



Resource assessment: targets and tools

Geochemical Methods for geothermal exploration

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Tasks of geochemistry in exploration, development and exploitation of geothermal resources

Exploration (prospection):

- 1) *Location of recharge areas and direction of underground fluid flows*
- 2) *Prediction of subsurface temperature*
- 3) *Evaluation of mixing and boiling processes in upflow areas*
- 4) *Assessment of water and steam quality*

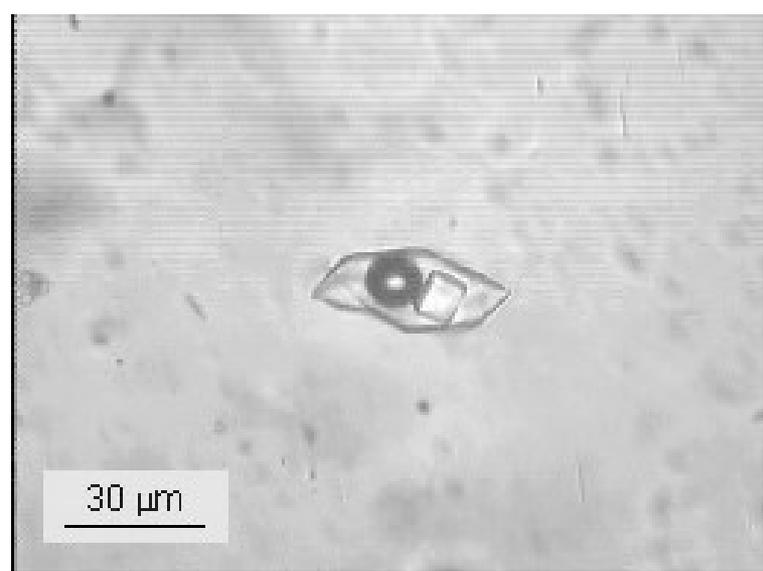
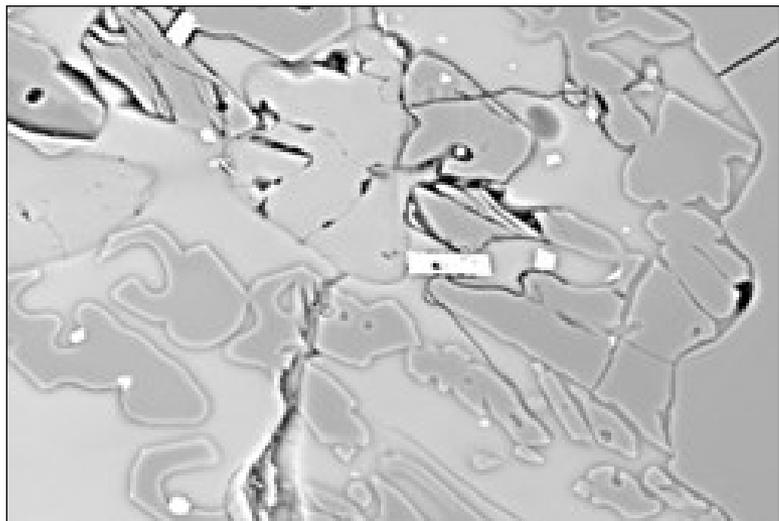
Development (after the first well drilled):

- 1) *Assessment of processes controlling the fluid composition of well discharges*
- 2) *Location of producing horizons in wells (Cl concentration)*
- 3) *Fluid movements within the geothermal system*
- 4) *Assessment of corrosion (HCl, H₂S) and scaling tendencies*
- 5) *Assessment of water and steam quality for the planned utilization*
- 6) *Assessing the environmental impact*

Exploitation (monitoring):

- 1) *Monitoring changes in the chemical composition of well discharges*
- 2) *Evaluation of boiling processes (formation of steam-dominated zones)*
- 3) *Assessment of natural water recharge (or cooling) into the reservoir*





