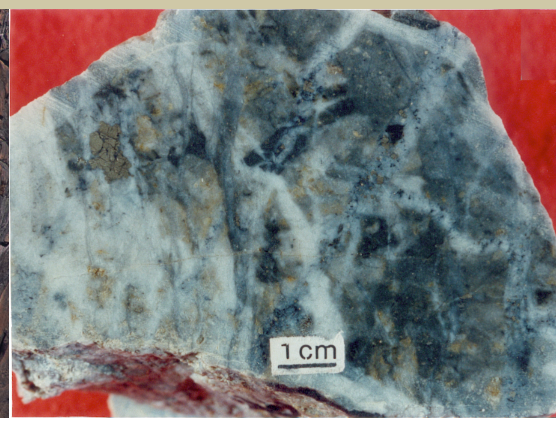
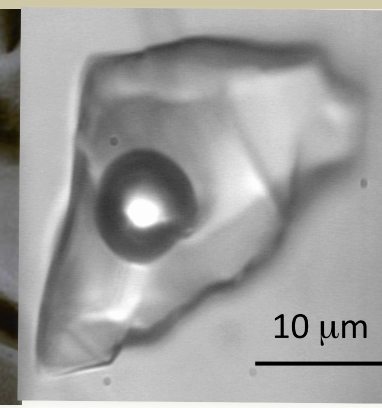
Ecole Thématique du CNRS

Ressources Minérales :
Du Terrain à l'expérimentation

Circulations fluides et concentrations métalliques l'analyse in situ des paléofluides





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The knowledge from the analysis of fluids to understand the process of ore formation

Source
(metal and fluid)

Transport
Fluid/ drains

Deposition

Redistribution
Dispersion/
accumulation

Interfaces

Biosphere/ Atmosphere

Identification of source rock and mineral

Fluid events
Time : When?
What duration?

Pressure –Temperature

Why at this time?
Relationship with Geodynamic
What are the fluids ?

Chemistry, Source
Metal content , ligands,
fO_2, fS_2

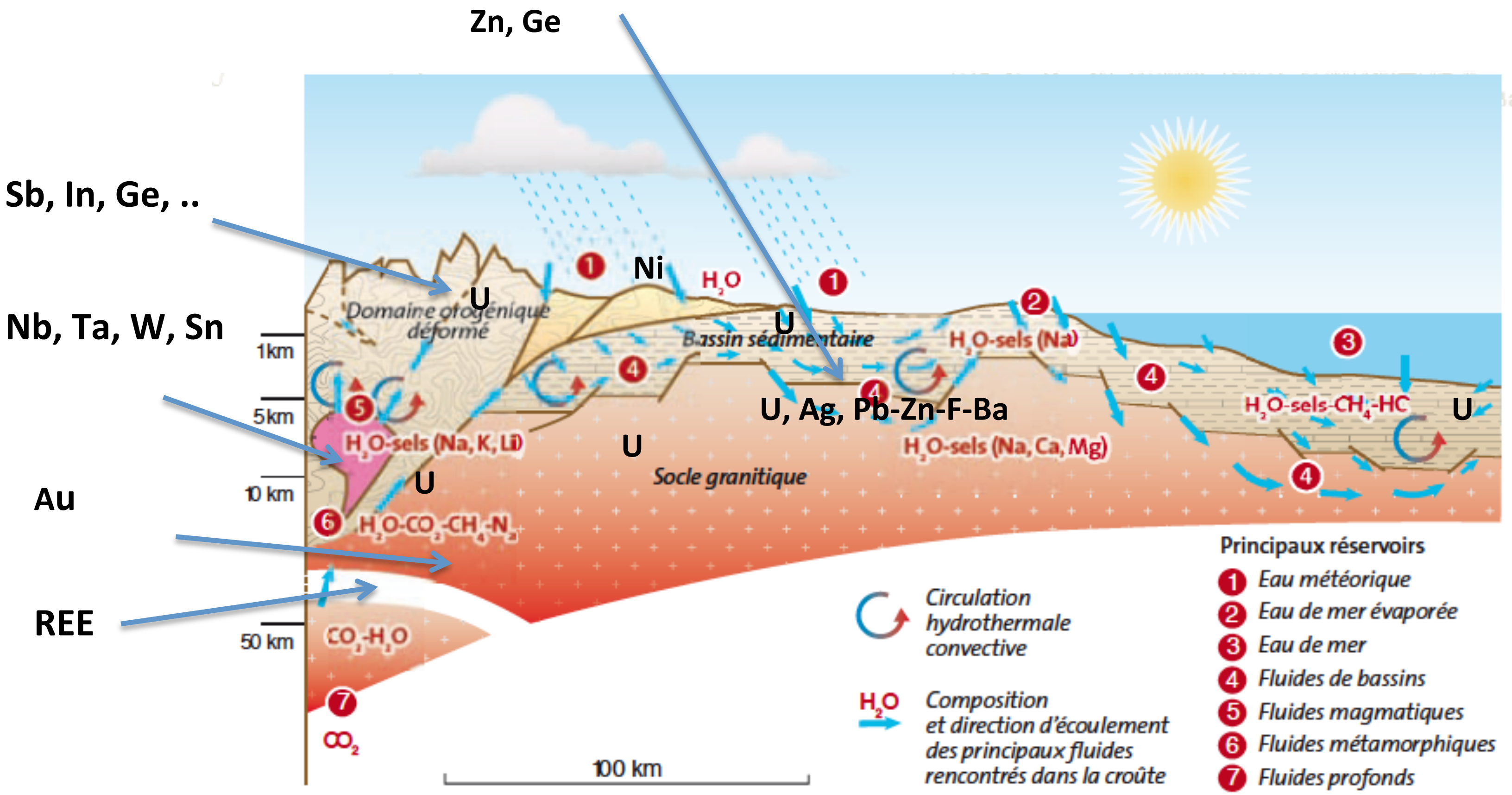
Traps

Physical-chemical Process

Fluid-rock and fluid – fluid Interactions

Mass balance calculations

Ore deposits and fluid transfers in the crust



What are the contributions and interactions between different fluid reservoirs

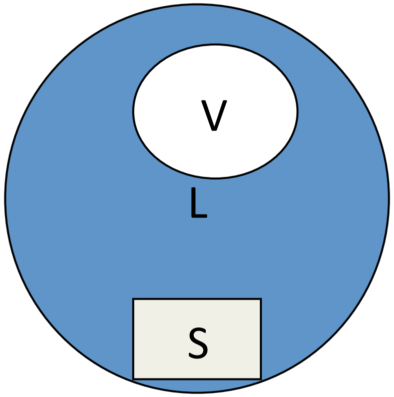
What are the interactions between fluids and host rocks ? Geochemical signatures, transfer and fluid chemistry

Fluid circulation and geodynamic context : Relationships between deformation, fracturing and fluid migration. What are the percolating zones in the crust?

What is a Fluid Inclusion?

Henry Clifton Sorby
(1826-1908)
English microscopist and geologist

Fluid inclusions are small cavities in a mineral that may contain 1 or more phases
vapor (V) - H_2O, CO_2, CH_4, N_2, H_2S
liquid (L)- H_2O, CO_2,CH_4 , Hydrocarbon
solid (S) - NaCl, KCl, hematite, anhydrite, muscovite, magnetite, carbonates, …..



Sample of fluids responsible
- of the host mineral precipitation (primary FI)
- or, of the crack healing by fluids circulating after the mineral precipitation (secondary FI)

The liquid of the inclusion is frequently an aqueous solution with dissolved ions of Na^+, Cl^-, Ca^{2+}, Mg^{2+}, SO_4^{2-}, HCO_3^{2-}, CO_3^{2-} + trace elements, metals
The concentration of the salts ranges from <1 wt. % to >50 wt. %

Density

Bulk composition

Gas

CO_2
CH_4
N_2
(H_2S, H_2, …)

H_2O

Salts

NaCl
KCl
$CaCl_2$
$MgCl_2$

Isotope signature

D/H
$\delta^{13}C$
($\delta^{18}O$, calc.)
$\delta^{37}Cl$

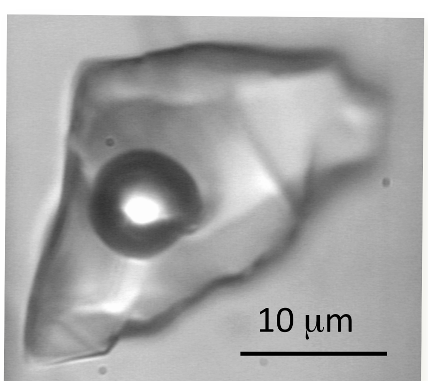
Trace element

Halogen (Br, I)
conservative tracer Cl/Br

Metal

U, Pb, Zn, Cu, Sn , W, Ag, Au, ….

Chemical composition of the fluids
at the scale of 10^{-9} g of matter



Fluid chemistry: key parameter, especially the metal content for the formation of significant ore deposits

What informations can we obtain from fluid inclusions?

1. Chemical composition of fluid (gas, major and trace element, metal contents)
2. Origin of salinity, of metals, ligands
3. Changes of fluid composition during mineral precipitation (mixing, dilution, boiling, cooling) – One fluid? Several fluids
4. Fluid-rock interactions- Fluid equilibrium during the different stages of fluid migration
5. Minimum temperature and pressure at the time of precipitation
6. True temperature and pressure applying pressure correction (i.e. independent geothermometer or boiling fluid)
7. Depth of formation (i.e. overlying deposits)

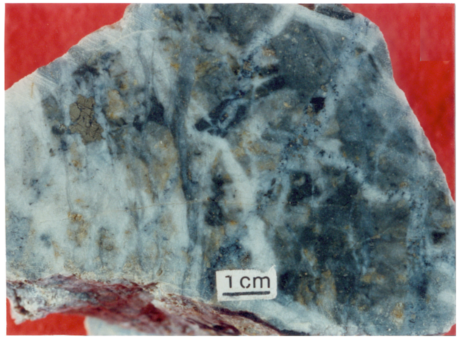
Major challenges to understand the ore formation processes

* to develop analytical techniques to measure the metal content in fluid inclusions

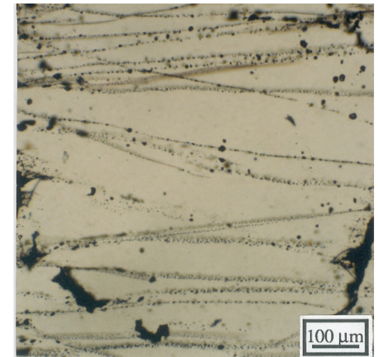
* to acquire data on metal solubility and themodynamic parameters concerning the different species in solution.

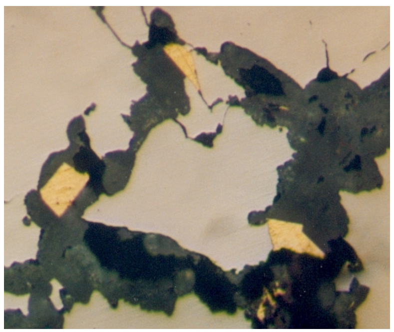
How to study fluid inclusions?

