Geothermometry in fluid phase in geothermal exploration

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Target(s) of exploration

Geological and geochemical parameters,
in terms of qualitative observations and
quantitative estimates (geothermometry *s.s.*)
shold drive, together, to the formation
of a coceptual modeling of fluid circulation
in the area under investigation

Foundation of geothermometry

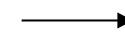Fluid composition and chemical equilibria attained at depth are maintained during transfert to the surface

if

No (or reduced) mixing

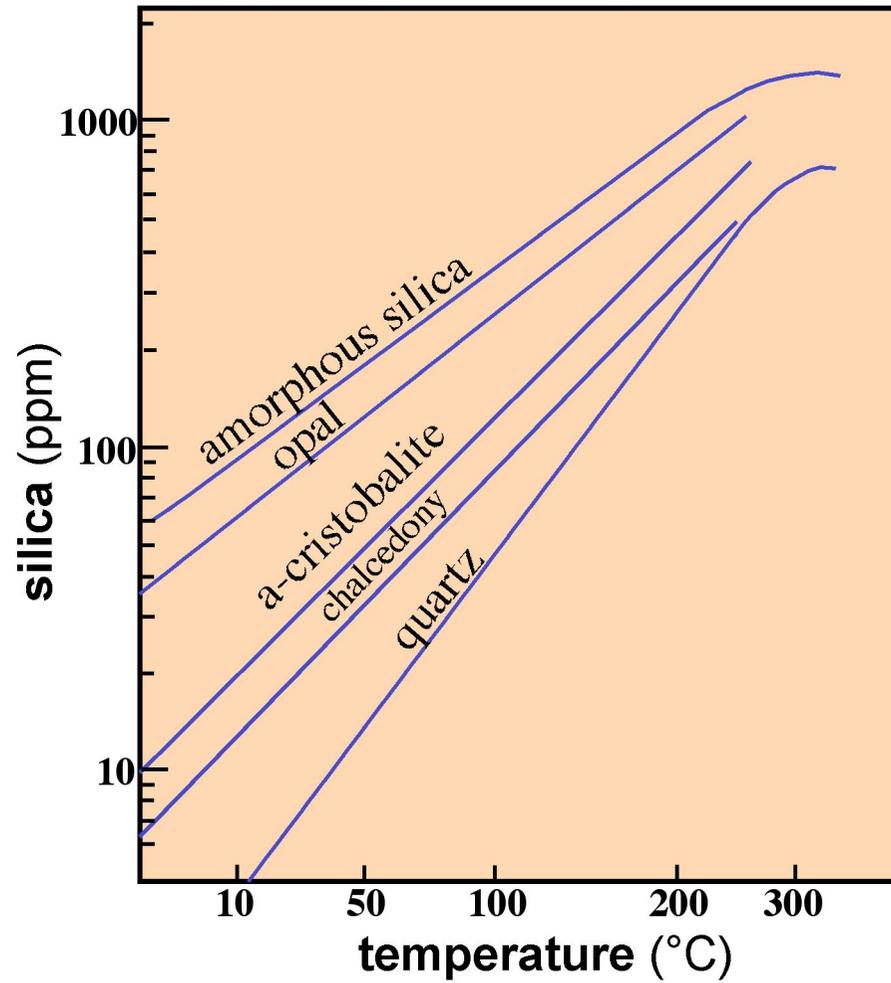*No (or reduced) dilution*

No re-equilibration

Conservative elements: Cl, B, Br, (N_2, He, noble gases) $\longrightarrow$ **tracers**

Geoindicators (of deep equilibria, temperature, pressure):
SiO_2, Na, K., Ca (CO_2, H_2, CH_4)

solubility of silica phases in water at the vapor pressure of solutions with increasing temperature (Fournier, 1991)

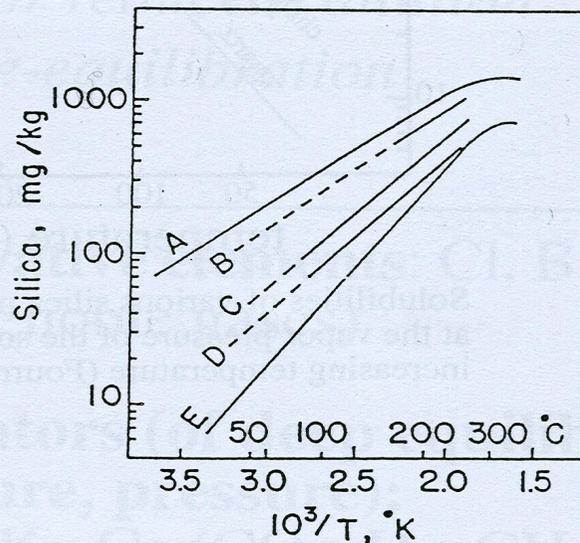Quartz–no steam loss $t°C = \dfrac{1309}{5.19 - \log S} - 273.15$ (1)

Quartz–maximum steam loss at 100°C $t°C = \dfrac{1522}{5.75 - \log S} - 273.15$ (2)

Chalcedony $t°C = \dfrac{1032}{4.69 - \log S} - 273.15$ (3)

α-Cristobalite $t°C = \dfrac{1000}{4.78 - \log S} - 273.15$ (4)

Opal-CT (β-Cristobalite) $t°C = \dfrac{781}{4.51 - \log S} - 273.15$ (5)

Amorphous silica $t°C = \dfrac{731}{4.52 - \log S} - 273.15$ (6)

Before applying any relation the n. of silica phases on which the solution is saturated must be calculate (speciation programs; i.e. Wateq, EQ3..etc.); only the still soluble phase (or the more soluble must be used for geothermometry, otherwise you will over estimate deep Temperatures.

Na/K geothermometry

$$\text{K-feldspar}+\text{Na}^+=\text{Na-feldspar}+\text{K}^+$$
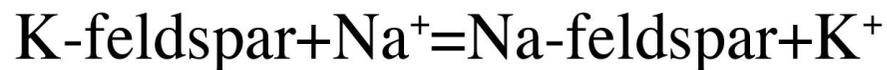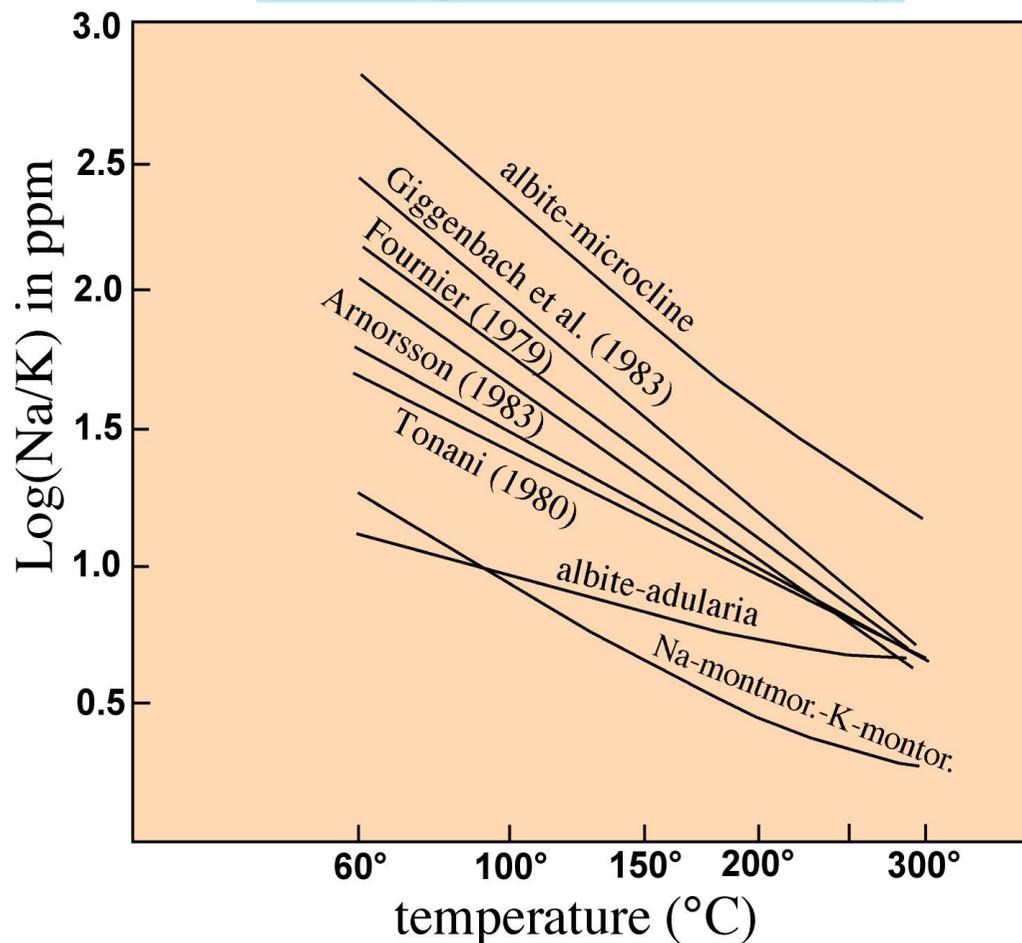
$$\text{K}_{(eq)}=a\text{K}^+/a\text{Na}^+$$