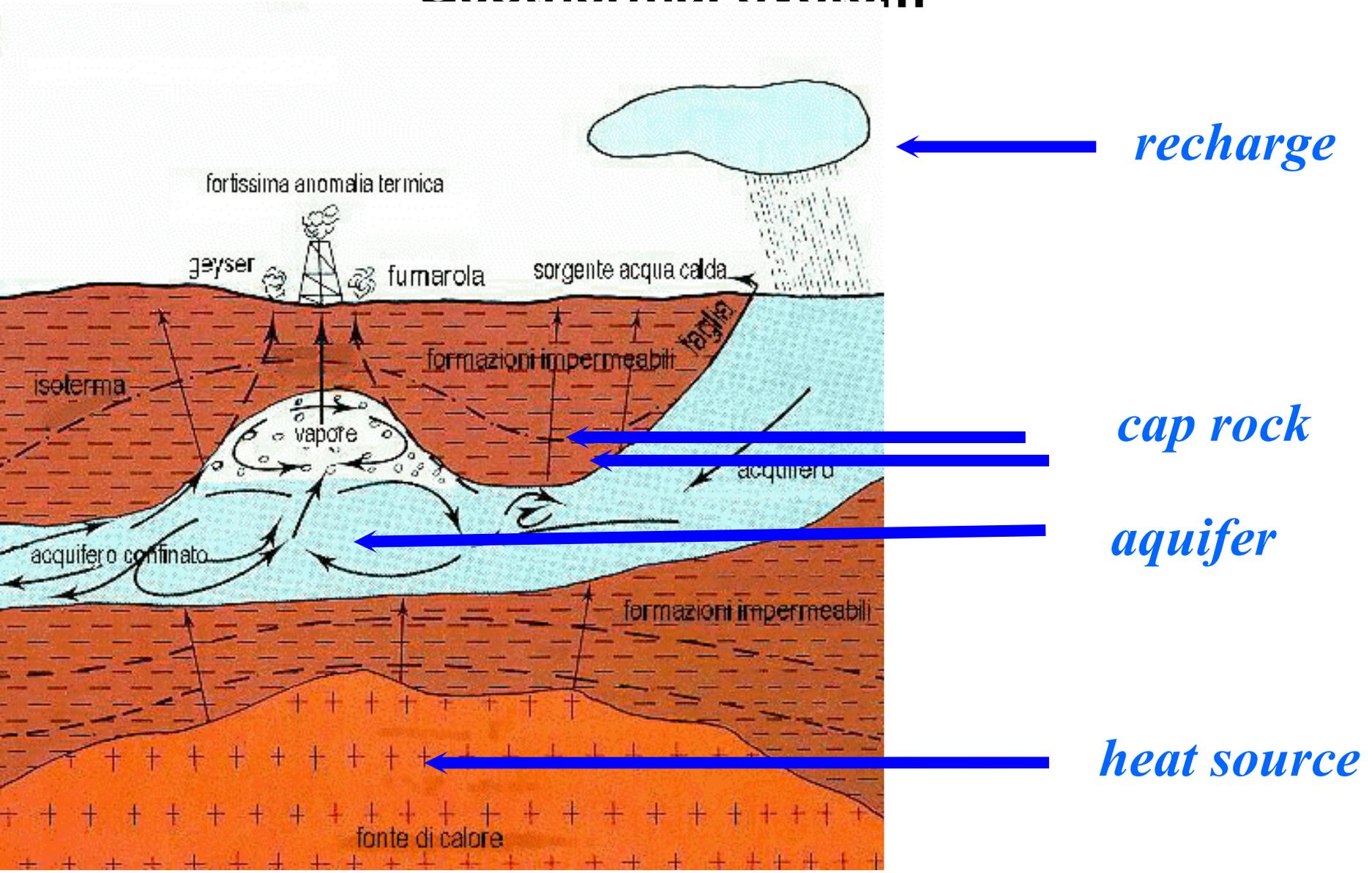


Types of fluid emissions

1. overheated (over the critical point of water=371° C) fumaroles (T up to 1150° C)
2. saturated fumaroles 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 90-100° C, generally very acidic (up to pH=0)
5. boiling springs (>90° C)
6. thermal springs (20-90° C)
7. cold gas bubbling pool (cold stagnant water, sometimes very acidic)
8. dry gas vent