Orientated sample



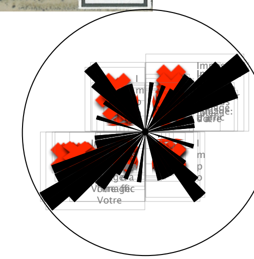
Petrography cathodoluminescence



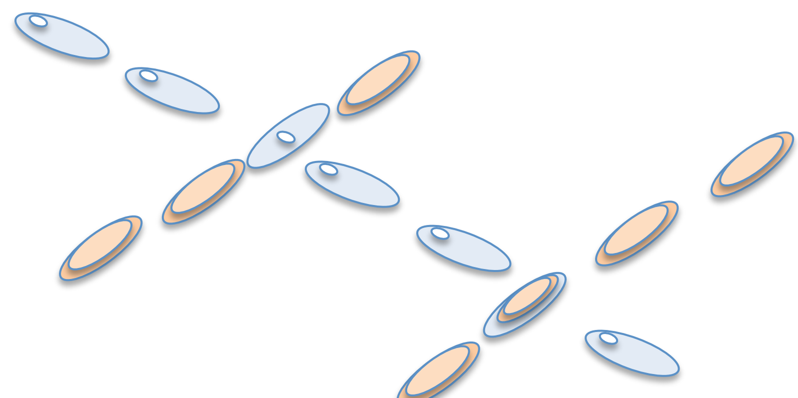


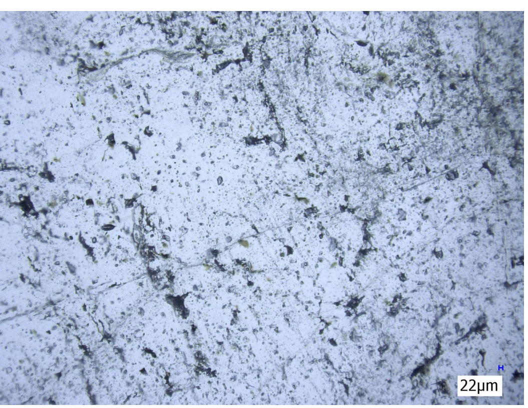
Relationships with ore and alteration paragenesis

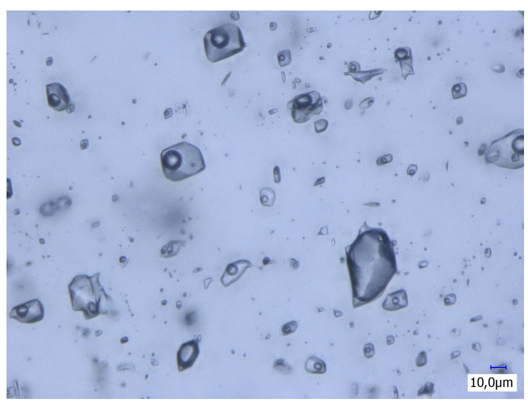
Relationships with tectonics



Typology and chronology of fluid events

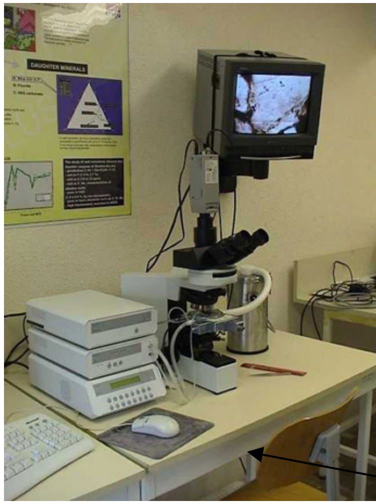




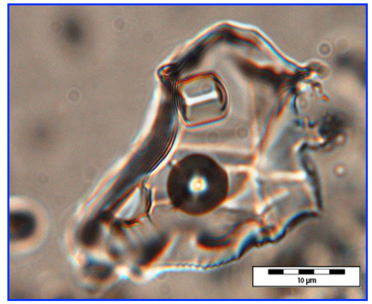


Opening and refilling of an older CO_2 rich inclusion by a water rich inclusion
Contamination of an older CO_2 rich inclusion by a water rich fluid

How to study fluid inclusions?



Individual fluid inclusion



Optical microscopy, infra-red, UV

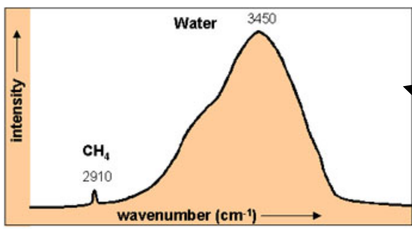
microthermometry

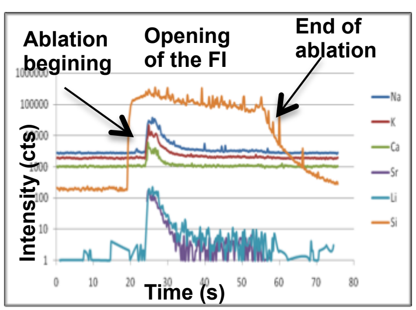
Inclusion water-gas-salts

Raman : gas, Cl

LIBS, LA-ICPMS : cations, metals

Equation of state
Liquid – vapor modelling



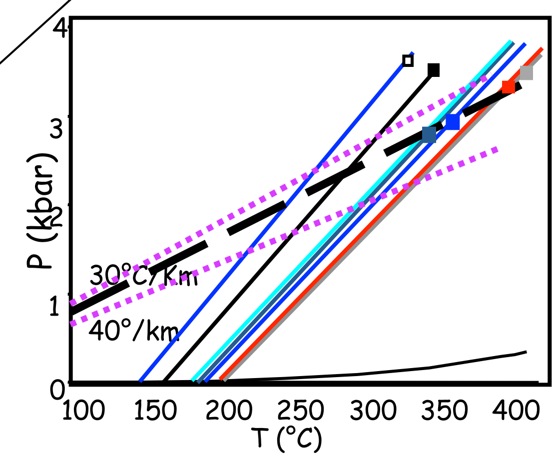


Micro-populations of fluid inclusions

Crush leach analysis
Cations anions metal halogens

Stable isotopes (C, O, H)

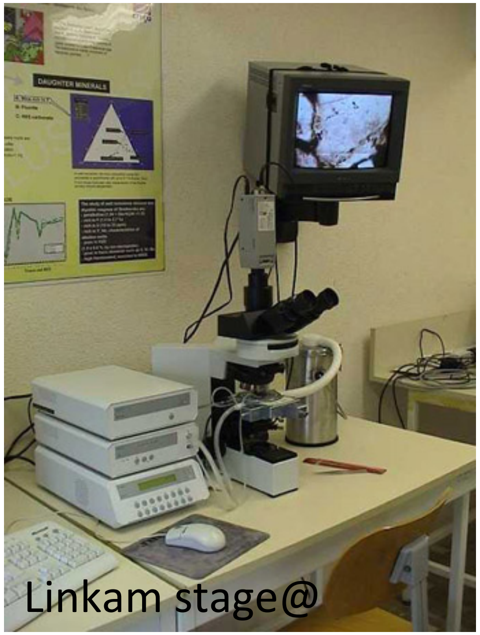
PTX of circulation



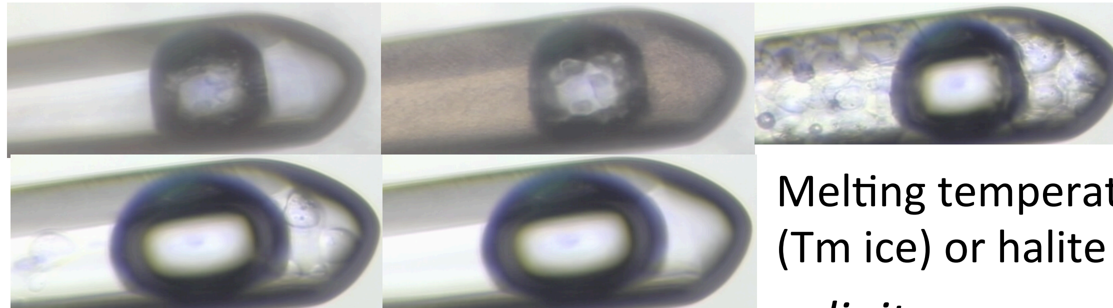
Fluids in capillaries- Synthetic fluid inclusions

EXPERIMENTAL APPROACH

Microthermometry



Observations of phase transitions during cooling and heating

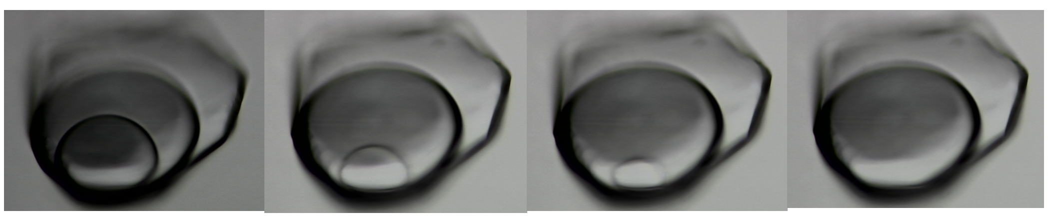


Melting temperature of ice (Tm ice) or halite (Tmh)

salinity

Melting temperature of volatile phase (Tm CO2)
indication on the presence of other gas than CO2 (CH4, N2)

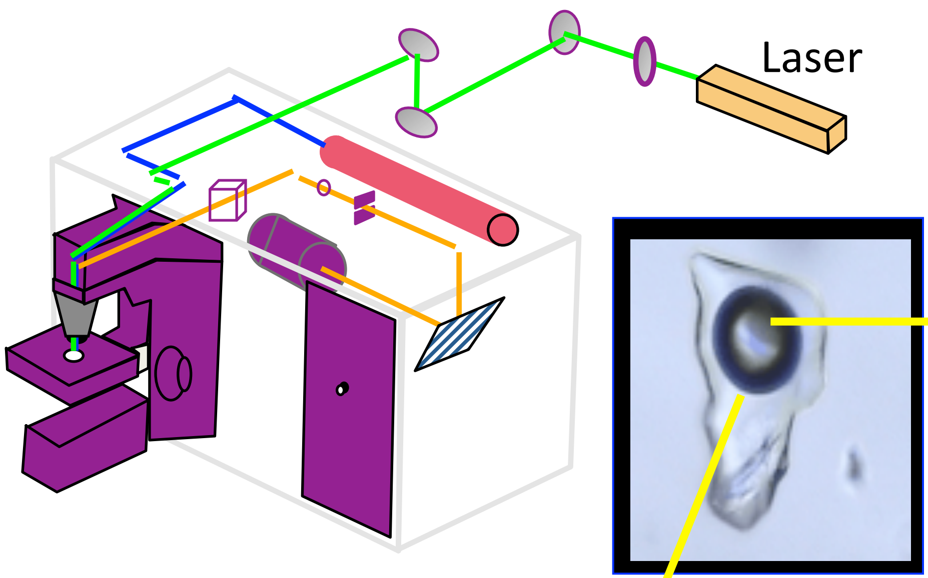
Melting temperature of chlatrate (Tm cl, gas hydrate)
salinity and density of the volatile phase

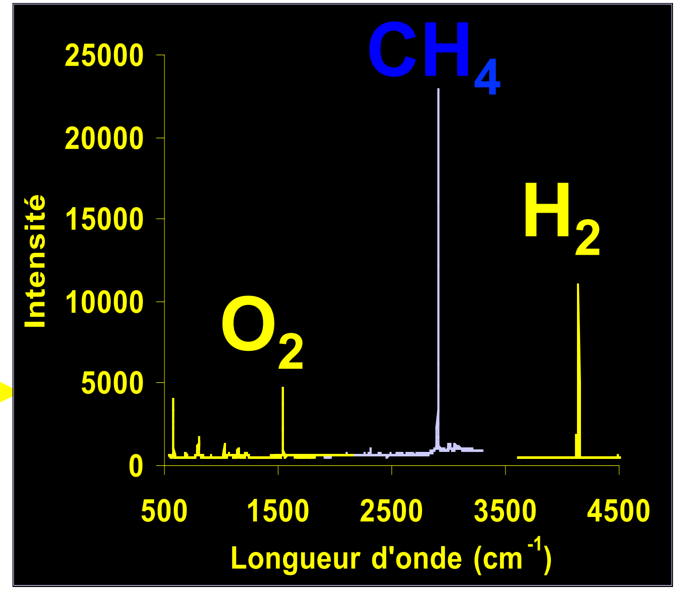


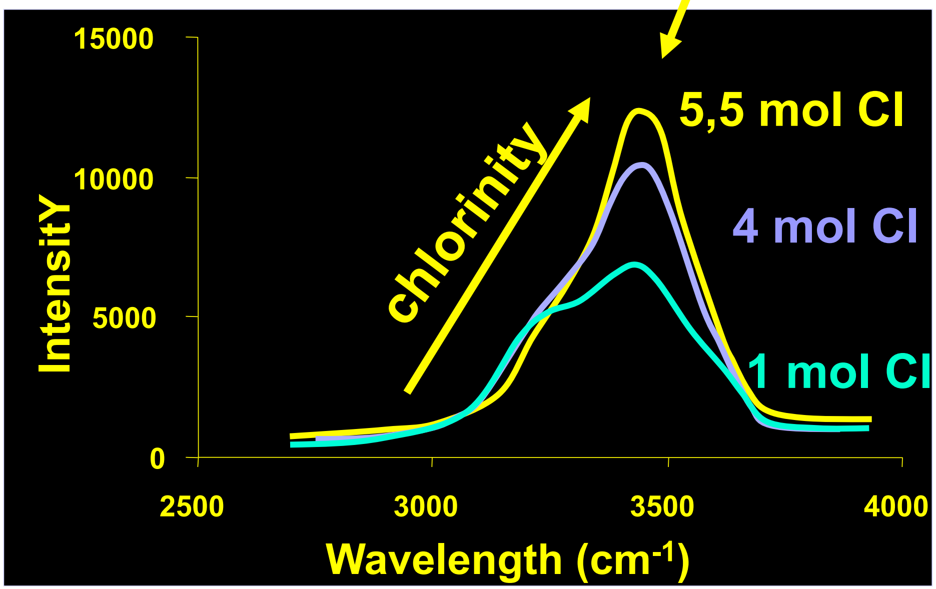
Homogenisation temperature of volatile phase (ThCO2)
density

