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Compelling hydrochemical evidence about limestone being dissolved as a result of the H_2S-induced acidity of the thermal brine that supplies Hercules karst spring

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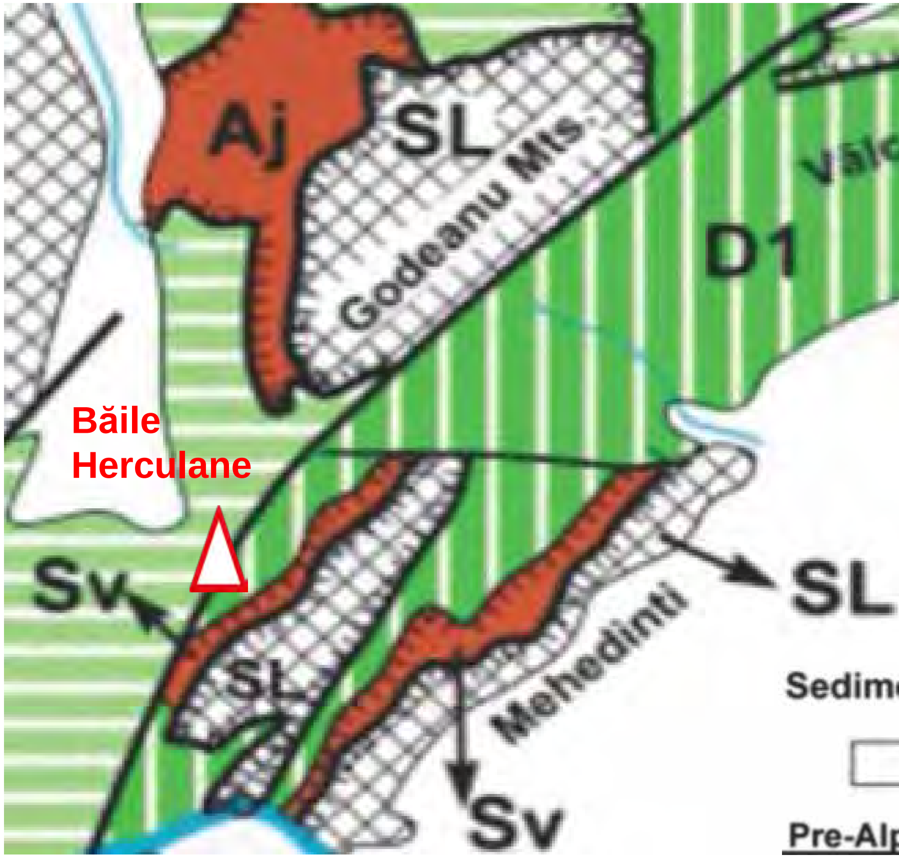
The present study addresses

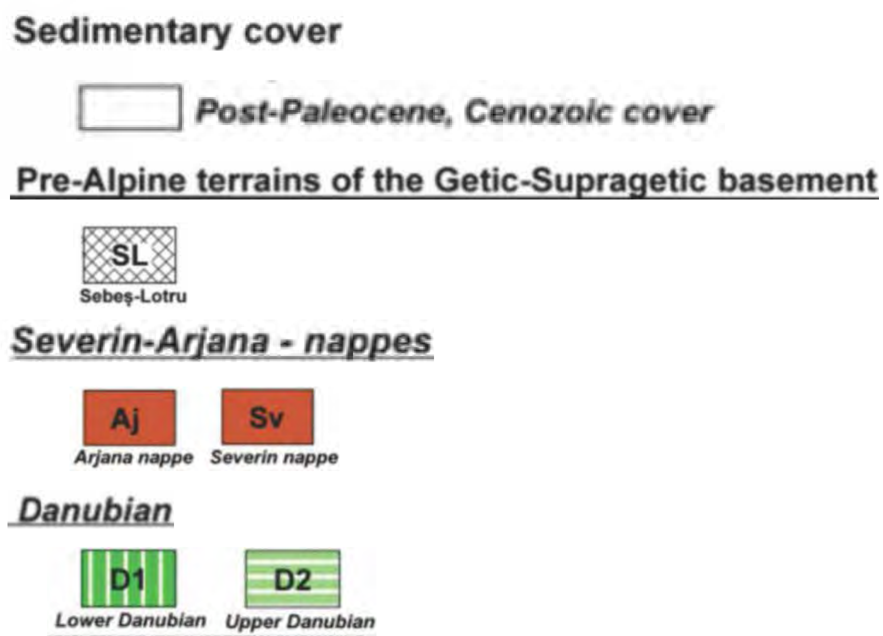
hydrochemical monitoring of
4 thermal water outflows (31-54 °C)
at **Băile Herculane**, over a period of
about 3 months:
mid-November 2013 to ***mid-February 2014***

A complicated nappe-structure in the Southern Carpathians

The thermal water discharges from **Upper Danubian nappes** formations

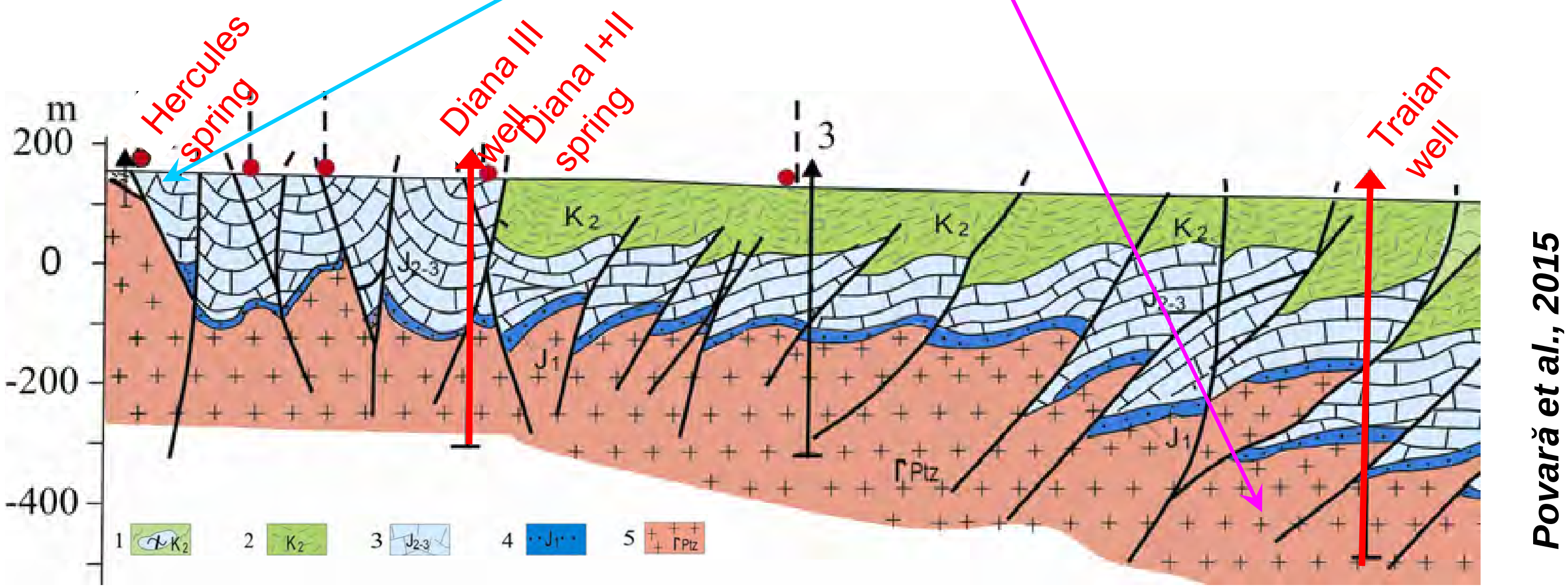
In that area, the **Cerna-Jiu major strike-slip fault** brings **Upper** and **Lower Danubian** nappes in lateral contact