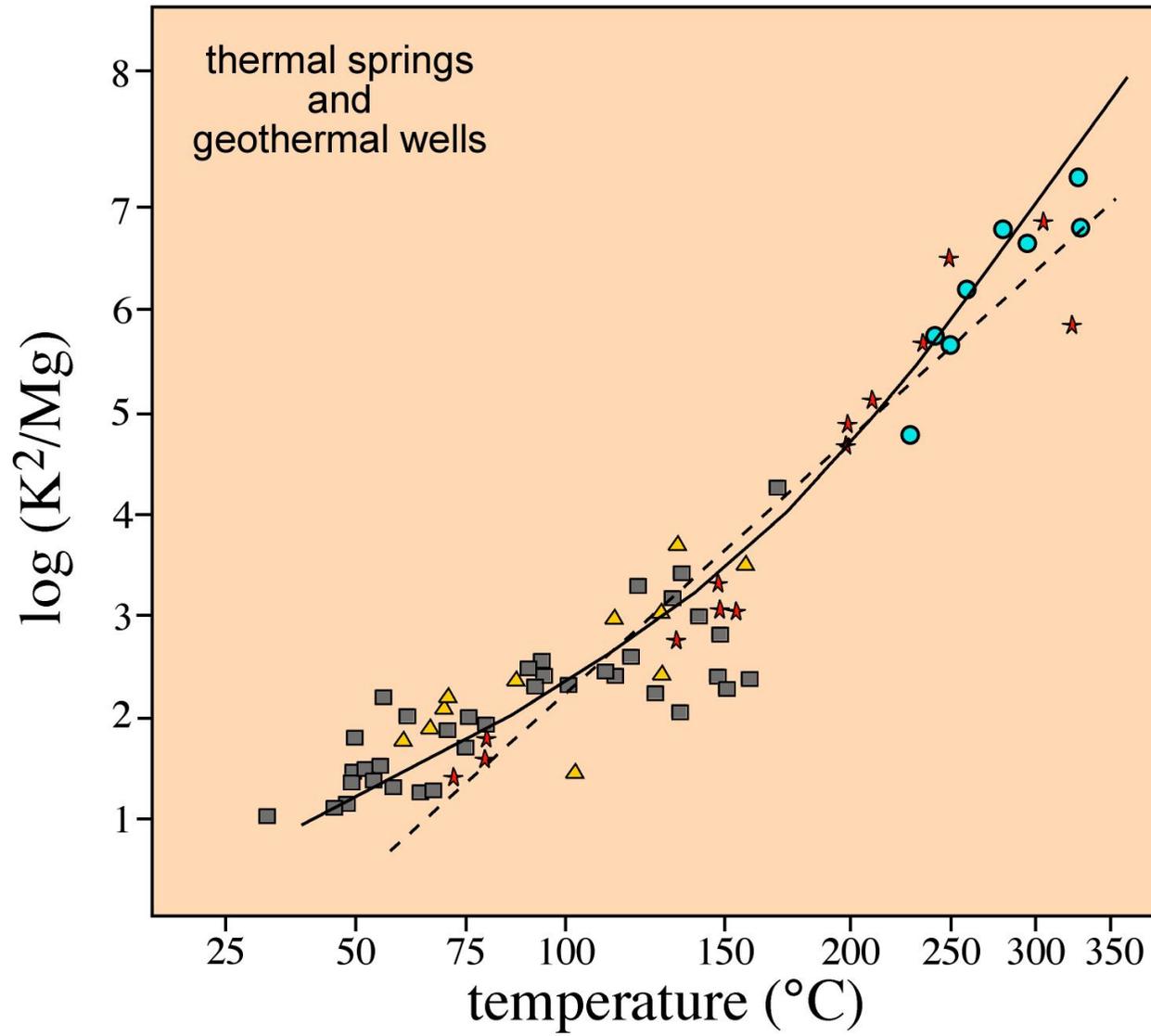$$\Delta\text{F}°= -\text{RT}ln\text{K}_{(eq)}$$

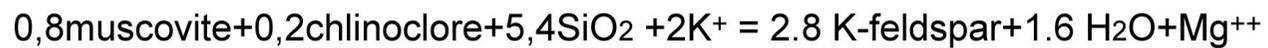$$\Delta\text{F}°=\Delta\text{H}°-\text{T}\Delta\text{S}$$

equations for cation geothermometers (concentrations in mg/kg)

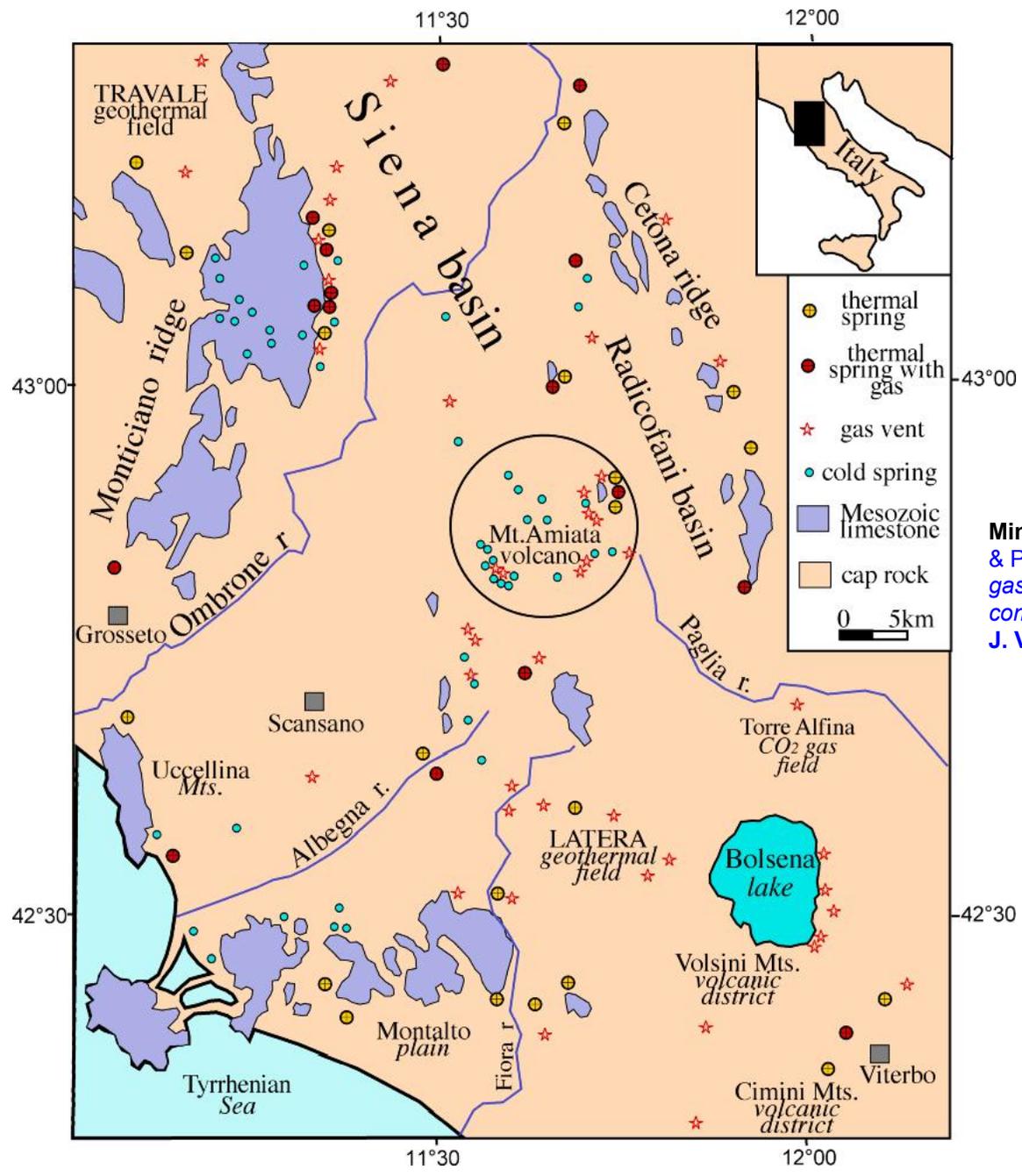| geothermometer	equation	author
Na/K	$t\,(°C) = \dfrac{856}{0.857+\log(Na/K)} - 273.15$	Truesdell (1976)
Na/K	$t\,(°C) = \dfrac{833}{0.780+\log(Na/K)} - 273.15$	Tonani (1980)
Na/K	$t\,(°C) = \dfrac{933}{0.993+\log(Na/K)} - 273.15$	Arnorsson (1983)
Na/K	$t\,(°C) = \dfrac{1319}{1.699+\log(Na/K)} - 273.15$	Arnorsson (1983)
Na/K	$t\,(°C) = \dfrac{1217}{1.483+\log(Na/K)} - 273.15$	Fournier (1983)
Na/K	$t\,(°C) = \dfrac{1178}{1.470+\log(Na/K)} - 273.15$	Nieva & Nieva (1987)
Na/K	$t\,(°C) = \dfrac{1390}{1.750+\log(Na/K)} - 273.15$	Giggenbach (1983)
K-Mg $\log(K^2/Mg)>1.25$	$t\,(°C) = \dfrac{2330}{7.350-\log(K^2/Mg)} - 273.15$	Fournier (199?)
K-Mg $\log(K^2/Mg)<1.25$	$t\,(°C) = \dfrac{1077}{4.033+\log(K^2/Mg)} - 273.15$	Fournier (199?)
Li-Mg	$t\,(°C) = \dfrac{2200}{5.470-\log(Li/Mg^{1/2})} - 273.15$	Kharaka & Mariner (1989)
Na/Li	$t\,(°C) = \dfrac{1590}{0.779+\log(Na/Li)} - 273.15$	Kharaka et al. (1982)
Na/Li	$t\,(°C) = \dfrac{1000}{0.389+\log(Na/Li)} - 273.15$	Fouillac & Michard (1981)
Na/Li	$t\,(°C) = \dfrac{1195}{0.130+\log(Na/Li)} - 273.15$	Fouillac & Michard (1981)
Na/Ca	$t\,(°C) = \dfrac{1097}{3.080-\log(Na/Ca^{1/2})} - 273.15$	Tonani (1980)
K/Ca	$t\,(°C) = \dfrac{1930}{3.861-\log(K/Ca^{1/2})} - 273.15$	Tonani (1980)
Na-K-Ca	$t\,(°C) = \dfrac{1647}{\log(Na/K)+\beta(\log(Ca^{1/2}/Na)+2.06)+2.47} - 273.15$	Fournier & Truesdell (1973)

