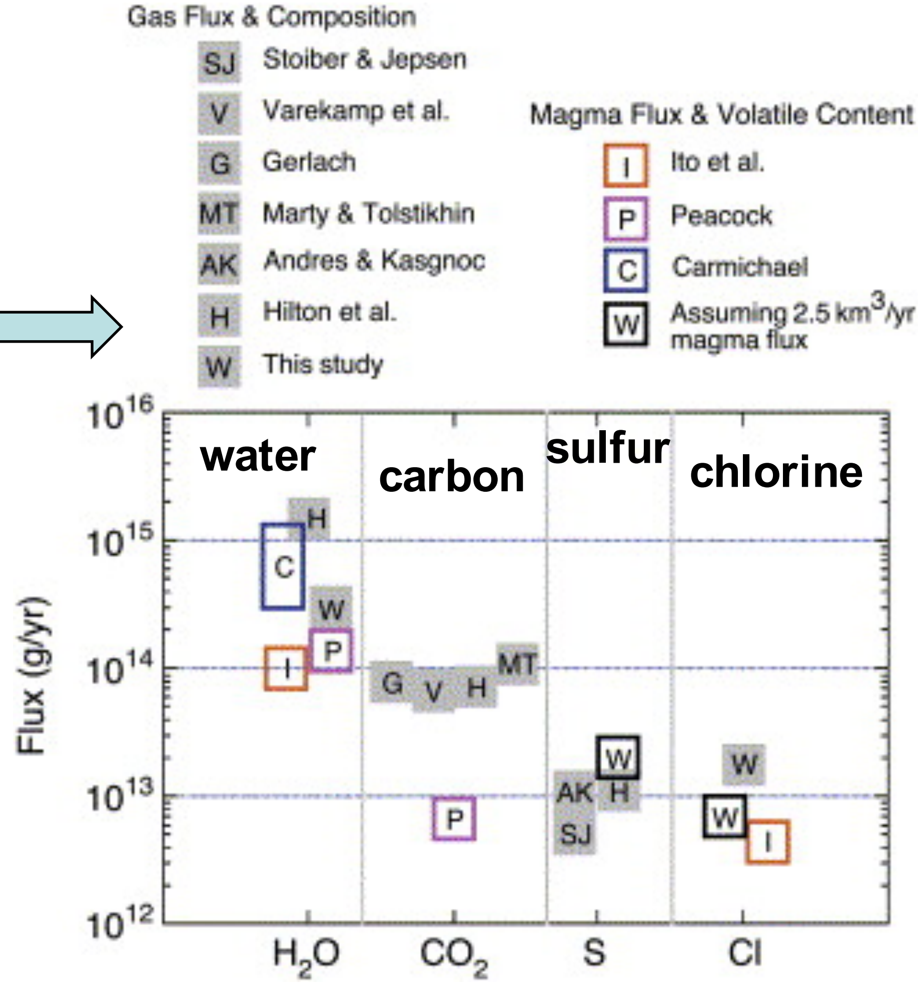
How to form an economic metal deposit ?



- ❖ Fluids enabling mobilization, transport and precipitation
- ❖ Solubility and chemical speciation of metals and volatiles

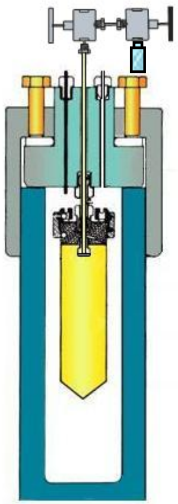
Fluxes of volatiles through the Earth's crust



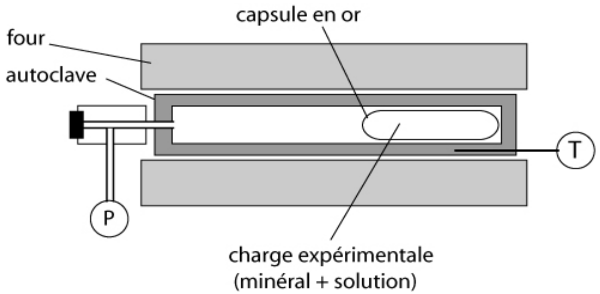


Wallace (2005) J. Volcanol. Geotherm. Res. 40, 217–240

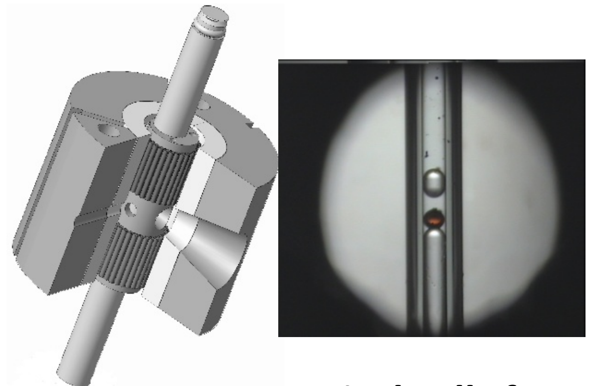
Tracking the deep and hot fluids



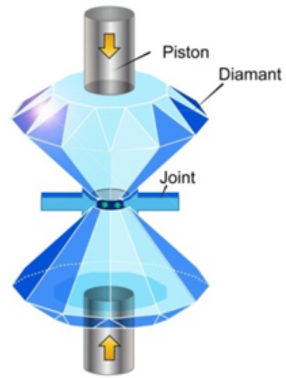
Hydrothermal reactors



Synthetic fluid inclusions

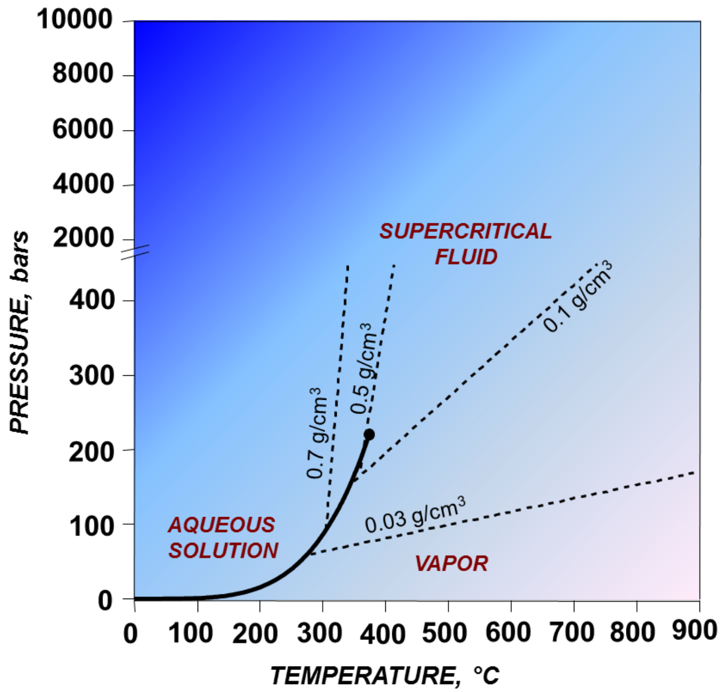


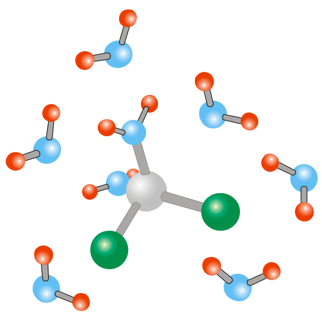
Low-pressure optical cells for Raman, IR, UV, XAS spectroscopy



High-pressure diamond-anvil cells

Trace element analyses (ICP-MS, ICP-AES)





Molecular silulations

Synchrotron techniques

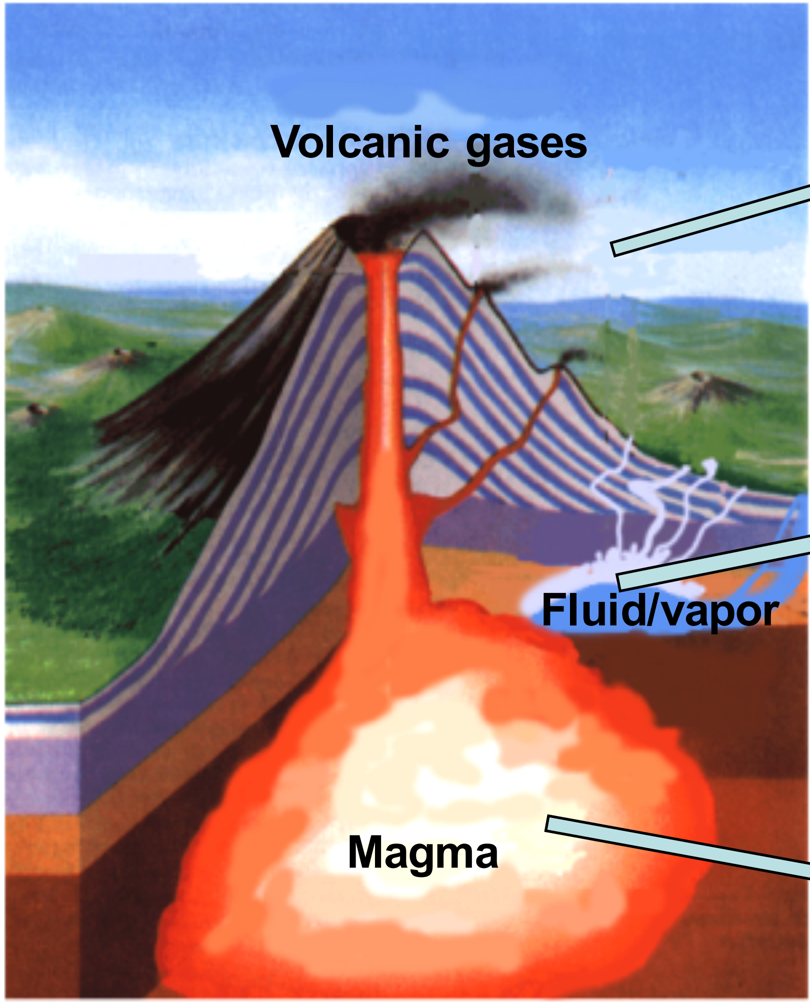
$$G_{i,TP} = G^{0}_{i,TP} + 2.3026RT \log a_i$$

$$G^{0}_{Born} = {}_{i} \cdot \frac{1}{\ {}_{mix}} \quad \frac{1}{\ {}_{water}}$$

Thermodynamic models

Sulfur

Known sulfur speciation in fluids, vapors and melts

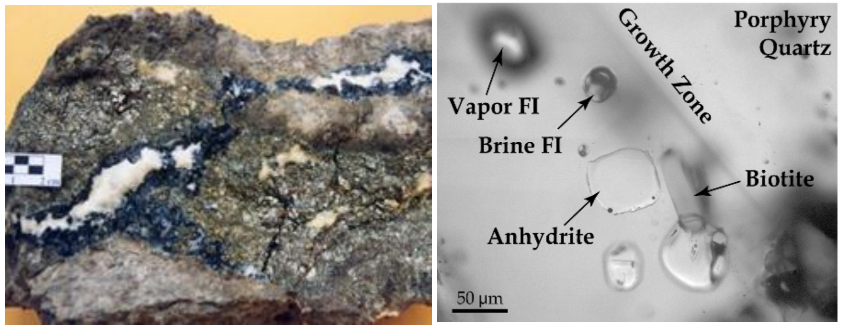


S^0, H_2S, SO_2, H_2SO_4

Volcanic fumaroles

H_2S, SO_4^{2-}
FeS_2, ZnS,
$CuFeS_2$
$CaSO_4$, $BaSO_4$

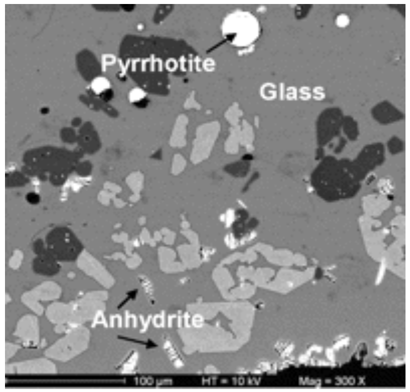
Hydrothermal minerals and fluid inclusions

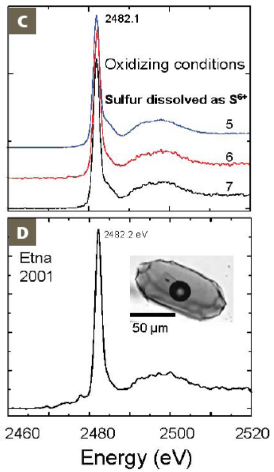


Kouzmanov et al., 2009, Miner. Deposita 44, 611

$S^{(2-)}$, $S^{(6+)}$
FeS, $CaSO_4$

Magmatic minerals and silicate glasses





Metrich & Mandeville, 2010, Elements 6, 81

→ Most data come from observations or analyses of final products at ambient conditions

Known metal speciation in hydrothermal fluids

(H_2O-NaCl-KCl-HCl-H_2S-SO_4)

As	$As(OH)_3^0$
Sb	$Sb(OH)_3^0$
B	$B(OH)_3^0$
Mo	$H_2MoO_4^0$, $HMoO_4^-$, MoO_4^{2-}, $(Na,K)HMoO_4^0$
W	$H_2WO_4^0$, HWO_4^-, WO_4^{2-}, $(Na,K)HWO_4^0$
Fe	$FeCl_2^0$, $FeCl_4^{2-}$
Zn	$ZnCl_2^0$, $ZnCl_3^-$, $ZnCl_4^{2-}$
Ag	$AgCl_2^-$
Cu	$CuCl_2^-$
Au	$AuHS^0$, $Au(HS)_2^-$ ($\pm$ $AuCl_2^-$)
Pt	$Pt(HS)_2^0$ ($\pm$ $PtCl_3^-$...)

Known sulfur control on metal solubility

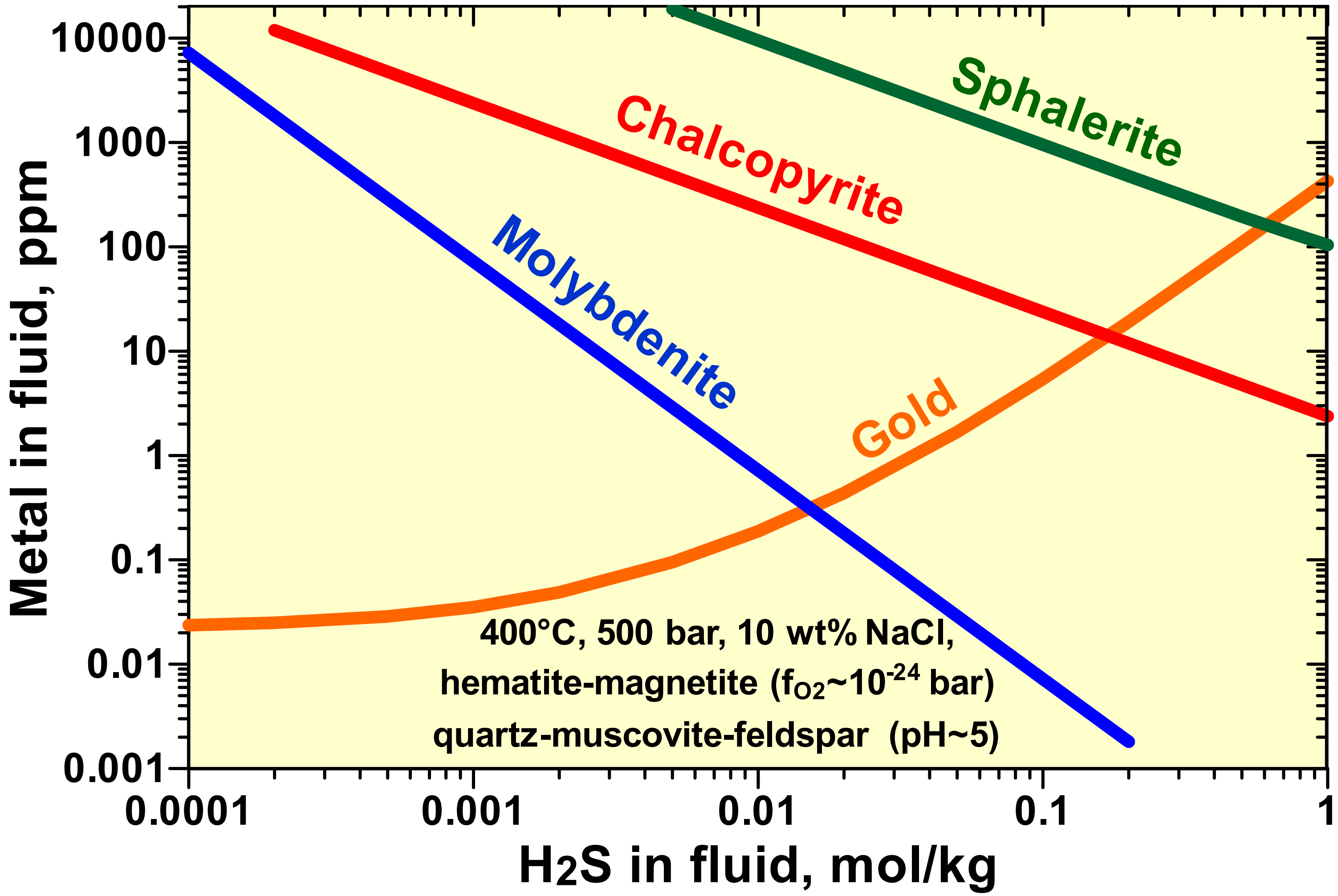
$CuCl_2^- + FeCl_2 + 2H_2S = CuFeS_2(s) + 0.5H_2 + 3H^+ + 4Cl^-$