Stremţan, 2014

Reservoir rocks:
- Middle-Late Jurassic limestone
- Variscan-age Cerna granite



1. Late Cretaceous wildflysch; 2. Middle Cretaceous turbiditic limestone;
3. Middle-Late Jurassic limestone; 4. Liassic sandstone; 5. Variscan granite

The thermal water outflows – two distinct categories:

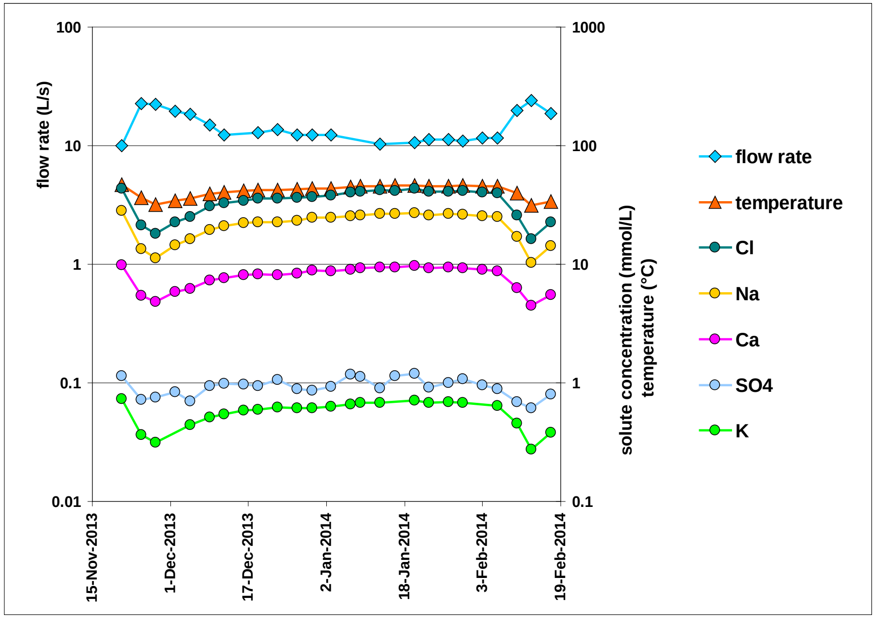
1. of *highly variable* discharge:
   Hercules karst spring

2. of *quasi-constant* and *relatively low* discharge:
   Diana III well
   Diana I+II spring
   Traian well

Correspondingly:

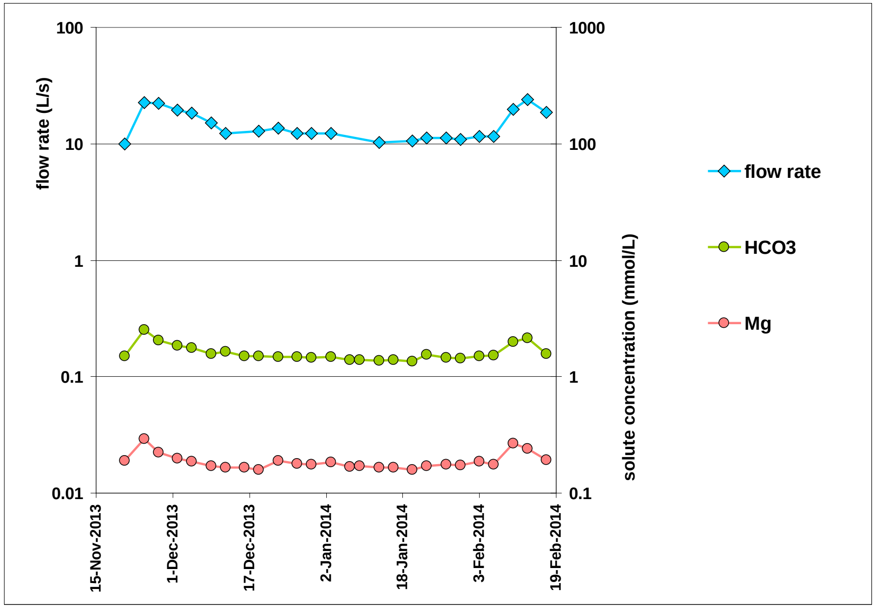
for Group 1 outflow (**Hercules spring**) both **temperature** and the **main chemical components'** concentrations **fluctuate significantly**:

temperature, Cl^-, Na^+, Ca^{2+}, SO_4^{2-} and K^+ opposite to the flow rate



and

Mg^{2+} and HCO_3^- concordantly to the flow rate



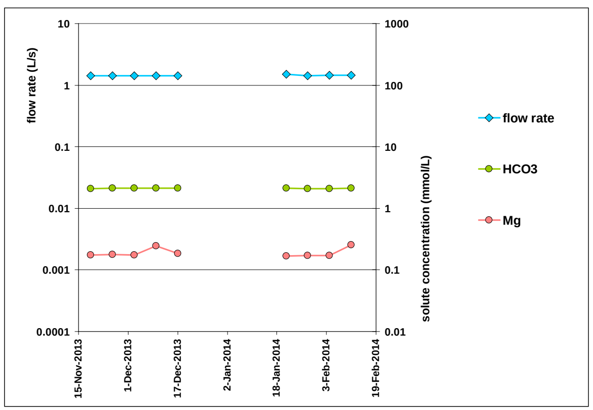
Sampling frequency adopted for this type of behavior: twice a week for Group 2 (**non-karst**) **outflows**:

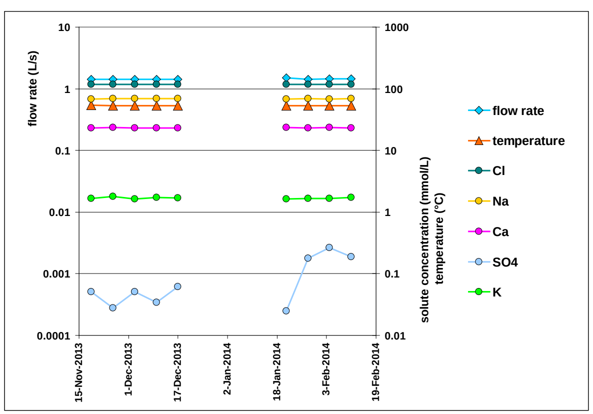
quasi-insignificant fluctuations of both temperature, and of the main chemical components' concentrations