$\beta=4/3$ for $t<100°C$ $\beta=1/3$ for $t>100°C$

K/Mg geothermometer

thermal springs
and
geothermal wells

log (K²/Mg)

temperature (°C)

Evaluation of Na-K-Mg temperatures

K-feldspar+Na$^+$ = Na-feldpar + K$^+$

0,8muscovite+0,2chlinoclore+5,4SiO$_2$+2Na$^+$ = 2albite+0.8 K-feldspar+1.6 H$_2$O+Mg^{++}

0,8muscovite+0,2chlinoclore+5,4SiO$_2$ +2K$^+$ = 2.8 K-feldspar+1.6 H$_2$O+Mg^{++}

TRAVALE geothermal field

Siena basin

Cetona ridge

Radicofani basin

Monticiano ridge

Ombrone r.

43°00

Grosseto

Mt.Amiata volcano

Paglia r.

Scansano

Uccellina Mts.

Albegna r.

Torre Alfina CO_2 gas field

LATERA geothermal field

Bolsena lake

Volsini Mts. volcanic district

Montalto plain

Fiora r.

Tyrrhenian Sea

Cimini Mts. volcanic district

Viterbo

11°30

12°00

43°00

42°30

42°30

11°30

12°00

Italy

○ thermal spring
● thermal spring with gas
✶ gas vent
○ cold spring
▨ Mesozoic limestone
▨ cap rock

0   5km
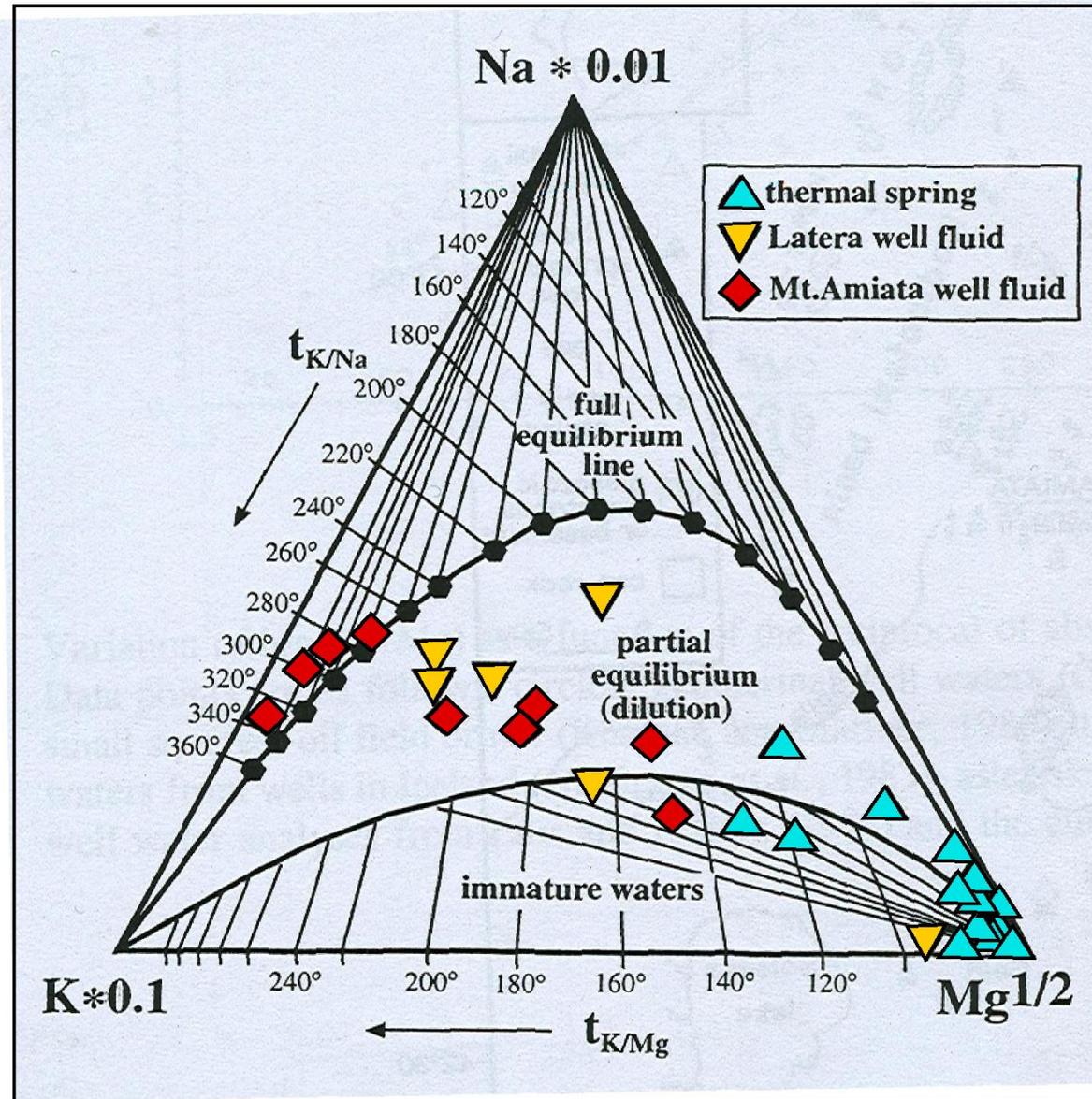
Minissale A., Magro G., Vaselli O., Verrucchi C. & Perticone I. (1997) *Geochemistry of water and gas discharges from the Mt. Amiata silicic complex and surrounding areas (central Italy).* **J. Volcanol. Geotherm. Res. 79**, 223-25 1

