Thermal springs and balneology in the Peri-Adriatic area: geochemical status and prospects

Riccardo Petrini, Pisa University

(with contributions by R. Cataldi and B. Della Vedova)

The Peri-Adriatic Region

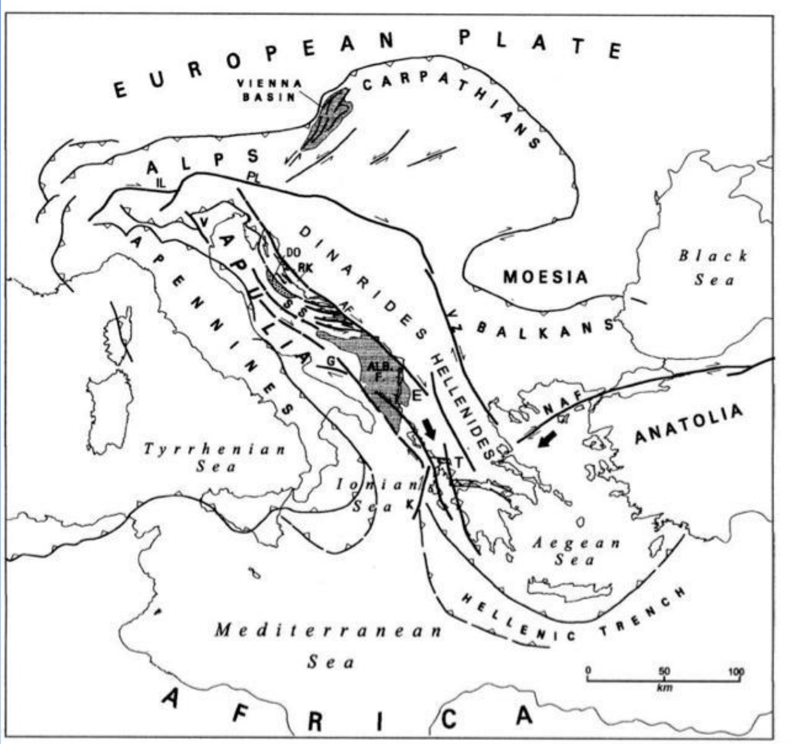
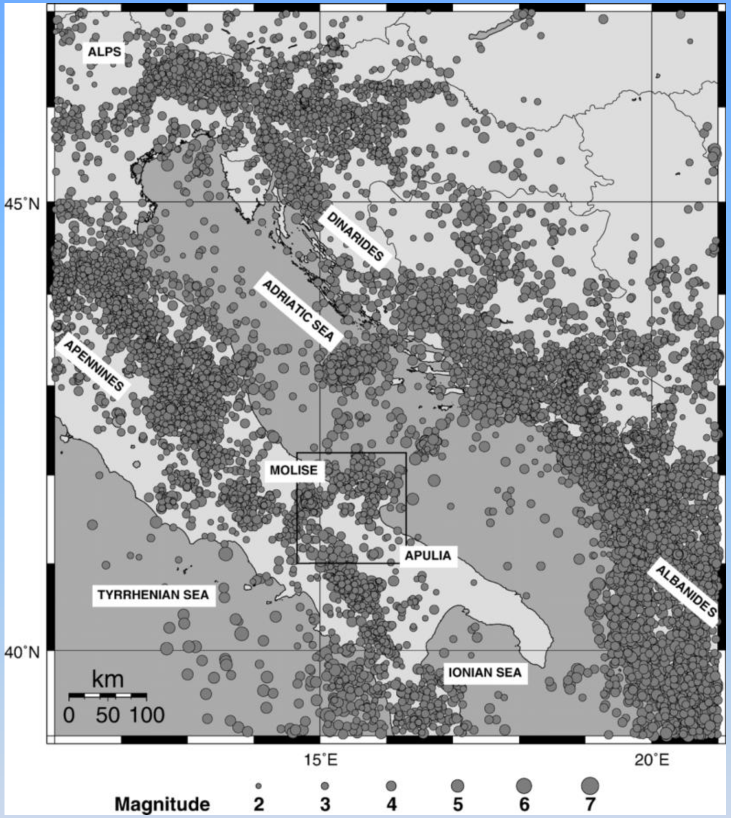


Figure 3 Schematic map of the Alpine system of Europe

(Picha F.J. 2002)



Epicenters of seismic events of magnitude > 2.0, from 1975 to 2005, U.S. Geological Survey Earthquake Database

(Del Gaudio et al., 2007)

Thermal Spas in Peri-Adriatic Region

COUNTRY	Number of active SPAs	Water volume used in 2010 (m^3/year, excluding pool uses)
Albania	5	140.000
Bosnia Herzegovina	20	1.290.000
Croatia	18	1.345.000
Greece	> 23 (up to 50?)	> 500.000
Italy	149	48.000.000
Montenegro	1	60.000
Slovenia	25	1.780.000
T O T A L	> 260	> 53.115.000

Including pool uses, a flow of about 112x10⁶ m³/year (3.55 m³/s) of thermal waters can be estimated to feed Spas of the Adriatic-Jonian Region

Thermal Spas in Peri-Adriatic Region: Q,T, V, MW, TJ

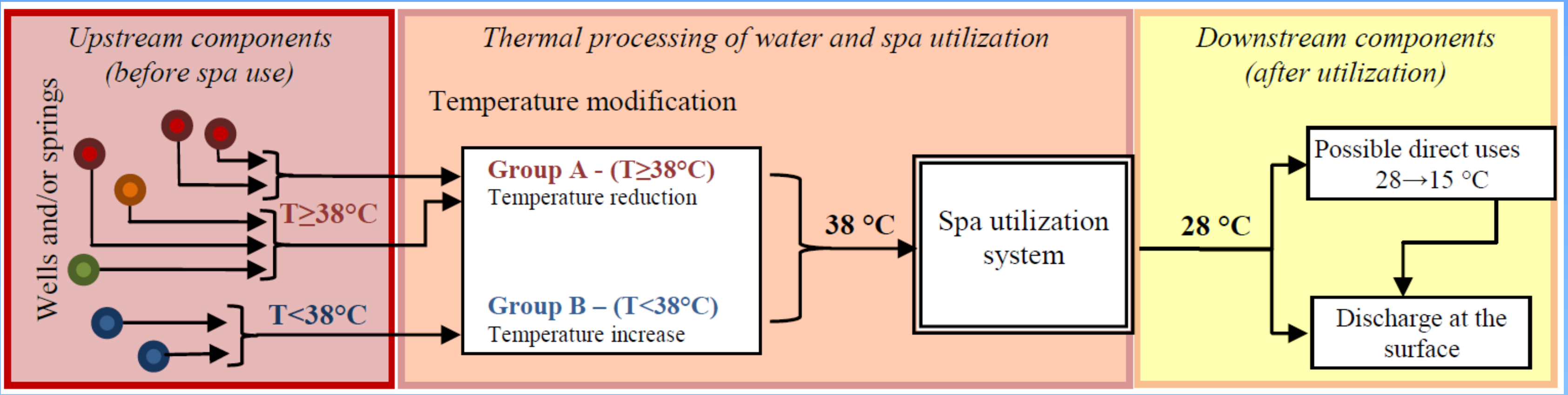
Country	N. of SPAs	Total average flow rate (kg/s)	Annual Total average water used (10^6*m^3)	T (°C)	Average T (°C)	Resource potential capacity (MWt)	Total geothermal energy used (TJ/yr)	Estimated number of tourists [1]	Source [2]
Slovenia	26	115*	3.6	23-63	33-38	25	311	751000 (2010) ?	WGC 2010
Croatia	18	96*	3.0	25-85	42-47	33	216	400000 (2010) ?	WGC 2010
Bosnia and Herzegovina	20	79*	2.5	21-76	39-44	13	100	192000 (2009) ?	WGC 2010
Montenegro	1	?		?	?	?	?	?	WGC 2010
Albania	6	21	0.7	27-60	45-50	12	8	?	WGC 2010
Greece	>60	>1500	≈ 47	18-100	?	39?**	238?**	>100000 (2010) ?	WGC 2010
Serbia	59	700-800 ?	≈ 23	29-96	45-50	40	647	?	WGC 2010
TOTAL	> 191	> 2.561	≈ 79,8			162	1520	>1.443.000	

(1) Data taken from different sources, they likely contain large uncertainties.
(2) Proceedings World Geothermal Congress 2010

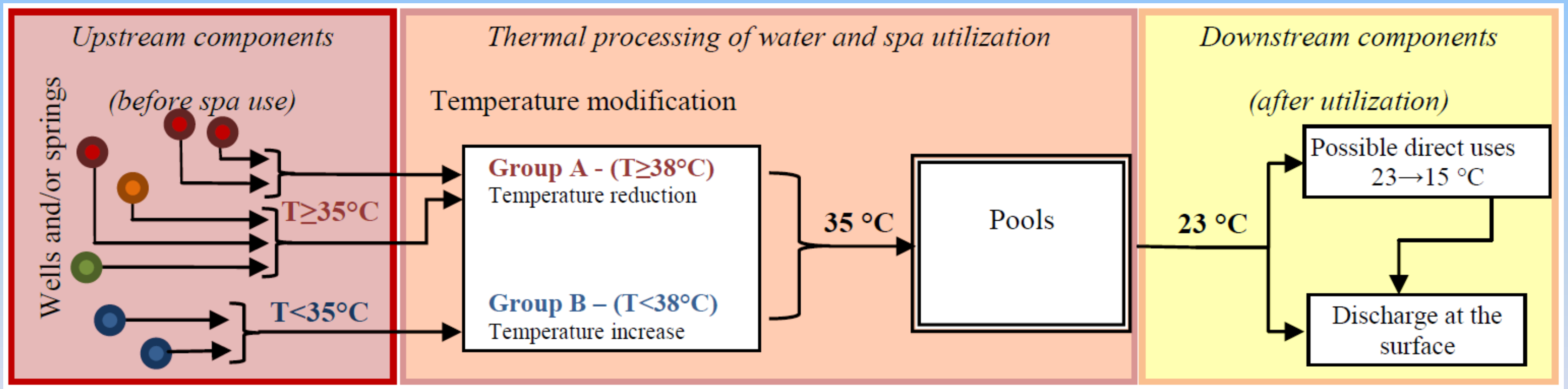
(*) *Water volumes have been estimeted starting from the Annual Energy Use of each country.*
For each spring we estimated the average mean annual energy (based on the average flow) for the effective temperature intervals (T_{in} –T_{out}), using the **Annual Energy Use (TJ/yr) = Ave. flow rate (kg/s) x [inlet temp. (°C) - outlet temp. (°C)] x 0.1319**

(**) *Figures largely underestimated*

Energy Potential of thermal springs and waters



Conceptual flow diagram for water and energy utilization in spa systems, excluding pools



Conceptual flow diagram for water and energy utilization of thermal pools associated to spa systems

Mass and energy balances are crucial for sustainable use of excess heat, up- and down-stream Spa uses, and are tools to develop the balneotherapy sector.

Thermal springs and waters in peri-Adriatic context

Geothermal reservoirs are often related to areas of active or recent magmatism, where heat is transferred from a magmatic source to the circulating fluids

However, low-enthalpy waters in different tectonic settings, including aquifers in deep carbonate-rocks and metamorphic basements, are receiving much attention, in particular for bathing and swimming

The Peri-Adriatic area has many favorable geothermal characteristics; however, long-term abstraction of resources should be carefully planned to avoid overexploitation

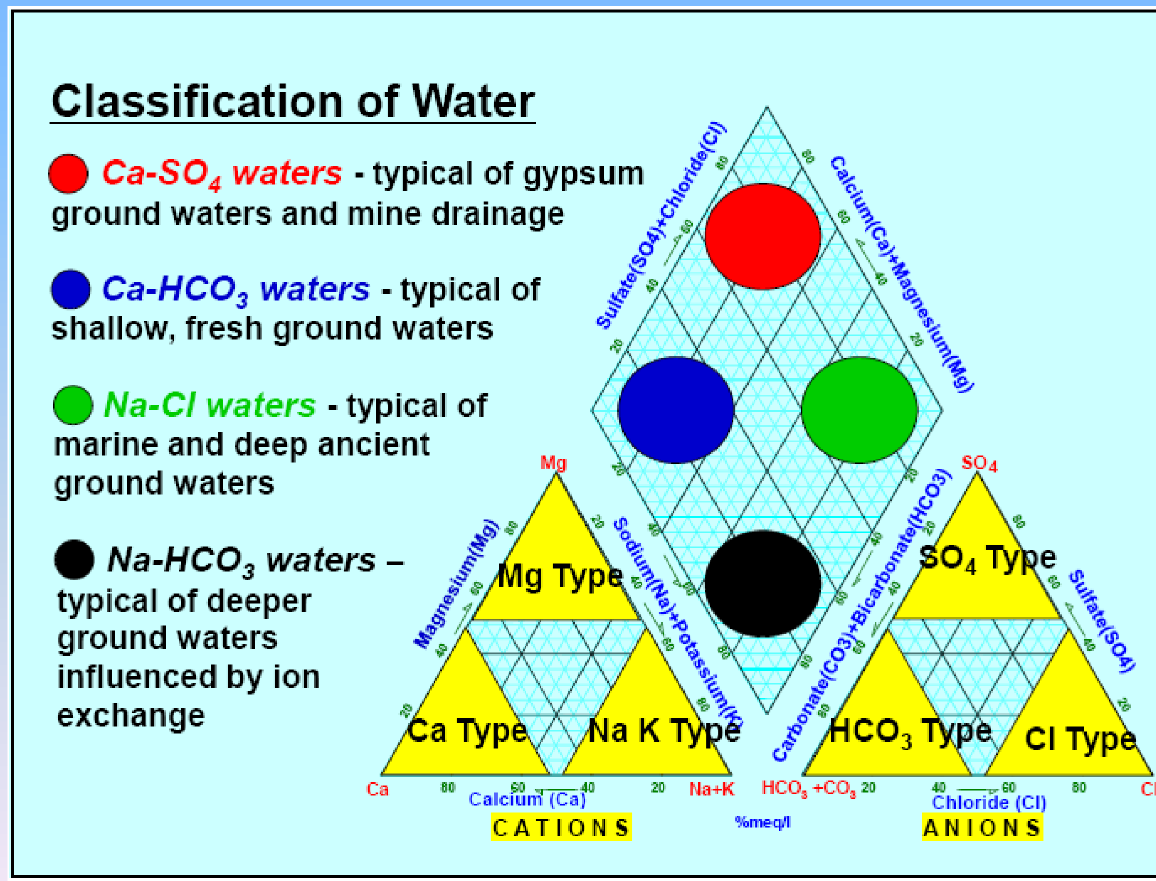
Water geochemistry: source aquifers for a sustainable exploitation policy

The major ions chemistry gives the basic information on water-type and processes

cations
Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}

anions
HCO_3^{-}, Cl^{-}, SO_4^{2-}

Piper diagram

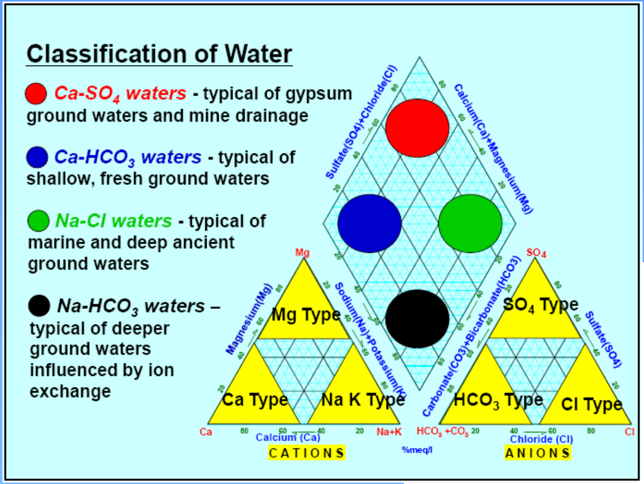


Geothermal manifestations in the Peri-Adriatic Region belong to different hydrofacies, reflecting different origin and nature of aquifers