Sampling frequency adopted for this type of behavior: once a week

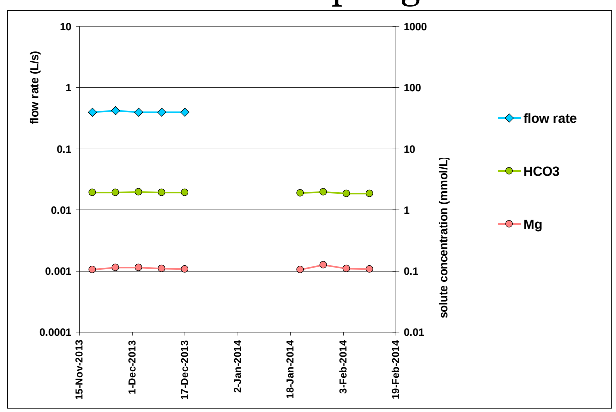
(yet no sampling during periods of spa activity - which involved repeated maneuvers of well-bore valves switching: this process seemingly induced disturbances in the discharged water chemistry)

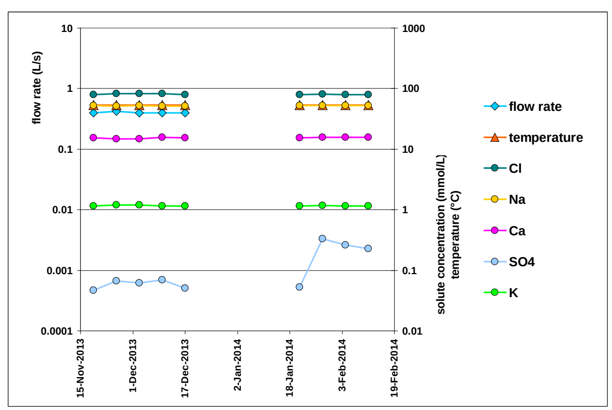
Traian well



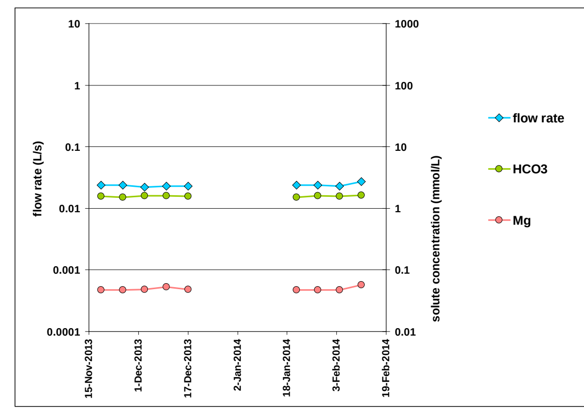


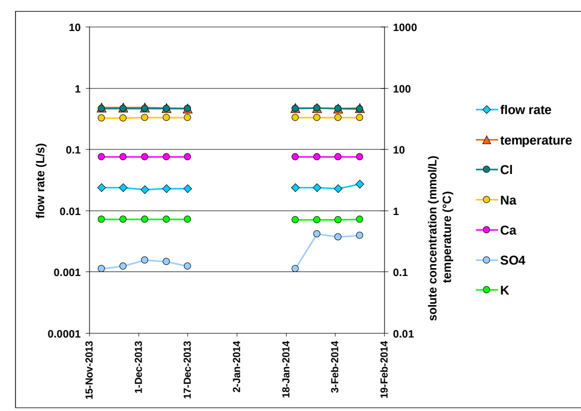
Diana I+II spring



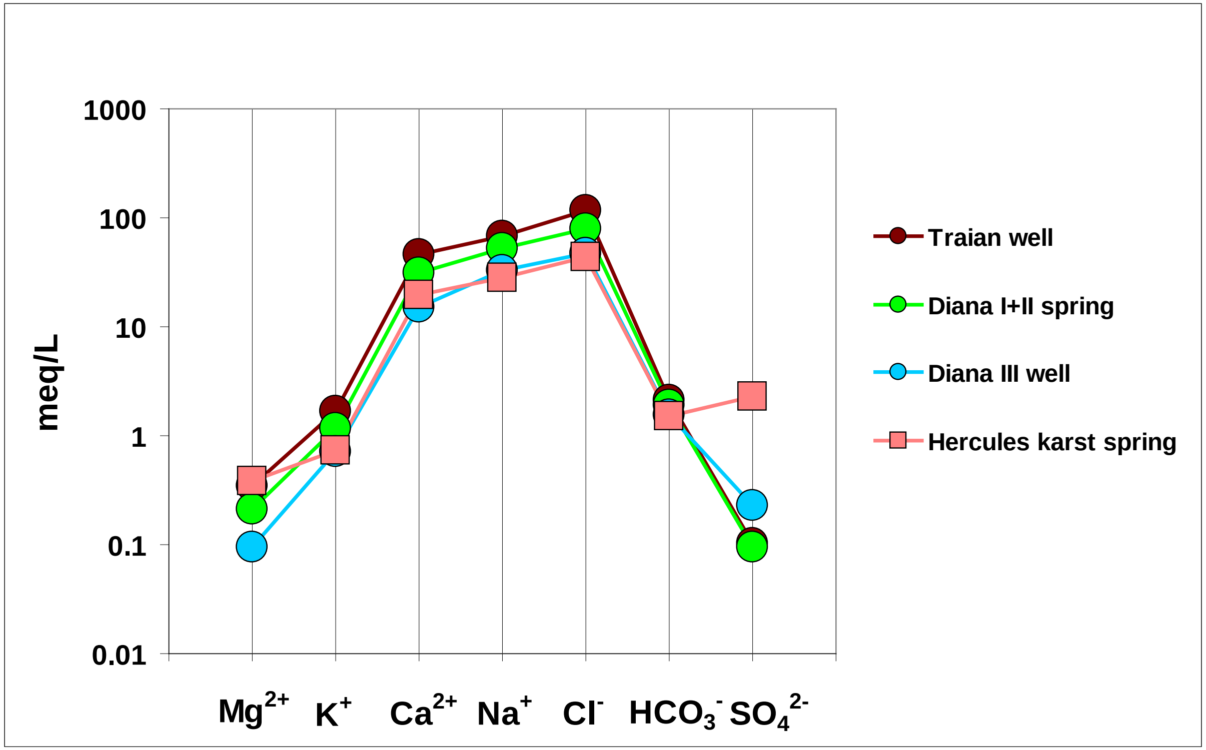


Diana III well





In spite of the contrasting hydrological behavior -
all those outflows have a very similar general chemical facies : Na-Ca-Cl



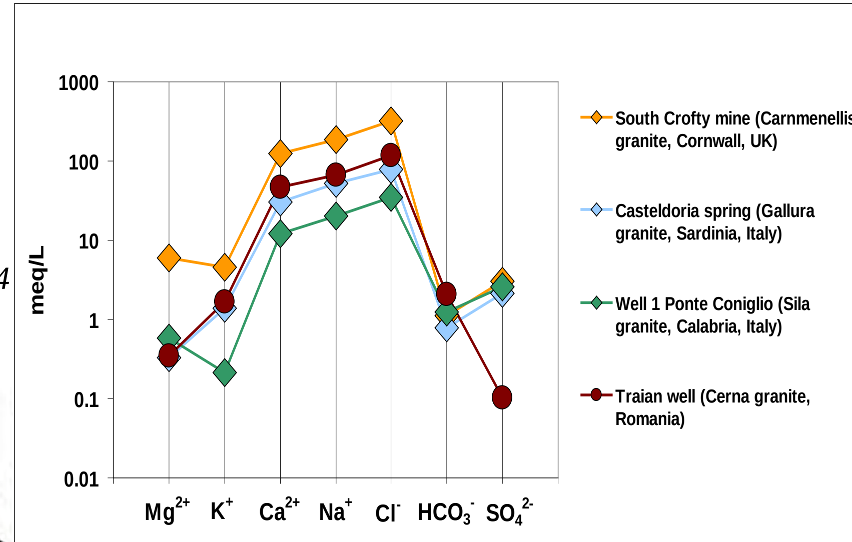
It was therefore inferred that some kind of mixing between:
a Na-Ca-Cl water
and
weakly mineralized fluids
operated within the entire geothermal system of Băile Herculane.