Mt. Amiata geothermal area

India and Madagascar
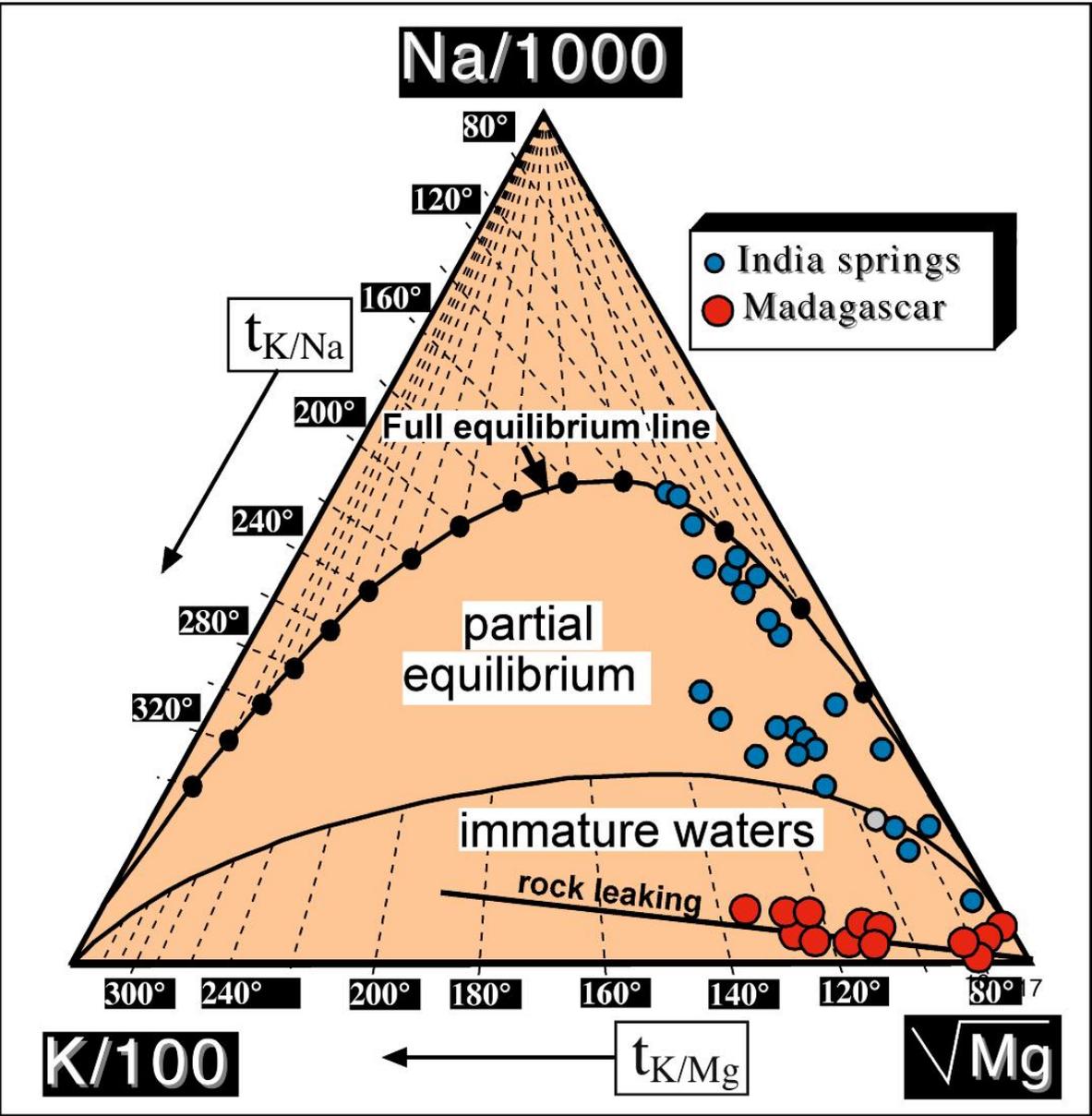
Geothermal indicators
(tracers)

NH$_4$ (Hg)

If steam condenses in shallow aquifer(s), surface (cold) springs should be anomalous in terms of ammonium with respect to the regional background

A closed anomaly in shallow aquifers in a active (or Quaternary) volcanic area, possibly assaciated to a pCO_2 anomaly, likely represents the outflow path of rising steam (condensation in the aquifer)

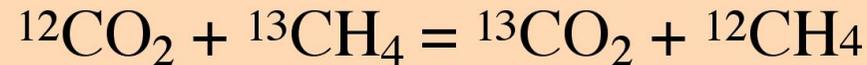*Because isotopes fractionate during chemical or physical processes and that the fractionation factor (α) is a function of temperature, several isotopic geothermometers have been proposed*

$$\alpha = \frac{\text{Isotopic ratio in phase or process (1)}}{\text{Isotopic ratio in phase or process (2)}}$$

$$^{12}CO_2 + {}^{13}CH_4 = {}^{13}CO_2 + {}^{12}CH_4$$

$$1000\, ln\alpha = \frac{15.25 *10^3}{T(°K)} + \frac{2.432*10^6}{T(°K)} - 9.56$$

$$HD + H_2O = H_2 + HDO$$
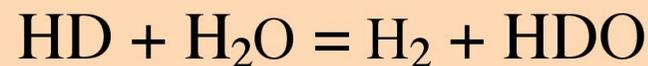
$$1000\, ln\alpha = \frac{396.8 *10^3}{T(°K)} + \frac{11.76*10^6}{T(°K)} - 217.3$$

Oxygen-18 shift with respect to the Global Meteoric Water Line

central Italy

Legend:
- spring T<15°C
- spring 15<T<20°C
- thermal spring (T>20 °C)
- Larderello geothermal well
- Vulsini Mts. geothermal well

δD (‰ SMOW)

$\delta^{18}O$ (‰ SMOW)

MMWL (Mediterranean Meteoric Water Line)
GMWL (Global Meteoric Water Line)

Mediterranean Sea

SMOW

$\delta D=-40$; $\delta^{18}O=-7$ (isotopic average composition of rain in central Itay ?)

1200 800 400 0 (altitude of recharge in m)

