



WATER-ROCK INTERACTION and MINERAL EXTRACTION

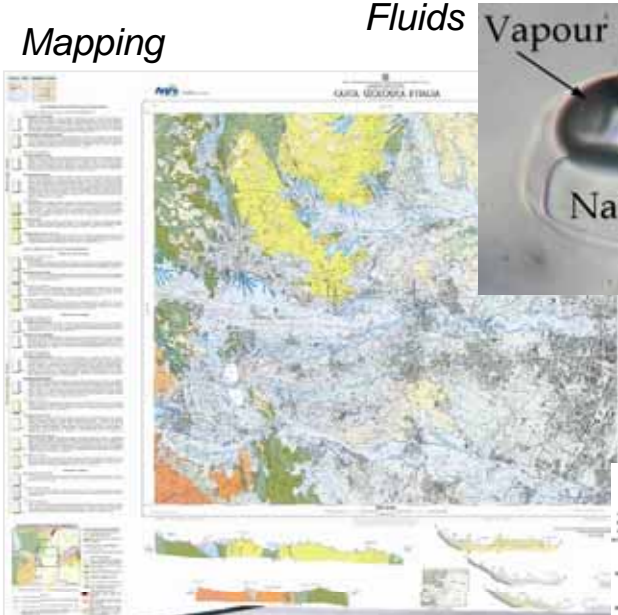
Andrea Dini

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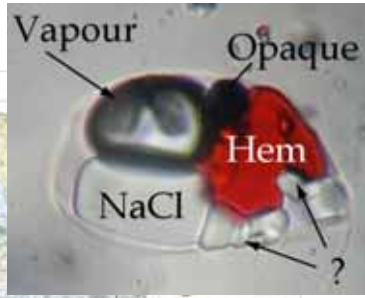


IGG-CNR: interdisciplinary approach

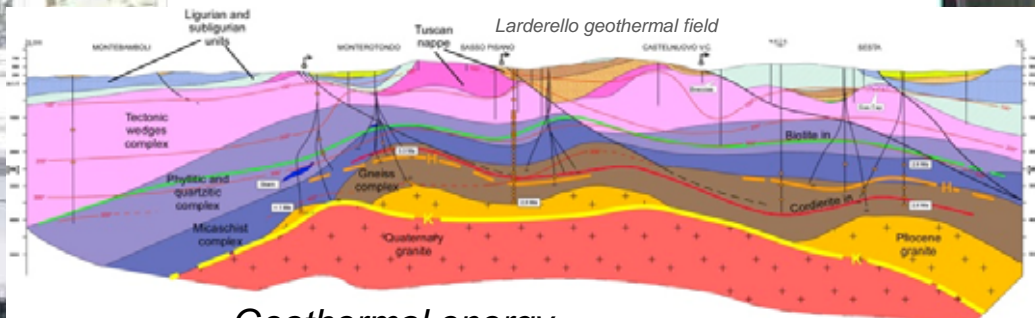
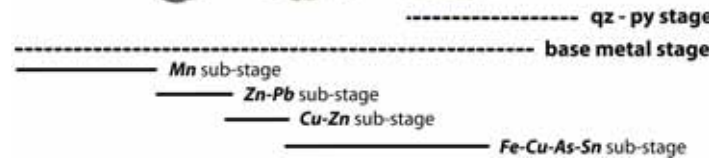
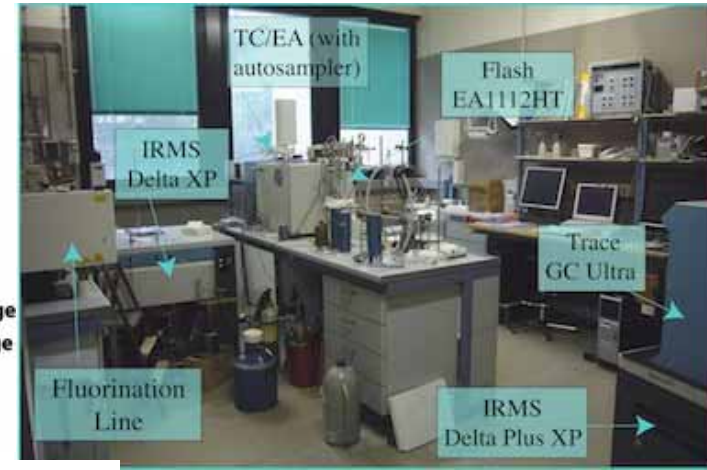
Stable isotopes



Fluids



Ore deposits



Geology



Geothermal energy

Geophysics
Modelling

... and much more

Radiogenic isotopes

Purpose of the seminar

First part - Water-rock interaction and hydrothermal alteration

Generalities, applications and limitations

Case study from Larderello geothermal field

Second part - Mobilization of critical elements in geothermal fluids

Generalities, energy transition, mineral extraction

Case study from Latium geothermal fields

Q: What is the difference between the two rocks?



A: Hydrothermal Alteration

“FRESH” ROCK

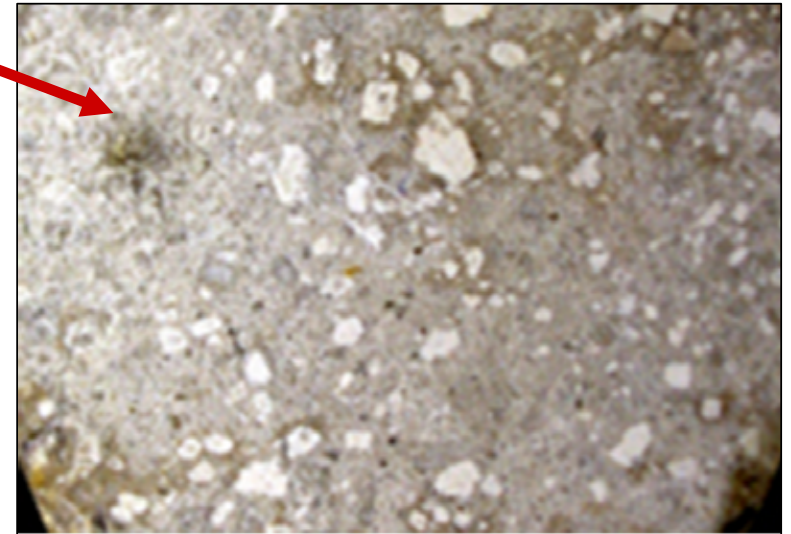


Mineral and
textural changes

WATER-ROCK INTERACTION

FLUID

Exchange of
chemical
components



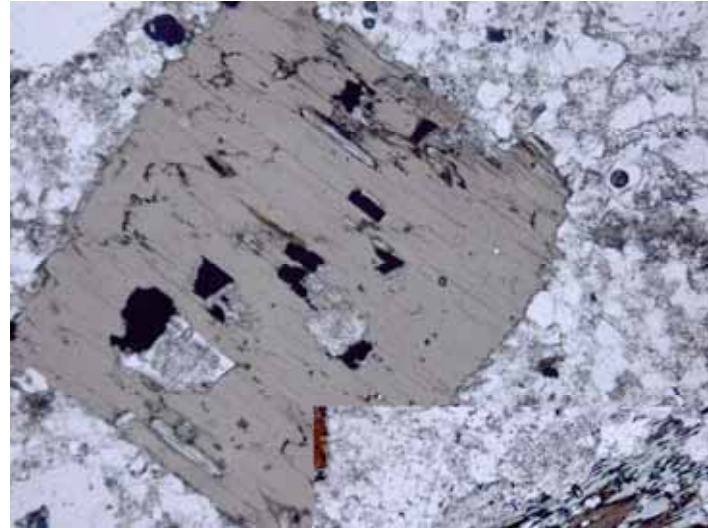
ALTERED ROCK

Hydrothermal alteration

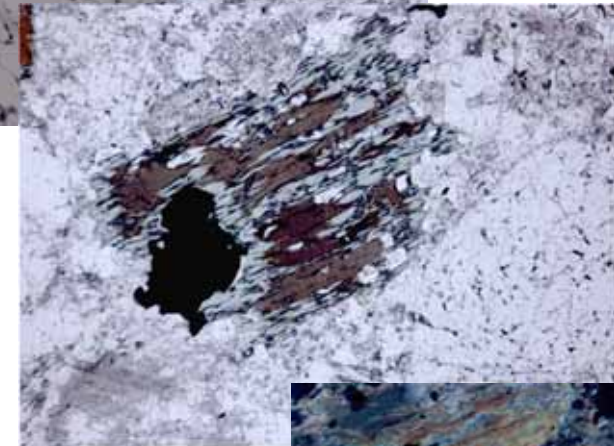
conversion of the original mineral association into a new mineral association stable in the new T-P-pH conditions, and in "equilibrium" with the hydrothermal fluids.

By definition: hydrothermal alteration is an *epigenetic* feature!

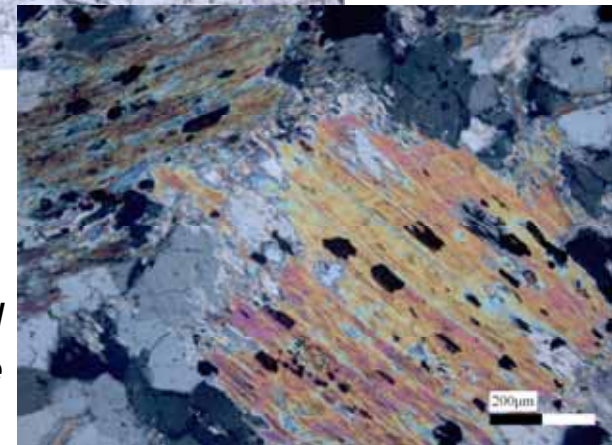
Original rock textures and structures can be slightly to completely modified by alteration processes: recognizing neo-formed alteration minerals and the original minerals is crucial for correct interpretation of alteration processes.



*magmatic
biotite*

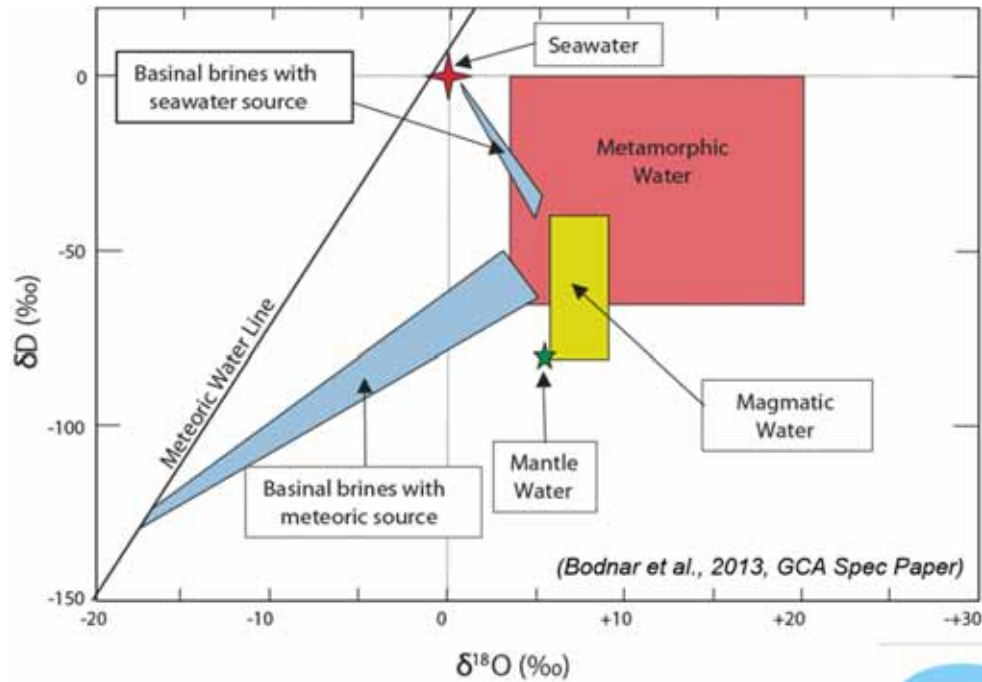


*chloritized
biotite*



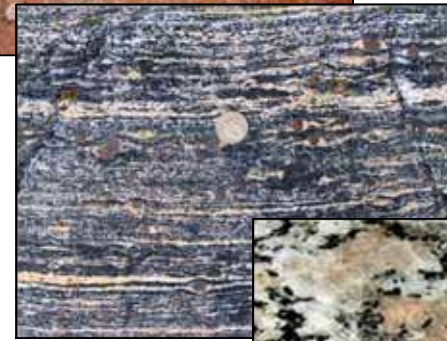
*sericitized
biotite*

Many type of “waters”, and rocks



Sedimentary

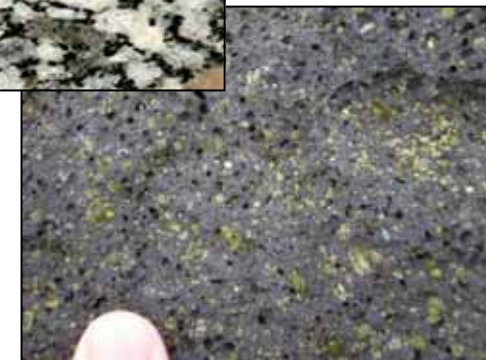
ROCKS



Metamorphic

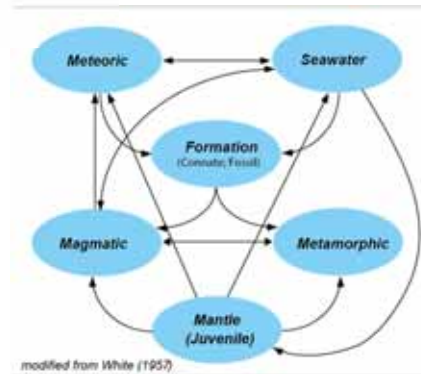


Magmatic



FLUIDS

- Magmatic
- Metamorphic
- Surface-derived (ex. meteoric, seawater)
- Formation (connate) waters; basinal brines



The parameters controlling hydrothermal alteration

Rock

- Permeability (fractures, pores)
- Composition
- P-T conditions
- Active deformation

Fluids

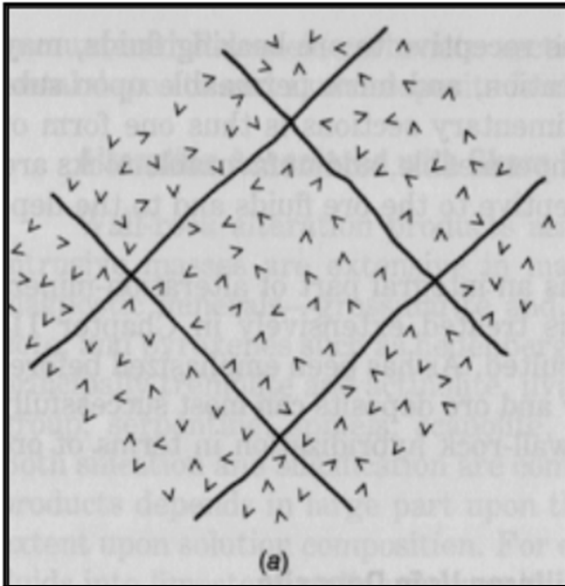
- Composition (original dissolved cations and anions)
- Initial P-T conditions

Reaction surfaces, Reactivity, Solubility

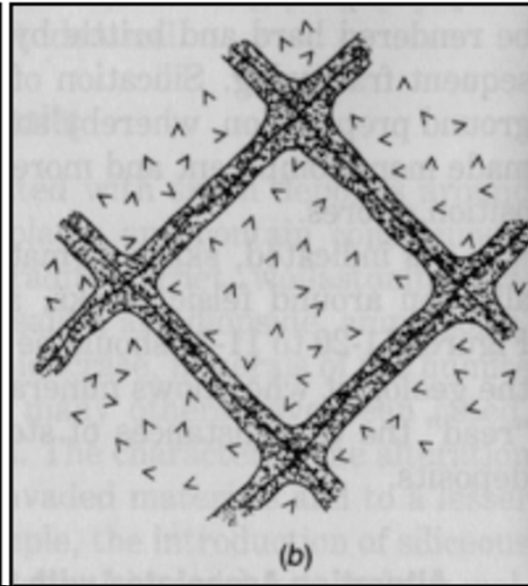
Open space vs. joints/boundaries

Infill vs. replacement

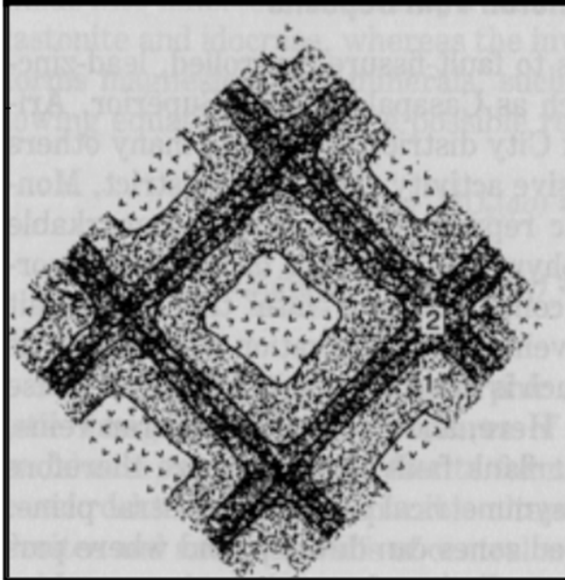
Fractured rock



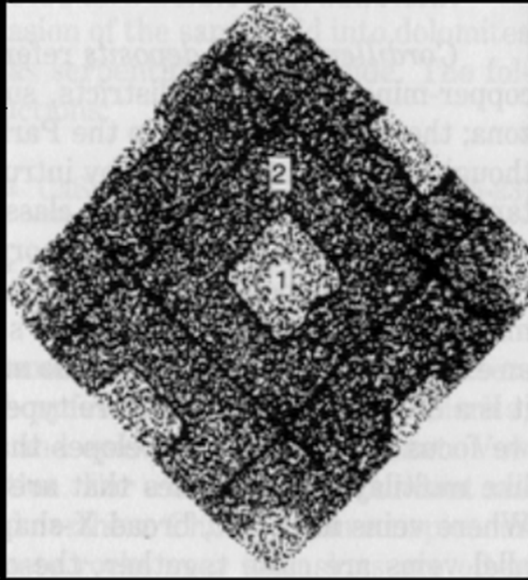
**Incipient, poorly
pervasive
alteration**