They include:

- Thermal waters in Mesozoic carbonate-rock aquifers
- Thermal waters in aquifers within the metamorphic basement
- Thermal waters in porous media in sedimentary basins
- Thermal waters of marine origin in coastal environments

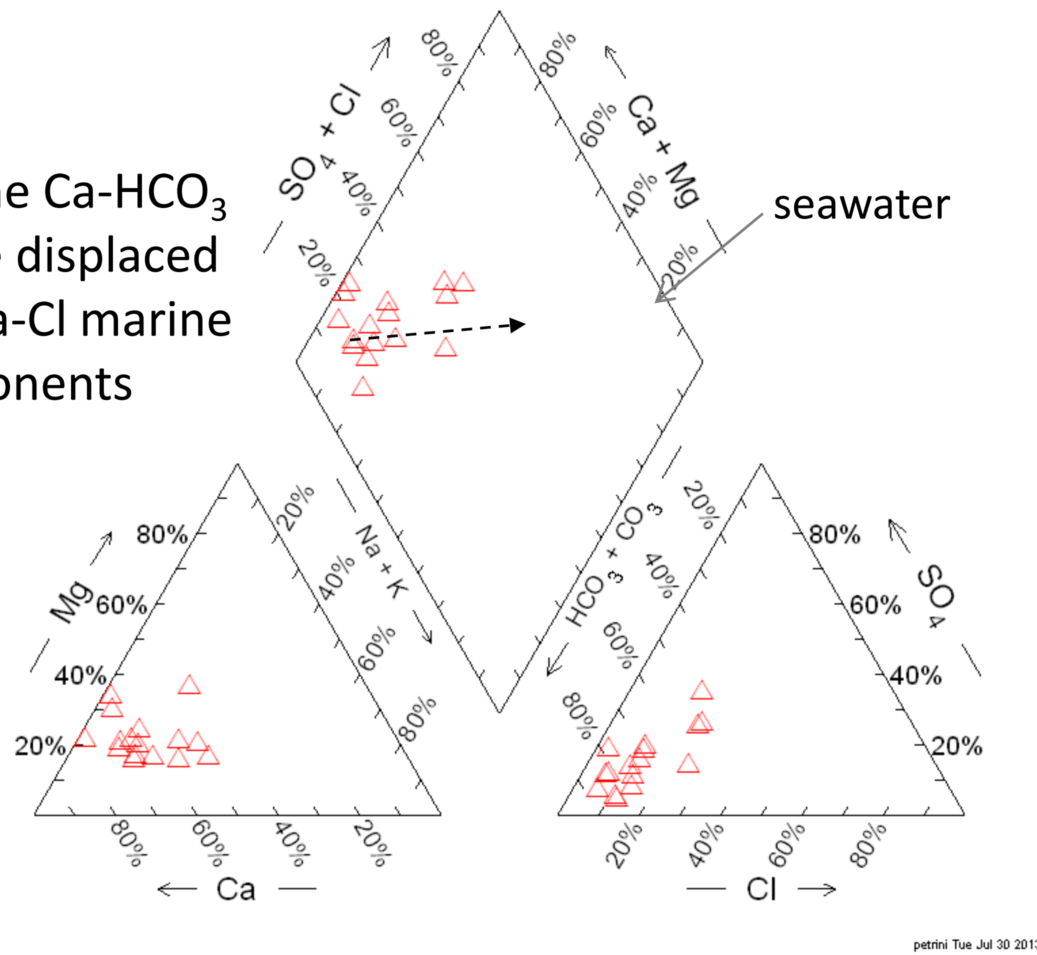
Each requires to enhance knowledge to reduce future quantitative and qualitative threats

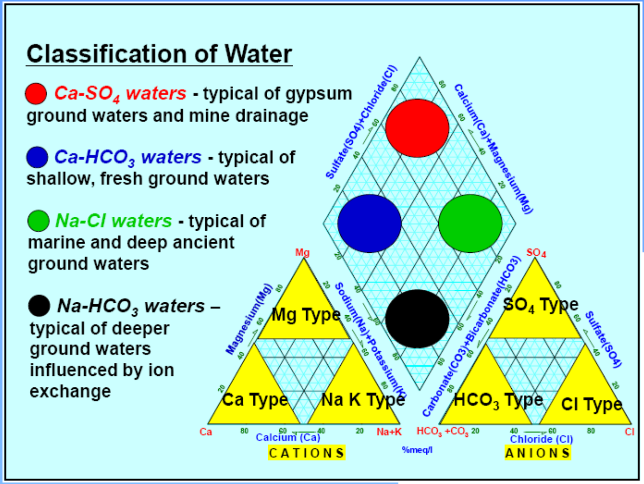


Hydrofacies: mostly of the Ca-HCO_3 type

Bosnia

Some of the Ca-HCO_3 waters are displaced towards Na-Cl marine components

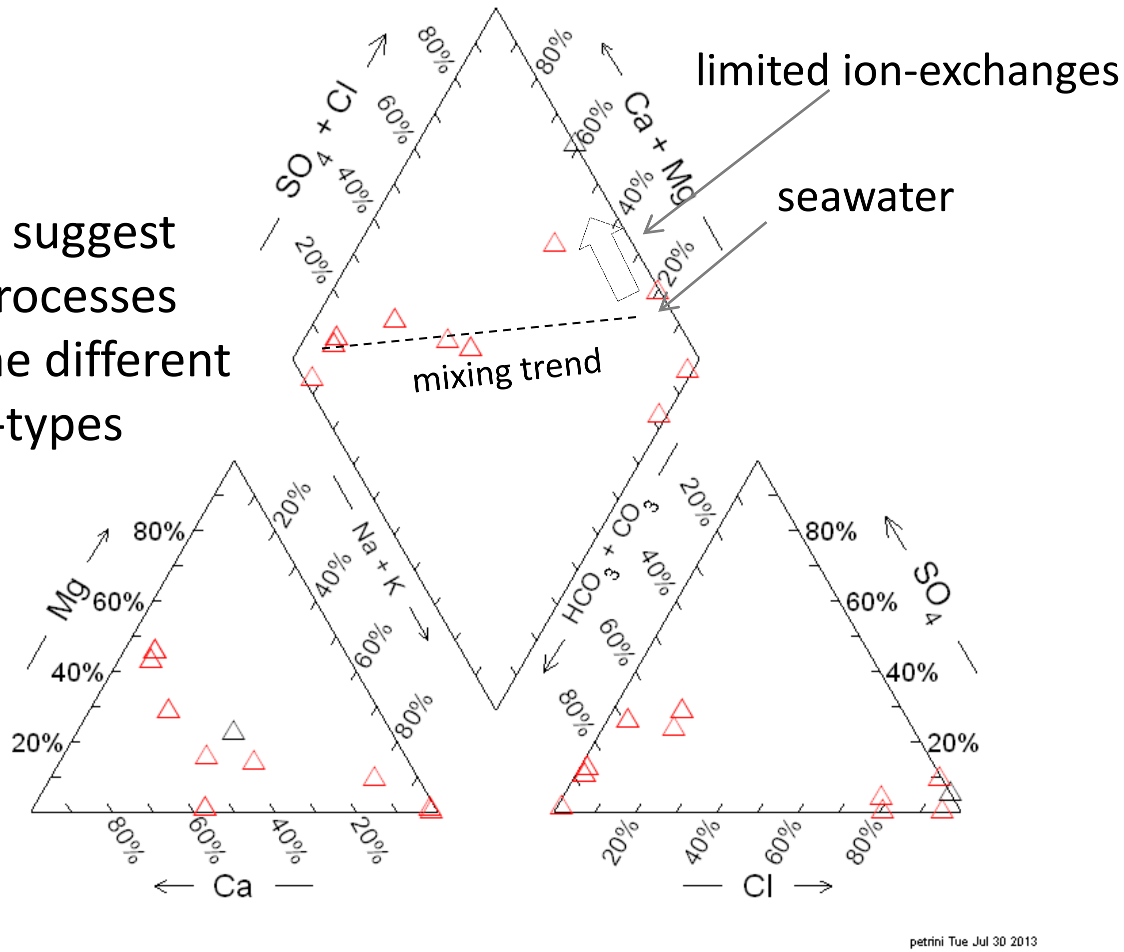


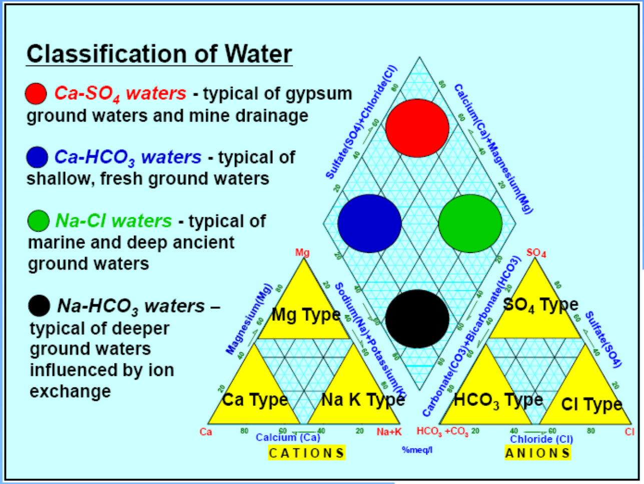


Hydrofacies: waters range from the Ca-HCO_3 to the Na-Cl, Ca-SO_4 type

Croatia

The data suggest mixing processes between the different water-types

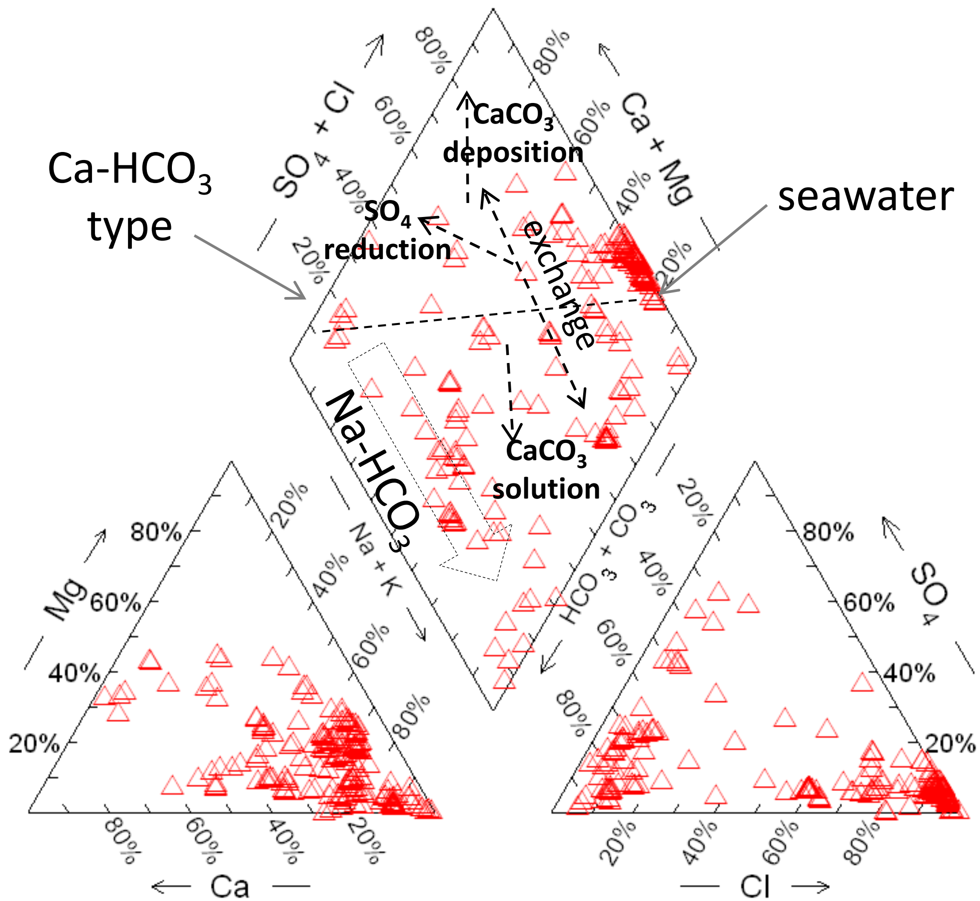




Hydrofacies: the Na-Cl type dominate; highly variable composition, including the <u>Na-HCO_3 type</u>.

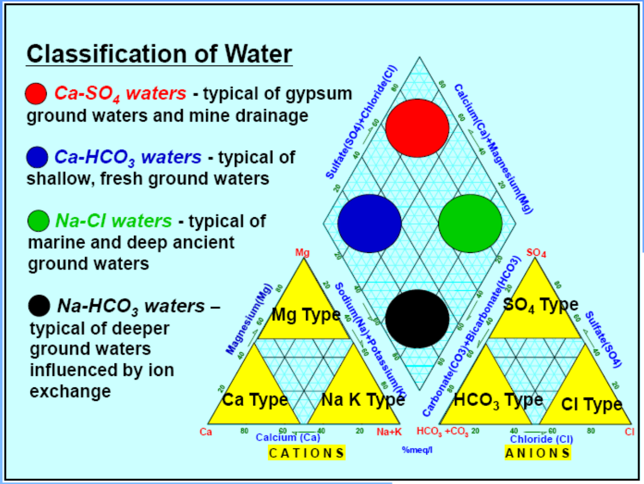
Greece

The data indicate that a number of different processes are active in the different environments, and that gases (in particular CO_2) have an active role in driving equilibria