135
33
36
18
46
40
39
35
98
38 43
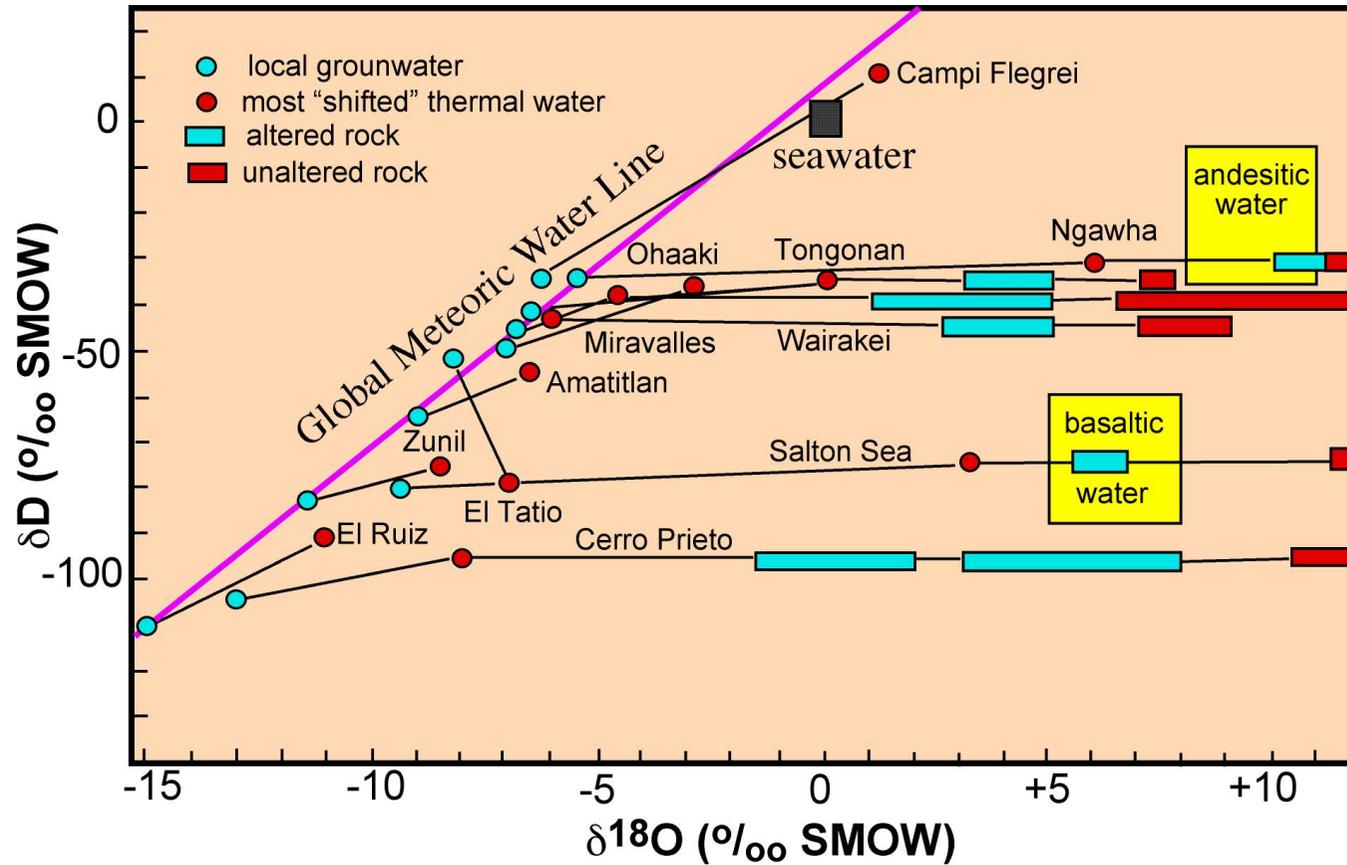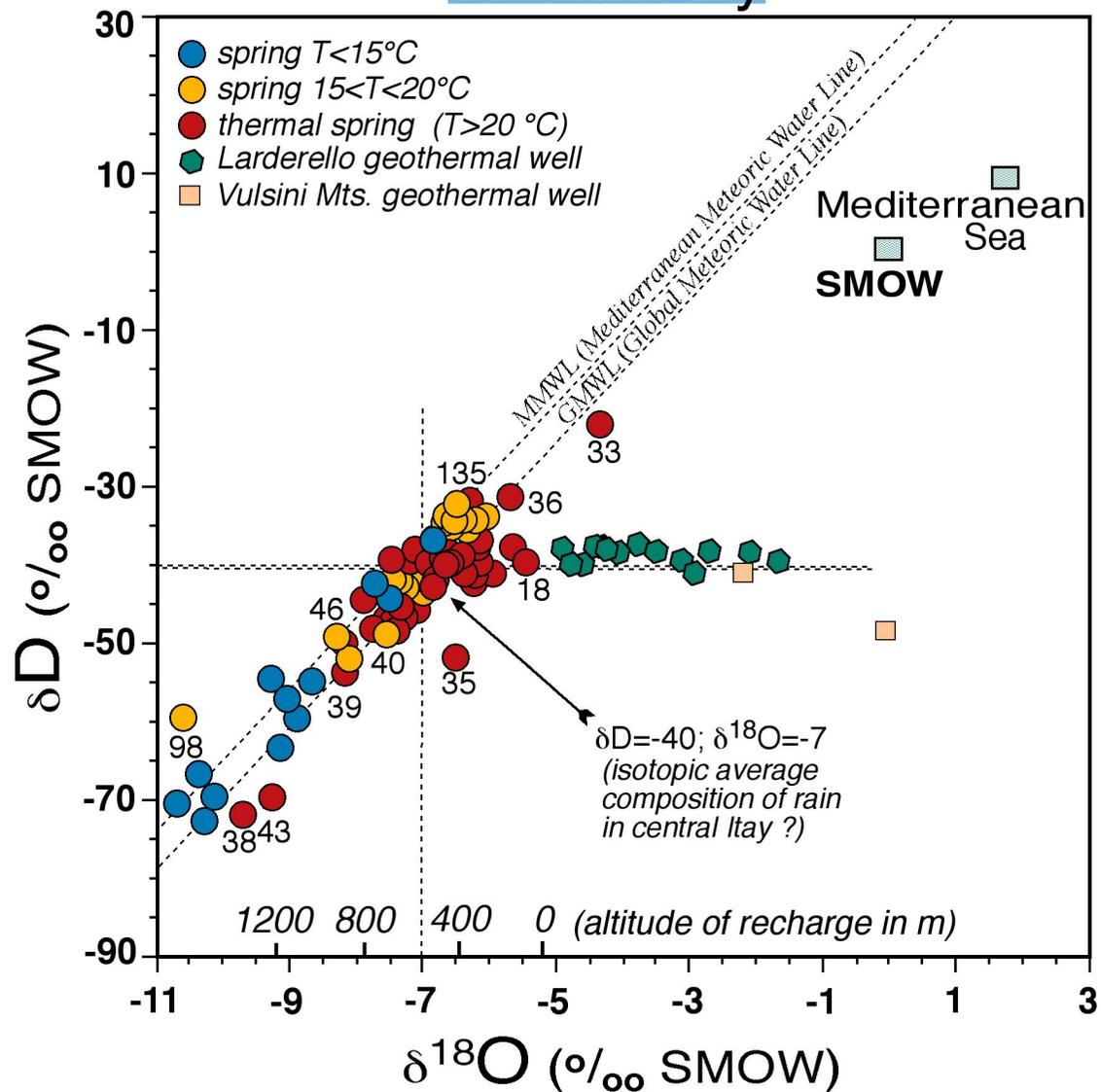
northern-central Apennines
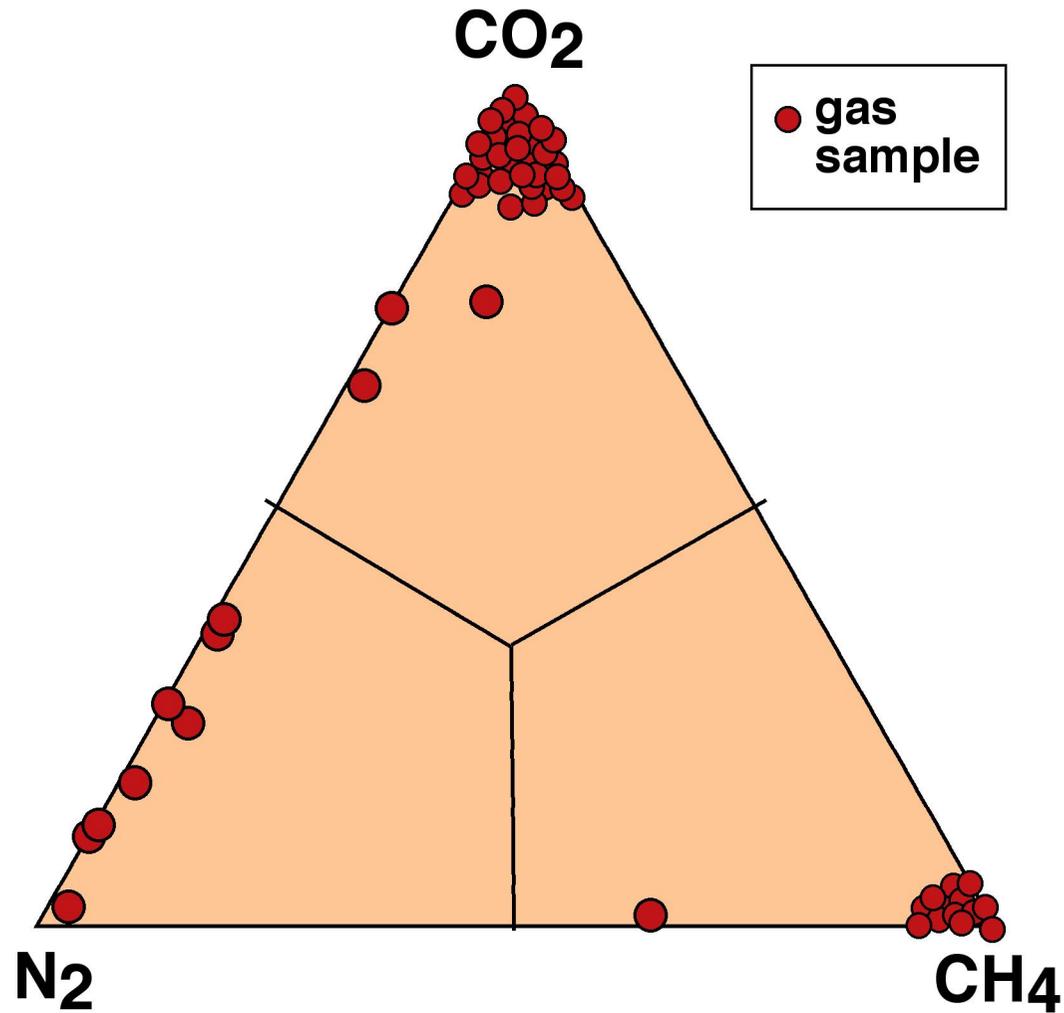
relative abundance of main components in gas vents in central Italy

schematic map of central Italy

Florence

Orciatico

Montecatini

Larderello
S. Vincenzo
Roccastrada
Campiglia
Elba I.
Gavorrano
Grosseto

Radicofani

Mt. Amiata

Perugia

S. Venanzo

Polino

Giglio I.

