Geochemistry: water-rock interaction, water and gas geochemistry, isotopes, geothermometry

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Georg Pawer (Agricola), 1556:

Non reagent nisi soluti

**The presence of fluids triggers most geological processes, which at their turn are regulated by geochemical processes:
WATER-ROCK INTERACTION (WRI)**

Differently from other geological disciplines operating in Geothermics, (Fluid) Geochemistry allows a direct contact with what it is commonly discharged from a geothermal reservoir

Thermal and mineral waters

Soil diffuse gas

Gas discharges: bubbling & boiling pools and fumaroles

ater) emissions

	evian® (mg/L)	
Sodium	Na⁺	6.5
Potassium	K⁺	1
Calcium	Ca²⁺	80
Magnésium	Mg²⁺	26
Chlorures	Cl⁻	6.8
Nirales	NO₃⁻	3.7
Bicarbonates	HCO₃⁻	360
Sulfates	SO₄²⁻	12.6
pH	pH	7.2
Silices	SiO₂	15
Fluorures		

The chemical composition of natural waters reflects the chemical weathering processes operated by the meteoric waters to the minerals they are interacting with (WRI). They are depending on the alterability degree (solubility) of the minerals: the higher it is the higher the ions getting into the solution. A solution may get saturated in certain ion pairs, which may originate precipitating salts.

Main sealing minerals in geothermal applications:

1) Calcite (almost always oversatutared)
2) Silica (strictly temperature-dependent)
3) Fe-hydoxides (strongly pH and Eh dependent)
4) Hg-Sb-As-sulphides (in volcanic areas)

Chemical weatheirng

Congruent dissolution

$$CaCO_3 + H_2O = \rightarrow Ca^{2+} + HCO_3^- + OH^-$$

Incongruent dissolution

$$NaAlSi_3O_8 + 11/2H_2O = \rightarrow Na^+ + OH^- + 1/2Al_2Si_2O_5(OH)_4$$

$$CaAl_2Si_2O_8 + 11/2H_2O = \rightarrow Ca^{2+} + OH^- + 1/2Al_2Si_2O_5(OH)_4$$

Redox reactions

$$FeS_{2(s)} + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$
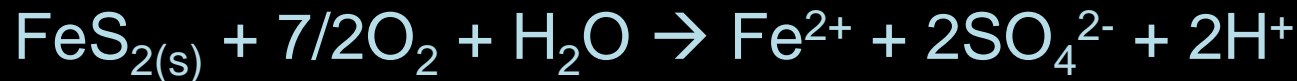
Each single chemical and isotopic composition we obtain is of paramount importance since it reflects a direct information from underground.
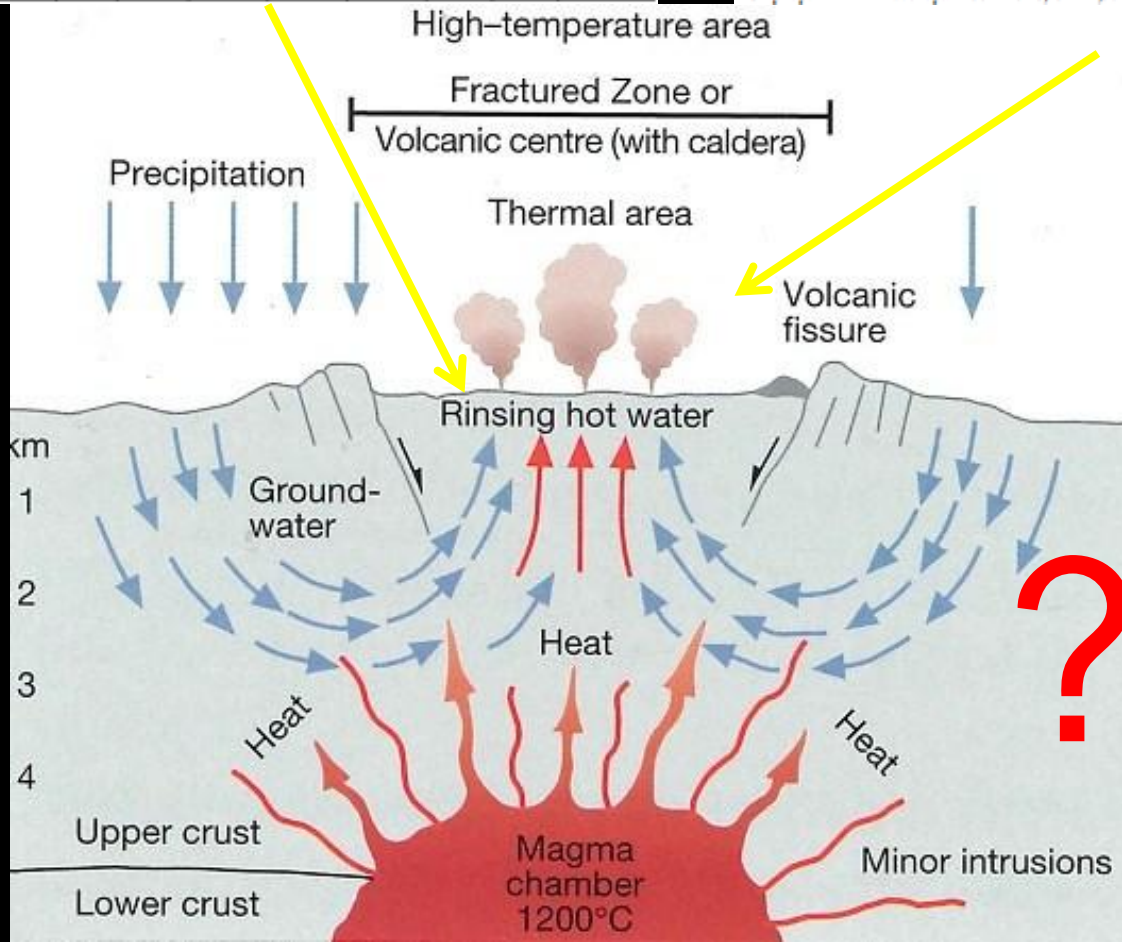
There is a (big) problem

Gas and isotopic composition

Water and isotopic composition

Locality	T°C	pH	HCO3	Cl	SO4	Na	K	Ca	Mg
Chianciano	39.6	6.09	884	17	1613	20	5.1	620	157.00

Name	Location	T, °C	CO_2	H_2S	N_2	Ar	O_2	Ne	H_2	He	CO	H_2O
El Playon	Ahuachapan	99.4	828,965	1,266	157,977	852.8	992.1	0.561	9,988	4.196	1.189	992,930
Chipilapa	Ahuachapan	99.7	948,492	2,954	46,294	92.18	1,463	0.056	698.6	8.170	1.216	996,116

High–temperature area

Fractured Zone or
Volcanic centre (with caldera)

Thermal area

Precipitation

Volcanic fissure

Which is the meaning of the chemical and isotopic compositions we measure at the surface?

Rinsing hot water

km

Ground-water

1

2

Heat

3

?

Heat

Heat

4

Upper crust

Magma chamber 1200°C

Minor intrusions

Lower crust

Physico-chemical Analyses

Components in liquid phase: Ca, Mg, Na, K, HCO_3, CO_3, SO_4, Cl, SiO_2, NH_4, NO_3, F, Br, Li, B, S^{II}, CO_2, Al, As, Ba, Be, Cd, Co, Cr, Cs, Cu, Fe, Hg, Mn, Mo, Ni, P, Pb, Rb, Sb, Se, Sn, Sr, Th, Tl, U, V, W, Zn, Zr

Physical parameters: T, pH, Eh, pH$_2$S, pNH$_4$, pO$_2$, pCO$_2$

Gas: H_2O, CO_2, N_2, HCl, HF, Ar, CH_4+hydrocarbons, O_2, Ne, H_2, He, H_2S

Dissolved gas: CO_2, N_2, Ar, CH_4, O_2, Ne, H_2, He

Isotopes: $^{18}O/^{16}O$; D/H; $^{13}C/^{12}C$ in DIC (Dissolved Inorganci Carbon) ;$^{13}C/^{12}C$ in CO_2, $^{3}He/^{4}He$, $^{87}Sr/^{86}Sr$

Conceptual model of a volcano in a convergent margin.
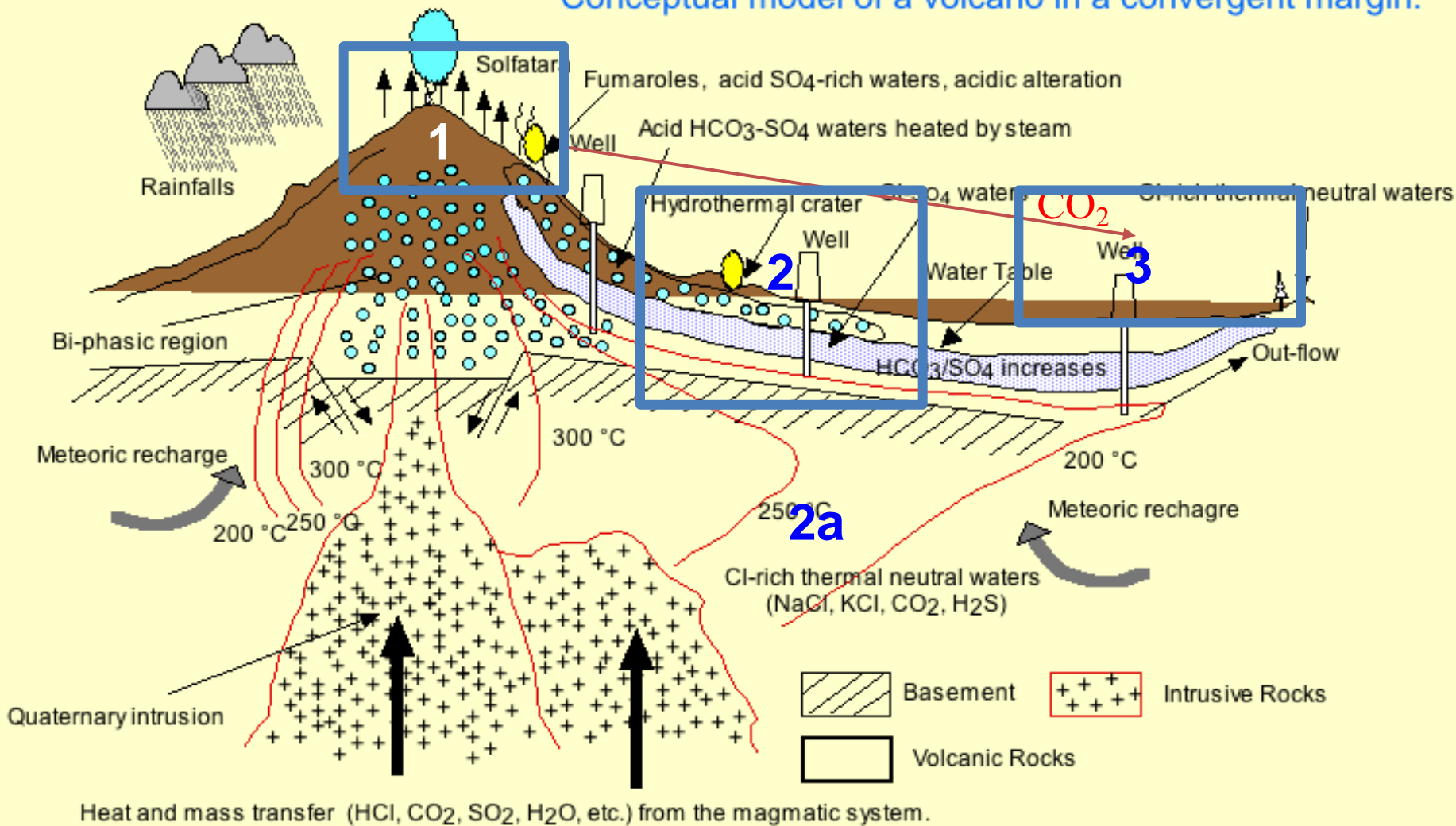
"Magmatic gas scrubbing"

"any process able to reduce emissions during reactions between gas, water and rocks (dissolution, formation of precipitates, gas-water chemical reactions etc.)"

Main volcanic gases

H_2O

SO_2

H_2S

HF

HCl

CO_2

CO

CH_4 + hydrocarbons

Noble gases (He, Ar, Ne, Kr, Xe, Rn)

H_2

NH_3

N_2

CFC, COS, S_2, heavy metals
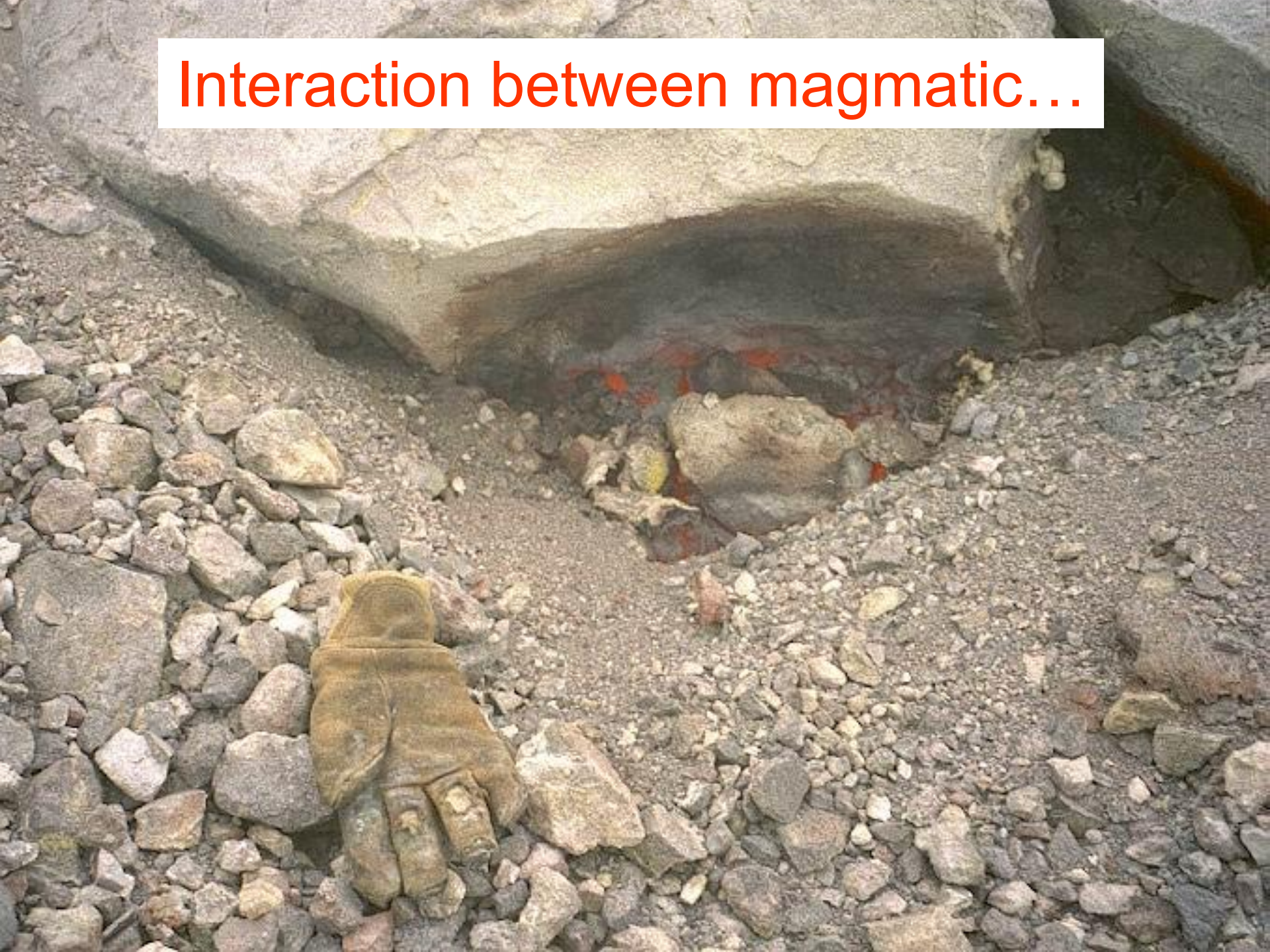
Typical magmatic gases

Acidic gases

Isotopes

- Essential: $\delta^{18}O$ and δ^2H in H_2O, $^3He/^4He$, $\delta^{13}C$ in CO_2;

- Very Useful: ^3H in H_2O, $\delta^{34}S$ in S-bearing species,

- Useful: $\delta^{13}C$ and δ^2H in CH_4, δ^2H in H_2, $\delta^{15}N$ in N_2, $^{40}Ar/^{36}Ar$, etc.