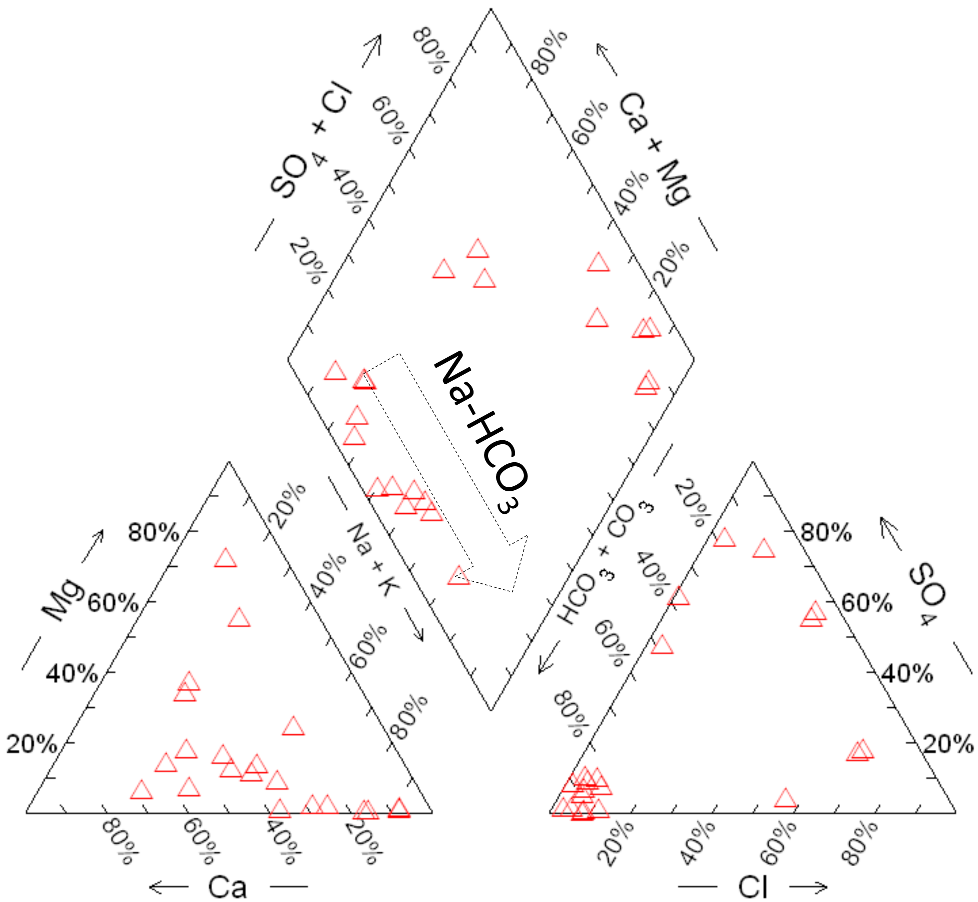


petrini Tue Jul 30 2013

Hydrofacies: waters range from Ca-HCO_3, Na-Cl and the Na-HCO_3 type



Macedonia



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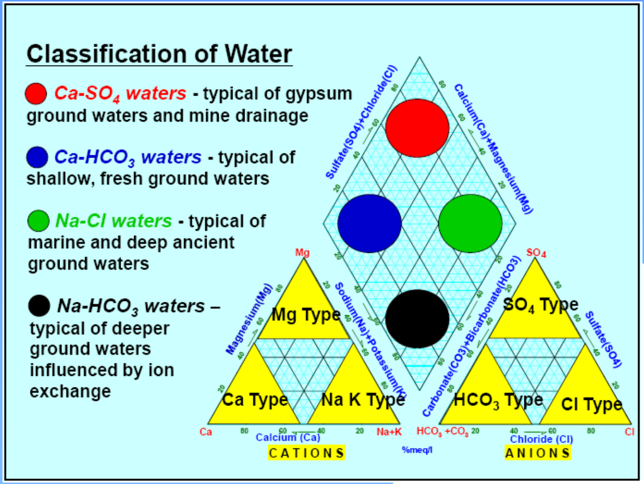
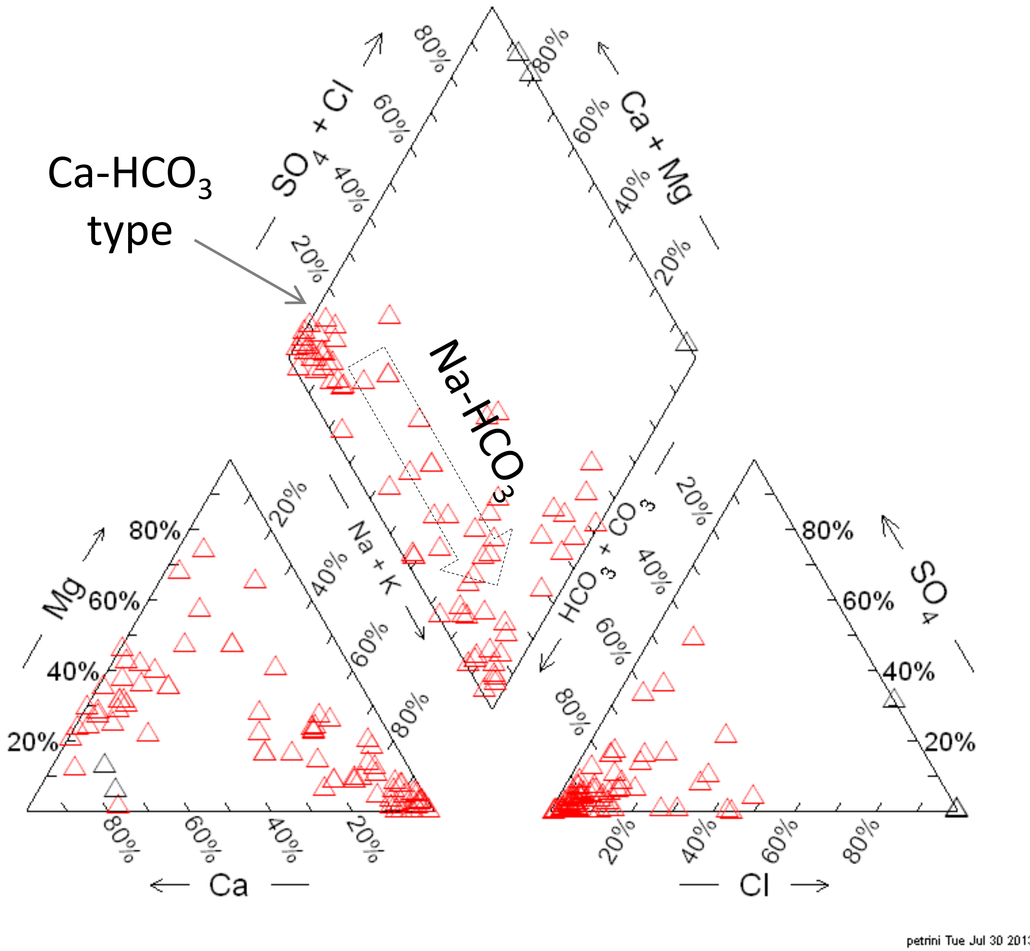
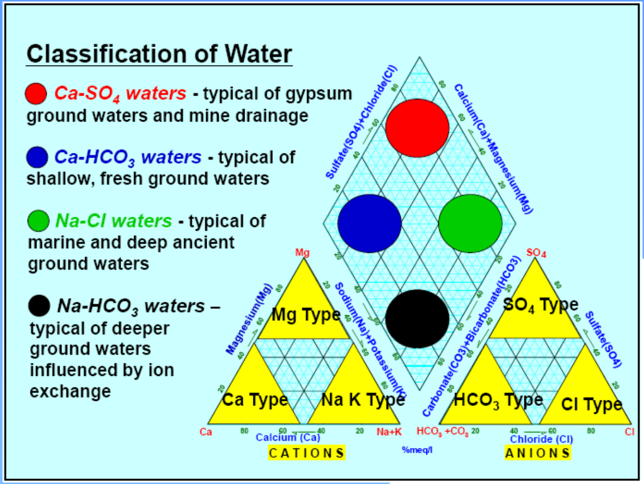
Most waters range from the Ca-HCO_3 to the <u>Na-HCO_3 type</u>



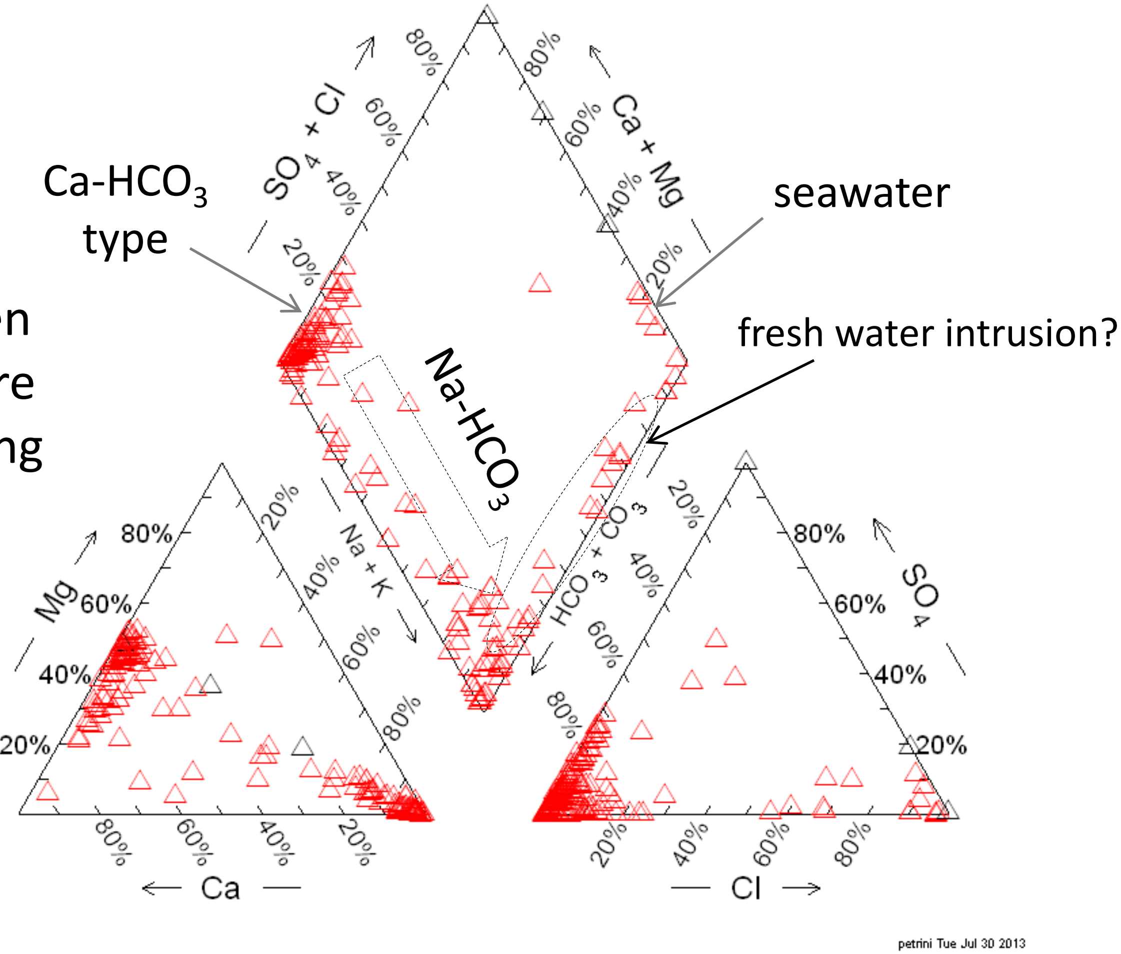
Serbia





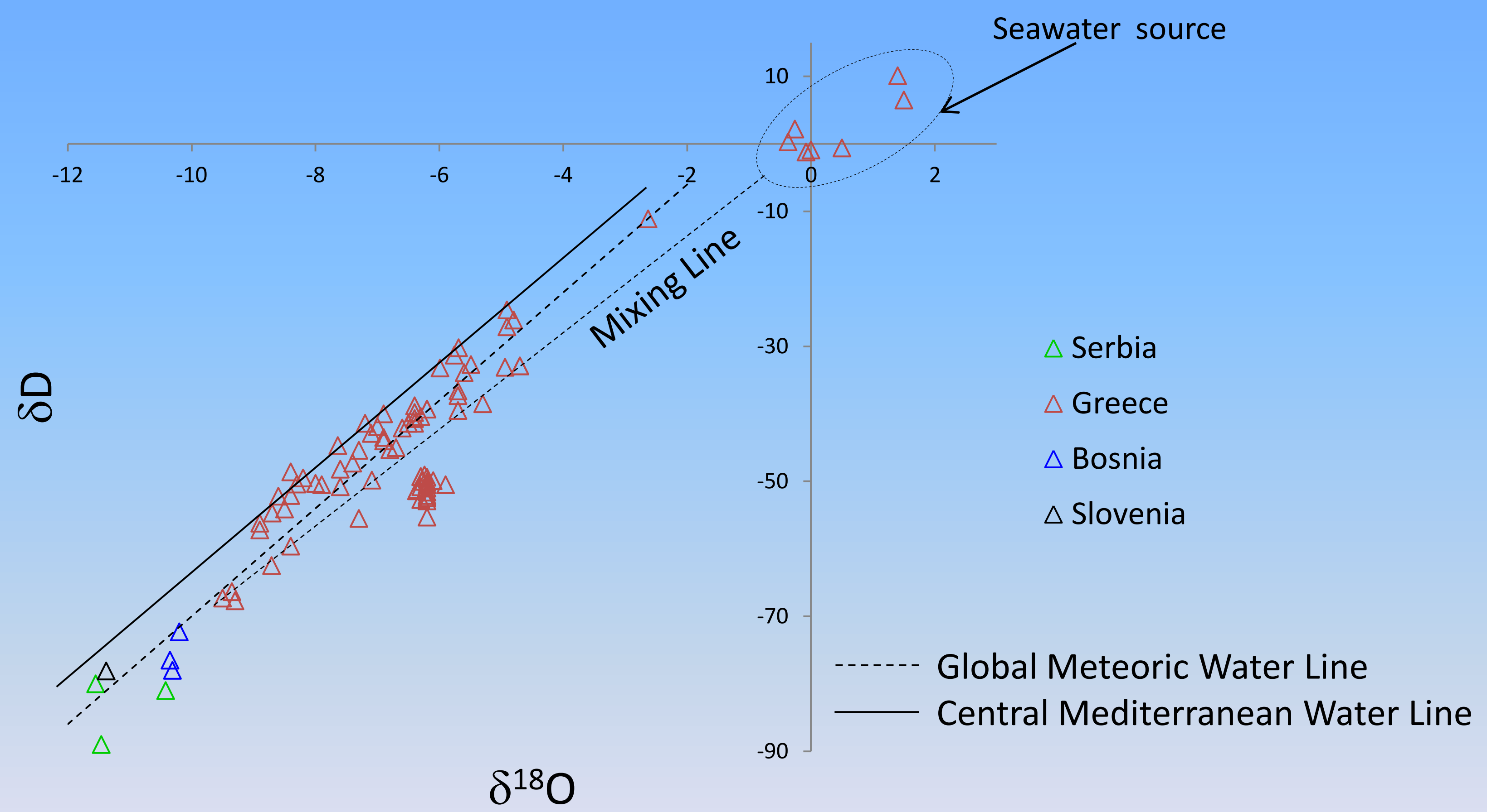
Hydrofacies: mostly waters range from the $Ca\text{-}HCO_3$ and $Na\text{-}HCO_3$ type Na-Cl waters are limited

Slovenia



Conservative mixing between $Ca\text{-}HCO_3$ and Na-Cl waters are absent or negligible, indicating non-interacting reservoirs. Possible processes of freshwater intrusion are highlighted

