Sampling and analytical methods in geochemical exploration for geothermal research

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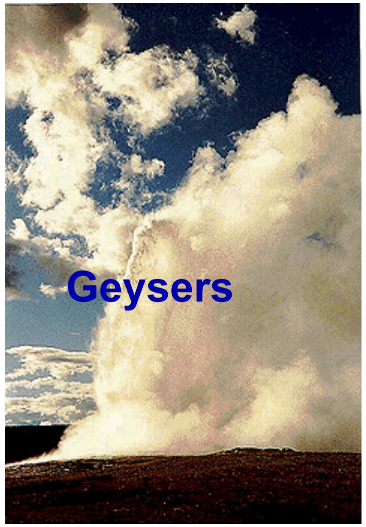
All (almost) hydrothermal systems leak fluids to the surface

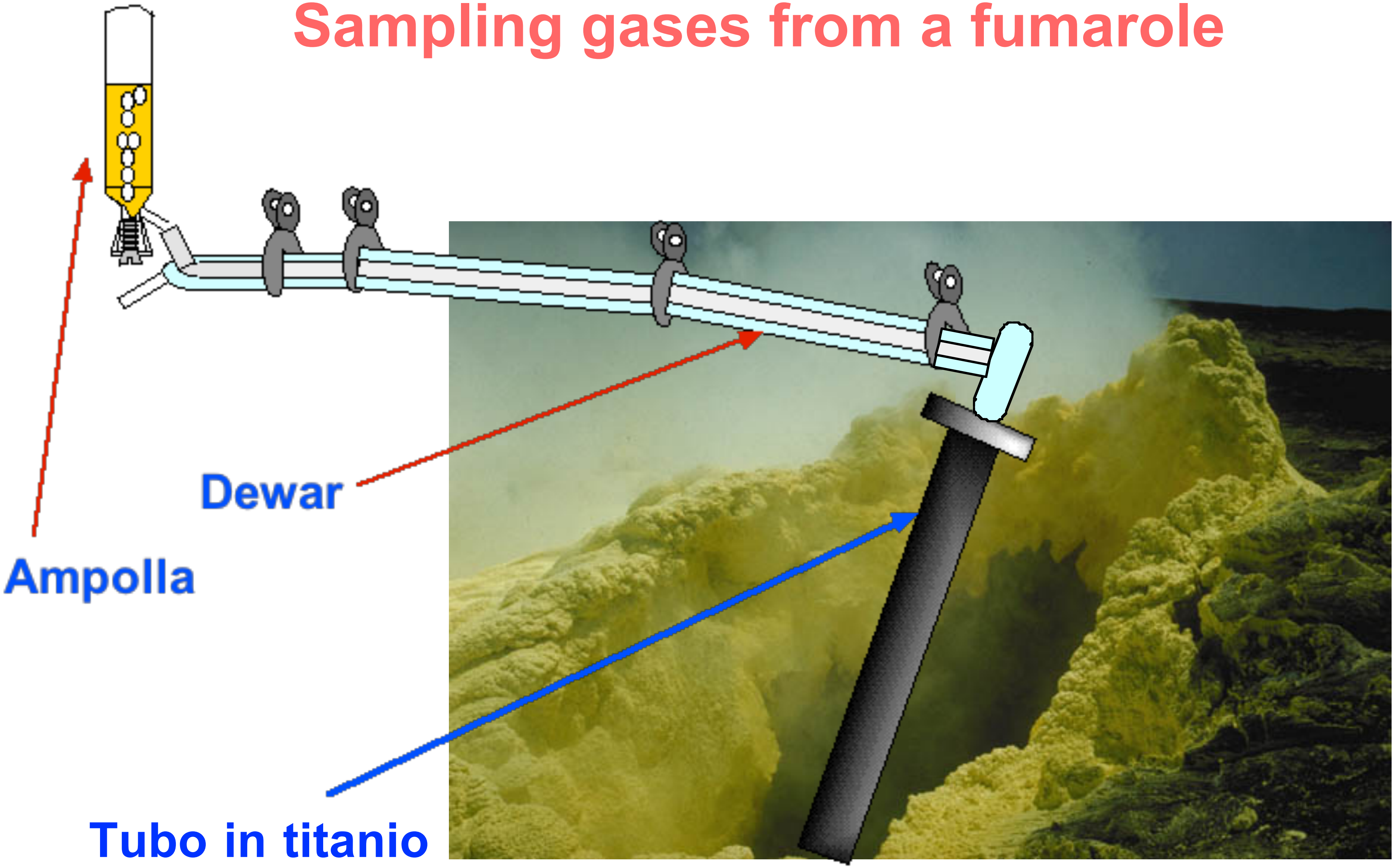
Most hydrothermal systems have at surface active and/or fossil thermal manifestations (fumaroles, thermal springs..etc.)