Irrutupuncu, N. Chile

Interaction between magmatic…

…and hydrothermal fluids

N$_2$, H$_2$O, O$_2$, Ar, CO$_2$

CO$_2$ H$_2$O   H$_2$S   Noble gases + N$_2$ H$_2$ CO

boiling

CO$_2$ H$_2$S   SO$_2$ Hydrothermal systemCl$^-$ H$_2$O   H$^+$ F$^-$

C > S > Cl > H$_2$O > F

H$_2$O CO$_2$ SO$_2$ H$_2$S H$_2$ HCl HF CO

Mass and hear transfer
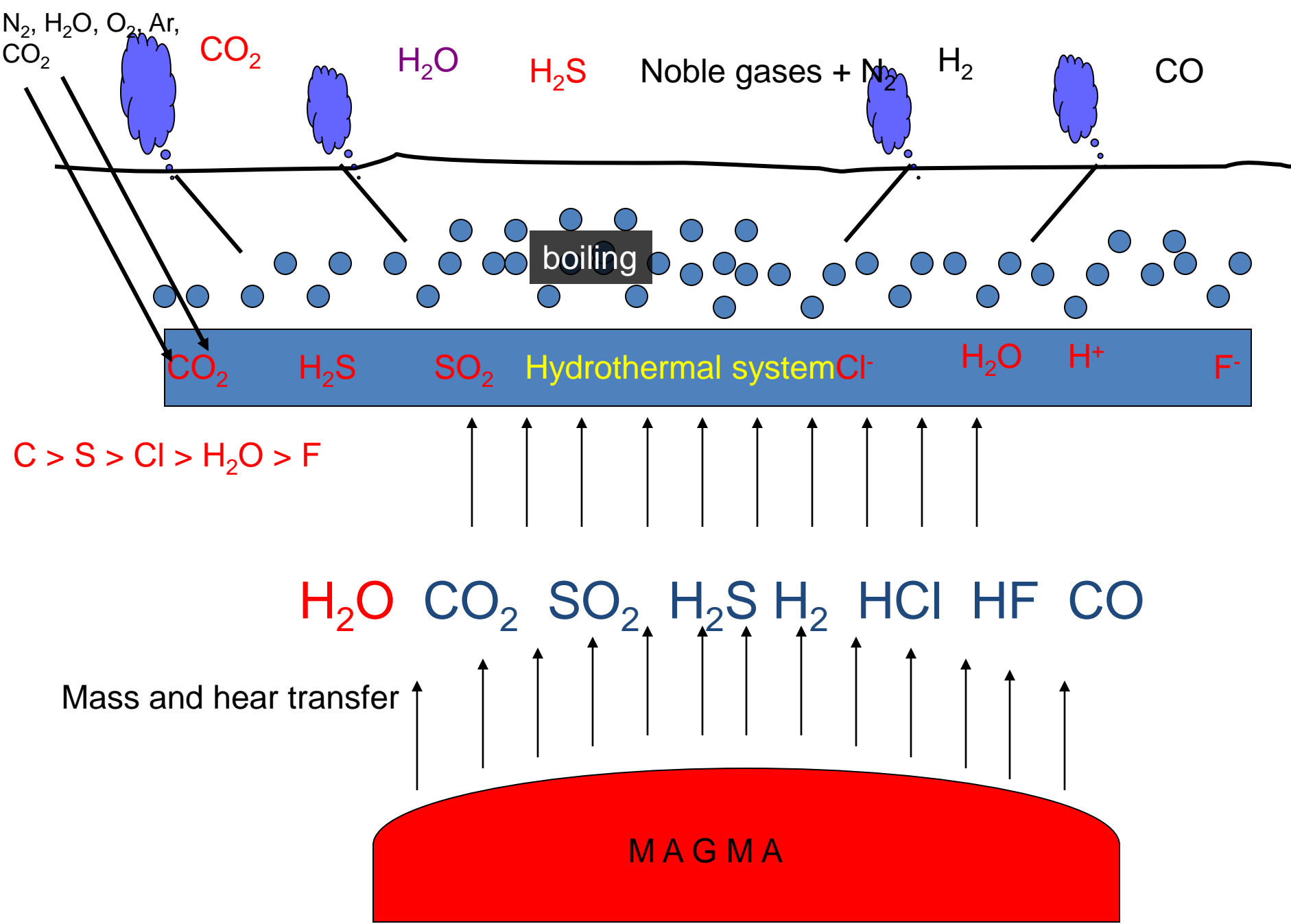
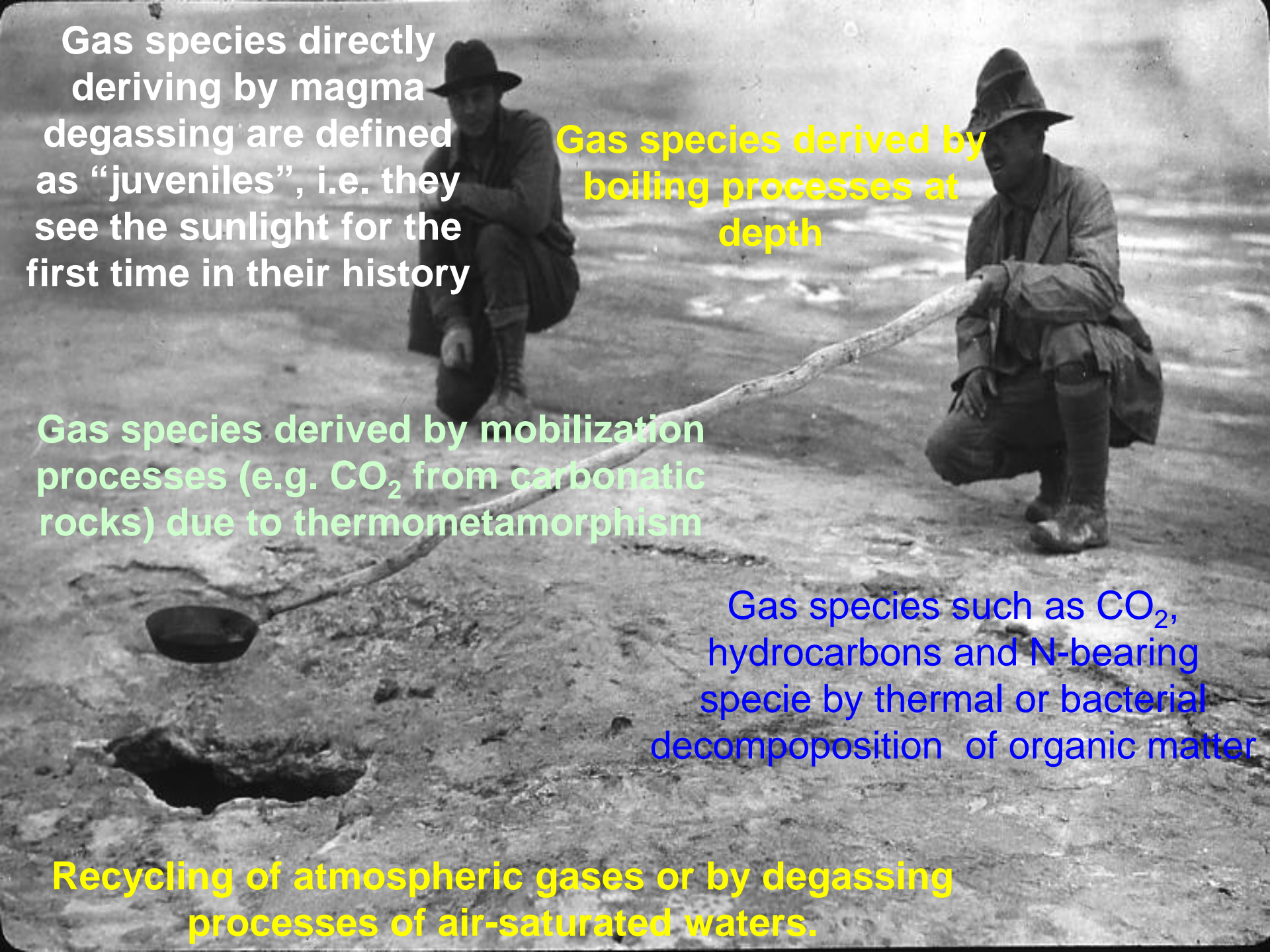M A G M A

Gas species directly deriving by magma degassing are defined as "juveniles", i.e. they see the sunlight for the first time in their history
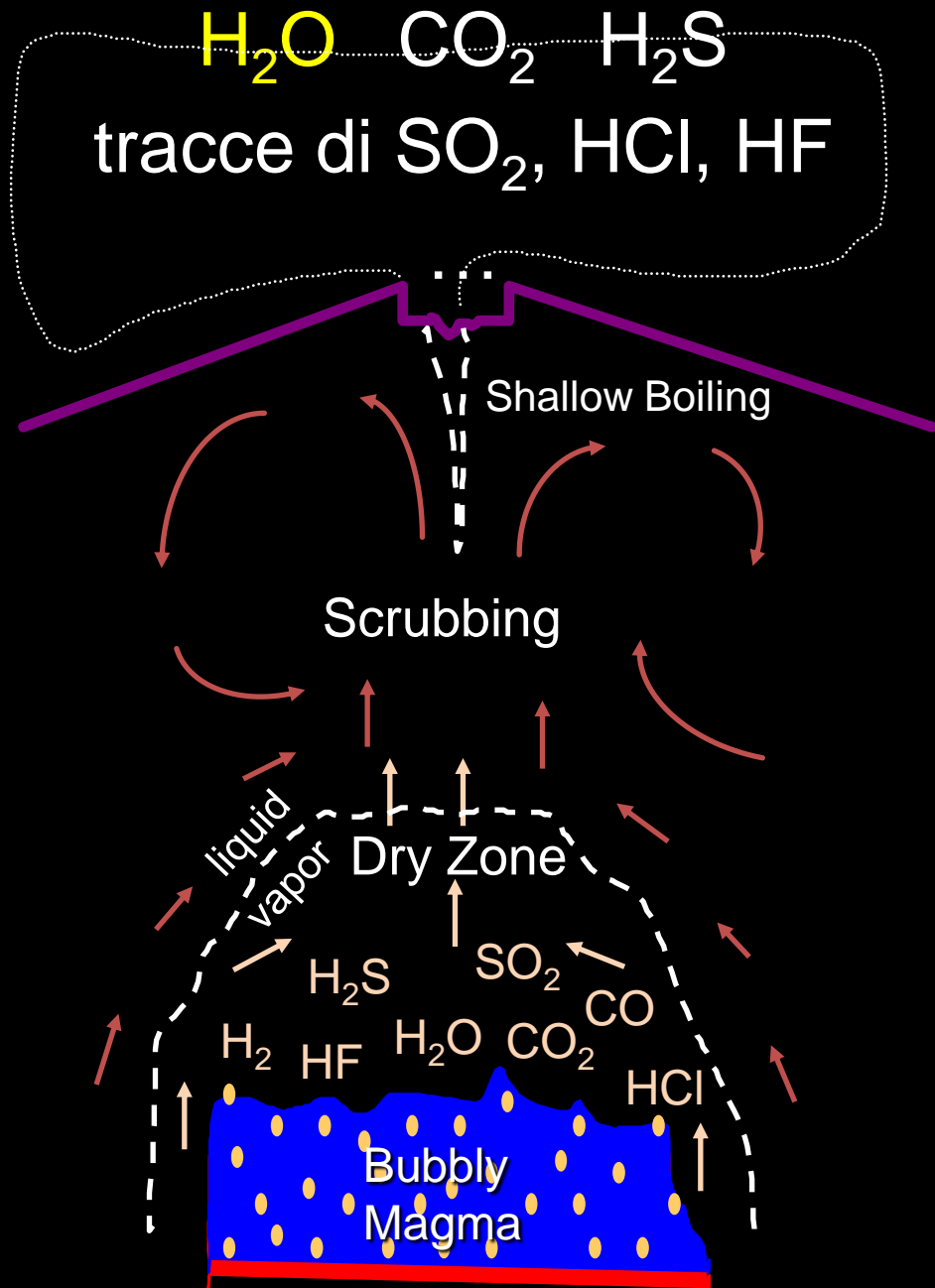
Gas species derived by boiling processes at depth

Gas species derived by mobilization processes (e.g. CO_2 from carbonatic rocks) due to thermometamorphism

Gas species such as CO_2, hydrocarbons and N-bearing specie by thermal or bacterial decompoposition of organic matter

Recycling of atmospheric gases or by degassing processes of air-saturated waters.

Secondary interactions

"Magmatic gas scrubbing"

"any process able to reduce emissions during reactions between gas, water and rocks (dissolution, formation of precipitates, gas-water chemical reactions etc.)"

Crustal contamination

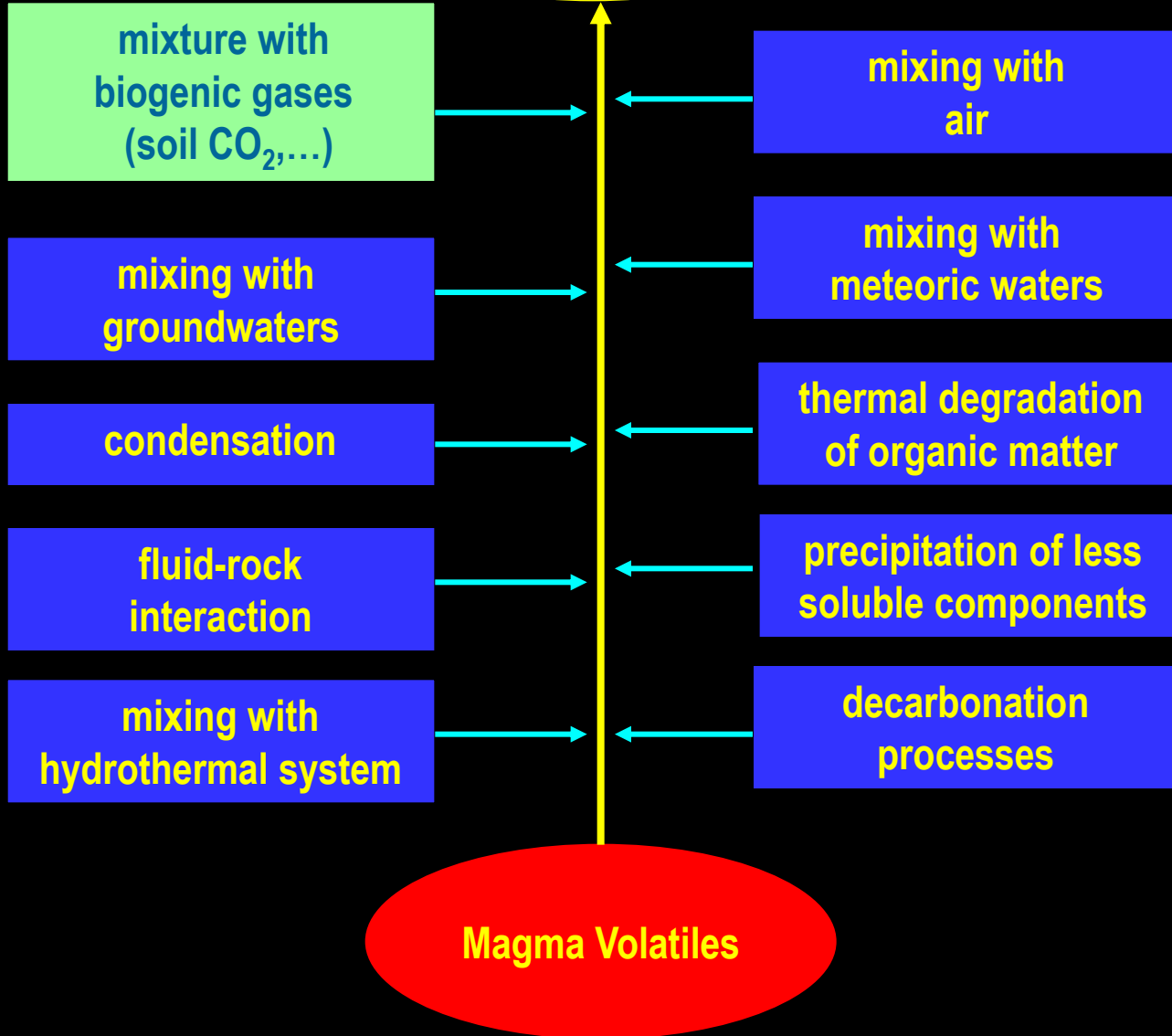Inputs derived by biological activity and/or radioacrive decay

Addition of air

ASW (Air Saturated Water) and/or direct contamination of air

Generally speaking, it can be said that the magmatic systems are are dominated by oxidizing conditions, whereas in the hydrothermal systems reducing conditions prevail. Consequently, the former will have SO_2 and other magmatic gases, whereas the latter show CO_2, H_2S, H_2, CO and CH_4, which are also favored by *scrubbing* processes.
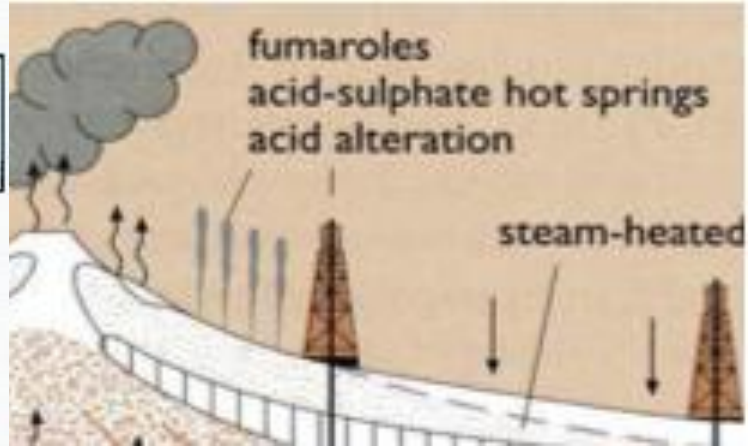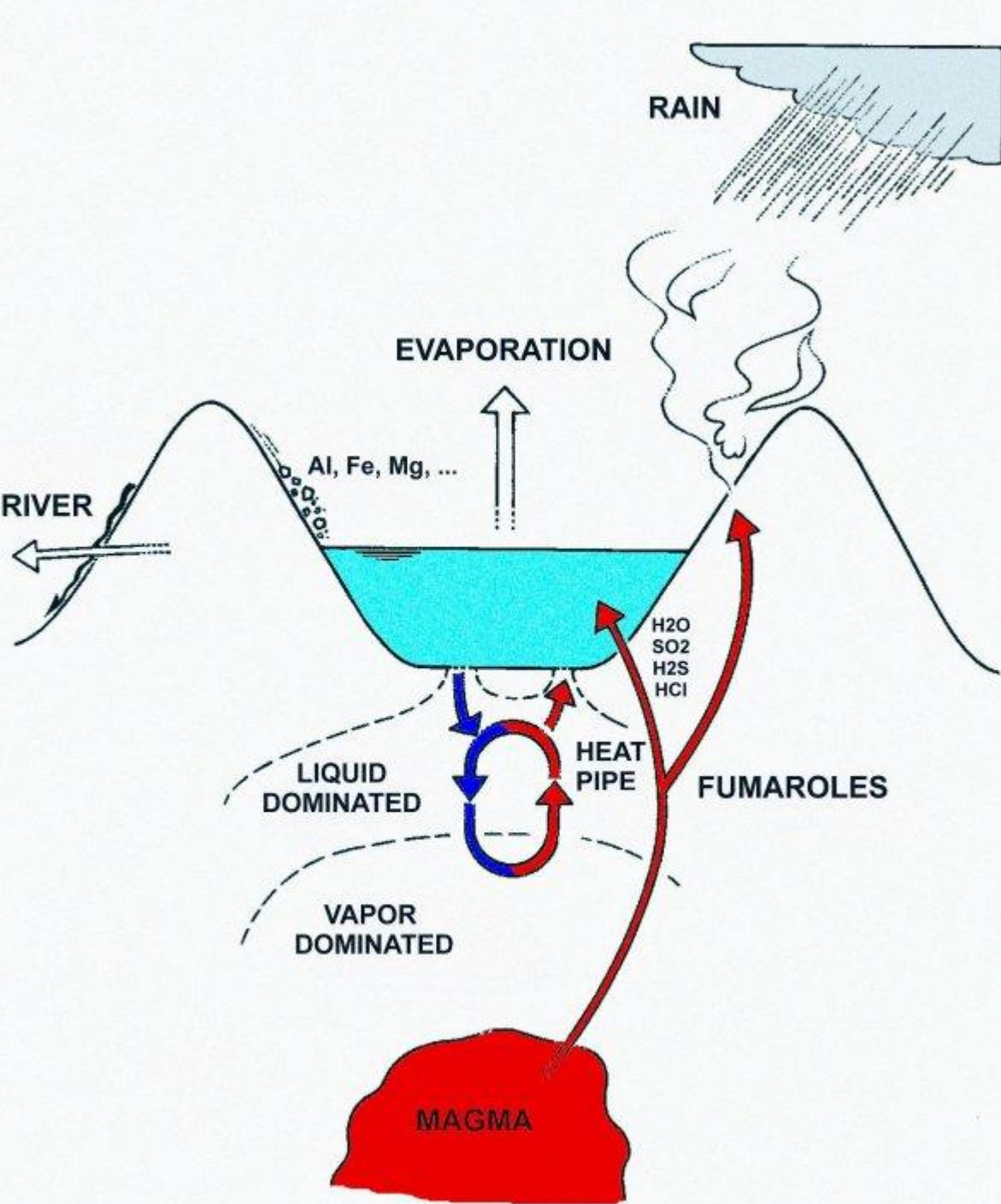
... H$_2$S, whose dissolution ... sive to the rocks.