$ZnCl_2^0 + H_2S = ZnS(s) + 2H^+ + 2Cl^-$

$HMoO_4^- + 2H_2S + H^+ + H_2 = MoS_2(s) + H_2O$

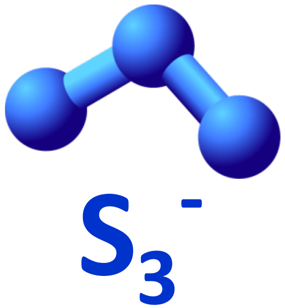
$Au(HS)_2^- + 0.5H_2 + H^+ = Au(s) + 2H_2S$

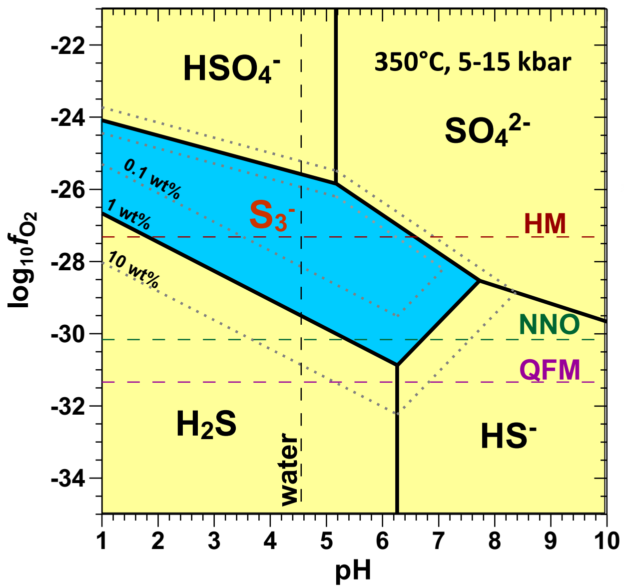
$AuHS^0 + 0.5H_2 = Au(s) + H_2S$

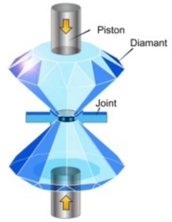


→ Amount and speciation of sulfur is a key control on the transport of most metals

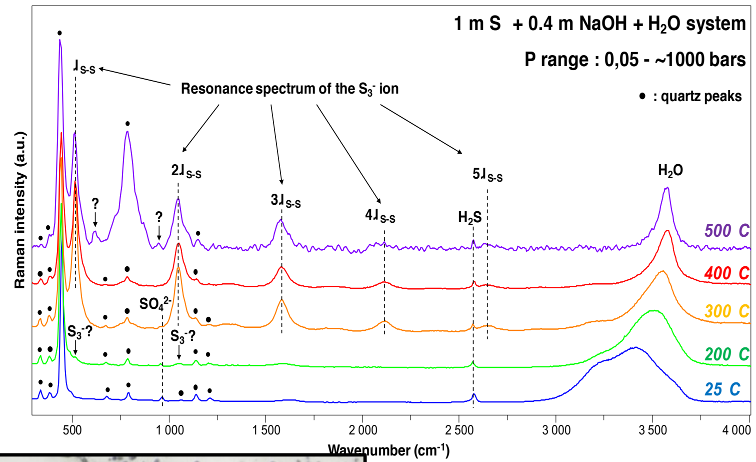
New sulfur species in hydrothermal fluids revealed by in-situ Raman spectroscopy

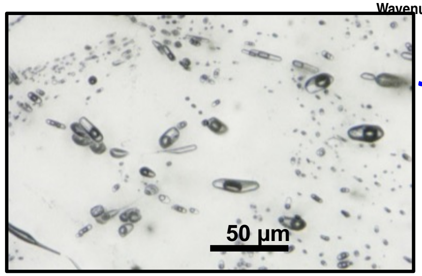




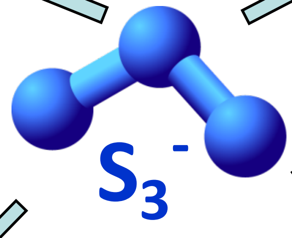


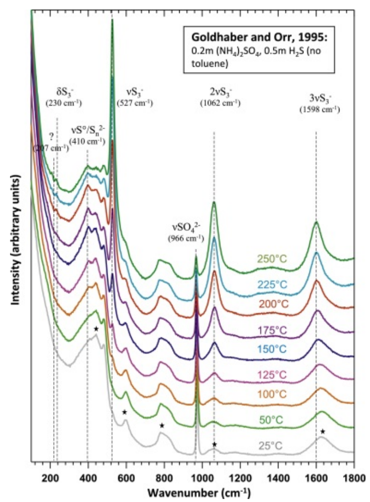
Pokrovski & Dubrovinsky (2011)
Science 331, 1052



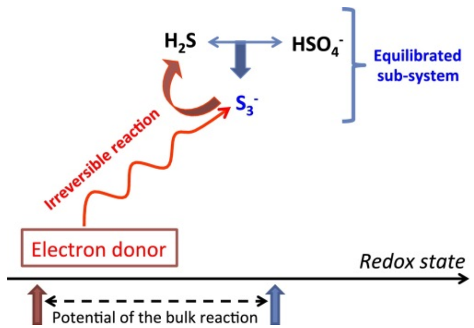


Jacquemet et al. (2014)
Amer. Miner. 99, 1109



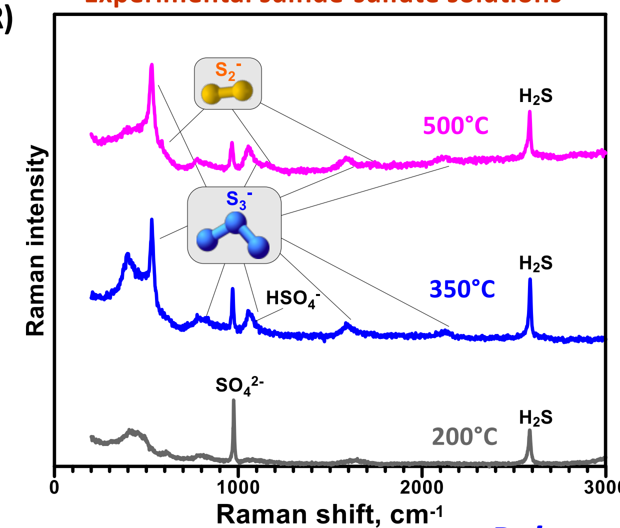


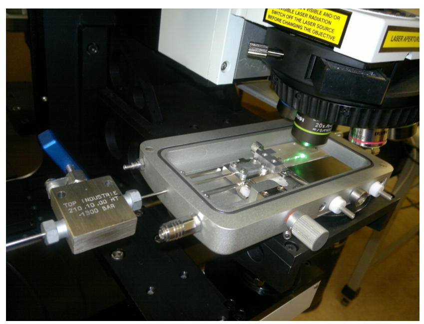
Thermochemical sulfate reduction (TSR)



Truche et al. (2014)
Earth Planet. Sci. Lett. 396, 190

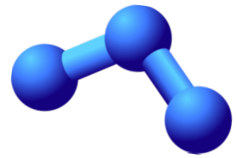
Experimental sulfide-sulfate solutions

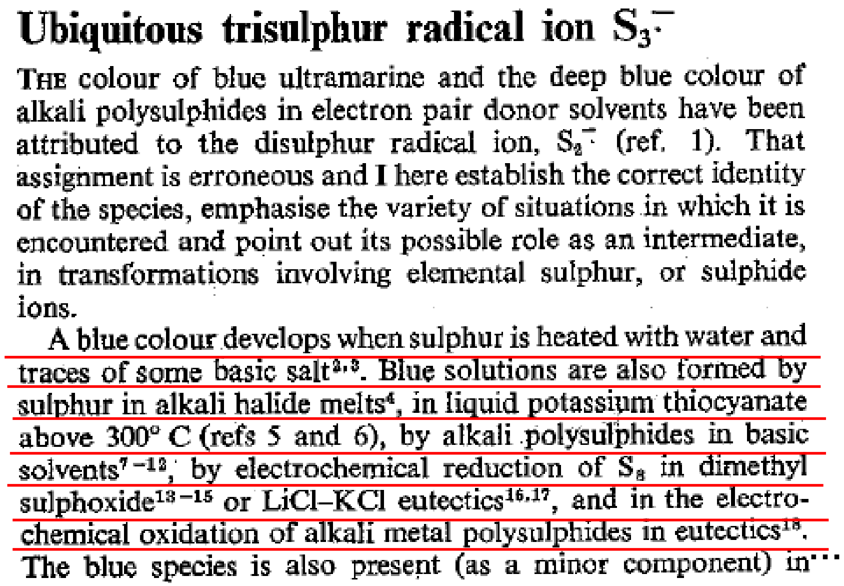




Pokrovski & Dubessy (2015)
Earth Planet. Sci. Lett. 411, 298

A very old sulfur chemical form



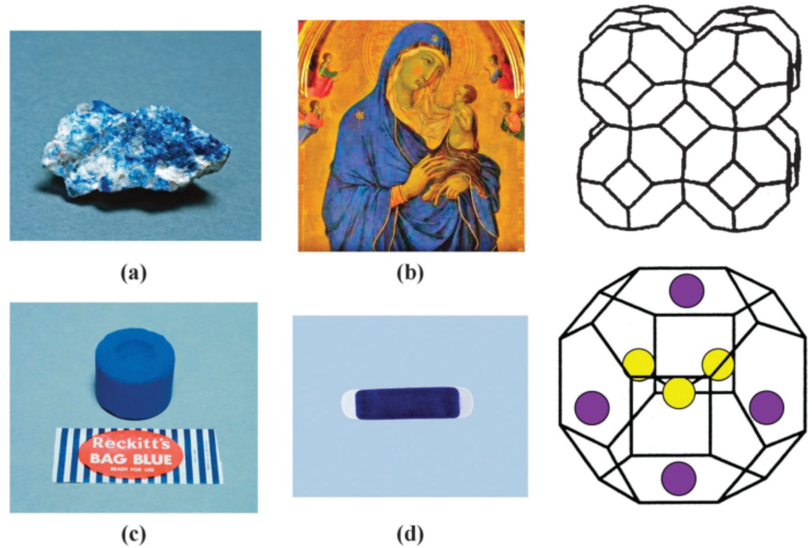


Ubiquitous trisulphur radical ion $S_3^{\cdot -}$

THE colour of blue ultramarine and the deep blue colour of alkali polysulphides in electron pair donor solvents have been attributed to the disulphur radical ion, $S_2^{\cdot -}$ (ref. 1). That assignment is erroneous and I here establish the correct identity of the species, emphasise the variety of situations in which it is encountered and point out its possible role as an intermediate, in transformations involving elemental sulphur, or sulphide ions.

A blue colour develops when sulphur is heated with water and traces of some basic salt[2,3]. Blue solutions are also formed by sulphur in alkali halide melts[4], in liquid potassium thiocyanate above 300° C (refs 5 and 6), by alkali polysulphides in basic solvents[7–12], by electrochemical reduction of S_8 in dimethyl sulphoxide[13–15] or LiCl–KCl eutectics[16,17], and in the electrochemical oxidation of alkali metal polysulphides in eutectics[18]. The blue species is also present (as a minor component) in…

Chivers (1974) Nature 252, 32-33

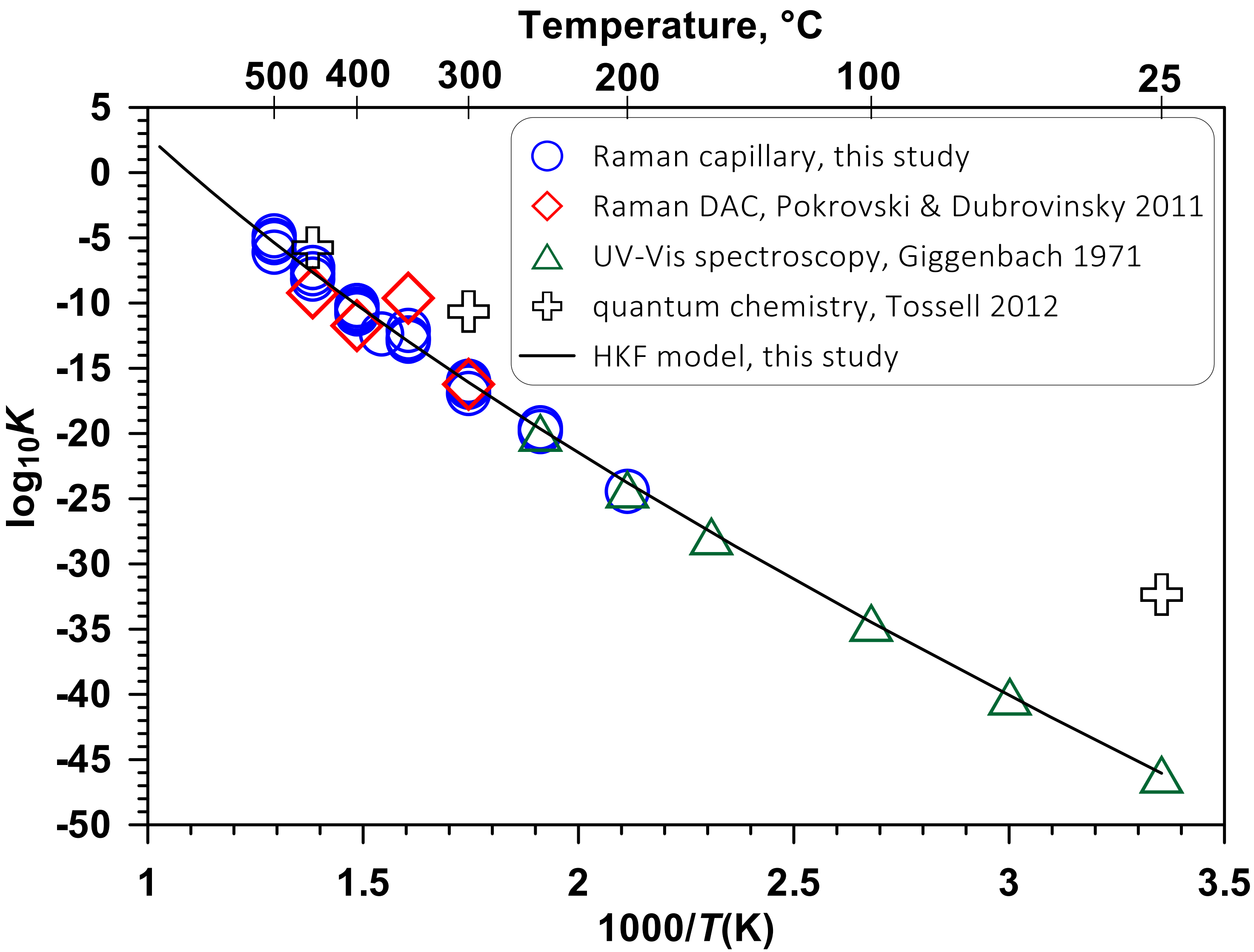


Chivers & Elder (2013) Chem. Soc. Rev. 42, 5996

- **Organic and inorganic solvents (e.g., S in NH_3 , dimethylformamide)**
- **Borosilicate glasses and melts ($S\text{-}B_2O_3\text{-}Al_2O_3\text{-}SiO_2$)**
- **Alkali halide melts (e.g., S in $NaCl\text{-}AlCl_3$)**
- **Alkali metal - sulfur batteries**
- **Water sensors**

