



Stable and radiogenic isotopes: a geological perspective in Critical Zone studies

Use of isotopes in environmental investigations

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Mission 4 "Education and Research" - Component 2: "From research to business" - Investment
3.1: "Fund for the realisation of an integrated system of research and innovation infrastructures"

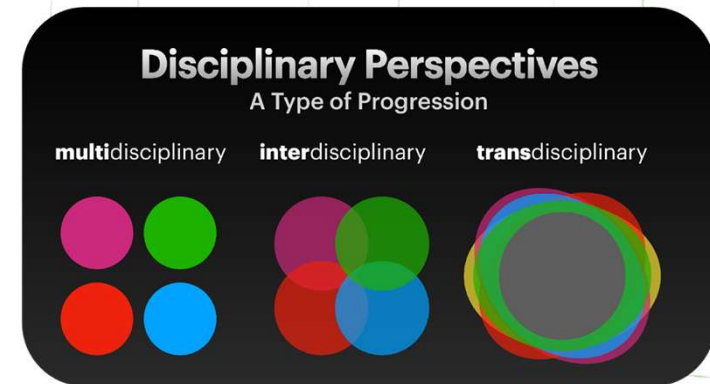


Using Stable and Radiogenic Isotopes in environmental investigations:

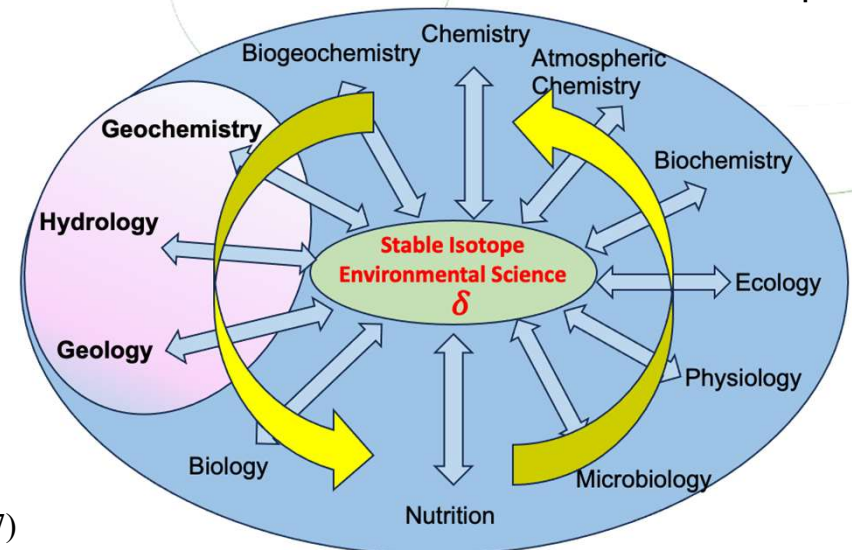
Why a geological and geochemical approach?

- Sources and process identification
- State of the art mass spectrometer allow to produce isotope data in earth science researches and environmental studies
- Multi-isotope toolbox of traditional, non traditional and state of the art isotopic systematics (Sr, Nd, Pb, and B, Cr, Li, and Fe, Ca, Mg....)
- **A multi disciplinary & Interdisciplinarity approach in environmental investigations**