... ervoirs associated with

... and remove cations from the ... ydrite, pyrite and kaolinite.

... contents of waters and rocks ... t is at depth the Na-Cl-rich

Water types

Circulating waters in deep-seated geothermal reservoirs and high enthalpy: **Na-Cl** with Cl up to thousands of mg/L (155.000 mg/L; Salton Sea, California) and acidic to neutral pH values with high SiO_2, K, Li, B and F, whereas Mg is low. The main dissolved gases are CO_2 and H_2S.
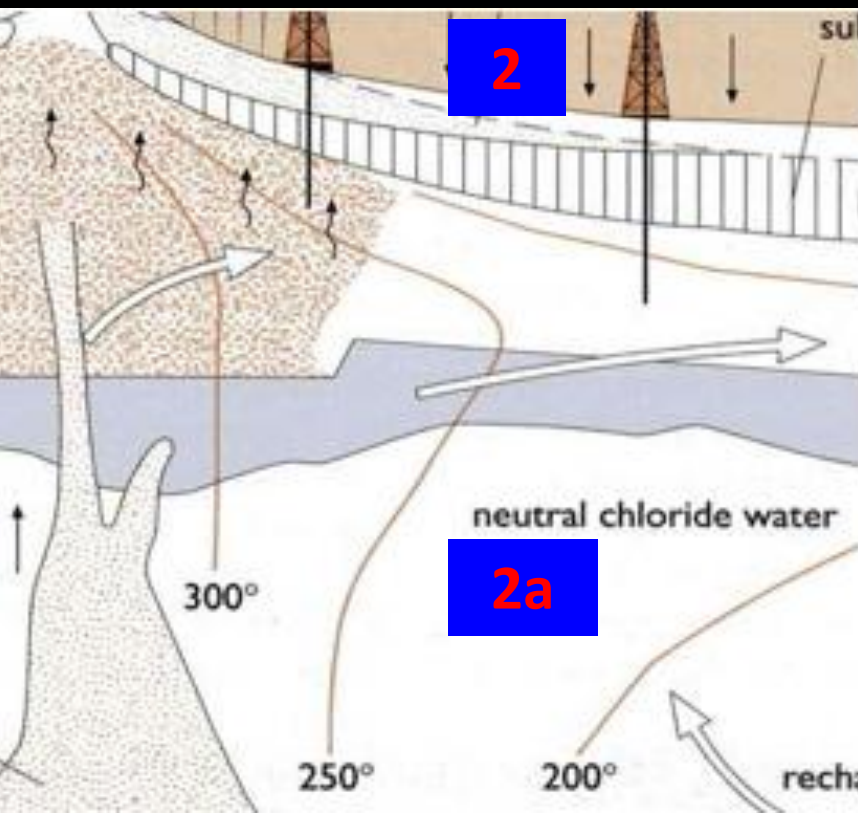These waters are usually fed by meteoric waters, although connate or magmatic waters can be present.

The waters at depth are initially acidic and turn to be neutral Na-Cl waters due to WRI processes and removal of magmatic sulfur species by transformation to sulfate/sulfide.

The deep Na-Cl waters can get to the surface or mix with shallow aquifers to produce Cl-diluted waters. Often they can be found at several kms from the volcanic edifice.

They a
above
system
phase

As a b
phase

The s
Here,

At thei
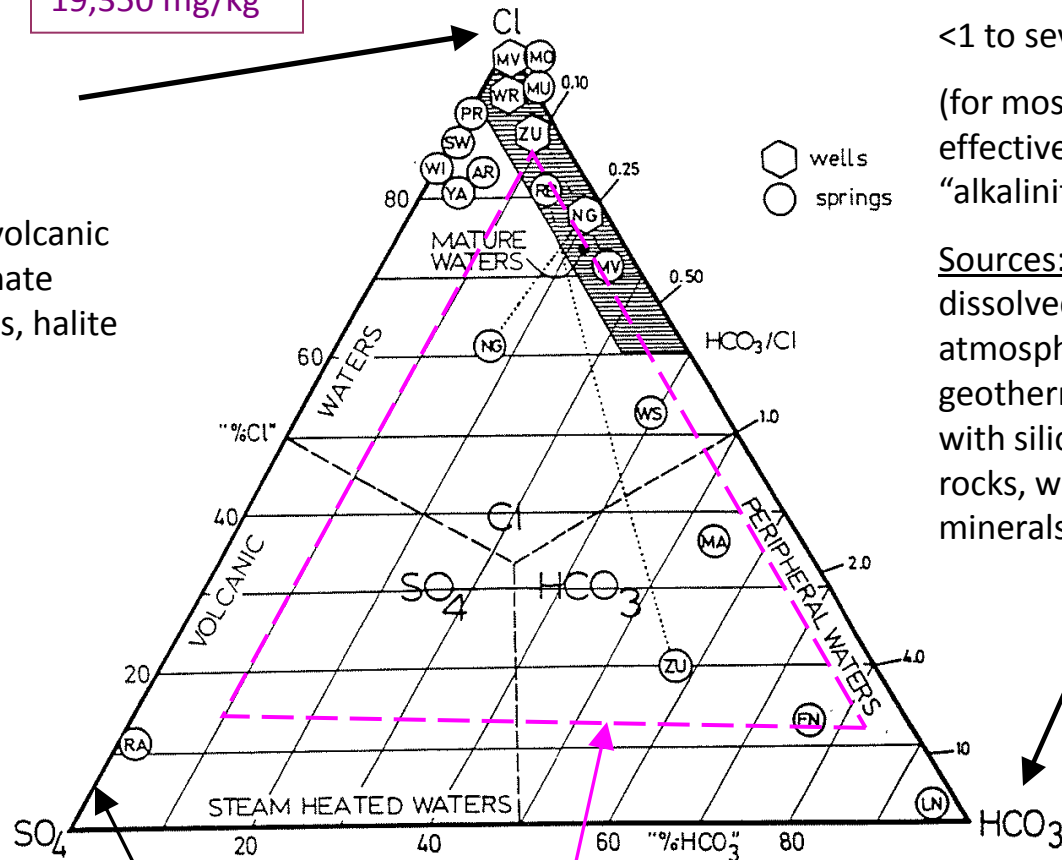vapor

Solutes: main anions

Chloride

~50 to ~20,000 mg/kg

(to ~200,000 mg/kg in hypersaline brines)

Sources: traces of Na-K-Cl in volcanic rocks (seawater origins), connate seawater in sedimentary rocks, halite deposits

Sulfate

~10 to ~1500 mg/kg

(to ~100,000 mg/kg in acid volcanic steam condensates

Sources: oxidized sulfide minerals and H_2S, sulfate mineral deposits (gypsum, anhydrite)

seawater Cl 19,350 mg/kg

W.F. Giggenbach

## Bicarbonate

<1 to several 1000 mg/kg

(for most purposes, effectively the same as "alkalinity")

Sources: reactions of dissolved CO_2 from atmosphere and/or in geothermal/volcanic steam, with silicate minerals in rocks, with carbonate minerals (limestone)

Extremes of volcanic and steam heated are acidic (no HCO_3)

Approximate range among non-volcanic geothermal systems (higher SO_4 exist)

$$CaCO_{3(s)} + CO_{2(g)} + H_2O \longleftrightarrow Ca^{2+}_{(acq)} + 2HCO_3^-{}_{(acq)}$$
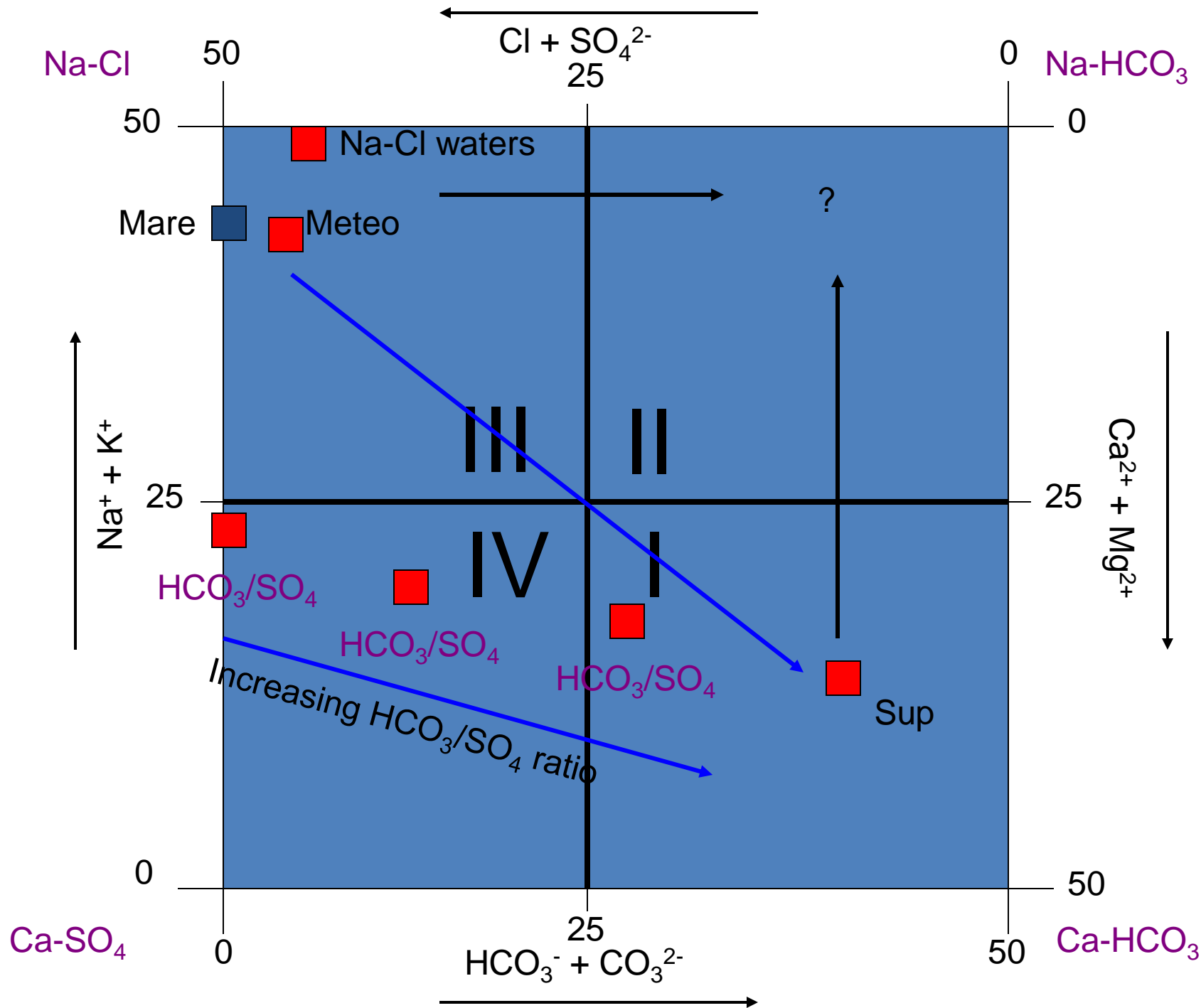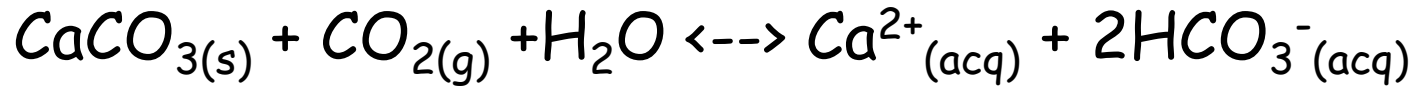
Ion-exchange reactions

If a mineral is able to adsorb ions onto its surface when in an electrolytic solution, some ions can be "captured" by the mineral from the solution while others may "leave" the mineral.

$$Na\text{-clay} + Ca^{2+} \longleftrightarrow Ca\text{-clay} + 2Na^+$$

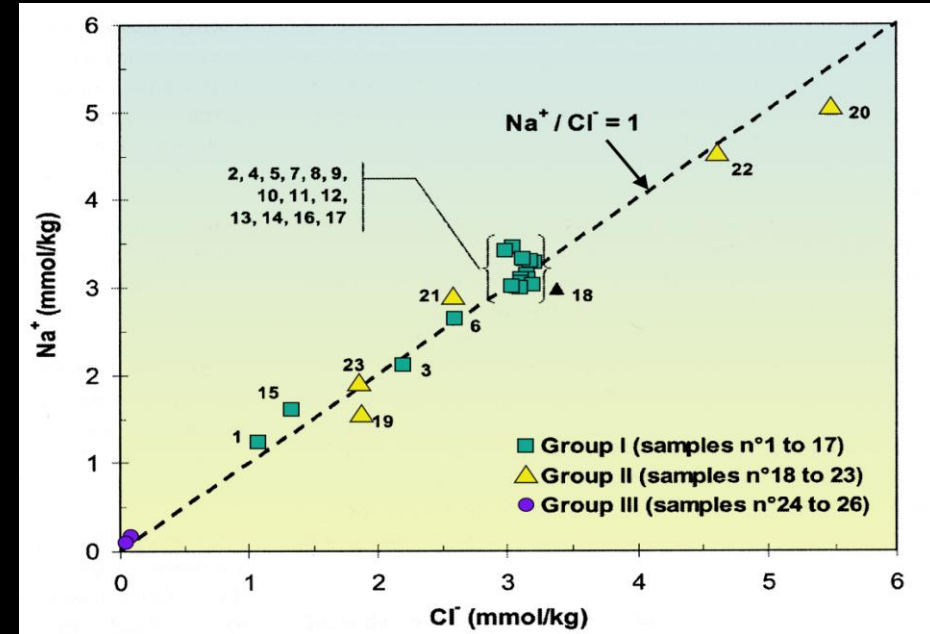# Source of water solutes
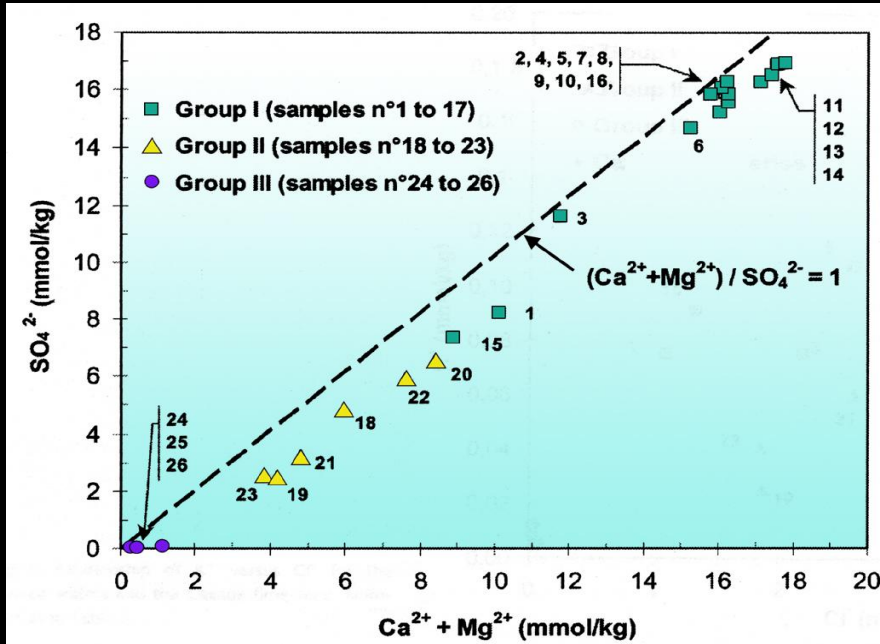
All samples are close to $SO_4/Ca+Mg = 1$:
→ stoichiometric dissolution of sulfate minerals (gypsum, anhydrite)
$$(Ca-Mg)SO_4 + H_2O \rightarrow Ca^{++} (+Mg^{++}) + SO_4^{--} + H_2O$$

All samples are close to $Na/Cl = 1$:
→ stoichiometric dissolution of evaporitic minerals (halite) or Na-Cl waters as seen before
$$NaCl + H_2O \rightarrow Na^+ + Cl^- + H_2O$$

$$\delta^{18}O\ ‰ = \left\{ \frac{^{18}O/^{16}O_{sample} - {}^{18}O/^{16}O_{V\text{-}SMOW}}{^{18}O/^{16}O_{V\text{-}SMOW}} \right\} \times 1000$$

$$\delta^{2}H\ ‰ = \left\{ \frac{^{2}H/^{1}H_{sample} - {}^{2}H/^{1}H_{V\text{-}SMOW}}{^{2}H/^{1}H_{V\text{-}SMOW}} \right\} \times 1000$$

$$\delta^{13}C\ ‰ = \left\{ \frac{^{13}C/^{12}C_{sample} - {}^{13}C/^{12}C_{V\text{-}PDB}}{^{13}C/^{12}C_{V\text{-}PDB}} \right\} \times 1000$$