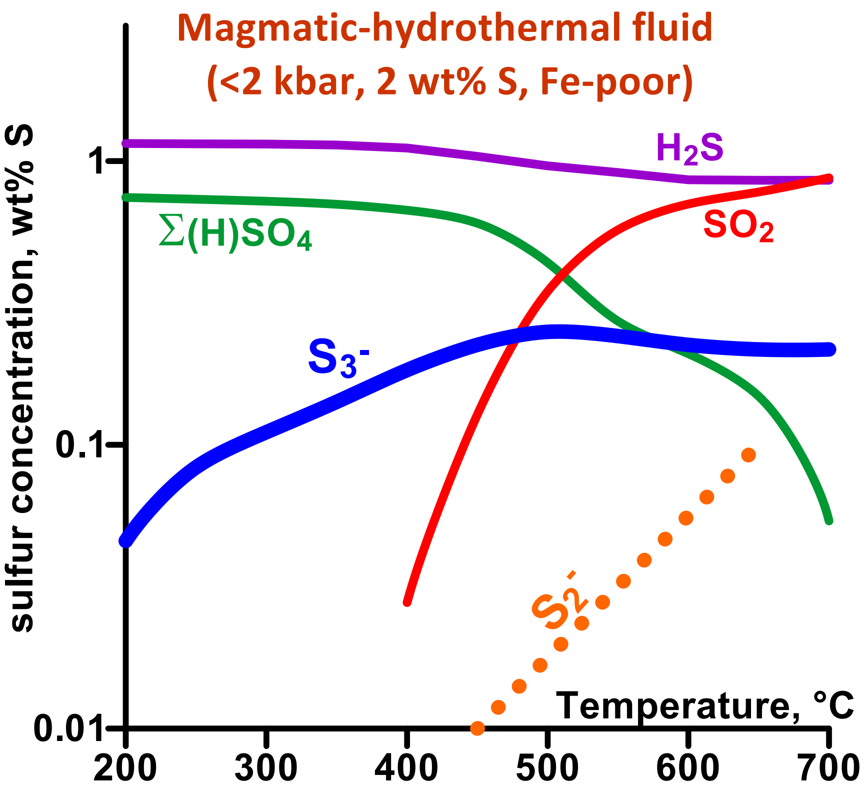
Stability constant of S_3^-

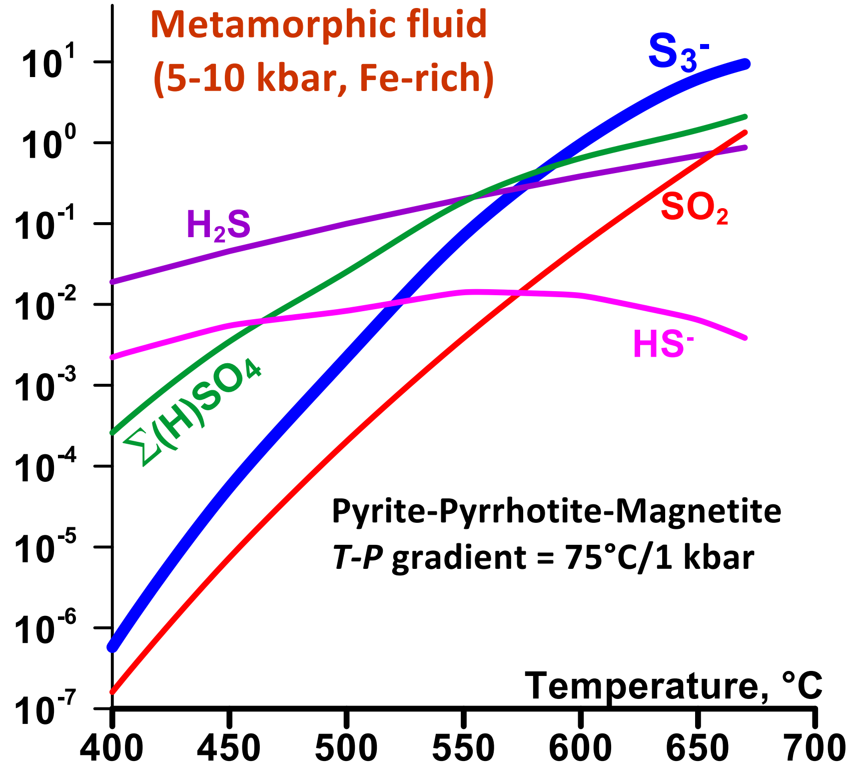
$$2\ H_2S + SO_4^{2-} + H^+ = S_3^- + 0.75\ O_2 + 2.5\ H_2O$$

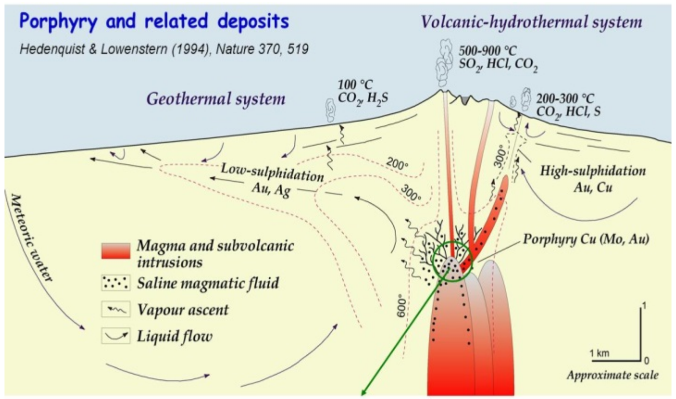


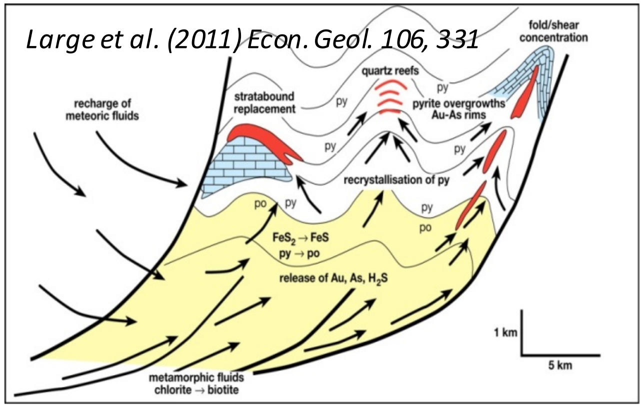
Pokrovski & Dubessy (2015) Earth Planet. Sci. Lett. 411, 298

Abundance of S_3^- ion in geological fluids







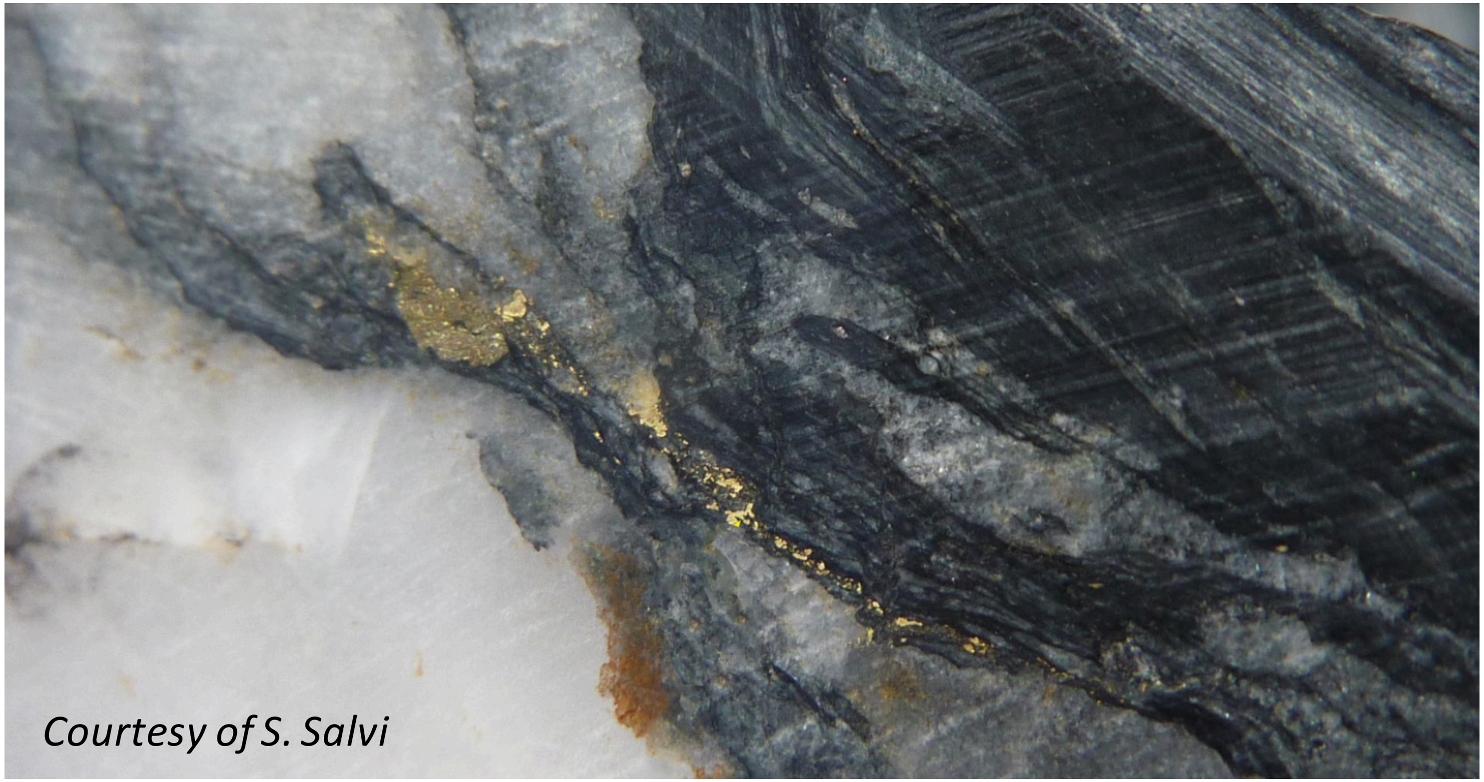


Pokrovski & Dubessy (2015) Earth Planet. Sci. Lett. 411, 298

Does S_3^- control the transport and precipitation of metals in hydrothermal fluids ?

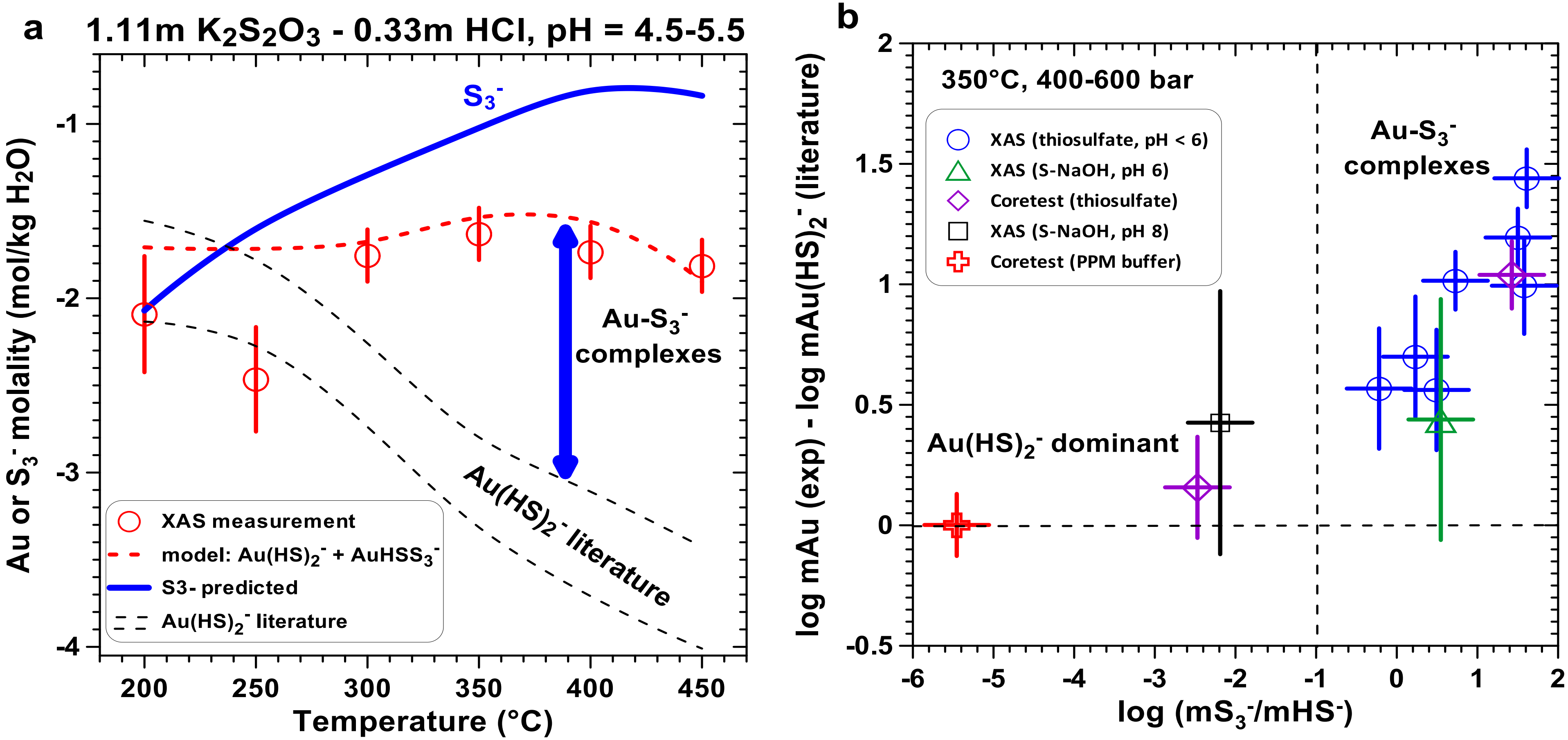
Example of gold

Enigmas of gold deposits



- **Gold is the most chemically inert metal of the Periodic Table.**
- **Low capacities of salt (Cl-) and sulfur (H_2S/HS^-) to solubilize gold (few ppm).**
- **Existence of large Au deposits (>100s tons) and Au-rich veins (100-1000 ppm Au).**
- **Deep Au-rich sources from mantle or flow of huge volumes Au-poor fluids.**
- **Rareness of known Au economic ressources (Au in deposits/Au in the Earth's crust = $1:10^7$).**

