Geochemical exploration in geothermal research: introduction

types of fluid emission

1 - overheated (over the critical point of water = 371°C) fumaroles (T up to 1150 °C)

2 - saturated fumarole along the water boiling curve (generally up to 160°C steam)

3 - boiling fumaroles at atmospheric pressure (90-100 °C)

4 - boiling mud pool containing steam condensate at 90-100°C, generally very acidic (up to pH=0)

5 - boiling springs (>90°C, high flow rate)

6 - thermal springs (>20-90 °C)

7 - cold gas bubbling pool (cold stagnant water, sometimes very acidic)

8 - dry gas vent

Geodynamic environments

-subduction zone — back arc / main thrust / foredeep

- back arc
- main thrust
- foredeep

-accretionary complexes

-rift areas (intraplate)

-cratonic areas (stable)

-strike-slip faults (San Andreas-type)

cratons

- -no active volcanism
- -thermal springs along regional faults
- -gases N_2-and ^4He-rich; low $^3He/^4He$
- -low fluid pressure along faults

strike-slip faults (San Andreas)

- -N_2 (CO_2 e CH_4)-rich thermal springs
- -variable $^3He/^4He$ ratio (sometimes high)
- -high fluid pressure in faults

accretionary complex

- -sediments loading (subsidence)
- -formation of hydrocarbons (CH_4)
- -saline diapirs, connate waters, mud volcanoes

intraplate rift

- -fluids similar to orogenic areas since they are activated by subcrustal magmas (CO_2, ^3He)

subduction zones

back arc areas

- -crust in extension
- -mantle magma intrusions (^3He)
- -granites
- -metamorfism and metasomatism (skarns)
- -hydrothermal (geothermal) systems
- -condensazion zones (CO_2, H_2S, H_2 escape)
- -water-rock interaction (t-dependent)
- -fumaroles, thermal springs, CO_2

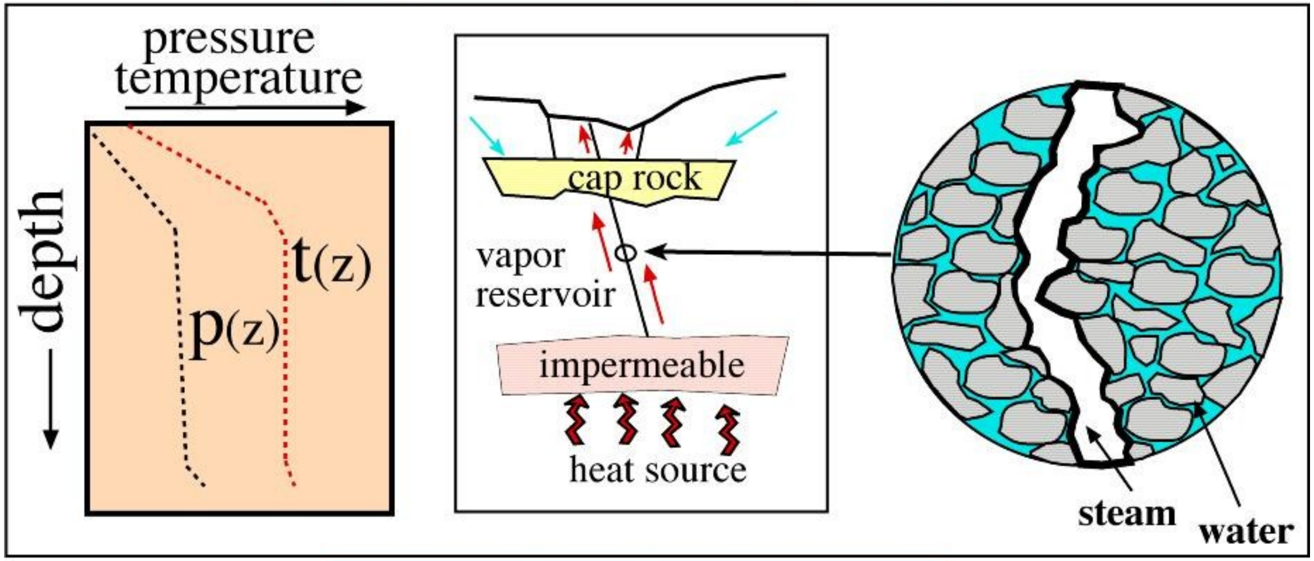
main thrust

- -compression (^4He)
- -fluids squeezing (CH_4)
- -thermal springs (N_2 e/o CH_4)