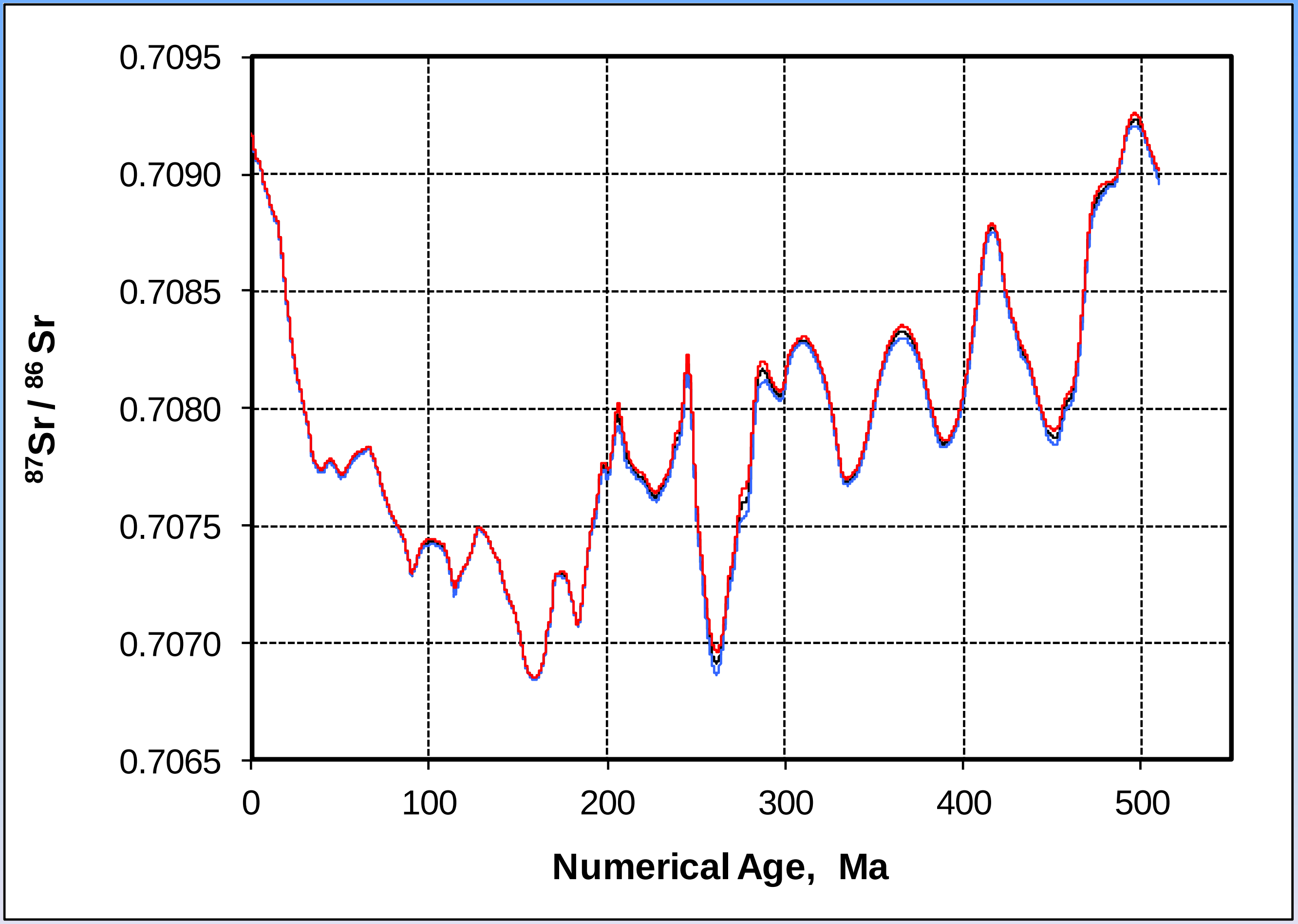
Waters origin: oxygen and hydrogen stable isotopes



Most water-types have a meteoric origin. Na-Cl waters have a marine origin. Modern or ancient seawater?

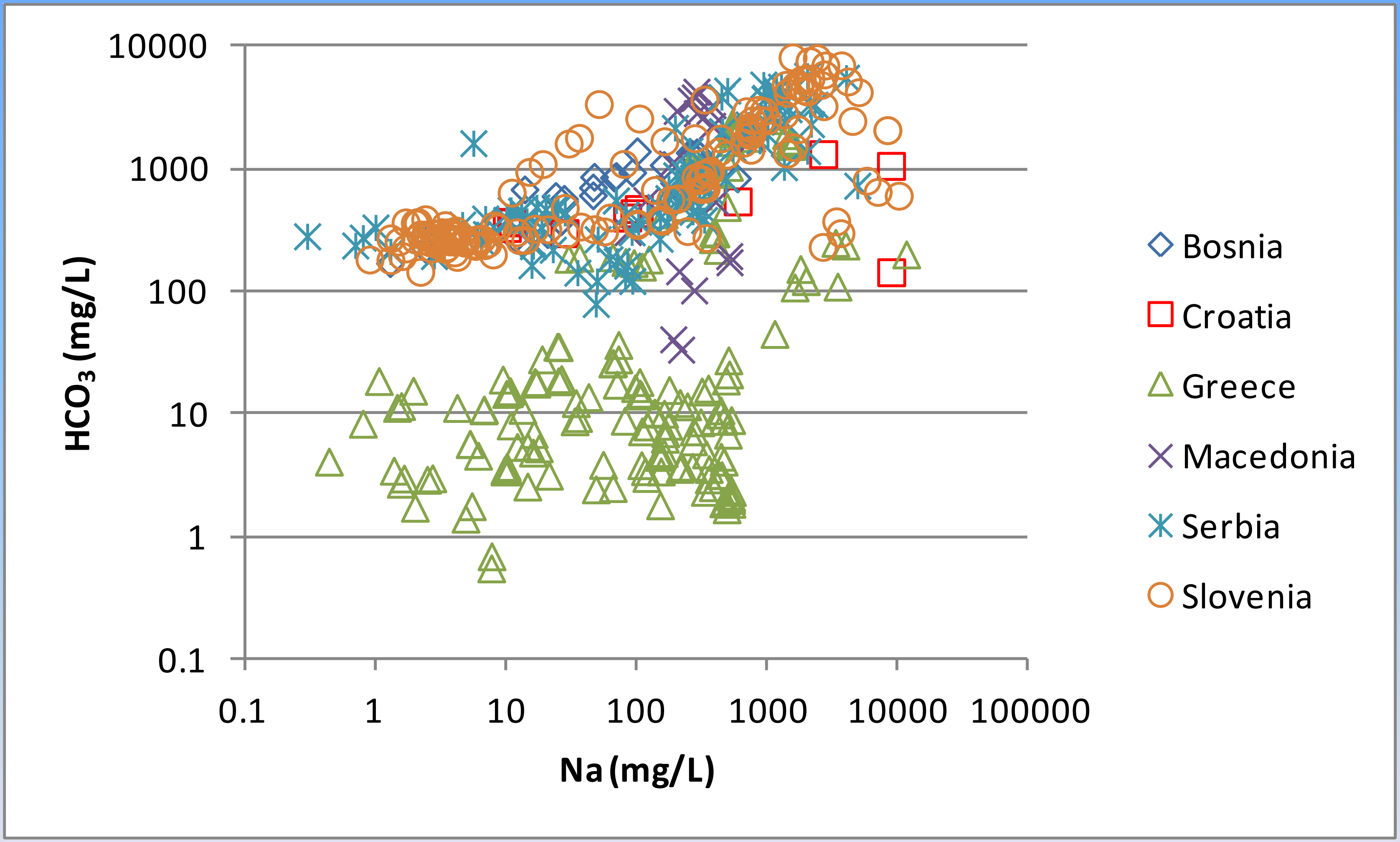
Strontium isotopes: the modern or ancient origin of the marine Na-Cl type waters

The $^{87}Sr/^{86}Sr$ ratio in seawater changes through geological time, allowing the “age” of the saline reservoir to be inferred



Mc Arthur et al, 2001, 2007

The Na-HCO_3 waters: extreme compositions through water-rock interaction



The waters from the Peri-Adriatic region show a Na vs. HCO_3 scattered distribution, in some cases with high HCO_3. Most waters from Greece are displaced towards low HCO_3

Some of the Na HCO_3 thermal waters likely reflect silicate weathering:

silicates have low solubilities ($NaAlSi_3O_8$: $6x10^{-7}$ mol/L) and low dissolution rates

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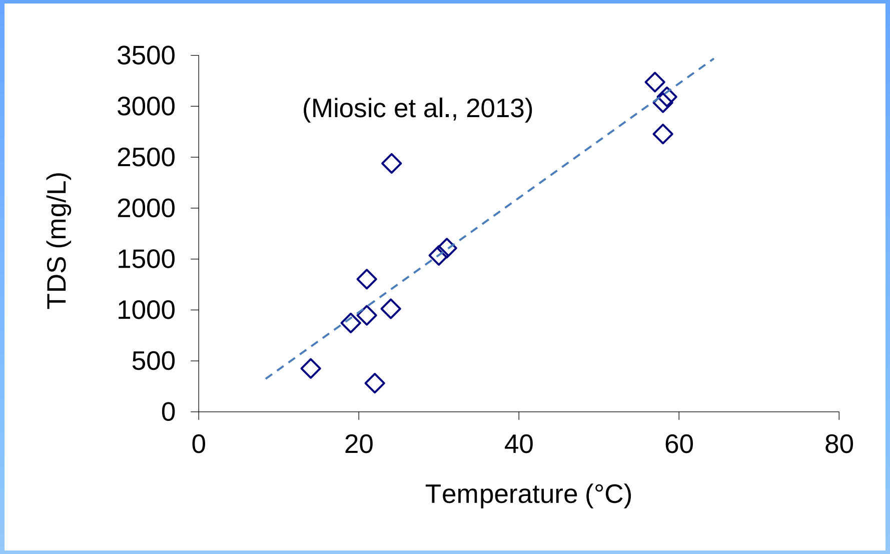
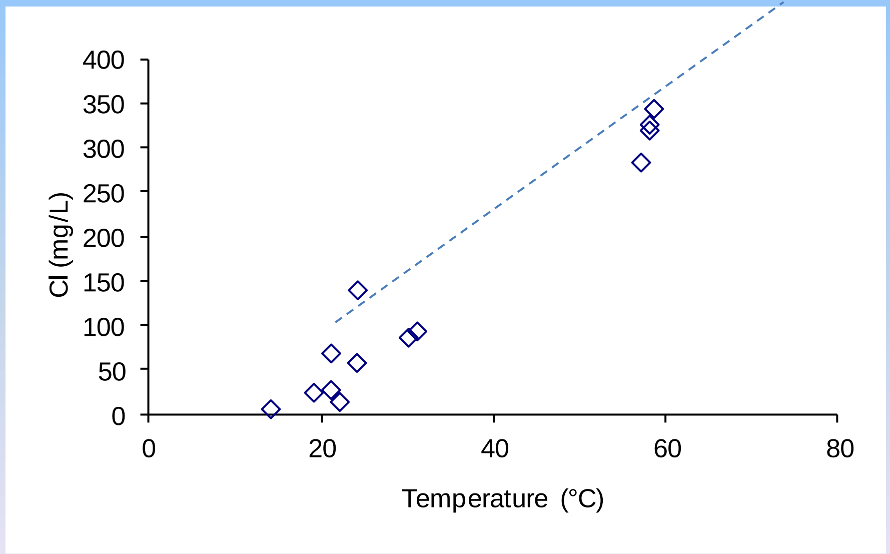
the ***Na-HCO_3 signature reflects long residence times*** of waters in deep environments

These thermal reservoirs are of particular interest

Temperature

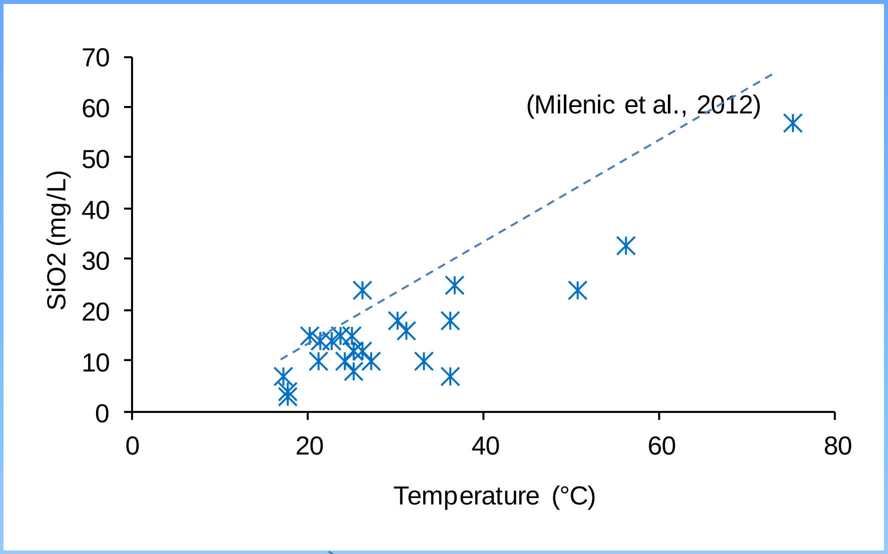


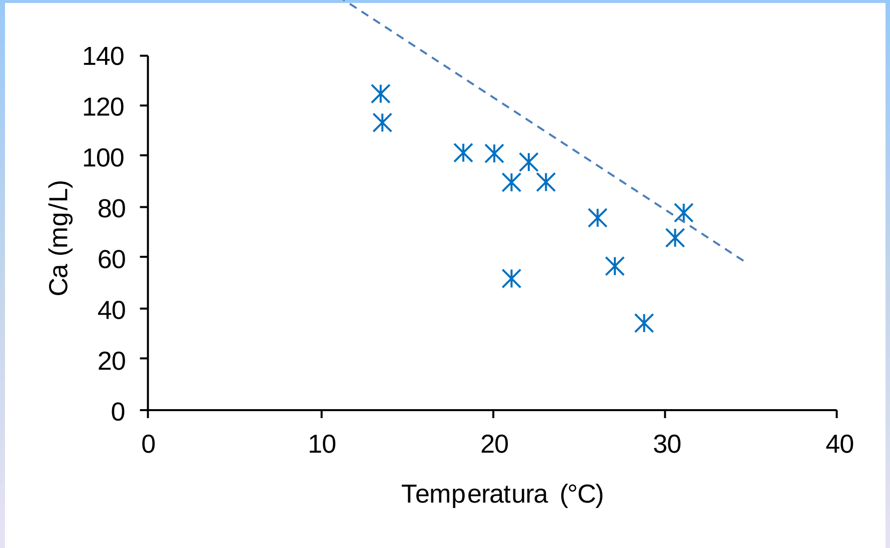


Bosnia

the trends of increasing temperature with increasing salinity and chloride content suggest, at least in some cases, the role of a high-thermal component of marine origin

Temperature



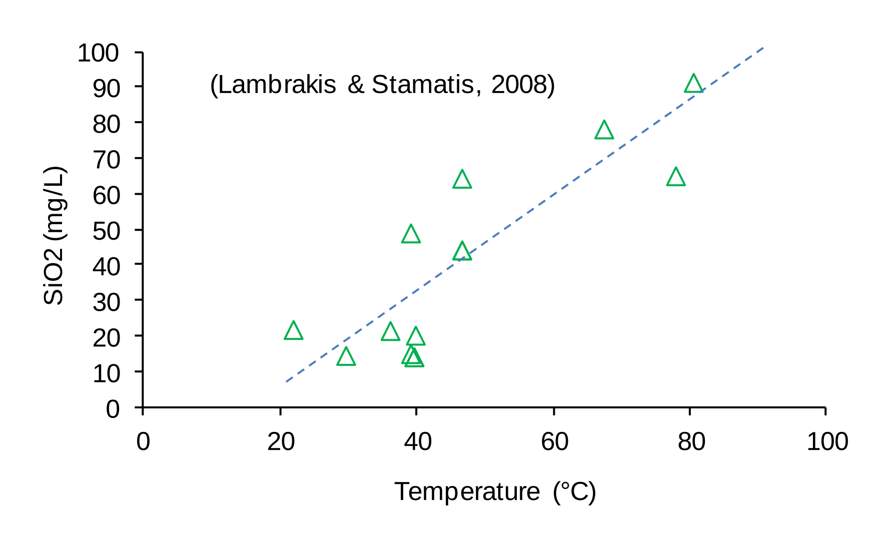


Serbia

Despite some scatter, the trend of increasing temperature with increasing silica likely indicate the role of high-thermal components related to silicate dissolution.

The pattern of decreasing calcium with increasing temperature could reflect the saturation state of carbonates, yielding cement precipitation

Temperature



Greece

Also in this case, some of the waters likely reflect the role of high-thermal, deep components related to silicate dissolution.