Helium isotopes
R/Ra: R is the measured $^{3}He/^{4}He$ ratio and Ra is the $^{3}He/^{4}He$ ratio in the **AIR**: **1.39×10^{-6}**
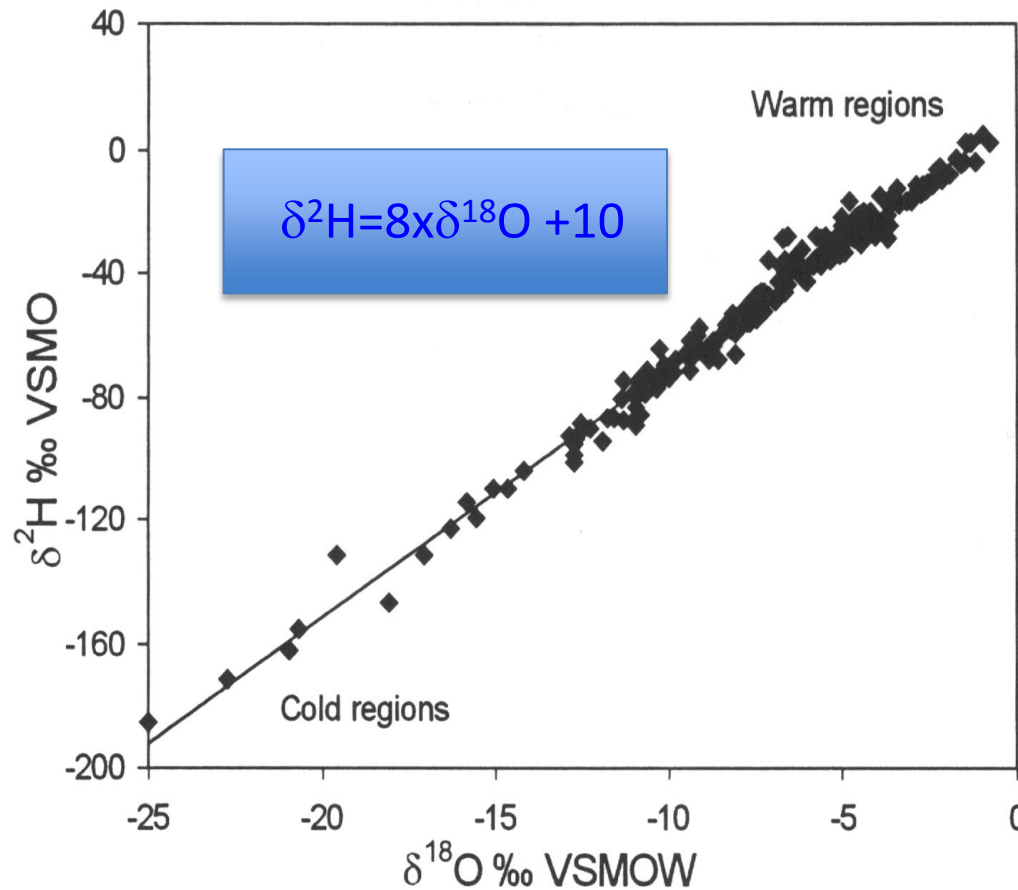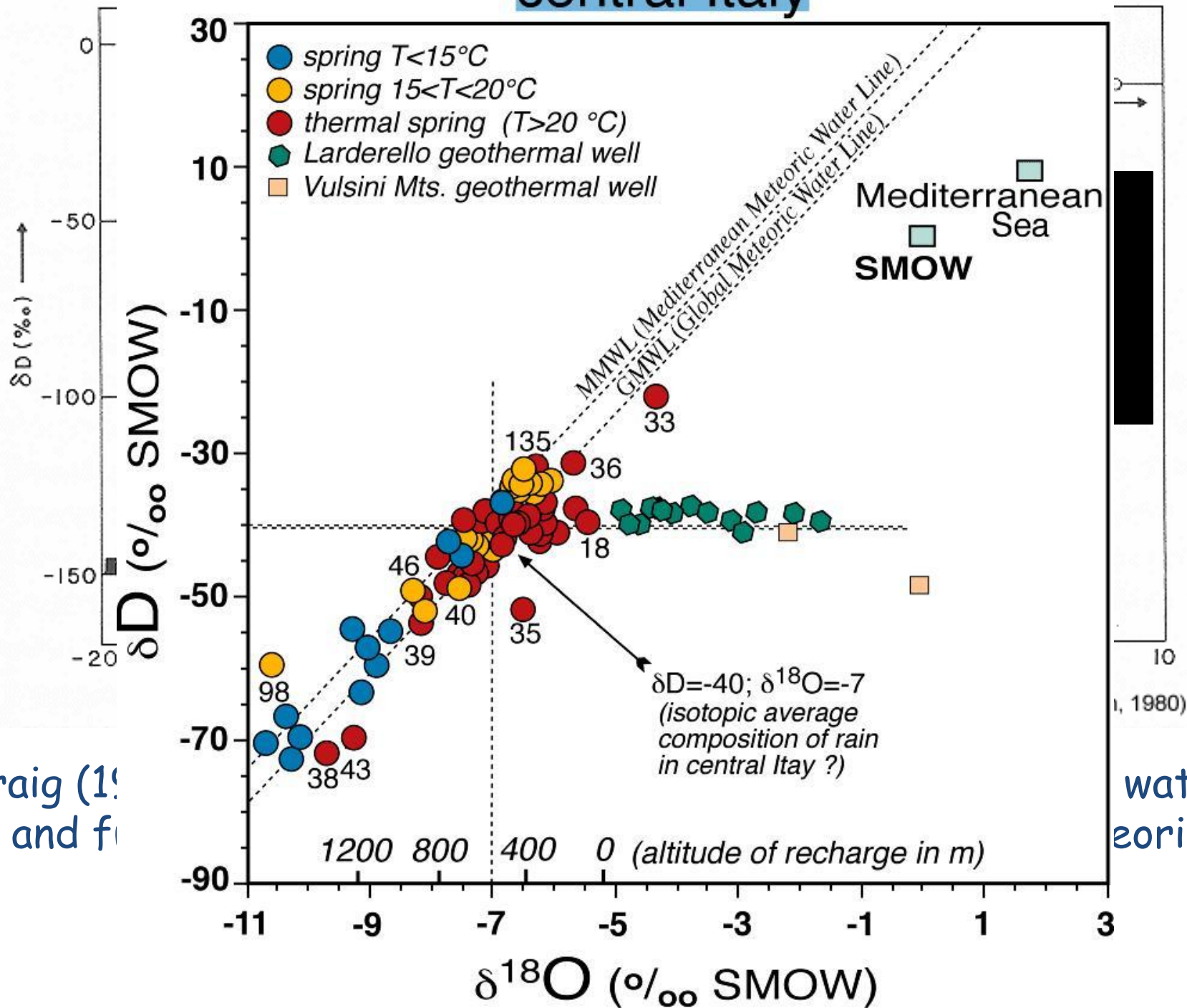
Fig. 2-1 The meteoric relationship for ^{18}O and ^{2}H in precipitation. Data are weighted average annual values for precipitation monitored at stations in the IAEA global network, compiled in Rozanski et al. (1993).

☐ δD and $\delta^{18}O$ values for the global precipitation.
• The slope of ca. 8 equals the condensation value of rainwater in the Rayleigh distillation process.

central Italy

- ● spring T<15°C
- ● spring 15<T<20°C
- ● thermal spring (T>20 °C)
- ⬠ Larderello geothermal well
- ▢ Vulsini Mts. geothermal well

Mediterranean Sea

SMOW

MMWL (Mediterranean Meteoric Water Line)

GMWL (Global Meteoric Water Line)

135

33

36

18

46

40

35

39

98

38 43

δD=-40; δ¹⁸O=-7
(isotopic average
composition of rain
in central Itay ?)

1200 800   400   0 (altitude of recharge in m)

δD (‰ SMOW)

δ¹⁸O (‰ SMOW)

δD (‰)

, 1980)

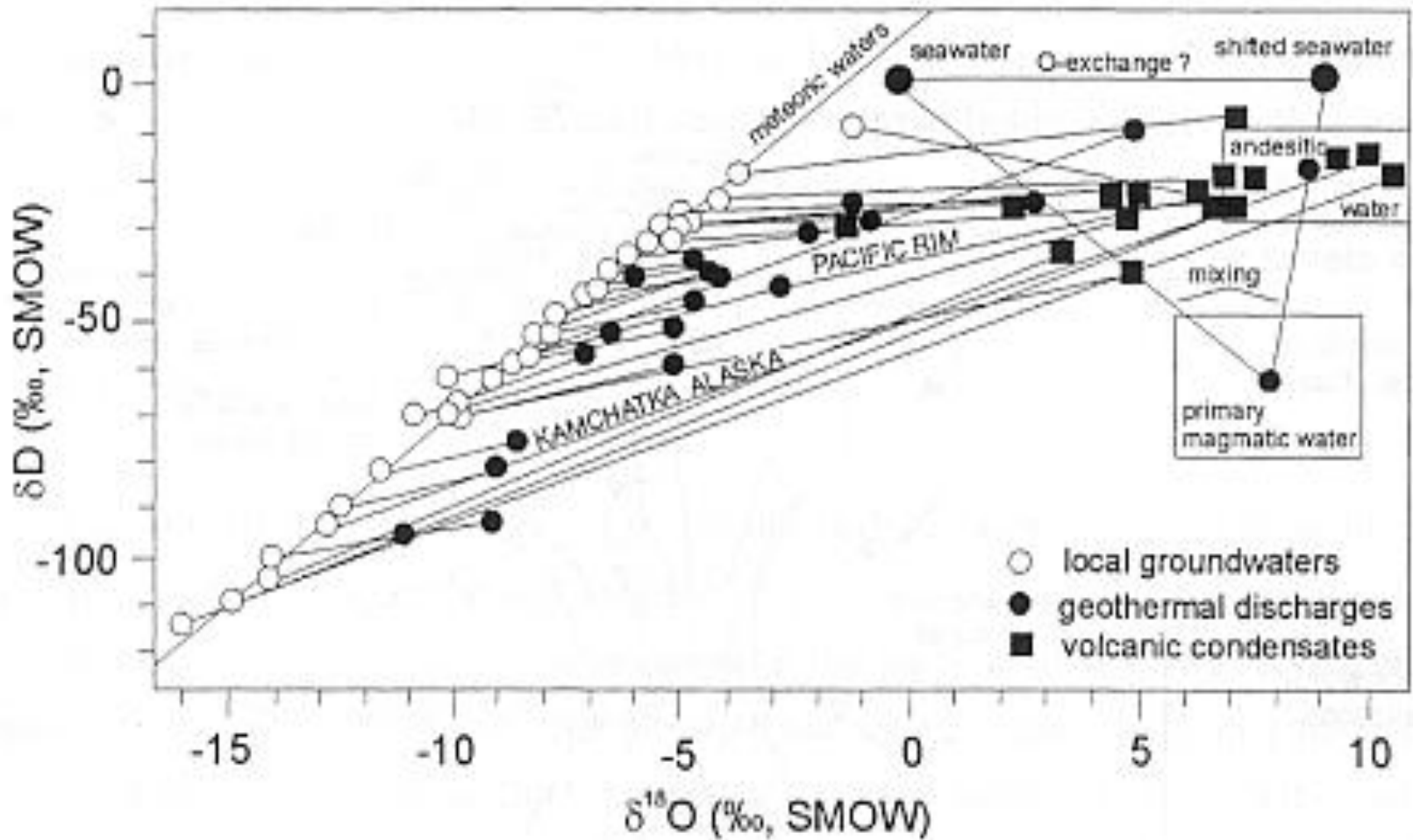Craig (19...   waters
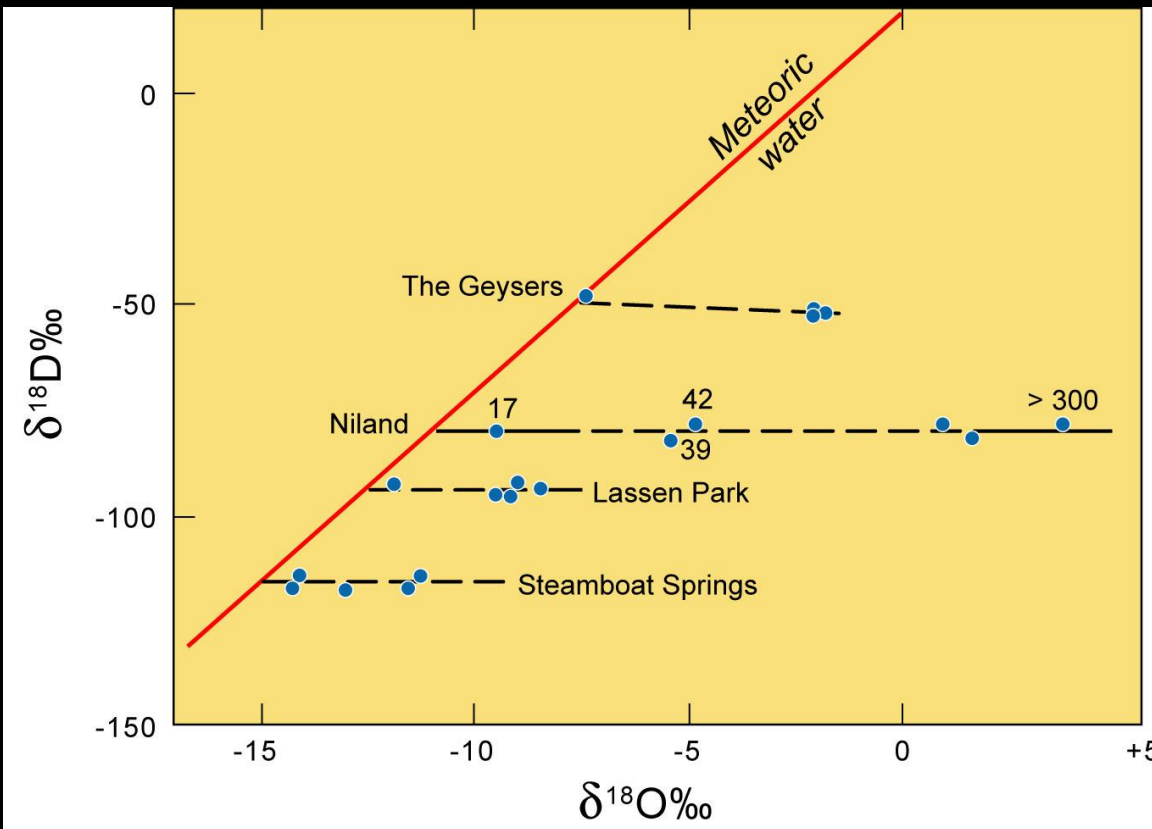   and f...   eoric

The volcanic condensates have allowed to identify a magmatic *end member* (namely andesitic magmatic water with δD of -20 $\pm$ 10 ‰), whereas the geothermal vapors are rich in the local meteoric component.

The O-H isotopic plot: high equilibrium temperatures between carbonate and silicate rocks and geothermal waters

Geothermal waters

❑ The isotopic composition is controlled by the progressive equilibrium between O-H_2O and O-rock (carbonates and silicates)

❑ δD in the discharging waters is not modified (low H content in rocks)

❑ the higher the O-shift, the higher the reservoir temperaturs

➤ **Marker di WRI**

❑ Generally speaking, the O-shift occurs for T>200 °C

Main features of hydrothermal fluids (HF)

1. Hydrothermal fluids have a variable composition whose most species are in chemical equilibrium with the altered hosting rocks;

2. Water has mainly a marine or meteoric origin;

3. CO_2 and S can be controlled by carbonate and sulfide precipitation. This partly jeopardizes their magmatic contribution.