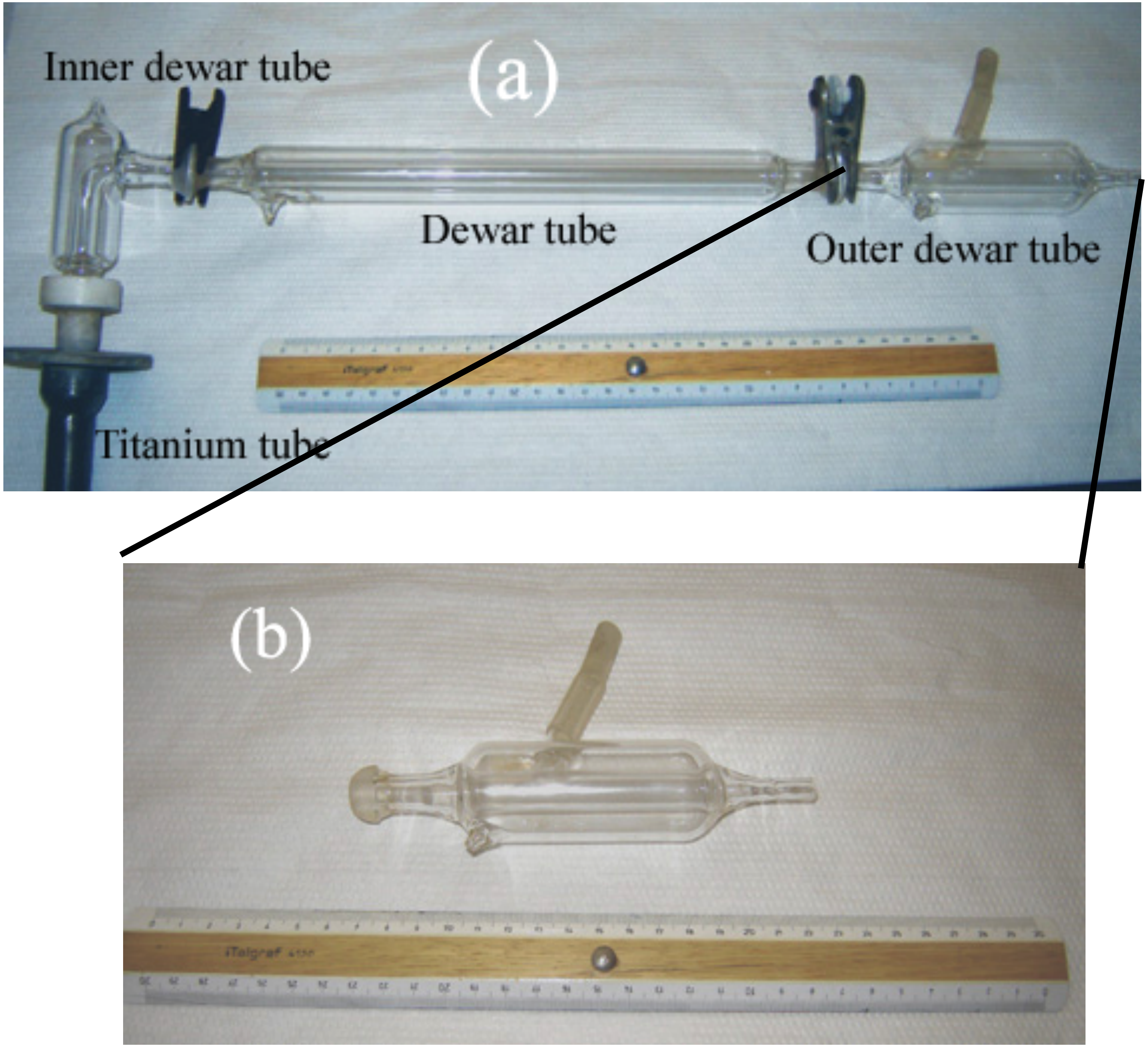


Steam pipelines, Wairakei Power Station

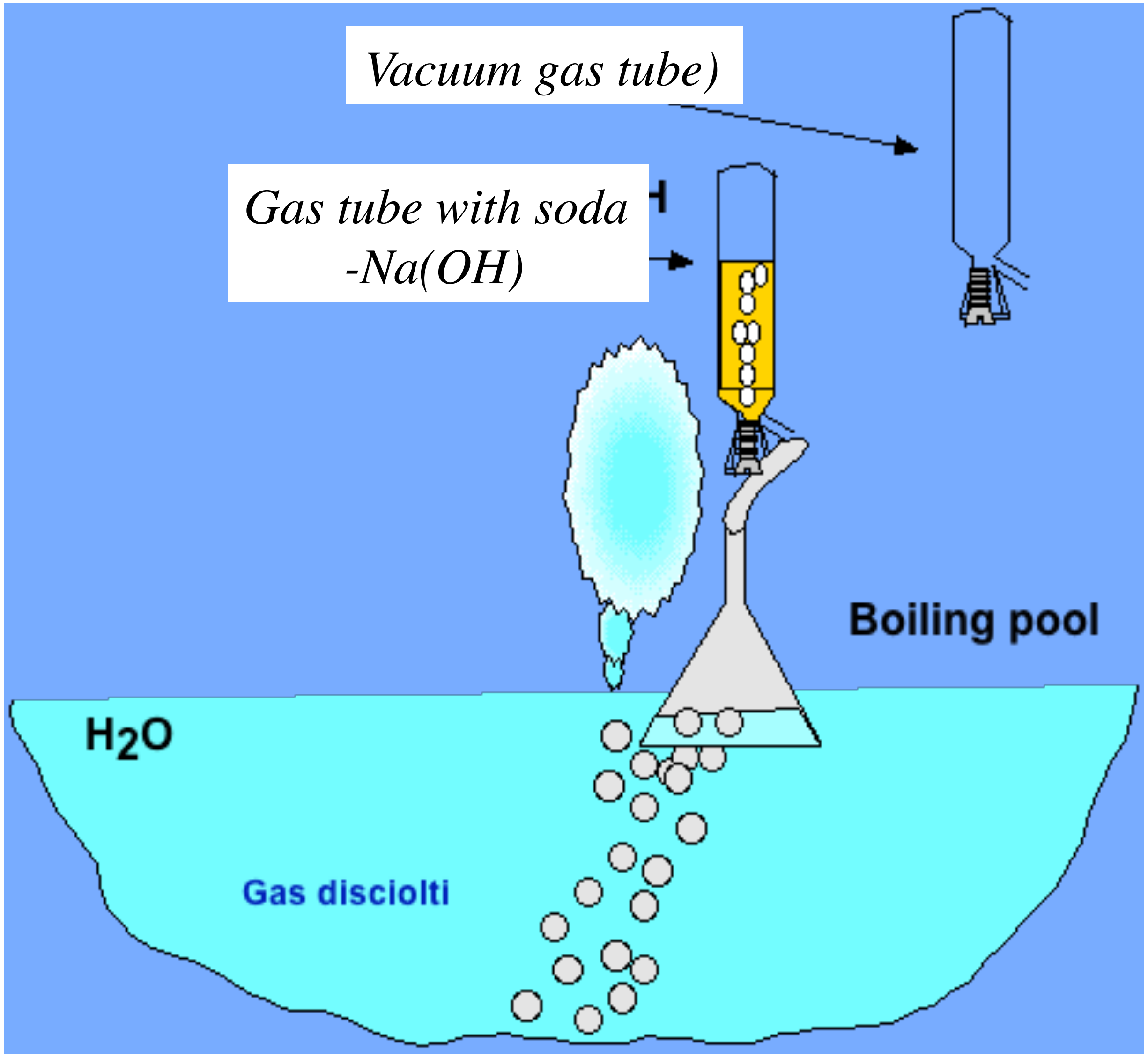
Sampling fumaroles and geothermal gases

Sampling gases from a fumarole




Inner dewar tube
(a)
Dewar tube
Outer dewar tube
Titanium tube
(b)


Bubbling gases from water



Vacuum gas tube)
Gas tube with soda
-Na(OH)
Boiling pool
H2O
Gas disciolti

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, N2..etc)

concentrate in the vacuum up to 100 times

(analysis with gas chromatography)

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

(analysis with a Gas-Mass)

Sampling of thermal springs (and gas)

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

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

1) promising *or*

2) measleading

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:

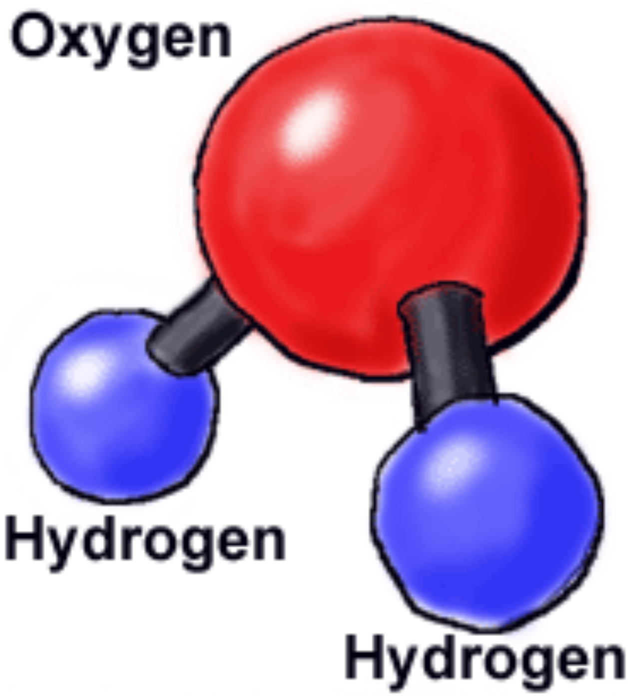
1) Near boiling temperature (85<T<99 °C)
2) High flow rate (up to 1 t/sec)
3) High salinity (deep, long circulation)
4) Neutral to highly basic *p*H (up to 12)
5) N_2 gas phase (up to 99 %)
6) High He (up to 10% of total volume)
7) Low $^3He/^4He$ ratio (^4He in the crust)

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 is too hot) in a glass bottle for isotopes
4) Aliquotes of stabilized free CO2 and H2S

During water (and gas) sampling

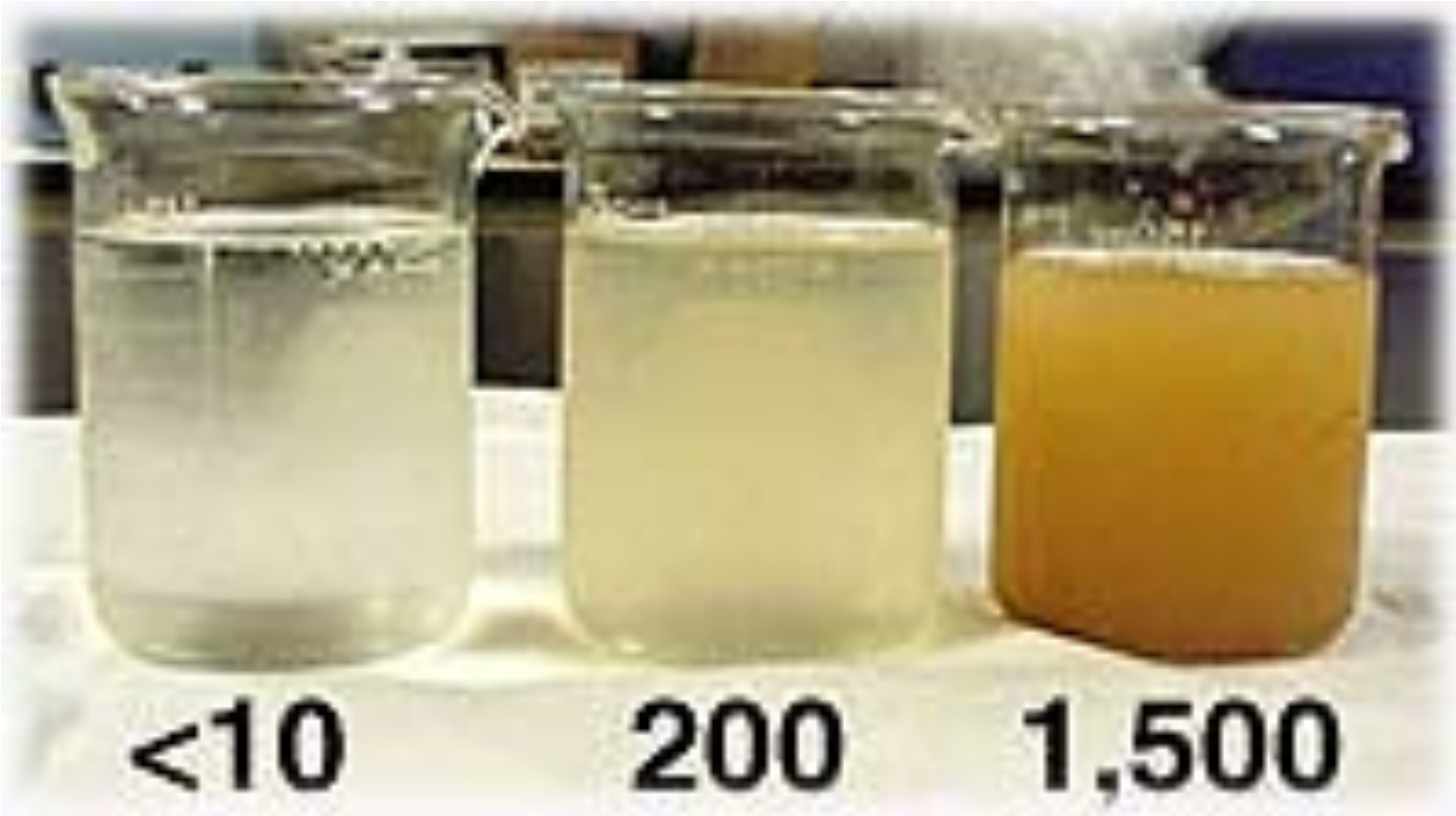
The aliquot of water (and gas) sampled must keep unaltered, as much as possible, the physical-chemical properties of the source.