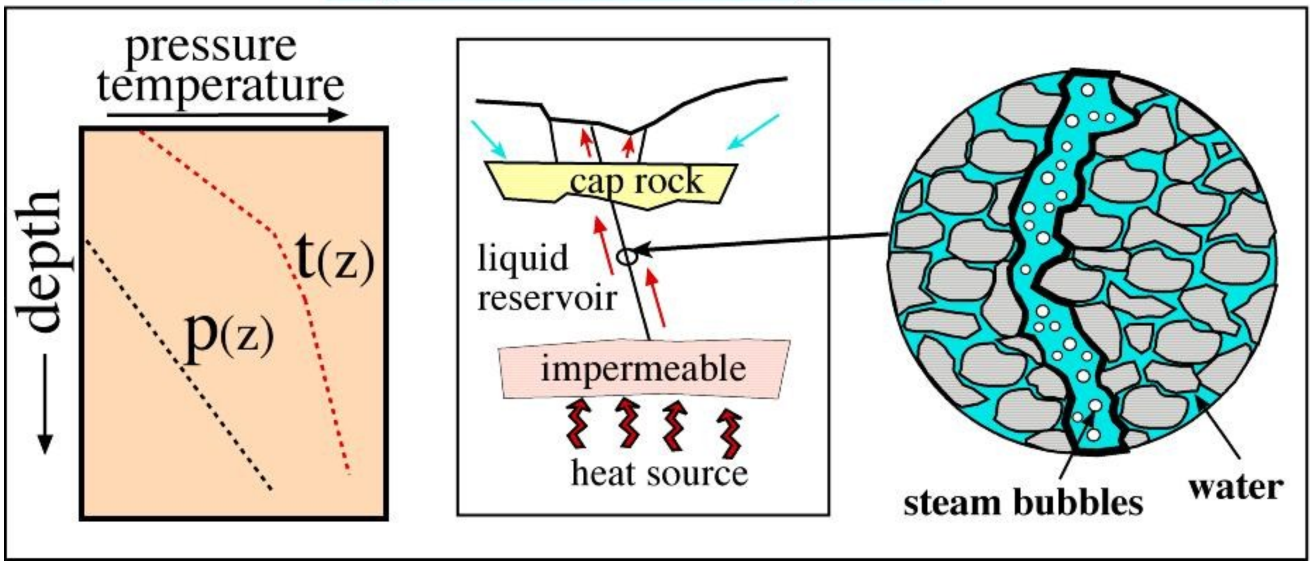
foredeep

- -compression
- -sediments accumulation
- -CH_4 formation (saline domes)
- -mud volcanoes

vapor-dominated system



liquid-dominated system



Promising surface features

1) Steam fumaroles at T~ 160 °C

2) Steam emission at boiling temp.
(very high local thermal gradient)

3) Thermal springs with high P_{CO_2}

4) Gas CO_2 emissions (rich in H_2)

$$CH_4 + 2H_2O = CO_2 + 4H_2$$

5) Hydrothermal alterations
(ore deposits)

Steam fumaroles at 160° C at atmospheric pressure means that underground there is a hydrothermal system at the maximum enthalpic point (236 ° C and 32 bars) whose abiabatic expansion at atmospheric pressure generates fumaroles at 160 ° C (typical of volcanic environment, but e.g. present at Larderello in Tuscany)

Steam at surface at **boiling temperature** (no matter the flow rate) always meens high thermal gradient where steam derives by secondary boiling of aquifers located at “intermediate” depth between a deep hydrothermal reservoir and the surface.

If steam temperature is much **lower than boiling temperature** it may derive by the boiling of a convective aquifer whoose depth can be high.

Promising thermal springs have the following characteristics:

1) Relatively low temperature ($30<T<70°C$)

2) Low-to-very low flow rate (~ 1 L/sec)

3) Low salinity (shallow circulation and/or steam condensation)

4) Neutral to slightly acidic *p*H (CO_2)