A simple and useful diagram to discriminate the gas sources
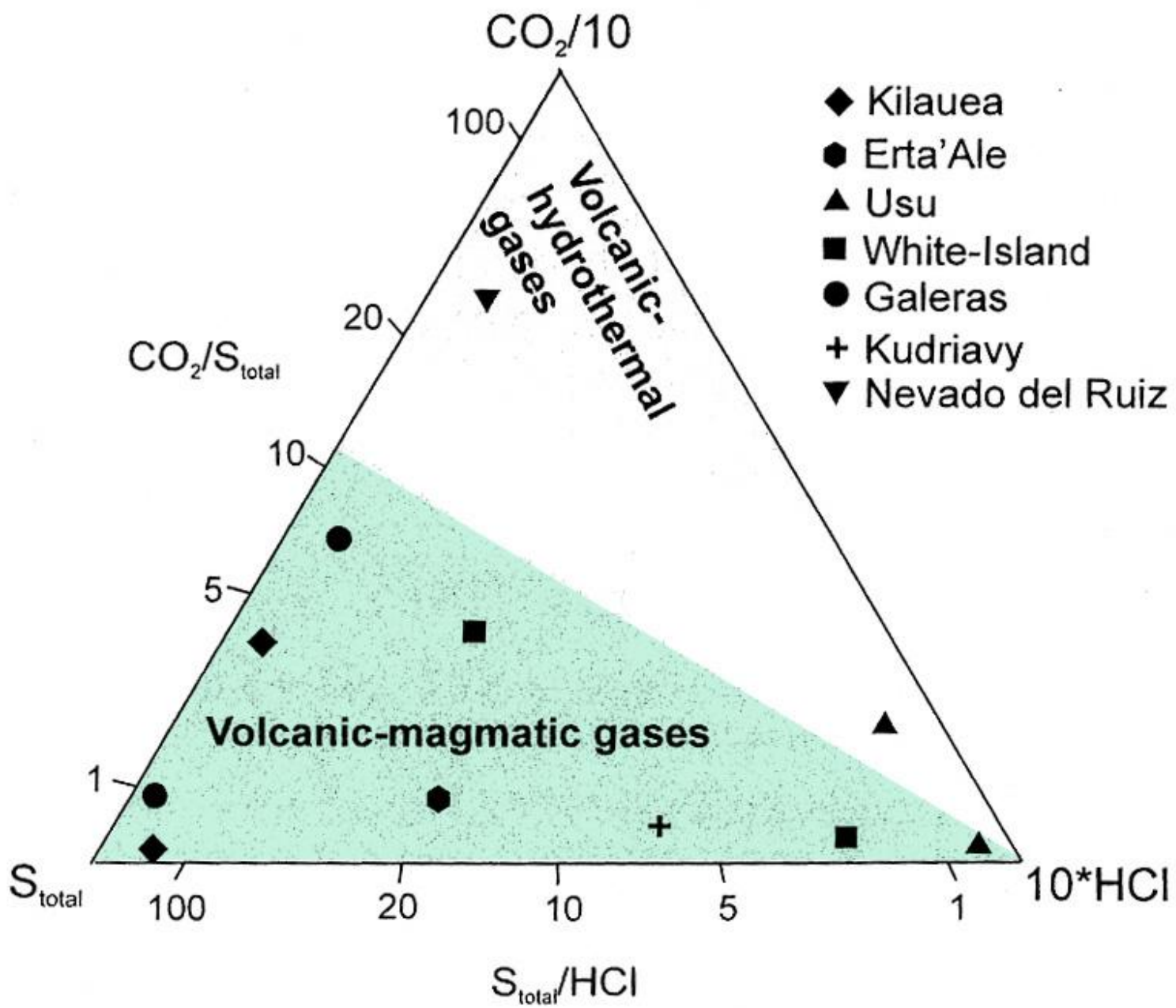
…and to discriminate the noble gases…
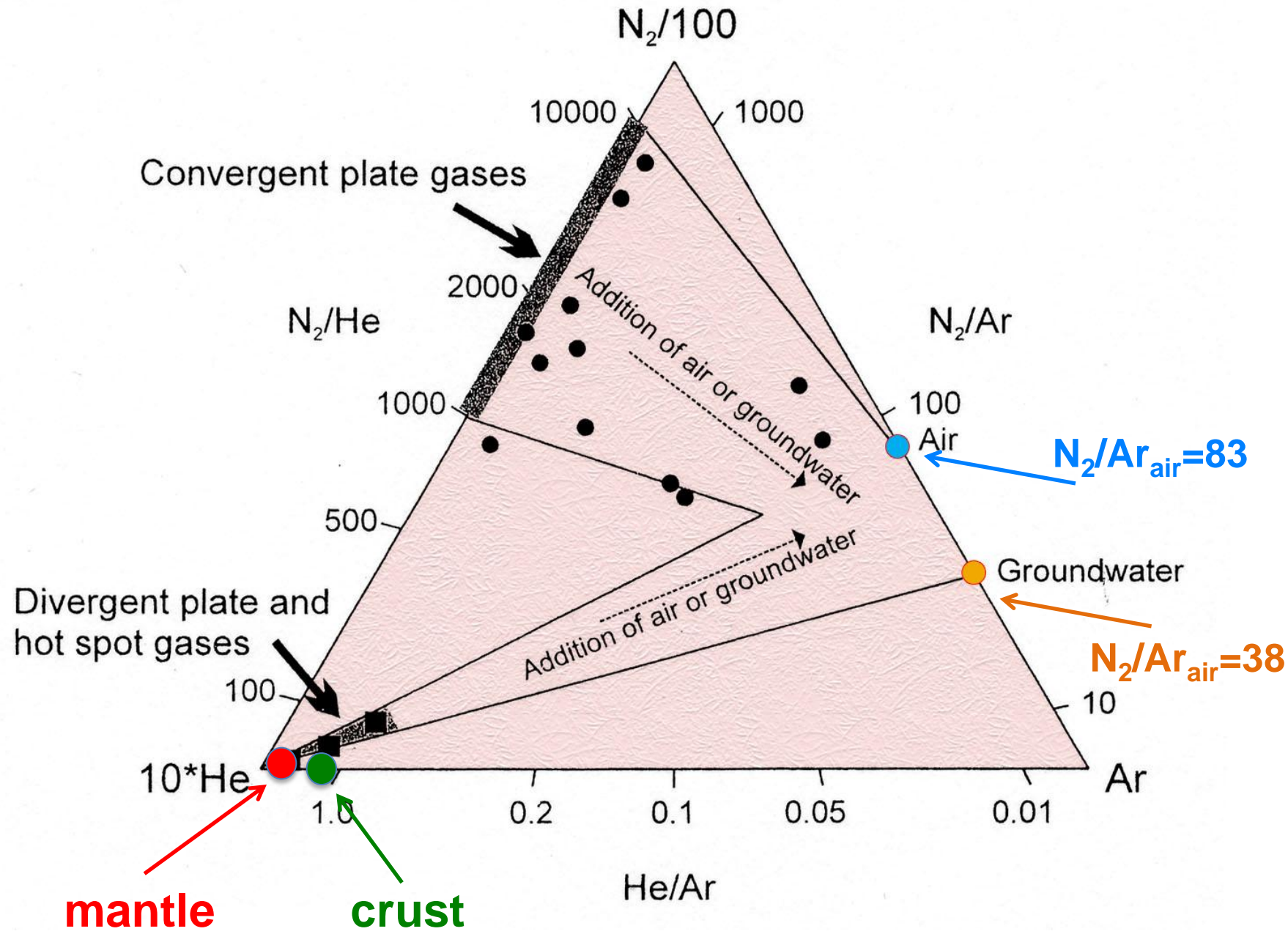
Origin of the CO_2 – $CO_2/^3He$ ratio
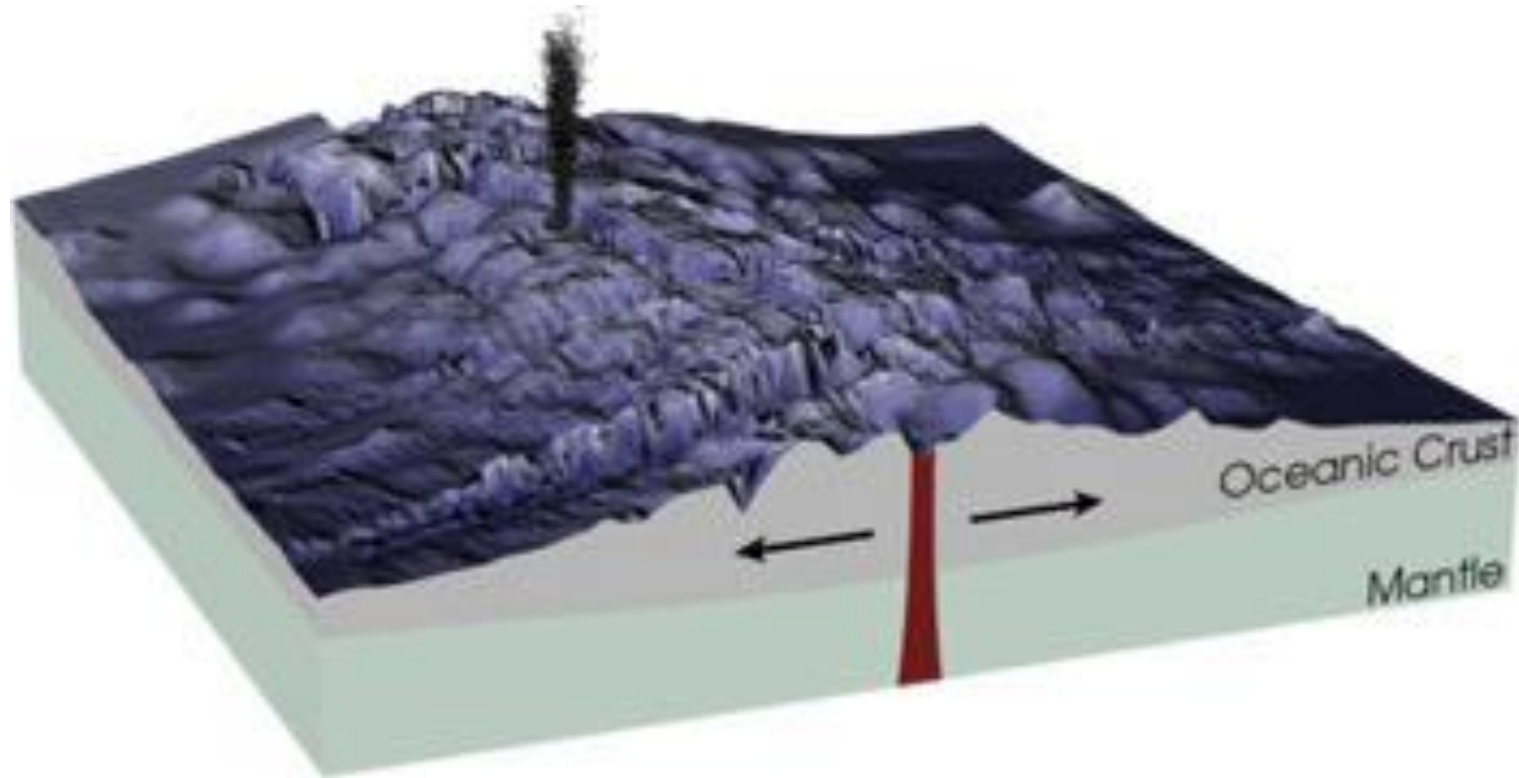
- Mantle $CO_2/^3He$ range: $1 \times 10^9 - 1 \times 10^{10}$
- Measured from Mid Ocean Ridge Basalts - MORBs

Origin of the CO_2 – $CO_2/^3He$ ratio

Above 1×10^{10}:

Crustal CO_2

Mantle (MORB) range: 1×10^9 – 1×10^{10}

Below 1×10^9:

CO_2 lost relative to ^3He

Y-axis: $CO_2/^3He$ Ratio

X-axis: CO_2 Concentration (%)

Origin of the CO_2 – $CO_2/{}^3He$ ratio

Green River Seeps

1 - 16%

Mantle CO_2

Mantle (MORB) range: $1 \times 10^9 - 1 \times 10^{10}$

CO$_2$/^{3}He Ratio

CO$_2$ Concentration (%)
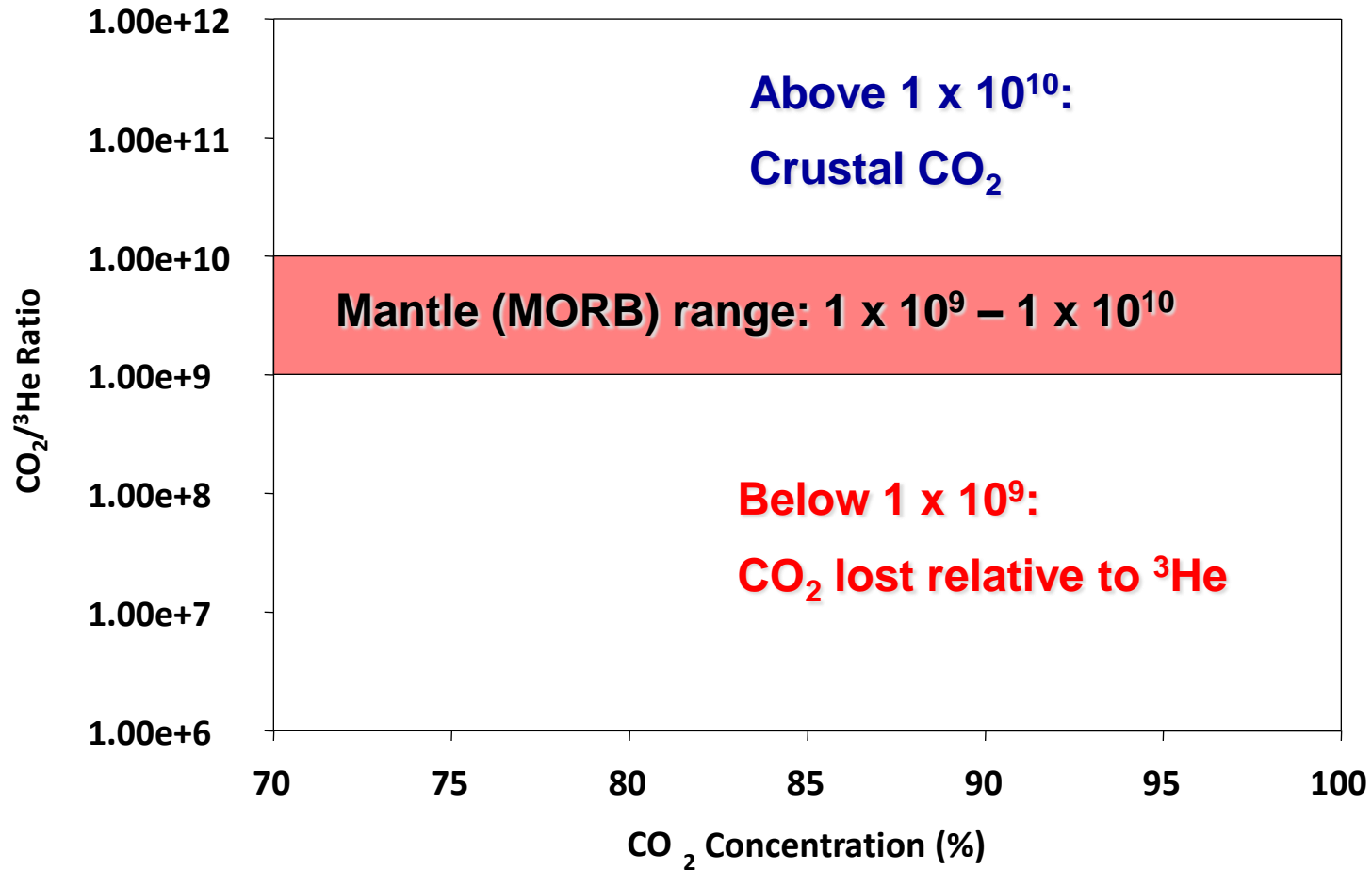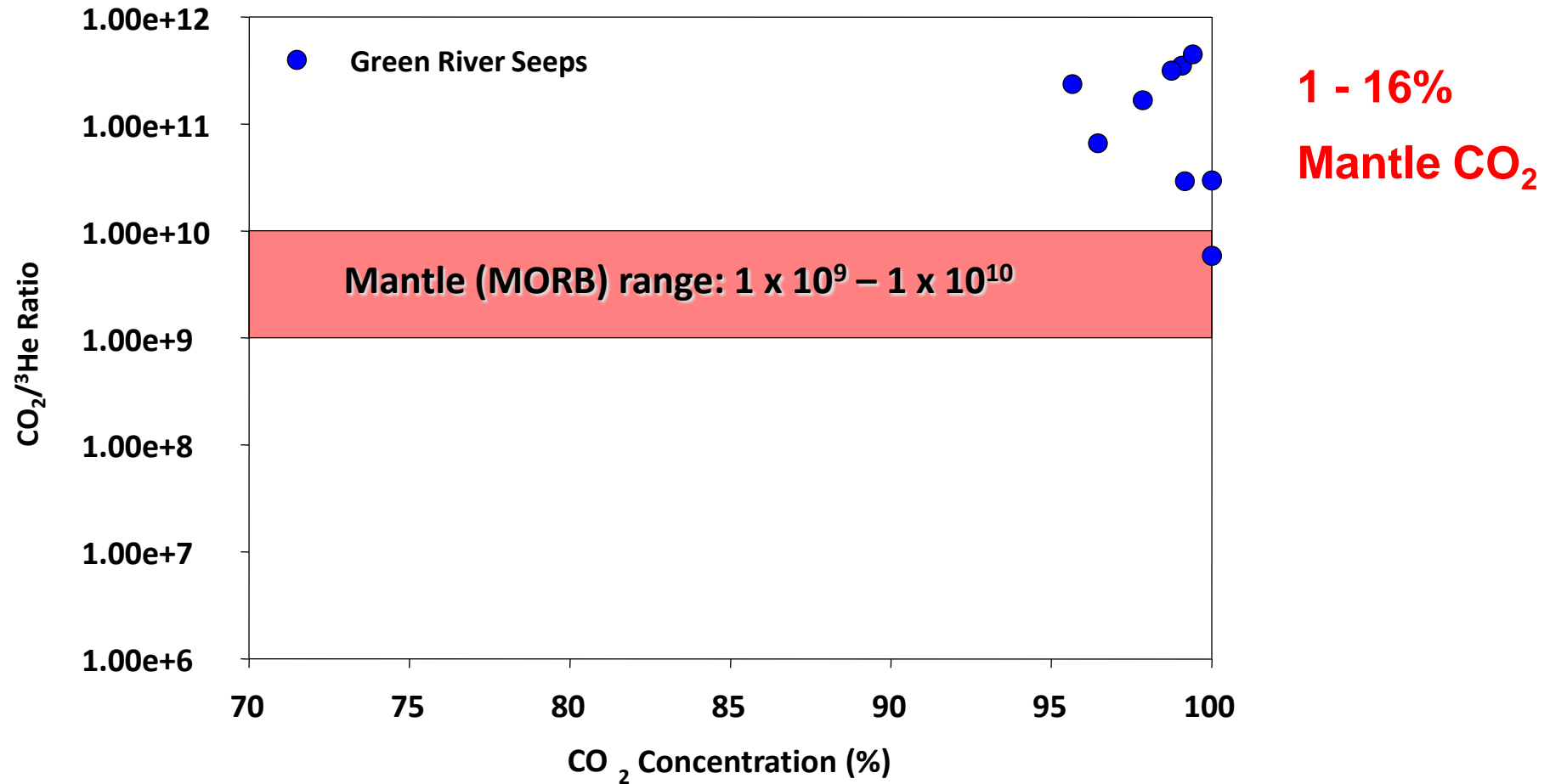
- Predominantly crustal derived CO_2 erupted from the Green River seeps.
- Small mantle component → 1 – 16%

$$M + S + L = 1$$

M: mantle degassing; L: limestone; S organic-rich sediments.

$$(\delta^{13}C - CO_2)_{obs} = M(\delta^{13}C - CO_2)_{MORB} + L(\delta^{13} C - CO_2)_{Lim} + S(\delta^{13} C - CO_2)_{Sed}$$

$$\left(\frac{1}{CO_2/^3He}\right)_{Obs} = \left(\frac{M}{CO_2/^3He}\right)_{MORB} + \left(\frac{L}{CO_2/^3He}\right)_{Lim} + \left(\frac{S}{CO_2/^3He}\right)_{Sed}$$

$$(\delta^{13}C - CO_2)_{MORB} = -6.5\text{‰}$$

$$(\delta^{13}C - CO_2)_{Lim} = 0\text{‰}$$

$$(\delta^{13}C - CO_2)_{Sed} = -30\text{‰}$$

$$\left(CO_2/^3He\right)_{MORB} = 1.5 * 10^9$$

$$(CO_2/^3He)_{Lim} = 1 * 10^{13}$$
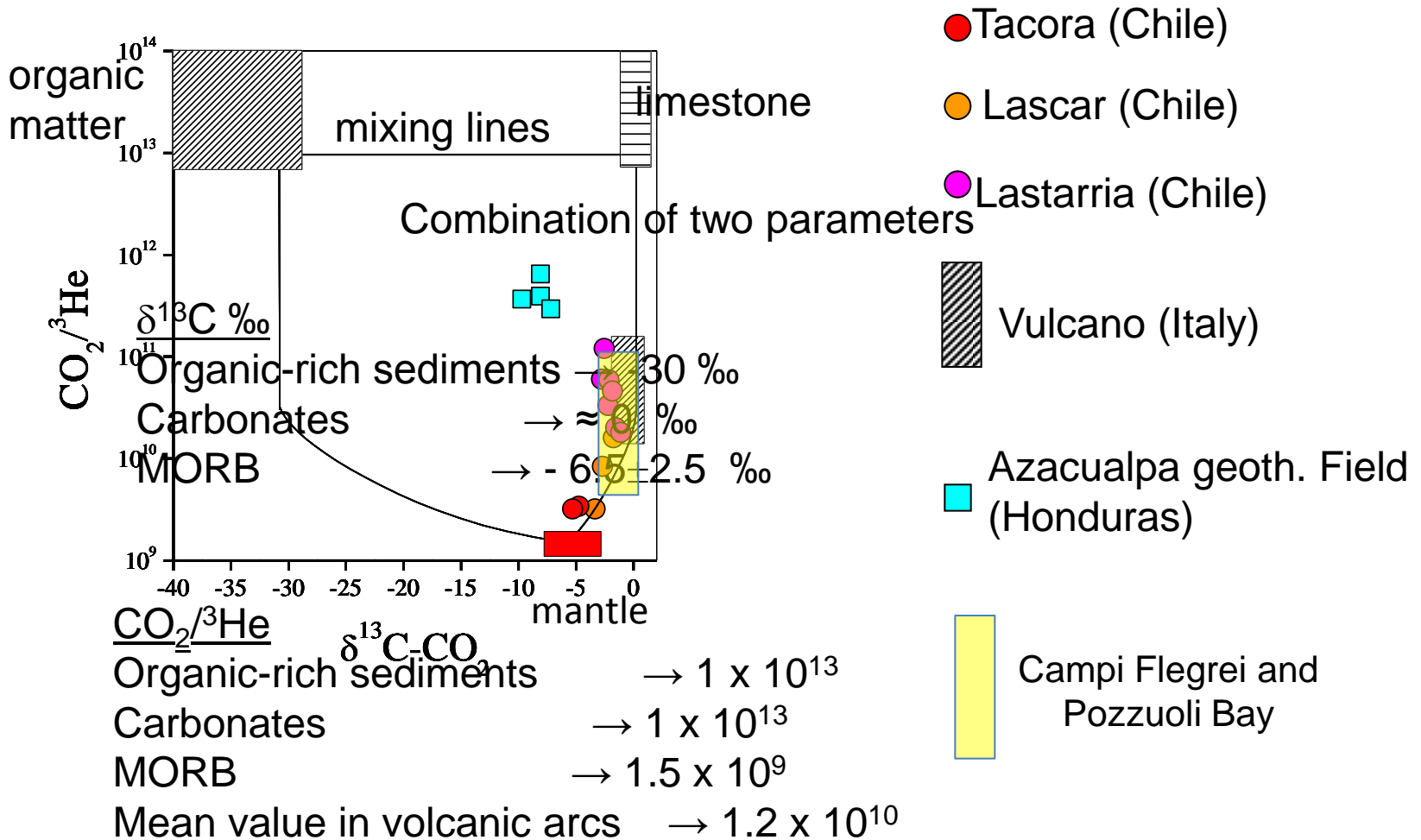
$$(CO_2/^3He)_{Sed} = 1 * 10^{13}$$

Different sources of CO_2 :
Sediments (carbonates vs organic-rich sediements)
Mantle degassing
How can the CO_2 source be recognized?