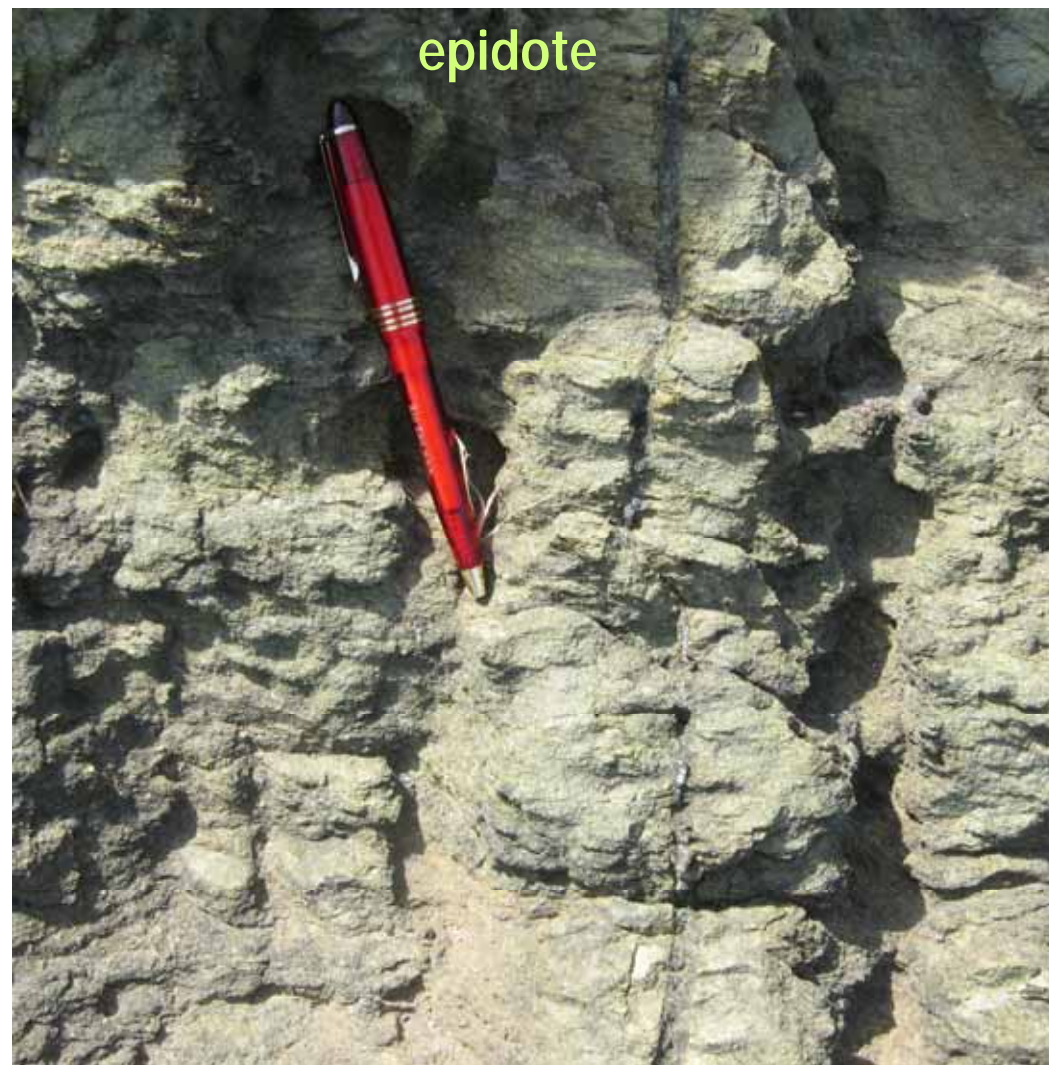
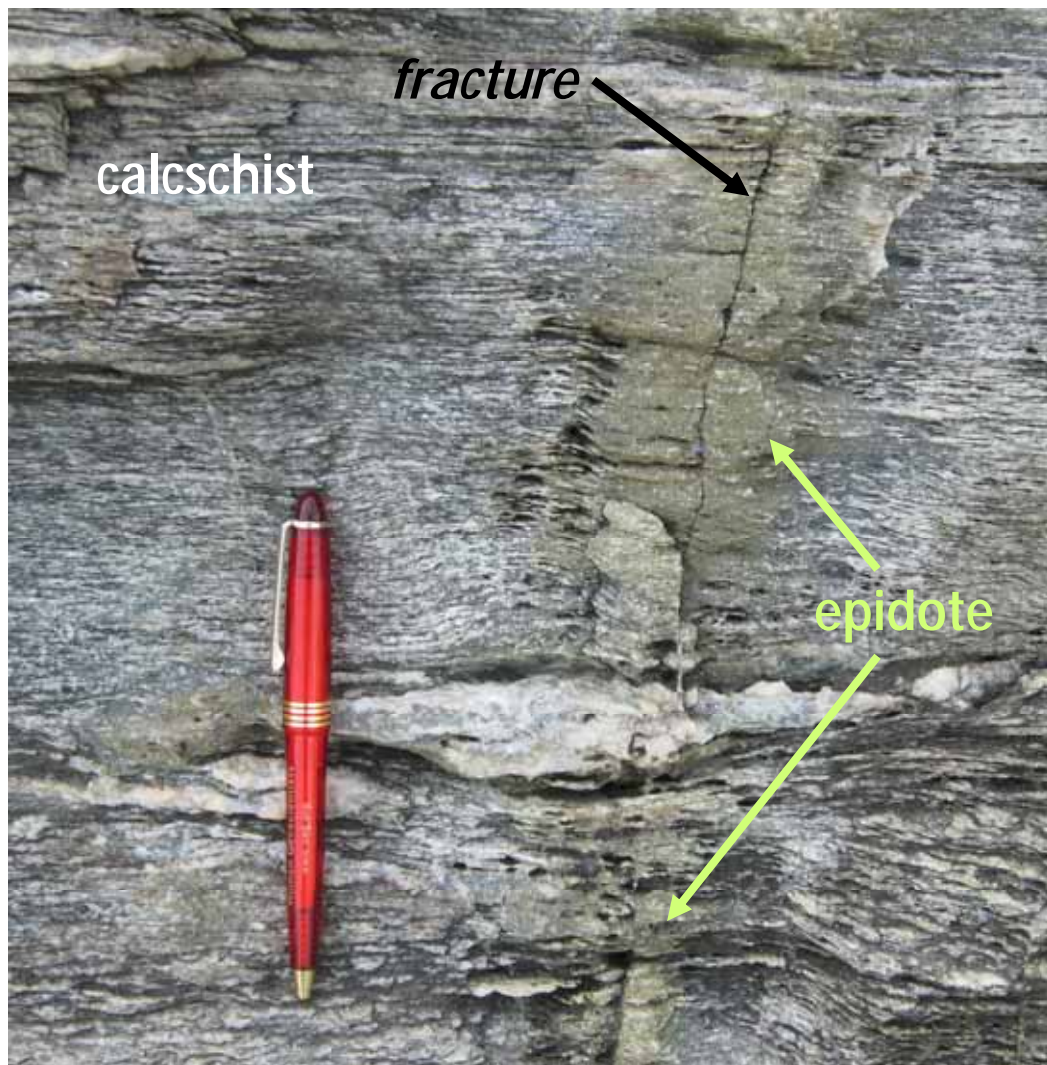


**Medium pervasive
alteration with relics
of original rock**



**Pervasive alteration
without relics
of original rock**





Epidote: $(\text{Ca}_2)(\text{Al}_2\text{Fe}^{3+})(\text{O},\text{OH})(\text{SiO}_4)(\text{Si}_2\text{O}_7)$

FLUID/ROCK RATIO IS VERY IMPORTANT ...

The fluid/rock ratio during the hydrothermal alteration of a rock mass is controlled by the permeability, the rate of fluid flow and the time of reaction.

The instantaneous fluid/rock ratio is generally controlled by the architecture of permeability: e.g. for a certain volume of rock, it is higher in case of a pervasive network of fractures (larger total reaction surface), and lower in case of a single large fracture (smaller total reaction surface).

For a certain network of fractures, the volume of reacting rock may be increased by large rates of fluid flow. If the new hydrothermal assemblage does not seal the fracture, large rates of fluid flow can produce a very high, final, cumulative fluid/rock ratio.

For certain initial rock and fluid compositions, variable fluid/rock ratios can produce different hydrothermal alteration and different chemical modification of the "exhausted" hydrothermal fluid.

... BUT THE REACTIVITY OF THE ROCK TOO



Hedenbergite replacing marble starting from a network of fractures

Carbonatic rocks are extremely reactive with HT magmatic fluids exsolved by granite intrusions

“Mature” hedenbergite-ilvaite-epidote skarn body replacing marble



Geochemical effects of Hydrothermal alteration

The geochemical characters of the rocks can be totally changed: METASOMATISM

The rocks can loose/gain/exchange part of their cations: HYDROLISIS

A significant amount of water can be added to the rocks: HYDRATION

Metasomatism



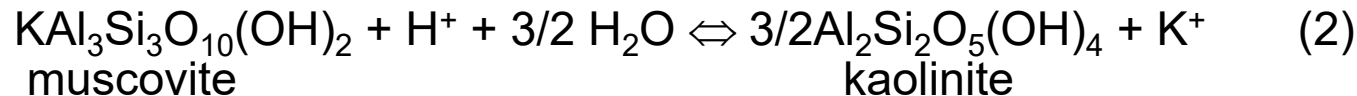
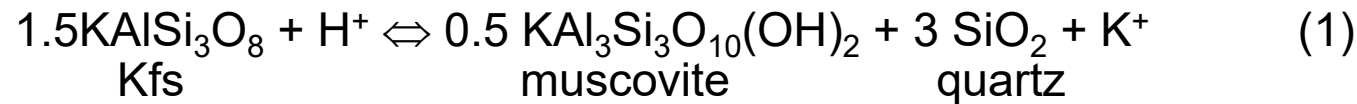
ilvaite

Hedenbergite + epidote

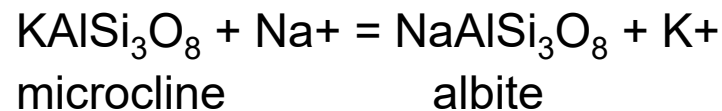
Hydrolysis

- Don't mix up with «hydration »! It occurs at low pH conditions (high H⁺ activity)

- Stability of feldspars, micas and clay minerals is by the *hydrolysis* which is a phenomenon, by which K⁺, Na⁺, Ca²⁺, Mg²⁺ and other cations are transferred from the mineral to the solution and H⁺ is fixed in the solid mineral phase. e.g.: stability of Kfs and micas at a given T (~300 ° C) is controlled by the following reactions:



During these reactions, an exchange of cations between the fluid and the mineral phase, is possible.



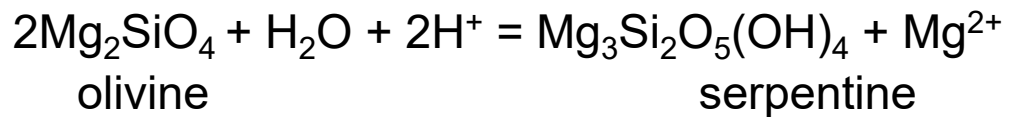
Hydration

Commonly, hydrolysis goes in parallel with hydration.

An example is the hydration of mantle peridotite by circulation of seawater at ocean spreading ridges with the formation of the rock called serpentinite.

Olivine, the main constituent of peridotite, is transformed in serpentine minerals
Only addition of water to the rock.

Peridotite contains ZERO water. Serpentinites up to 14 weight % H₂O.

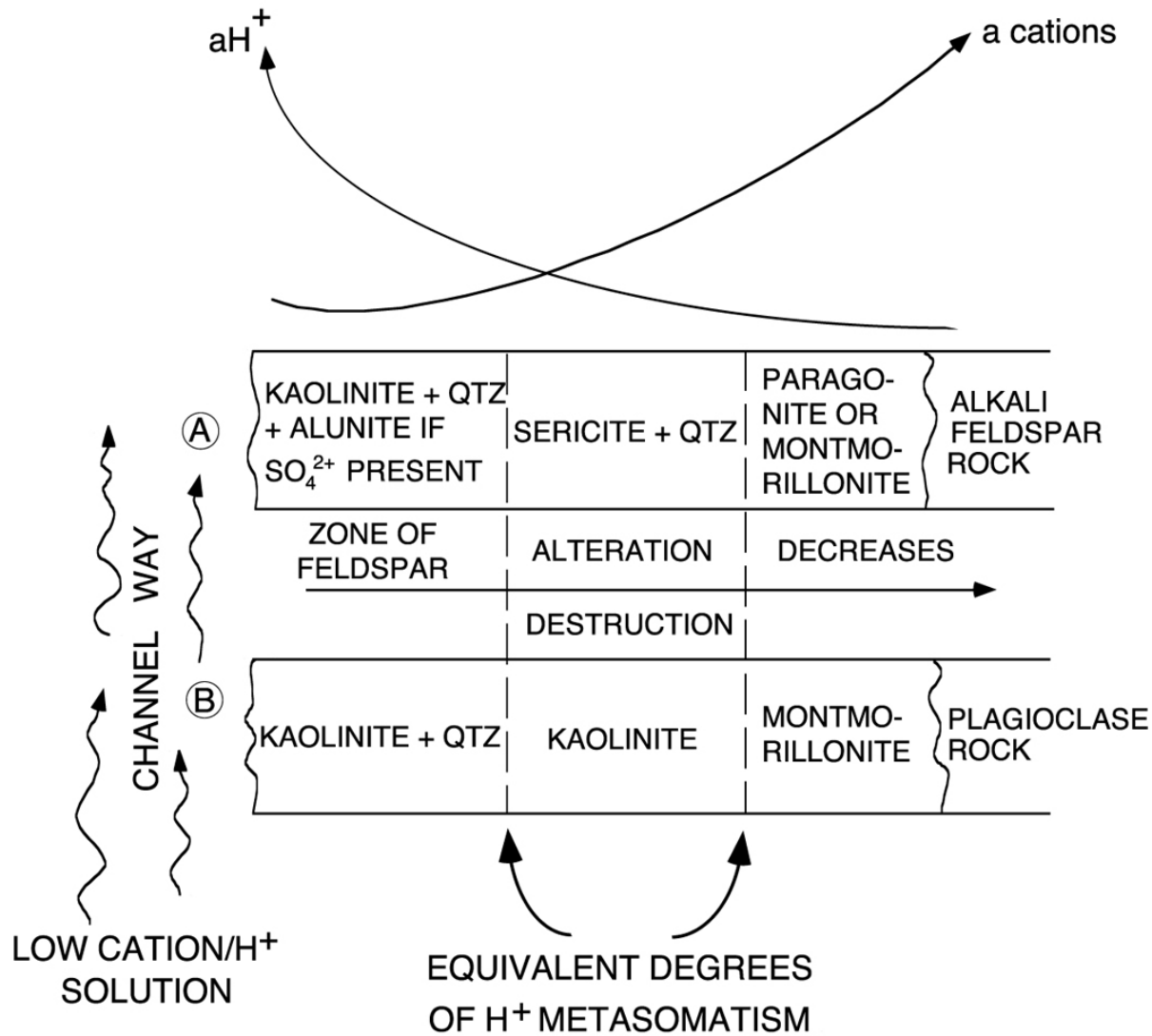


Serpentinite



Peridotite

The role of the rock mineralogy

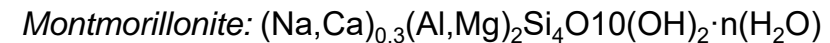


Schematic representation of hydrothermal alteration in rocks containing:

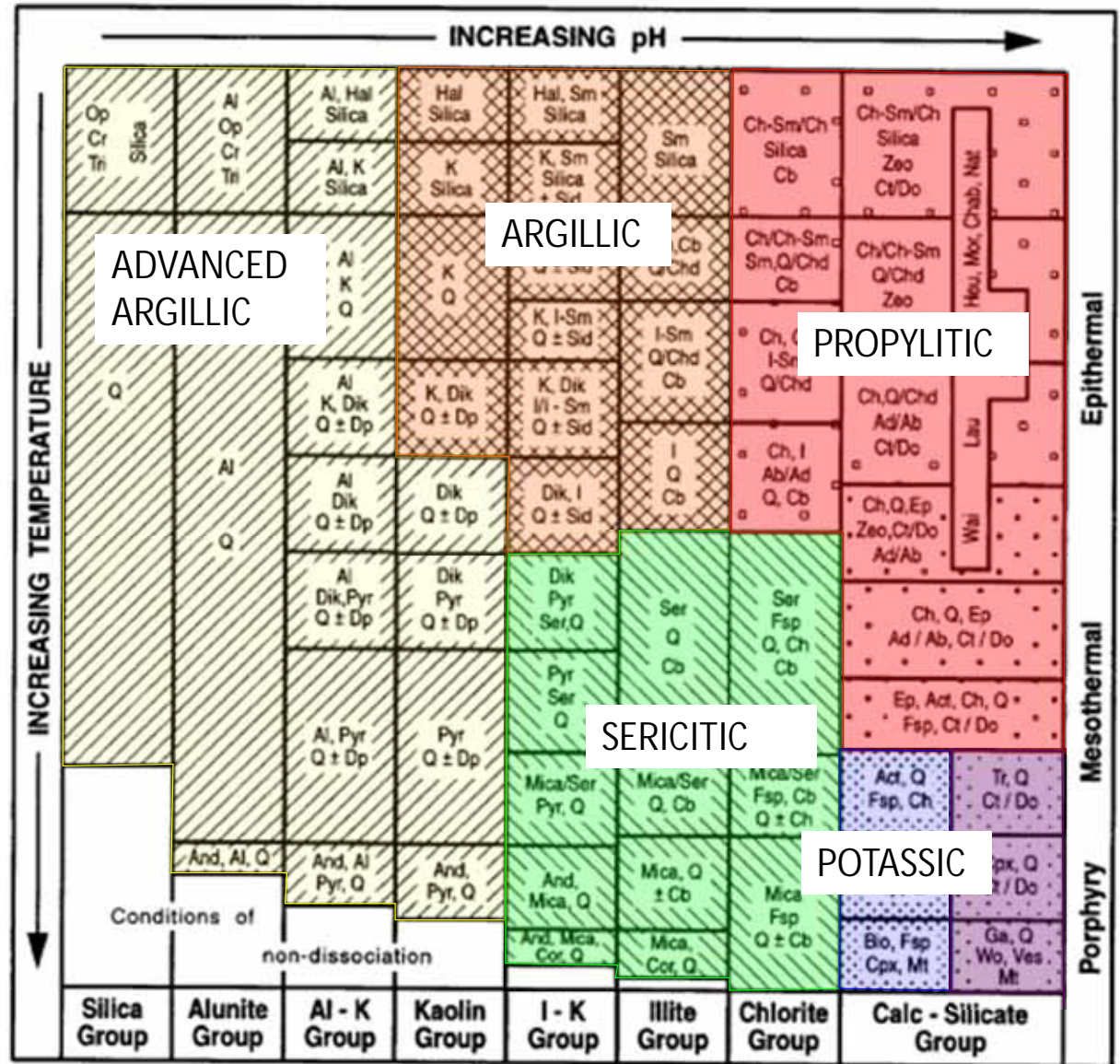
(A) KFs dominant;

(B) Ca-plagioclase dominant

(after Hemley and Jones, 1964)