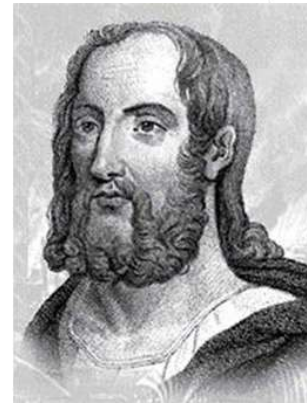
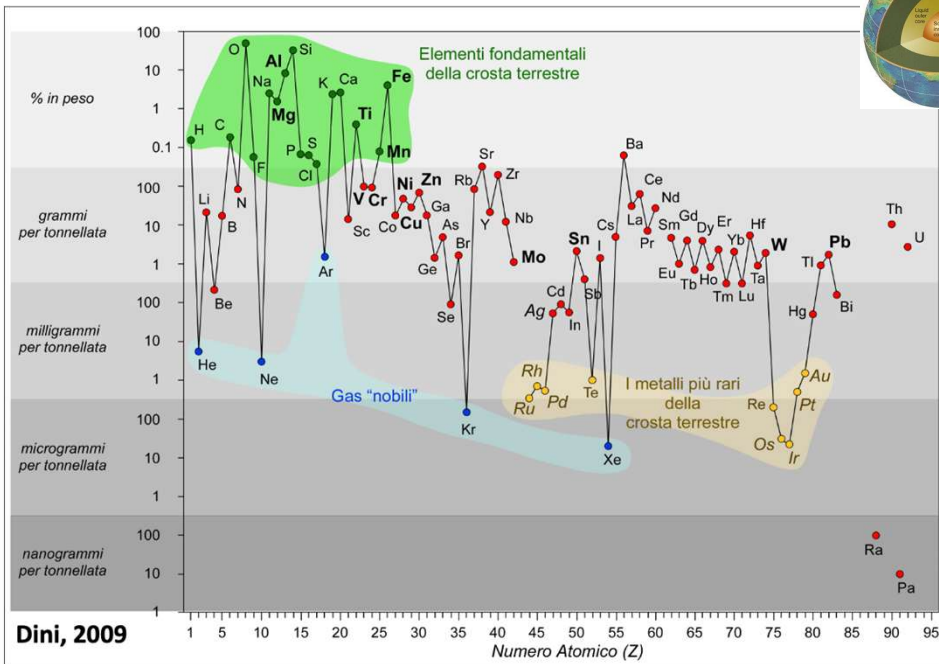
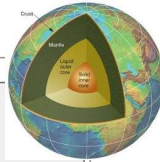
Growing new generations of Critical Zone Scientists (Wymore et al., 2017)



...and social science and additional disciplines



The Geochemical Approach: Elements distribution on earth: Intrusive, sedimentary, metamorphic, volcanic rocks



«Tales sunt aquae qualis est terra per quam fluunt»

«water inherits characteristics of the ground in which it flows»

Vernadsky & Goldschmidt
Chemical analyses of rocks, minerals and soils
Processes governing the distribution of elements in the Earth's System

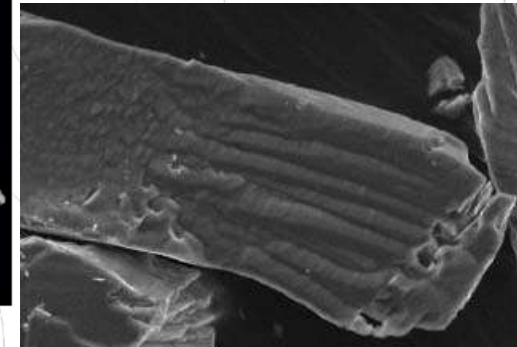
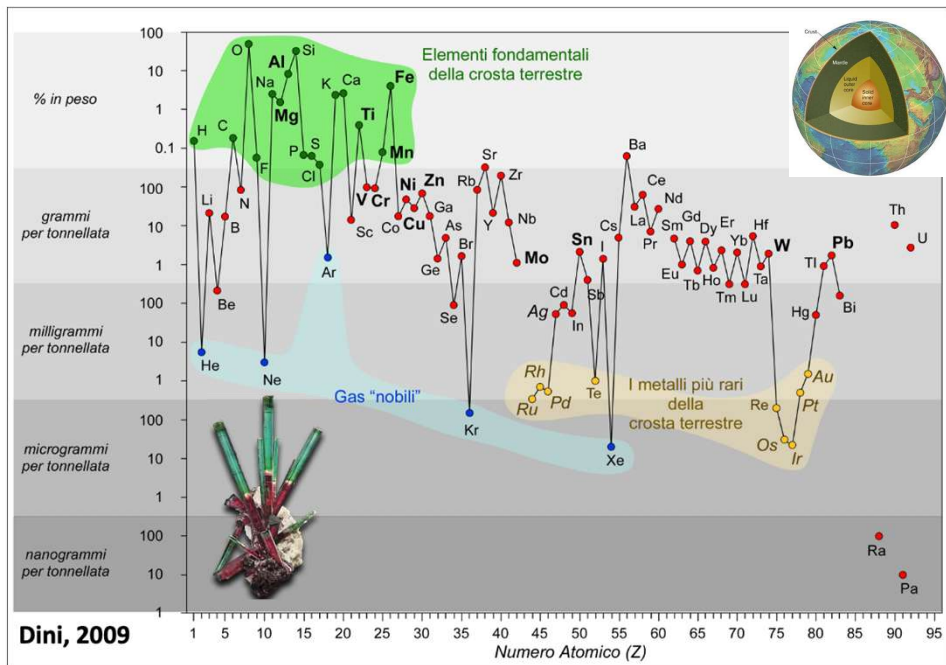