Homogenisation temperature (Th) : *minimal trapping temperature*

Raman Spectroscopy







in situ analysis of gas
CO_2, CH_4, N_2, O_2, H_2, H_2S, …
Calculation of fO_2, fS_2

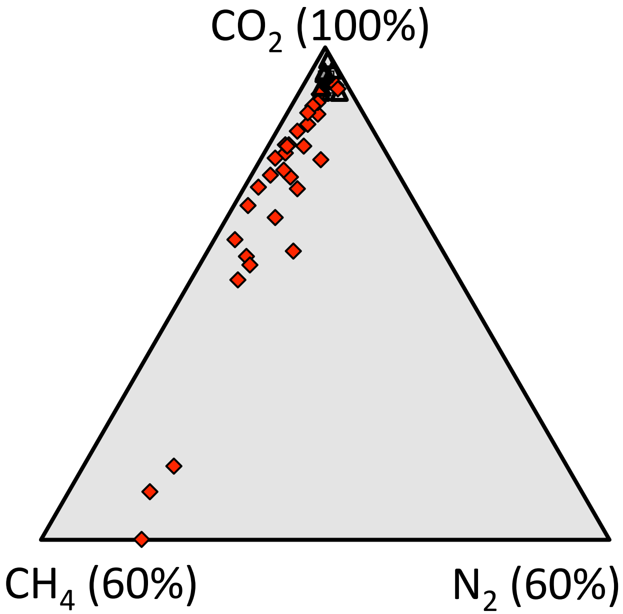
Chlorinity *(Dubessy et al. 2002, Caumon et al., 2013)*

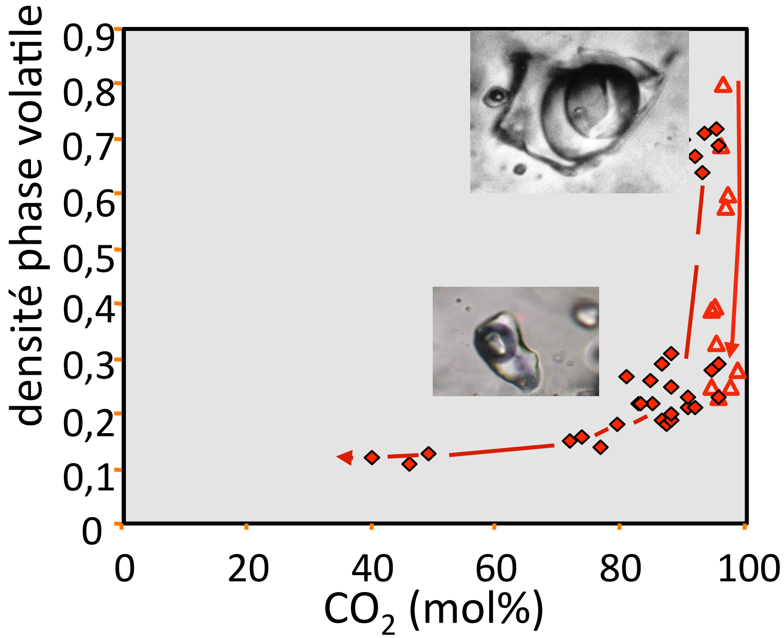
SO_4^{--}/HSO_4^- ,pH
(Boiron et al., 1999)

Determination of solids in fluid inclusions

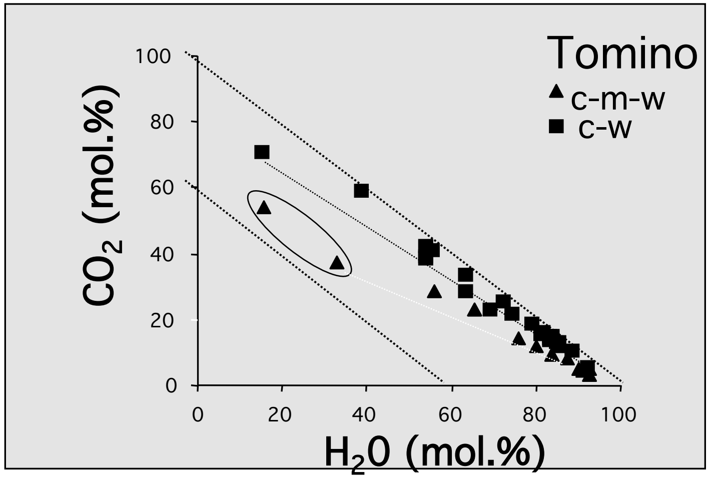
Fluids in Gold deposits from the hercynian belt

Composition of the volatile phase





Bulk composition



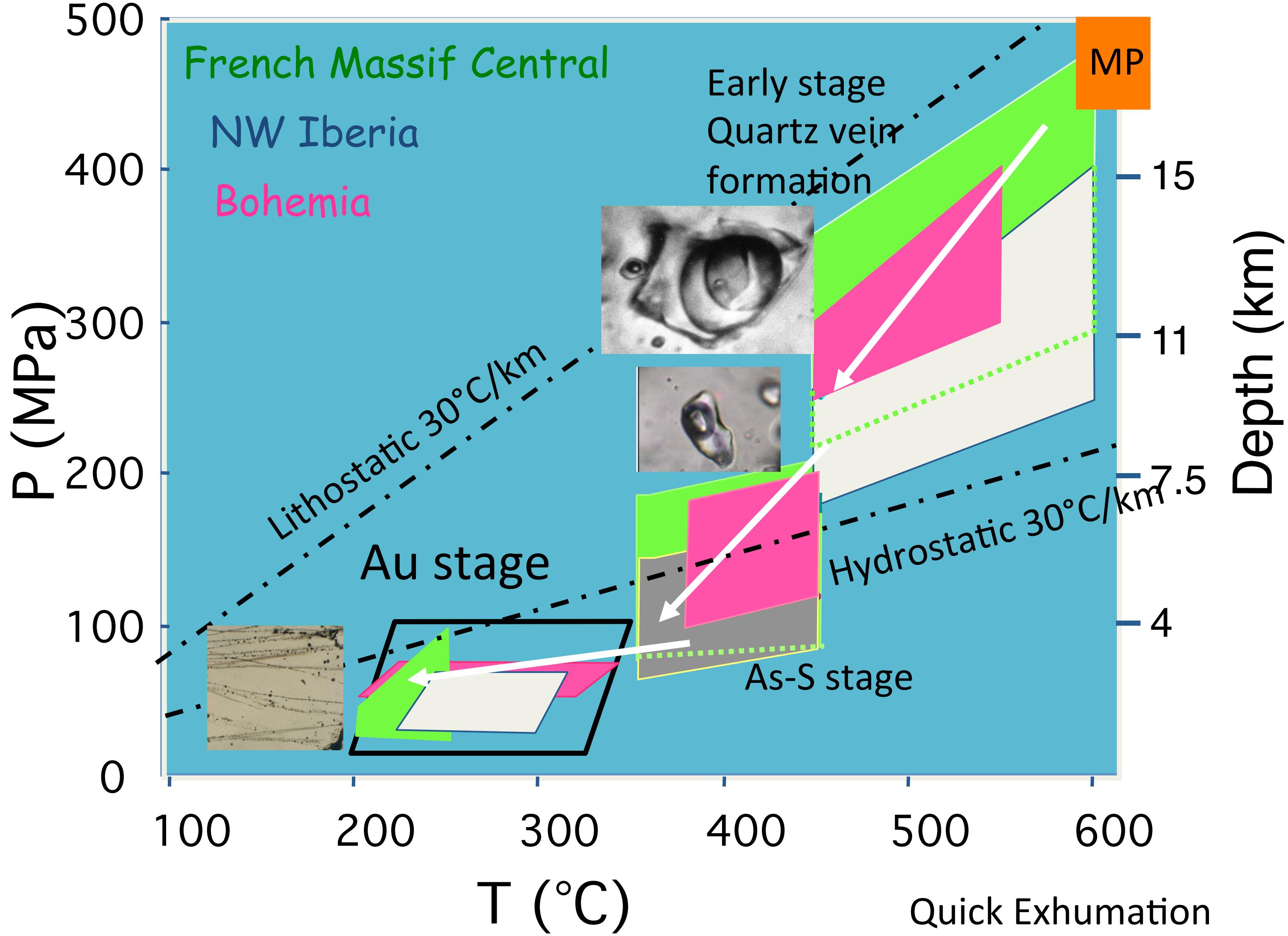
- ✧ CO_2 dominated fluids equilibrated with metamorphic host rocks

- ✧ Decrease of the density of the volatile phase
- ✧ Increase of CH_4 content
- ✧ Pressure drop

Boiron et al., 2003, Chem. Geol

Gold deposits in Western Europe

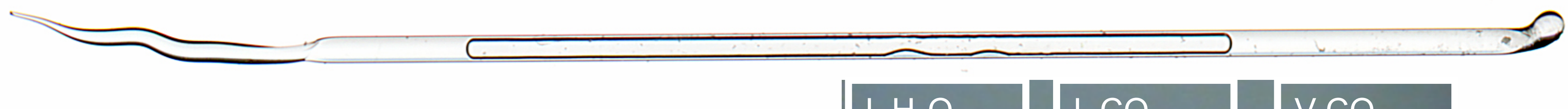
Pressure - temperature conditions

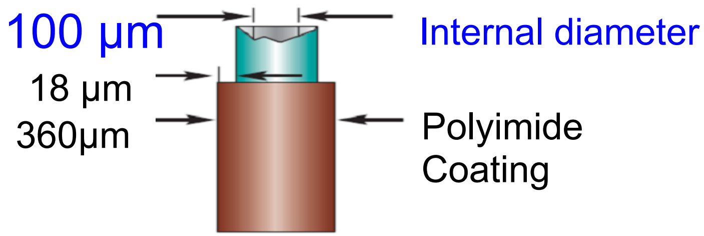


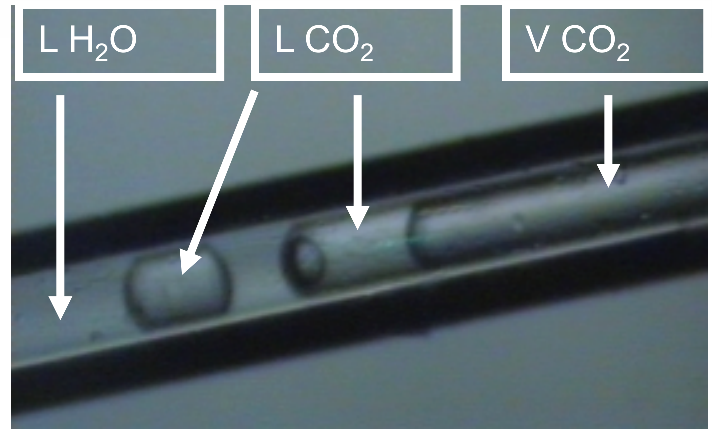
Boiron et al., 2003, Chem. Geol

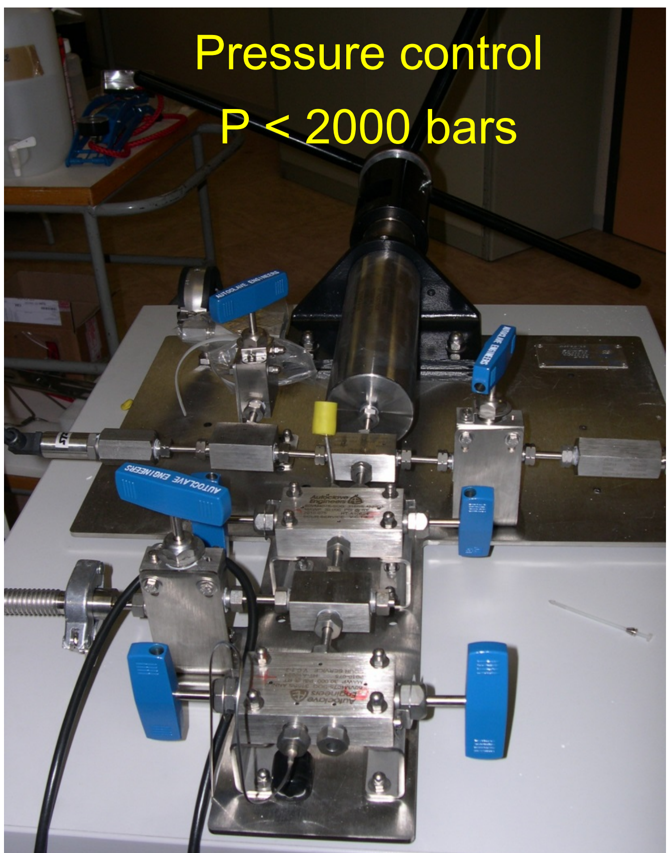
Quick Exhumation
Lithostatic -> hydrostatic