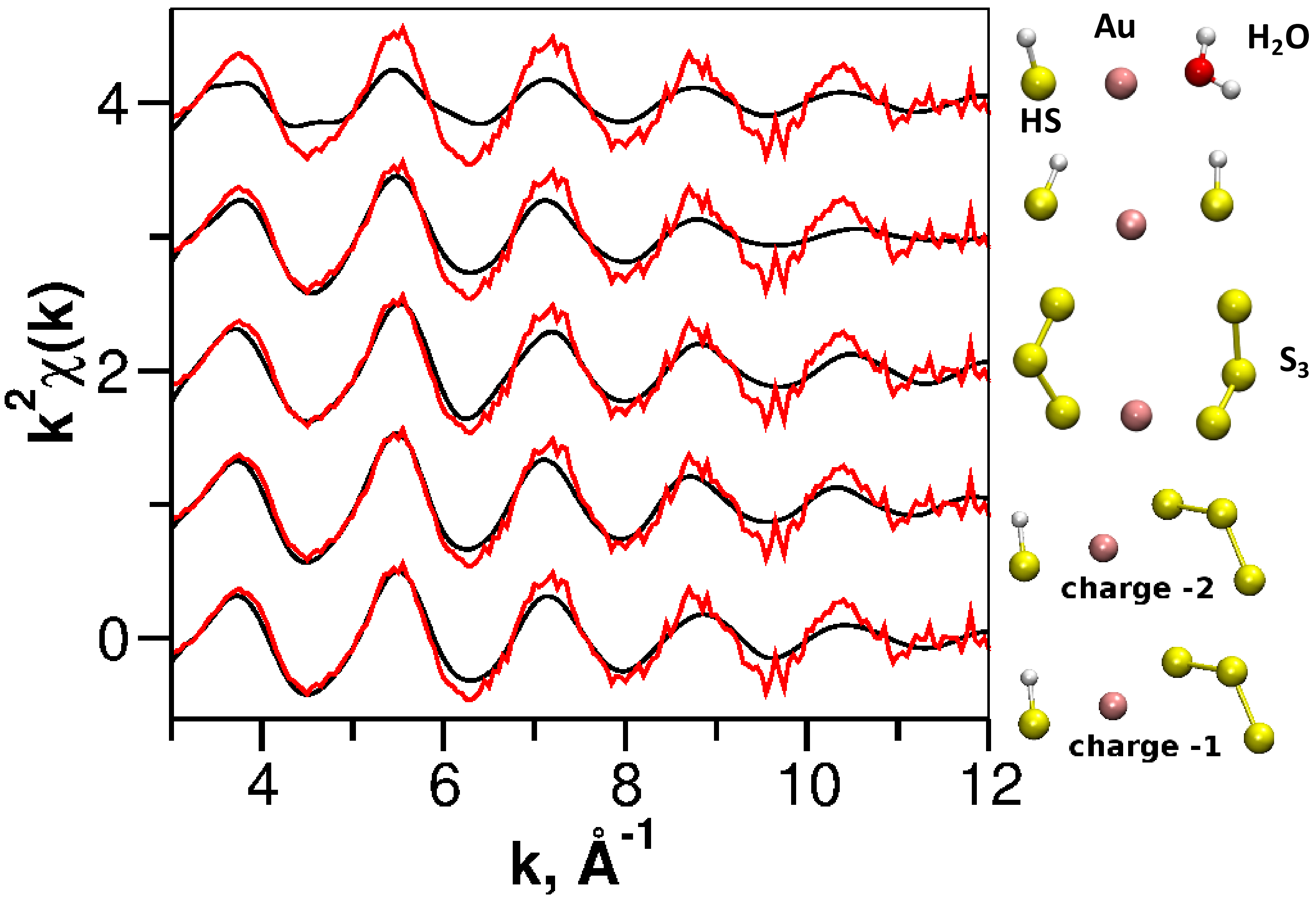
Gold solubility in S_3^- - bearing solutions



Direct experimental evidence for Au-S_3^- complexes; Competition between HS^- and S_3^- for Au

EXAFS spectroscopy and molecular dynamics simulations

Calculated EXAFS spectra of different Au-HS-S3- clusters (black) versus the experimental EXAFS spectrum of a S_3^--rich solution at 400°C (red)



➡ **The best match of experimental spectra is for HS-Au-S_3 type complexes**

Speciation model

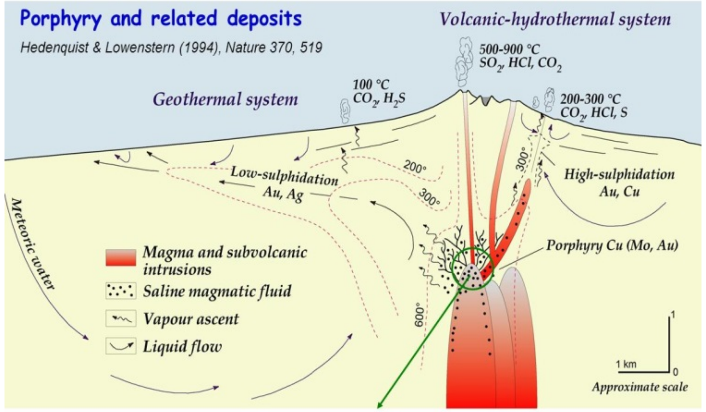
$Au(HS)_2^- + S_3^- = Au(HS)S_3^- + HS^-$ (R1), $K_{R1} \approx 1$ at all *T-P*

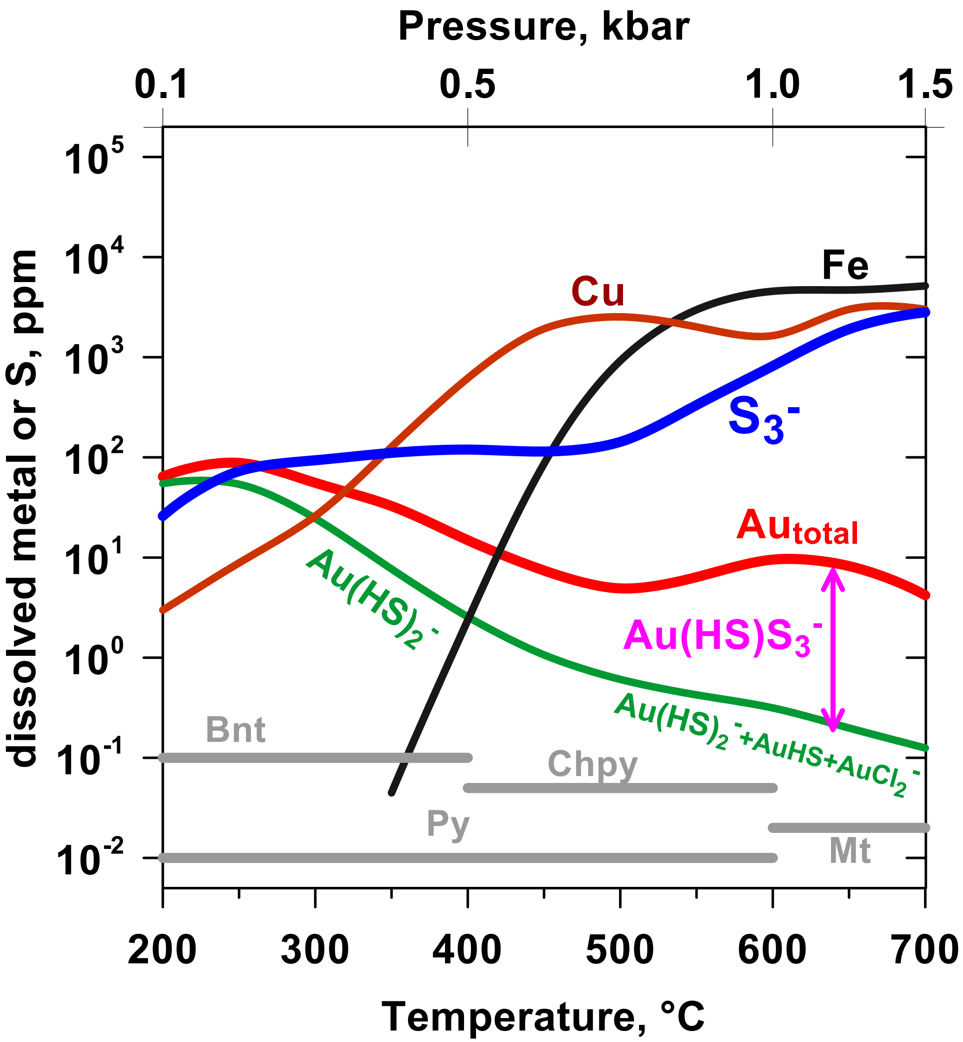
T °C	P, bar	Number of data points	$Log_{10}\ K_{R1}$	Error ±2 s.d.
300	600	12	**-0.3**	0.6
350	500	15	**0.0**	0.5
400	600	12	**-0.1**	0.6
450	600	14	**0.0**	0.6
500	700	2	**-0.3**	0.7

Important role of S_3^- in the formation of gold deposits

Porphyry-epithermal fluids

Cooling and rise of a fluid degassed from magma at 700°C and 1.5 kbar in equilibrium with Au metal and carrying:
2 wt% S, H2S:SO2 = 1, 10 wt% NaCl,
7500 ppm Fe, 3000 ppm Cu
pH 5-6 (Quartz-Muscovite-K feldspar)

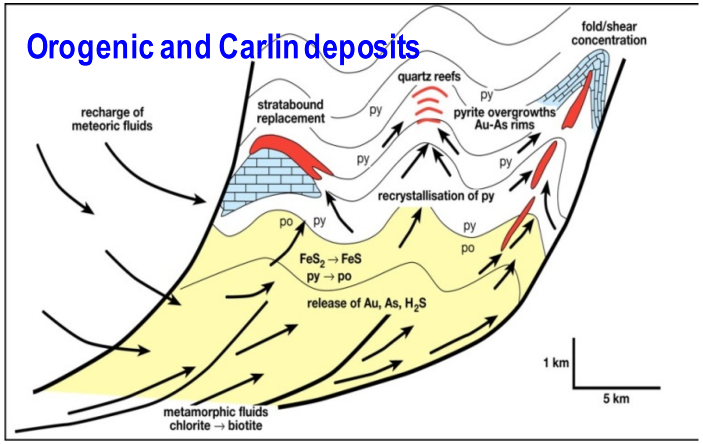


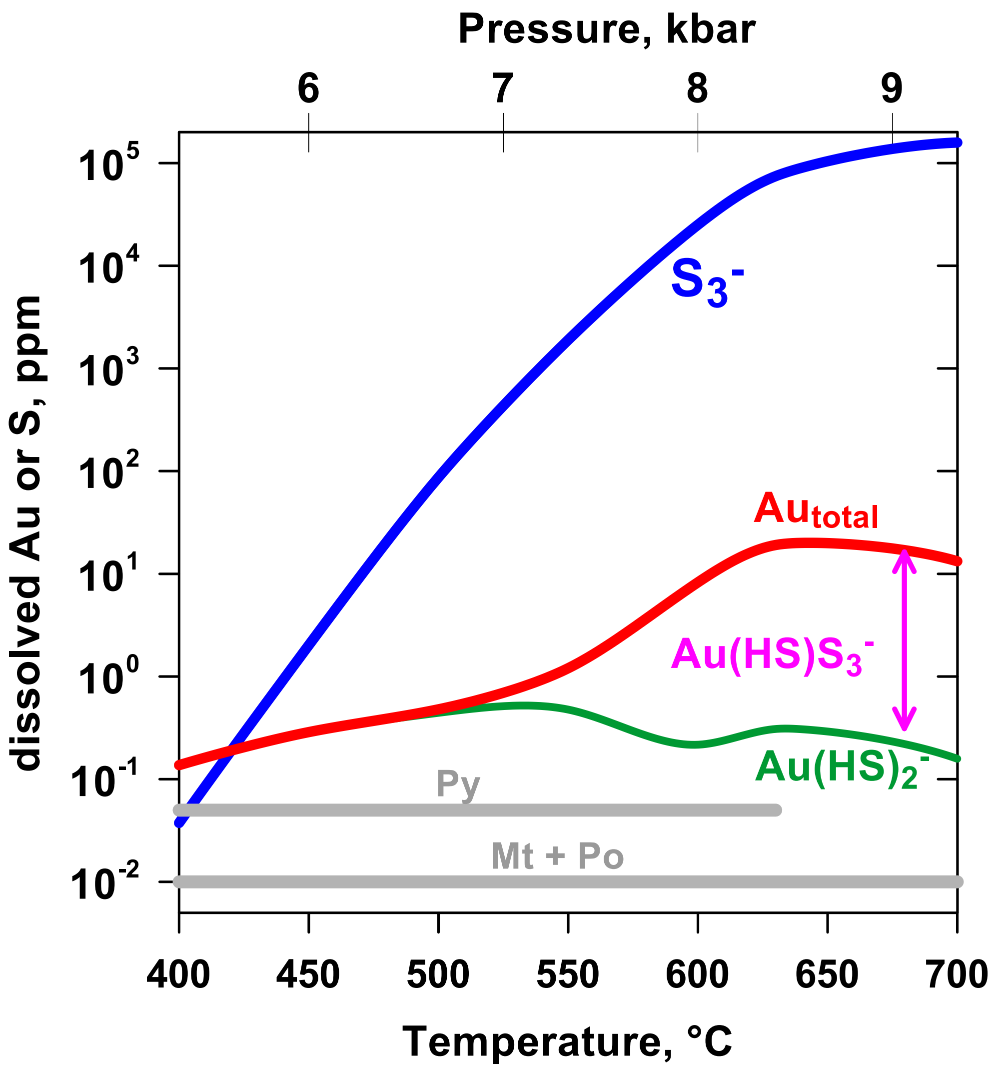


S_3^- enhances, by a factor of 10 to 100, the fluid capacity to extract Au from magma and to transport it to ore deposition sites

Orogenic fluids

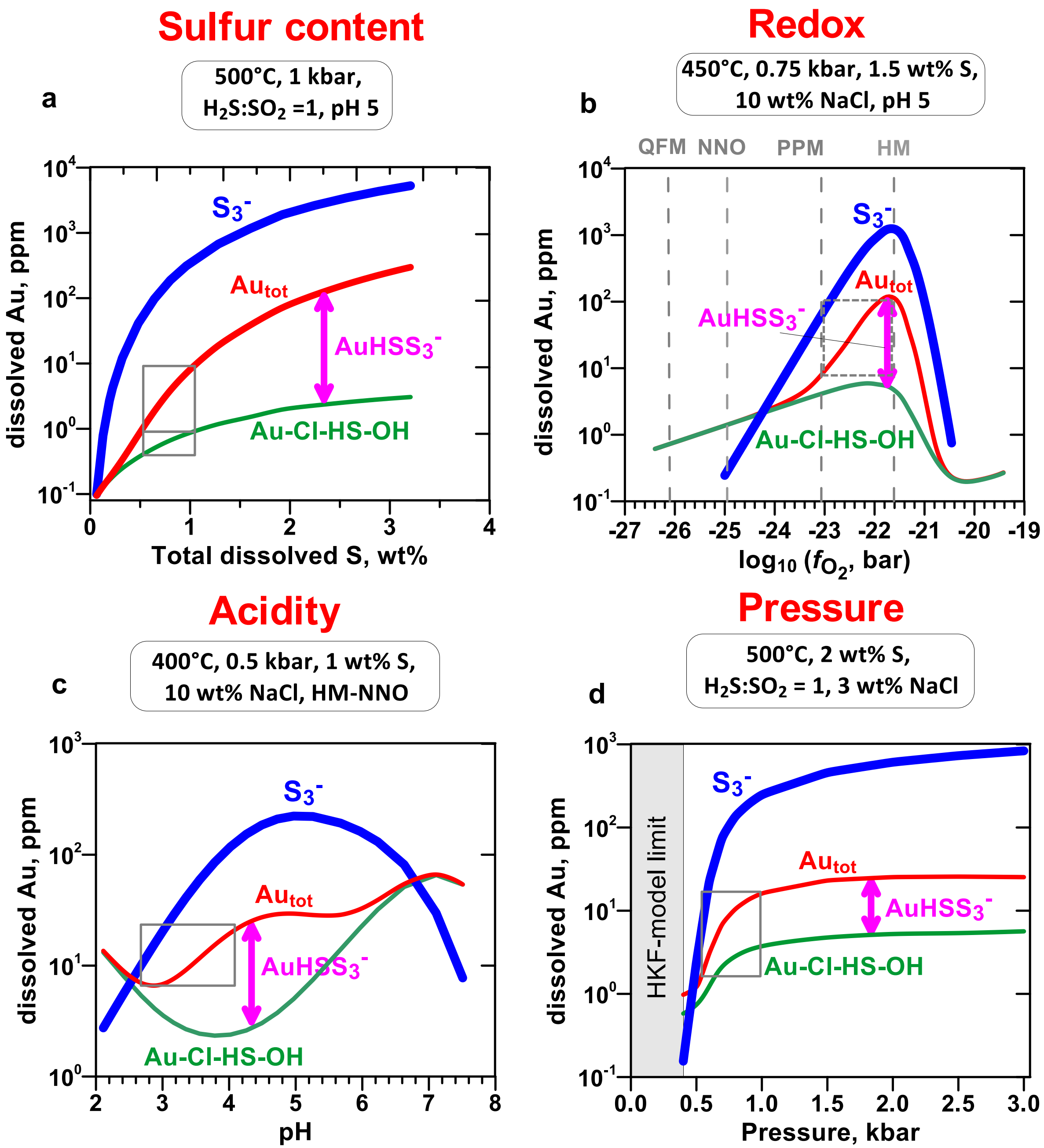
A sea-water salinity fluid during subduction of pyrite-bearing rocks (geothermal gradient =75°C/1kbar):
3 wt% NaCl, pH 5-6 (Quartz-Muscovite-K feldspar-Albite)
Pyrite-Pyrrhotite-Magnetite