V.M. Goldschmidt
1888 – 1947

V. Vernadsky
1863 – 1945

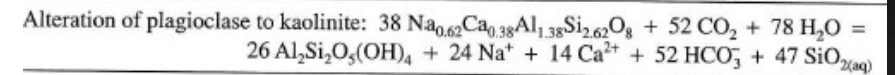
20th century
 A new scientific discipline:
GEOCHEMISTRY

The concepts of Geosphere, Biosphere (1926), Noosphere (including human activities)



ITINERIS

Plagioclasio $(Na,Ca)(Si,Al)_4O_8$

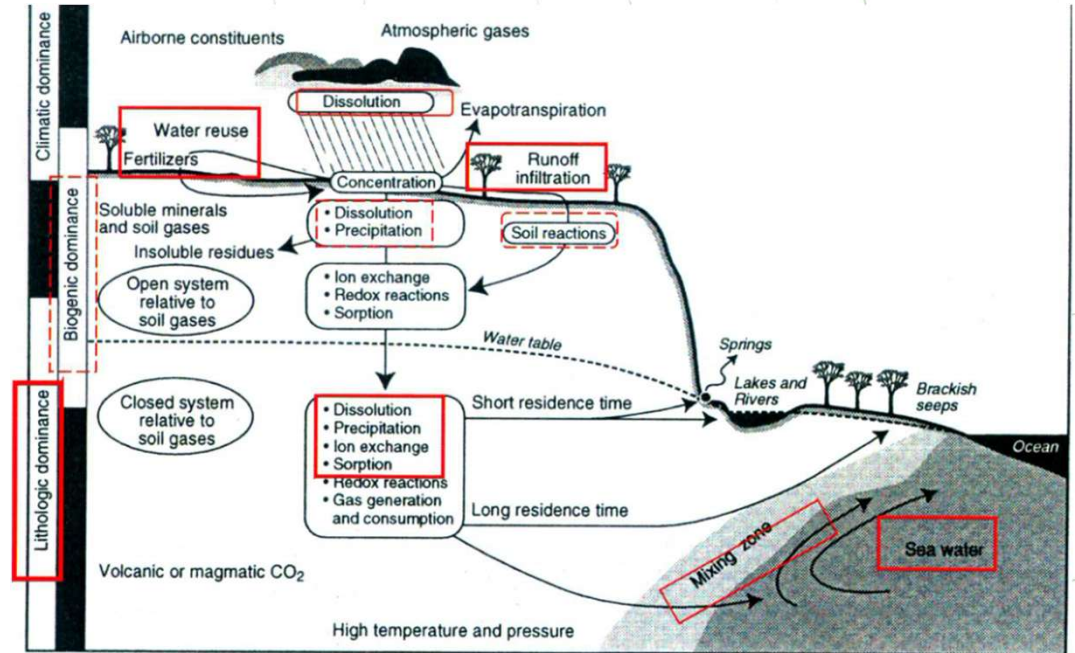
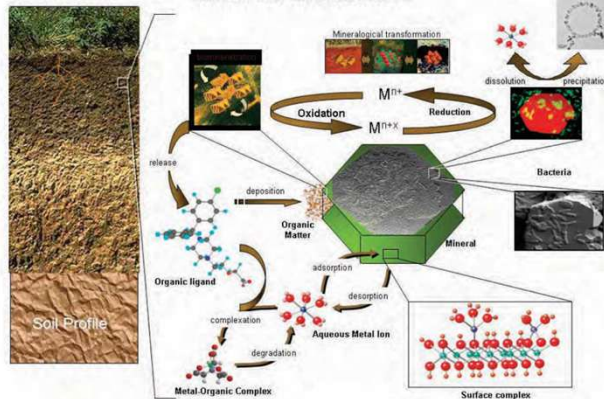


Processes investigated using geochemistry and isotope geochemistry

- 🌐 Chemical weathering
- 🌐 Adsorption
- 🌐 Desorption
- 🌐 Precipitation

- 🌐 Ion Exchange
- 🌐 Redox
- 🌐 Mixing (geogenic and anthropogenic sources)