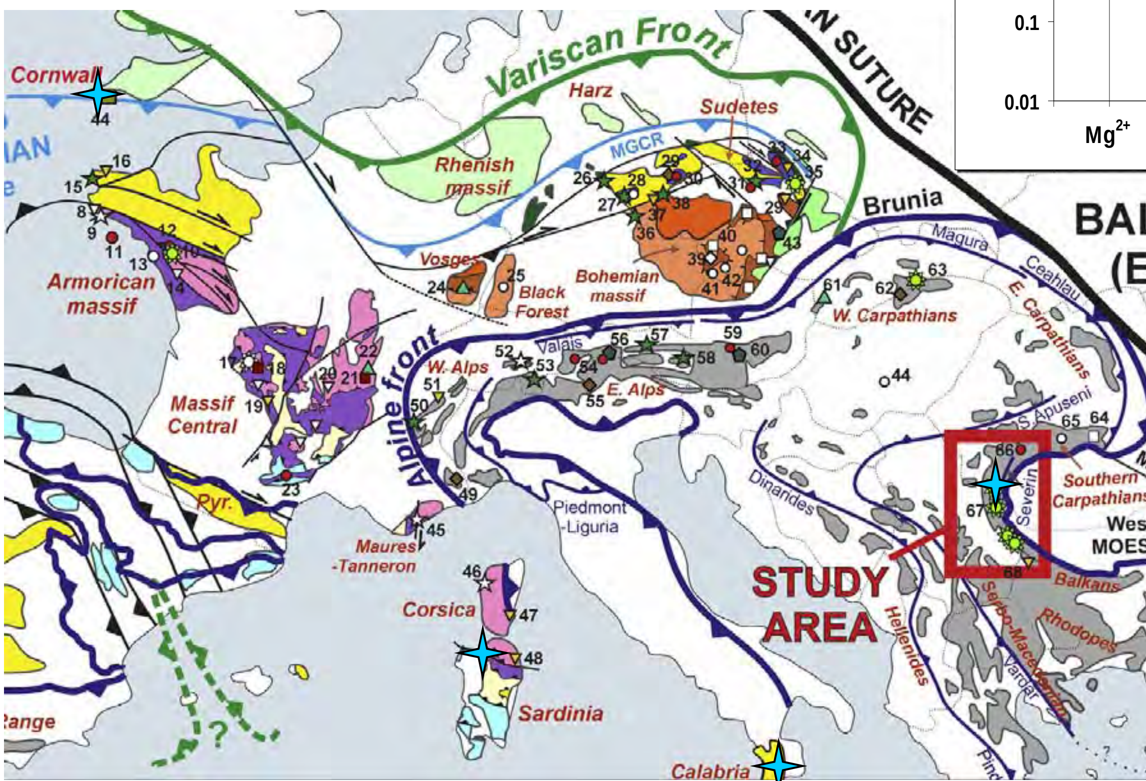
The highly mineralized Na-Ca-Cl water origin:

likely, the **Variscan-age Cerna granite.**

Very similar - Na-Ca-Cl - chemical facies - also **other thermal waters** discharging from **Variscan-age granites in Europe:**

Carnmenellis granite (Cornwall, UK) – *Edmunds et al., 1984*
Gallura granite (Sardinia, Italy) – *Angelone et al., 2005*
Sila granite (Calabria , Italy) – *Apollaro et al., 2016*





Variscan map of Europe
(*Plissart et al., 2017*)

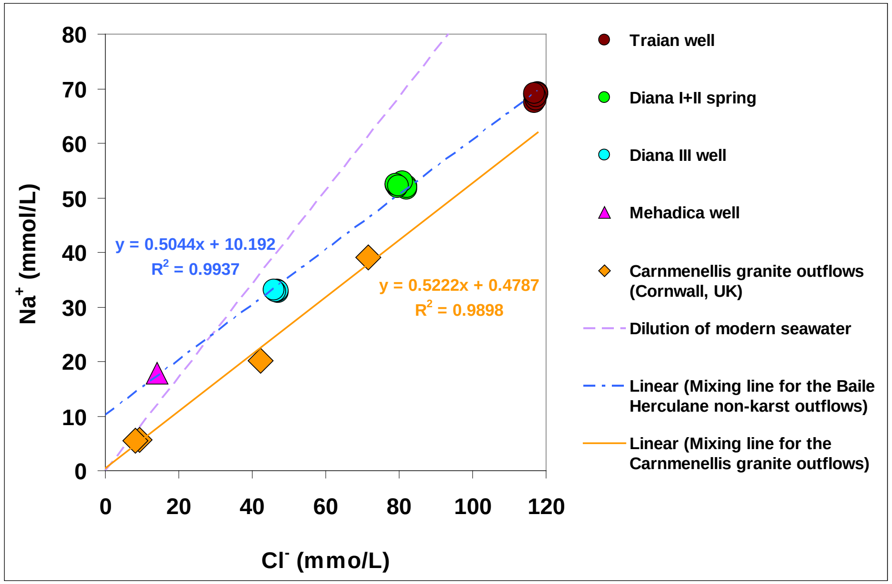
The diluting fluid(s) origin ?

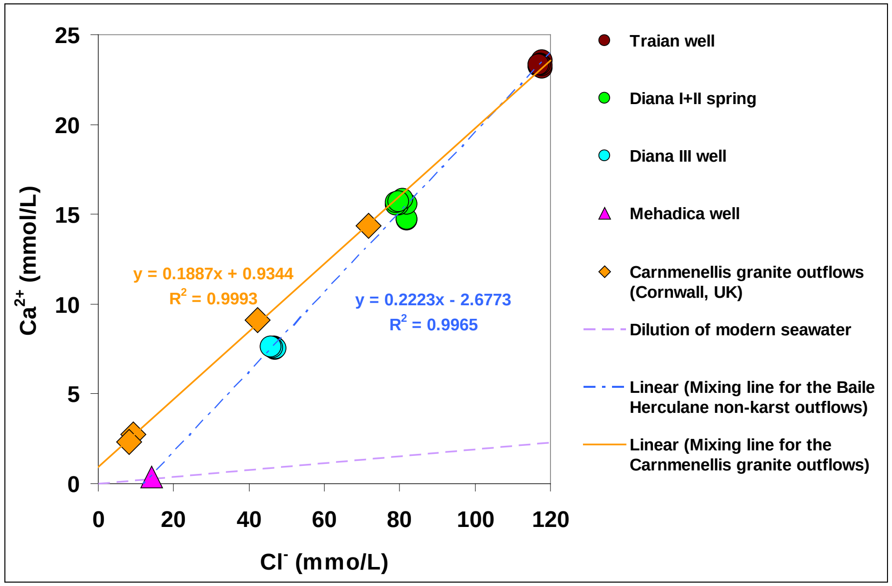
There are considered **conservative natural tracers**; (**“conservative”** - negligible chemical interaction with the host rock)

The most widely used conservative natural tracer – **chloride** (Cl^-)

In the Băile Herculane **non-karst outflows** - also Na^+ and Ca^{2+} behave conservatively (similar behavior was also recorded for **Na-Ca-Cl outflows** discharging from the **Carnmenellis granite**, UK - *Edmunds et al., 1984*)

The concentration of one conservative tracer is plotted against the concentration of the other conservative tracer (**“reciprocal concentration plots”**):





Since both tracers in a diagram are conservative, **each sample** (data-point) is assumed to mirror **ONLY** a specific **mixing ratio** between two **parent waters**.