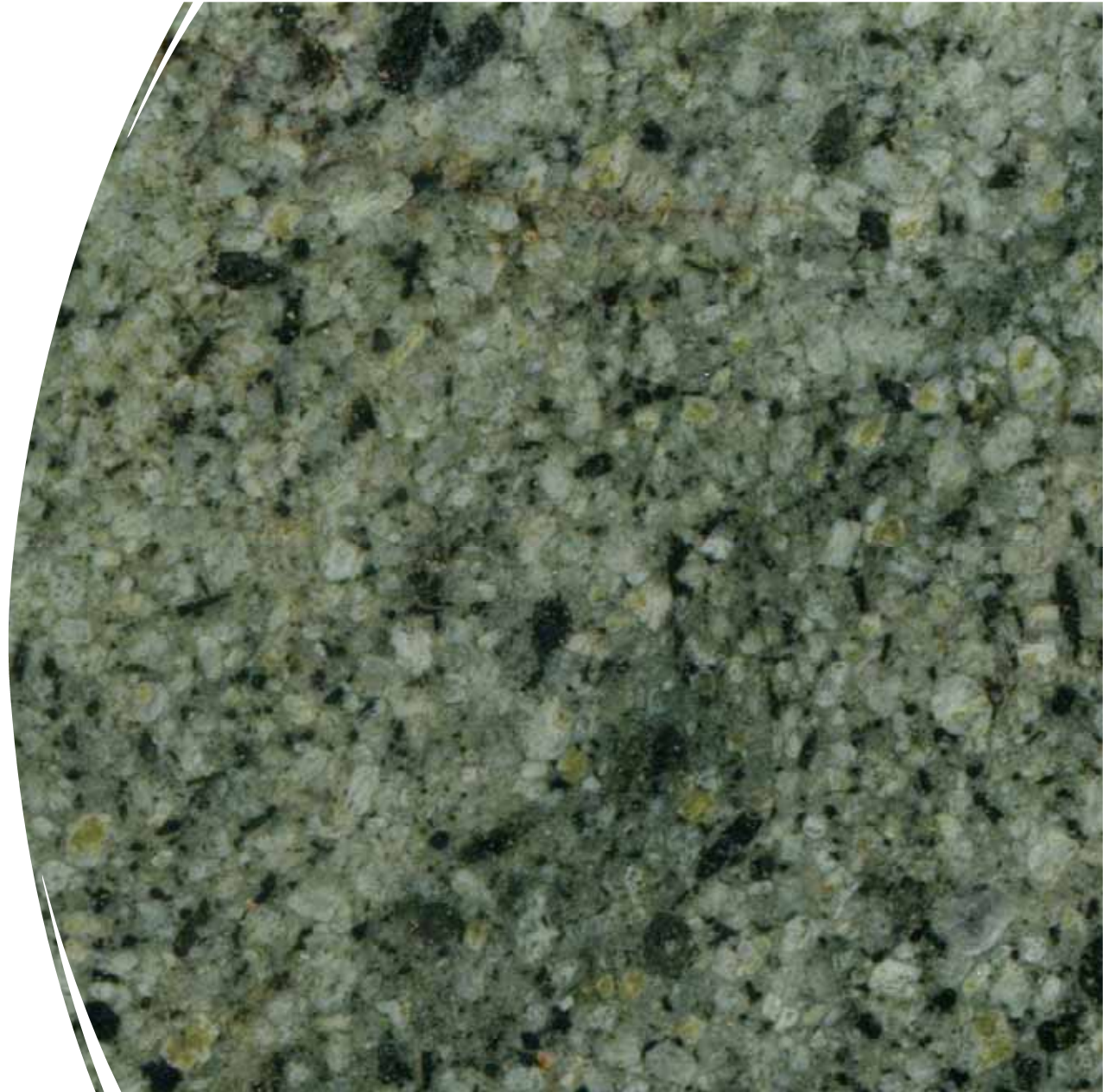


Classification of Hydrothermal Alteration



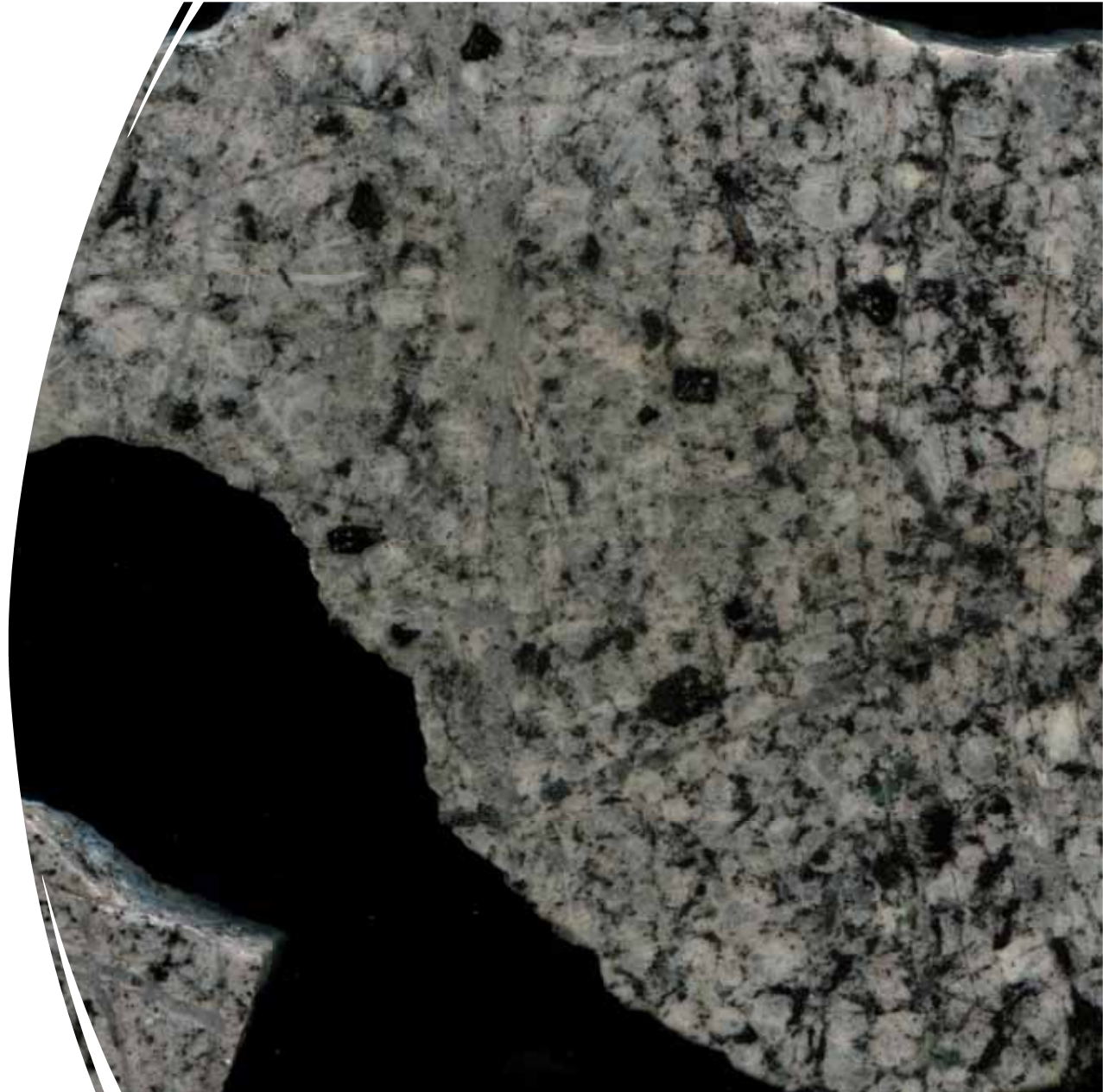
Principal alteration types (according to increasing acidity)

- **Propylitic alteration**
 - preservation of original rock textures
 - no major chemical changes
 - addition of H_2O , CO_2 and locally S.
 - epidote, chlorite, carbonate, albite, K-feldspar and pyrite.
 - transition towards unaltered rocks



- **Alkali metasomatism, in particular potassic alteration**

- T = 500 ° to 650 ° C
- interaction with saline magmatic fluid exsolved from crystallizing silicate melt.
- pH close to neutrality
- K-feldspar ± biotite ± albite ± magnetite.



Na-Ca Alteration

-
- **Na-Ca alteration**
 - Typical for deep parts of certain Porphyry copper deposits (e.g. Yerington, Morococha)
 - Albite or oligoclase (frequently after plagioclase or Kfs), actinolite (frequently after Hbl and/or biotite), epidote, sphene
 - Leaching of K, Fe and sulfides
 - It has been suggested that it is produced by saline basinal brines

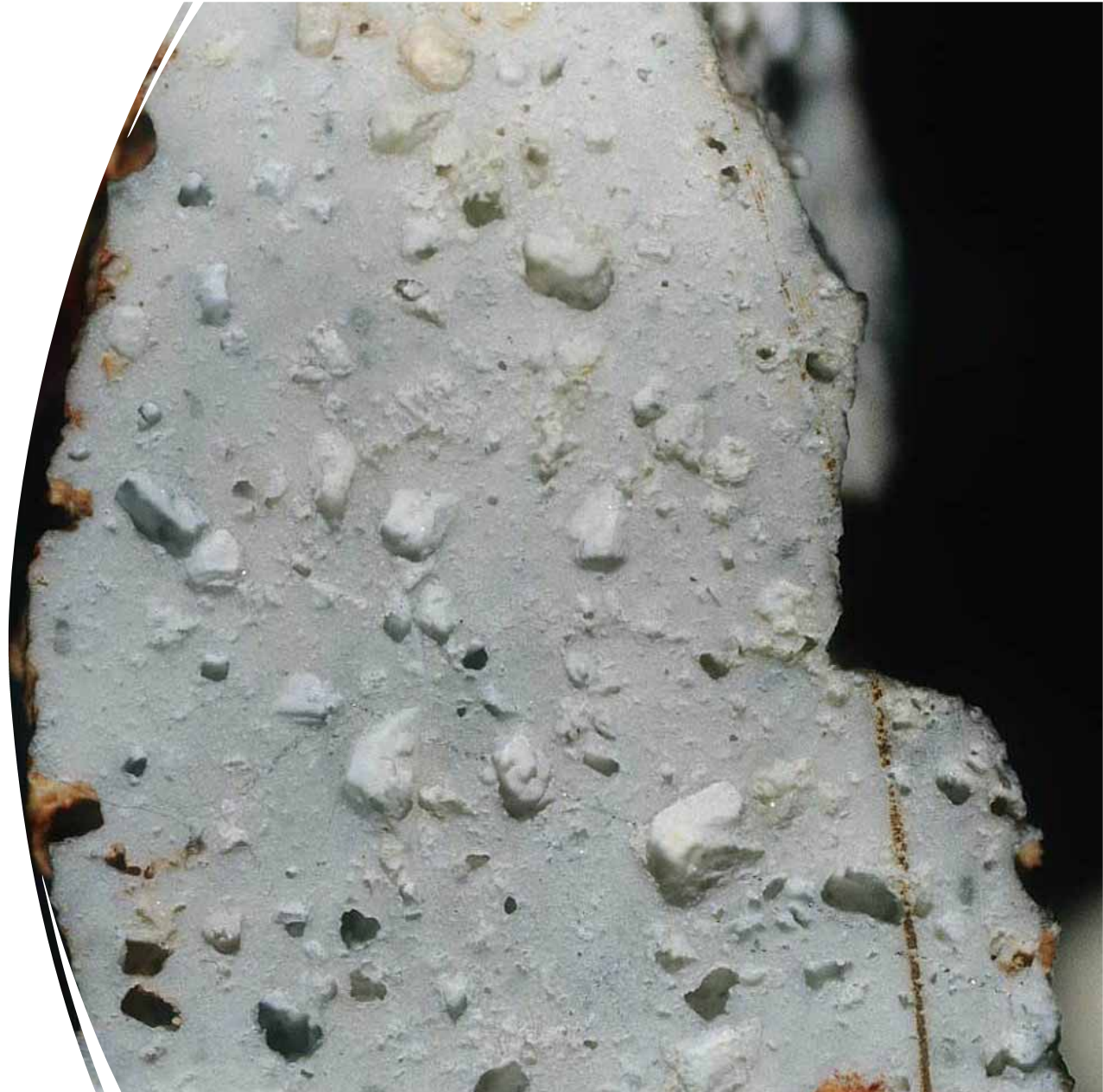


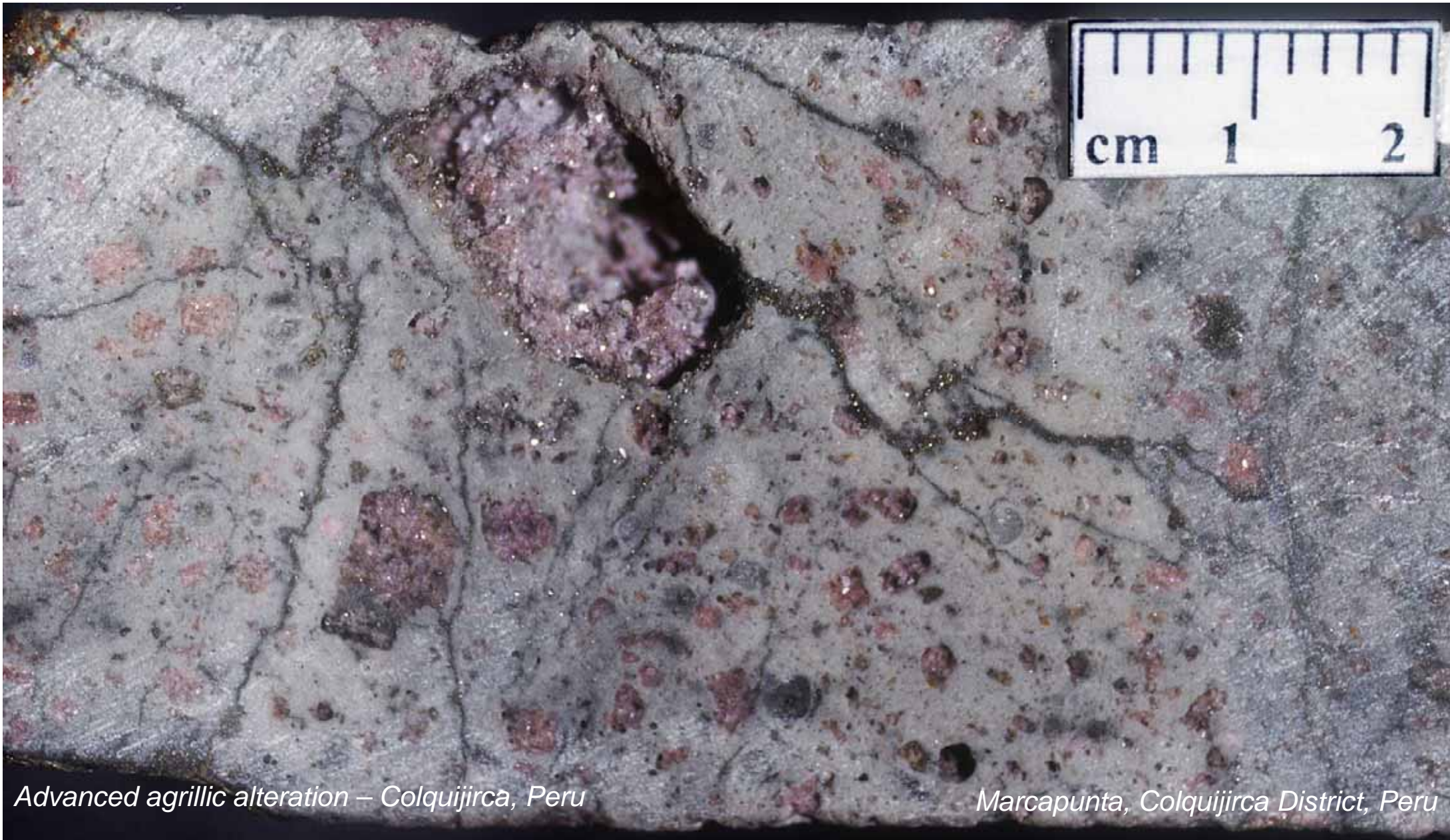
-
- **Sericitic alteration (phyllic / quartz-sericite-pyrite, QSP)**
 - *quartz-sericite-pyrite* association (rarely Kfs, kaolinite, tourmaline, calcite, biotite, rutile, anhydrite and apatite).
 - Always present if fluids develop certain acidity. Typical of destabilization of feldspars in presence of H^+ , OH^- , K, and S to form quartz, muscovite-sericite and sulfides, mainly pyrite.



- **Advanced argillic alteration (AAA)**

- Under more acidic conditions feldspars and mafic minerals can be completely destroyed - "*advanced argillic alteration*". Al liberated by the destruction of silicates will be fixed as mineral of the kaolinite group (clays), alunite $KAl_3(SO_4)_2(OH)_6$ and diaspore. In addition, barite, native sulfur, topaz, tourmaline and other clay minerals may form. AAA is typical of hydrothermal epithermal systems of "high-sulfidation" type.
- "vuggy silica" / "residual silica" – typical alteration texture for AAA. The formation of "residual silica" does not imply silicification, no Si added to the system !
- H_2SO_4 forms by "disproportion" of magmatic SO_2 (disproportion: separation of S^{-2} and SO_4^{-2}). SO_4^{-2} is used to form alunite, barite.





Advanced argillic alteration – Colquijirca, Peru

Marcapunta, Colquijirca District, Peru

WHY IT IS IMPORTANT TO STUDY W/R INTERACTION?

Until now, the study of hydrothermal alteration has been performed for four main purposes:

- define the 3D mineralogical zonation of geothermal systems or hydrothermal envelopes of ore deposits, in order to individuate the “hot” or “high-grade” core of the system (mineralogical vectoring).
- define the geometry of impermeable cap rocks in geothermal systems.
- define the physical-chemical properties of the reservoir rocks.
- Define the physical-chemical characters of the causative fluid.

GEOHERMAL SYSTEMS

Which is the scientific/industrial value of this information?

HUGE !

Very good definition of reservoir and cap rocks

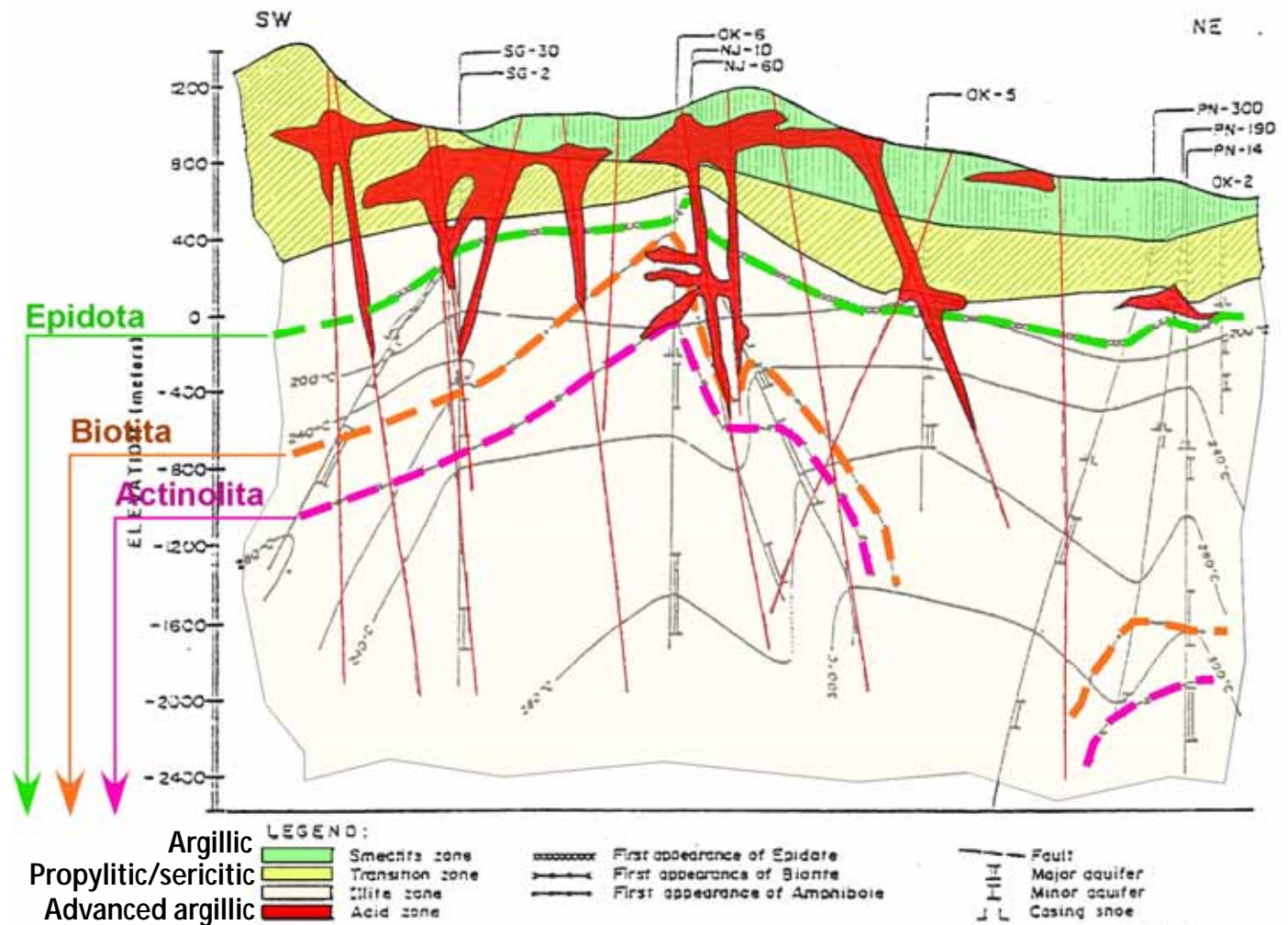


Fig. 7.1(d). The distribution of alteration zones and measured isotherms in the Palinpinon geothermal system, Southern Negros, Philippines. (From Reyes, 1990).