Trends of decreasing calcite and dolomite saturation states with decreasing temperature are also observed, indicating the role of CO_2-mediate carbonate equilibria

- ✓A variety of hydrofacies characterize the active geothermal manifestations used for thermal balneology in the Peri-Adriatic region

- ✓Waters have both a meteoric origin or maintain a marine signature, likely attributable to modern or to remnants of ancient seawater. Isotopic studies would help to clarify this point

- ✓Some of the waters are diagenetically modified by long-lasting interactions with the aquifer lithologies, suggesting high residence times and/or slow flowpaths. In particular, the interactions with low-solubility silicate minerals is likely responsible for the particular Na-HCO_3 signature of the thermal, deeper reservoirs. These waters would deserve further studies.

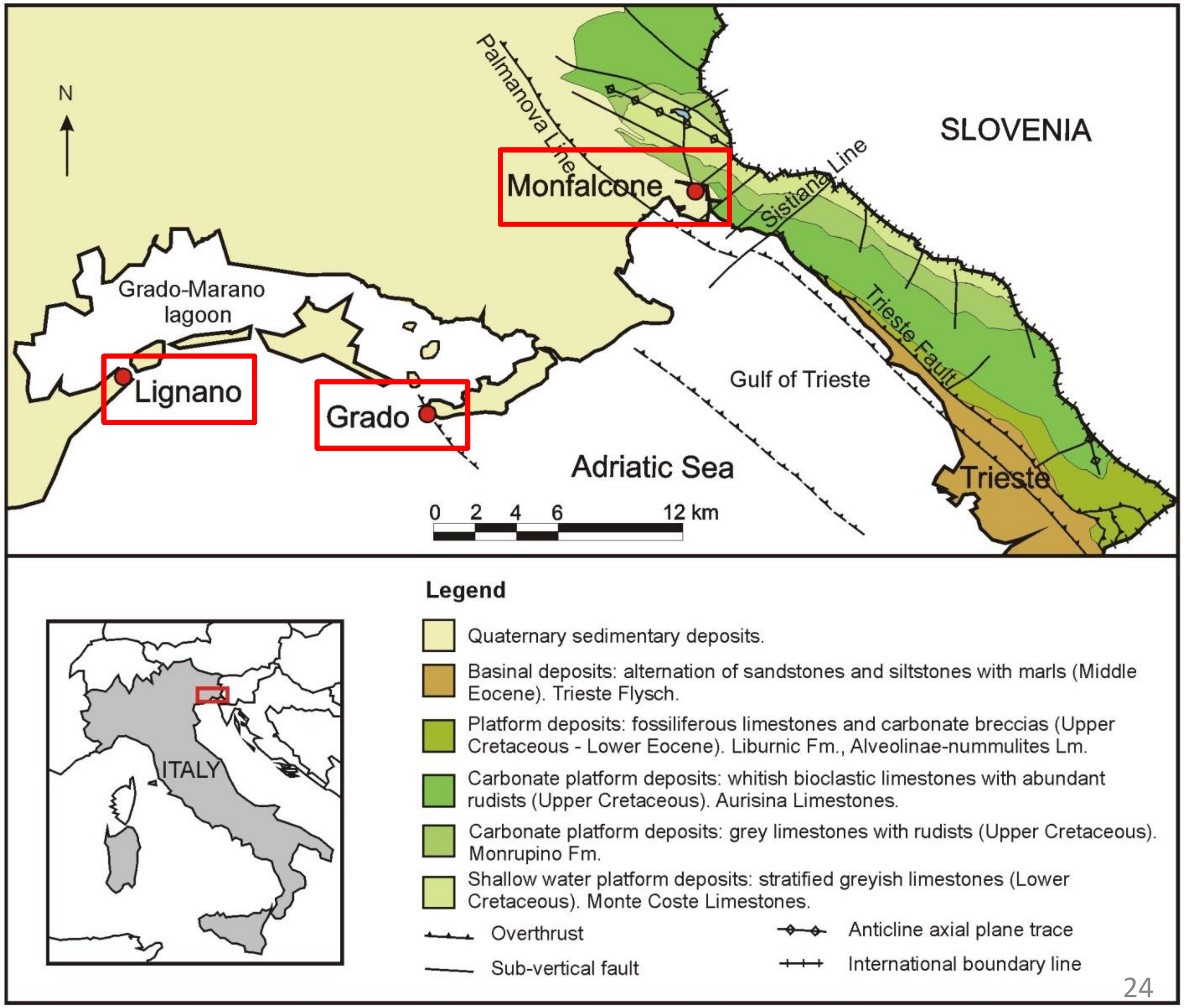
- ✓For these waters, long-term abstraction should be carefully planned

- ✓In some cases, mixing of waters with different geochemical signature occurs

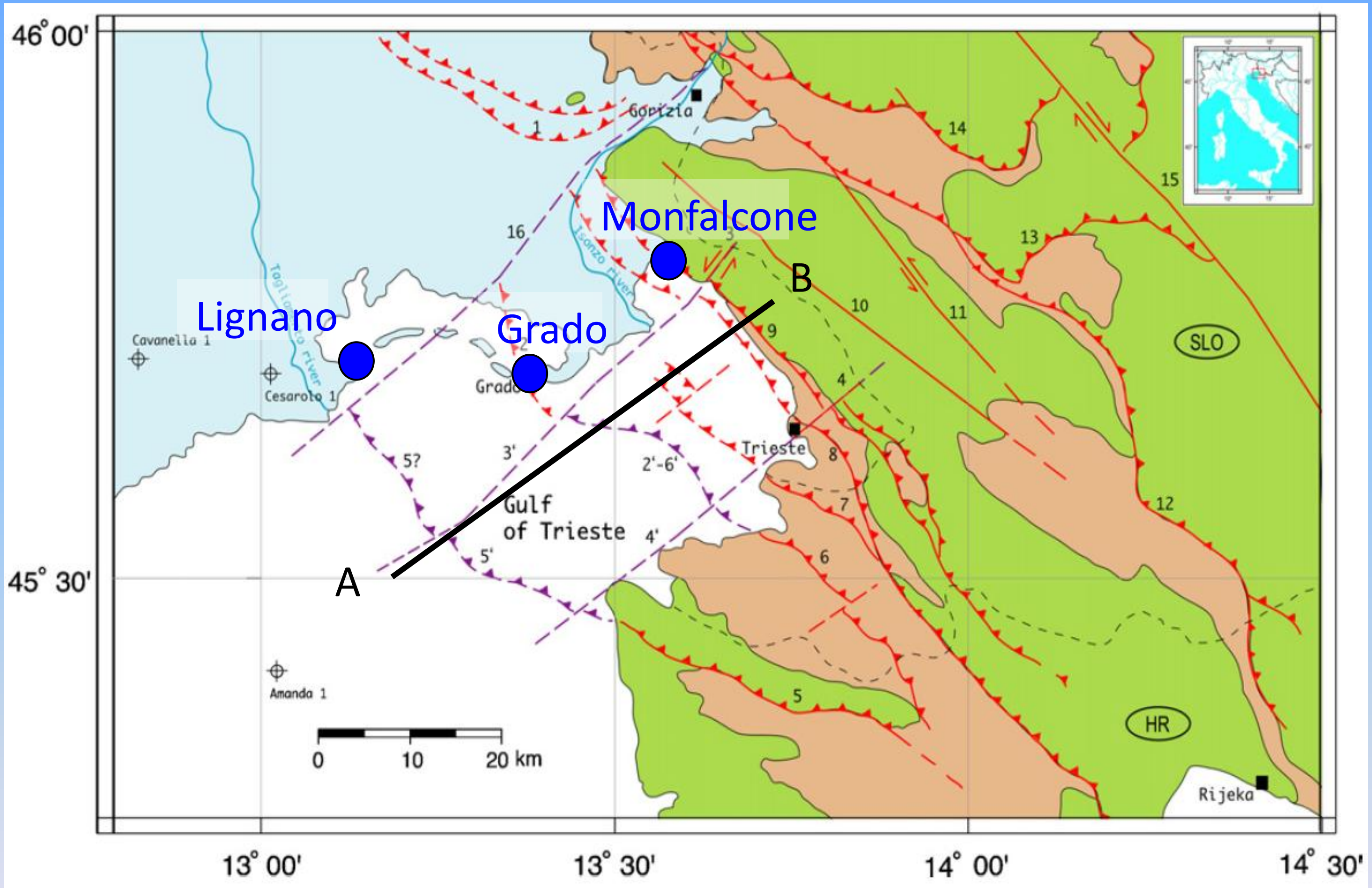
The Monfalcone (Grado – Lignano) thermal waters in the coastal area of the Friuli Plain (NE-Italy): a case history

Sites of study

Monfalcone: natural springs (34-40 °C)
Grado: Grado-1 well (1100 m depth; 43 °C)
Lignano: SIL well (≈2000 m depth; 53 °C)