Geothermal system





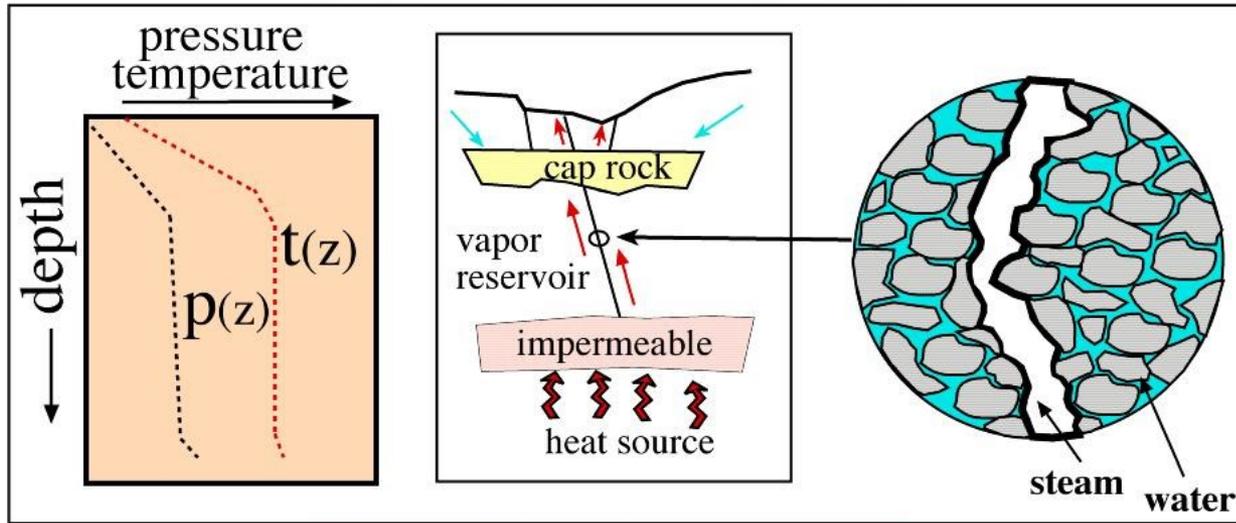
Geothermal reservoirs must have:

- 1) A heat source
- 2) A potential permeable reservoir
- 3) Sealed and impermeable cap-rock
- 4) Sealed or low permeability boundaries
- 5) A recharge of the system (possibly)

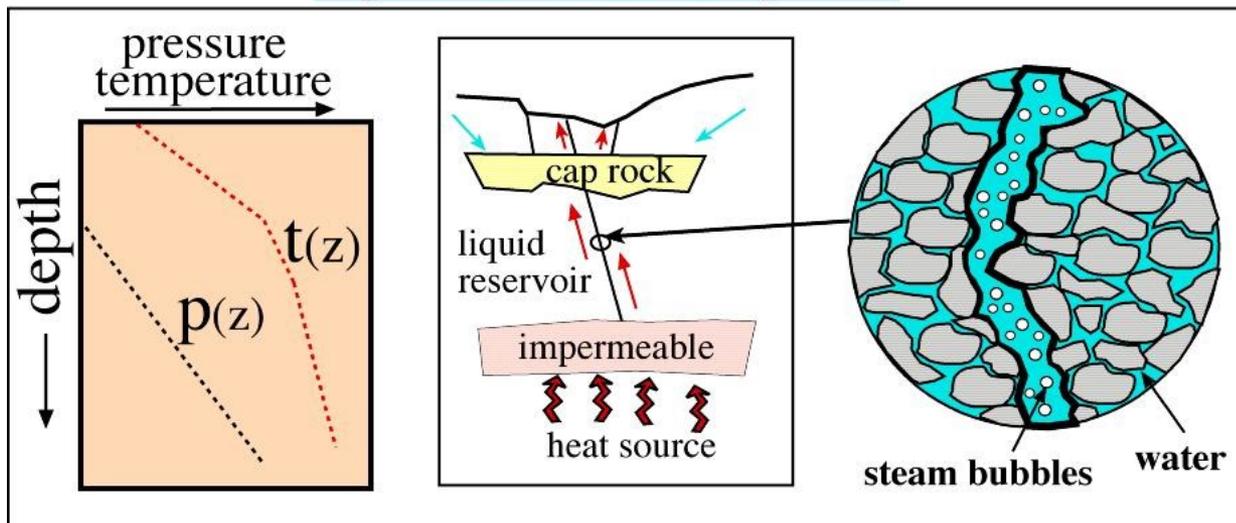
Geothermal reservoirs may have:

- 1) A steam-dominated fluid
- 2) A two phase (liquid and vapor) fluid
- 3) A liquid-dominated fluid (eventually flashing in the well)

vapor-dominated system



liquid-dominated system





Sampling fumaroles, springs and gases



GAS EMISSION SOURCES:

- Geyser, Fumarol
- Wells (during well testing operation)
- Production Plant



GEO THERMAL FLUID

VAPOUR
85-98%

UNCONDENSATE GASES 2-15%

PM
trace

CO₂
95%

H₂S
1%

CH₄
1%

H₂
2%

N₂
1%

O₂, Ar, He, CO, Idroc.
trace



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

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

- 1) promising *or*
- 2) misleading



Promising surface features

- 1) Steam fumaroles at $T \sim 160 \text{ } ^\circ\text{C}$
- 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)
$$\text{CH}_4 + 2\text{H}_2\text{O} = \text{CO}_2 + 4\text{H}_2$$
- 5) Hydrothermal alterations
(ore deposits)



Steam fumaroles at 160°C at atmospheric pressure means that on the 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 means 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 lower than boiling temperature it may derive by the boiling of a convective aquifer whose depth can be higher.

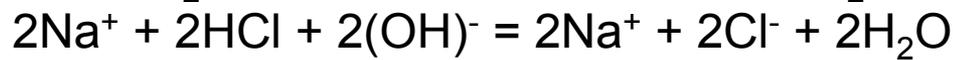
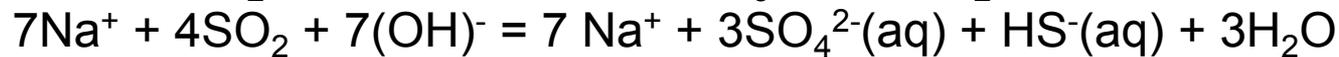
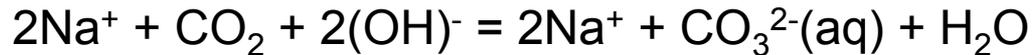
Misleading thermal springs have the following characteristics:

- 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 *pH* (up to 12)
- 5) N₂ gas phase (up to 99 %)
- 6) High He (up to 10% of total volume)
- 7) Low ³He/⁴He ratio (⁴He in the crust)



Acidic gases react with the soda

Steam => condensation



(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)



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 (Nitric Acid) for Ca and metal cations
- 3) 25-50 ml of water (as fast as possible, eventually using gloves is too hot) in a glass bottle for isotopes
- 4) Aliquots of stabilized free CO_2 and H_2S (Hydrogen sulfide)



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 $^{13}\text{C}/^{12}\text{C}$ in CO_2
- 2) A pre-evaquated and pre-weighted gas for the determination of the $^3\text{He}/^4\text{He}$ ratio
- 3) A gas tube for hydrocarbons (ethane, buthane, benzene...etc.)