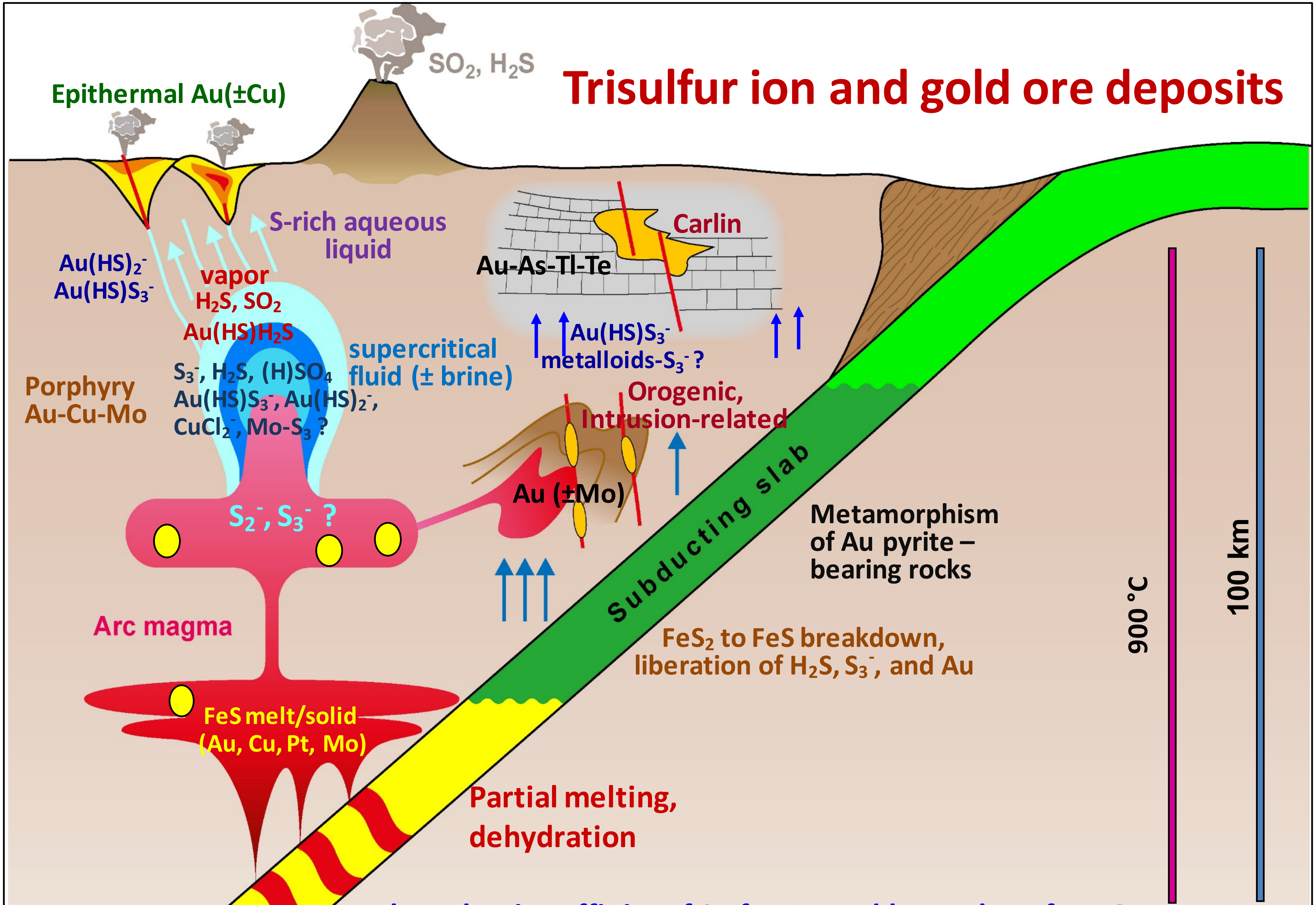
S_3^- may enhance, by a factor of 100, Au extraction from the rocks and concentration in metamorphic fluids above 500°C

Effect of major fluid parameters on Au solubility and speciation



Breakdown of S_3^- within a narrow *T*-*P*-pH-f_{O_2} window yields focused Au deposition in high tenors from a small fluid volume

Trisulfur ion and gold ore deposits



The selective affinity of S_3^- for Au and by analogy for PGE, Mo, As, Te might explain the elements signatures of the different deposit types

Sulfur summary

- Au strongly binds to S_3^- in the fluid phase
- Enhanced extraction, transport et precipitation de Au
- Control on metal signatures in different types of gold deposits
- Making the formation of gold deposits easier than we thought

PNAS

Sulfur radical species form gold deposits on Earth

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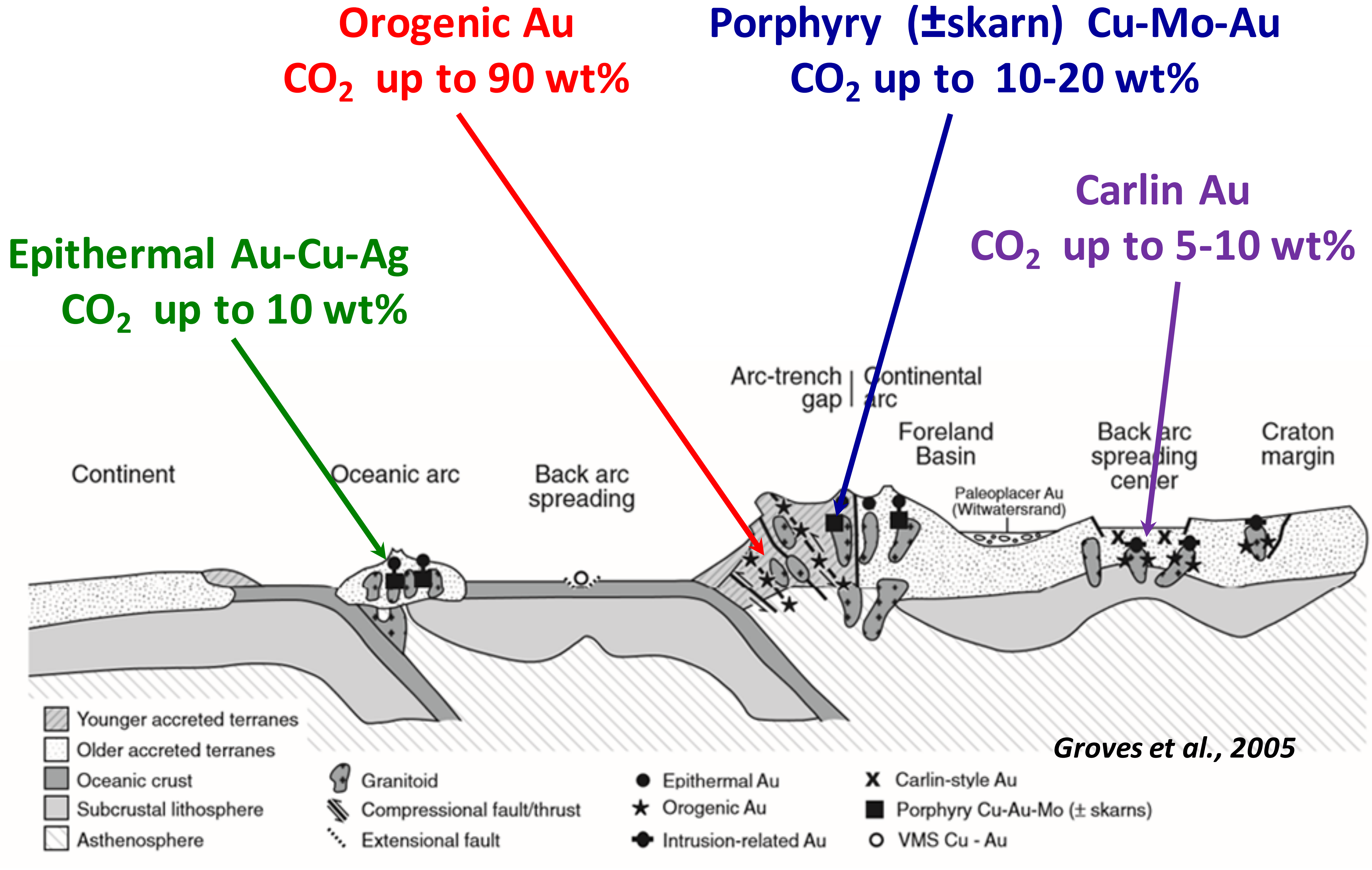
13484–13489 | PNAS | November 3, 2015 | vol. 112 | no. 44

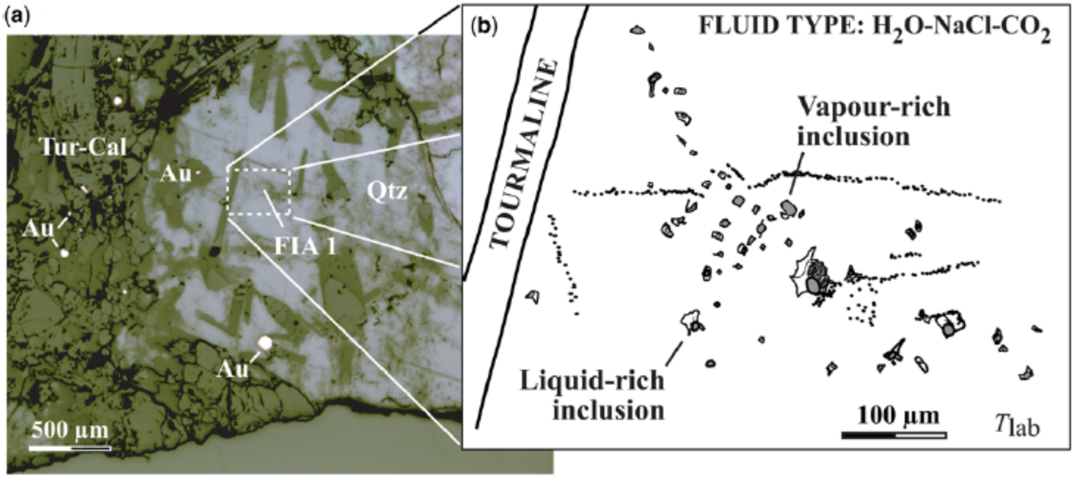
Carbon



Orogenic Au
CO_2 up to 90 wt%
Porphyry (±skarn) Cu-Mo-Au
CO_2 up to 10-20 wt%
Carlin Au
CO_2 up to 5-10 wt%
Epithermal Au-Cu-Ag
CO_2 up to 10 wt%
Arc-trench gap
Continental arc
Foreland Basin
Back arc spreading center
Craton margin
Continent
Oceanic arc
Back arc spreading
Paleoplacer Au (Witwatersrand)
Younger accreted terranes
Older accreted terranes
Oceanic crust
Subcrustal lithosphere
Asthenosphere
Granitoid
Compressional fault/thrust
Extensional fault
Epithermal Au
Orogenic Au
Intrusion-related Au
Carlin-style Au
Porphyry Cu-Au-Mo (± skarns)
VMS Cu - Au
Groves et al., 2005

Evidences directes du transport des métaux par les fluides carboniques

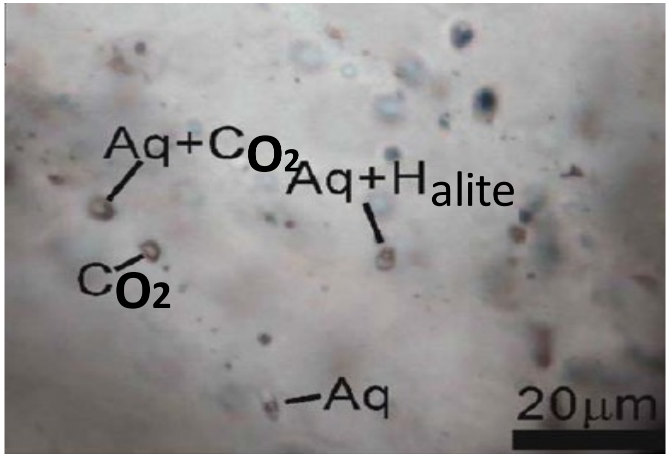
Inclusions à CO_2, 1000 ppm B, 100 ppm As, 1-5 ppm Au



Sigma, Canada

Garofalo et al. (2014) Geol. Soc. London Spec. Publ. 402, 71

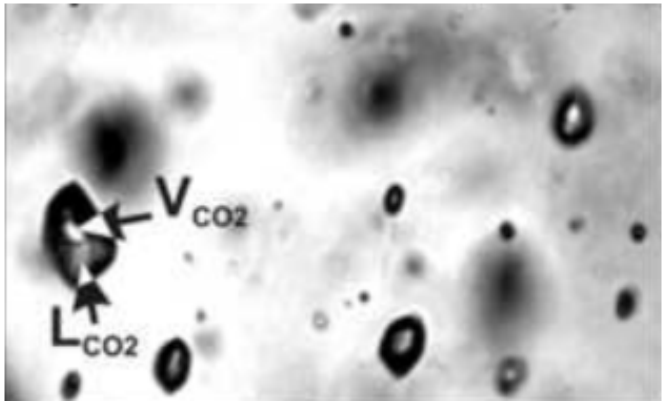
Inclusions à CO_2, 0.1-3.4 wt% Cu



Fenghuangshan, Chine

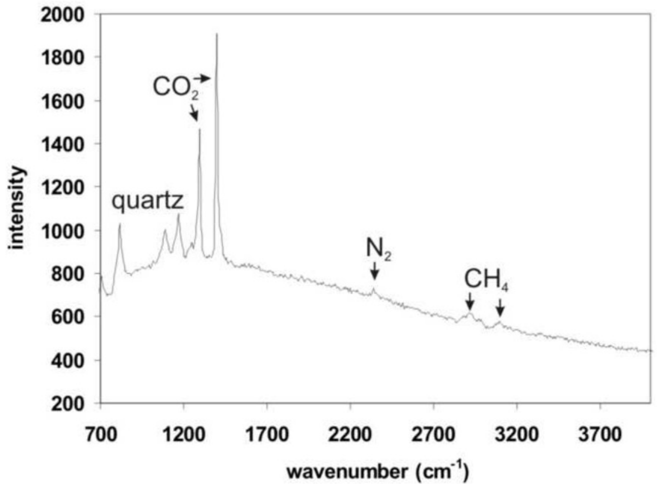
Lai & Chi (2007) Min. Dep., 42, 293

Inclusions à CO_2, 100s ppm Pd, Cu, Ni



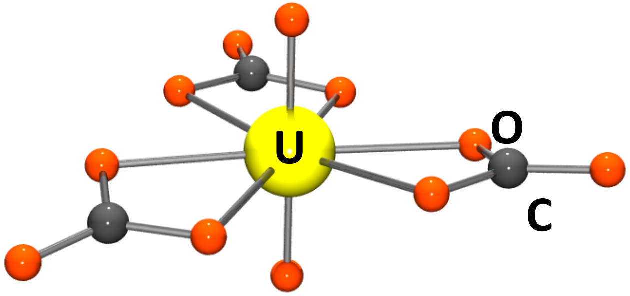
Pegmatites du Lac des Iles, Canada

Hanley & Gladney (2011) Econ. Geol. 106, 33

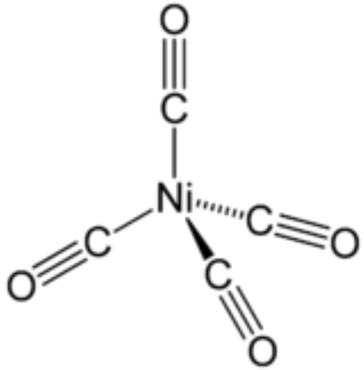


What is the effect of CO_2 on metal transport ?

carbonates and bi-carbonates
(e.g., U, Sn?, Zr?, Nb?, REE?...)