“mixing line” – straight line connecting the **two parent waters** (each of them of assumedly constant concentration) which **mix** in order to result the **sampled fluid**;

For the **mixing line** corresponding to the **non-karst outflows** (**Traian**, **Diana I+II**, **Diana III**), a **proxy for** the **diluting parent-water** could be the **Mehadica well** thermal **(23.6°C) outflow**.

Mehadica well:

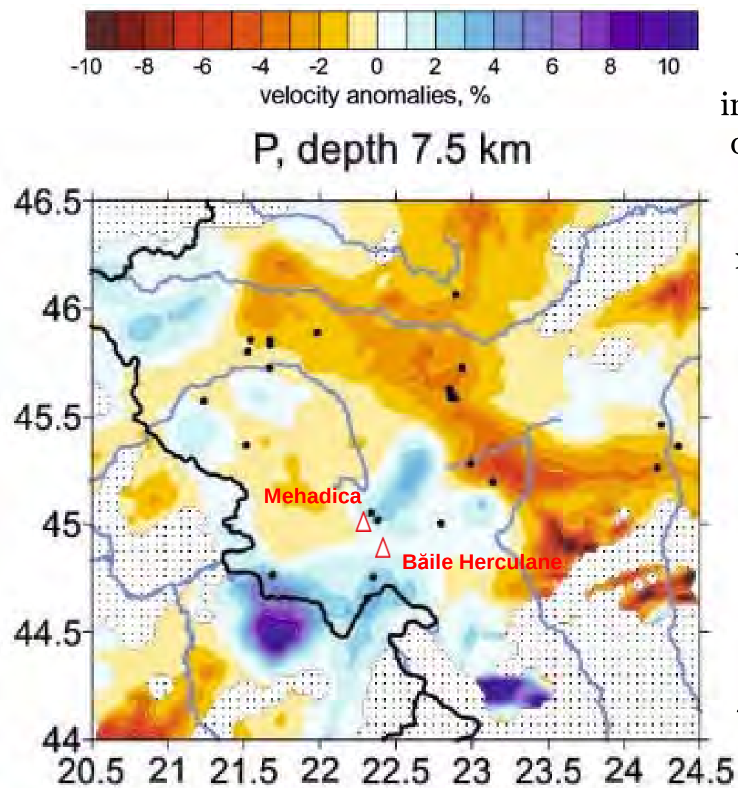
located 20 km away from Băile Herculane, in a Neogene, post-nappe sedimentary basin

- no information about depth, completed interval, tapped aquifer(s)

A connection between “Mehadica-type” water, and the Băile Herculane outflows appears unlikely, given:

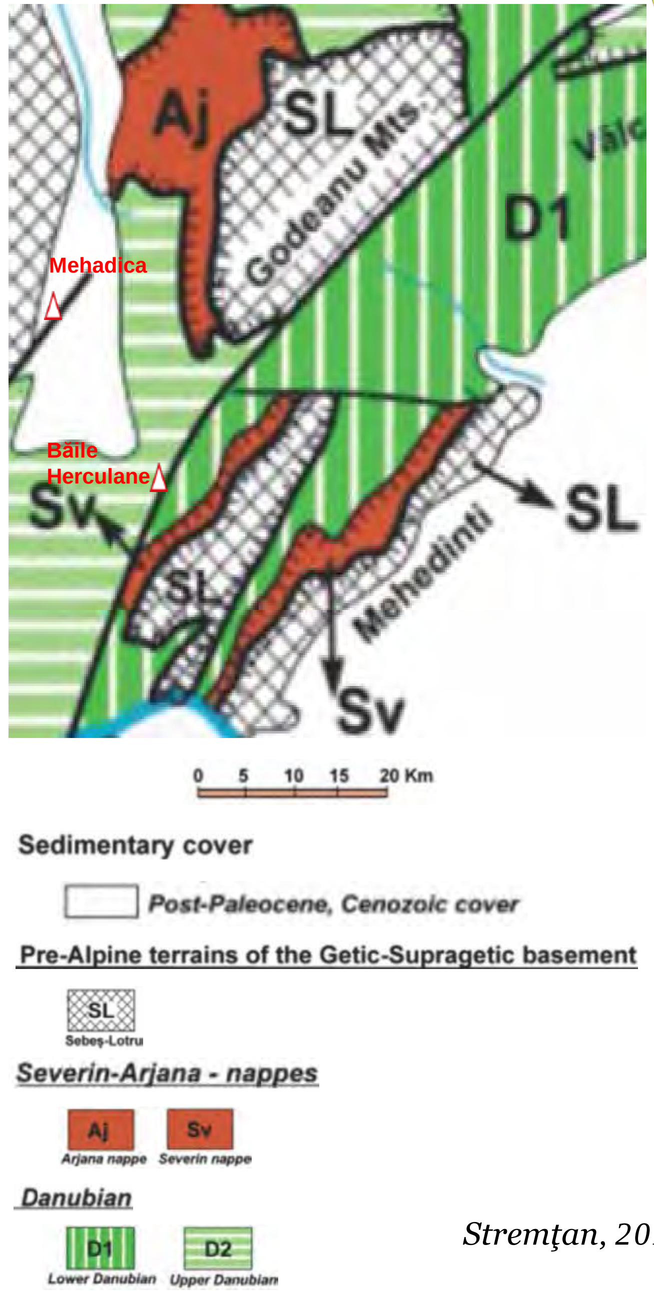
- the different basement units outcropping next to the two regions

- the general SW-NE strike of the major tectonic structures



Yet recent seismic tomography clearly indicates a WNW-ESE oriented low-velocity structure (intensely fractured basement region ?) connecting Mehadica and Băile Herculane