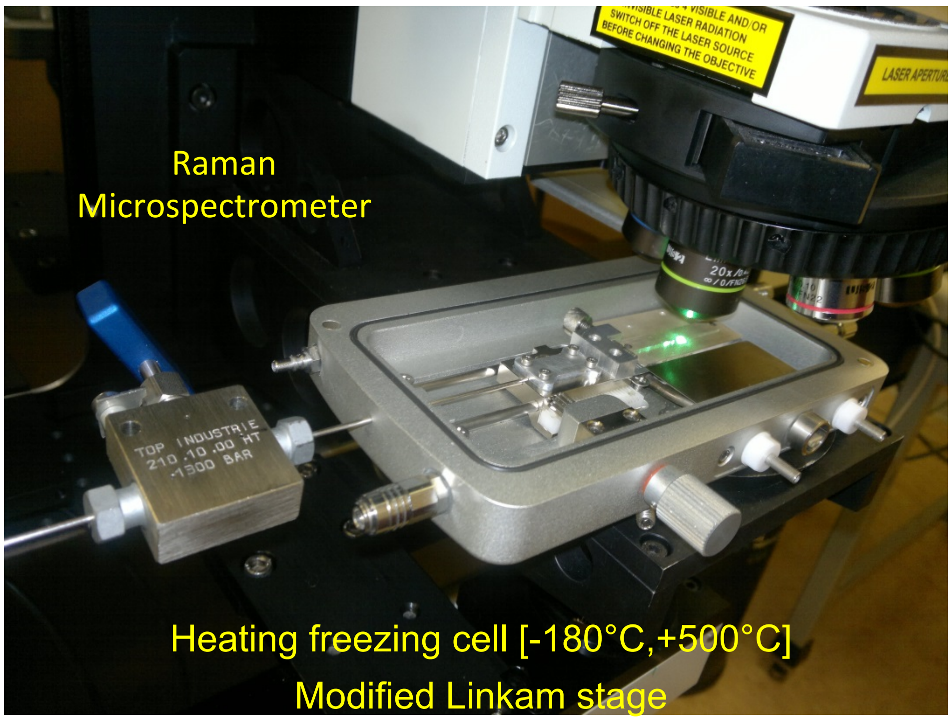
Experimentation using silica capillaries











Developped by J. Dubessy

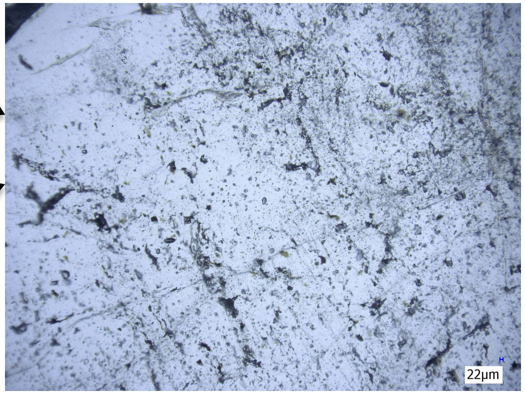
Isotopic signature of the fluids

*The **mineral hosting fluid inclusions** (quartz, carbonate, $\delta^{18}O$, $\delta^{13}C$) and recalculation of isotopic signature of the fluid ($\delta^{18}O$) for the temperature of fluid circulation

*The **gas and liquid** extracted from **fluid inclusions** after decrepitation or crushing (H_2O - CO_2- CH_4), $\delta^{13}C$, δD

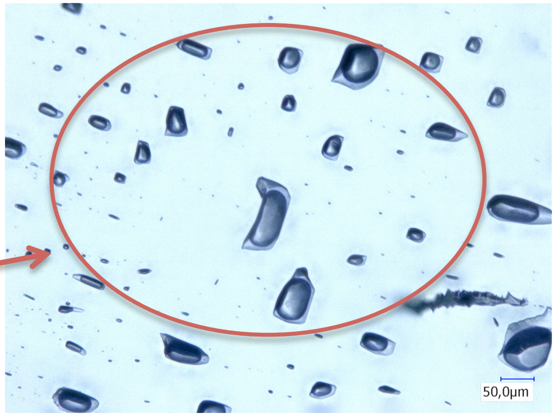
* Noble gas He, Ar, Ne, Xe, Kr,

***extracted liquid** (crush-leach) from fluid inclusions
+ Cl, $\delta^{37}Cl$
+ radiogenic isotopes U, Pb, Sr, Rb after separation on columns

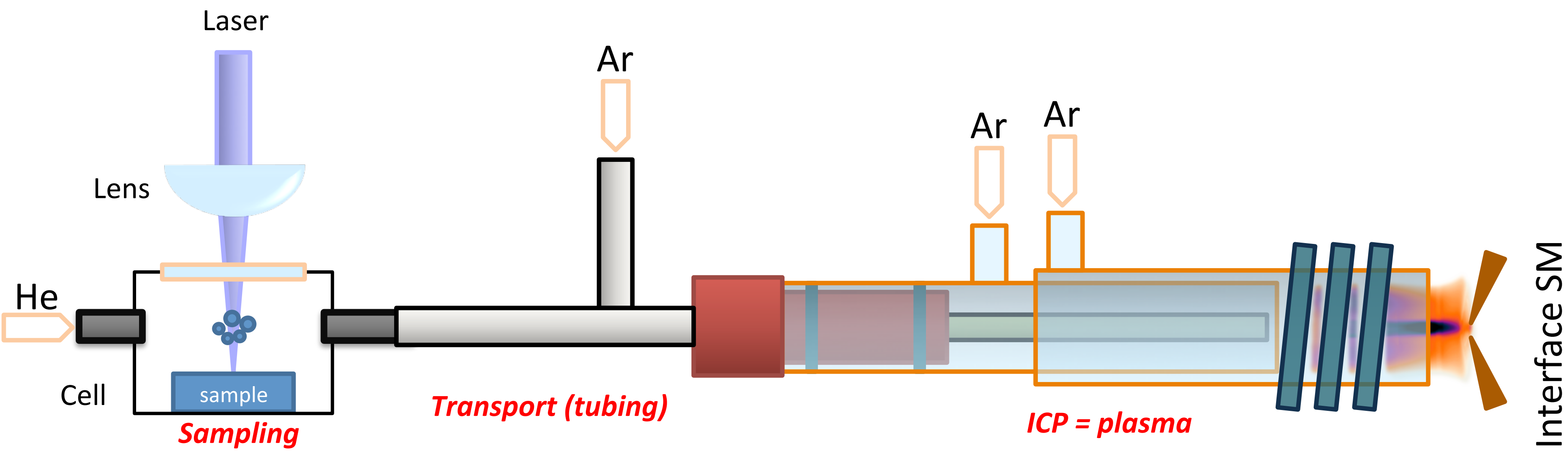


Mixing fluid inclusion populations

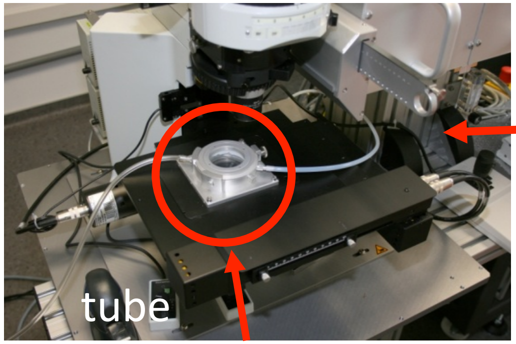
The challenge : to decrease the sample volume from small chips of wafer to **individual fluid inclusions** or **a group of fluid inclusions**



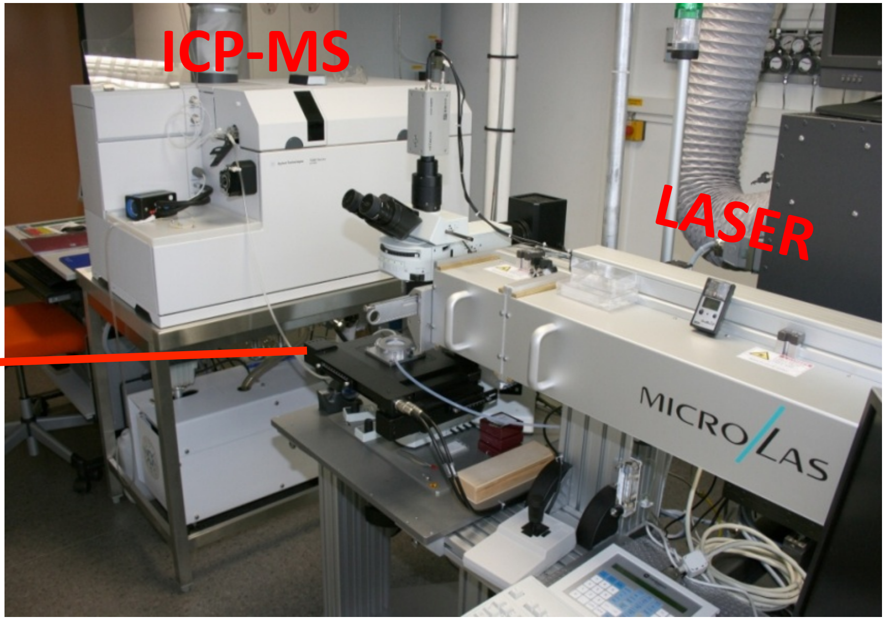
Laser Ablation-ICPMS

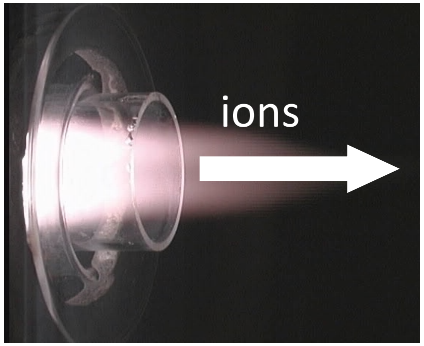


(MicroLas Pro - Agilent 7500)