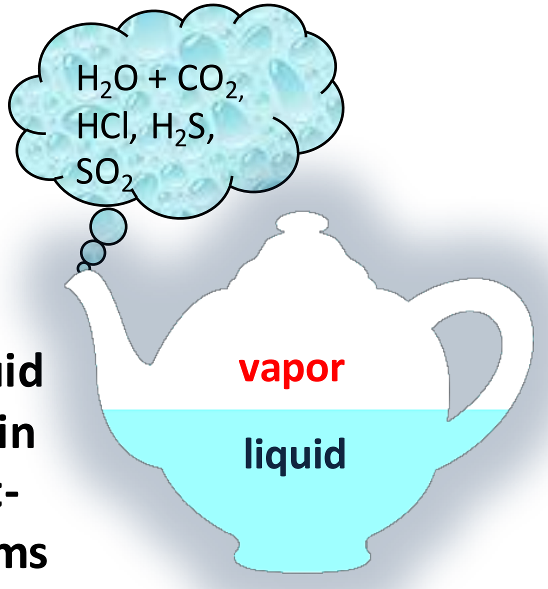


other (minor) C-bearing ligands (e.g., CO)



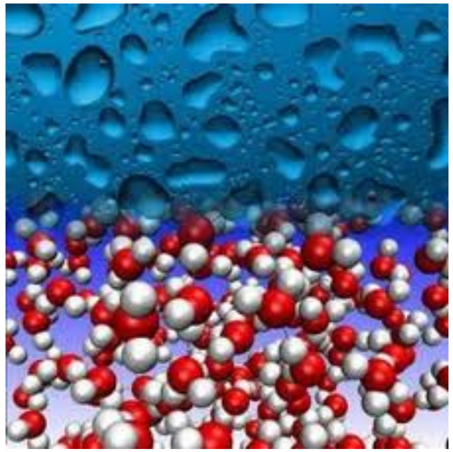
CO_2

Vapor-liquid equilibria in water-salt-CO_2 systems



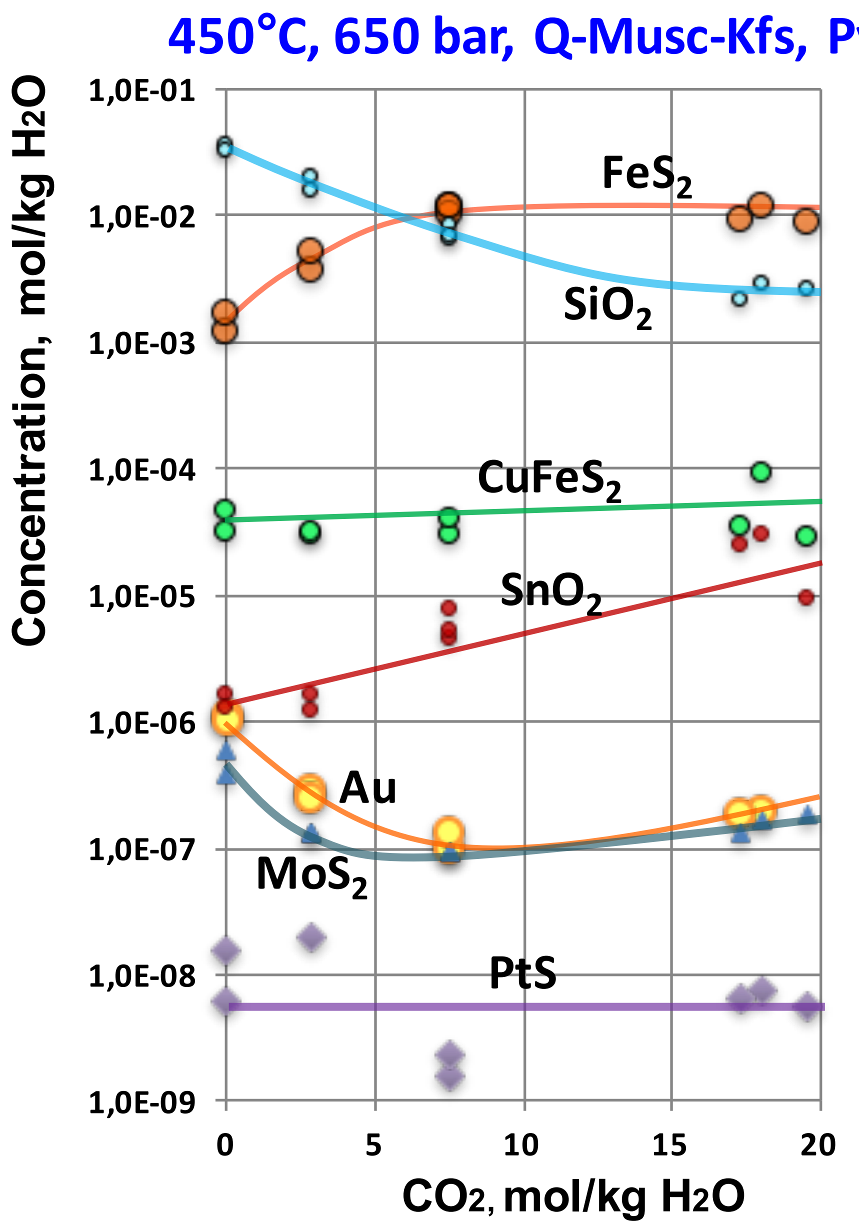
$$CO_2 + H_2O = HCO_3^- + H^+$$

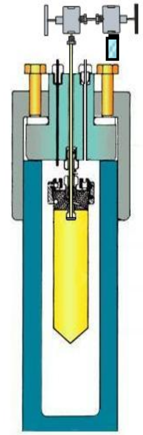
Decrease in dielectric constant ε_{mix} and water activity a_{H_2O} of the solvent



→ *Decrease in solubility ?*

Solubility of metals in supercritical H_2O-CO_2 fluid





Si ↓

Cu, Pt =

Sn, Fe ↑

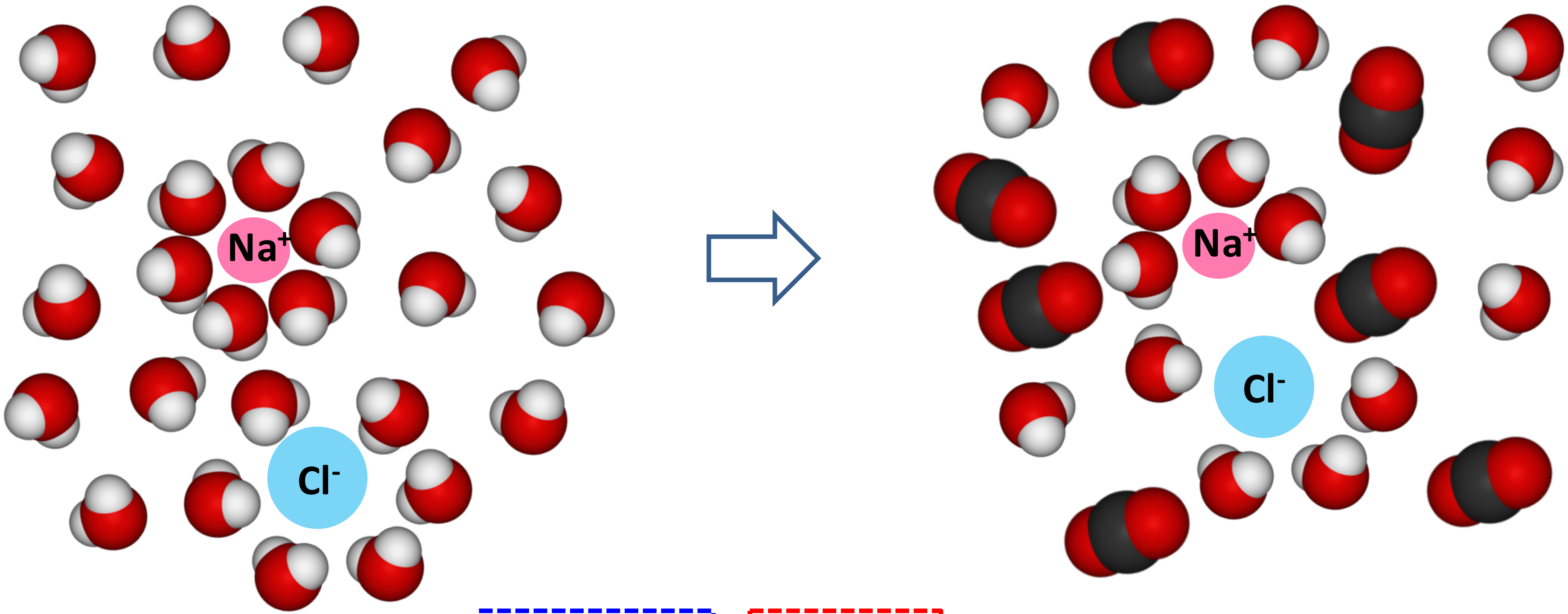
Au, Mo ↓ and ↑

- Metal speciation in the fluid phase
- Thermodynamic model for a multicomponent fluid-mineral system

Kokh M. (2016) PhD thesis, University of Toulouse

Electrostatic model

H_2O fluid **H_2O-CO_2 fluid**



$$\Delta G^\circ_i = \Delta G^\circ_i \text{ Born} + \Delta G^\circ_i \text{ DH}$$

interactions species – solvent

$$G^0_{Born} = \;_i \cdot \quad \frac{1}{\;_{mix}} \quad \frac{1}{\;_{water}}$$

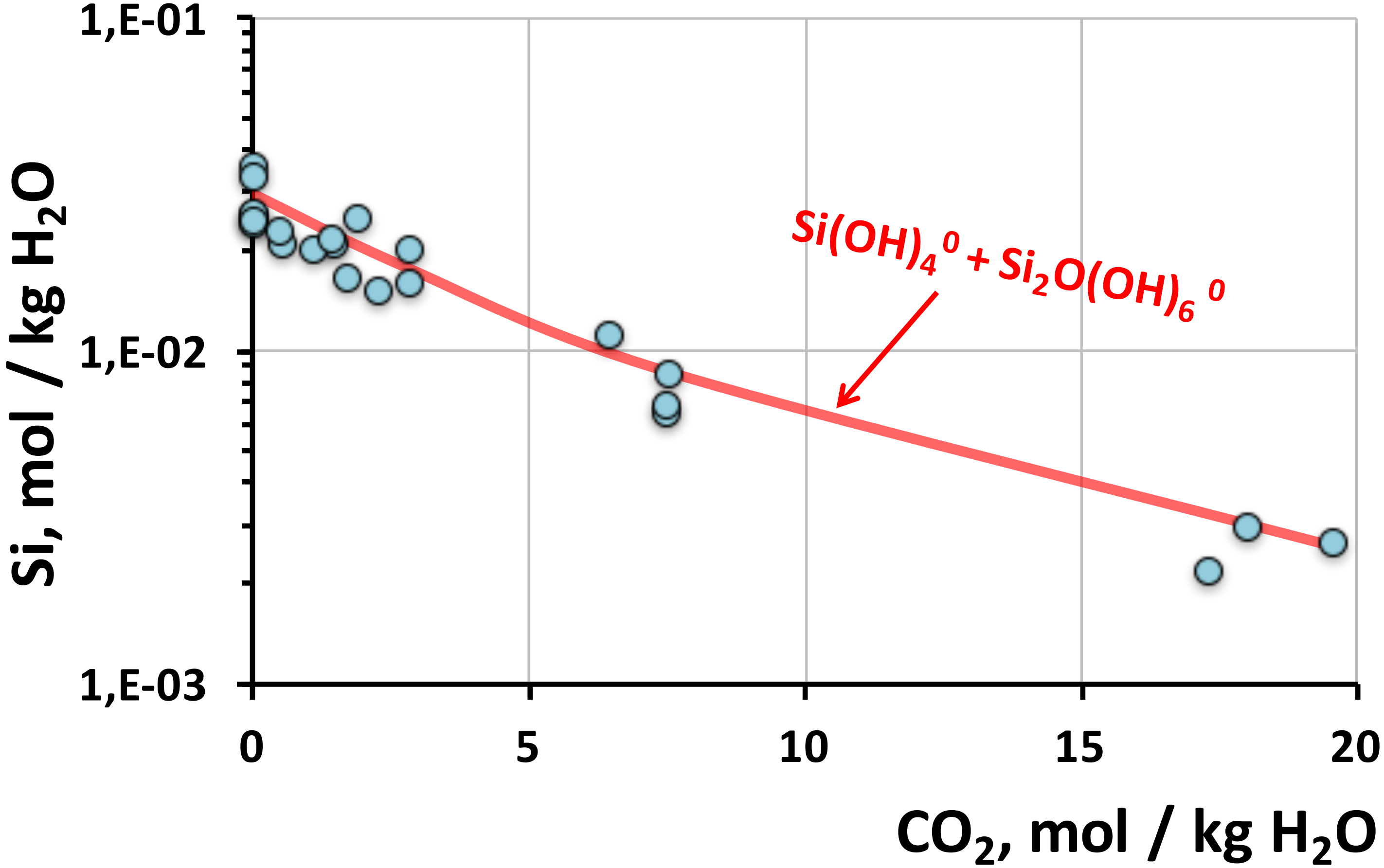
interactions species – species

$$\log(\gamma) = \frac{-A \cdot Q^2\sqrt{I}}{1 + B \cdot r\sqrt{I}}$$

Helgeson et al. (1981); Dandurand and Schott (1992)

Solubility of quartz in H_2O-CO_2-salt-sulfur fluid

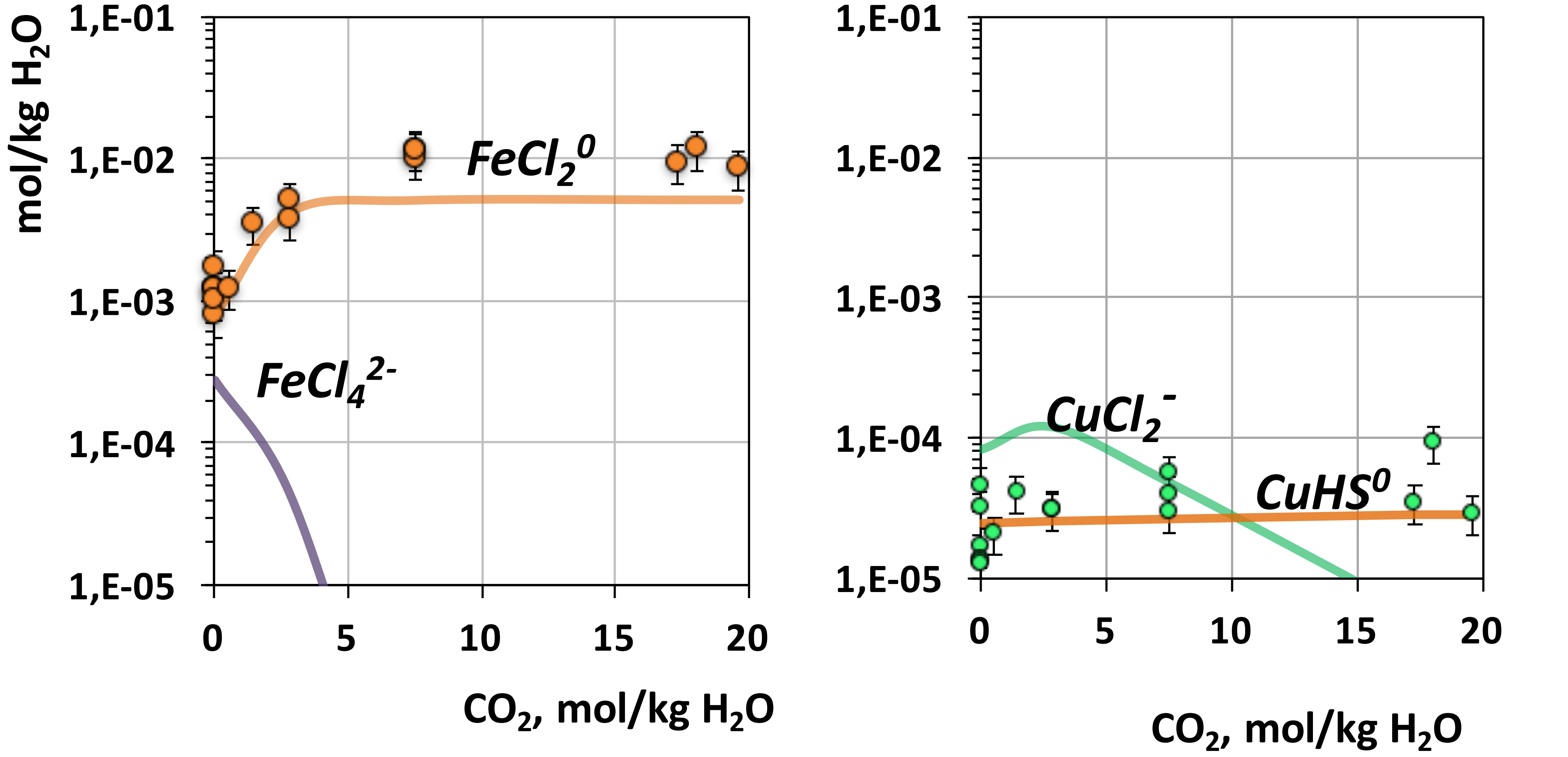
450°C, 650 ± 40 bar, 0.01-0.1 mol KCl / kg H_2O