GOLD EPITHERMAL SYSTEMS

Which is the scientific/industrial value of this information?

HUGE !

The gold is concentrated in the most altered axial zone

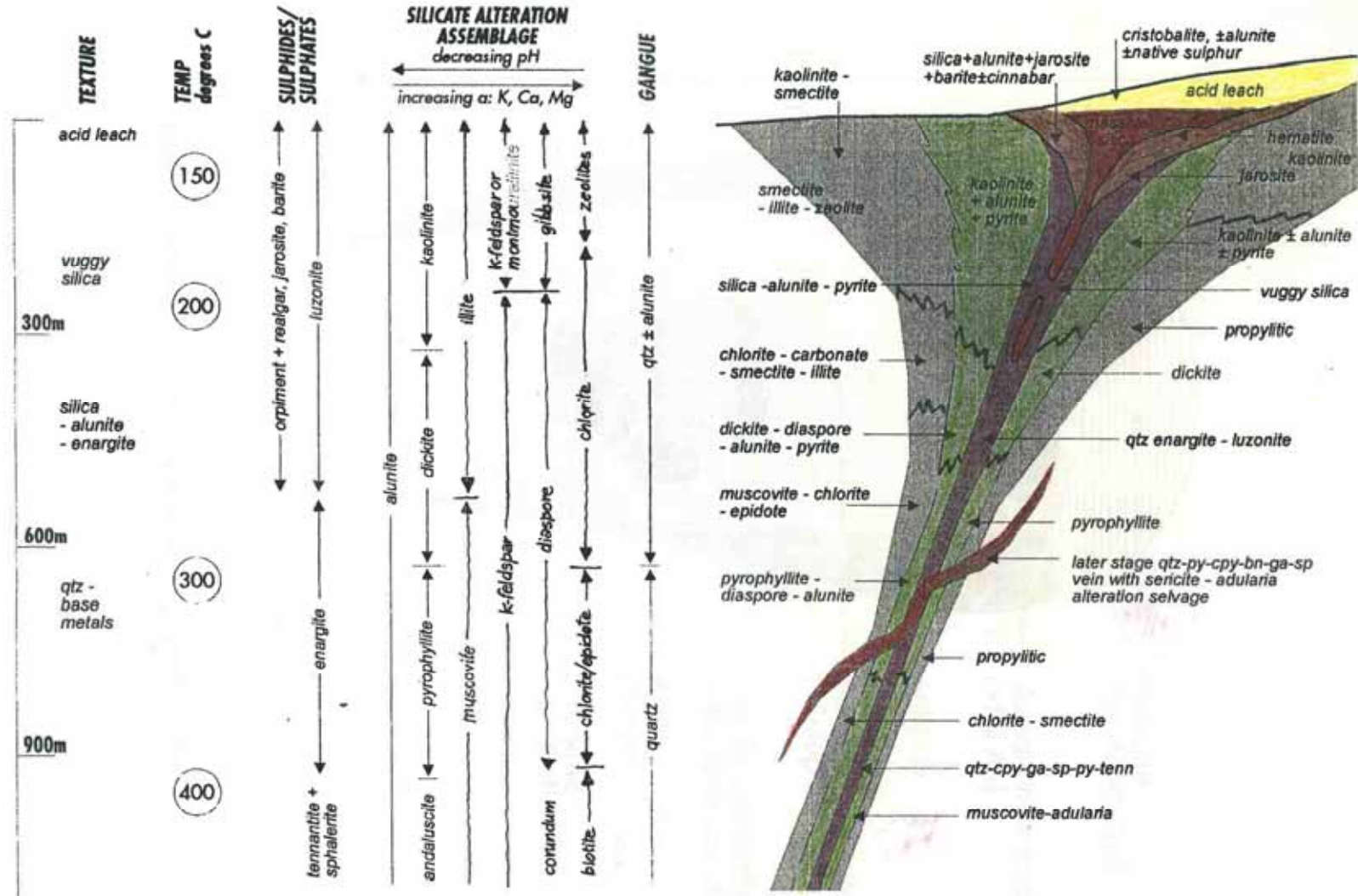
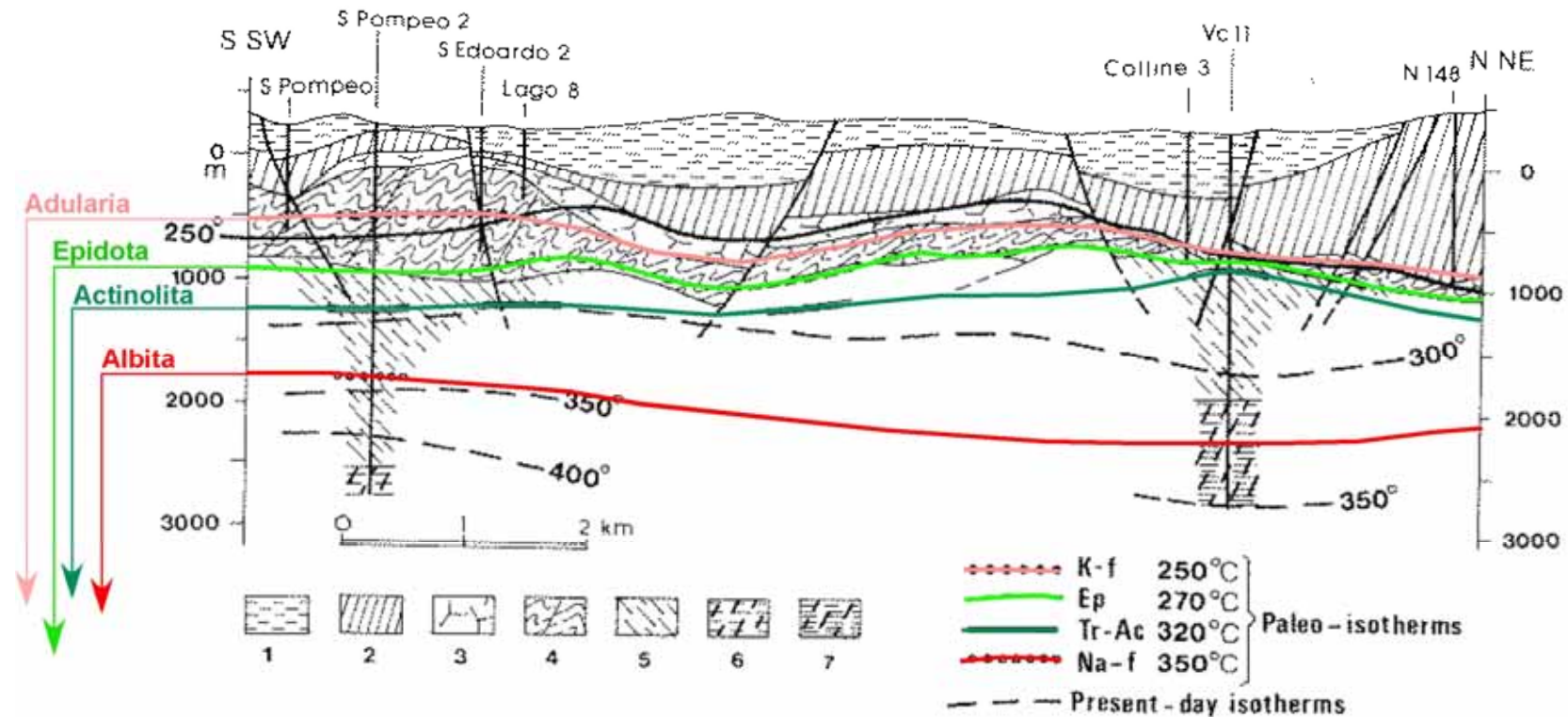


Figure 3 Schematic section through a high-sulphidation epithermal system

ALTERATION ZONING IN LARDERELLO GEOTHERMAL FIELD



Which is the scientific/industrial value of this information?

NEGLIGIBLE ! WHY?

The zoning is not related to the present day geothermal system!

Larderello: boron and steam

The boron-rich character of Larderello fluids is known since Roman and Medieval time.

In 1818 started the industrial extraction of boric acid by condensation of steam.

Production of boron compounds continued until few decades ago.

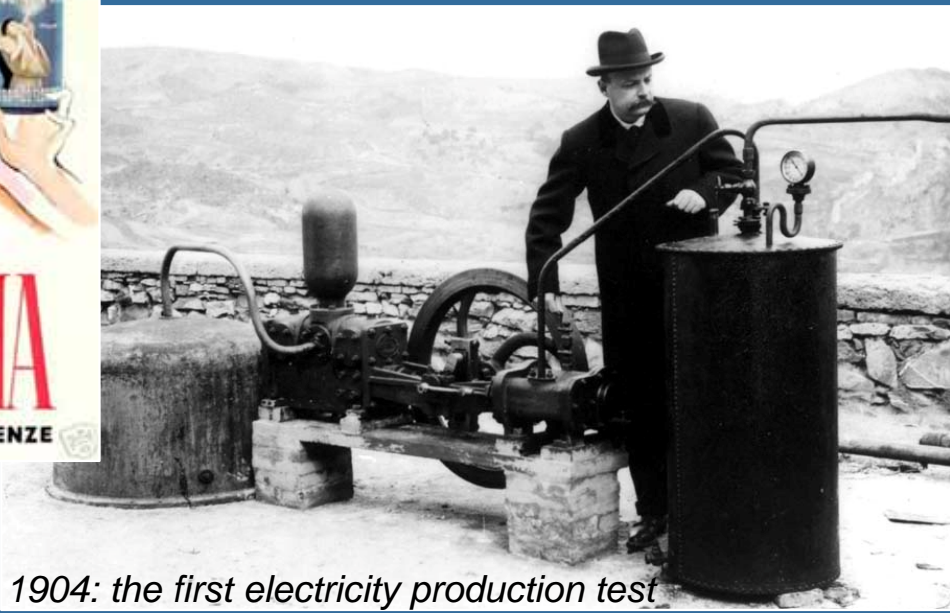
In 1904, the first attempt to use steam for producing electric energy.



Larderello in the XIX century



*"Florentia":
the boric talcum
produced at Larderello*



1904: the first electricity production test

Early interpretation: B-rich magmas = B-rich fluids

Tourmaline is a common mineral in granites, pegmatites and hydrothermal veins from Tuscany.

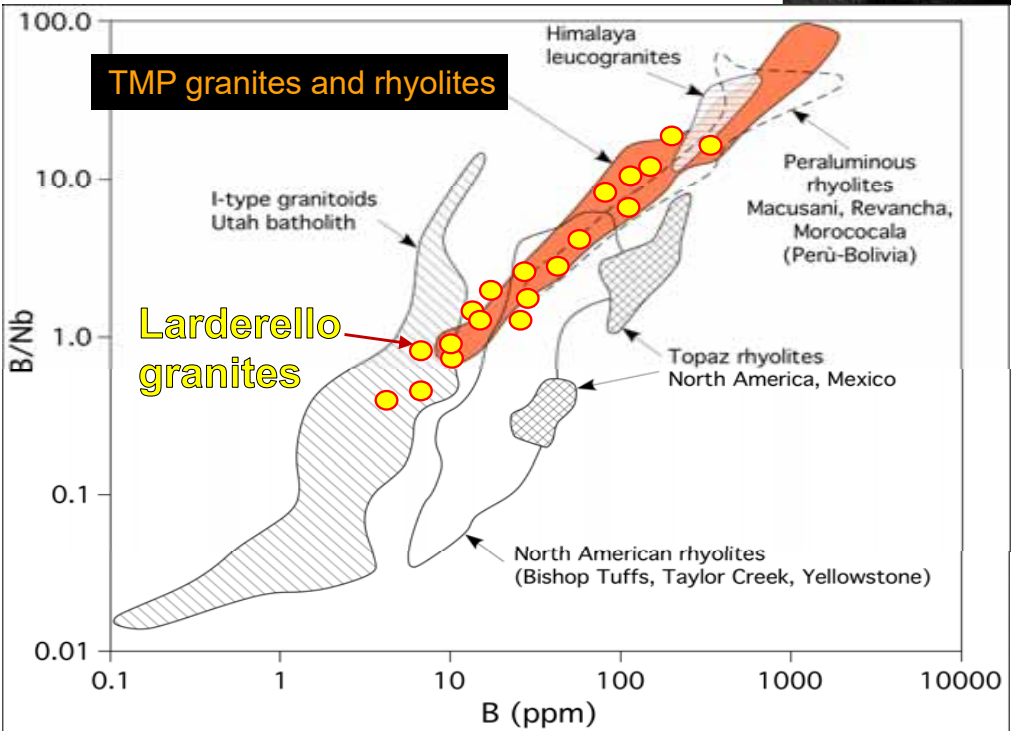
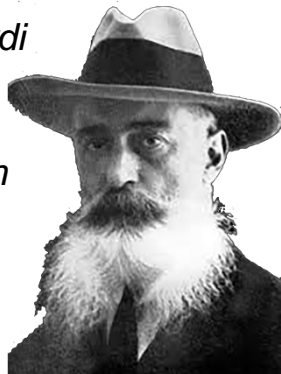
Since XIX century, early Tuscan geologists/mineralogists recognized the boron-rich character of this “young” magmatic rocks.

They explained both thermal anomaly and B-rich fluids at Larderello (B = 5-100 ppm) as originated by the presence of granite magmas at depth (magmatic origin).

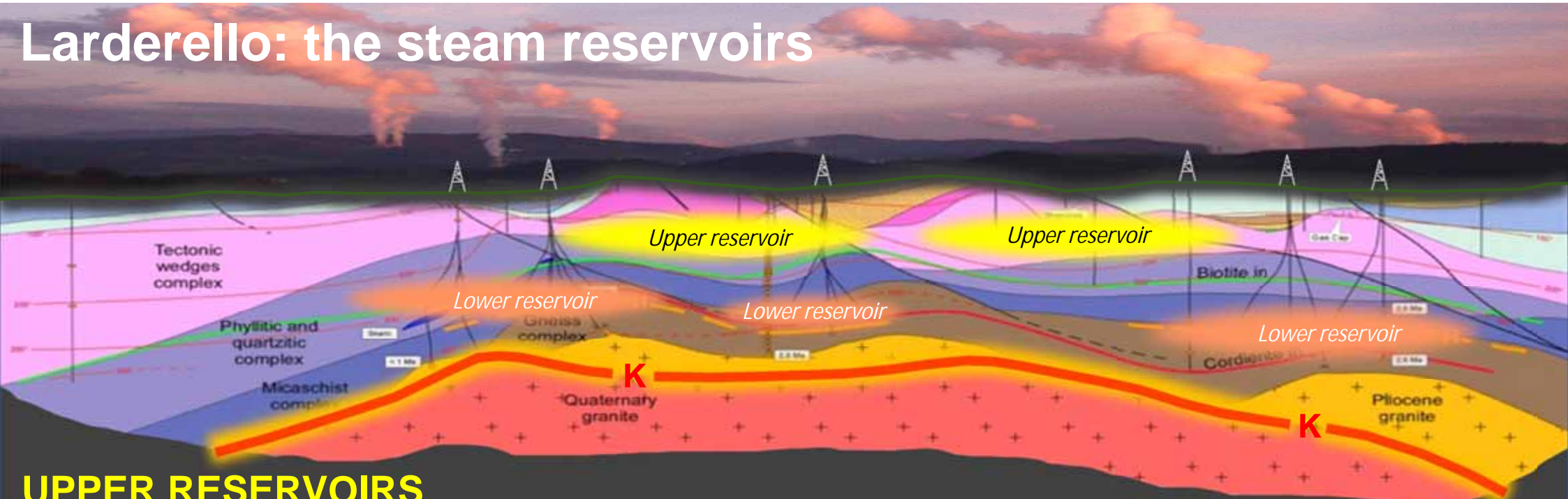


Sassolite (H_3BO_3) from Larderello fumaroles

Giovanni D’Achiardi (1872-1944): he studied boron minerals from both Tuscan granites and Larderello condensates



Larderello: the steam reservoirs



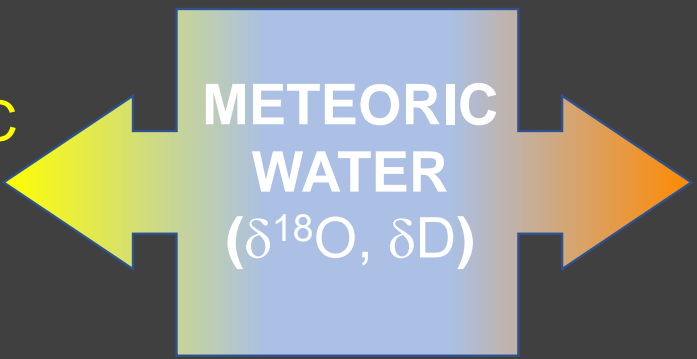
UPPER RESERVOIRS

Host rocks: Sedimentary (carbonates, argillites)

Depth: 200-1500 m

Temperature: 120-260°C

Pressure: 5-60 bars



LOWER RESERVOIRS

Host rocks: Metamorphic (metapelites)

Depth: 1500-4500 m

Temperature: 300-360°C

Pressure: 40-70 bars

Larderello: a multipulse, long-lived intrusive system

Modified after Dini et al., 2005

New U-Pb ID-TIMS zircon dating of granites (Farina et al., 2018) are coherent with ^{40}Ar - ^{39}Ar ages. Larderello is a multi-pulse magmatic system including five main stages:

1) Monteverdi (4.3-4 Ma)



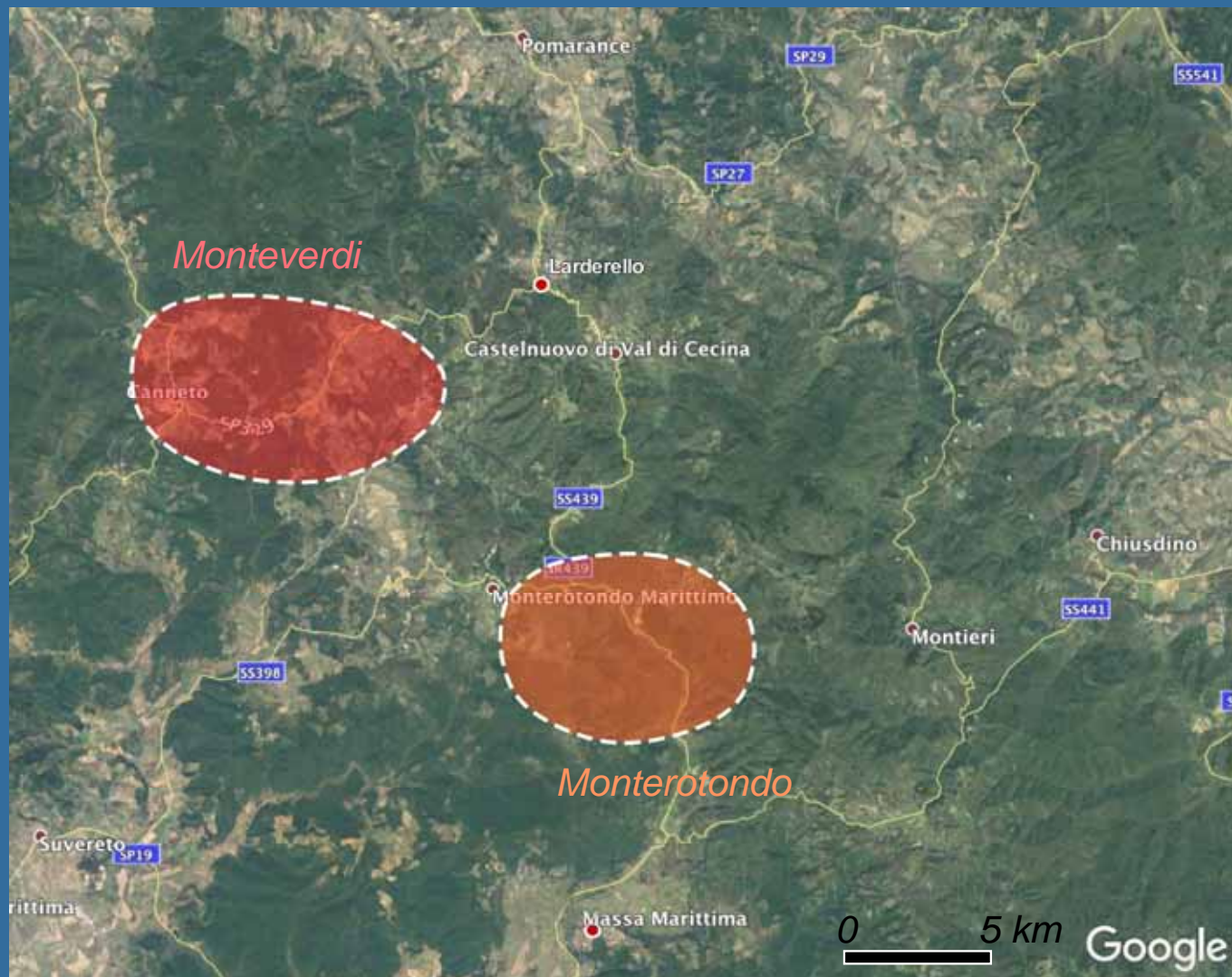
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- 1) Monteverdi (4.3-4 Ma)
- 2) Monterotondo (3.5-3.8 Ma)