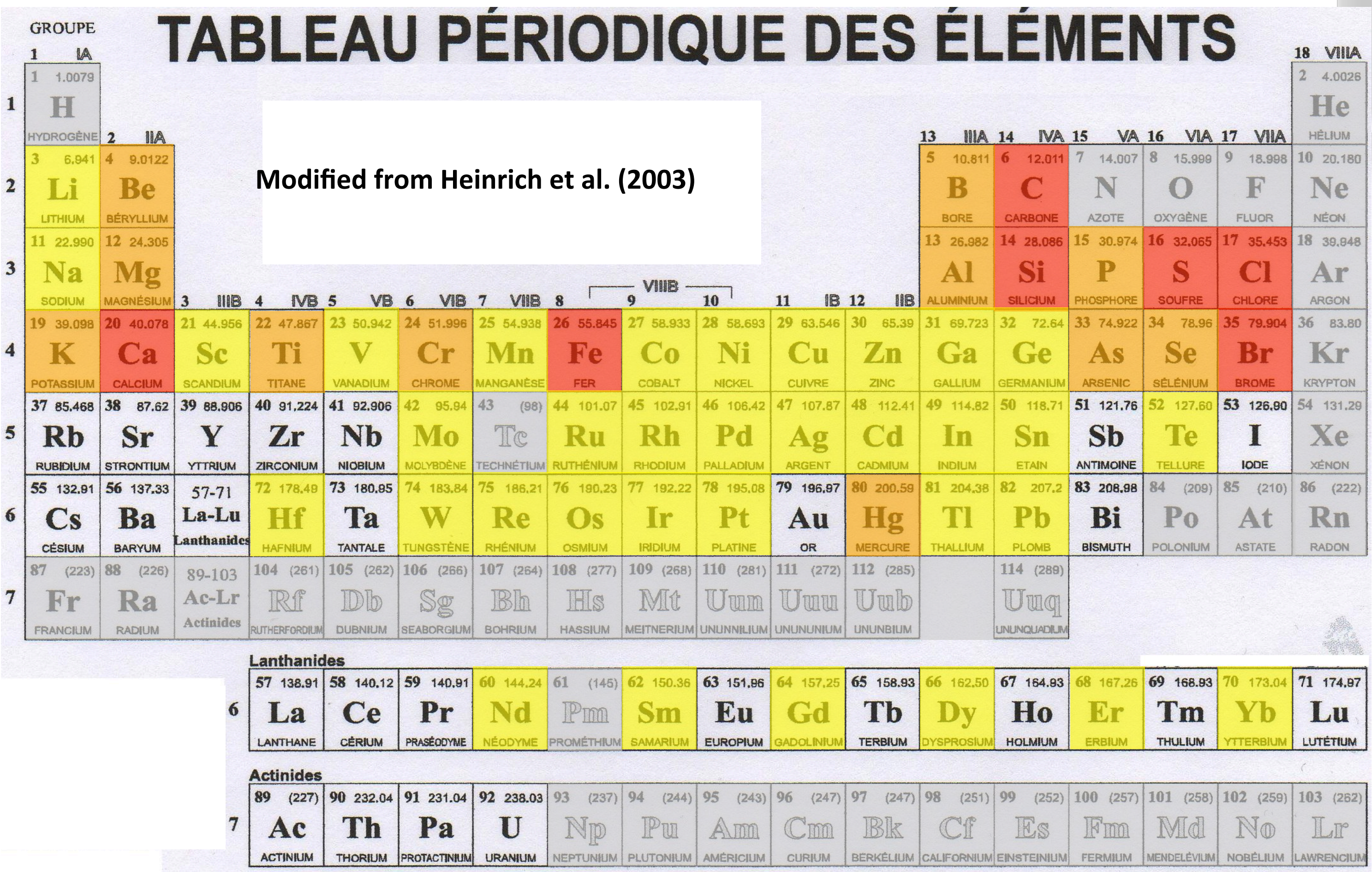
Ablation cell





Plasma torch

Ionisation



Detection limit

$Ø_{cratère}$: 40 µm

solide

- 10 µg/g (ppm)
- 1 µg/g
- 100 ng/g (ppb)
- 10 ng/g
- undetectable

ICP-MS Quadripolar

For fluid inclusions: X 10-20

Most of metals can be measured at concentration around 1 ppm in fluid inclusions (depending on salinity and size of the inclusions)

Laser Ablation-ICPMS : The chemistry of individual fluid inclusion

Formation of a Magmatic-Hydrothermal Ore Deposit: Insights with LA-ICP-MS Analysis of Fluid Inclusions

Andreas Audétat,* Detlef Günther, Christoph A. Heinrich

Science, 279, 2091-2094

Gold concentrations of magmatic brines and the metal budget of porphyry copper deposits

T. Ulrich*, D. Günther*† & C. A. Heinrich*

** Isotope Geology and Mineral Resources, Department of Earth Sciences, ETH Zentrum 8092 Zürich, Switzerland*

Nature, 399, 676-679

Giant uranium deposits formed from exceptionally uranium-rich acidic brines

Antonin Richard[1]*, Christophe Rozsypal[1], Julien Mercadier[1†], David A. Banks[2], Michel Cuney[1], Marie-Christine Boiron[1] and Michel Cathelineau[1]

Nature Geoscience, 5, 142-146

Metal Concentrations in Crustal Fluids and Their Relationship to Ore Formation

Bruce W. D. Yardley†

School of Earth and Environment, University of Leeds, Leeds LS2 9JT, United Kingdom

Economic Geology, 100, 613-632

Anomalously Metal-Rich Fluids Form Hydrothermal Ore Deposits

Jamie J. Wilkinson,[1,2]*† Barry Stoffell,[1]‡ Clara C. Wilkinson,[1,2]† Teresa E. Jeffries,[2] Martin S. Appold[3]

Science, 323, 764-767

Determination of Cl and Br concentrations in individual fluid inclusions by combining microthermometry and LA-ICPMS analysis: Implications for the origin of salinity in crustal fluids

Mathieu Leisen, Marie-Christine Boiron *, Antonin Richard, Jean Dubessy

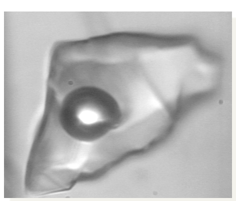
Université de Lorraine, G2R, CNRS, CREGU, Boulevard des Aiguillettes, B.P. 70239, F-54506, Vandoeuvre-lès-Nancy, France

Chemical Geology, 330-331, 197-206

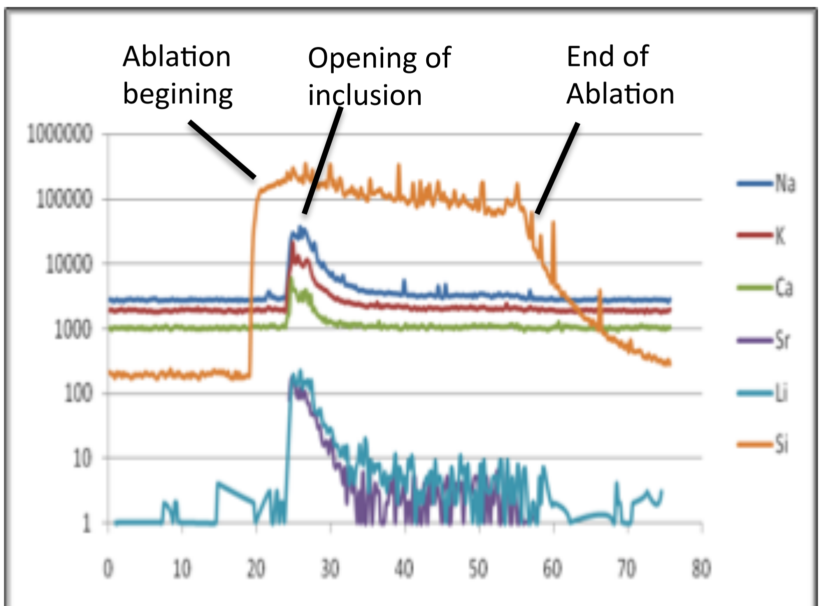
Recent developments in element concentration and isotope ratio analysis of individual fluid inclusions by laser ablation single and multiple collector ICP-MS

Thomas Pettke [a,*], Felix Oberli [b], Andreas Audétat [c], Marcel Guillong [d], Adam C. Simon [e], Jacob J. Hanley [f], Leonhard M. Klemm [g]

Ore Geology Review, 44, 10-38



10^{-9} g to be analyzed



[Major] : Na, Ca, K, Mg, …

[Metal] : Cu, Zn, Pb, Sn, W, Au, U, …

[Trace] : Li, B, Br ,…

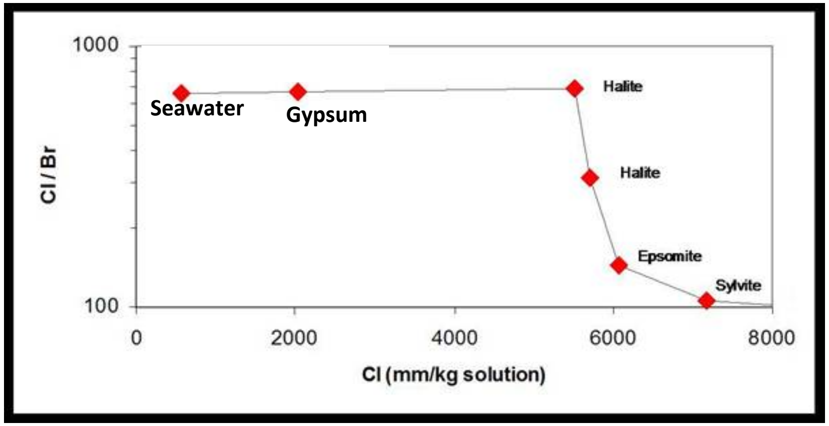
Origin of salinity – Halogen signature

Primary Brines

- Exsolution during crystallisation of magmas.

Granitoids and associated mineralisations
Cu-Mo-Ag-Au porphyries , rare metal granites

- Seawater evaporation



U, Pb Zn, Ag deposits
(unconformity sedimentary
basin/crystalline basement

Fontes et Matray, 1994.

Secondary Brines :

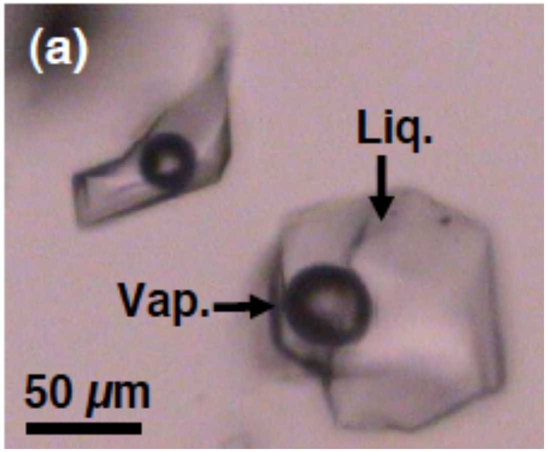
- dissolution of salt deposits (evaporites)

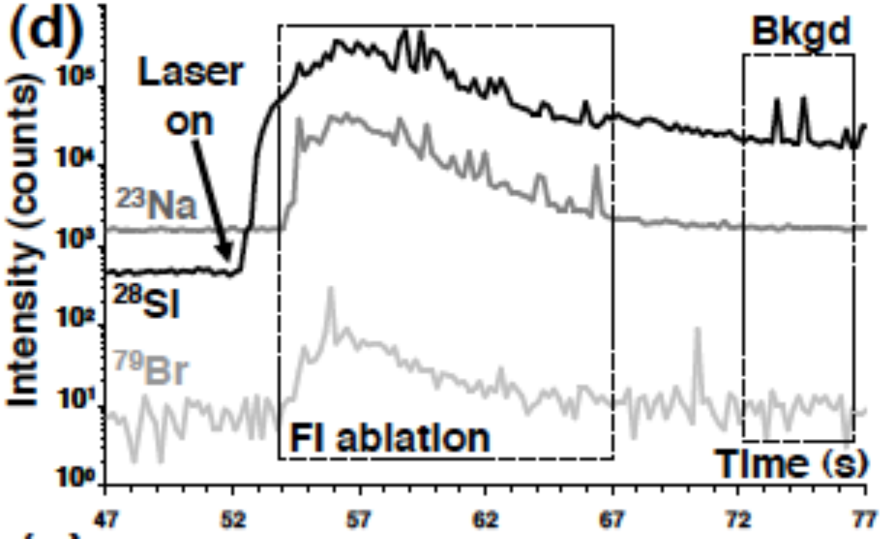
Emeralds

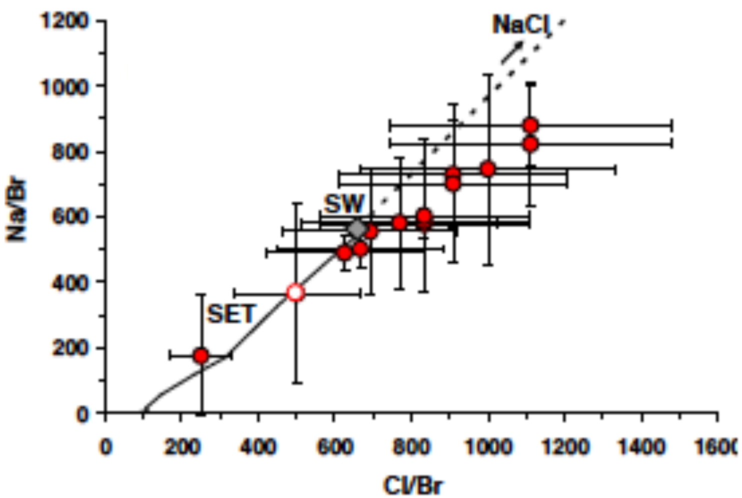
- Water loss of chlorine solution during hydration reactions (retrograde metamorphism)