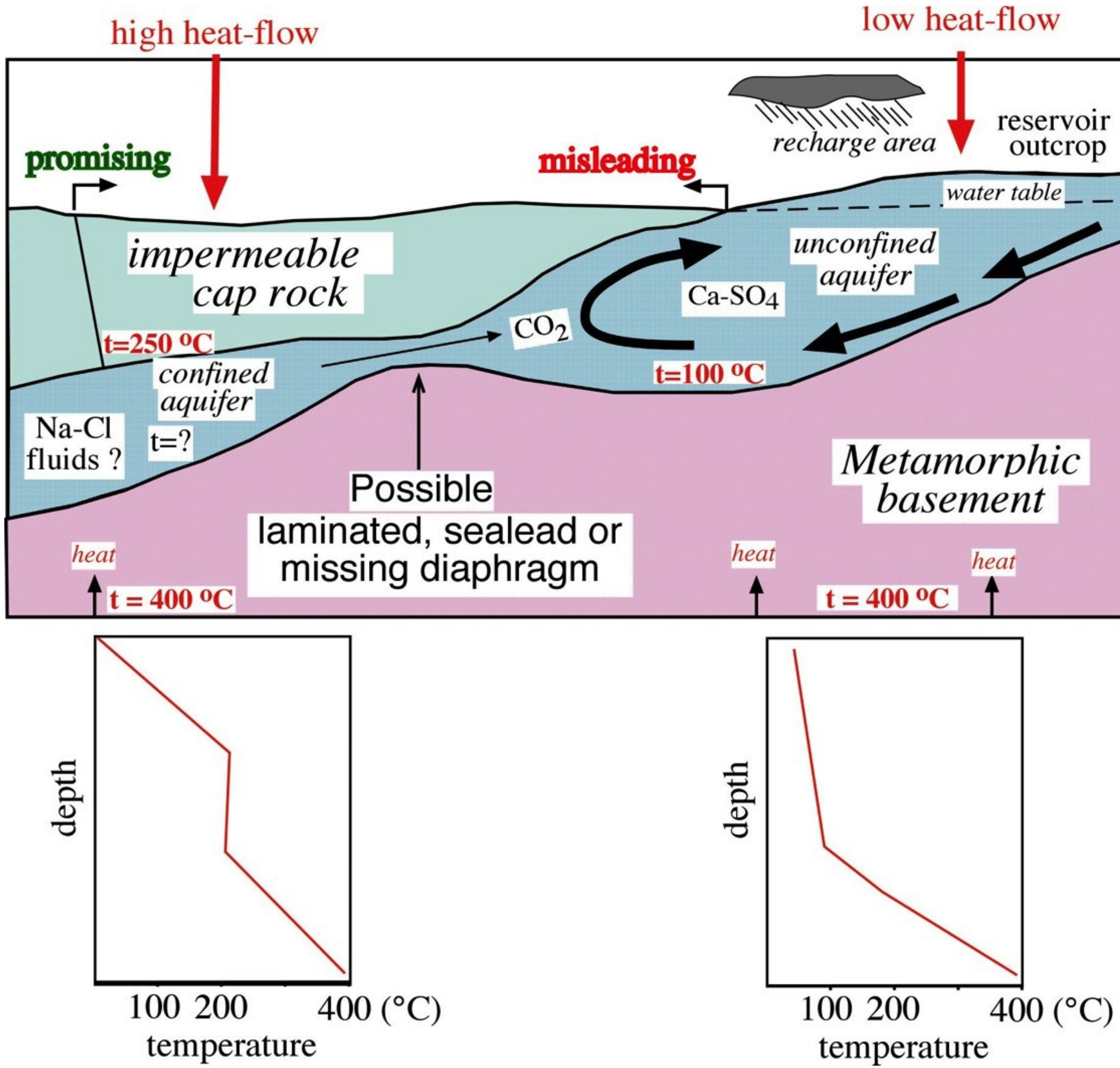
5) CO_2 (H_2S) as main associated gas phase

6) Low He (diluted by hydrothermal CO_2)

7) High $^3He/^4He$ ratio (mantle magmas)

Misleading thermal springs have the following characteristics:

1) Near boiling temperature (85<T<99 °C)
2) High flow rate (up to 1 t/sec)
3) High salinity (deep, long circulation)
4) Neutral to highly basic *p*H (up to 12)
5) N_2 gas phase (up to 99 %)
6) High He (up to 10% of total volume)
7) Low $^3He/^4He$ ratio (^4He in the crust)



high heat-flow
low heat-flow
promising
misleading
recharge area
reservoir outcrop
water table
impermeable cap rock
unconfined aquifer
Ca-SO4
CO2
t=250 ºC
t=100 ºC
confined aquifer
Na-Cl fluids ?
t=?
Possible
laminated, sealead or missing diaphragm
Metamorphic basement
heat
heat
heat
t = 400 ºC
t = 400 ºC
depth
100 200 400 (°C)
temperature
depth
100 200 400 (°C)
temperature