Geological framework of the Trieste Gulf



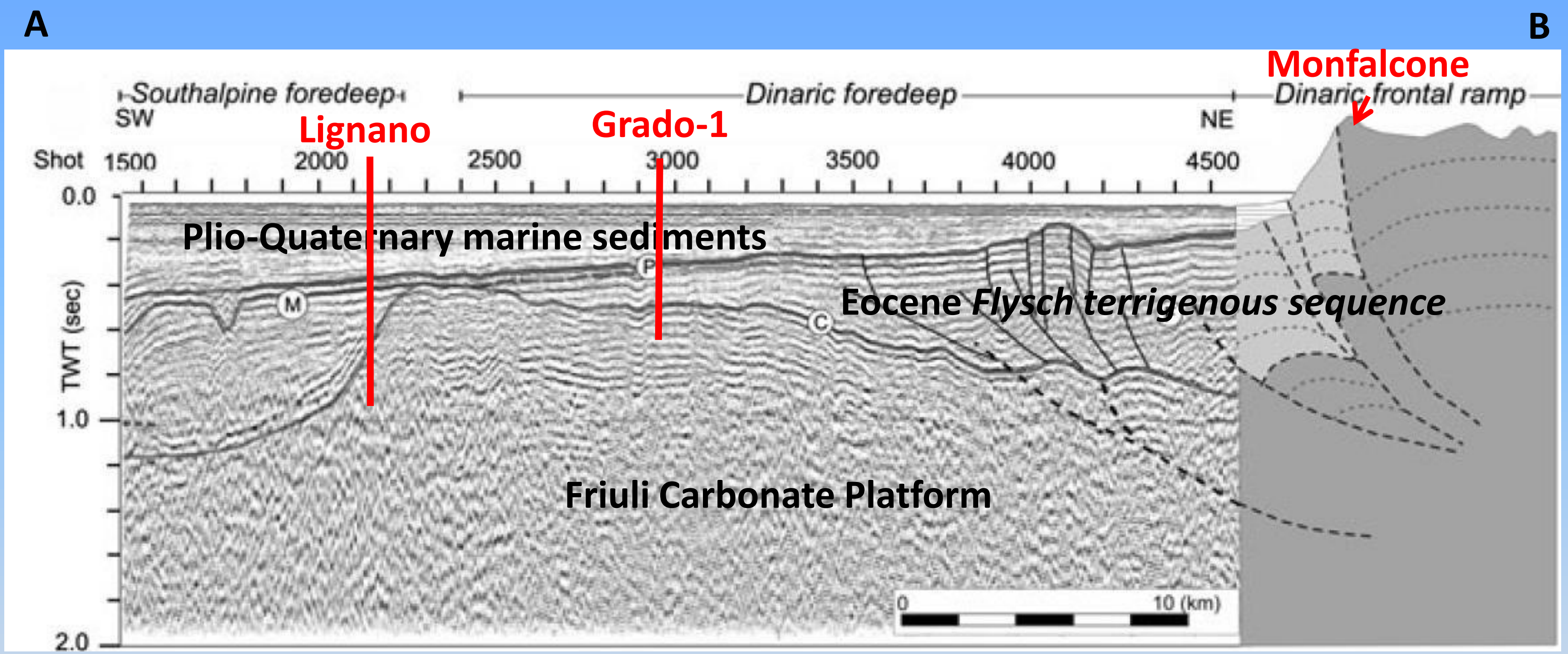
Mesozoic-Cenozoic carbonate Units

Paleogene Terrigenous Units

Quaternary alluvial sediments

After Carulli (2011) J. Geodyn. 51, 156-165

Multichannel seismic profile across the Trieste Gulf

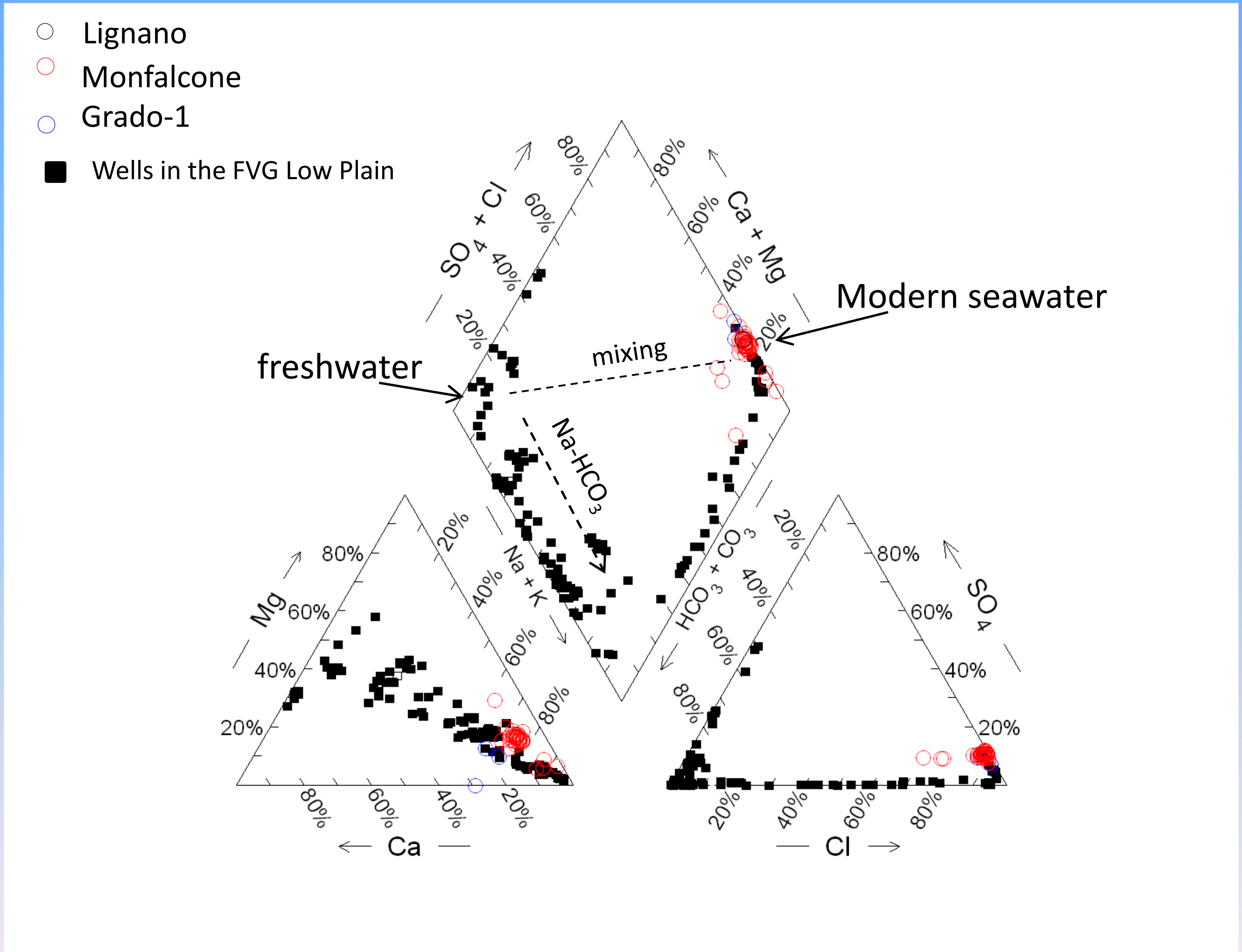


Busetti et al 2010

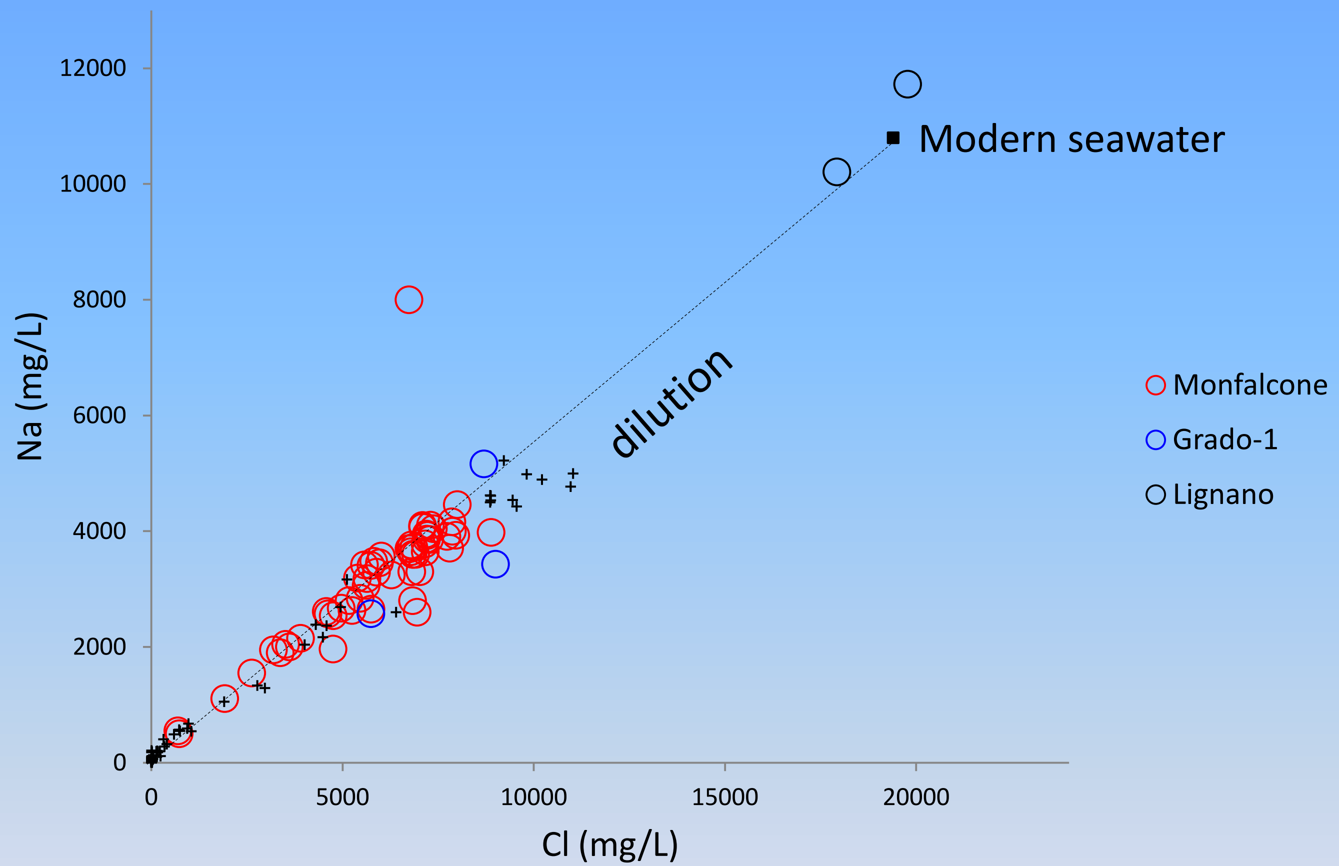
Hydrochemistry

The Monfalcone, Grado-1 and Lignano deep waters have all the chemical signature like modern seawater

NOTE
Some of the waters from geothermal wells in the FGV Low Plain are of the Na-HCO_3 type



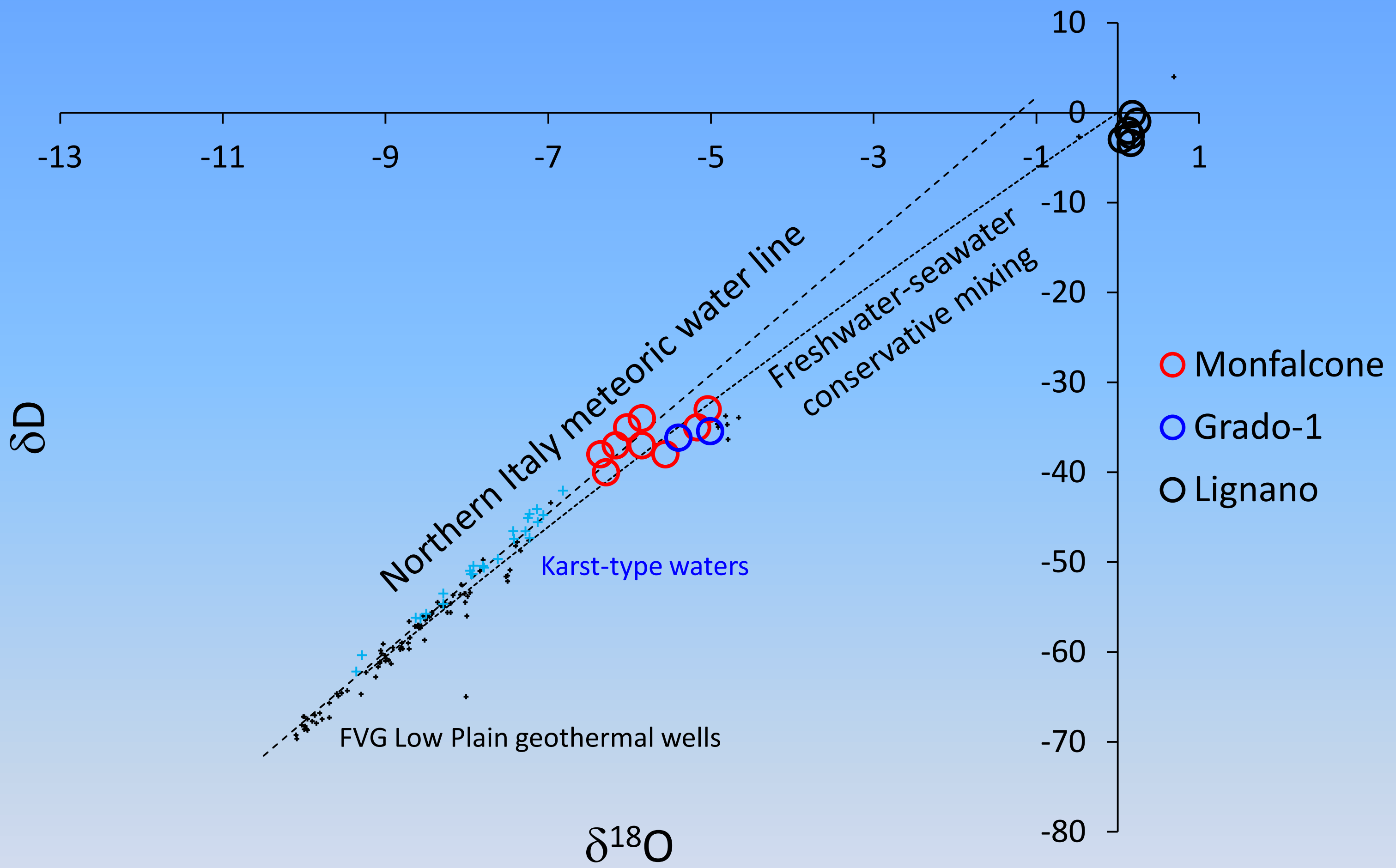
The marine signature



- ✓Waters from the Lignano well are the most representative of the marine end-member
- ✓Dilution processes are active at the Monfalcone springs and Grado-1 well to a lower extent

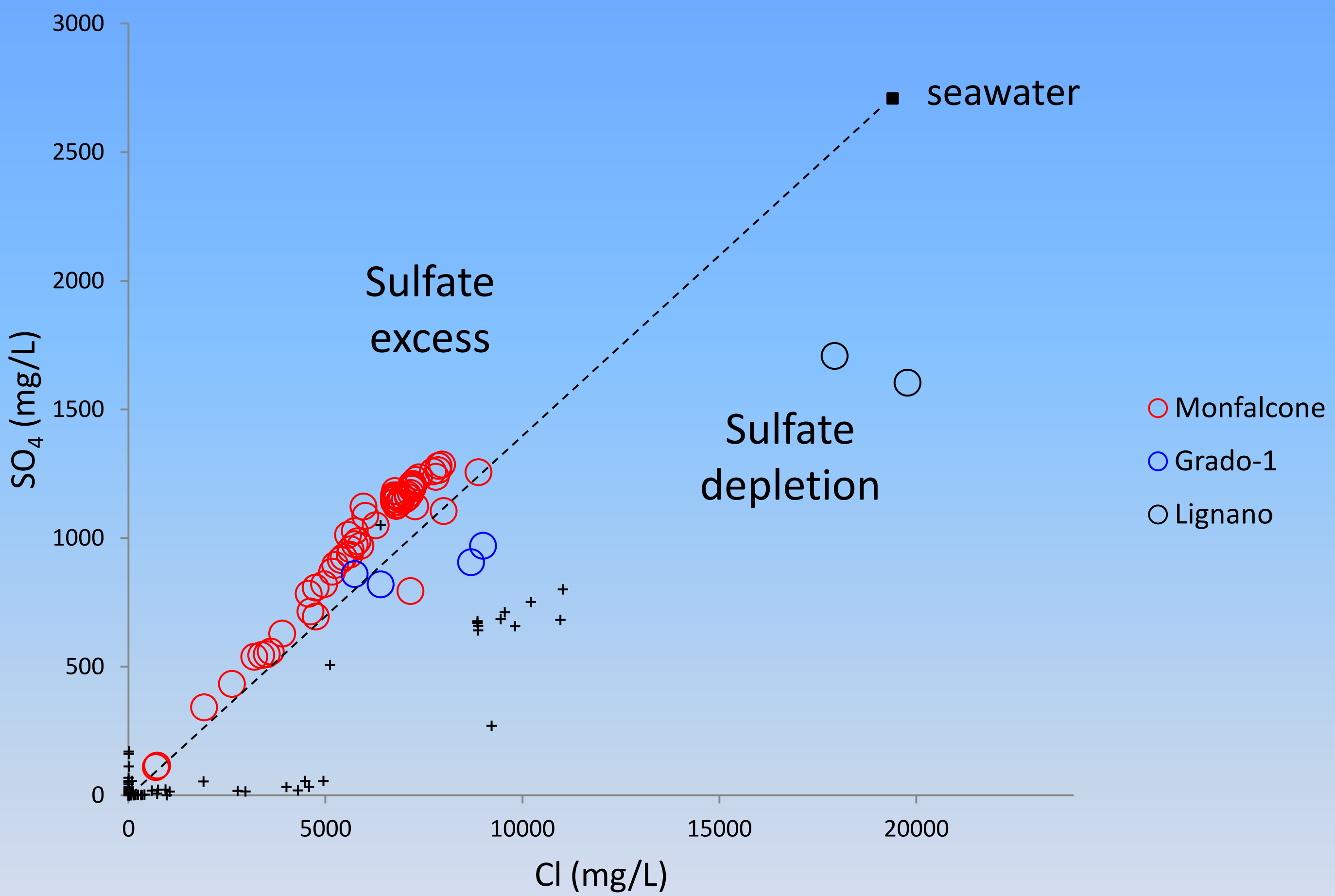
- ✓A marine component also contributes to waters from geothermal wells in the FVG Plain (crosses)