Zaharia et al., 2017

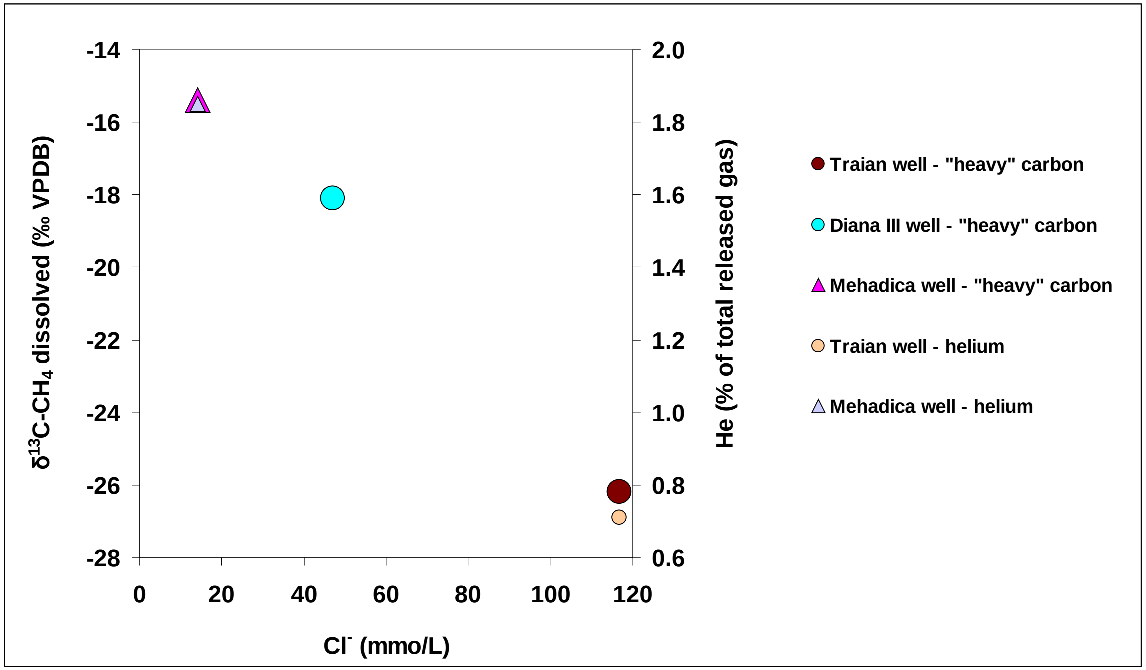


Stremţan, 2014

Additional support for the inferred **mixing relationship** involving the **Mehadica well** and the **non-karst outflows** at Băile Herculane:

the **associated gas composition**

The **“Mehadica-type” fluid** (which progressively dilutes, at Băile Herculane, the brackish Na-Ca-Cl parent-water) has a corresponding **contribution** - with **He** and with **abiotic-origin CH_4** - to the gas phase associated to the **non-karst outflows**



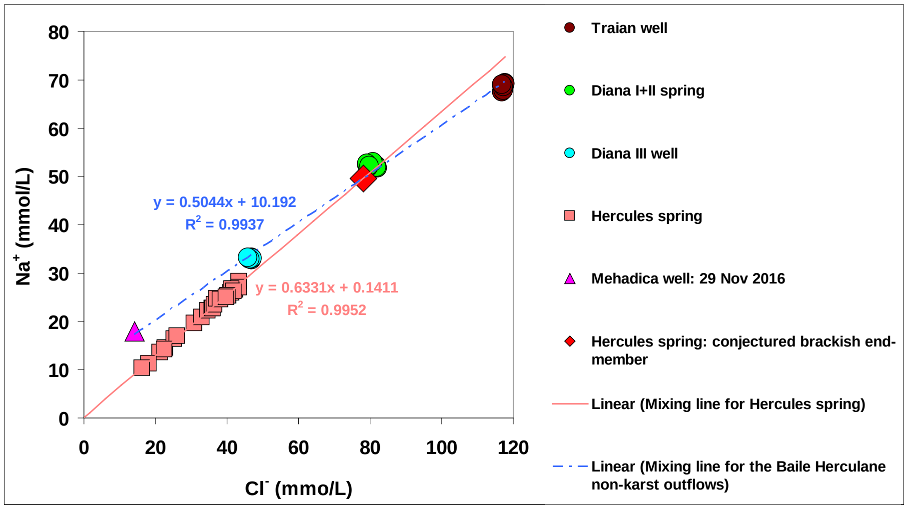
- contribution of **abiotic methane** (mirrored by **large ^{13}C concentrations**) to the total content of dissolved CH_4 (*Ionescu et al., 2017*): progressively **increases from Traian well, toward Mehadica well** (while, correspondingly, the thermogenic methane contribution, decreases)

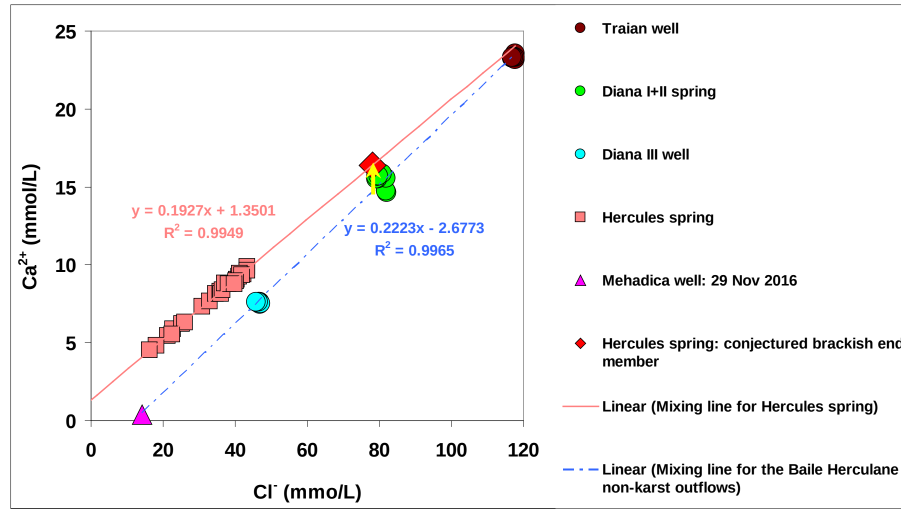
- **He** percentage in the total released gas (*Cosma & Ristoiu, 1999*) also **increases from Traian well, toward Mehadica well**

For the **non-karst outflows**:
the **mixing ratios vary** mainly ***from one sampling site to another*** (while each such separate sampling site displays virtually no time-fluctuations of the concerned solute contents): therefore, mixing lies are fitted to the data-points comprehensively aggregated for all the dates when the non-karst outflows are sampled

For the **Hercules karst spring**:

- the **mixing ratios vary between** samples collected ***at different time-moments*** (**different mixing ratios** between the **brackish parent-water**, and the **meteoric-derived** inflow of **karst freshwater**)





In the Na vs Cl reciprocal concentration plot, the two mixing lines intersect at a Cl^- concentration of about 78 mmol/L, suggesting that:
- the brackish end-member which supplies Hercules spring originates in a mixing process which involves the same end-members as those which contribute to the non-karst outflows;

and

-in the case of the brackish end-member which supplies Hercules spring, the mixing ratio between those two end-members is roughly the same as the one displayed by the Diana I+II spring.

