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
BRGM

Geological studies and definition of the structural setting

Isotopic studies

Water-rock interaction experiments
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 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

- recharge
- cap rock
- aquifer
- heat source
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
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  

2) misleading
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 Pco2

4) Gas CO2 emissions (rich in H2)
   \[ \text{CH}_4 + 2\text{H}_2\text{O} = \text{CO}_2 + 4\text{H}_2 \]

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
2Na\(^{+}\) + CO\(_2\) + 2(OH\(^{-}\)) = 2Na\(^{+}\) + CO\(_3^{2-}\)(aq) + H\(_2\)O
7Na\(^{+}\) + 4SO\(_2\) + 7(OH\(^{-}\)) = 7 Na\(^{+}\) + 3SO\(_4^{2-}\)(aq) + HS\(^{-}\)(aq) + 3H\(_2\)O
Na\(^{+}\) + H\(_2\)S + (OH\(^{-}\)) = Na\(^{+}\) + HS\(^{-}\)(aq) + H\(_2\)O
2Na\(^{+}\) + 2HCl + 2(OH\(^{-}\)) = 2Na\(^{+}\) + 2Cl\(^{-}\) + 2H\(_2\)O

(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)
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 HNO₃ (Nitric Acid) 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 (Hydrogen sulfide)
What to sample for components in the gas phase:

1) A pre-evauated and pre-weighted gas tube for main (CO$_2$, N$_2$, H$_2$S, CH$_4$...etc) and trace (He, Ar, CO...etc) components, and $^{13}C/^{12}C$ in CO$_2$

2) A pre-evauated and pre-weighted gas for the determination of the $^3$He/$^4$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 (NH₄)
5) Silica (SiO₂)
6) Elevation
7) Coordinates

Measurements in the laboratory:
1) Main components (Na, K, Mg, Ca, HCO₃, SO₄, Cl)
2) Some trace elements (B, Br, Sr, NO₃, Li, F)
3) ¹⁸O/¹⁶O and ²H/H ratios in water
4) ¹³C/¹²C 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):
CO$_2$, H$_2$S, CH$_4$, N$_2$, O$_2$,
Ar, He, Ne
$\delta^{13}$C in CO$_2$
$^3$He/$^4$He
Multiple sources of CO\textsubscript{2}

Carbon isotopes and the origin of CO\textsubscript{2} (courtesy of Minissale)

Multiple origin of CO\textsubscript{2} in central Italy having different isotopic signature (Minissale et al. 1997; 2002).
Some elements have both stable and radiogenic isotopes

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

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

e.g., in water boiling, $^{18}\text{O}$ will tend to stay in the liquid, $^{16}\text{O}$ 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 \(\text{CO}_2\) (for the origin of \(\text{CO}_2\) and travertine)

\(^{13}\text{C}/^{12}\text{C}\) in \(\text{CH}_4\) (for the origin of \(\text{CH}_4\) 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 \(\text{H}_2\text{S}, \text{SO}_4\) (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 $1.39 \times 10^{-6}$*

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

Because of radioactivity of U and Th and formation of $\alpha$ particles ($^{4}\text{He}$) 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
$^{3}\text{He}/^{4}\text{He}$ ratio is very sensitive to the presence of mantle magmas residing in the crust

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

$R \sim 0.005$ 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 (CH4+H2O=CO2+H2)

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.: \( \log(X_{CH_4}/X_{CO_2}) = 5280/T(°K) - 11.12 \) )

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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