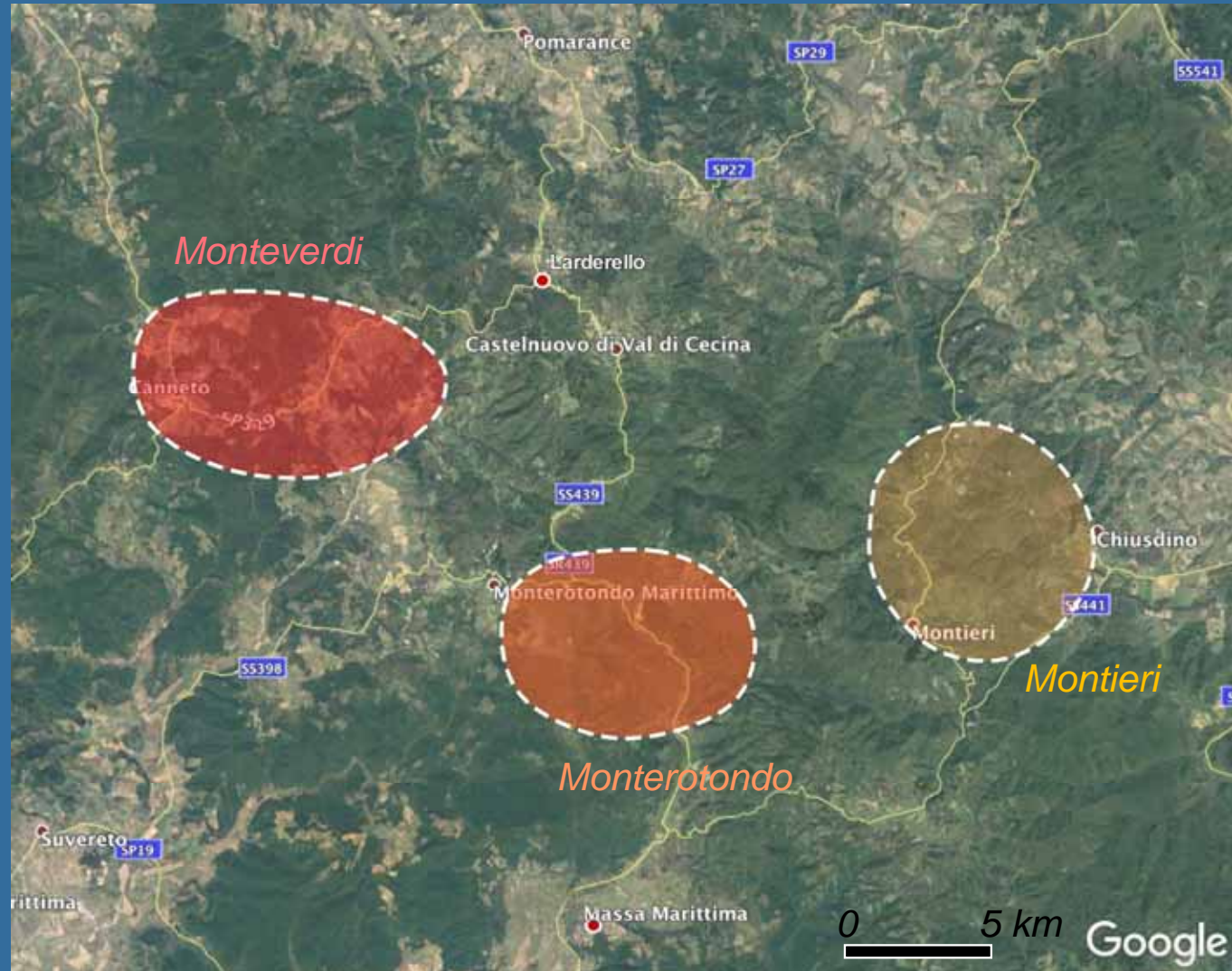
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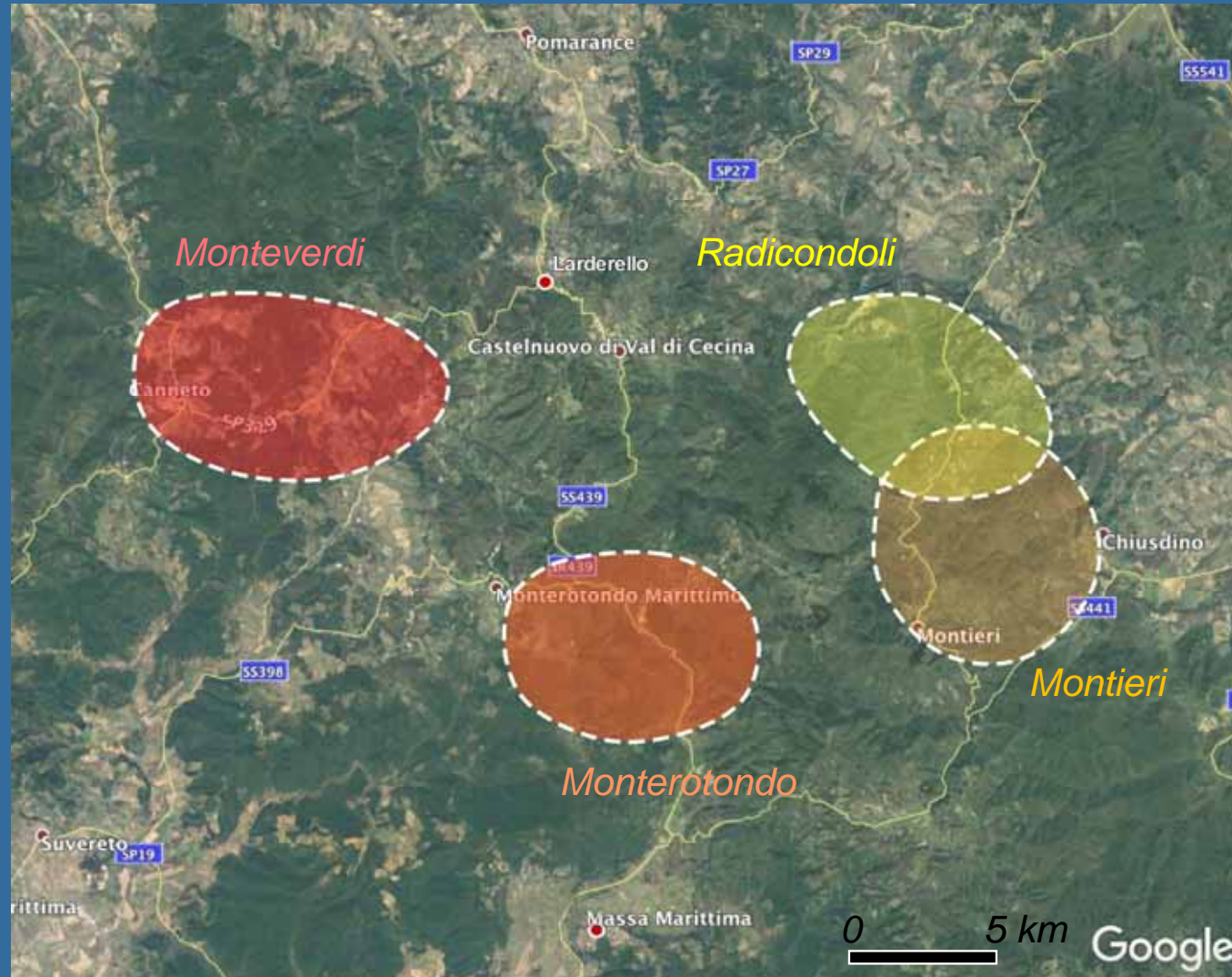
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- 4) Radicondoli (2.7-2.5 Ma)



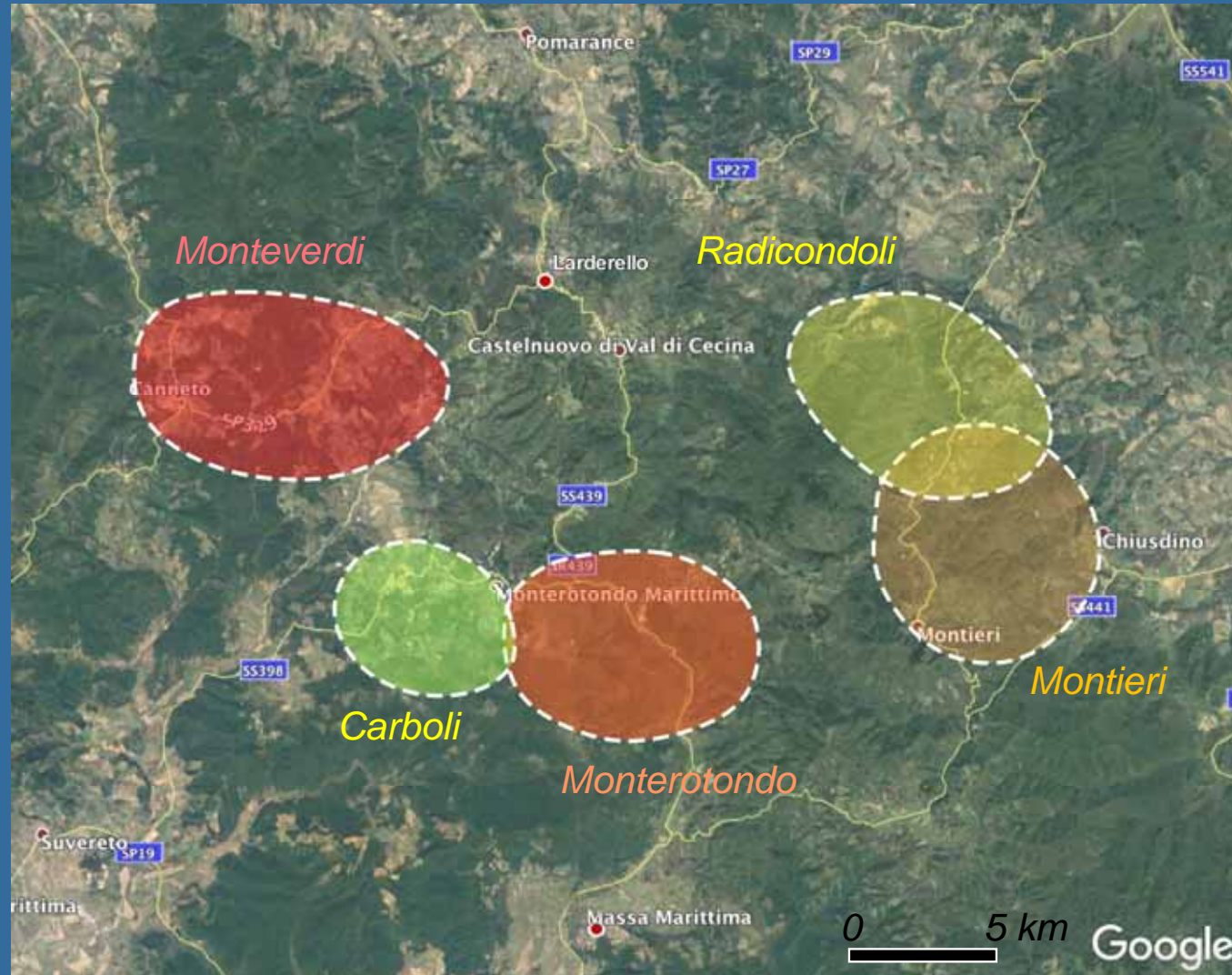
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- 4) Radicondoli (2.7-2.5 Ma)
- 5) Carboli (1.9-1.6 Ma)



Larderello: a multipulse, long-lived intrusive system

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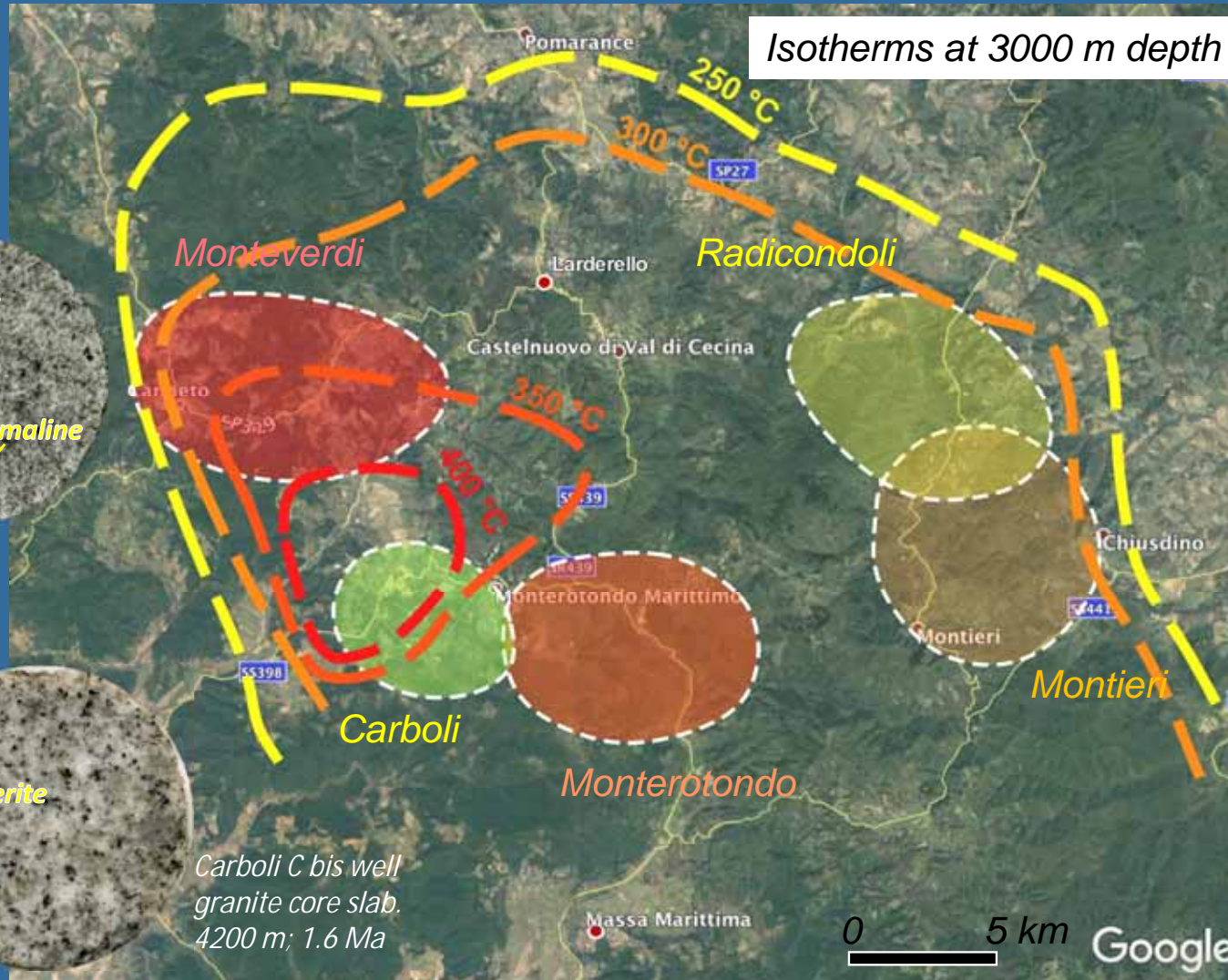
The youngest, known granite is “too old” (1.9-1.6 Ma) to sustain the present day geothermal system.

- 1) Monteverdi (4.3-4 Ma)
- 2) Monterotondo (3.5-3.8 Ma)
- 3) Montieri (3.3-3.1 Ma)
- 4) Radicondoli (2.7-2.5 Ma)
- 5) Carboli (1.9-1.6 Ma)
- 6) **ACTIVE INTRUSION ?**