Components of waters

- dissolved components (ions)
- solids in suspension (clay)
- Organic and inorganic compounds
- dissolved gases (N_2, O_2, CO_2..)
- Colloids and gels
- Organo-metal compounds

Filtering (0.45 μm)



Types of waters:

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

Temperature (in temperate climate)

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

Salinity

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

Relation between salinity (TDS) and electrical conductivity (Ω)

TDS (ppm) = Ω × 0.67

Measurements in the field on spring water samples:

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

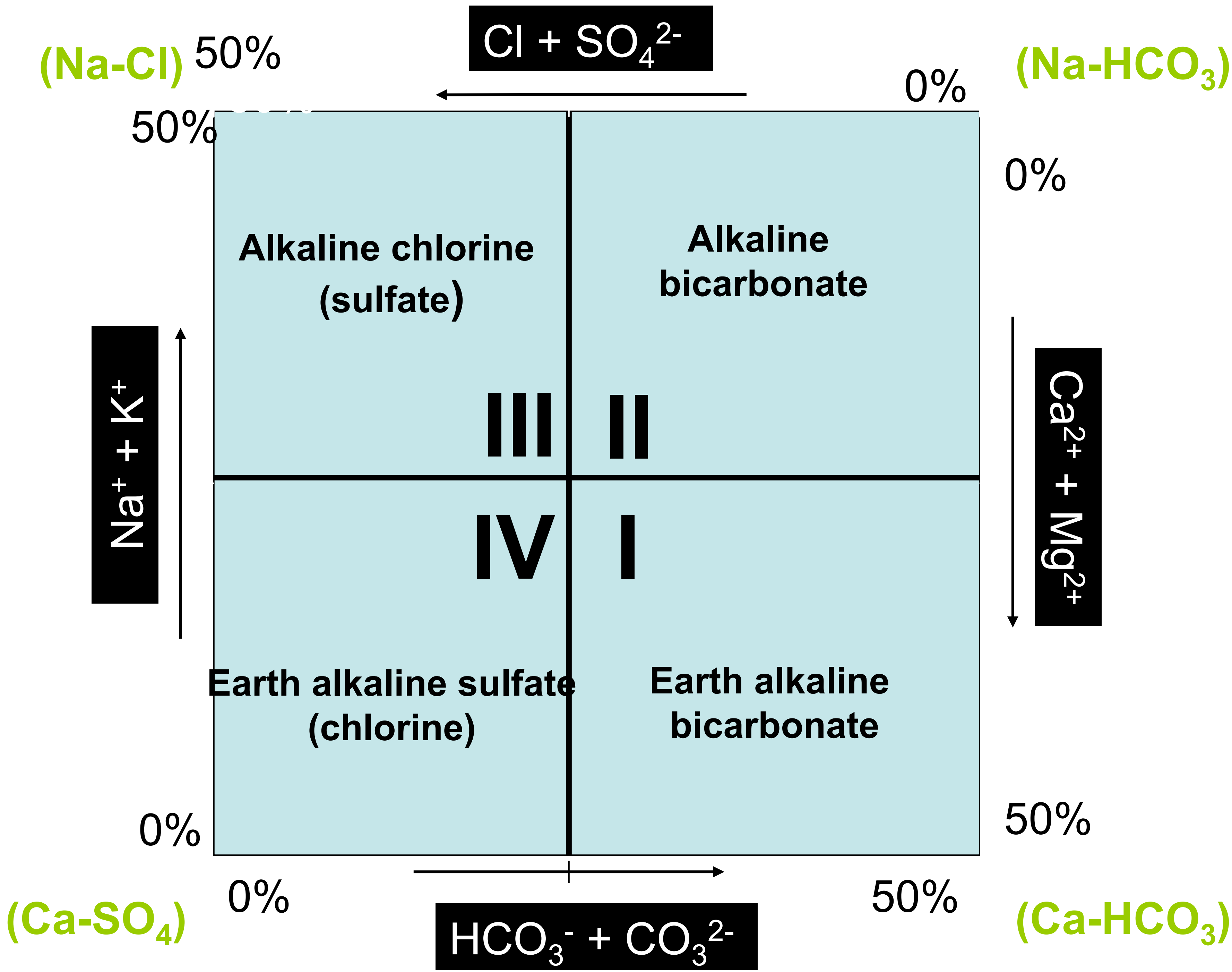
Measurements in the laboratory:

1) Main components ($Na, K, Mg, Ca, HCO_3, SO_4, Cl$)
2) Some trace elements (B, Br, 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)

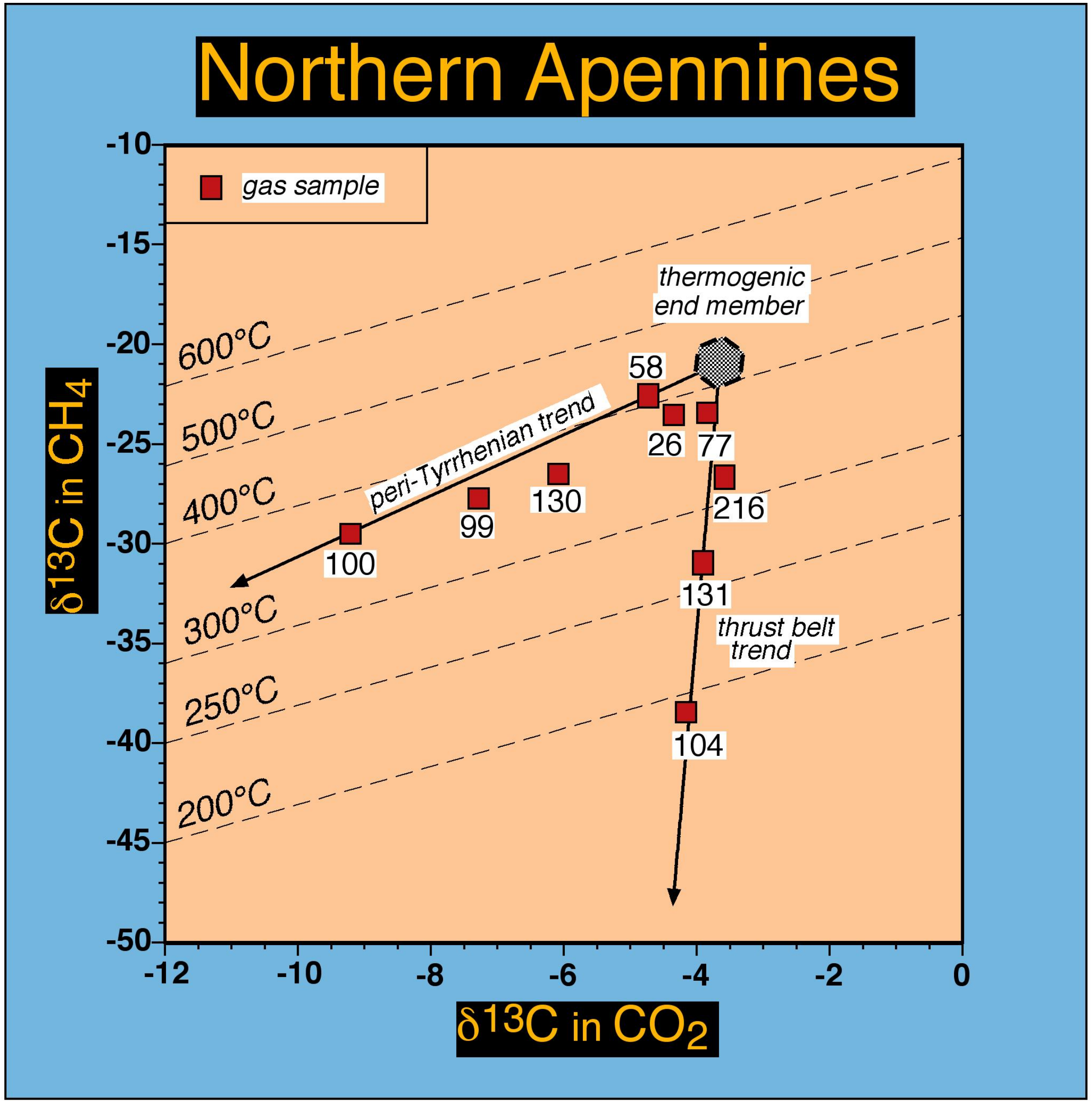
Minimum data set necessary for the elaboration of liquid and gas phase:

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

Gas phase (either exolved from water or as dry emission):
CO2, H2S, CH4, N2, O2,
Ar, He, Ne
$\delta^{13}C$ in CO_2
$^{3}He/^{4}He$



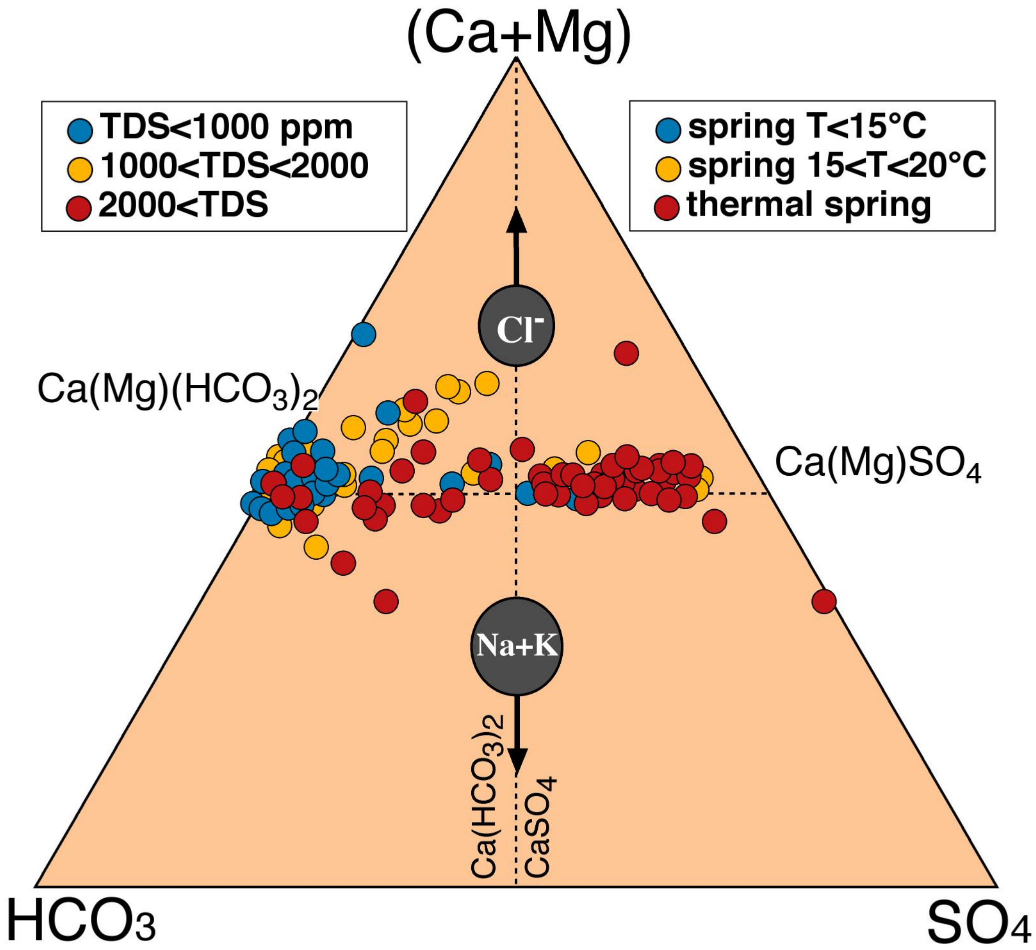
Cl + SO_4^{2-}
(Na-Cl) 50%
0%
(Na-HCO_3)
50%
0%
Alkaline chlorine (sulfate)
Alkaline bicarbonate
III
II
IV
I
$Na^+ + K^+$
$Ca^{2+} + Mg^{2+}$
Earth alkaline sulfate (chlorine)
Earth alkaline bicarbonate
0%
50%
(Ca-SO_4)
0%
50%
(Ca-HCO_3)
$HCO_3^- + CO_3^{2-}$