Sampling fumaroles, springs and gases

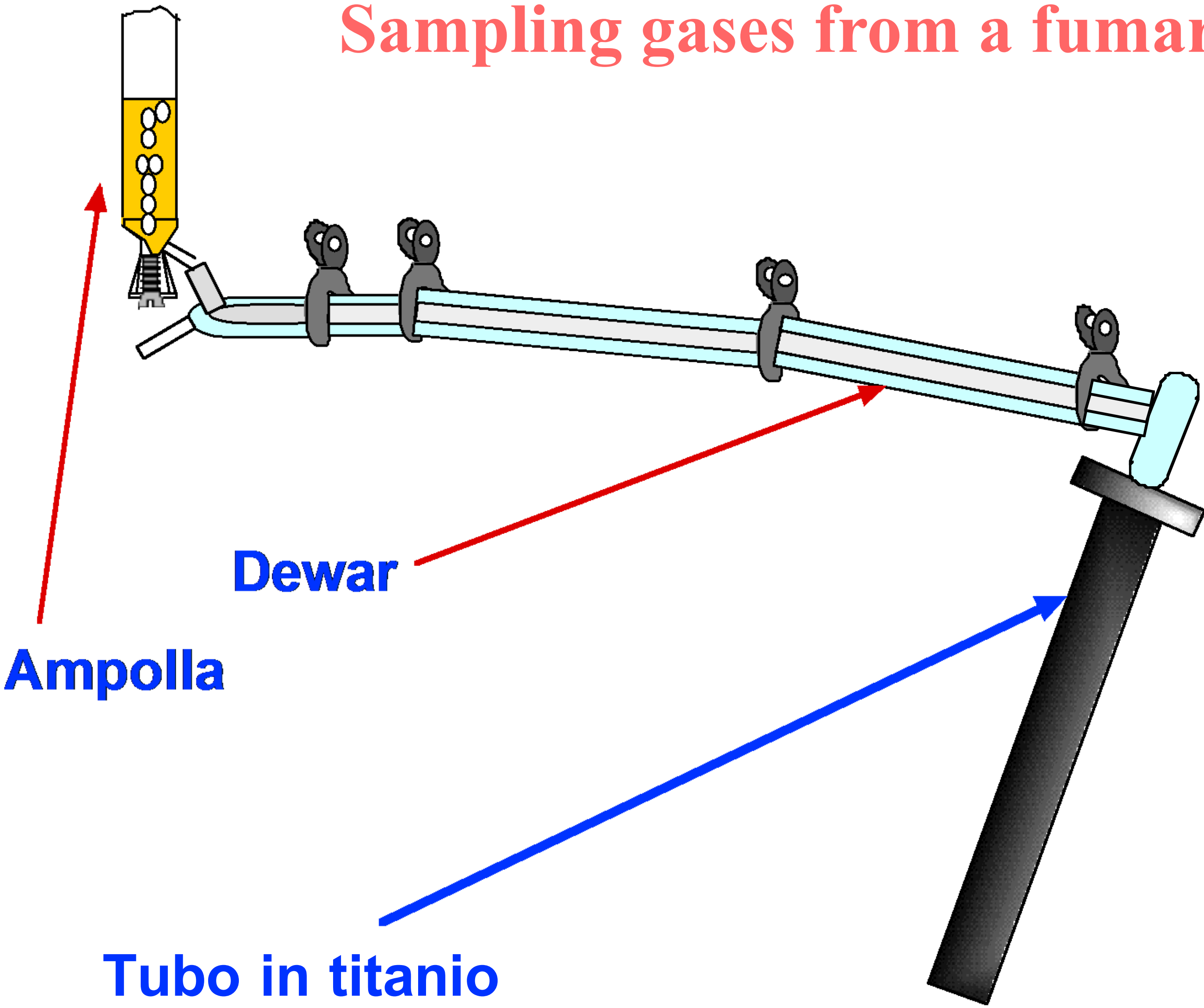
The main gol of Fluid Geochemistry during the exploration phase is to understand the relation between the fluids emerging at the surface with the "*parent*" fluid in depth (reservoir ?).

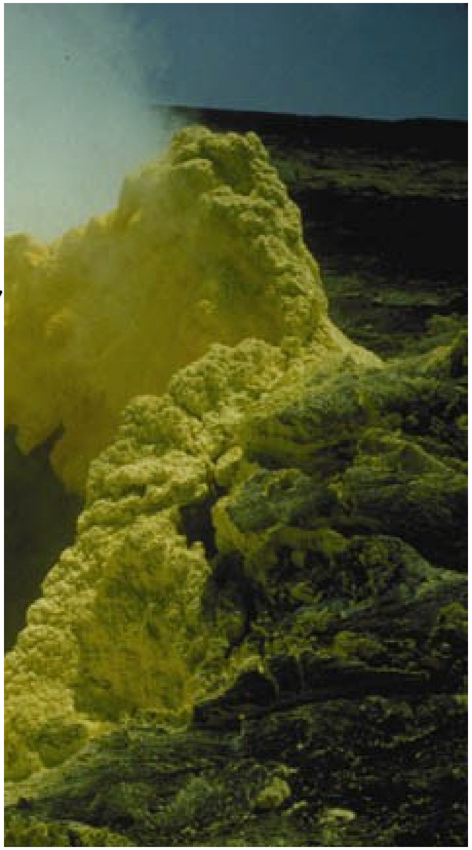
In particular, in case of springs, if they can be considered:

1) promising *or*

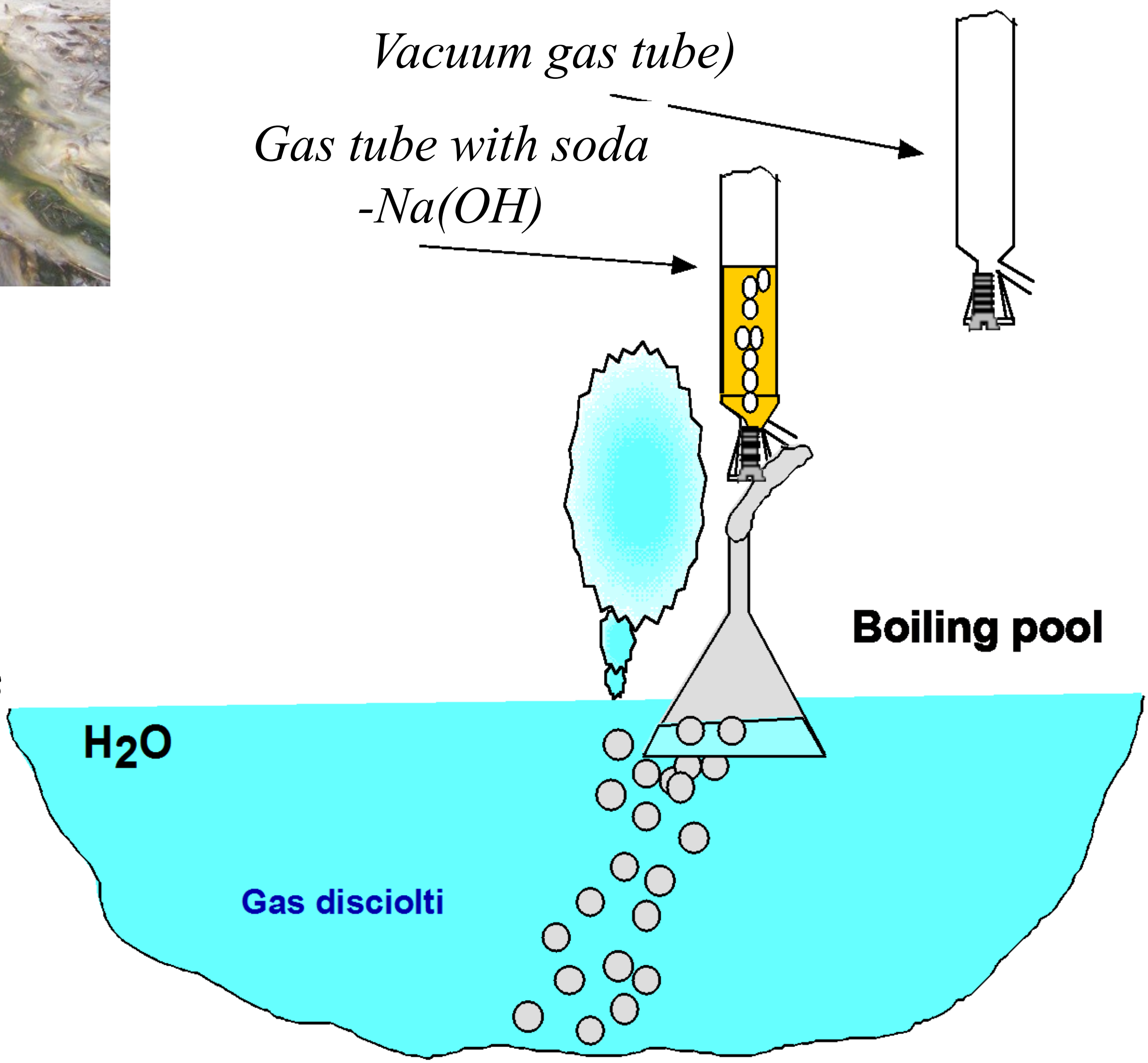
2) measleading

Sampling gases from a fumarole





Sampling gases from a gas vent



What to sample for components in the gas phase:

1) A pre-evaquated and pre-weighted gas tube for main (CO_2, N_2, H_2S, CH_4…etc) and trace (He, Ar, CO…etc) components, and $^{13}C/^{12}C$ in CO_2

2) A pre-evaquated and pre-weighted gas for the determination of the $^3He/^4He$ ratio

3) A gas tube for hydrocarbons (ethane, buthane, benzene…etc.)