Gems

Br analysis in individual fluid inclusions
Origin of fluid responsible of talc deposition



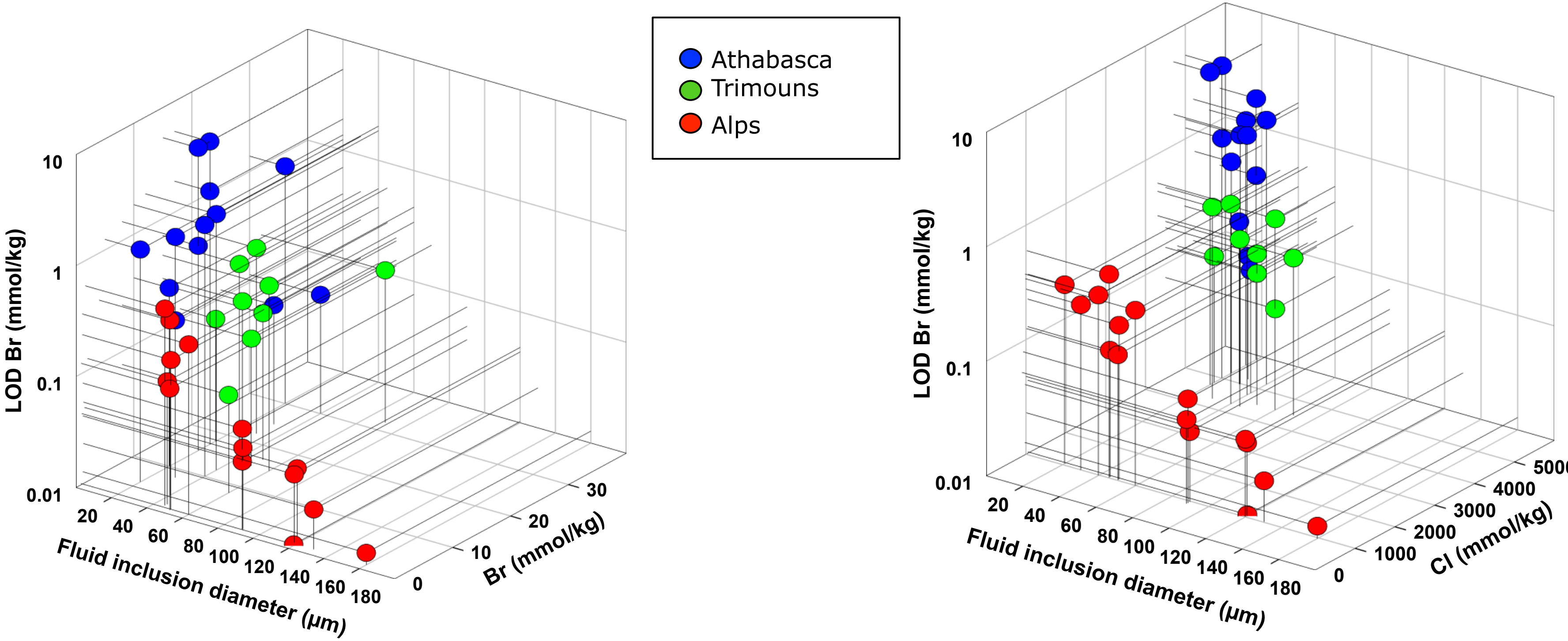


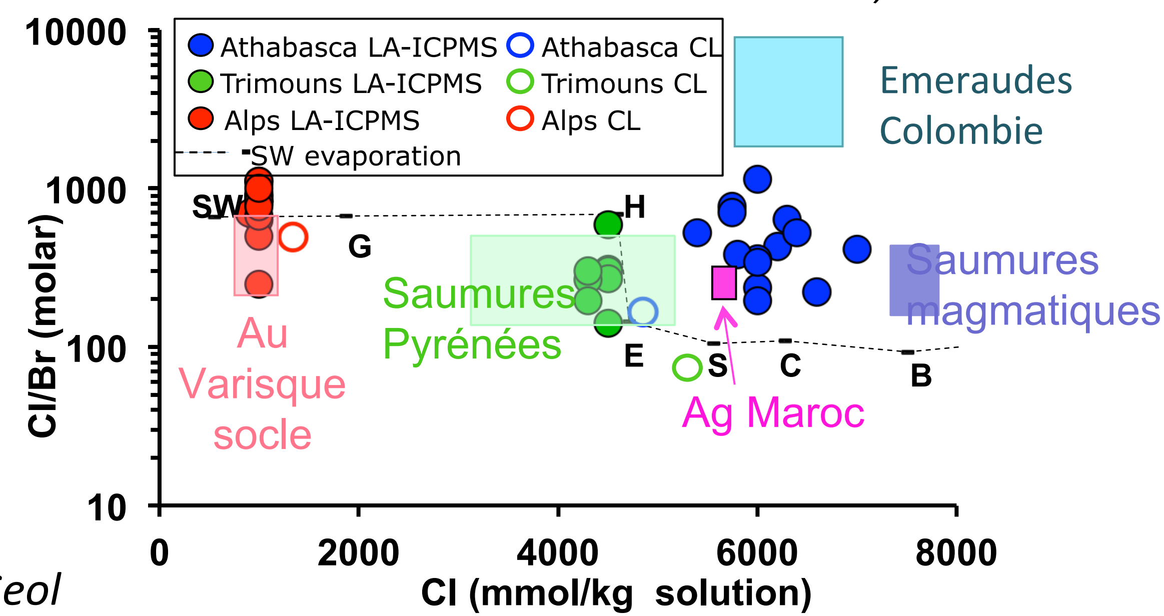


Cl : 5 mole/kg
Br : 8 à 30 mmole/kg

Cl / Br ratio typical of seawater having passed halite saturation

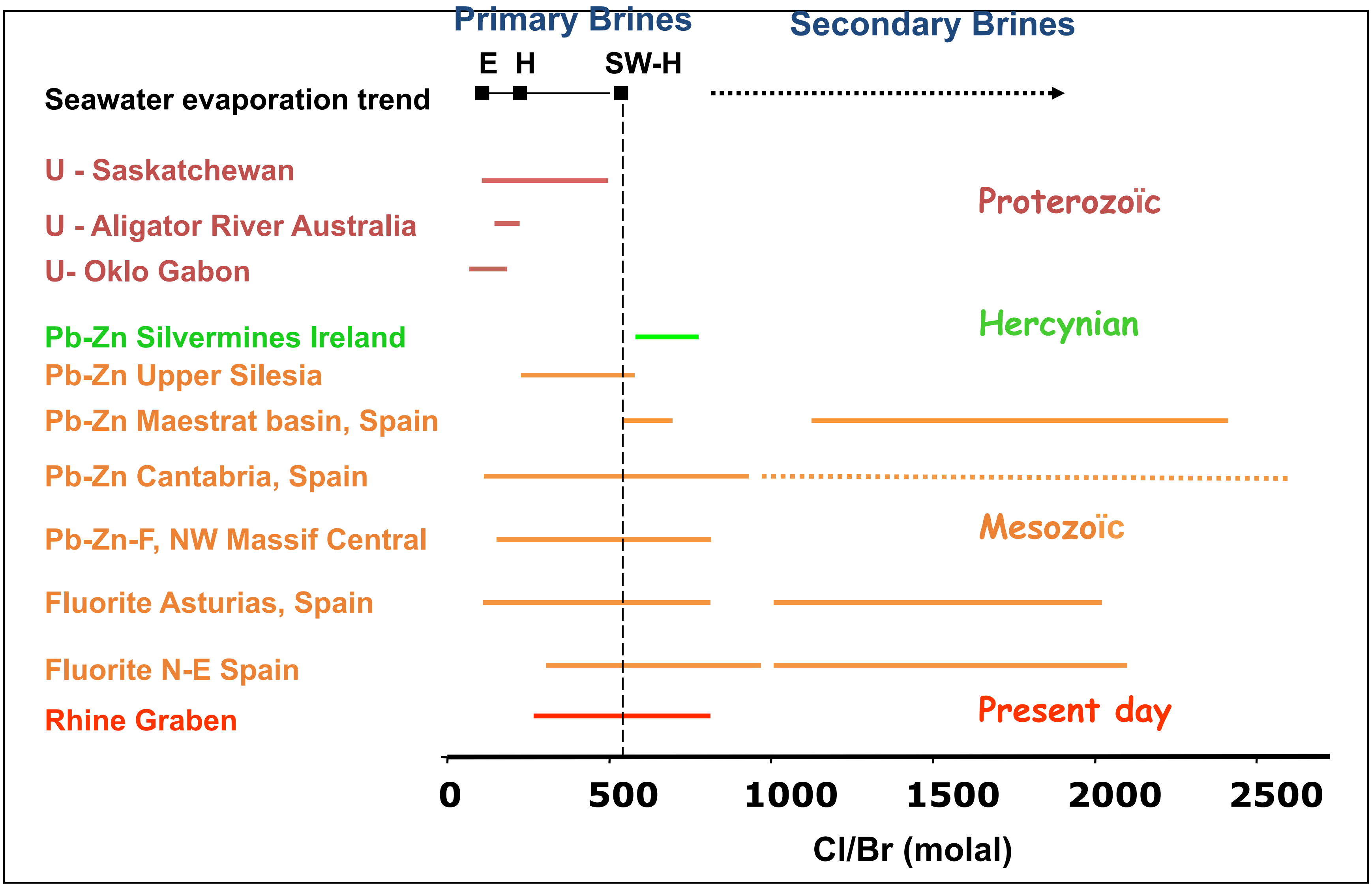
Leisen , Boiron, Richard and Dubessy, Chemical Geology, 2012





Leisen et al., 2012, Chem Geol

Origin of fluids - Halogen signature



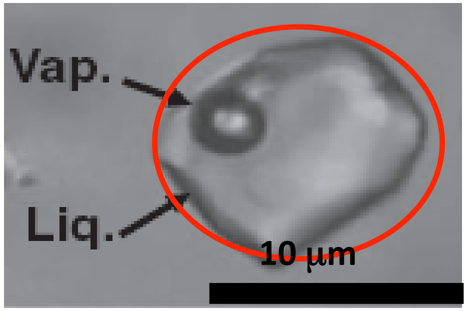
Brines circulating at the unconformity between basement and sedimentary cover

Boiron et al, 2010, Geofluids

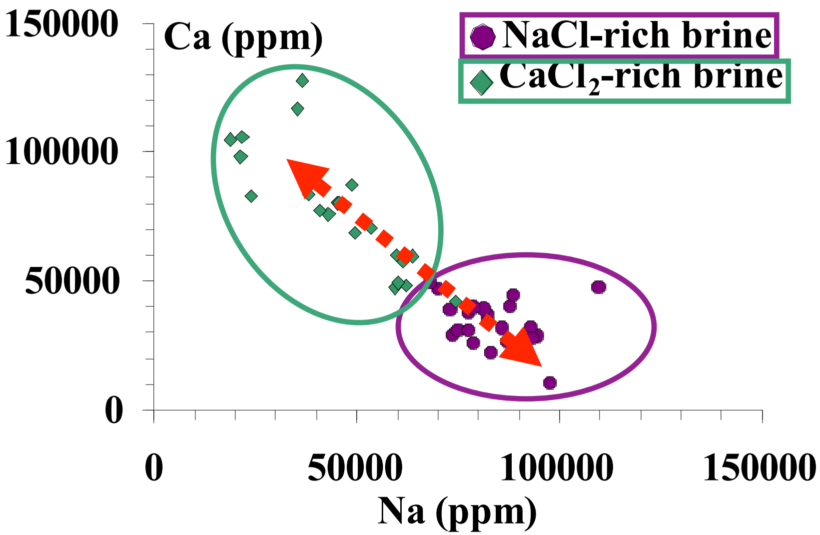
Uranium deposits –Athabasca basin - Canada