Monteverdi 3 well granite core slab. 3860 m; 3.8 Ma



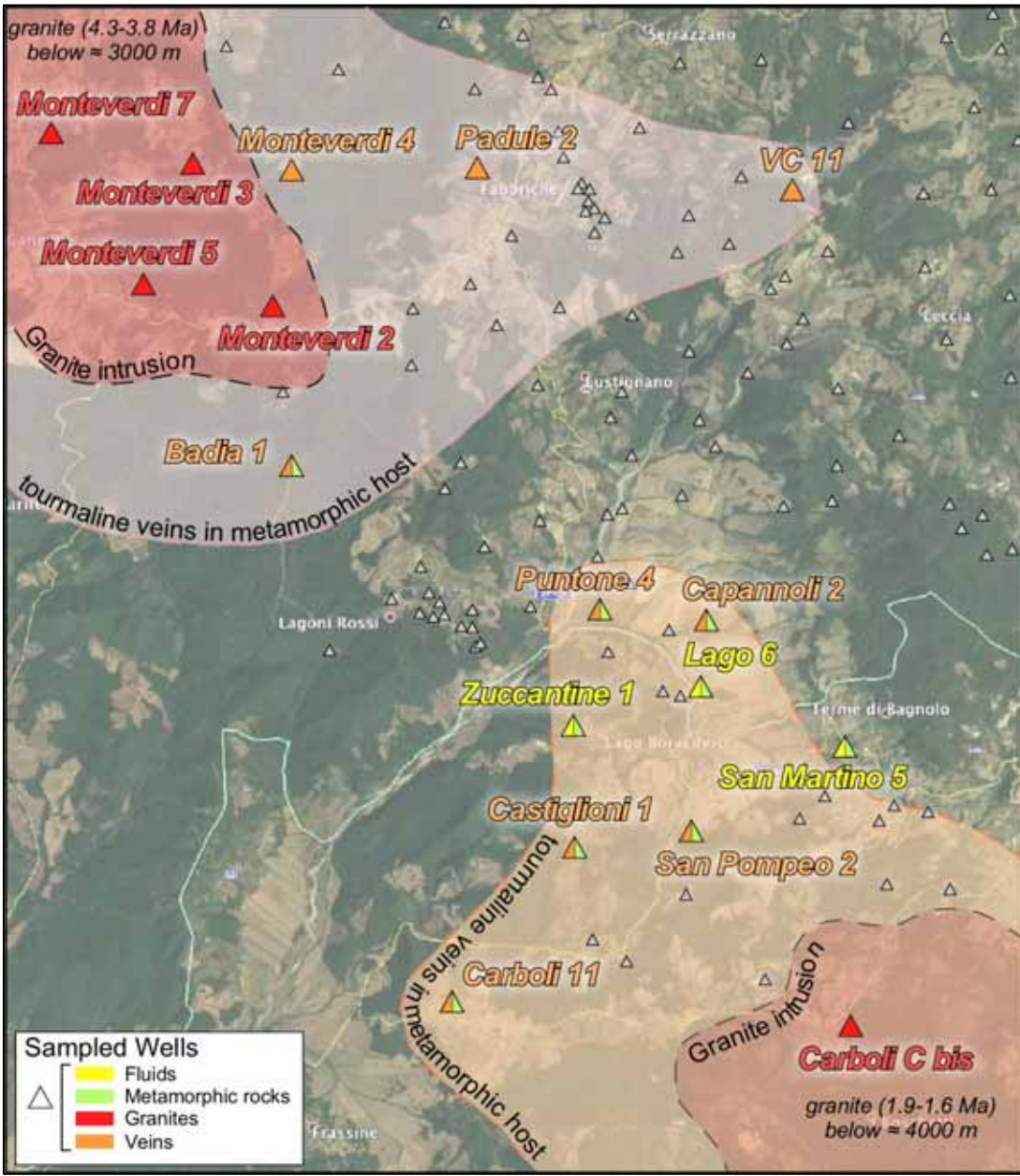
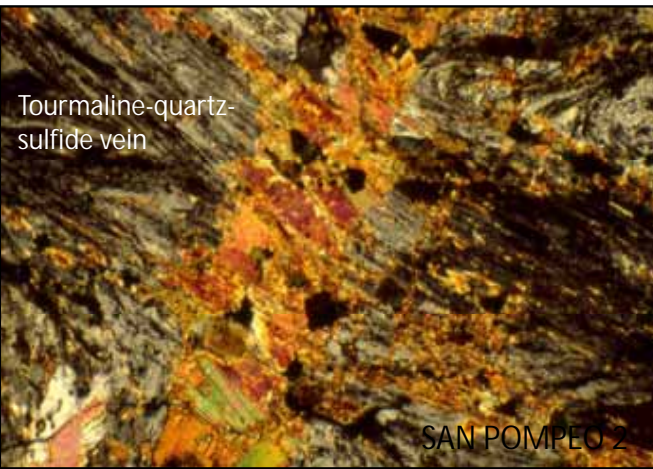
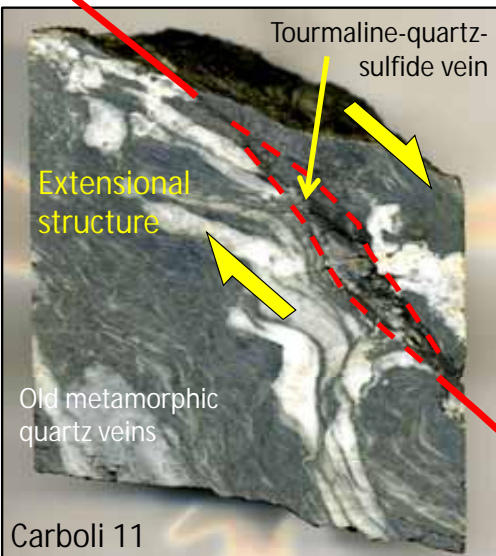
Carboli C bis well granite core slab. 4200 m; 1.6 Ma



Multiple intrusions: multiple contact & hydrothermal events

Metamorphic host rock and granite intrusions recorded the formation of tourmaline bearing quartz-sulfide veins, metasomatic masses and hydraulic breccias.

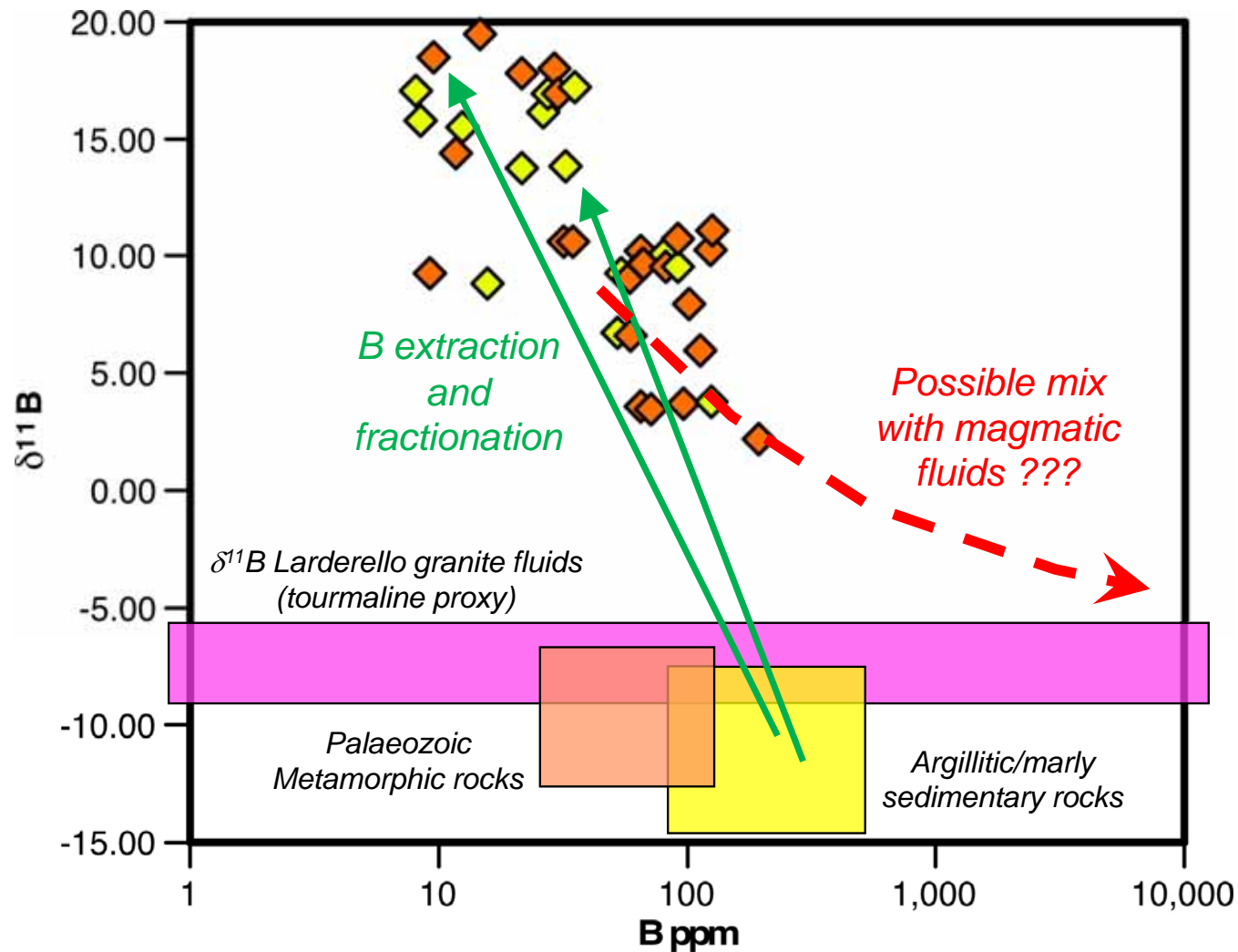
Every intrusion has its tourmaline bearing “shell”



The positive $\delta^{11}\text{B}$ of geothermal fluids is not compatible with a magmatic (S-type granite) origin.

Boron cannot be extracted from Palaeozoic basement by present day steam.

The only suitable source for boron are the sedimentary rock (from 0 to 1500 m depth).



Granite magmas are there, but they “just” provide heat

HYDROTHERMAL ALTERATION + GEOCHEMISTRY AND ISOTOPES

Mineral extraction from geothermal fluids represent a challenge and an opportunity for the future.

Rocks that have undergone hydrothermal alteration have been greatly modified but, in turn, the fluids themselves have experienced profound chemical changes.

The study of hydrothermal alteration of rocks can unveil the mobility of specific elements and allow us to hypothesize the existence of fluids enriched in critical elements.

Metals from geothermal: a challenge and an opportunity

Poor knowledge of these metal unconventional resources

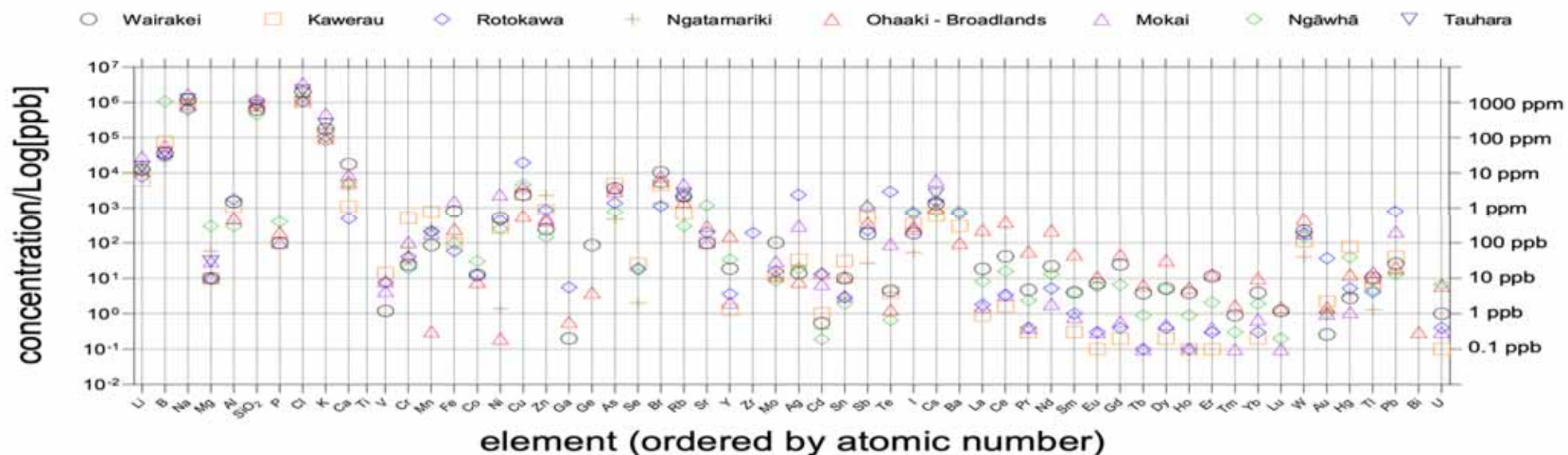
There is a need for an integrated approach involving Research Institutions and Industry:

- Scientific Research: geological-petrological-geochemical conceptual models; Origin of metals.
- Industrial Research: Direct Lithium Extraction
- Mining Exploration : New mining strategy (defining resources and reserves; environmental sustainability and social acceptans)



Figure 1.4 Geo40 silica-recovery plant (Ohaaki Northern Plant) in New Zealand (source: Geo40).

Geographic Provinces	Potential Minerals	Remarks
Basin and Range	SiO ₂ , Ag, B, Cs, Cu, Li, K, Mn, Pb, Rb, and Zn	SiO ₂ and K can be recovered from numerous brines; Ag, Cu, Li, Mn, Pb, Zn have recovery potential from Salton Trough Section of this province; Li could be recovered from some brines in the Great Basin Section in Utah and Nevada; B, Cs, and Rb could be recovered from some brines in the Great Basin and Salton Trough Sections.
Columbia Plateau	SiO ₂ , Ag, Au	Some brines from Walla Walla, Harney, and Blue Mountains Sections have Ag and Au in µg/kg (ppb) levels of concentration. Several brines in this province are identified with positive attributes for SiO ₂ recovery.
Northern Rocky	SiO ₂	SiO ₂ concentrations are relatively low (<125 mg/kg) in most of the brines. One sample is identified with SiO ₂ and TDS level suitable for recovery (Figure 9b).
Middle Rocky	SiO ₂ , Ag, Li	The geothermal features with some recovery potential of these minerals are located in Yellowstone National Park, Wyoming.
Wyoming Basin	Ag	A small number of samples are reported to have about 50 µg/kg (ppb) silver content.
Southern Rocky	SiO ₂ , Li	Li could be recovered from brines around Vales Caldera National Preserve. Only two brine samples are identified with good attributes for SiO ₂ recovery.
Colorado Plateau	Li, K	Li can be recovered from brines located in the Datil and Navajo Sections; K has higher recovery potential from brines in the Canyon Lands Section
Cascade-Sierra	SiO ₂ , B, Li	A small number of sites have SiO ₂ recovery potential; a small number of geothermal waters in the Northern Cascade have B and Li concentrations up to 40 mg/kg and 10 mg/kg, respectively.
Pacific Border	SiO ₂ , Li,	A small number of sites have SiO ₂ recovery potential; a small number of sites have Li concentrations between 10-33 mg/kg.



Lithium in Italy: is there any under our feet?

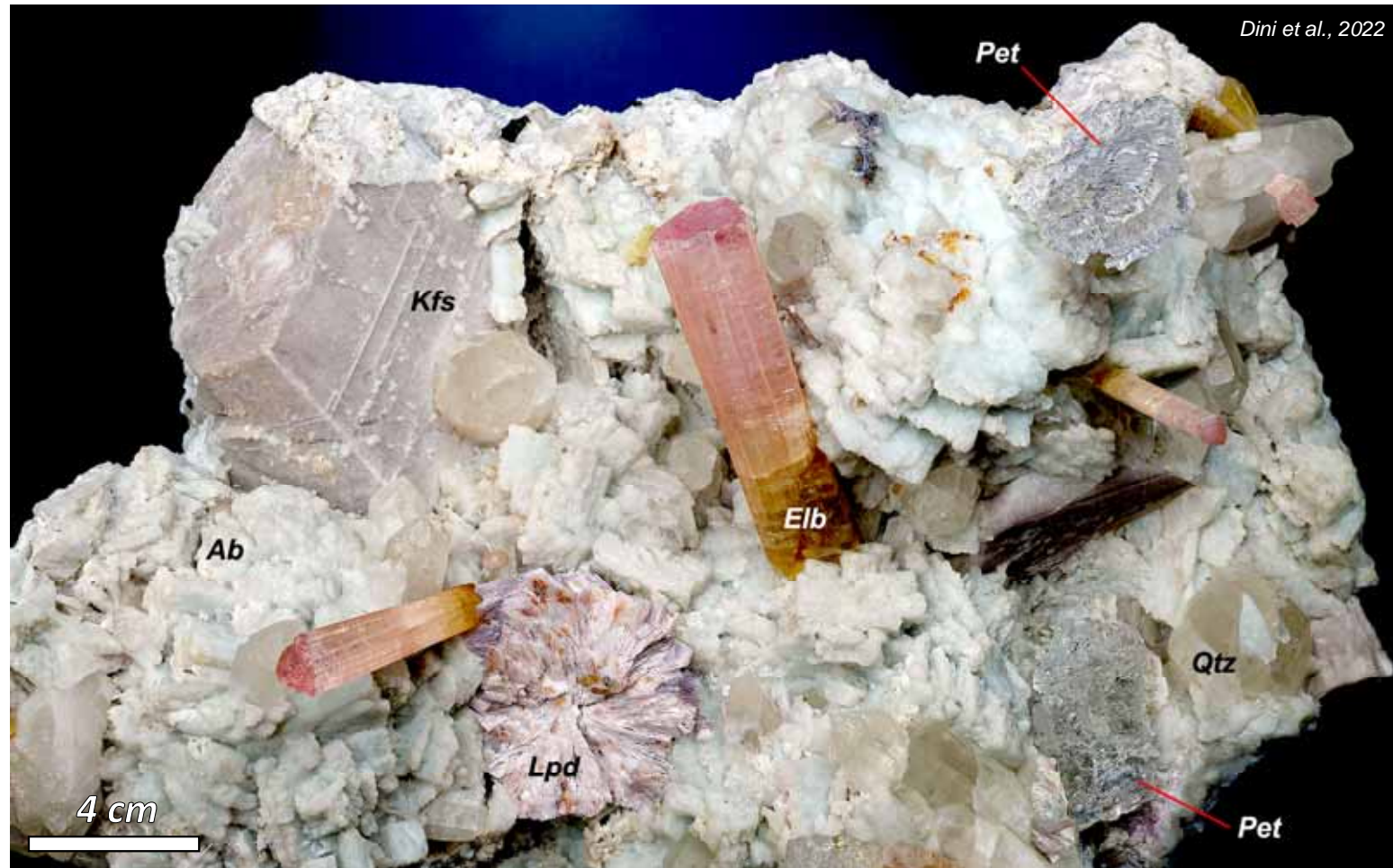
Beautiful crystals of Li-rich minerals collected at Elba Island well before Arfwedson discovered lithium in 1817!

Lithium was separated by Italian chemists in 1827 using lepidolite from Elba Island.

Type-locality for elbaite: the most precious and amazing lithium-rich member of the tourmaline supergroup.

In spite of two centuries of collecting and science:

Italy has no record of lithium production



Elbaite (Elb), lepidolite (Lpd) and petalite (Pet) crystals from a pegmatite dyke at Elba Island, Italy

Lithium Occurrence in Italy—An Overview

Andrea Dini ¹, Pierfranco Lattanzi ², Giovanni Ruggieri ^{2,*} and Eugenio Trumpy ¹





Minerals 2022, 12, 945. <https://doi.org/10.3390/min12080945>

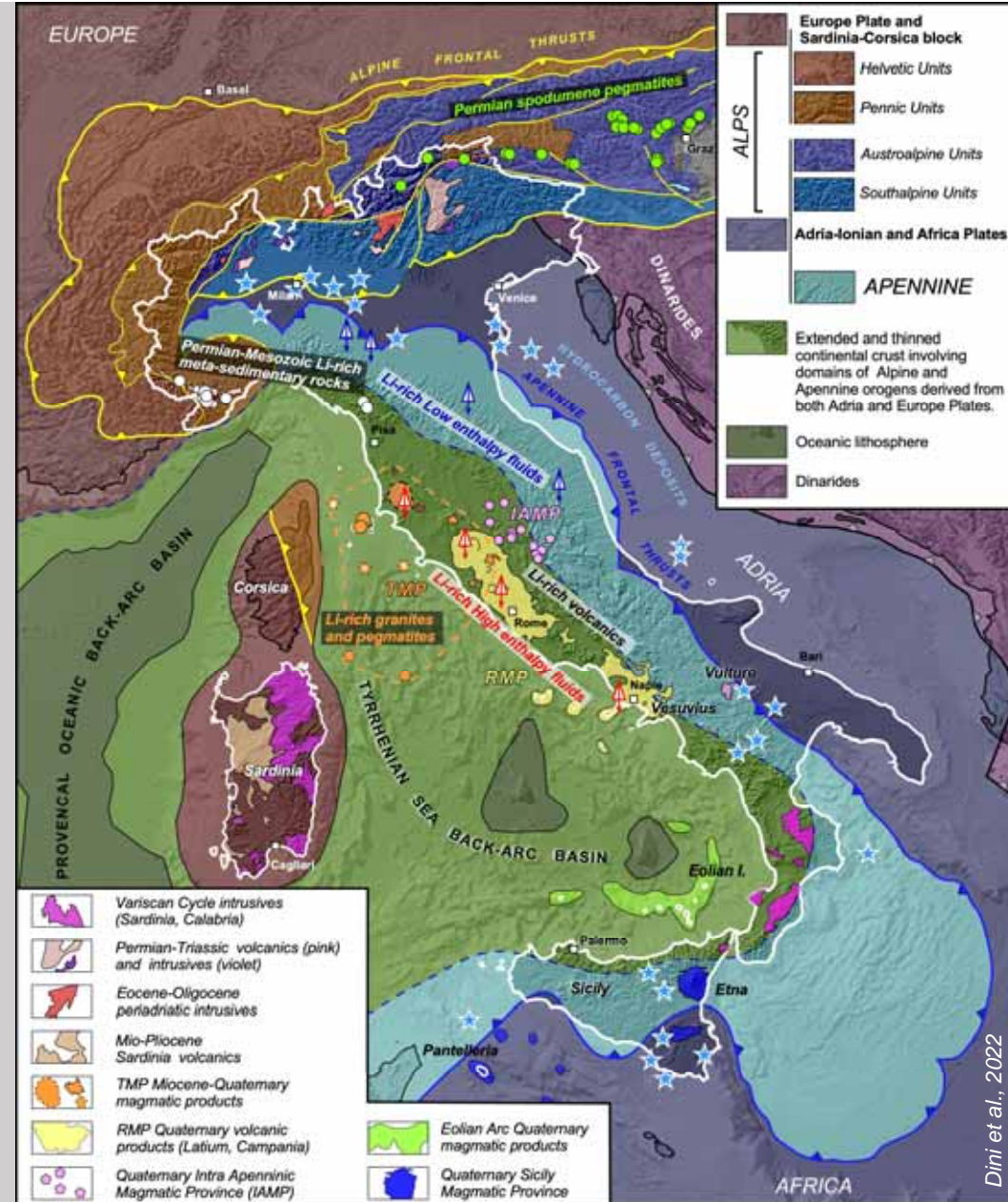
<https://www.mdpi.com/journal/minerals>

Overall geological-climatic features **unfavorable for conventional** hard rock (spodumene pegmatites) and brine (salars) deposits.