Acidic gases react with the soda

Steam => condensation

$2Na^+ + CO_2 + 2(OH)^- = 2Na^+ + CO_3^{2-}{}_{(aq)} + H_2O$

$7Na^+ + 4SO_2 + 7(OH)^- = 7\ Na^+ + 3SO_4^{2-}{}_{(aq)} + HS^-{}_{(aq)} + 3H_2O$

$Na^+ + H_2S + (OH)^- = Na^+ + HS^-{}_{(aq)} + H_2O$

$2Na^+ + 2HCl + 2(OH)^- = 2Na^+ + 2Cl^- + 2H_2O$

(analysis of Cl, S species, F…etc. with chemical procedures)

Inert gases (He, Ar, N_2..etc)

concentrate in the vacuum up to 100 times

(analysis with gas chromatography)

Organic gases (ethane, propane…benzene..etc)

(analysis with a Gas-Mass)

After filtering

What to sample for components in liquid phase?

1) 250 ml of water in plastic bottle (for main components and some trace elements)
2) 50 ml of water in a plastic bottle acidified with a few drops of concentrated HNO_3 for Ca and metal cations
3) 25-50 ml of water (as fast as possible, eventually usings gloves if too hot) in a glass bottle for isotopes
4) Aliquotes of stabilized free CO_2 and H_2S for isotopes

Types of waters:

Juvenile (very rare)
Hydrothermal (hot springs)
Fossil (in the sediment pores since the beginning)
Formation (filling the pores)
Brines (hyper-saline waters)

Temperature (temperate latitude)

- ✓Cold waters ($T<20$ ° C)
- ✓Hypothermal ($20<T<30$ ° C)
- ✓Thermal ($30<T<40$ ° C)
- ✓Hyperthermal ($T>40$ ° C)

Salinity (Total Dissolved Solids)

Fresh waters: $TDS<1000$ ppm
Brackish waters: $1000<TDS<20000$ ppm
Salt (marine) water: ≈35000 ppm
brines: >35000 ppm

Measurements in the field on spring water samples:

1) Temperature
2) *p*H
3) Electrical conductivity
4) Ammonia (NH_4)
5) Silica (SiO_2)
6) Elevation
7) Coordinates

Measurements in the laboratory:

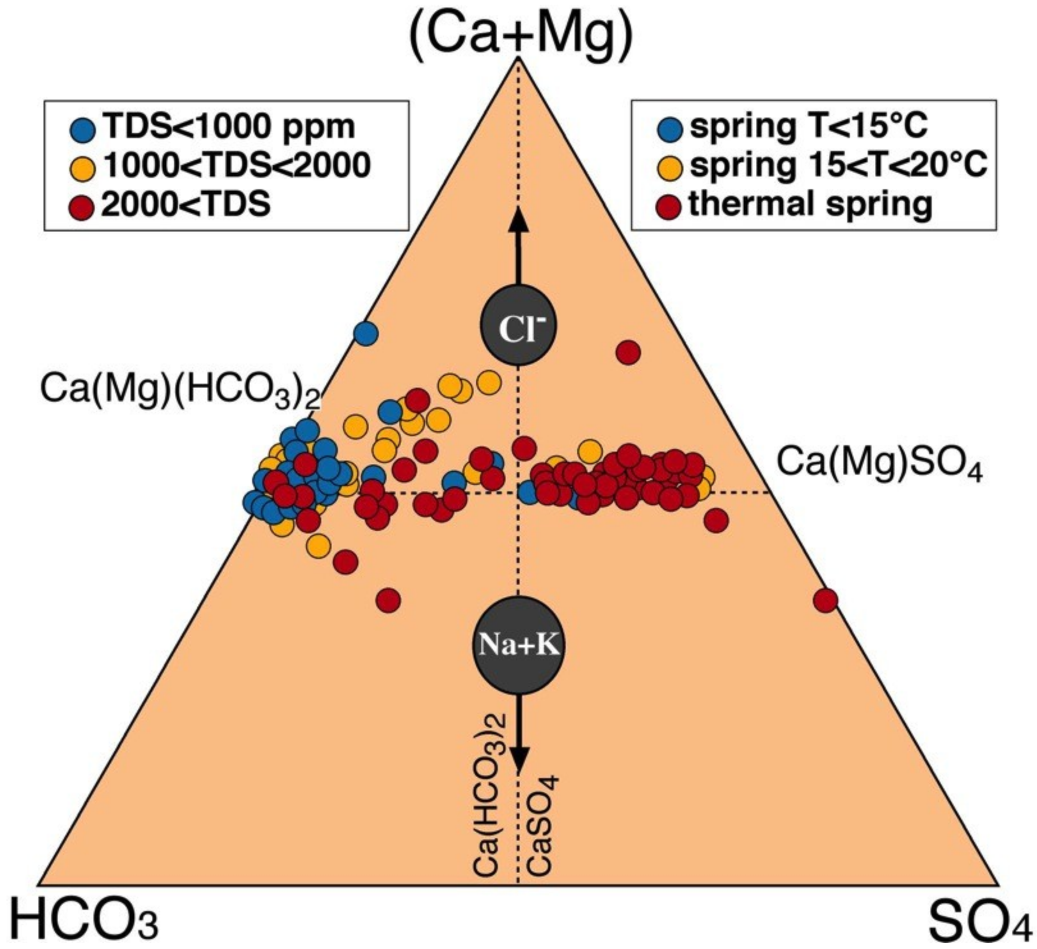
1) Main components (Na,K,Mg,Ca,HCO_3,SO_4,Cl)
2) Some trace elements (B, Br, Sr, NO_3, Li, F)
3) $^{18}O/^{16}O$ and $^{2}H/H$ ratios in water
4) $^{13}C/^{12}C$ in DIC (dissolved inorganic carbon)
5) $^{35}S/^{34}S$ in sulfur species