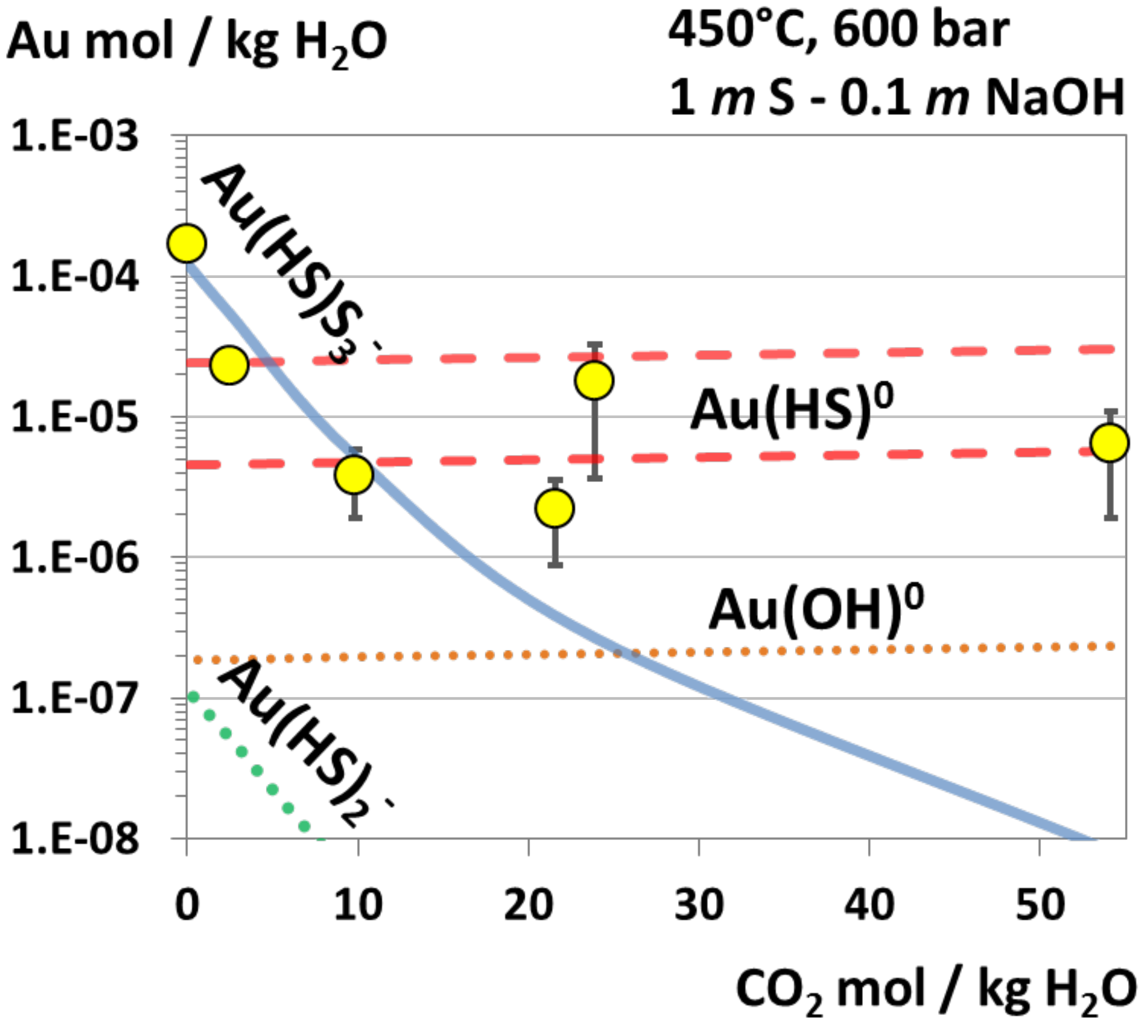
$Si(OH)_4$, $Si_2O(OH)_6$ – Sverjensky et al., 2014

Fe and Cu solubility in H_2O-CO_2 fluids

450°C, 650 bar, Q-Musc-Kfs, Py-Po-Mt-Chpy, KCl = 0.1 mol/kg water



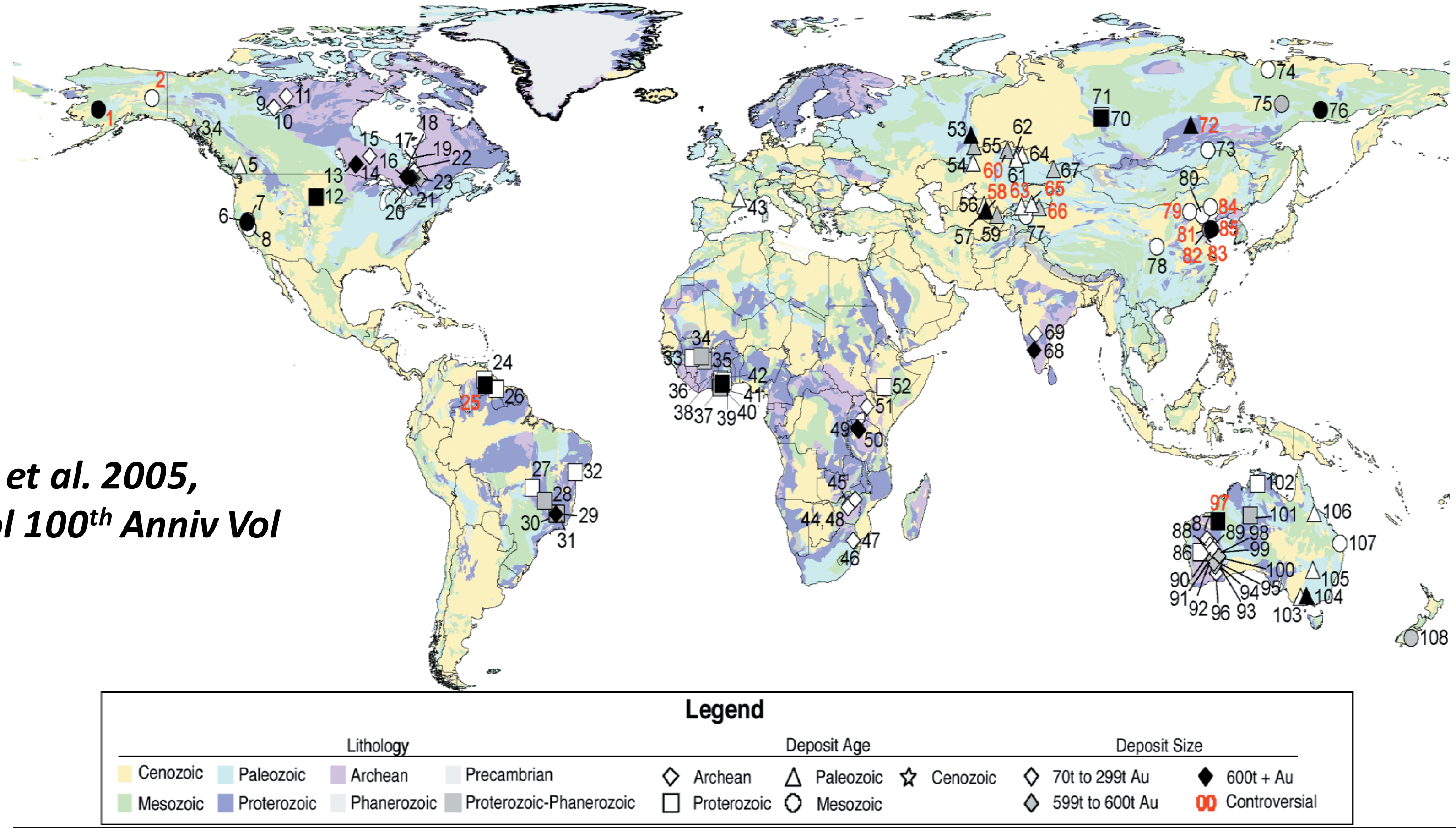
Gold solubility in S-rich H_2O-CO_2 fluid



$Au(HS)S_3^-$: Pokrovski et al., 2015, PNAS, 112(44), 13484

Applications to natural systems

Gold deposits in metamorphic belts



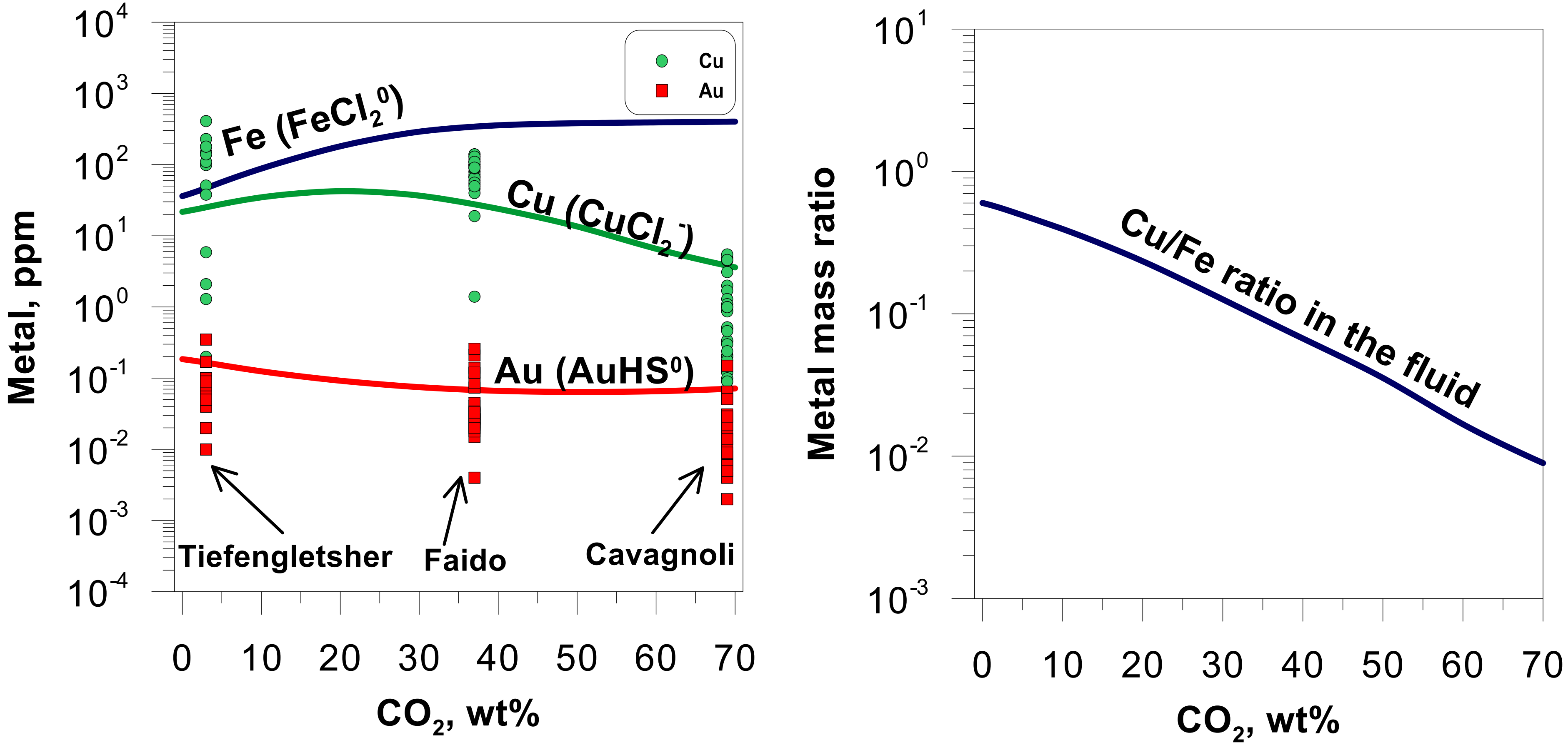
Goldfarb et al. 2005,
Econ Geol 100th Anniv Vol

- > 30% of the total Au production
- Low-salinity H_2O-CO_2 fluids (to 50-90 wt% CO_2)
- 0.5-5.0 kbar, 200-600°C
- Pyrite-pyrrhotite, Au (Ag, As, B, Bi, Sb, Te, W), but uneconomic Cu

Orogenic gold deposits

Oxidizing S-poor fluids

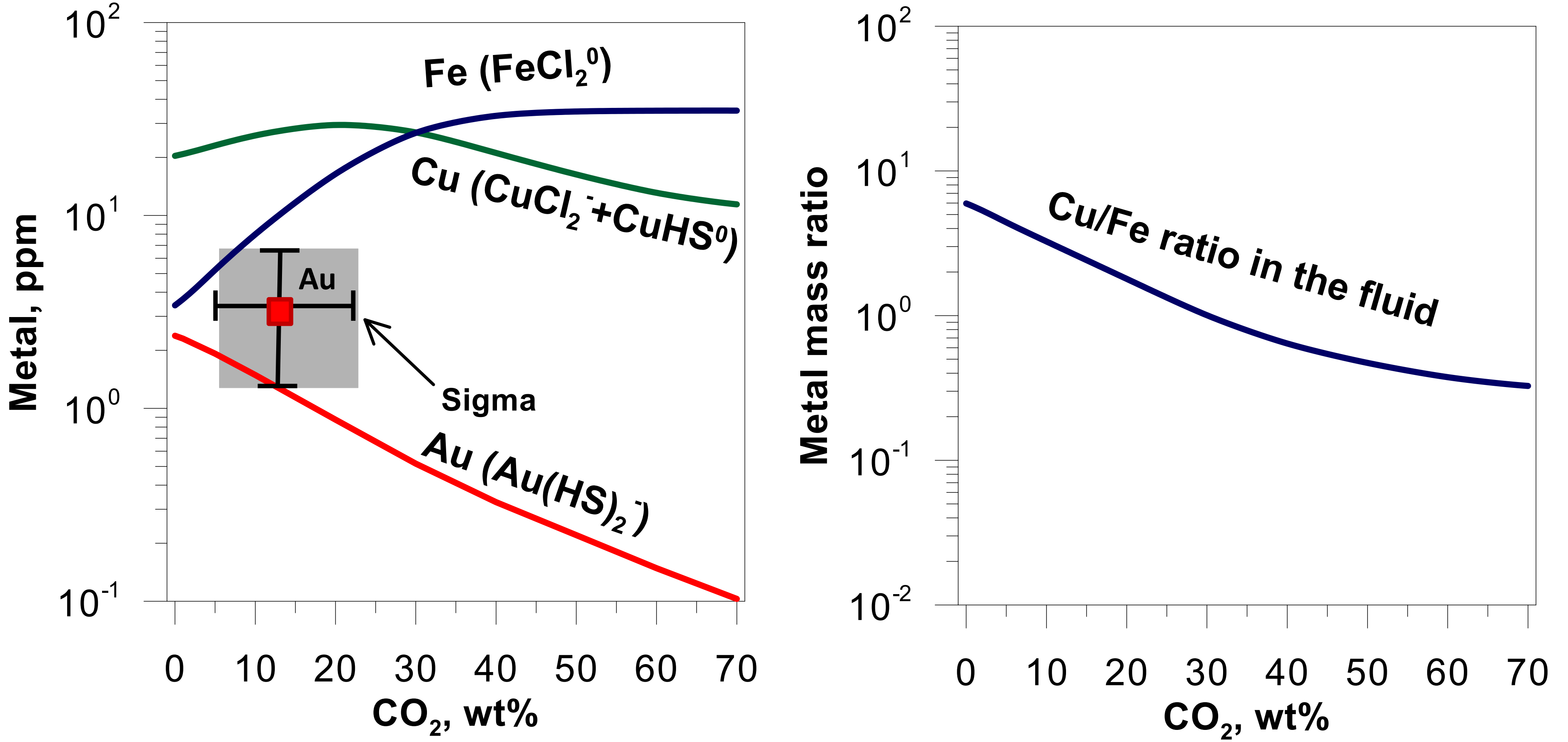
450°C, 2 kbar, 7 wt% (NaCl+KCl), *QMK, PMP*