Few spodumene pegmatites in eastern Alps.

Significant **potential for unconventional resources:**

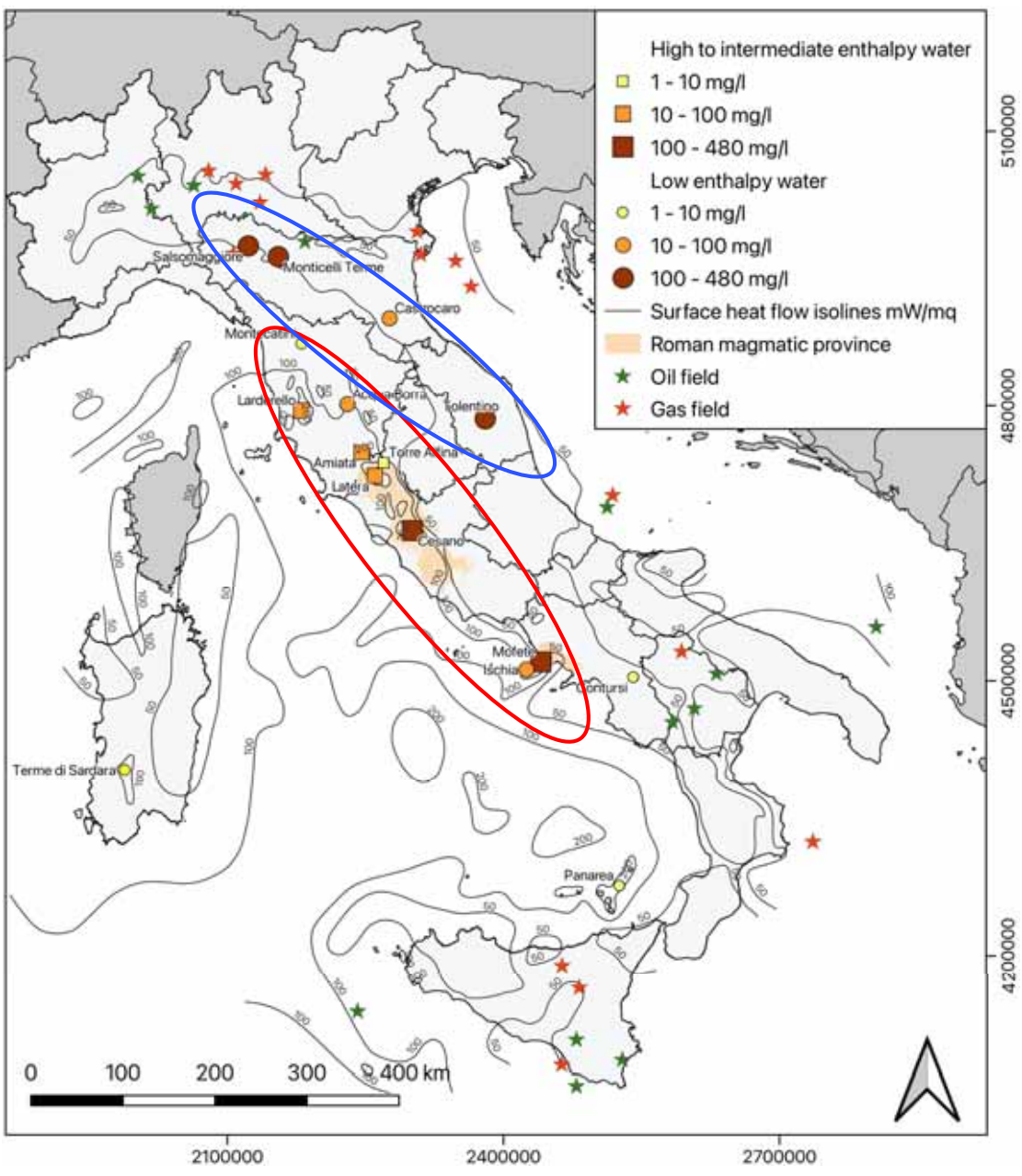
- Geothermal fluids in back-arc region (internal Apennine)  Li up to 500 mg/l
- Fluids in the foredeep-wedge region (Apennine front)  Li up to 400 mg/l
- Li-rich peraluminous granites (Tuscany)  Li up to 2500 µg/g
- Permian-Triassic volcano-sedimentary sequences (Alps)  100s to 1000s µg/g



Unconventional resources

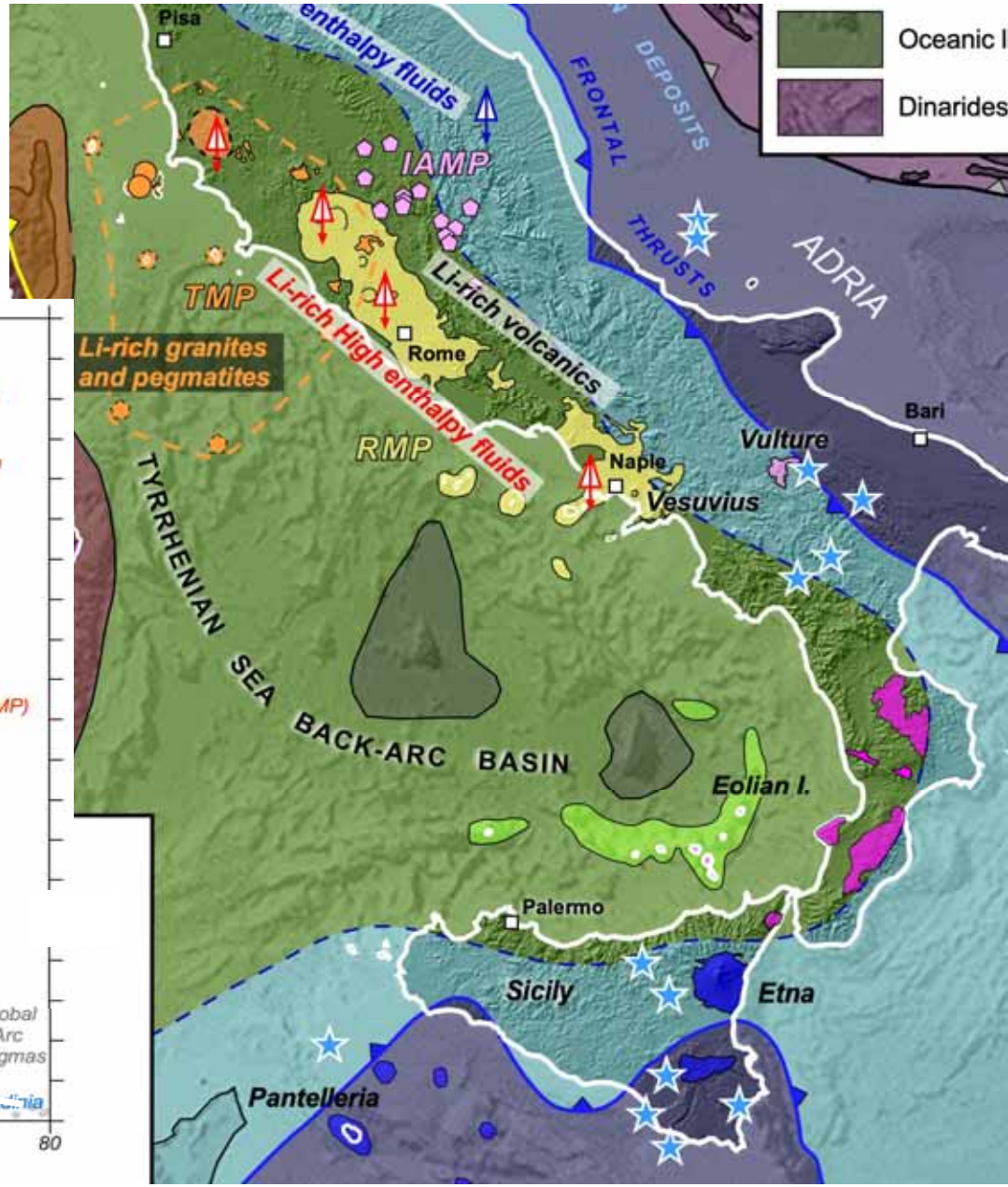
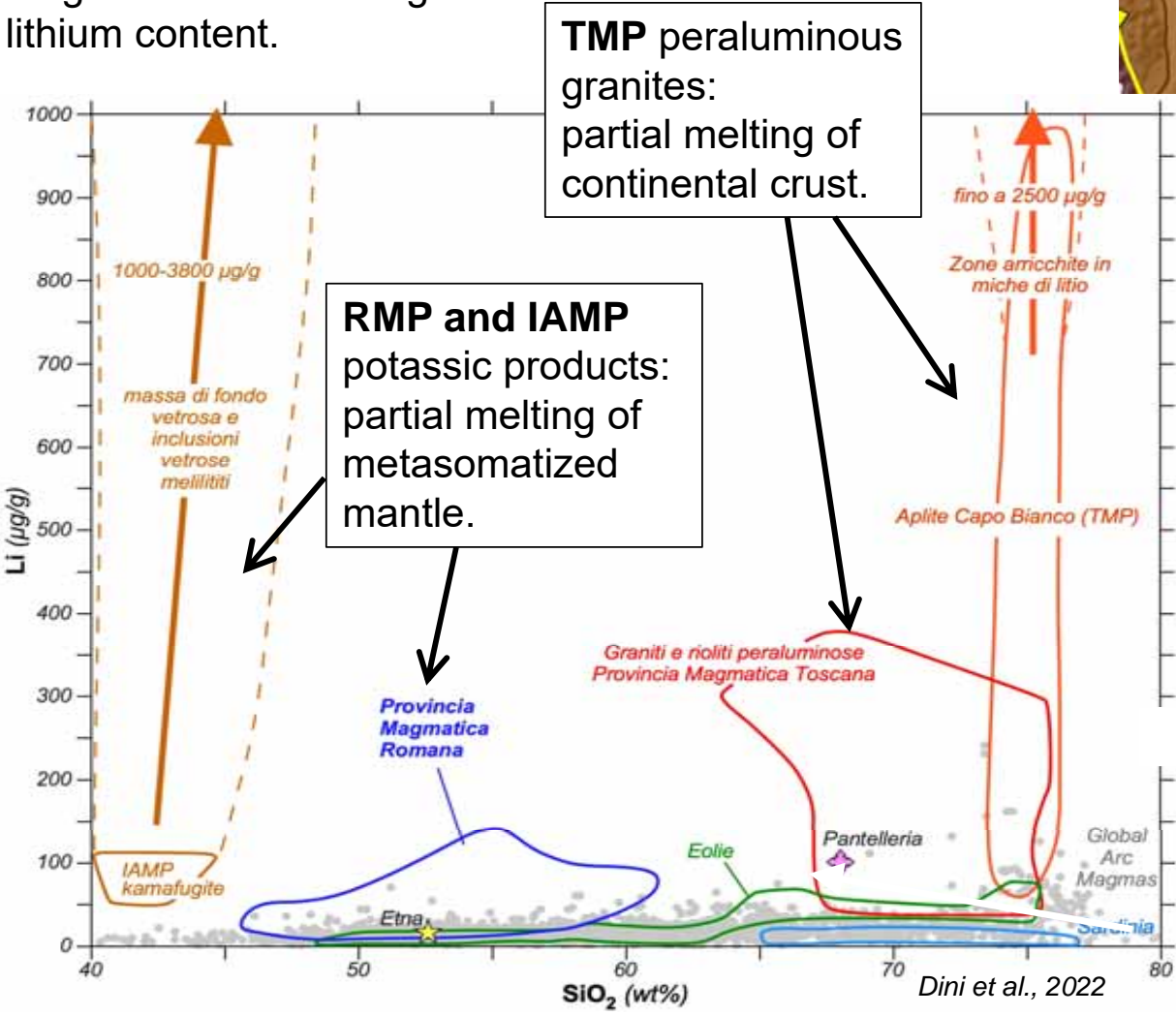
Brines with Li concentrations up to 500 mg/l were intercepted during the geothermal exploration in Tuscany-Latium-Campania area.

Low temperature fluids with Li content up to 400 mg/l are well known in the frontal zone of the Northern Apennine mountain belt.



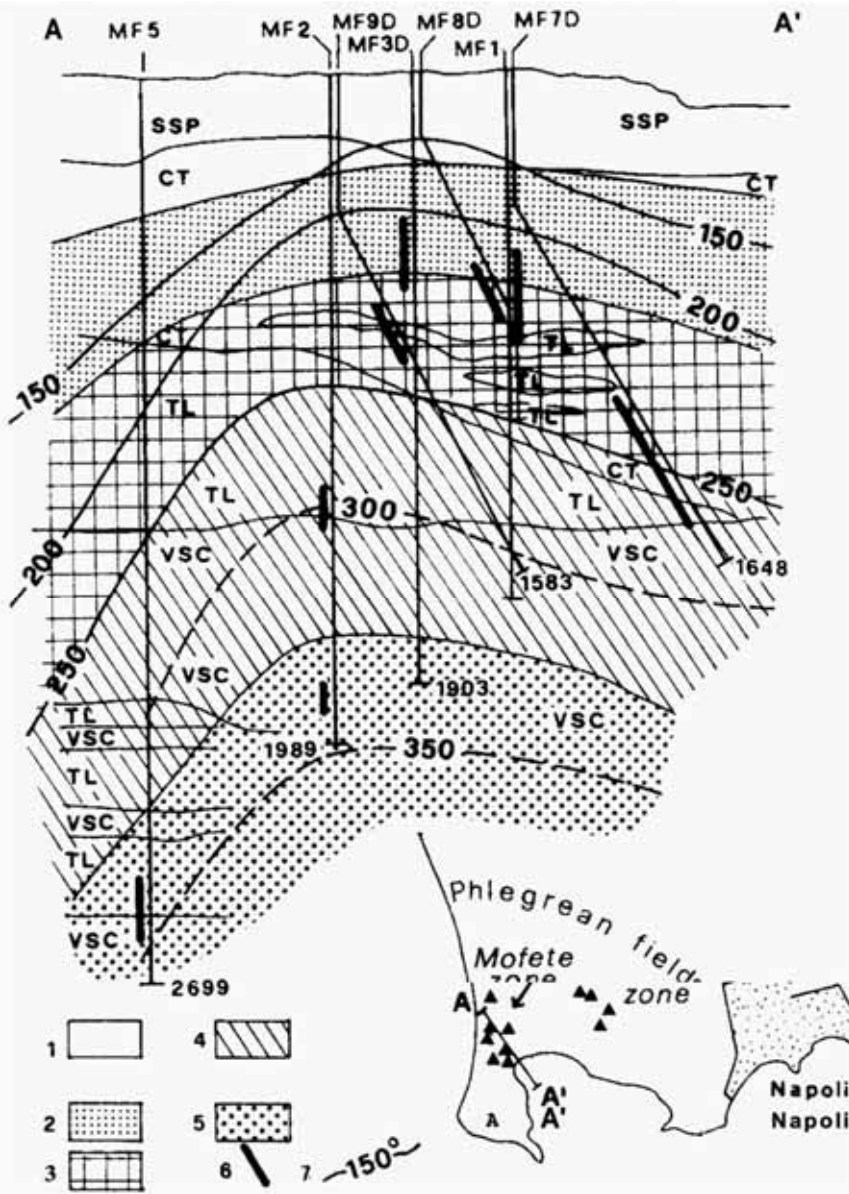
Miococene-Quaternary magmas

In Tuscany-Latium-Campania, magmatic rocks with high lithium content.

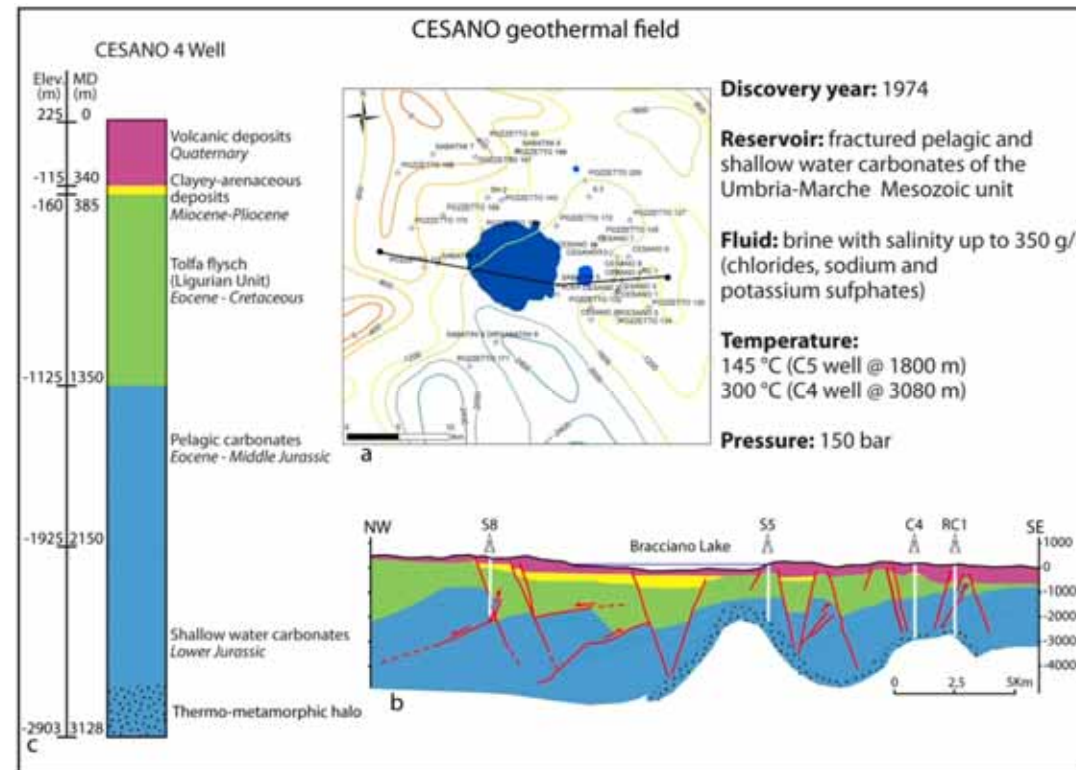


Unconventional resources

Enel Green Power and Vulcan Energy started a partnership to study the potential for geothermal lithium in the Cesano area (Latium)