Minimum data set necessary for the elaboration of liquid and gas phase:

Spring water: Ca, Mg, Na, K, HCO_3, SO_4, Cl (main)
SiO_2, NH_4, B, NO_3 (minor)
Li, Br, Sr, F (trace)
$\delta^{18}O$ and $\delta^{2}H$
$\delta^{13}C$ in DIC (Dissolved Inorganic Carbon)

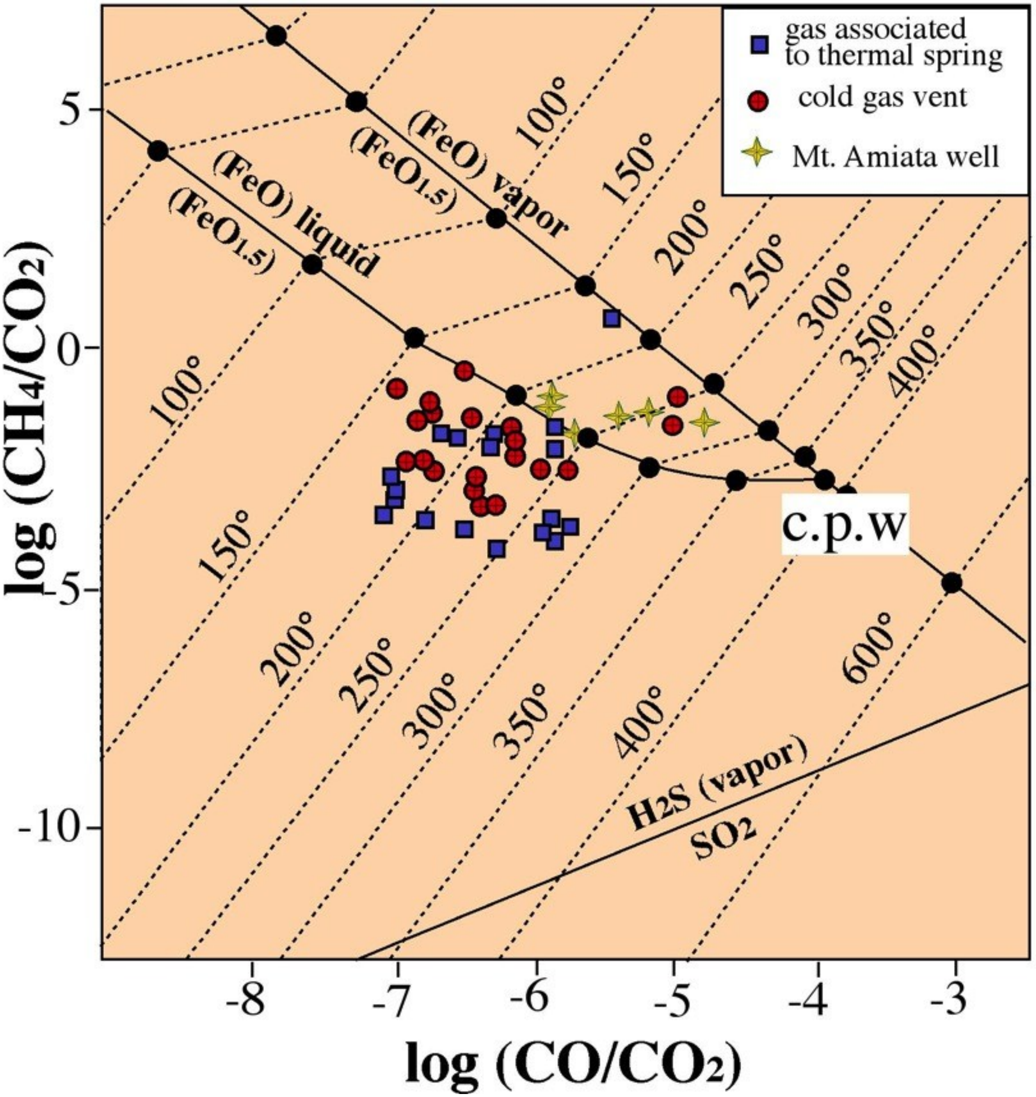
Gas phase (either exolved from water or as dry emission):
CO_2, H_2S, CH_4, N_2, O_2,
Ar, He, Ne
$\delta^{13}C$ in CO_2
$^{3}He/^{4}He$