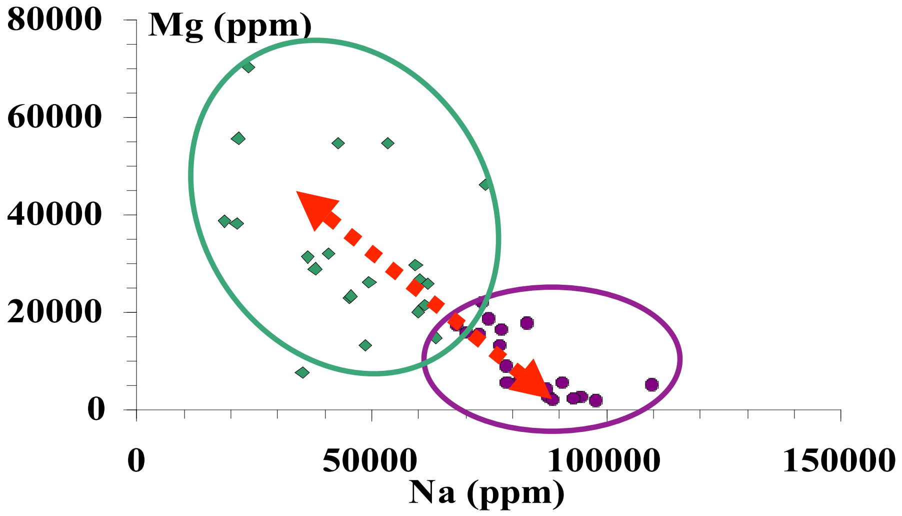
NaCl-$CaCl_2$ – ($MgCl_2$ – KCl) brines

150°C - 6 mol/l Cl



Fluid inclusion in quartz

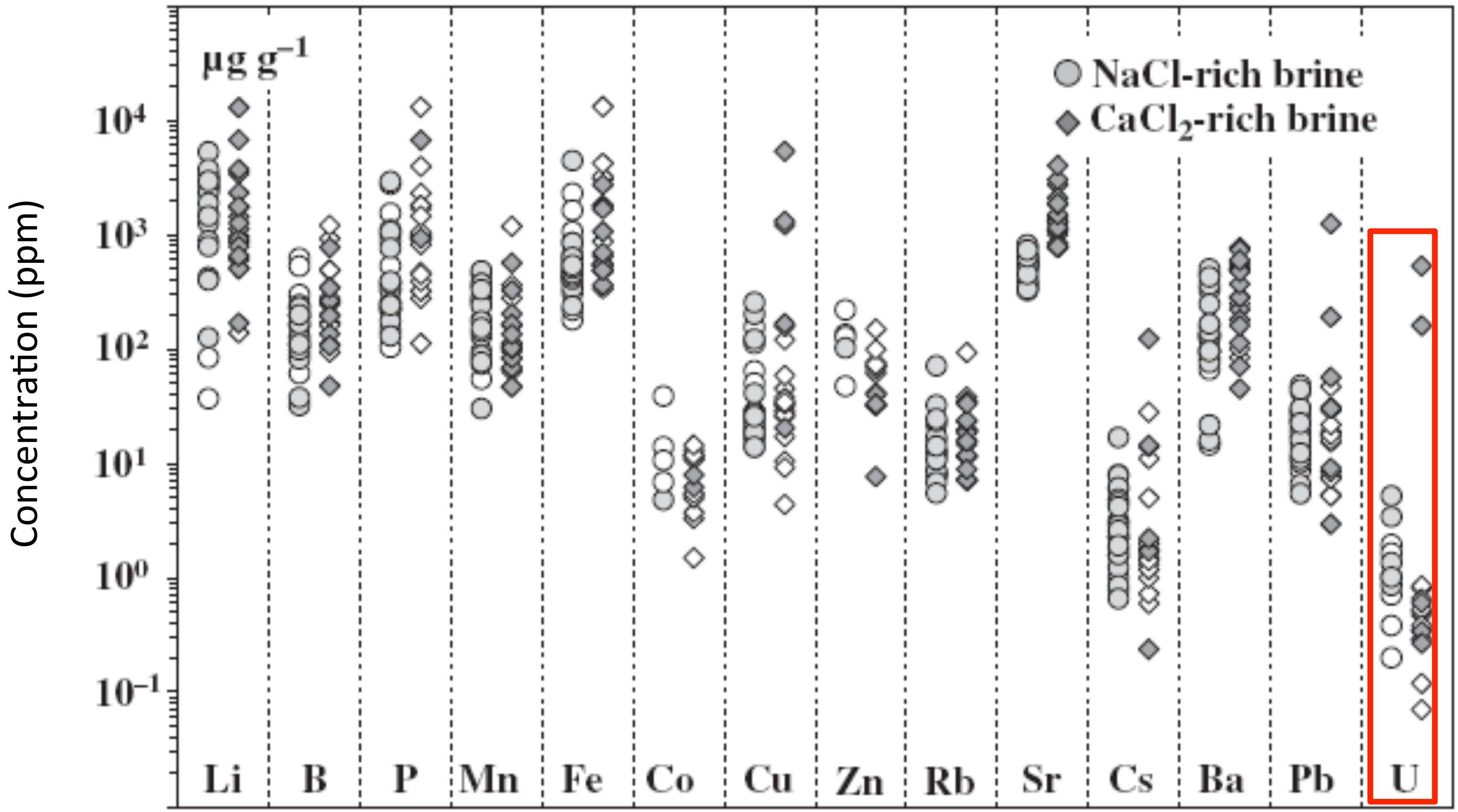




Sodic brine: Na-Ca-Mg-K-Sr with Na>Ca+Mg

Calcic brine: Ca-Mg-Na-K-Sr with Ca+Mg>Na

Chemistry of the brines

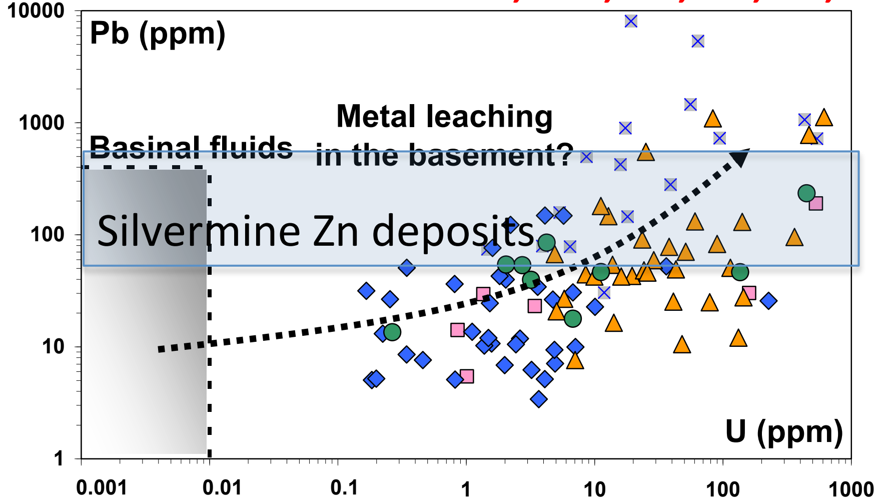


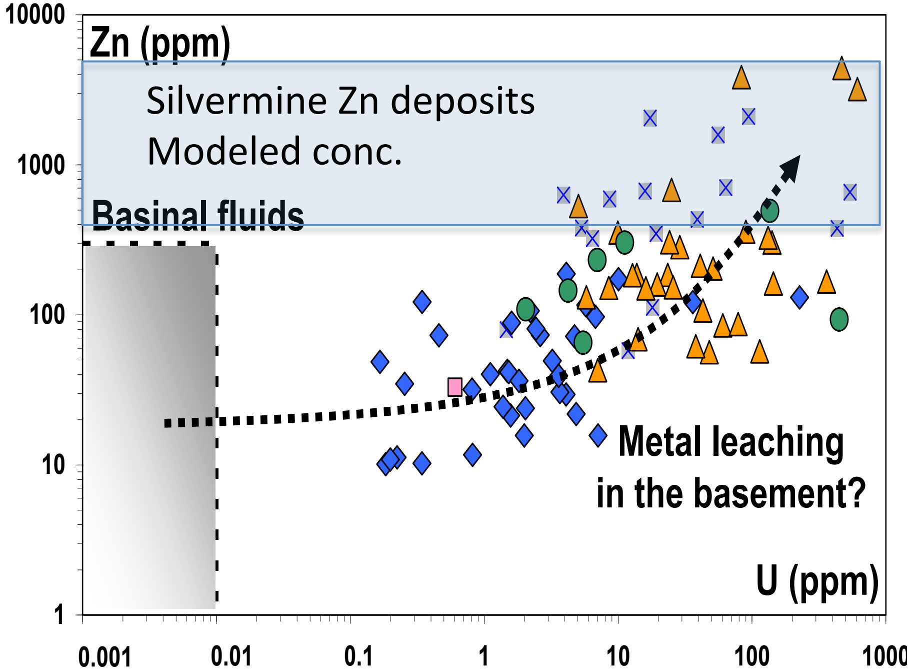
High contents of Uranium and other metals (Pb, Zn , Cu, …) in the two brines

Richard et al. , *Terra Nova, 22,* 303-308

Huge U concentration in fluids, but also in other metals

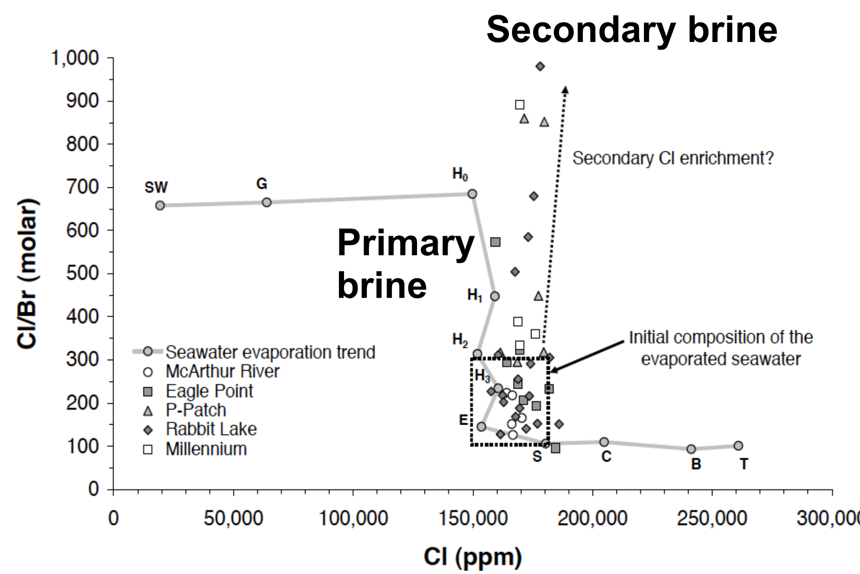
Fluid enriched in Fe, Mn, Cu, Pb, Zn, Li, Sr