Tacora (Chile)

Lascar (Chile)

Lastarria (Chile)

Vulcano (Italy)

Azacualpa geoth. Field (Honduras)

Campi Flegrei and Pozzuoli Bay

Combination of two parameters

$\delta^{13}C$ ‰
Organic-rich sediments → - 30 ‰
Carbonates → ≈ 0 ‰
MORB → - 6.5 -2.5 ‰

$CO_2/^3He$
Organic-rich sediments → 1 x 10^{13}
Carbonates → 1 x 10^{13}
MORB → 1.5 x 10^9
Mean value in volcanic arcs → 1.2 x 10^{10}

Basic concepts

- Geochemical prospection is economically sustainable and a lot of infos can be gathered;

- Waters and gases at the surface **"HAVE BEEN THERE"** and generally the carry "infos" from the depth... it has to be understood WHICH ARE THE INFOS!

- We can divide the fluid constituents into two groups:

    - **Inert (non reactive) constituents** that can be defined as **TRACER**! Once in solution or in the gas phase they do not change. They are a **TAG** to understand their origin;

    - Chemically reactive species. They are affected by the environment but their behavior is controlled and can be understood: **GEOINDICATORS**!

TRACER: Noble gas and N_2, Cl, B, Li, Rb, Cs

GEOINDICATORS: Na, K, Mg, Ca, SiO_2 (T-dependent when reacting with Al-sils); H_2, H_2S, CH_4 e CO_2 (PT-redox-dependent)

    Exceptions: at >250 °C Cesium is a **tracer** but it may be hosted in zeolites at lower temperatures

W.F. Giggenbach
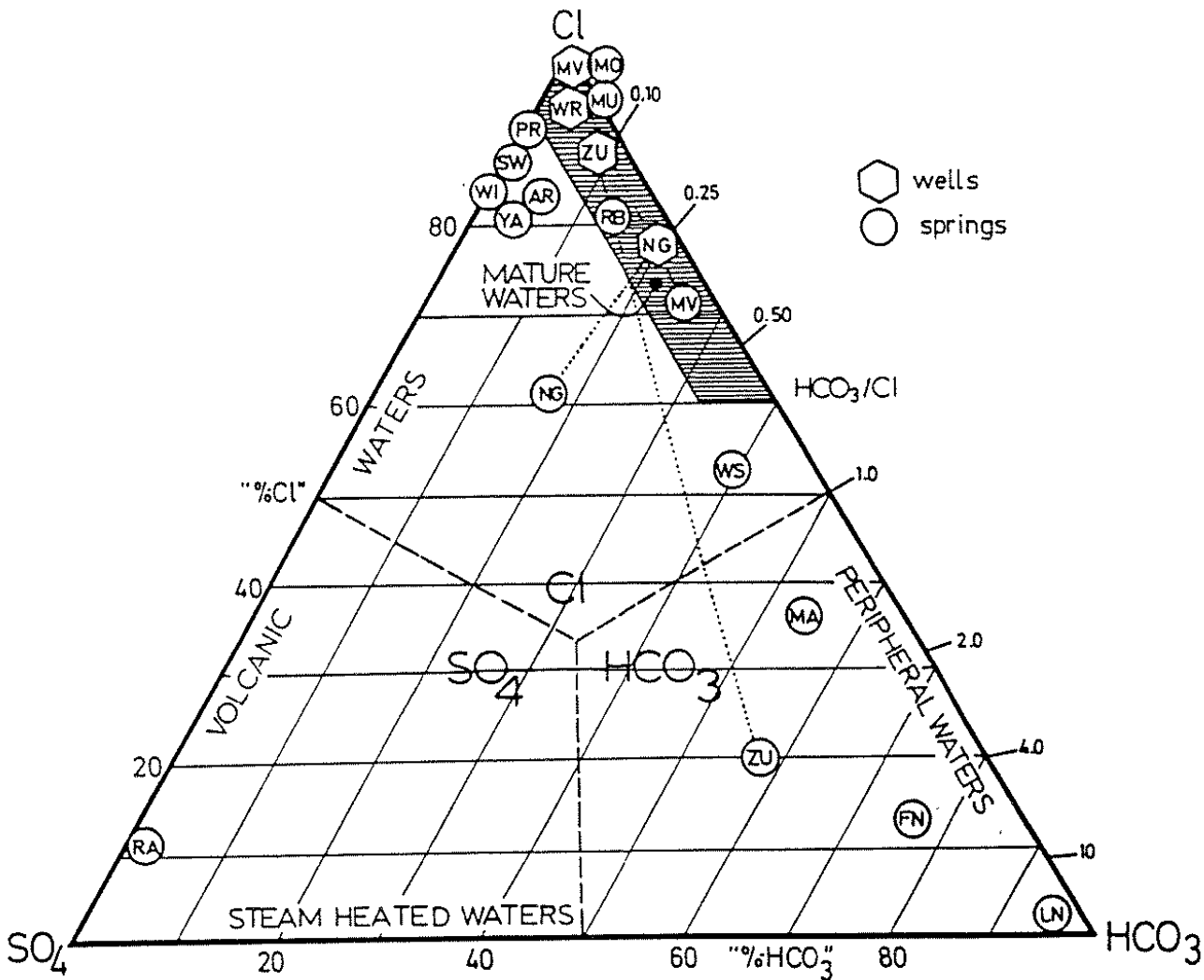
Advantages:
1) The main anions are considered; **2)** the mixing lines are straight lines; **3)** groups of waters can be recognized.
Limitations: 1) ratios → no concentrations; **2)** false correlations can be obtained.

Trace elements can be used to ascertain the deep origin of the waters by eliminating the shallow components if mobile alkaline elements (Li, Rb and Cs) are taken into account.

By comparing fresh and altered rhyolites in geothermal wells, Li, Cs and Rb do not seem to be leached but added by dissolution processes of deeper-seated rocks.
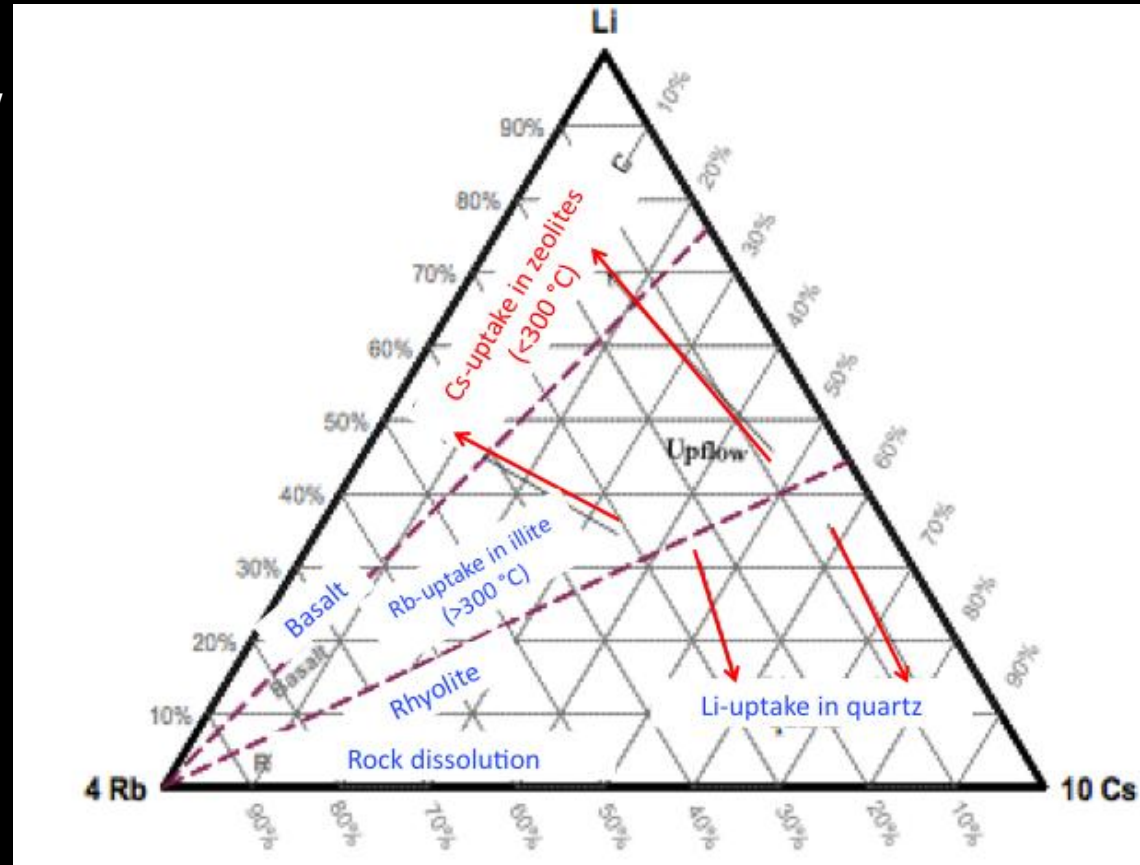
Although mixing with shallow waters may be occurring, the low contents of Li, Rb and Cs do not affect the relative ratios!

Rb behaves similarly to K and is hosted in K-minerals, e.g. illite:

Cs can enter zeolites when <250 °C.

Li is difficultly hosted, though possible, in quartz and chlorite.

This suggests that Li is more mobile than Rb and Cs…thus...

…Li is a good tracer of initial dissolution of altered rocks at depth and it can be coupled with two other mobile (conservative) tracer such as: Cl and B!

Only one sample is apparently characterized by rock-leaching (FN).

The other samples have higher Cl and B relative contents with respect to that of the rock:
1. Lost of Li. No way! No "hydrothermal sink" of Li;
2. Li stays in solution;
3. Cl and B are added;
4. At HT, Cl is as HCl;
5. At HT, B is as H_3BO_3;
6. Both are volatile and can be mobilized by the vapor phase at high T;
7. It can be hypothesized that they were part of the magmatic gases: formation of acidic brines and rock dissolution;
8. At low T, HCl is more acid and consumed by the alteration processes and it forms NaCl waters;
9. Boron prefers the volatile phase and can be carried by the vapor at lower temperatures.
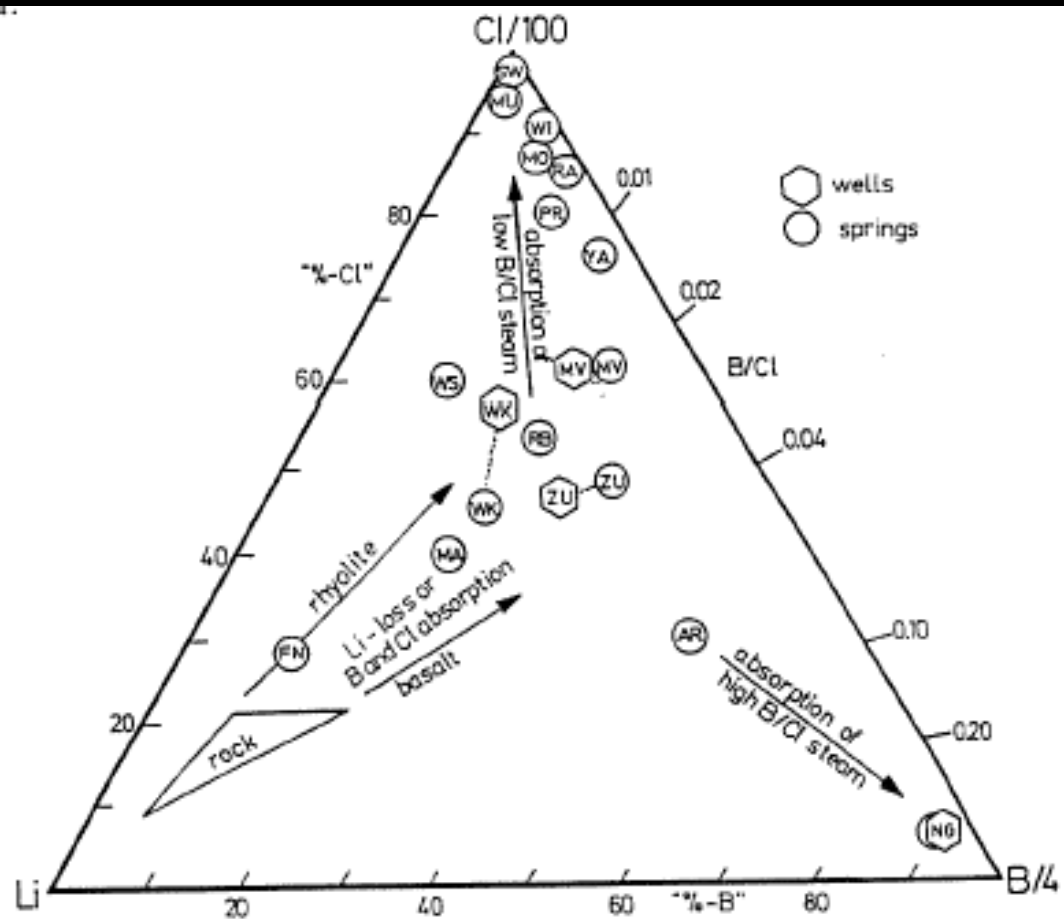
GEOTHERMOMETRY
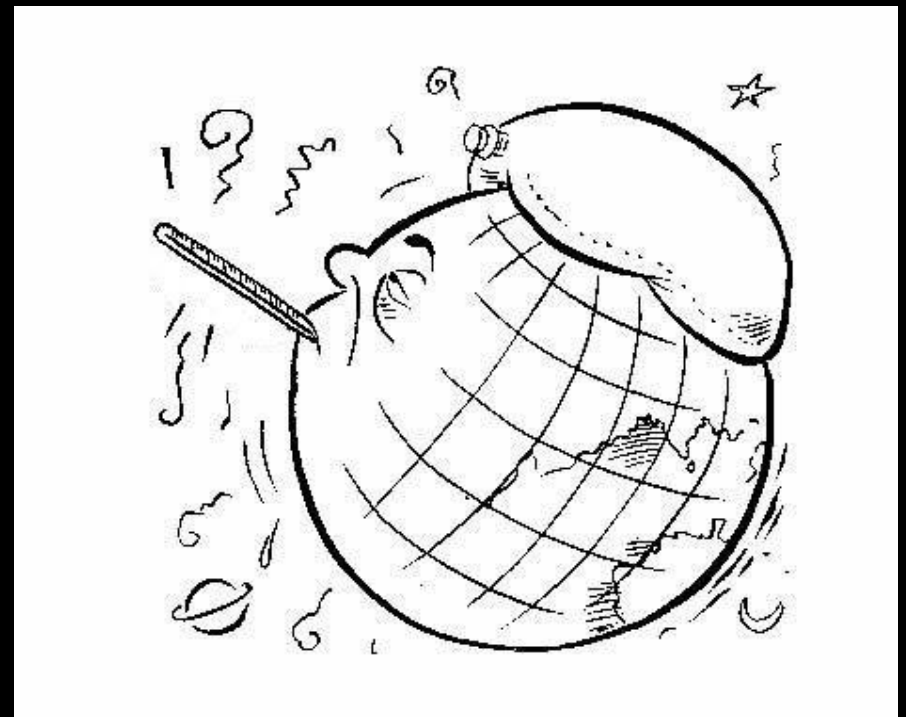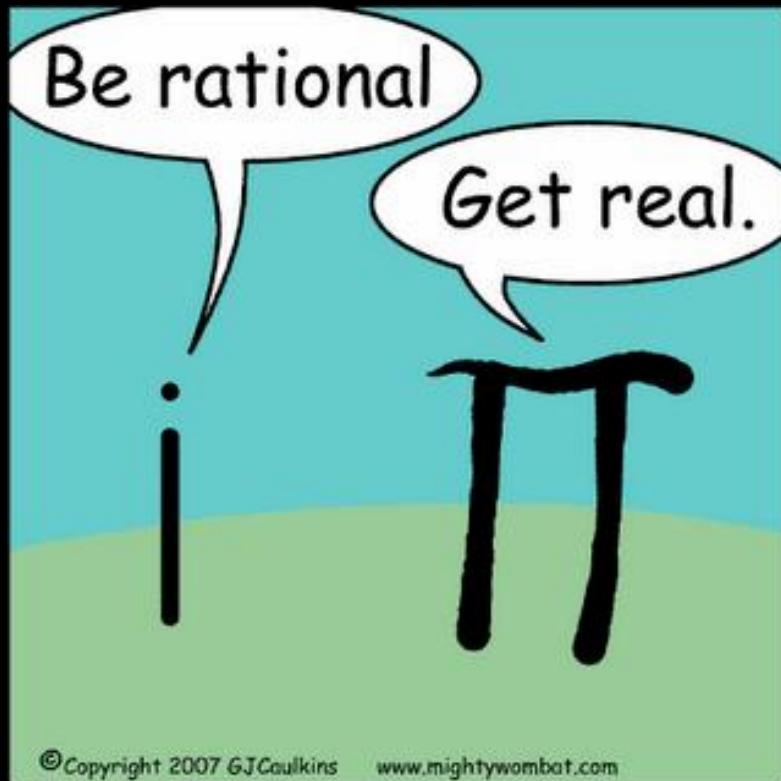
Geothermometry

Temperature estimations of the geothermal reservoirs by using mathematical equations that include analytical data

- Chemical GeoT
- Isotopic GeoT

- **minerals**
- **solutions**
- **gases**

Empirical Geothermometers

A comparison between concentrations or concentration/concentration ratios with measured T

➢ **It is important to have good measured temperatures at depth**

➢ **It is necessary to have a good temperature interval**

➢ **The Temperature vs. concentrations or concentration/concentration ratios must carefully be evaluated**

Thermodynamic Geothermometers:
at chemical/isotopic equilibrium

The equations are derived by calculating the concentration/concentration ratios for a specific reactions by using the thermodynamic constants related to that reaction

When can we apply geothermometry?