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 ($\text{Na}, \text{K}, \text{Mg}, \text{Ca}, \text{HCO}_3, \text{SO}_4, \text{Cl}$)
- 2) Some trace elements ($\text{B}, \text{Br}, \text{Sr}, \text{NO}_3, \text{Li}, \text{F}$)
- 3) $^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/\text{H}$ ratios in water
- 4) $^{13}\text{C}/^{12}\text{C}$ in DIC (dissolved inorganic carbon)



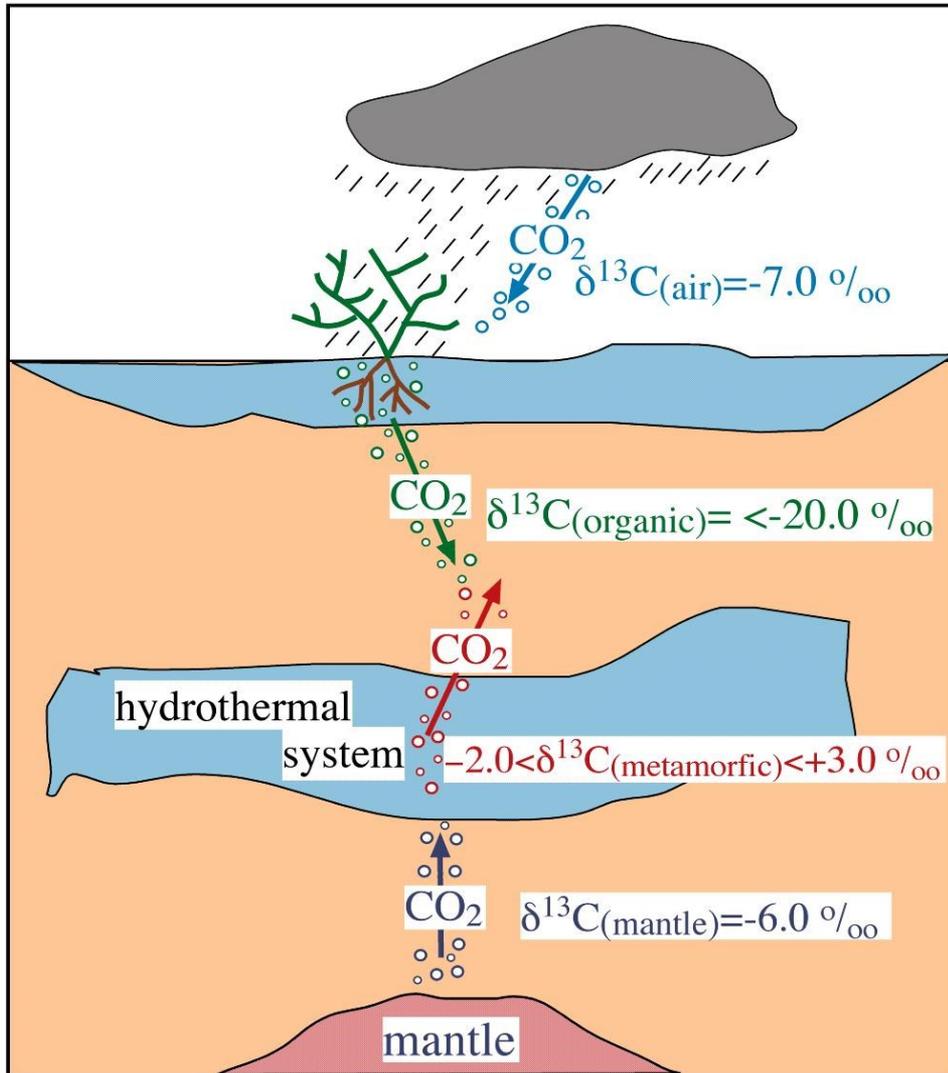
Minimum data set necessary for the elaboration of liquid and gas phase:

Spring water: Ca, Mg, Na, K, HCO₃, SO₄, Cl (main)
SiO₂, NH₄, B, NO₃, Br, Sr (minor)
 $\delta^{18}\text{O}$ and $\delta^2\text{H}$
 $\delta^{13}\text{C}$ in DIC (Dissolved Inorganic Carbon)

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



Multiple sources of CO₂



**Carbon isotopes
and the origin of CO₂
(courtesy of Minissale)**

Multiple origin of CO₂ in central Italy having different isotopic signature (Minissale et al. 1997;2002).