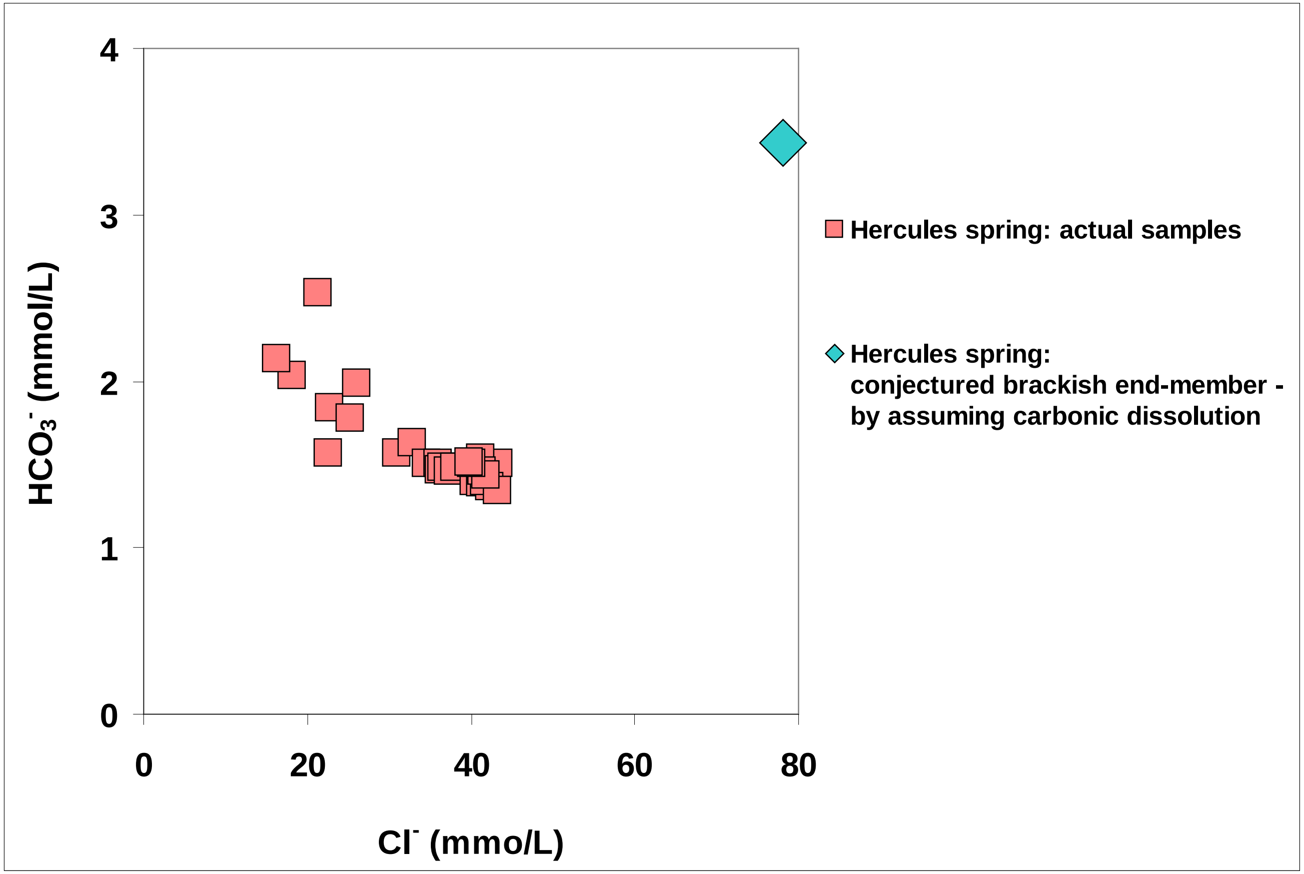
But the Ca^{2+} vs. Cl^- mixing lines intersection occurs at a Cl^- concentration of about 136 mmol/L, suggesting that:
- although originating in the binary mixing process outlined for the non-karst outflows, the brackish parent-water which supplies Hercules spring should be more concentrated even than the Traian well discharge.

One possible explanation:
The brackish parent-water which supplies Hercules spring indeed has a Cl^- concentration of about 78 mmol/L; but its Ca^{2+} content is larger than the one corresponding simply to the non-karst outflows mixing trend.
The accordingly conjectured **Ca^{2+} enrichment** (about **1.7 mmol/L**) – **likely**, a result of **limestone dissolution**.

Yet **NOT** the (habitually-encountered) **limestone attack by CO_2 and H_2O**:

$$H_2O + CO_2 + CaCO_3 = Ca^{2+} + 2HCO_3^-$$

The dissolved HCO_3^- amount which would result ensuing to the corresponding carbonic dissolution (3.4 mmol/L, needed for balancing the brackish parent-water Ca^{2+} enrichment of 1.7 mmol/L) plots significantly faraway from the HCO_3^- vs. Cl^- trend outlined by the Hercules spring data-points.



Additional clue - provided by the **fate of H_2S**

For the **non-karst outflows** - H_2S concentrations in the range **0.85 - 1.73 mmol/L**

For **Hercules spring** - H_2S concentration always **below the detection limit** (b.d.l.), of **2.9×10^{-3} mmol/L**

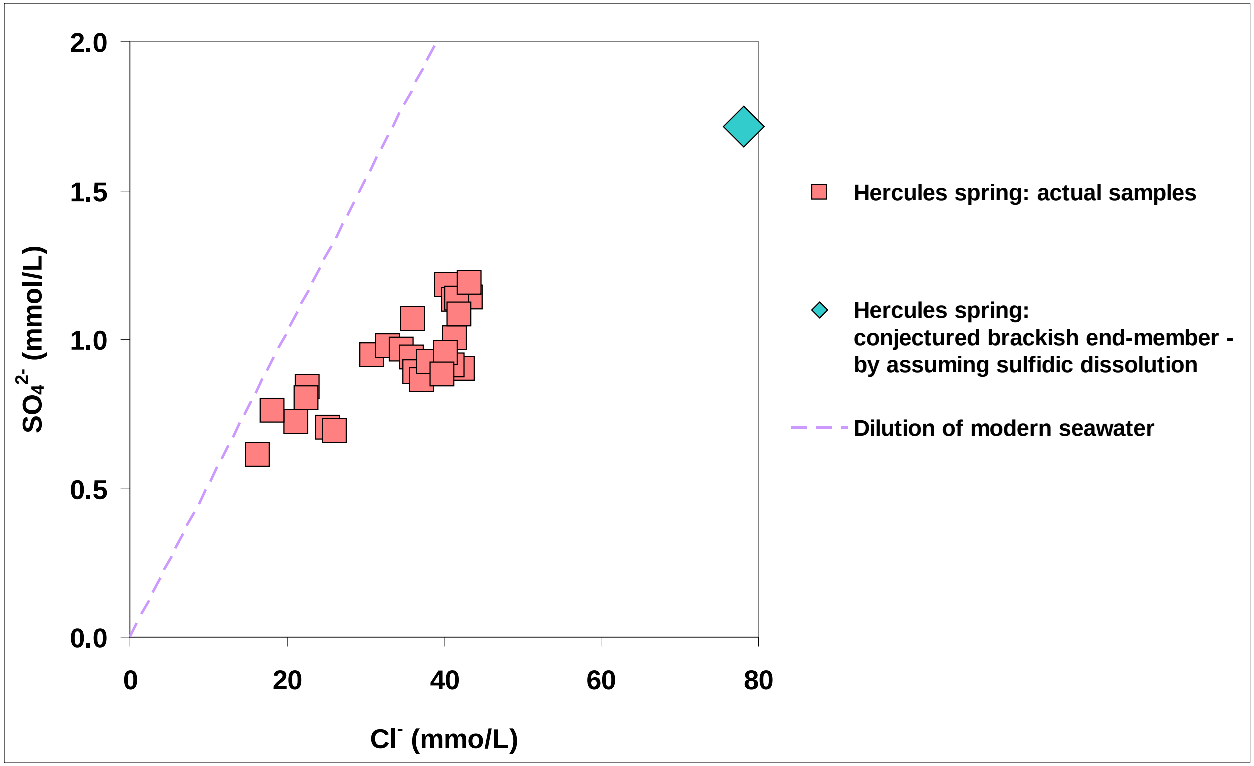
H_2S concentrations (mmol/L)