Richard A., et al., 2015, Mineralium Deposita

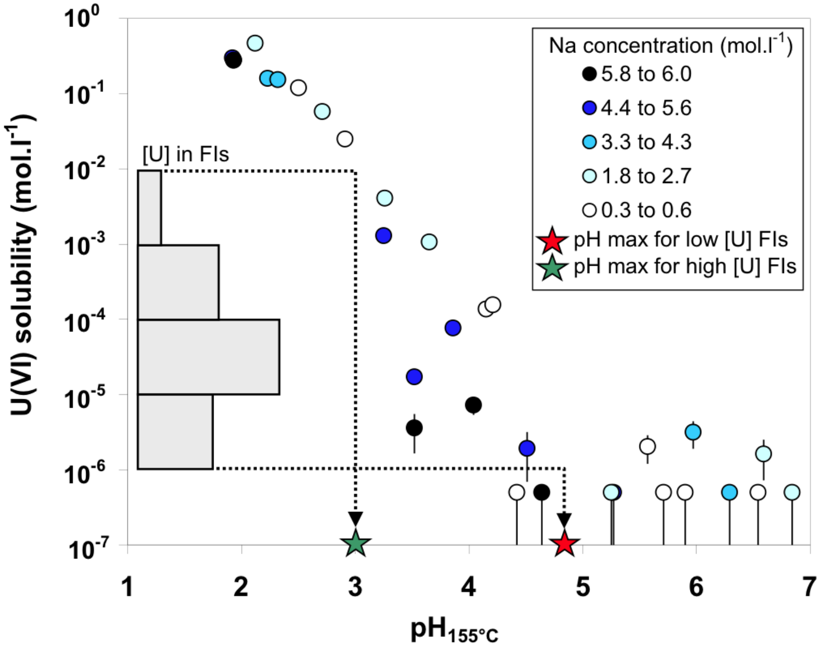
Origin of fluids



Brine resulting from seawater evaporation having passed halite saturation

Possible mixing with secondary brine percolating through evaporitic level

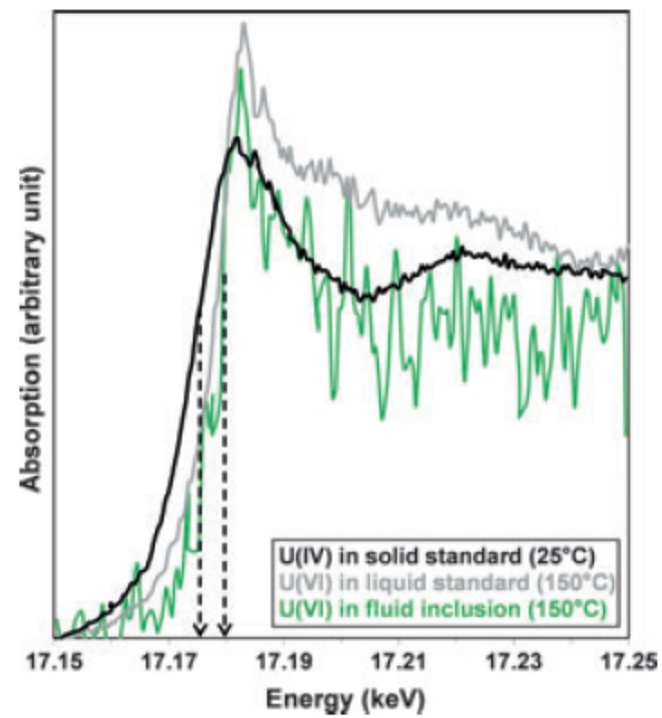
Experimental



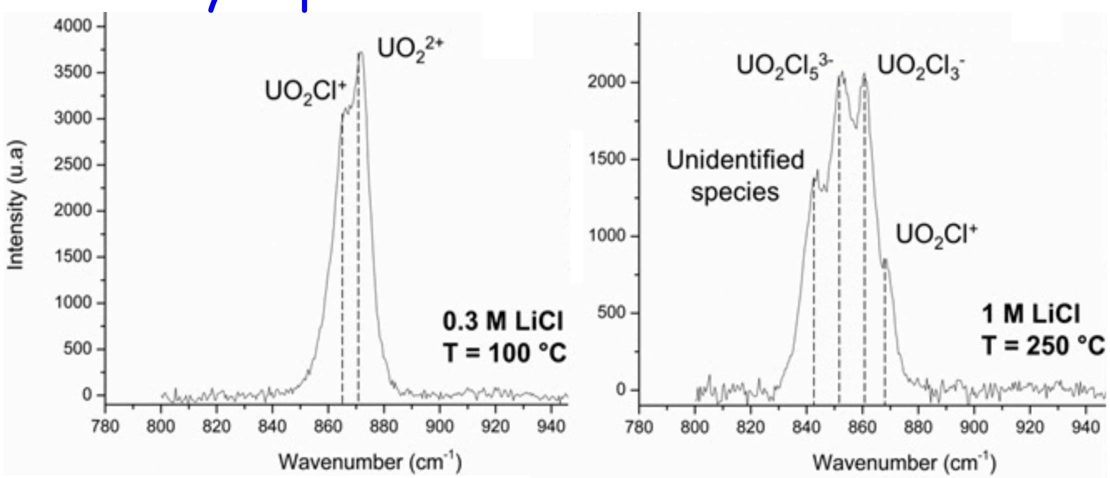
Brine enriched in U in agreement with experimental data in the NaCl-U(VI)-H_2O system at T=155°C and pH = 4-5

Richard et al., 2012, Nature Geosciences

Synchrotron XRF and XANES study of U speciation in fluid inclusions



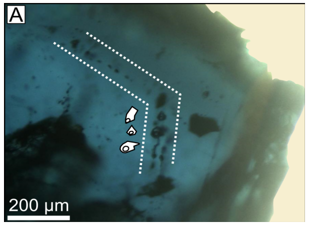
Raman Spectroscopy in silica capillary
Uranyl Speciation 20°C to 250 °C

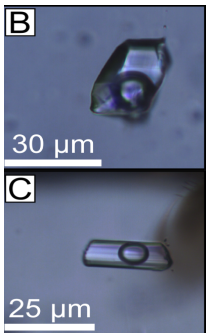


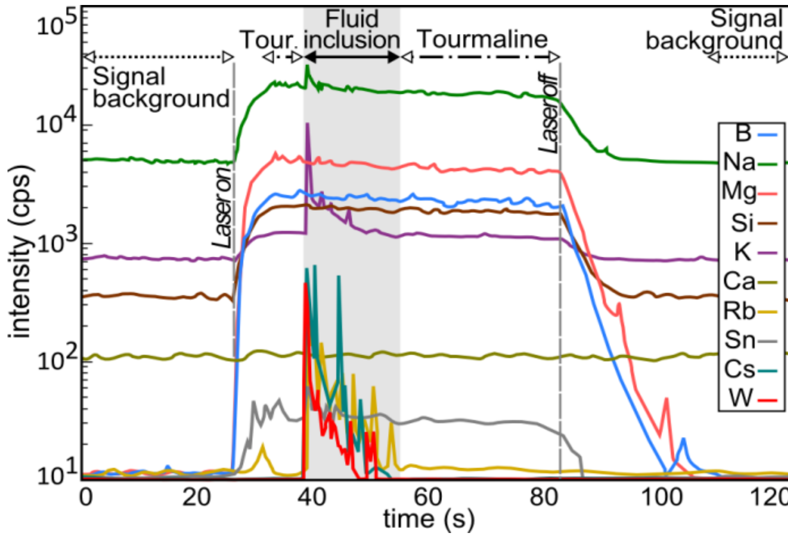
Dargent, 2014, PhD Thesis
Dargent et al., 2013, European Journal of mineralogy

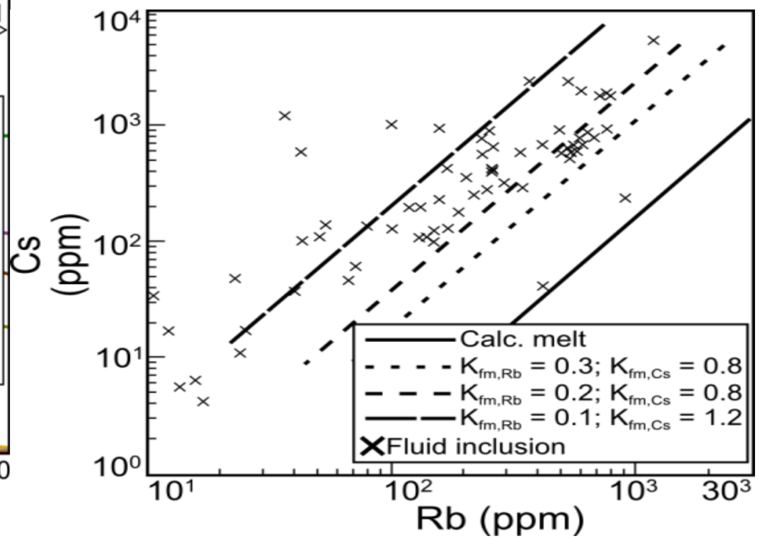
Richard et al., 2012, Geofluids

Fluid fractionation of Tungsten during granite pegmatite differentiation Karagwe –Ankore Belt - Rwanda



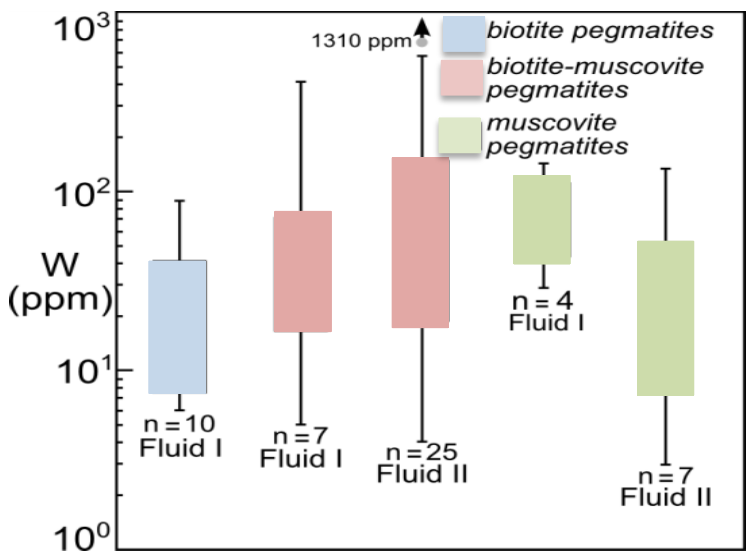


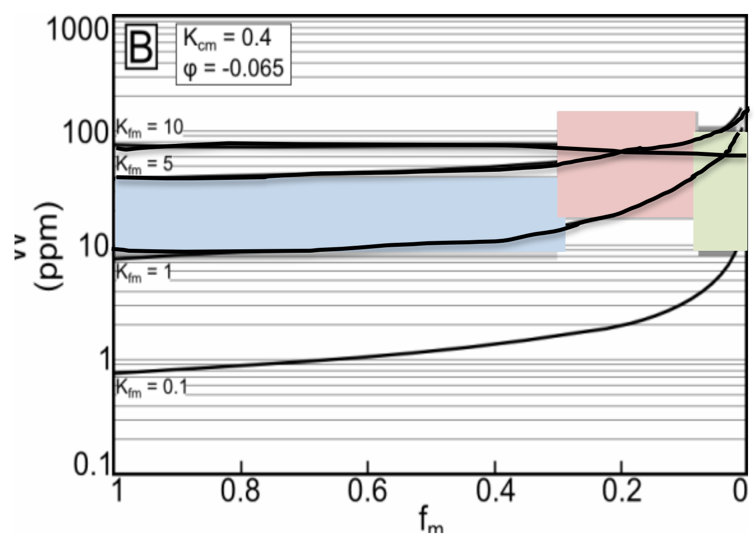




Fluid 1 : 9 wt % eq.NaCl
Th : 280°C

Fluid 2 : 17-20 wt % eq.NaCl
Th : 380°C





W : 5 to 500 ppm – Sn : 10-60 ppm

The fluid phase: experimentation and modeling : Property of fluids, metal speciation, fluid-rock interactions

Natural samples
Chemsitry of
(paleo)-fluids

Analysis

Paleofluids
Microthermometry
MicroRaman MicroLIBS
LA-ICP-MS
Fluorescence-synchrotron
Isotopic signature

Speciation
of metal
XANES, EXAFS
(experimentation, in situ analysis of experimental and natural fluids

Thermodynamic Modeling

- V-X,P-T; equations ofstate (water-gas-salts),
- organic species and thermodynamic todeling
- pH

- Fluids ⇔ Mineral equilibria

Role of solvent: HP-HT mixing H_2O-gas-salt
Raman

Structure and dynamic of fluids at the sacale of molecules(Spectroscopy)