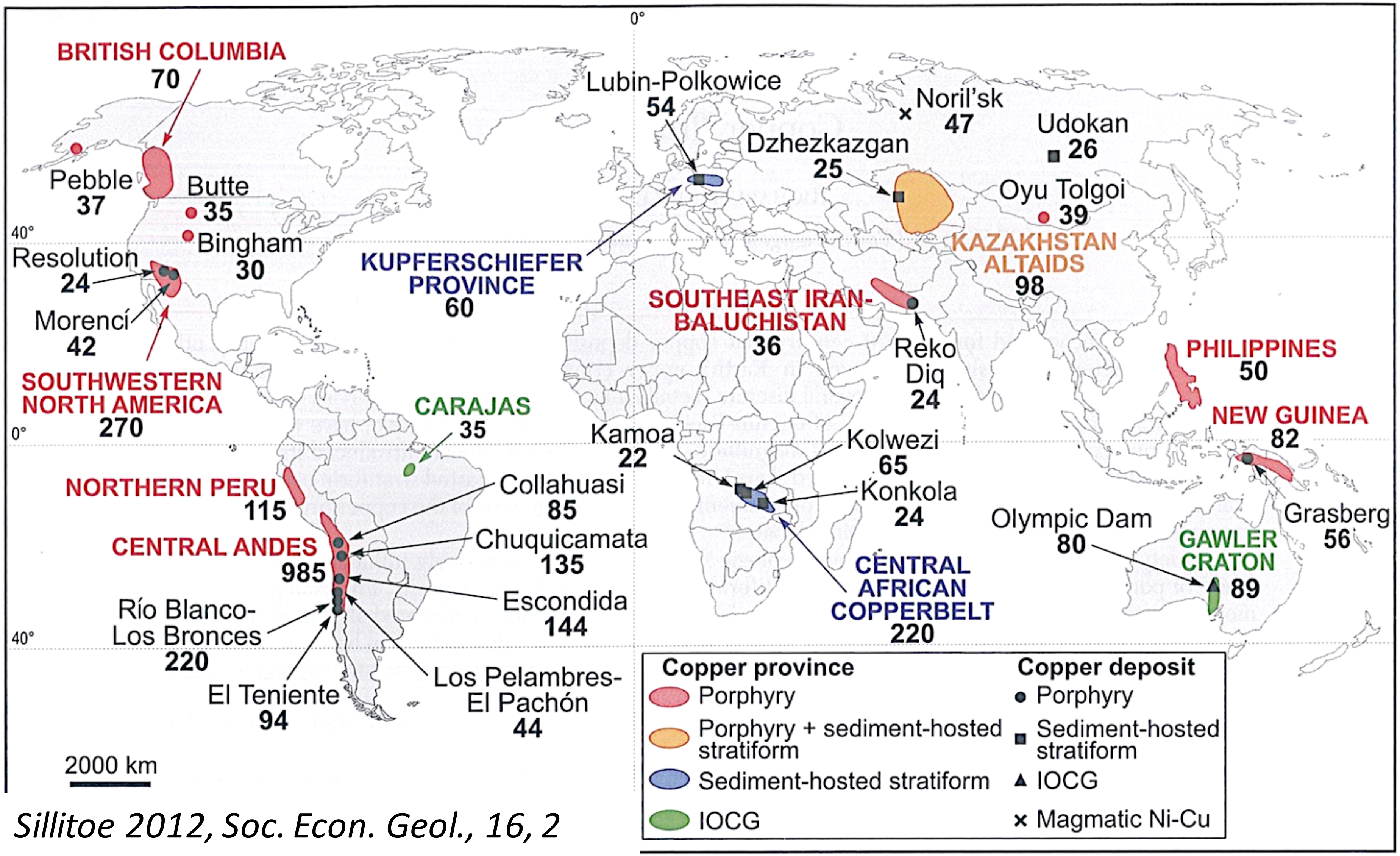
Orogenic gold deposits

Reducing S-rich fluids

450°C, 2 kbar, 7 wt% (NaCl+KCl), 1 wt% S, *QMK*, graphite



Les gisements de type porphyre et associés

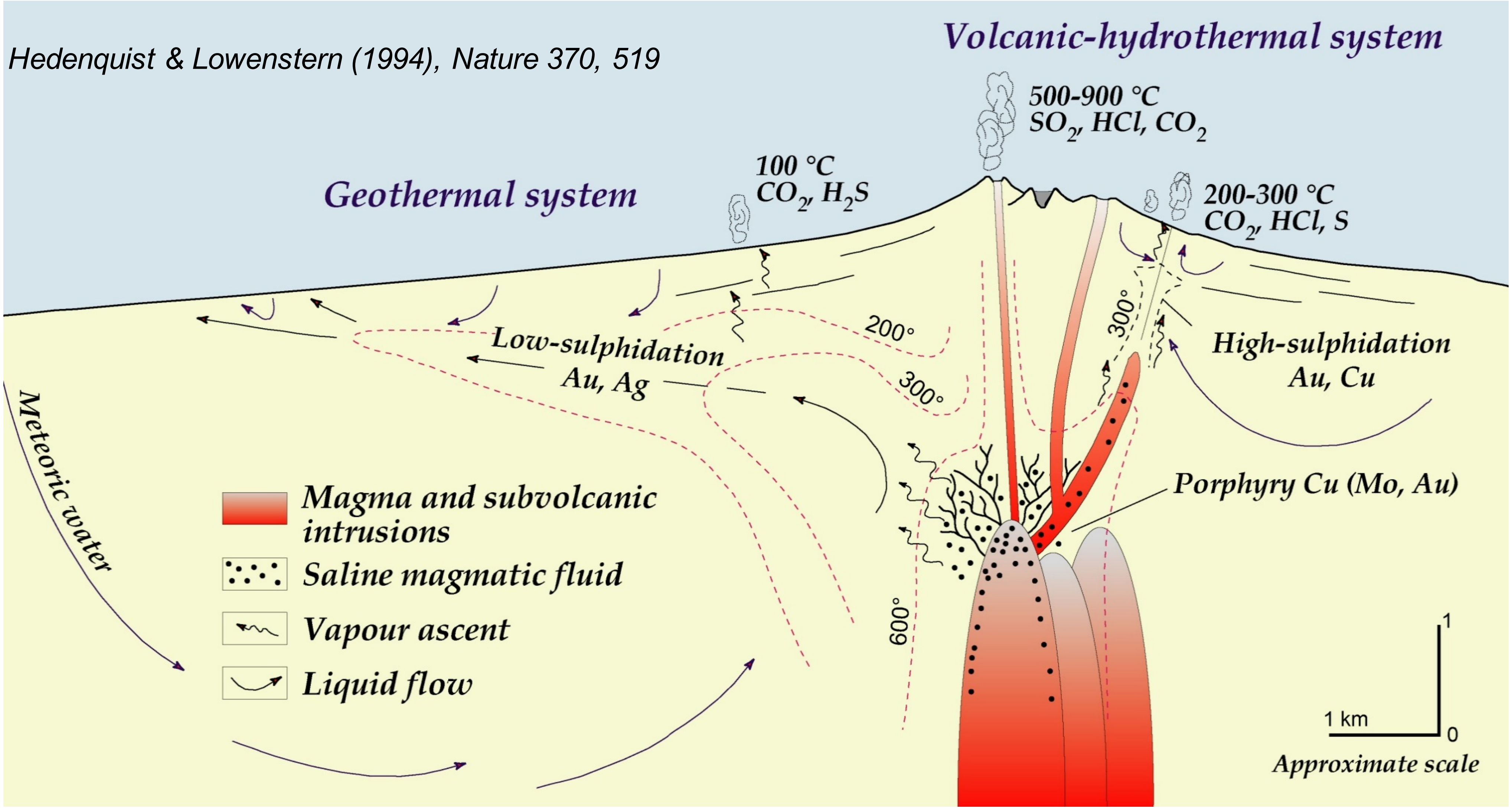


Sillitoe 2012, Soc. Econ. Geol., 16, 2

- **Plus de 75% de la production de Cu, 50% de Mo, 20% de Au**
- **Fluides de salinité variable (2-40 wt% NaCl) , CO_2 ≤ 20wt%, 0,5-1,5 kbar,**
- **300-600°C, riches en S, Pyrite-Magnétite-Hématite, $CuFeS_2$, Au, MoS_2**

Les gisements de type porphyre et associés

Modèle classique: dégazage d'un fluide magmatique riche en soufre et métaux, suivi de refroidissement/démixtion/altération avec les roches

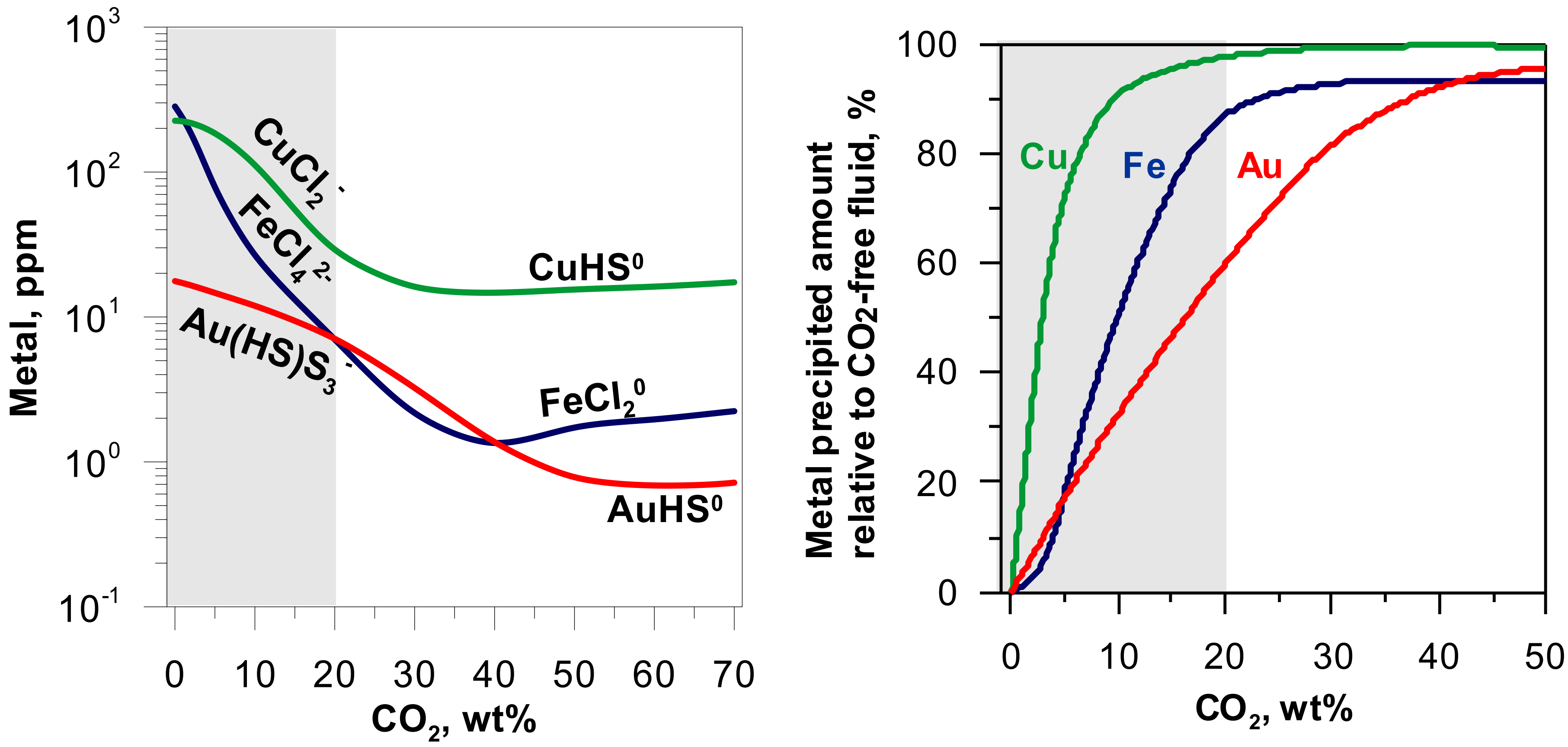


Les fluides de ces gisements contiennent jusqu'à 20 wt% CO_2. Quel est son rôle?

Porphyry deposits

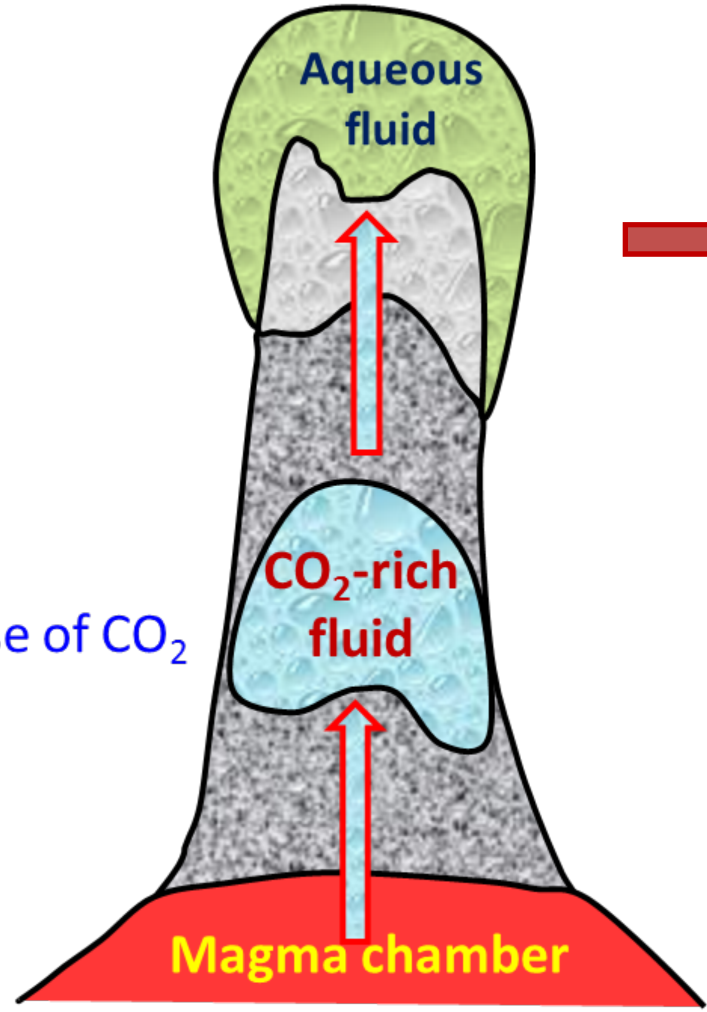
Saline oxidizing S-rich fluids

500°C, 1 kbar, 10 wt% NaCl, 1 wt% S, *QMK-QAK*



➡ **Injection de 20 wt% CO_2 dans un fluid porteur de métaux induit la precipitation de >60% de Au et >80% de Cu et Fe**

Mixture of the two fluids



Pulse of CO_2

Assimilation of carbonate rocks by magma

A new mechanism of metal precipitation by flushing magmatic CO_2 through a porphyry system?

Voir le poster de Maria Kokh

Carbon summary

- CO_2 changes the aqueous fluid properties, in particular, the dielectric constant
- Charged complexes become weaker, neutral complexes become stronger; the resulting metal solubility may increase or decrease depending on the fluid composition and metal speciation
- Control on Fe/Cu/Au ratios in metamorphic gold deposits
- New possible mechanism of metal precipitation in porphyry systems by CO_2 fluxing from magma

Kokh et al. (2016a) Geochim.Cosmochim. Acta (in press, doi:10.1016/j.gca.2016.05.010)
Kokh et al. (2016b) Geochim.Cosmochim. Acta (under revision)

Beyond our world…


Venus in true colors by Mariner 10

Near-surface atmosphere:

460 °C

90 bar CO_2

2 bar N_2

SO_2, H_2O, H_2SO_4

CO, COS, S_n

Carbothermal ore deposits ?