Springs circulating in Mesozoic limestone in central Italy



Ternary diagrams

geothermometry in the gas phase



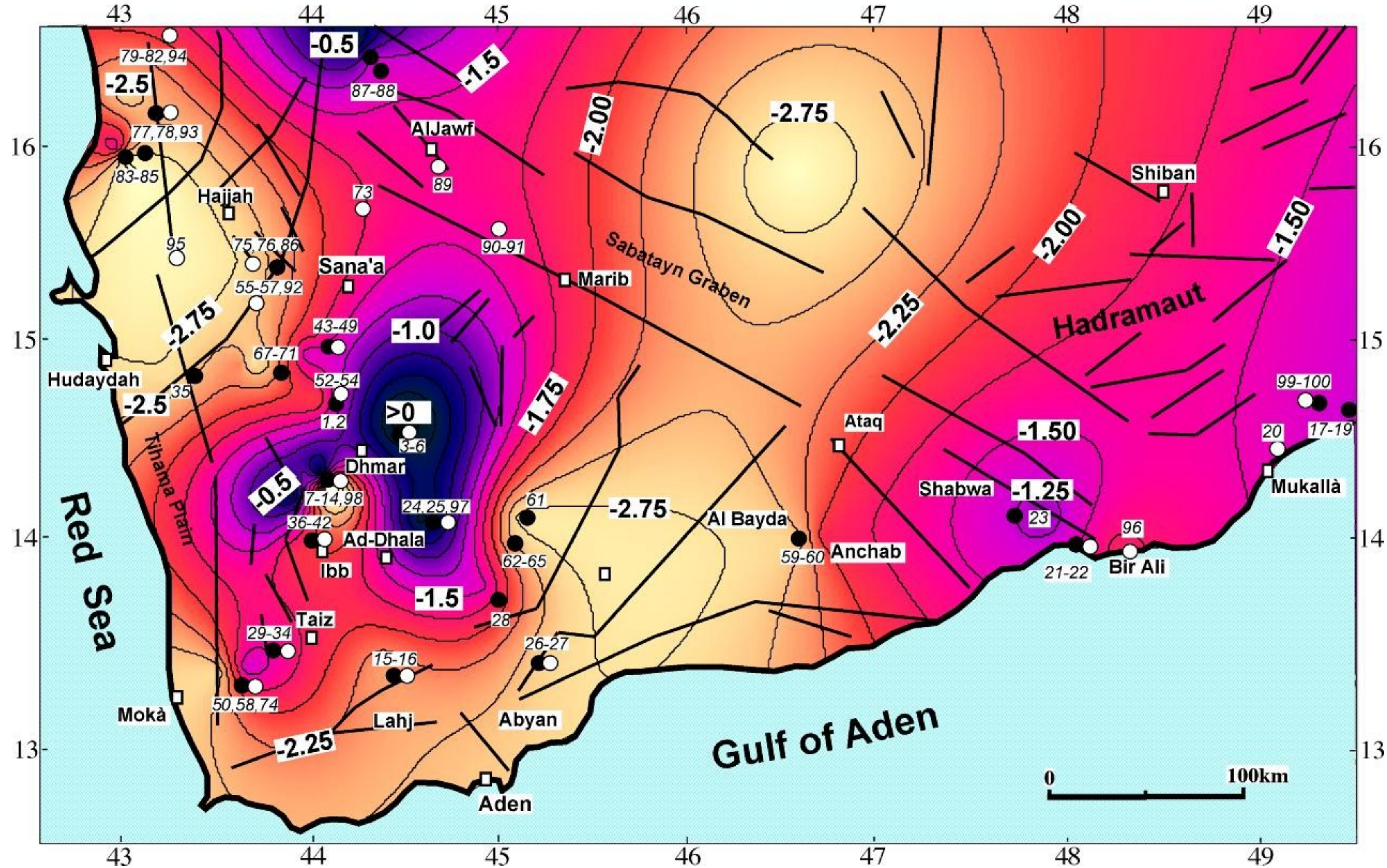
$CH_4 + 2H_2O \Longleftrightarrow CO_2 + 3H_2$

$CO + 0{,}5O_2 \Longleftrightarrow CO_2$

$FeO + 0.25\ O_2 \Longleftrightarrow FeO_{1.5} + 0.25\ e^-$

$H_2S + 2H_2O \Longleftrightarrow SO_2 + 6H^+ + 6e^-$

Distribution map of calculated *p*CO2 in thermal springs



West-East 100 *km* section across Yemen