Dilution processes and origin of non-marine component



The freshwater component might be represented by karst-type groundwaters

Evolutionary patterns of the marine component

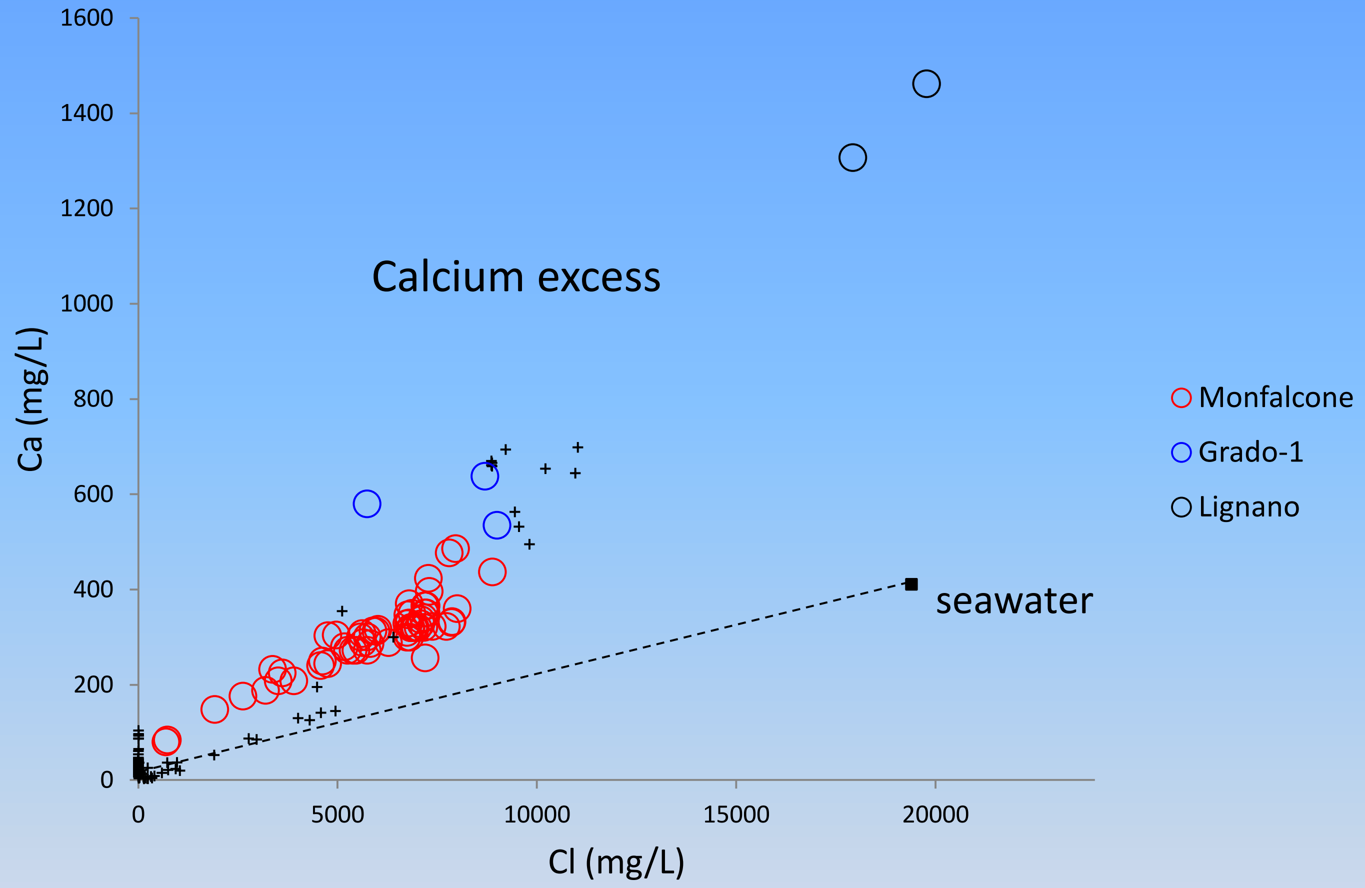


Sulfate excess and mixing corrosion

$$H_2S + 2O_2 = H_2SO_4$$

$$H_2SO_4 + 2CaCO_3 = 2Ca^{2+} + SO_4^{2-} + 2HCO_3^-$$

$$H_2S + 2O_2 + 2CaCO_3 = 2Ca^{2+} + SO_4^{2-} + 2HCO_3^-$$



Diagenetic reactions of seawater with the hosting carbonates

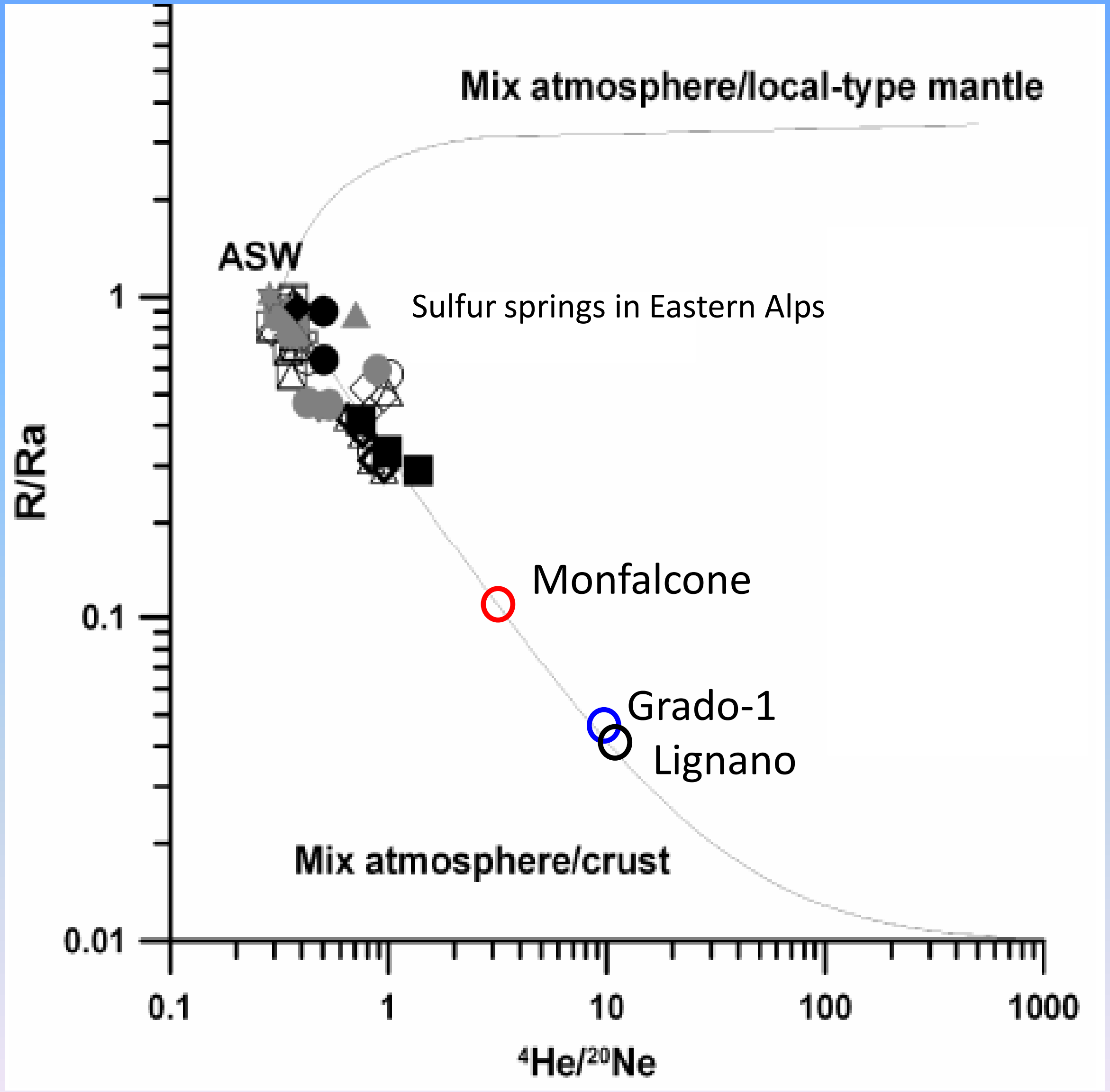
Crustal gas-water interactions

Samples deviate from the composition of air saturated water towards the admixing of crustal gases.

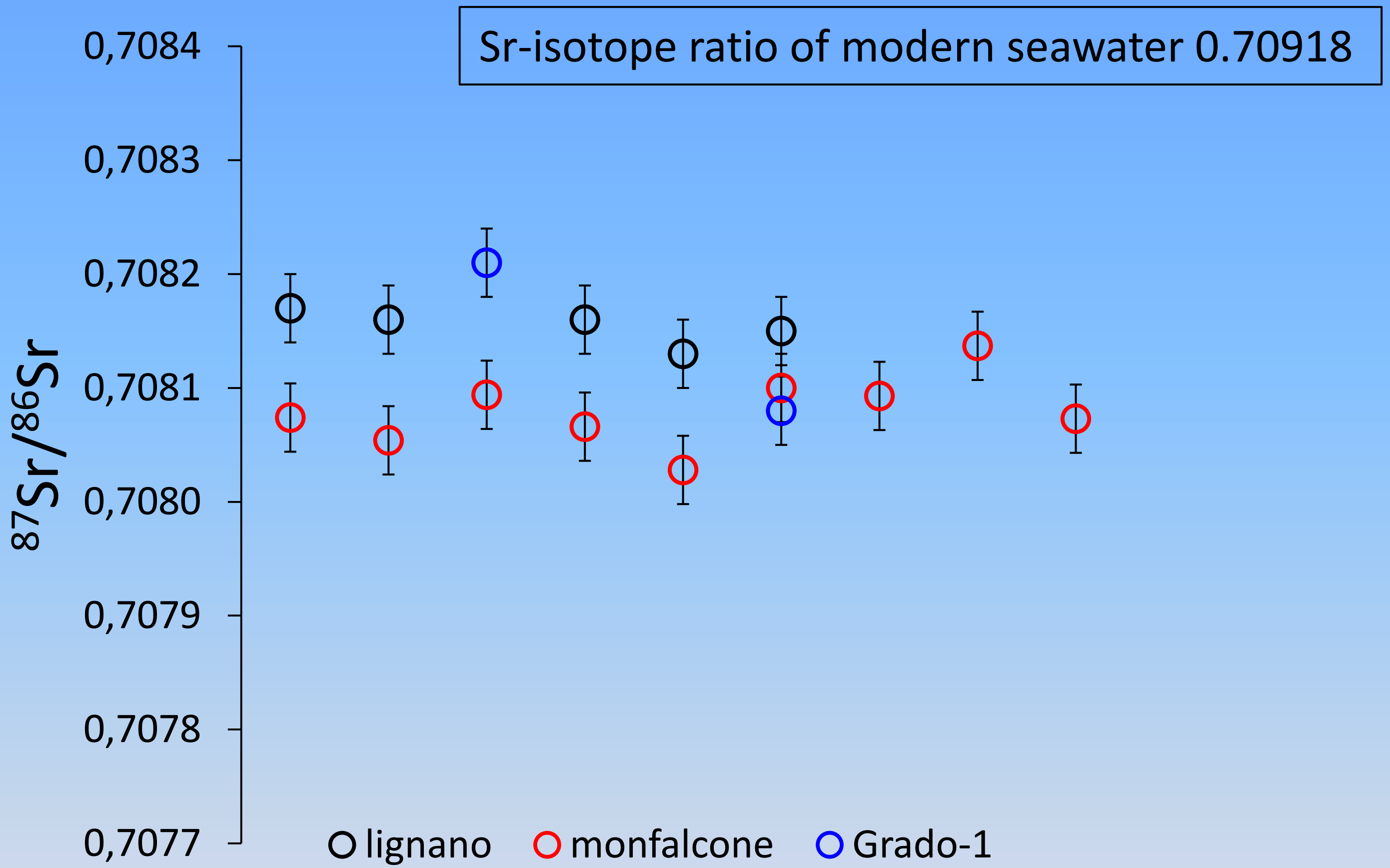
This has implication on the volume of the thermal reservoir, since the original atmospheric signature has been replaced by crustal components:

⇩

LOW WATER VOLUME OR DISCONTINUOUS WATER BODIES (?)



Modern or ancient seawater?



The thermal waters do not have the isotopic signature of present-day seawater !

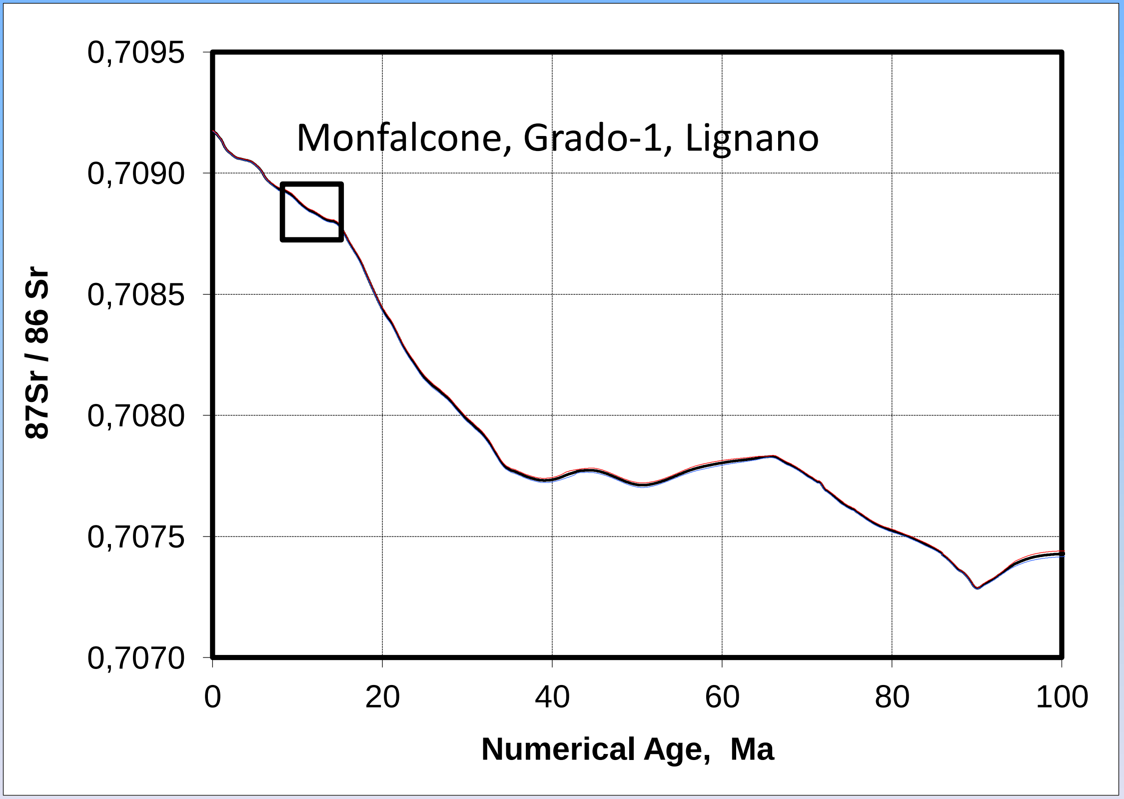
A possible common marine source for Monfalcone, Grado-1 and Lignano

Deconvolving the diagenetic chemical changes and "age" of the thermal component

Mass-balance equation

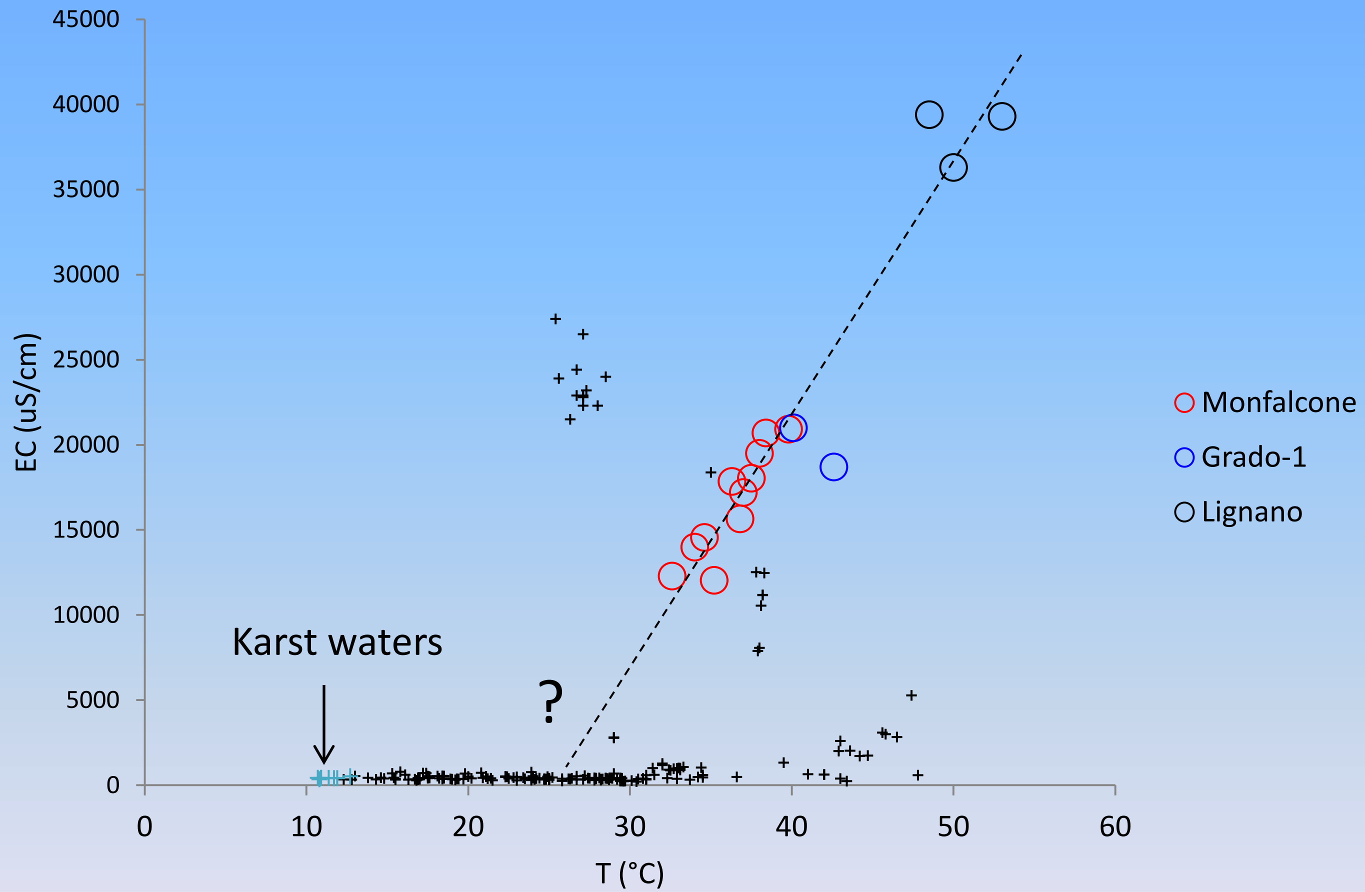
$$^{87}Sr/^{86}Sr_{reservoir} = {}^{87}Sr/^{86}Sr_{measured}\left(1+\frac{[Sr]_{excess}}{[Sr]_{reservoir}}\right) - {}^{87}Sr/^{86}Sr_{excess}\frac{[Sr]_{excess}}{[Sr]_{reservoir}}$$