Binary diagrams

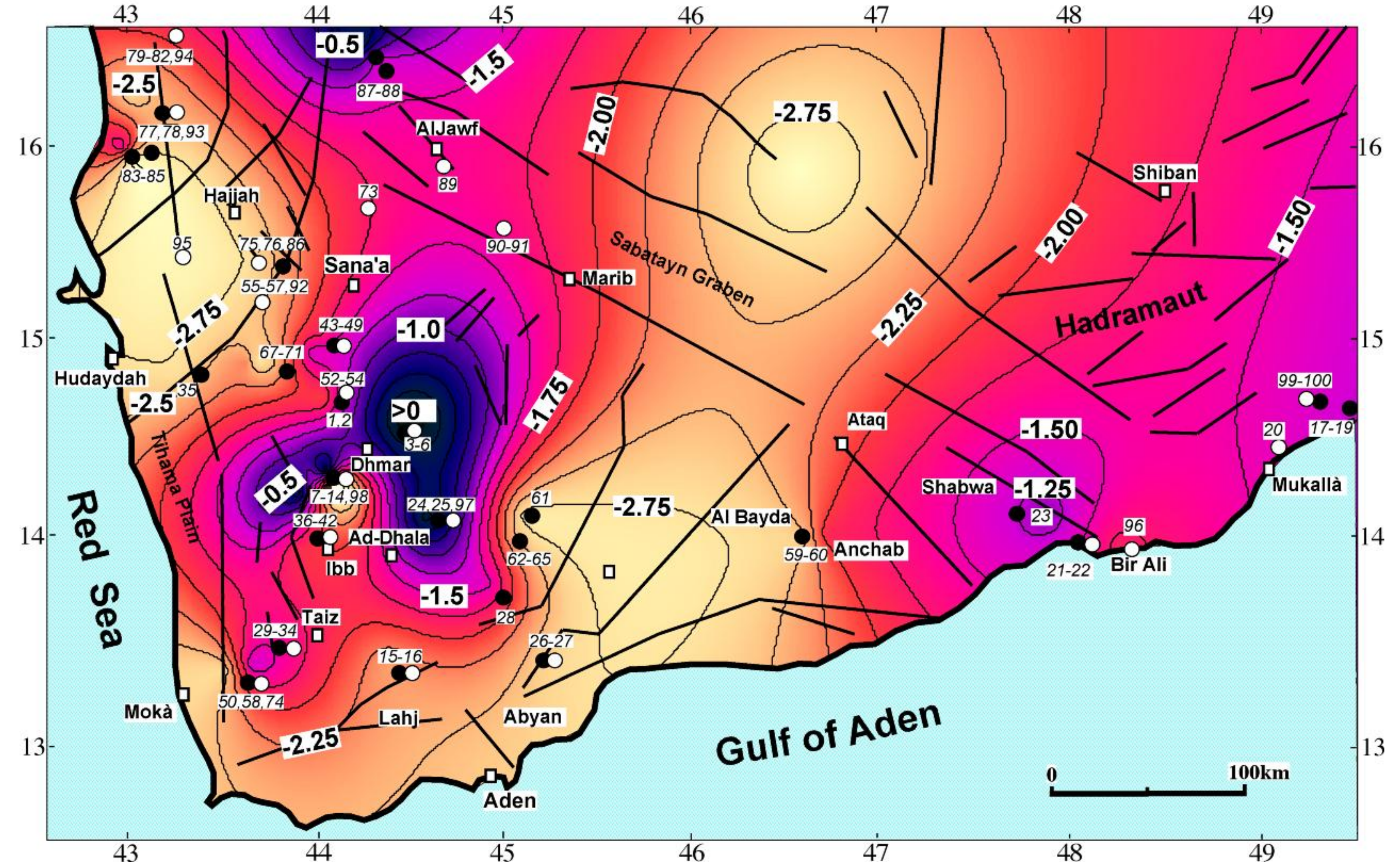
Minissale, Magro, Martinelli, Vaselli, Tassi (2000) **A fluid geochemical transect in the Northern Apennines: fluid genesis and migration and tectonic implications**. *Tectonophys. 319*, 199-222

Springs circulating in Mesozoic limestone in central Italy



Ternary diagrams

Distribution map of calculated *p*CO2 in thermal springs



West-East 100 *km* section across Yemen