Bolsena
Latera

Mt. Cimino
Vico
Tolfa
Bracciano
Sacrofano
Albano
Rome
Nepi

Cupaello

MAIN APENNINES

Ancona

Adriatic Sea

Pescara

Ernici

Campobasso

30

30

30

30

25

20

25

25

15

35

35

35

Roccamonfina

Phlegraean Fields
Ponza I.
Ischia I.
Vesuvius
Ventotene I.
Naples
Vulture

10

Tyrrhenian Sea

central Italy

Legend

- Quaternary volcanite
- Mesozoic limestones
- ▲ Quaternary volcano
- ▲ Pliocene volcanite
- ▼ Pliocene granite
- active fault
- Moho depth
- ● travertine
- ● thermal spring
- * gas vent

O ___ 50 km

northern-central Apennines

Northern Apennines

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 $CH_4 + 2H_2O = CO_2 + 4H_2$

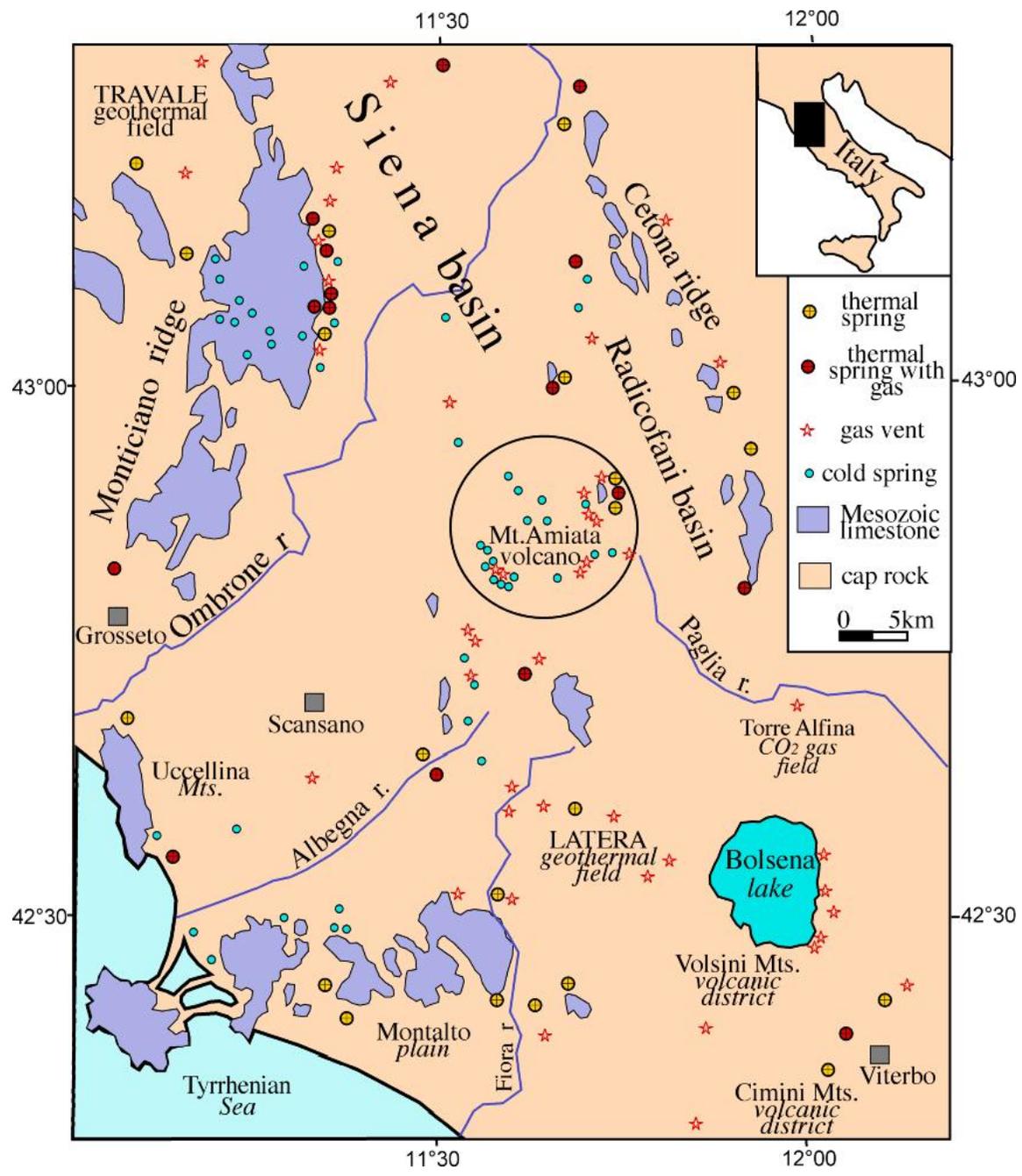2) Geothermal gases do not undergo dilution with shallow components (apart from CH4 in Neogene basin).

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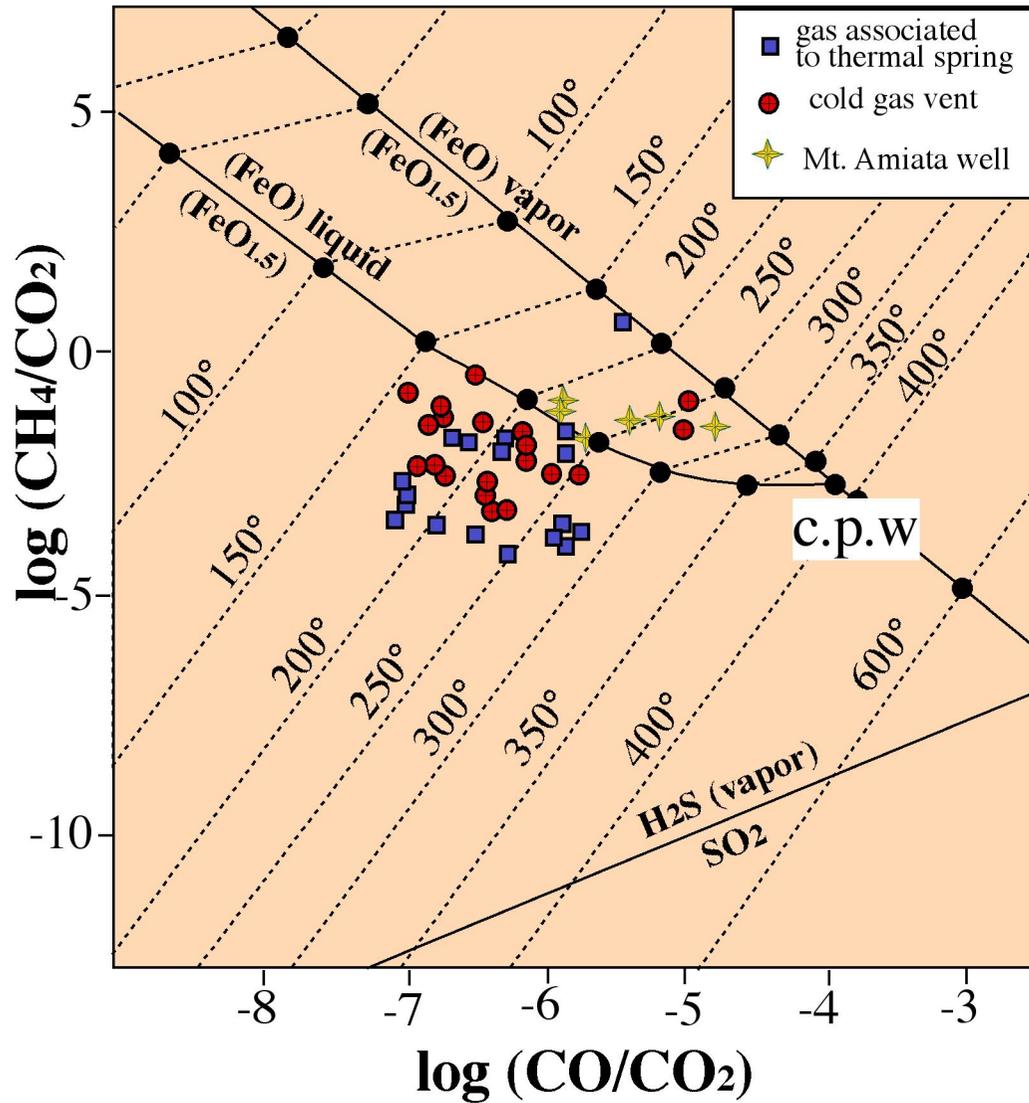
drowbacks

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

Mt.Amiata

geothermometry in the gas phase

Legend:
- gas associated to thermal spring
- cold gas vent
- Mt. Amiata well

Axis labels: log (CH_4/CO_2) vs log (CO/CO_2)

Curve labels: (FeO) liquid, (FeO$_{1.5}$), (FeO) vapor, 100°, 150°, 200°, 250°, 300°, 350°, 400°, 600°, c.p.w, H_2S (vapor), SO_2

Mt. Amiata geothermal field

$$CH_4 + 2H_2O \Longleftrightarrow CO_2 + 4H_2$$
$$CO + 0{,}5O_2 \Longleftrightarrow CO_2$$
$$FeO + 0.25\,O_2 \Longleftrightarrow FeO_{1.5} + 0.25\,e^-$$
$$H_2S + 2H_2O \Longleftrightarrow SO_2 + 6H + 6e^-$$

Map legend:
- methane vent
- CO₂ vent
- N₂-rich thermal spring
- CO₂-thermal spring
- CH₄-thermal spring
- fumarole