Sr isotopic changes in seawater through time



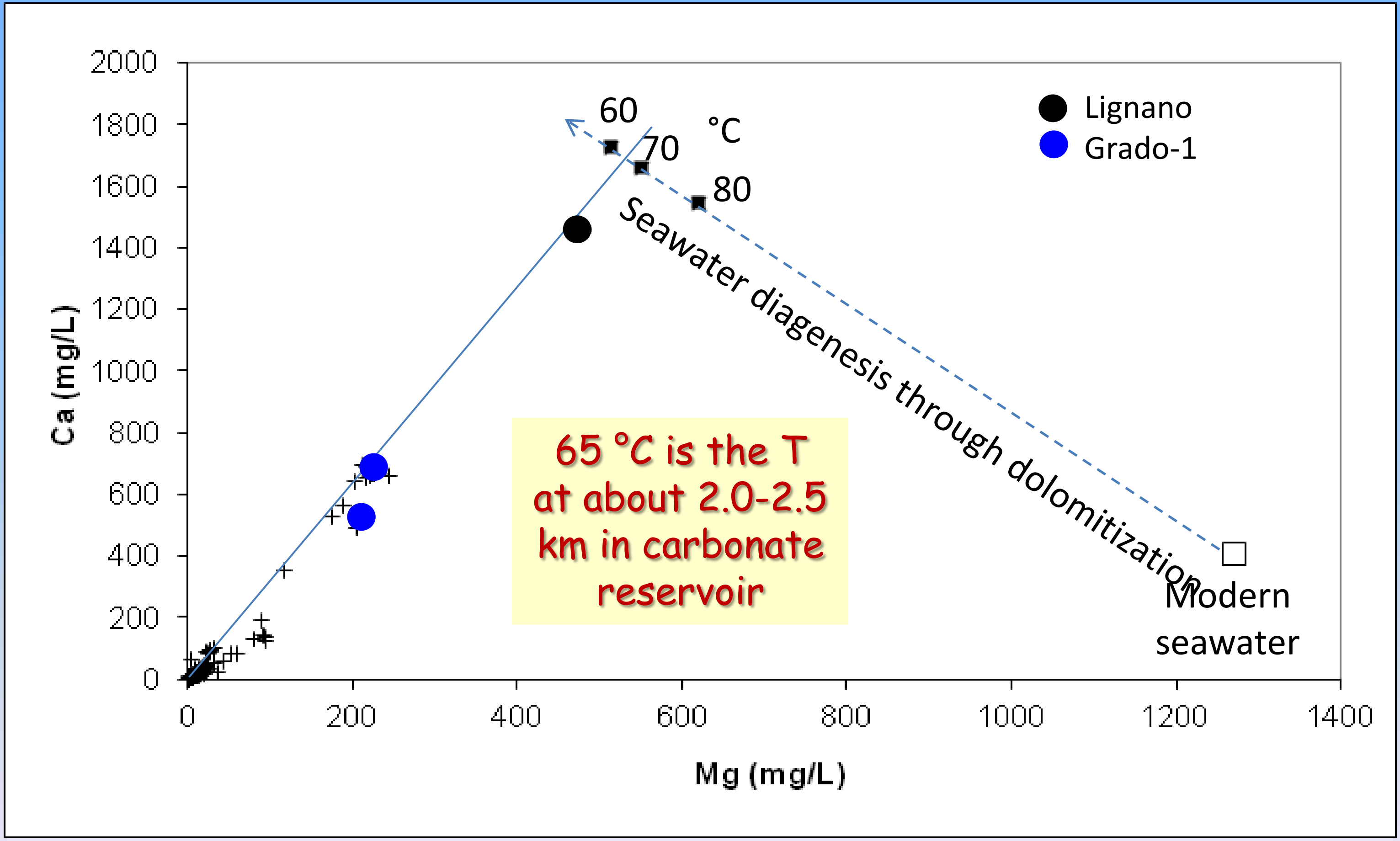
the marine reservoir would be represented by ancient seawaters "dated " at Miocene

Temperature



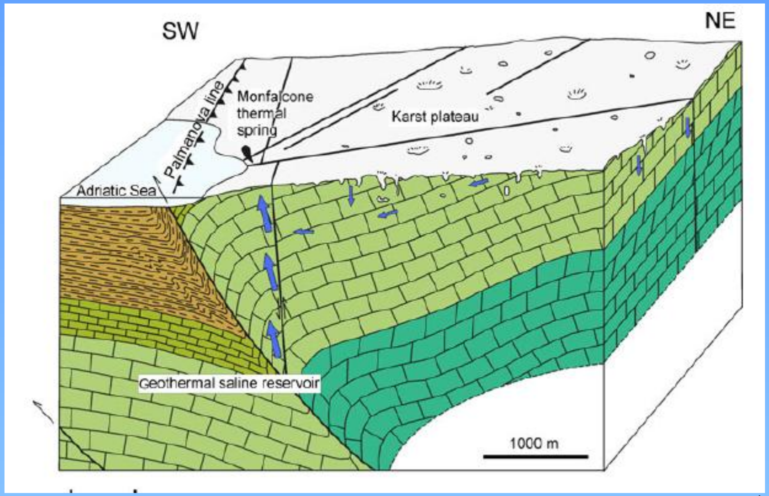
The thermal reservoir is best represented by the saline ancient seawater
Cooling by dilution is observed; however the karst-type waters of superficial aquifers are unsuitable as cold term

Deconvolution of the diagenetic processes of ancient seawater in the deep carbonate reservoir to estimate temperature of the geothermal component

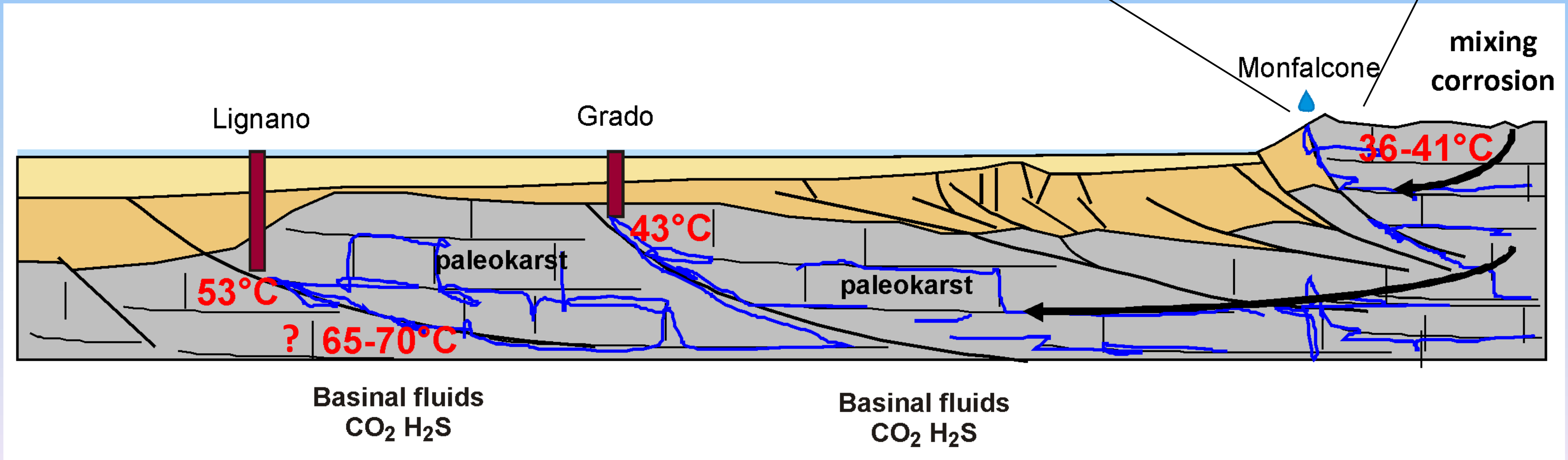


Concluding remarks

- Friuli thermal waters represent the ancient, diagenetically modified seawater of a low temperature geothermal system
- Deep saline reservoir might represent remnants of seawater entrapped in Mesozoic carbonates during the late Oligocene–Miocene sea transgression
- In some parts the deep thermal reservoir mixes and homogeneizes with colder kast(?)-type waters flowing in, through a deep and long-lasting circuit
- Thermal reservoir might be composed by discrete aquifers, or might not be widely extended
- Hydrothermal diagenesis including dolomite cementation might change the water flow dynamics at depth



Generalized geothermal model




TRIESTE
GRADO
VENEZIA
Thank you for your attention
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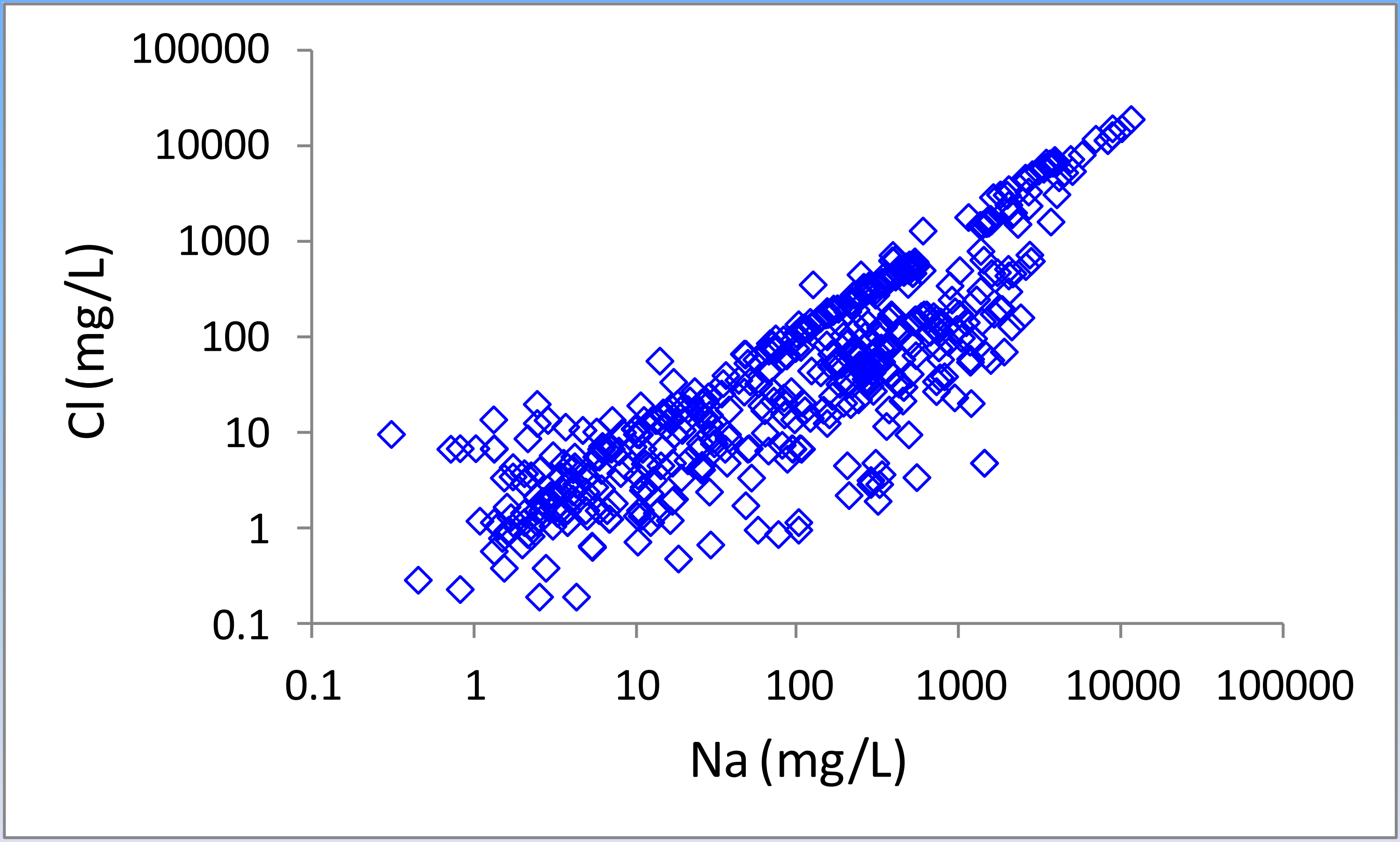
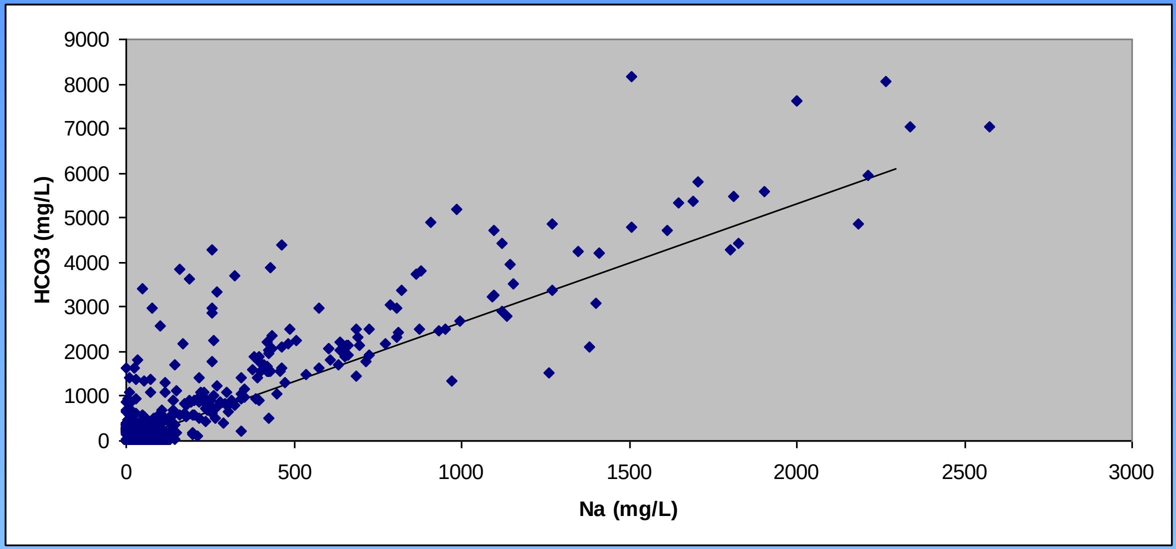
Some of the waters show a Na vs. Cl linear correlation, suggesting the role of seawater or dissolution of marine salts



On this ground, the contribution of the marine component can be removed



After correction a more clear correlation in observed, following the equimolar distribution of Na and HCO_3 ions (solid line)

This is consistent with the (incongruent) silicate dissolution to generate the Na-HCO_3 waters:

$$2NaAlSi_3O_8 + 3H_2O + 2CO_2 \Rightarrow \boxed{2Na^+} + \boxed{2HCO_3^-} + Al_2Si_2O_5(OH)_4 + 4SiO_2$$

as an example