❖**1) no significant input of the selected species from an external system, e.g. surface or shallow waters;**

❖**2) strong dependence of the concentration/concentration ratios between the species involved in a certain reaction (as described by the Equilibrium Constant) and temperature;**

❖**3) the chemical reaction have attained a thermodynamic equilibrium.**
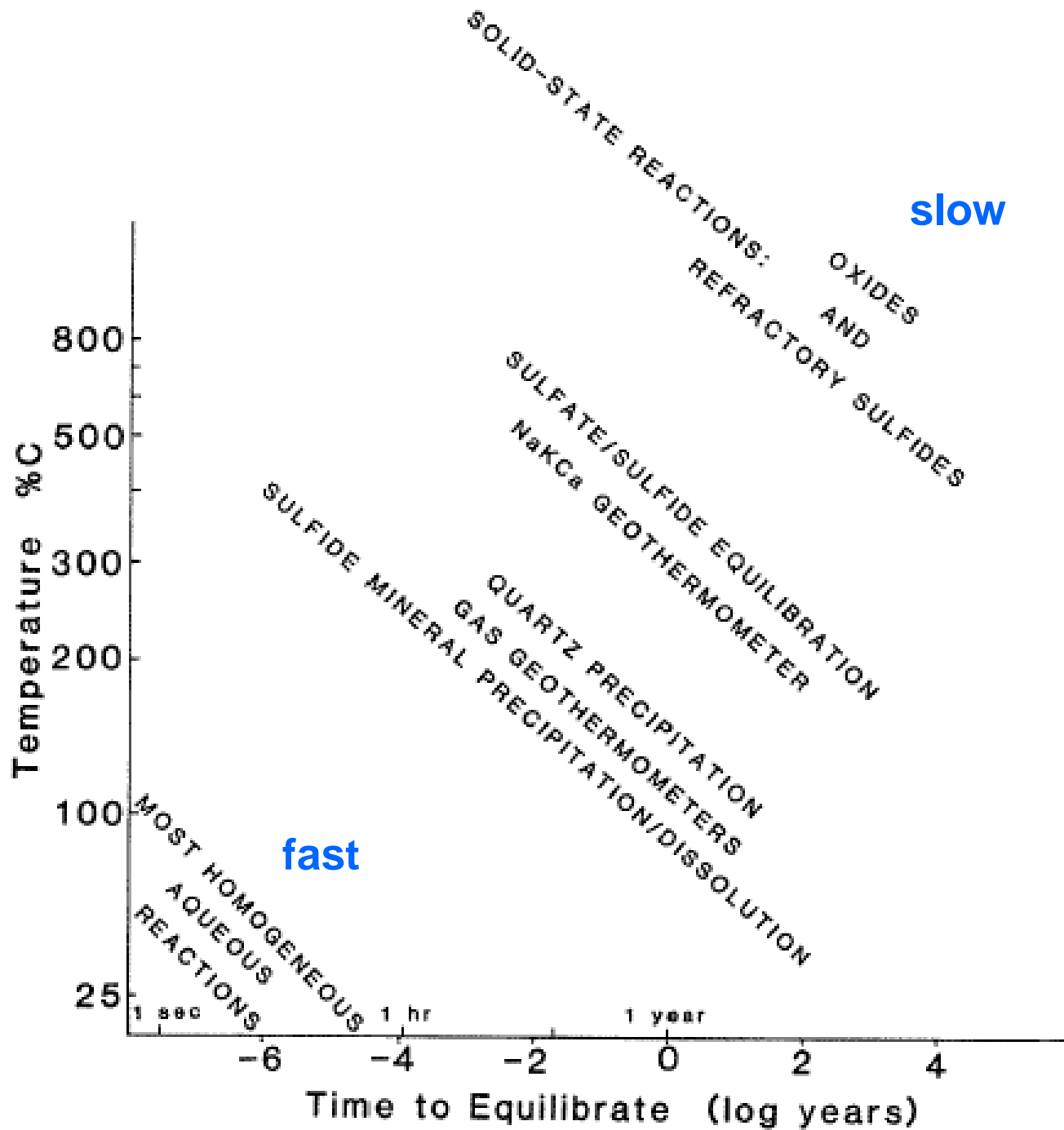
Principles

The liquid GeoTs are developed on the basis of:

- **The chemical equilibrium is dependent on T between water and minerals at the reservoir conditions**

- **Water maintains its chemical composition during the ascent to the surface:**

Possible secondary processes

  ➢ **cooling**

  ➢ **mixing with waters that have a different origin.**

- **GeoTs are not equations where the analytical data are simply added;**

- **The interpretation of the GeoTs requires that the geochemical processes in the geothermal systems are understood;**

- **It is necessary to verify whether the assumptions for which a certain GeoT has been applied are correct.**
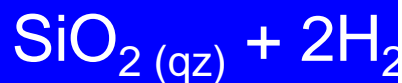
Two distinct liquid GeoTs:

1. Mineral solubility as a function of T, e.g. SiO_2;

2. Solution-mineral equilibrium where the temperature regulates specific concentration/concentration ratios of dissolved species, e.g. Na/K or K/Mg
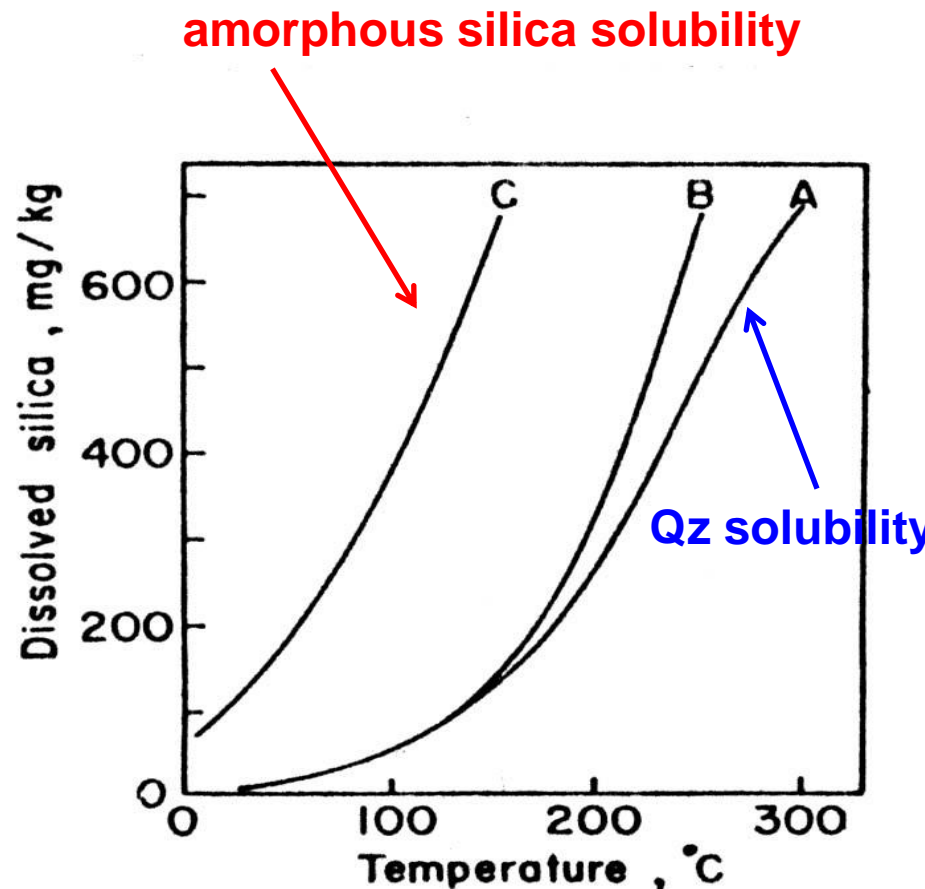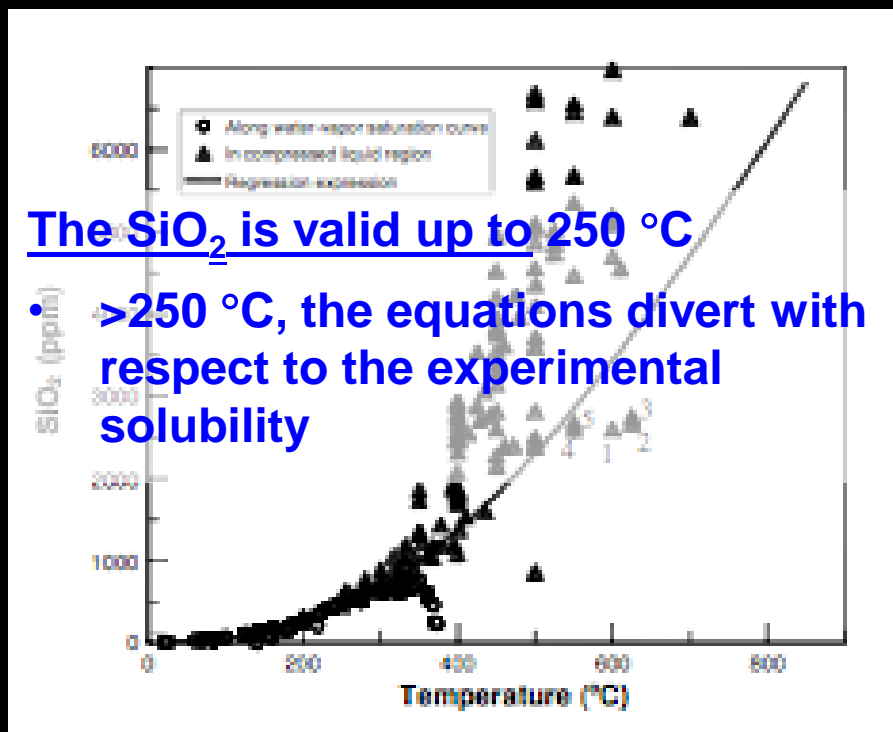
SiO₂

SiO$_2$ occurs as quartz, crystobalite, chalcedony, amorphous silica).

Thus, different GeoTs exist

The reaction to be taken into account is:

$$SiO_{2\,(qz)} + 2H_2$$

The solubility of SiO$_2$ changes as the te...

amorphous silica solubility

Qz solubility

The SiO$_2$ is valid up to 250 °C

- **>250 °C, the equations divert with respect to the experimental solubility**

Silica geothermometer

Geothermometer	Equation	Reference
Quartz-no steam loss	$T = 1309 / (5.19 - \log C) - 273.15$	Fournier (1977)
Quartz-maximum steam loss at 100 ºC	$T = 1522 / (5.75 - \log C) - 273.15$	Fournier (1977)
Quartz	$T = 42.198 + 0.28831C - 3.6686 \times 10^{-4} C^2 + 3.1665 \times 10^{-7} C^3 + 77.034 \log C$	Fournier and Potter (1982)
Quartz	$T = 53.500 + 0.11236C - 0.5559 \times 10^{-4} C^2 + 0.1772 \times 10^{-7} C^3 + 88.390 \log C$	Arnorsson (1985) based on Fournier and Potter (1982)
Chalcedony	$T = 1032 / (4.69 - \log C) - 273.15$	Fournier (1977)
Chalcedony	$T = 1112 / (4.91 - \log C) - 273.15$	Arnorsson et al. (1983)
Alpha-Cristobalite	$T = 1000 / (4.78 - \log C) - 273.15$	Fournier (1977)
Opal-CT (Beta-Cristobalite)	$T = 781 / (4.51 - \log C) - 273.15$	Fournier (1977)
Amorphous silica	$T = 731 / (4.52 - \log C) - 273.15$	Fournier (1977)

- **Steam separation;**
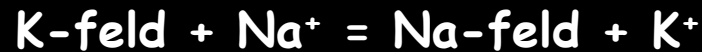- **Silica precipitation;**
- **Mixing**
- **pH**

Process   **Estimated temperature**

- Steam separation   ⇨   overestimation
- Precipitation   ⇨   underestimation
- High pH   ⇨   overestimation
- Mixing with shallow waters ⇨ underestimation

$V_2 < V_1$

$SiO_2\ (2) > SiO_2\ (1)$
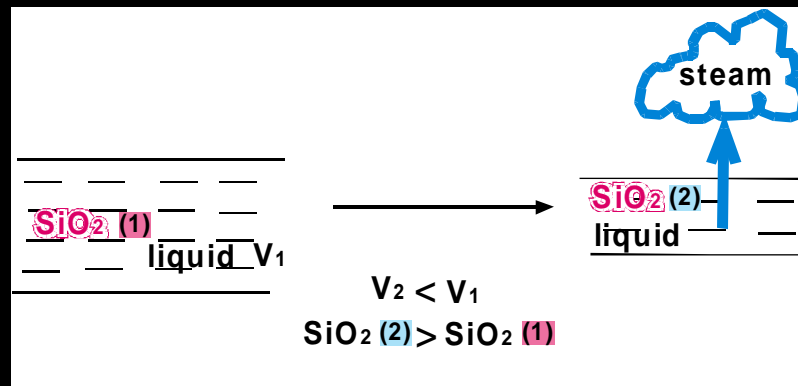
Two other liquid GeoTs

- **The Na-K Geothermometer**
- **The K-Mg Geothermometer**

$$K\text{-feld} + Na^+ = Na\text{-feld} + K^+$$

$$2.8\ K\text{-feld} + 1.6\ H_2O + Mg^{2+} = 0.8\ K\text{-mica} + 0.2\ Chlorite + 5.4\ SiO_2 + 2K^+$$

$$T_{kn} = 1390/(1.75 - L_{kn}) - 273 \qquad T_{km} = 4410/(14.0 - L_{km}) - 273$$

Where $L_{kn} = \log(c_K/c_{Na})$ and $L_{km} = \log(c_K^2/c_{Mg})$. C_i in mg/kg

The KM geothermometer re-equilibrates faster, e.g. mixing with cold waters, whereas the KN geothermometer is less affected by shallow processes. By applying the single geothermometers different equilibrium temperatures can be obtained but by combining them together:
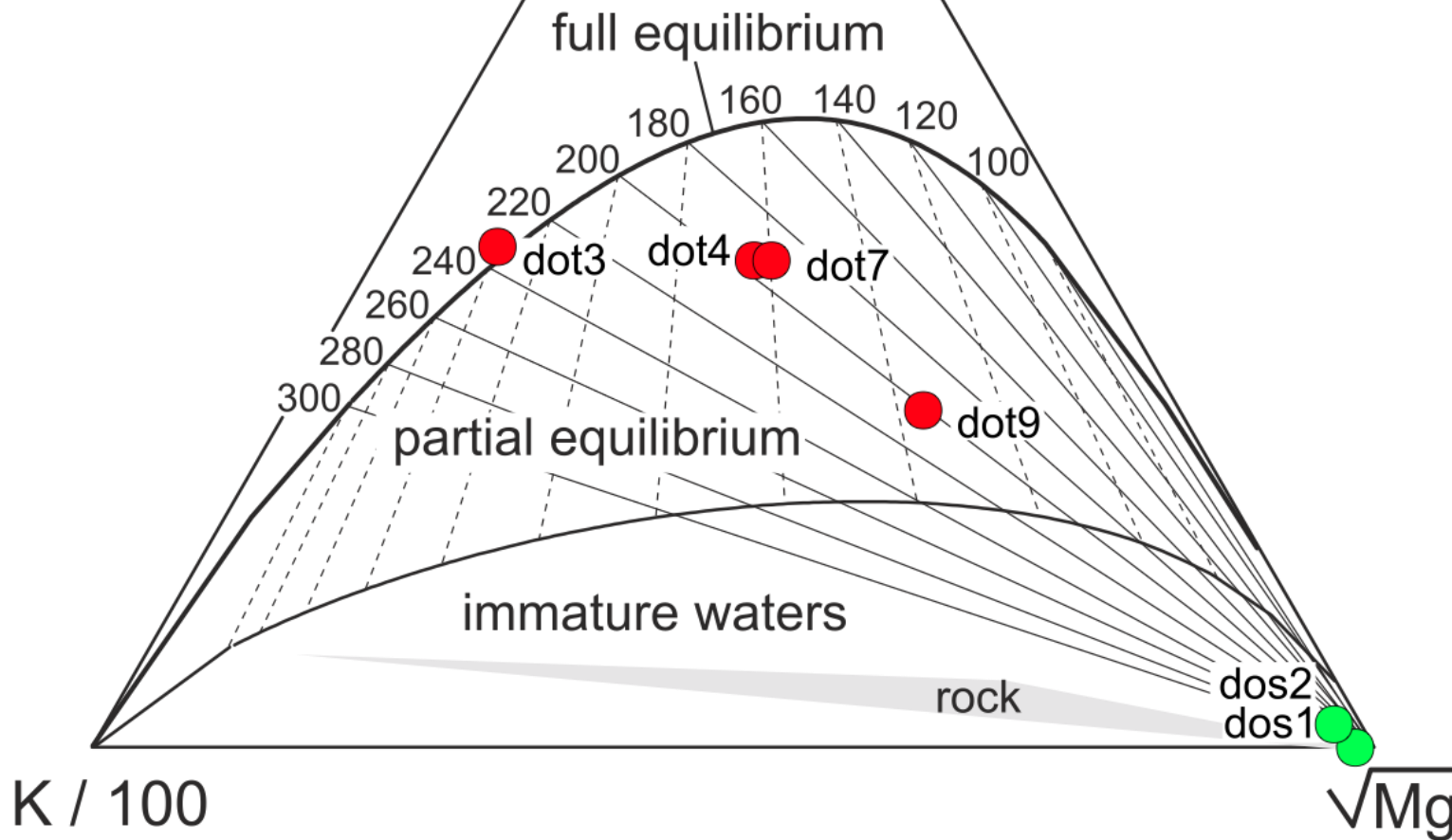
Na/K

Geotherm.	Equations	Reference
Na-K	T=[855.6/(0.857+log(Na/K))]-273.15	Truesdell (1976)
Na-K	T=[833/(0.780+log(Na/K))]-273.15	Tonani (1980)
Na-K	T=[933/(0.993+log (Na/K))]-273.15 (25-250 ºC)	Arnorsson et al. (1983)
Na-K	T=[1319/(1.699+log(Na/K))]-273.15 (250-350 ºC)	Arnorsson et al. (1983)
Na-K	T=[1217/(1.483+log(Na/K))]-273.15	Fournier (1979)
Na-K	T=[1178/(1.470+log (Na/K))]-273.15	Nieva and Nieva (1987)
Na-K	T=[1390/(1.750+log(Na/K))]-273.15	Giggenbach (1988)