Map labels: Reggio Emilia, Modena, Bologna, Po Valley, Apennine boundary, MAIN APENNINES, Apennine watershed, Imola, Faenza, Forlì, Cesena, Adriatic Sea, Apuan Alps, Garfagnana, Mugello, Middle Arno, Lucca, Sieve river, Casentin, Pisa, Arno river, Florence, Elsa river, Era river, Upper Arno, Arno river, Leghorn, Fine, Bra, Elsa, Arezzo, Larderello, Radicondo, Siena, Serrazzano, Chiana basin, Tyrrhenian Sea

Scatter plot: gas vents in the Northern Apennines

Axes: δ¹³C in CH₄ (vertical), δ¹³C in CO₂ (horizontal)

Legend: gas sample

Labels: thermogenic end member, peri-Tyrrhenian trend, thrust belt trend

Data points: 58, 26, 77, 130, 99, 216, 100, 131, 104

Temperature isolines: 600°C, 500°C, 400°C, 300°C, 250°C, 200°C
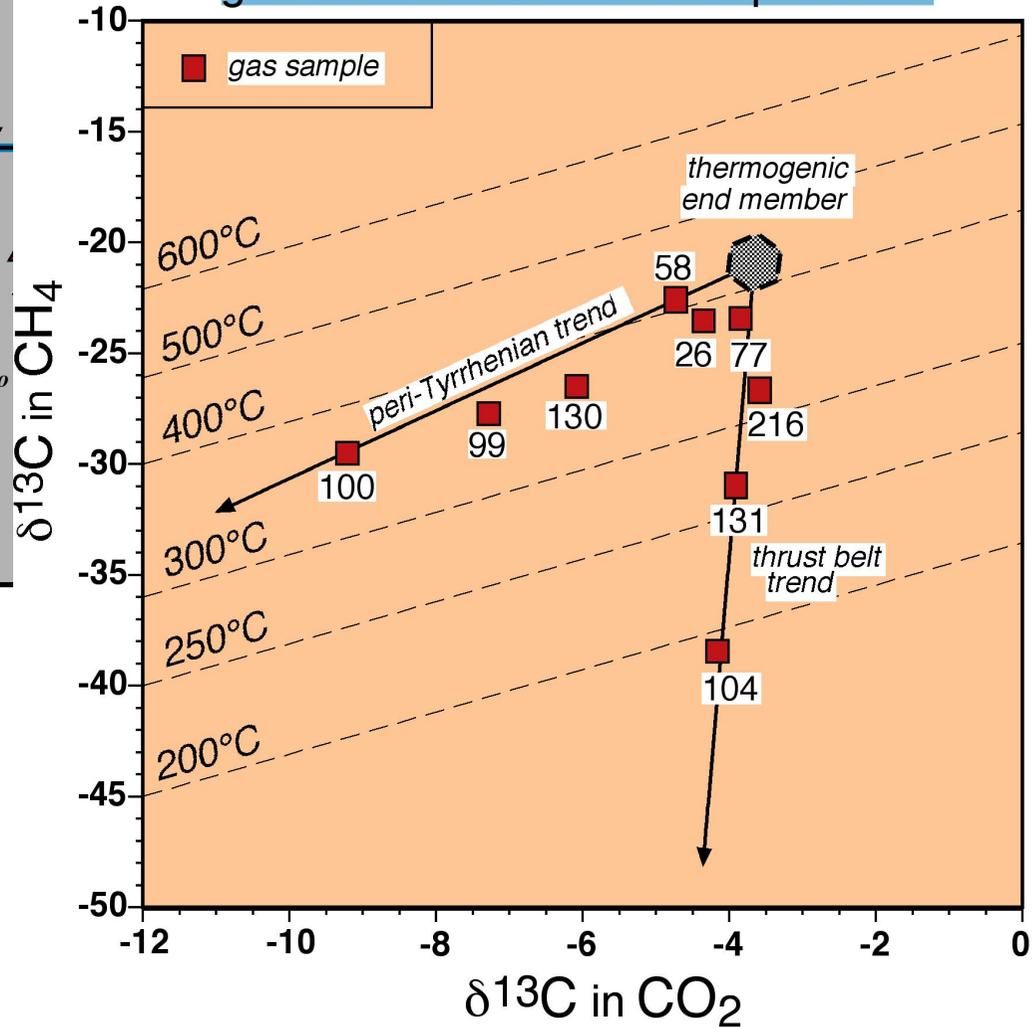
^{3}He/^{4}He

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

$$R = \frac{^3\text{He}/^4\text{He}_{(sample)}}{^3\text{He}/^4\text{He}_{(air)}}$$
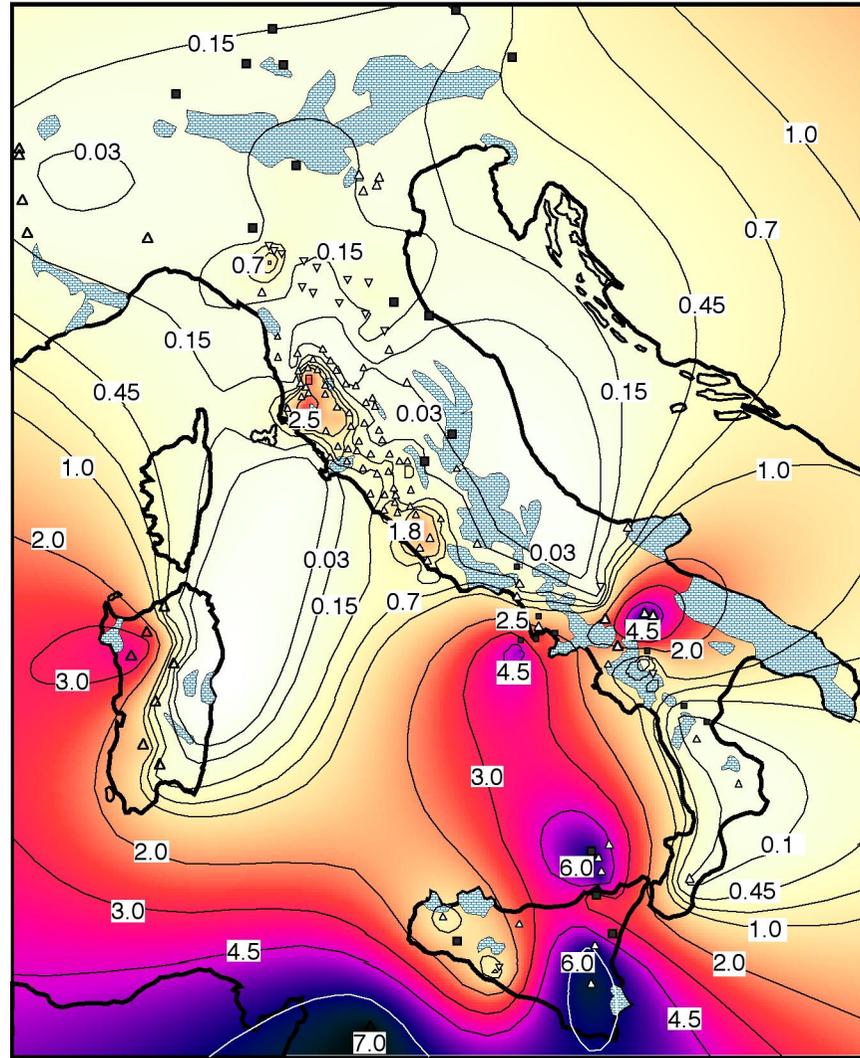
R ~ 0.005 in the crust
R ~ 1 in the air
R ~ 8 in M.O.R.B.
R >15 in O.I.B.