Sampling date	Traian well	Diana I+II spring	Diana III well	Hercules spring
19-Nov-2013	1.616	1.348	0.948	
21-Nov-2013				b.d.l.
25-Nov-2013				b.d.l.
26-Nov-2013	1.534	1.206	1.020	
28-Nov-2013				b.d.l.
02-Dec-2013				b.d.l.
03-Dec-2013	1.509	1.301	1.015	
05-Dec-2013				b.d.l.
09-Dec-2013				b.d.l.
10-Dec-2013	1.331	1.283	0.965	
12-Dec-2013				b.d.l.
16-Dec-2013				b.d.l.
17-Dec-2013	1.560	1.049	1.006	
19-Dec-2013				b.d.l.
23-Dec-2013				b.d.l.
27-Dec-2013				b.d.l.
30-Dec-2013				b.d.l.
03-Jan-2014				b.d.l.
07-Jan-2014				b.d.l.
09-Jan-2014				b.d.l.
13-Jan-2014				b.d.l.
16-Jan-2014				b.d.l.
20-Jan-2014				b.d.l.
21-Jan-2014	1.506	1.602	1.021	
23-Jan-2014				b.d.l.
27-Jan-2014				b.d.l.
28-Jan-2014	1.397	1.469	0.927	
30-Jan-2014				b.d.l.
03-Feb-2014				b.d.l.
04-Feb-2014	1.665	1.605	0.852	
06-Feb-2014				b.d.l.
10-Feb-2014				b.d.l.
11-Feb-2014	1.730	1.378	0.985	
13-Feb-2014				b.d.l.
17-Feb-2014				b.d.l.

Still likely, the **brackish end-member** involved in the **Hercules spring** supply had, **initially**, **comparably large amounts of H_2S.**

The latter were able to **provide**, **by oxidation**, the **1.7 mmol/L** of SO_4^{2-} needed **for balancing** the Ca^{2+} which – assumedly - was **up-taken into solution** ensuing to the **limestone attack by the dissolved H_2S**

$$H_2S+2O_2+CaCO_3 = Ca^{2+}+SO_4^{2-}+CO_2+H_2O$$



This **SO_4^{2-} content estimated** for the **brackish end-member** (**1.7 mmol/L**) is also **consistent with** the **SO_4^{2-} vs. Cl^- trend** outlined for Hercules spring.

And because of the complete oxidation to SO_4^{2-}, virtually no H_2S remained in the Hercules spring discharge

What is the resulting **limestone dissolution rate**?

karst freshwater supplying Hercules spring - has negligible Cl^- input;

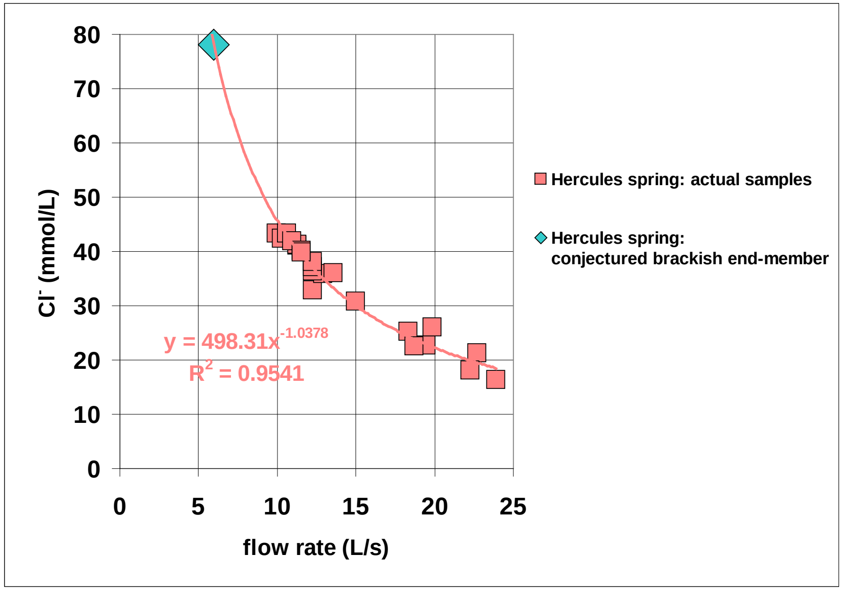
hence

Hercules spring output of Cl^- ($Q_o c_o$) is fully balanced by the Cl^- input due to the brackish parent-water ($Q_b c_b$),

namely:

$$c_o = Q_b c_b Q_o^{-1}$$

If a **power-law** with an **exponent** ≈ **-1** can be **fitted to** the **c_o vs Q_o** plot, this indicates that the product **$Q_b c_b$** is **constant**.



Q_o – total flow rate discharged by Hercules spring
c_o – Cl^- concentration recorded at Hercules spring
Q_b – brackish parent-water flow rate
c_b – brackish parent-water Cl^- concentration

c_b itself is also **constant** (otherwise no tight mixing lines could have been fitted to the conservative tracers' concentrations); hence **Q_b must be constant** as well.

Assessing **Q_b**:

the **power-law line** is **extrapolated to** the **Cl^- content** of about **78 mmol/L** (estimated for the **brackish parent-water which supplies Hercules spring**)

It results: **Q_b = 6 L/s** – the **brackish parent-water flow rate**

The amount of **Ca^{2+} up-taken** by **sufidic dissolution** and **carried by this flow rate**: 1.7 mmol/L x 6 L/s = **10.2 mmol/s**
The amount of correspondingly **dissolved $CaCO_3$** is also **10.2 mmol/s** - namely ≈ **1 g/s**, or ≈ **2.6 tons/month**, or ≈ **1 m^3/month**.

In fact, the **limestone amount dissolved by sufidic attack** is likely **double (≈ 2 m^3/month)** – since a mine gallery having been excavated in the late 1980'ies, currently diverts half of the discharge that was originally flowing through Hercules karst spring.

CONCLUSIONS

It had been conjectured - since long time ago, e.g. *Popescu-Voiteşti, 1921* - that the **Băile Herculane thermal water composition** resulted from **mixing** between several (three?) **different water types**

And it was quite reasonable to assume that the **H_2S-bearing waters** were **dissolving limestone**

So, what's new about that?

Actually, **no quantitative evidence** had been **so far** provided **for any of those two inferences**.

And accordingly, **no quantitative estimates** had been issued **for** the involved amounts – namely:

- **solute concentrations** of **contributing parent-waters**;

and

- **sulfidic dissolution rate**

Acknowledgements

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