Some elements have both stable and radiogenic isotopes

i.e. for carbon: ^{12}C , ^{13}C , ^{14}C (unstable)

Elements with more isotopes involved in chemical reactions and/or physical processes “**fractionate**” isotopes.

e.g., in water boiling, ^{18}O will tend to stay in the liquid,
 ^{16}O will tend to move in the steam



The most used isotopic ratios in geothermics are:

$^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/\text{H}$ (for the origin of waters)

$^3\text{H}/\text{H}$ (for the age of geothermal fluids)

$^{13}\text{C}/^{12}\text{C}$ in CO_2 (for the origin of CO_2 and travertine)

$^{13}\text{C}/^{12}\text{C}$ in CH_4 (for the origin of CH_4 and geothermometry)

$^3\text{He}/^4\text{He}$ (for the very deep origin of the gas phase)

$^{15}\text{N}/^{14}\text{N}$ (for the origin of nitrogen)

$^{35}\text{S}/^{34}\text{S}$ in H_2S , SO_4 (for the origin of sulfur)



The $^3\text{He}/^4\text{He}$ (R) is a powerful tectonic tool

In air the $^3\text{He}/^4\text{He}$ (Ra) is $1,39 \cdot 10^{-6}$

The ratio (R/Ra) in the mantle > 35

Because of radioactivity of U and Th and formation of α particles (^4He) the ratio (R/Ra) in the crust can be as low as 0.0001

The $^3\text{He}/^4\text{He}$ ratio can be used to trace the presence of mantle magmas and deep gases



$^3\text{He}/^4\text{He}$

$^3\text{He}/^4\text{He}$ ratio is very sensitive to the presence of mantle magmas residing in the crust

$$R = \frac{^3\text{He}/^4\text{He}_{(\text{sample})}}{^3\text{He}/^4\text{He}_{(\text{air})}}$$

$R \sim 0.005$ in the crust

$R \sim 1$ in the air

$R \sim 8$ in M.O.R.B.

$R > 15$ in O.I.B.



Foundation of geothermometry

Fluid composition and chemical equilibria attained at depth are maintained during transfer to the surface

if

No (or reduced) mixing

No (or reduced) dilution

No re-equilibration

Conservative elements: Cl, B, Br,
(N₂, He, noble gases)

**Geoindicators (of deep equilibria,
temperature, pressure):**

SiO₂, Na, K., Ca (CO₂, H₂, CH₄)



Gas geothermometers

- 1) Apart from H₂S and CO₂ partly soluble in water, H₂, CO, CH₄ and noble gases are poorly soluble, so, they keep recorded their deep equilibrium ($\text{CH}_4 + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$)
- 2) Geothermal gases do not undergo dilution with shallow components (apart from CH₄ in Neogene basin).
- 3) Gases do not re-equilibrate at shallow conditions
- 4) Ar and Ne can be used as atmospheric tracers
- 5) Relative ratios in surface gas vents can be used as geothermometers (i.e.: $\log(X_{\text{CH}_4}/X_{\text{CO}_2}) = 5280/T(^{\circ}\text{K}) - 11.12$)

drowbacks

- 1) Solubilities of gas components in liquid phase are different among them and is variably different at different temperature
- 2) Gas components have different fractionation factors between liquid phase and steam in case of phase separation



Thank you!

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I would like to thank A. Minissale (CNR-IGG, Florence, Italy)
who provided some of the slides included in this presentation.