helium-3 distribution in gas vents of Italy

^{3}He/^{4}He ratio in gas vents in central Italy

Florence

Ancona

0.2

0.05

2.6

2.8

1.4

Perugia

**Adriatic
Sea**

0.2

Grosseto

0.8

0.4

0.2

0.6

0.6

0.2

0.4

Pescara

L'Aquila

0.2

0.6

1.2

2.0

0.4

Rome

0.8

Campobasso

0.4

0.4

0.4

0.2

1.4

2.8

4.0

central
Italy

Mesozoic
limestones

* CO$_2$ gas vent

O   5O km

**Tyrrhenian
Sea**

2.8

1.6

Naples

1.6

1.2
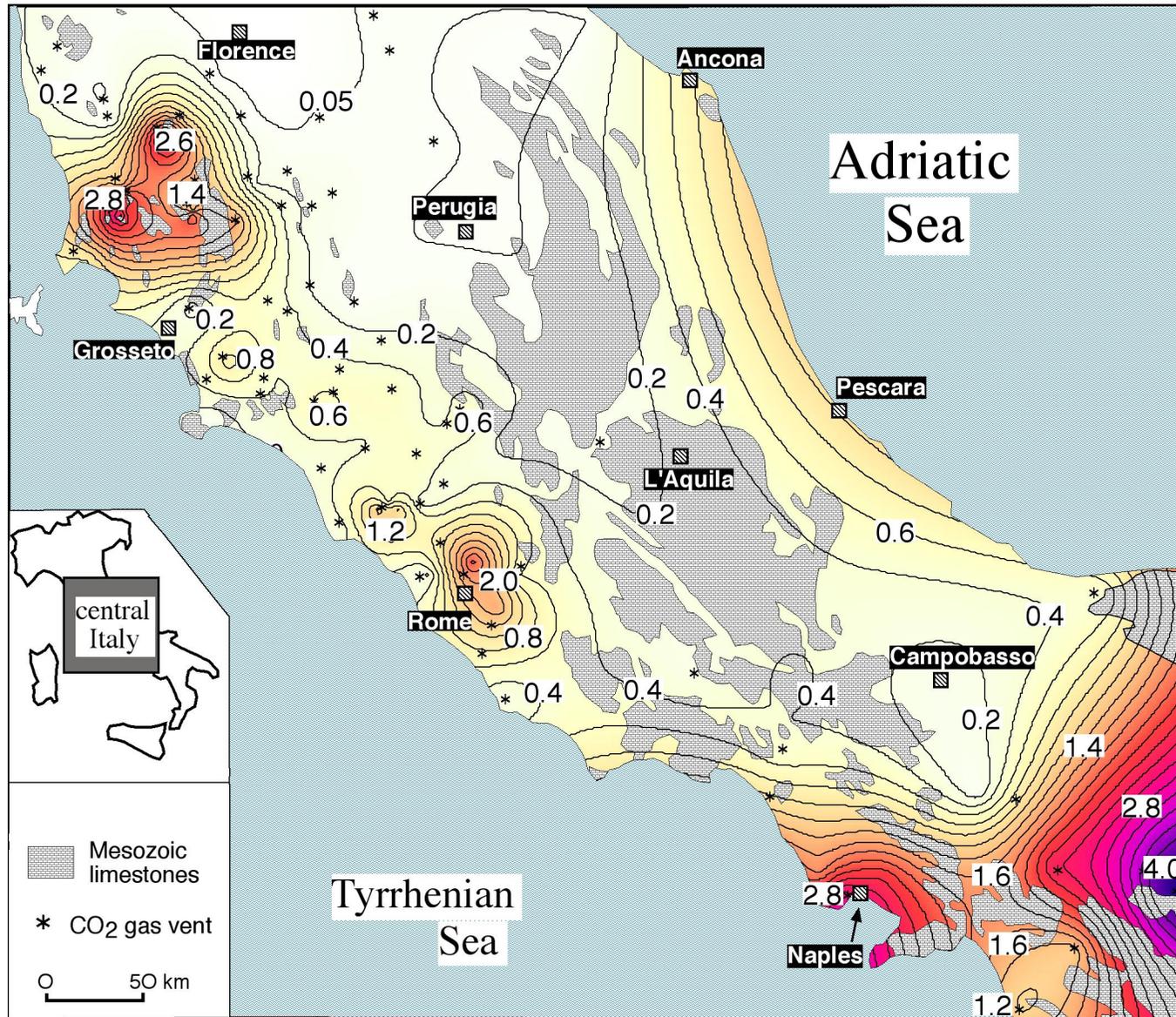
1) together with temperature

2) together with saline fluids (geothermal brines are very saline)

The shallower the hot geothermal reservoir the more evident is at the surface the presence of closed conductivity anomalies

drowbacks

Cold saline fluids in Neogene marine and/or continental sediments (unconsolidated)

Prospection through the heat-flow

$$\Phi_{(c)} = K \, dt/dz$$
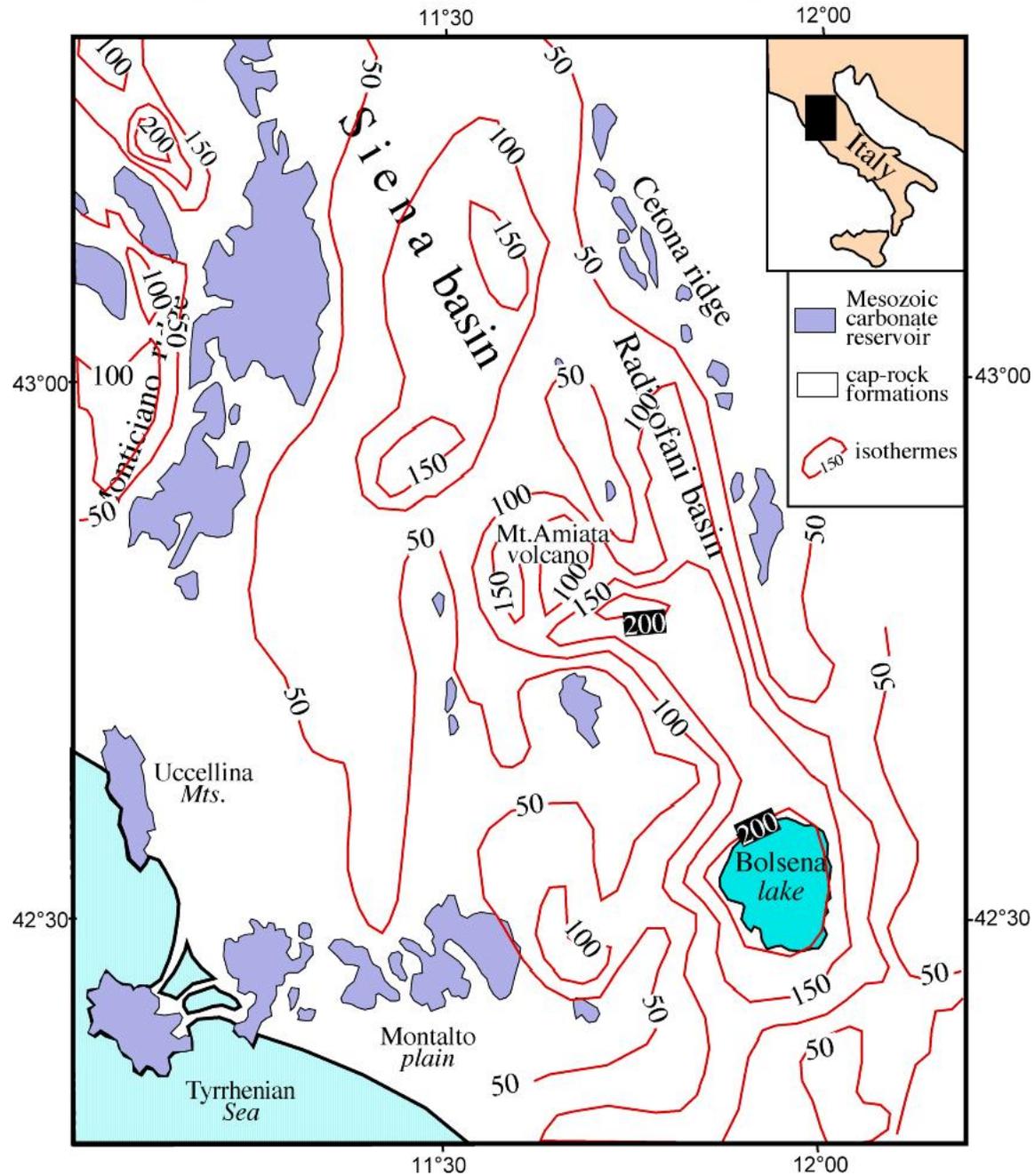
K= rock thermal conductivity
dt/dz=geothermal gradient

$\Phi_{(c)} = 60mW/m^2$ in cratonic areas
$\Phi_{(c)}$ even >400 mW/m^2 in orogenic areas

drawbacks

1) $\Phi_{(c)}$ in convective systems is near 0

2) shallow $\Phi_{(c)}$ are strongly influenced by the presence of shallow convective relatively thermal aquifers

Estimated temperature at the top of the carbonate formations in the Mt. Amiata region

Heat-flow in mW/m² in central Italy

Florence

Ancona

70 80 90 60 40 30 40

100

150 50

200 70

400 50 80

100 90 60 50

Perugia

150 50 30

200 30

100 40 30 30

Grosseto 200 30

150 100 50

150 200 Pescara

100 200 40

150 150

200 400 50 50 60

Tyrrhenian 200 60

Sea 150 100 40 60 Isernia 40 60

Rome 150 40

150 60

175 50 60 50

150

100 50 60 50

100 100 80

Naples

75

200

100 150

75 150 100

central Italy

Adriatic Sea

Mesozoic limestones

70 iso heat-flow in mW/m²