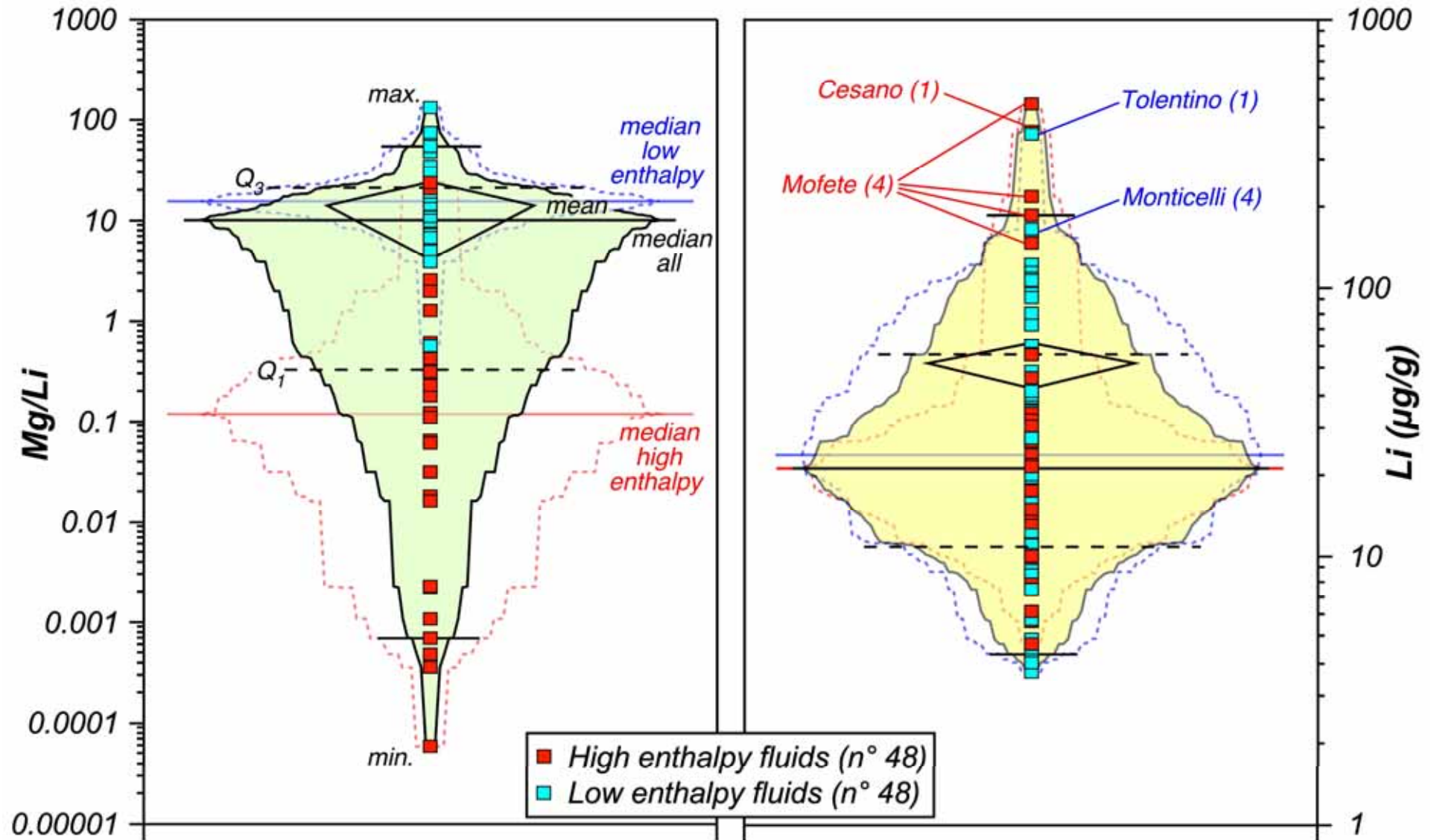


Mofete, Campi Flegrei

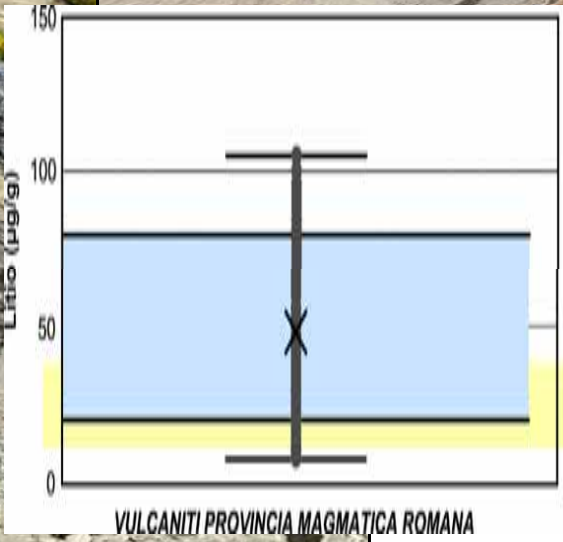


Cesano, Bracciano

Unconventional resources



Volcanic rocks from Latium



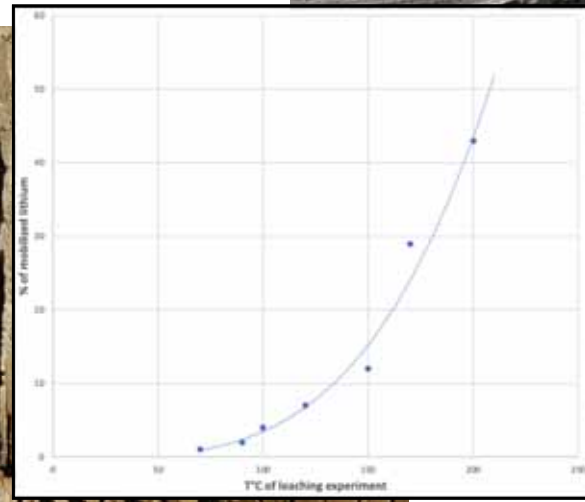
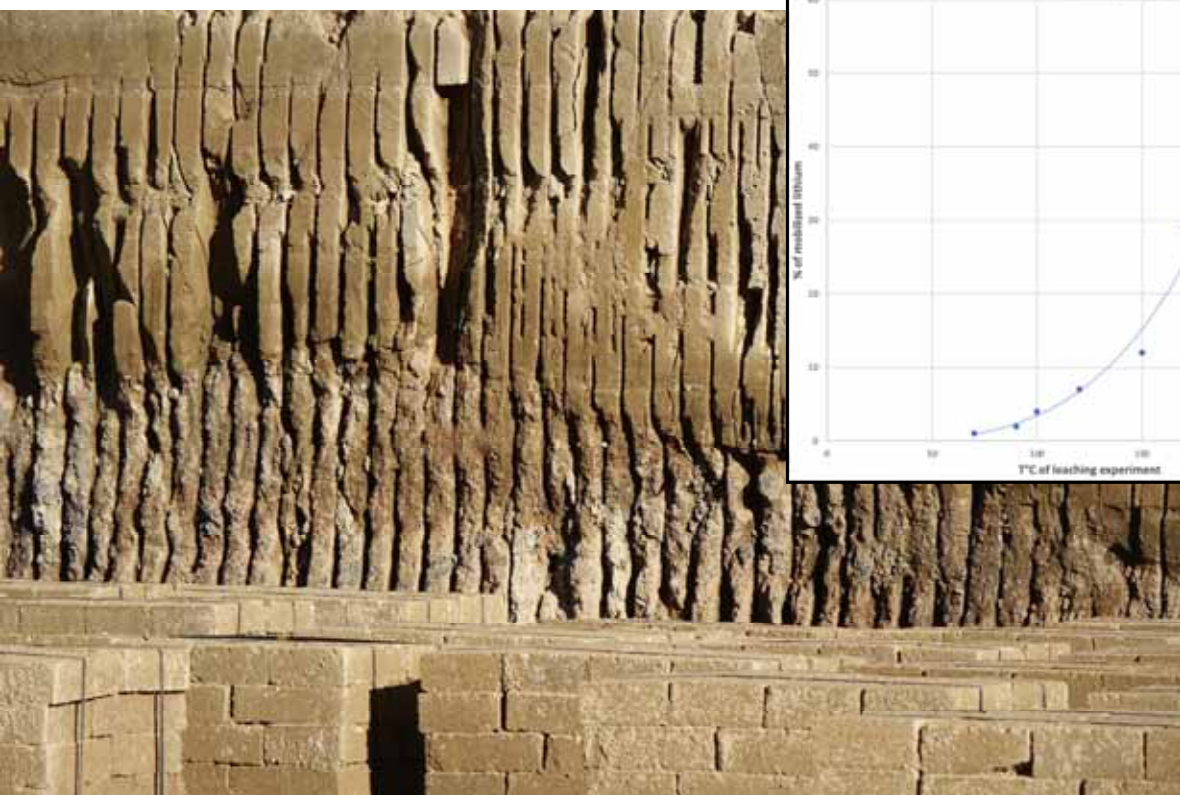
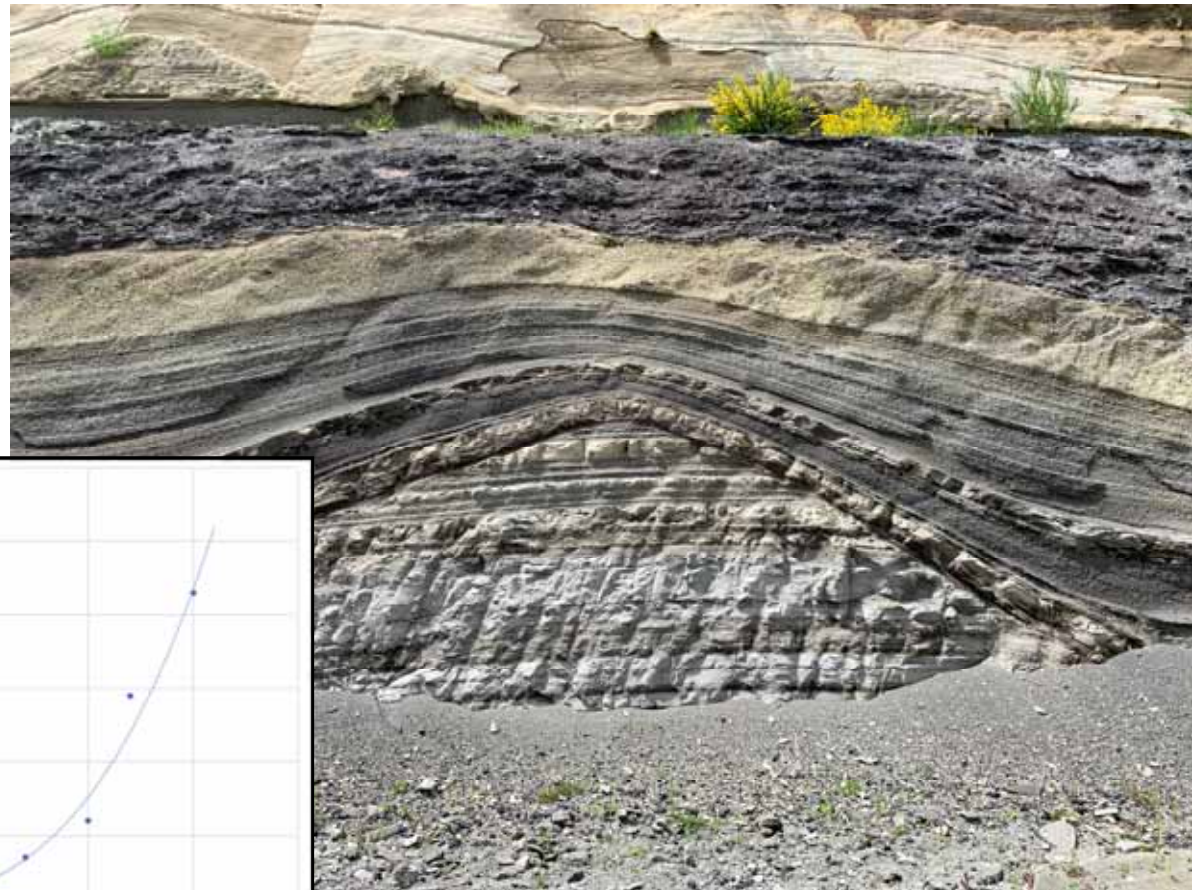
Huge pyroclastic sequences with large volumes of fresh glassy pumices.

These rocks contain up to ≈ 100 mg/kg of lithium

The average (50 mg/kg) is twice the values of «normal» rocks from volcanic arcs.

Volcanic rocks from Latium

Large volumes of pyroclastic rocks have been altered by fluids. The rocks are massively replaced by zeolites (chabazite, philipsite)



Fresh pyroclastic rocks contain up to 100 mg/kg of lithium.

Zeolitization of pyroclastic rocks has mobilized 50-70% of the original lithium content.

What metal in a geothermal system?

Boron is an abundant element in Larderello geothermal fluids because it was easily mobilized at relatively low-T from illite-smectite minerals in the sedimentary covers.

Lithium shows significant concentration in granite minerals (tourmaline, biotite) that cannot be easily leached.

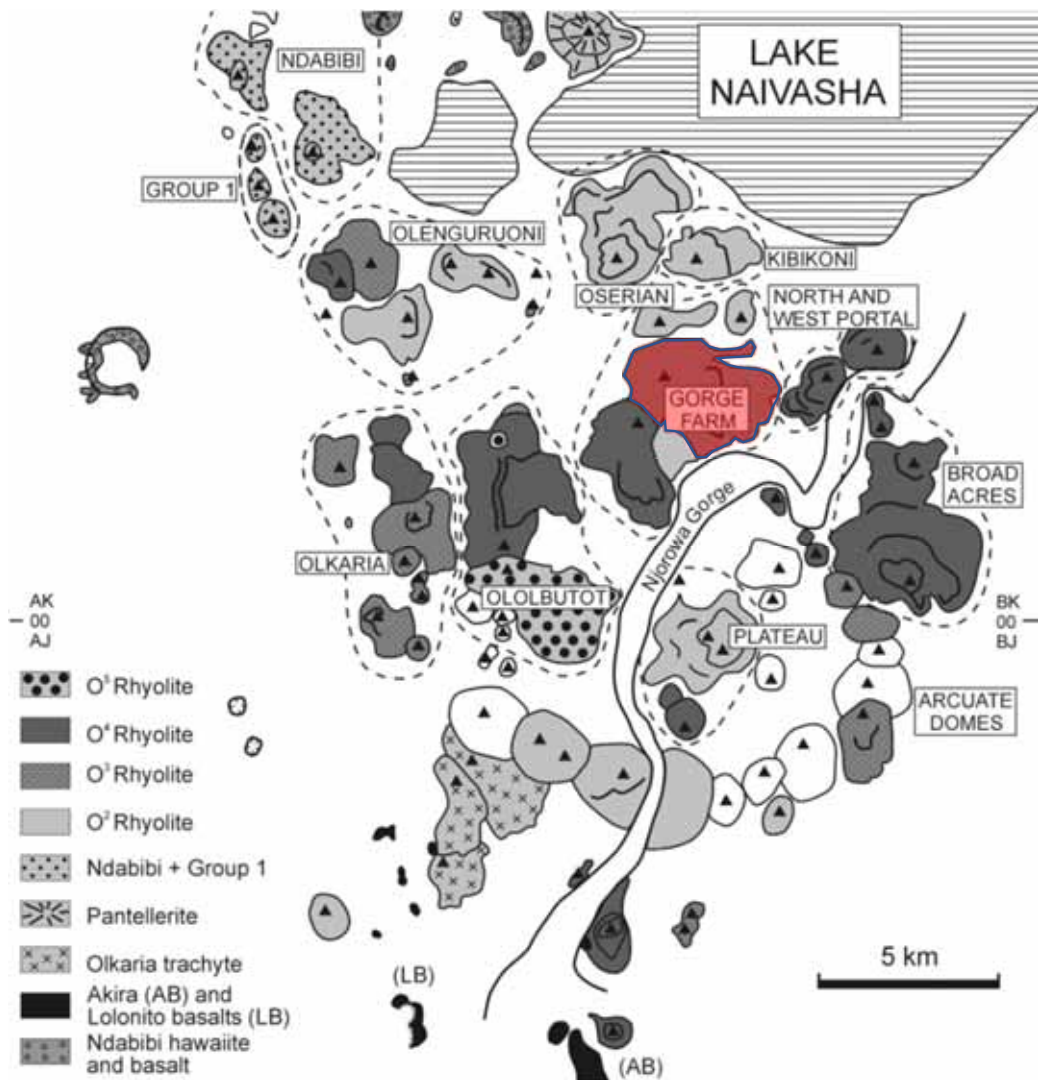
Lithium and boron show very high concentration in Latium-Campania geothermal fluids because they were concentrated in the residual volcanic glass, and easily mobilized by hydrothermal fluids interacting with pyroclastic sequences.

A very detailed knowledge of the geology, petrography, mineralogy and geochemistry of the geothermal areas is crucial to understand the potential for metals in geothermal fluids.

Hydrothermal alteration of rocks provides clues on metal potential in fluids.

What metal for Kenya geothermal systems?

I don't know but don't stop the investigation !



Volcanic glass in Gorge Farm rhyolites has lithium concentration up to 150 mg/kg !

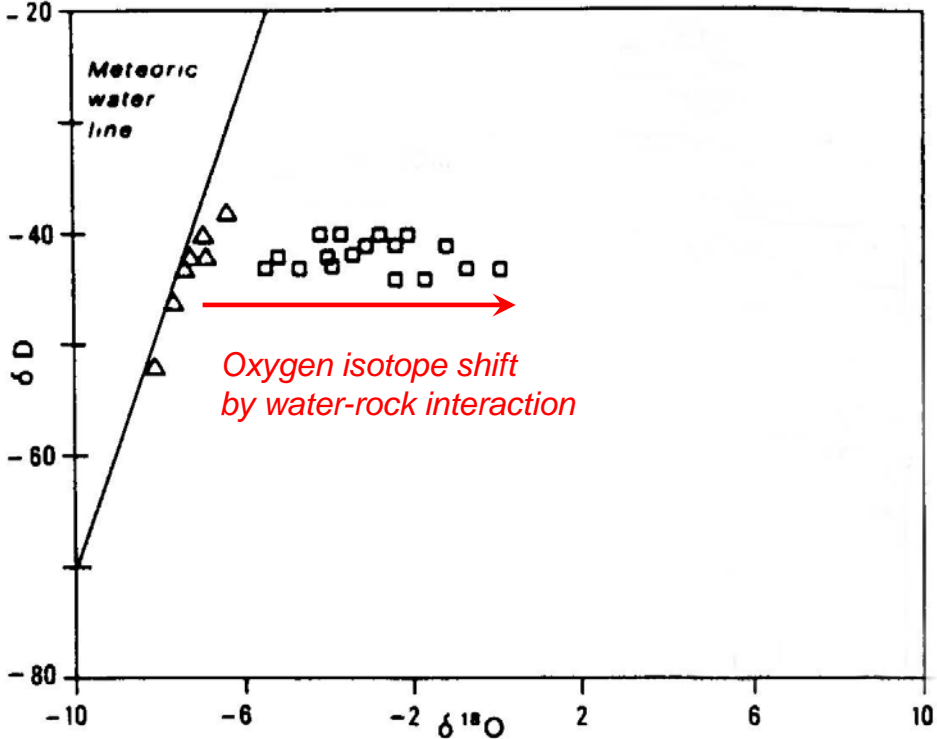
Super-heated steam: modified meteoric water

Average composition of geothermal fluids

H ₂ O ≈ 95 %	NH ₄ ≈ 100-300 ppm
Gases: ≈ 5% (mostly CO ₂)	B ≈ 10-200 ppm
	Cl ≈ 5-30 ppm

O and D isotopes suggest a dominantly meteoric origin of the water. Tritium is absent and there are estimates of storage time greater than 1700 y (see Minissale, 1991).

In spite of the different P, T and host rocks, the steam in the two reservoirs is quite similar in both chemical and isotopic composition.



**IF WATER IS METEORIC,
WHERE DOES THE BORON
COME FROM?**

Boron isotope composition of geothermal fluids

Significant variation and negative correlation between boron content/isotopic composition.

Several sampled wells define a cluster with low B content and very positive $\delta^{11}\text{B}$.

For increasing B content, samples are more dispersed pointing to lower $\delta^{11}\text{B}$ (still positive).