The intersection of each Na-K and K-Mg isotherm corresponds to water compositions in equilibrium with a mineralogical assemblage that controls both geothermometers and delineates the so-called "full equilibrium" curve.
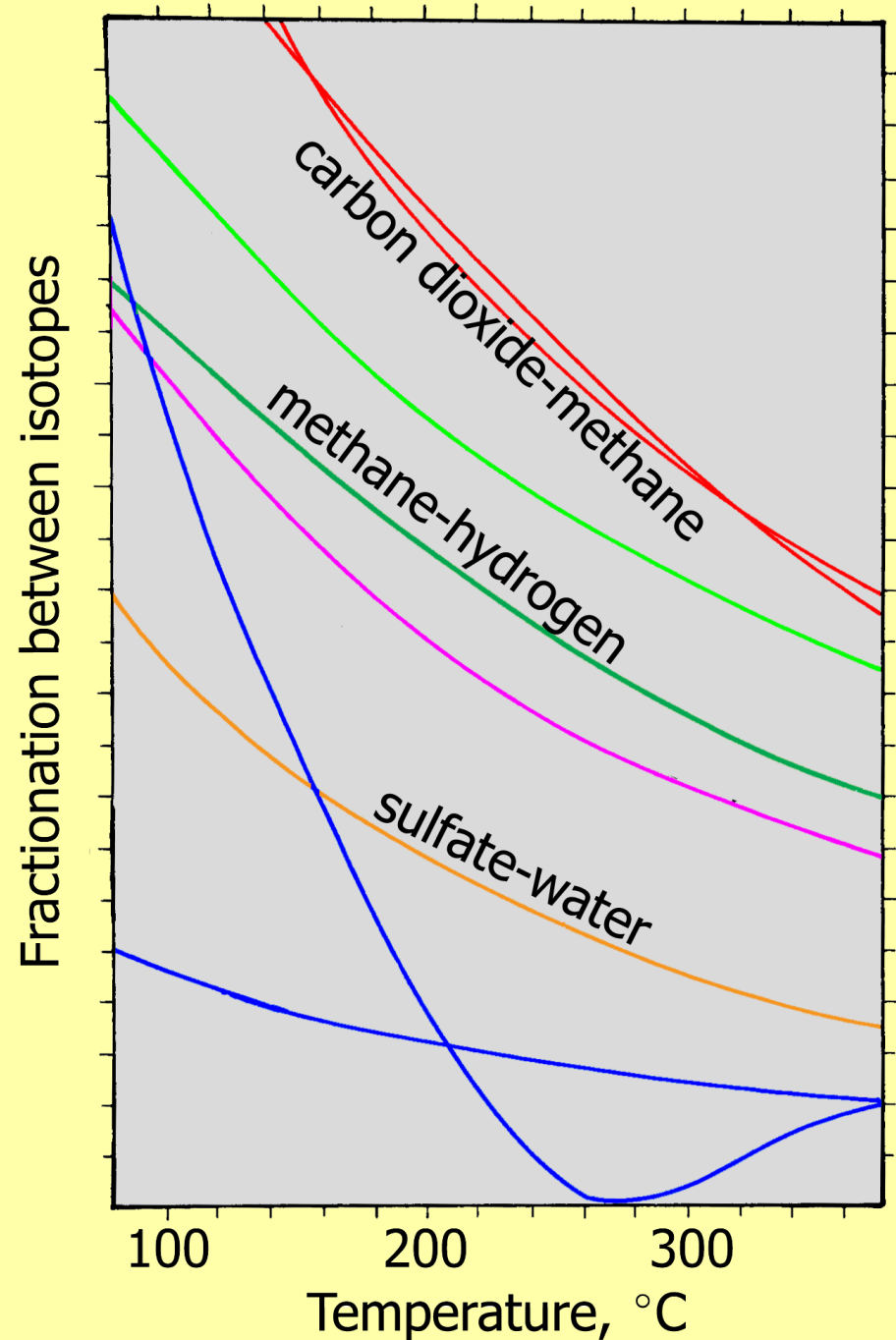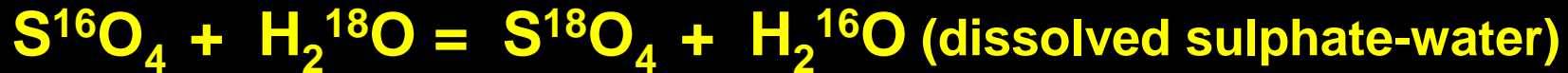
Isotope geothermometers

- Less dependant by WRI.
- They can be affected by mixing/boiling processes

Ohaaki Pool 2001

Fractionation between isotopes

carbon dioxide-methane

methane-hydrogen

sulfate-water

Temperature, °C

100   200   300

Isotope Geothermometers

$^{12}CO_2 + {}^{13}CH_4 = {}^{13}CO_2 + {}^{12}CH_4$ (CO$_2$ gas - methane gas)

$CH_3D + H_2O = HDO + CH_4$ (methane gas – water vapor)

$HD + H_2O = H_2 + HDO$ (H$_2$ gas – water vapor)

$S^{16}O_4 + H_2{}^{18}O = S^{18}O_4 + H_2{}^{16}O$ (dissolved sulphate-water)

⬇

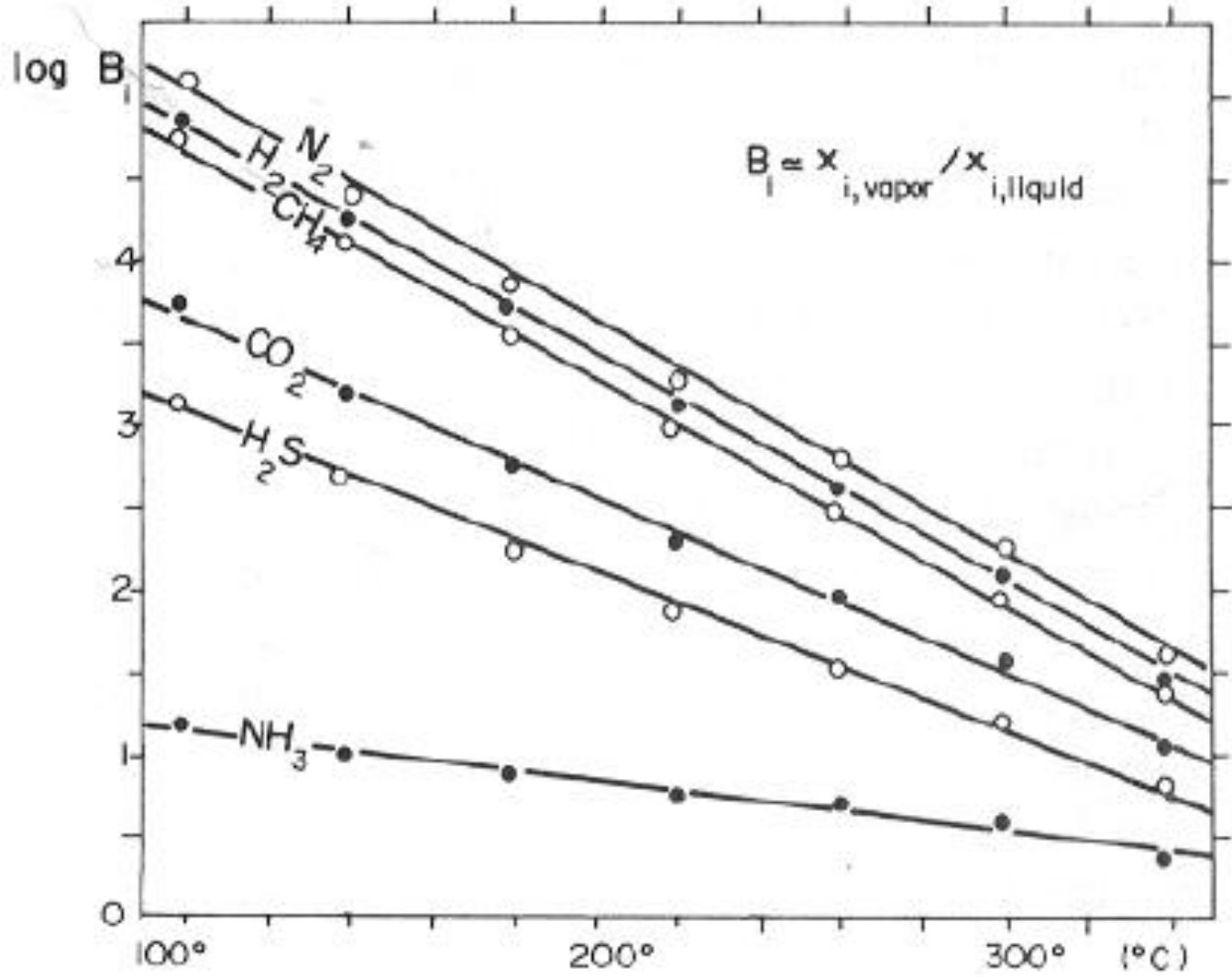$1000 \ln \alpha_{(SO4 - H2O)} = 2.88 \times 10^6/T^2 - 4.1$

(T = degree Kelvin = K)

Partial pressure (fugacity) is dependant on the temperature
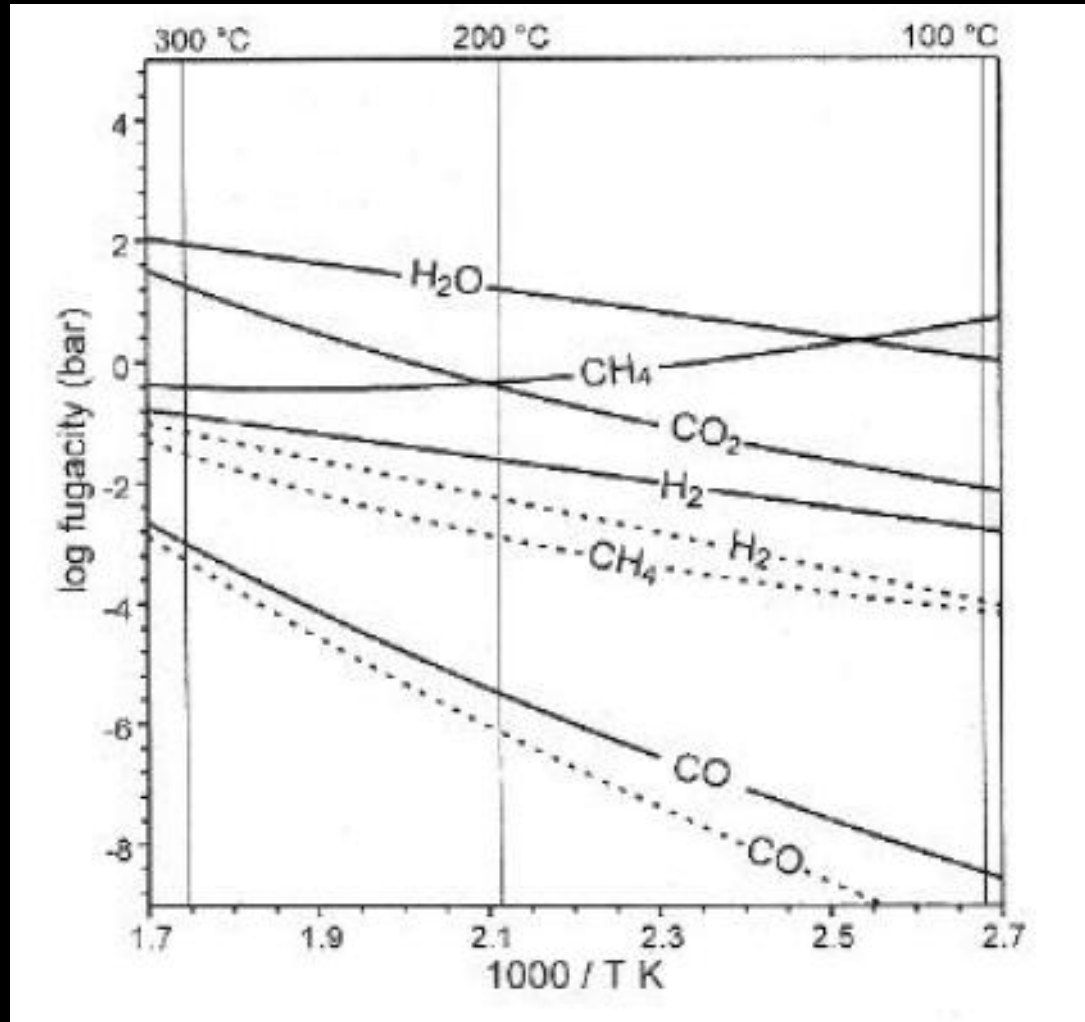
Liquid-vapor separation

Gas equilibria

- The chemical equilibrium can only be achieved among ideal gases.

- The behavior of the real gases divert from that of the ideal gases as a function of their concentrations.

- If real gases are diluted we may assume that their behavior mimics that of the ideal gases.

By combining the equilibrium constant of a reaction with the temperature we may have the opportunity to "suggest" some gas geothermometers.

Why gas geothermometry?

No water no geothermometric estimations!

Our assumption: LogK = $\Sigma logP_{products}$ – $\Sigma logP_{reactants}$

Buffering system

Reactions can be dependent on the redox conditions

Gas buffers:

SO_2-H_2S
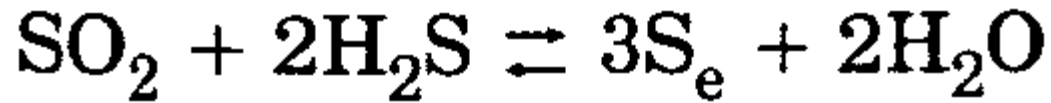
CO_2-CH_4

CO_2-CO

Rock buffers:

FeO-$FeO_{1.5}$

Ni-NiO

HM, FMQ, etc

They are required if redox-sensitive species are present, e.g. H_2 e O_2

Gas buffer

$$SO_2 + 2H_2S \rightleftharpoons 3S_e + 2H_2O$$

$$t_s = (10744/(L_s + 3.66)) - 273.2$$

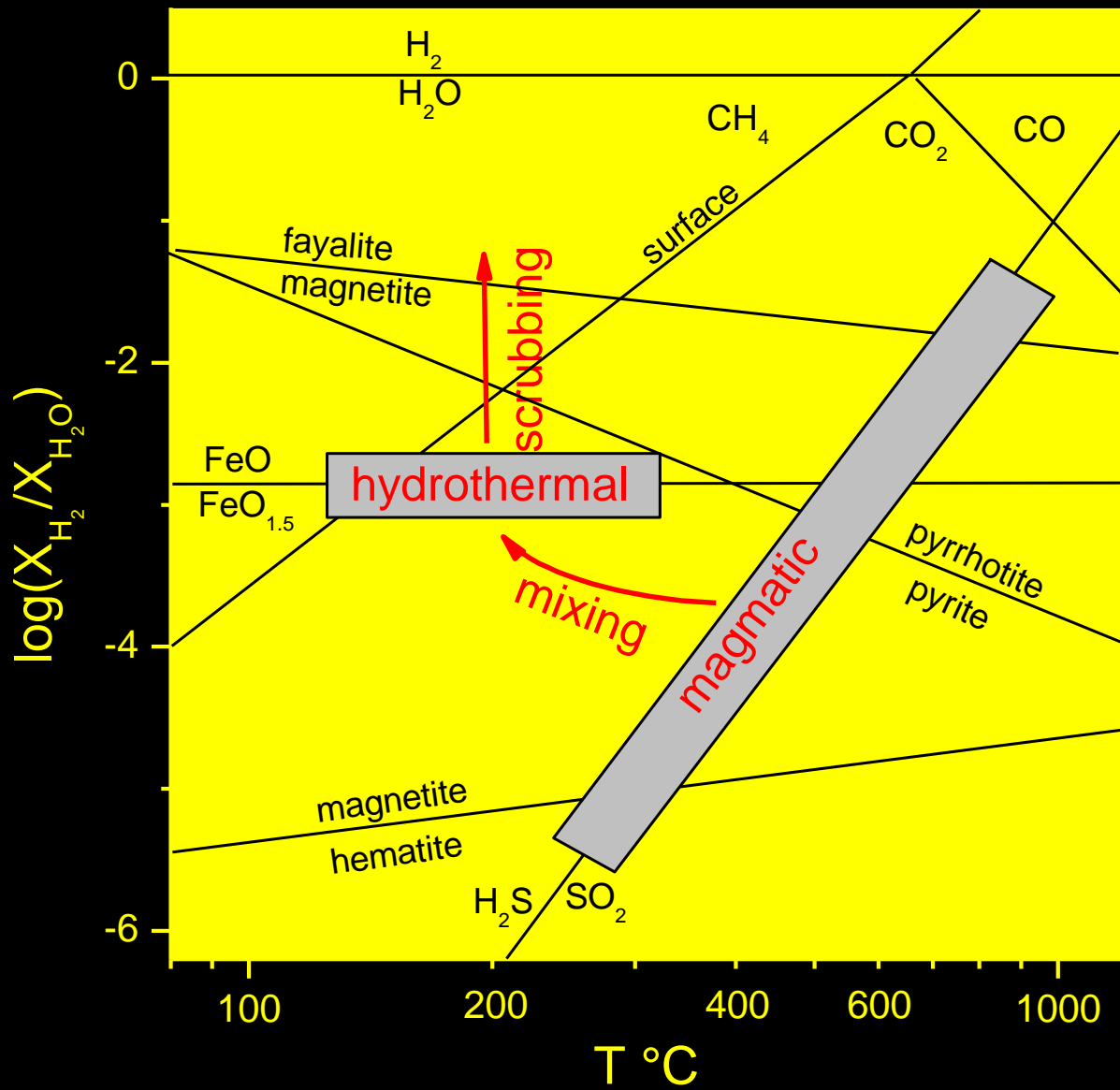## Rock buffer

$$2(FeO) + H_2O = 2(FeO_{1.5}) + H_2$$

$\log(H_2) = 2.1 - 1820/T(K)$

$\log(H_2O) = 4.9 - 1820/T(K)$

It is OK up to 1200 °C and it assumes that the redox conditions are controlled by the Fe^{2+}/Fe^{3+} rock buffer.

In a geothermal system fully-equilibrated the redox conditions can be represented by

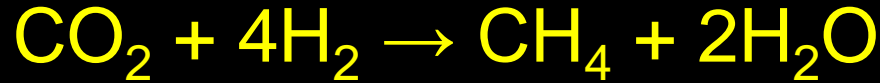$R_H = \log(H_2/H_2O) = -2.8$

Fischer-Tropsch Geothermometer (FT)

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

$$\log P_{CO_2} + 4\log P_{H_2} - \log P_{CH_4} - 2\log P_{H_2O} = 10.76 - 9323/T$$

No mineralogical buffer → H$_2$ geothermometer

Hydrogen Sulfide – Hydrogen (HSH)

$$3FeS_2 + 2H_2 + 4H_2O = Fe_3O_4 + 6H_2S$$
$$FeS_2 + H_2 = FeS + H_2S$$
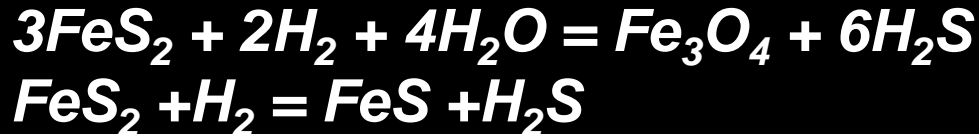
$$3\log P_{H_2S} - \log P_{H_2} = 15.71 - 10141/T \text{ (py-mag)}$$
$$\log P_{H_2S} - \log P_{H2} = 4.94 - 2874/T \text{ (py-pyh)}$$

Grazie