Intergrated Processes Controlling Elemental Cycling within the Critical Zone



Isotopes of metals and semimetals to investigate the Earth system



STABLE ISOTOPES

RADIOACTIVE ISOTOPES

RADIOGENIC ISOTOPES

Classic now routine

Research

State of the art

1 H 1.008																	2 He 4.00	
3 Li 6.94	4 Be 9.01																	10 Ne 20.18
11 Na 23.00	12 Mg 24.31																	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.71	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80	
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98.91	44 Ru 101.07	45 Rh 102.90	46 Pd 106.40	47 Ag 107.90	48 Cd 112.40	49 In 114.80	50 Sn 118.70	51 Sb 121.80	52 Te 127.60	53 I 126.9	54 Xe 131.30	
55 Cs 132.90	56 Ba 137.30	57 La* 138.90	58 Ce 140.10	59 Pr 140.90	60 Nd 144.20	61 Pm (145)	62 Sm 150.40	63 Eu 152.00	64 Gd 157.30	65 Tb 158.90	66 Dy 162.50	67 Ho 164.90	68 Er 167.30	69 Tm 168.90	70 Yb 173.00	71 Lu 175.00		
87 Fr (223)	88 Ra (226)	89 Ac** (227)	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.00	94 Pu 239.10	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (254)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)		

C "Classical" now routine
U "Research"
Fe State of the art

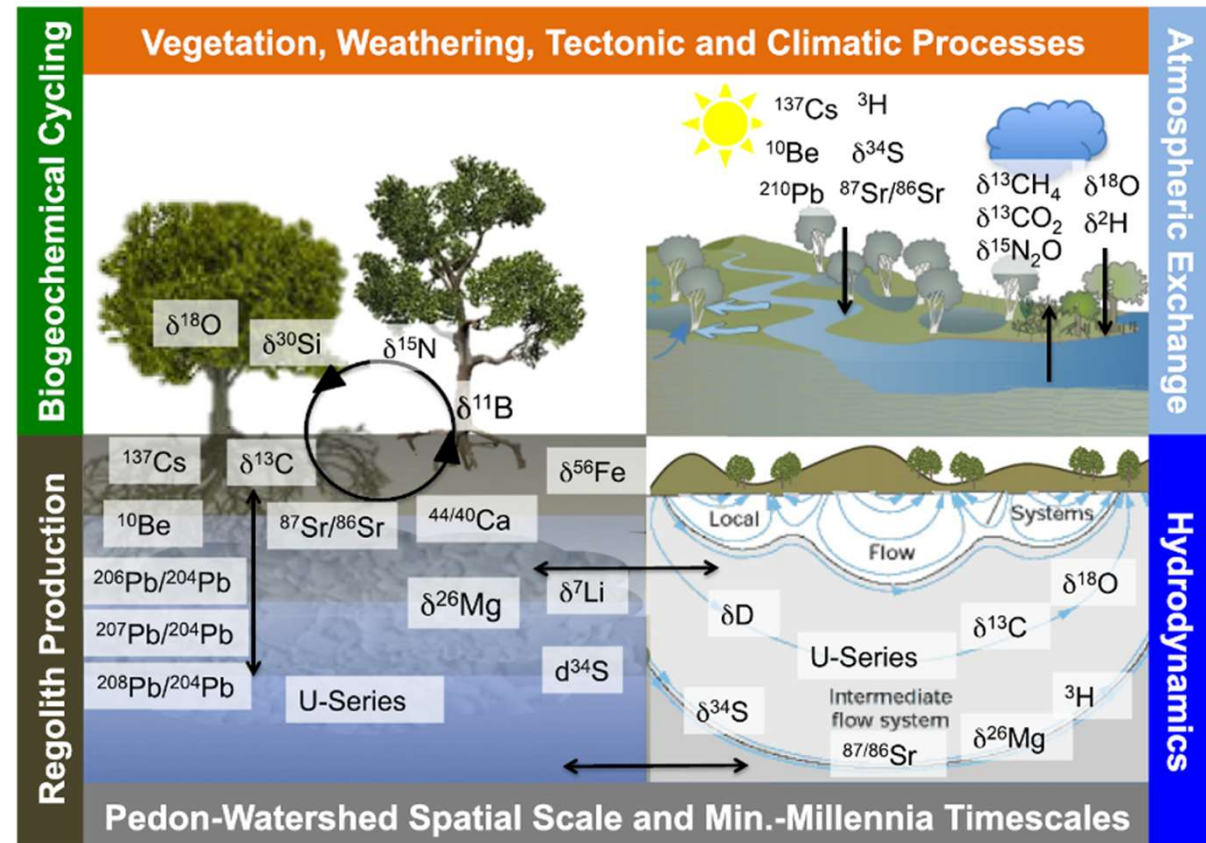
The isotopic systematic of a given element has peculiar geochemical characteristics:
the multi-isotopes toolbox

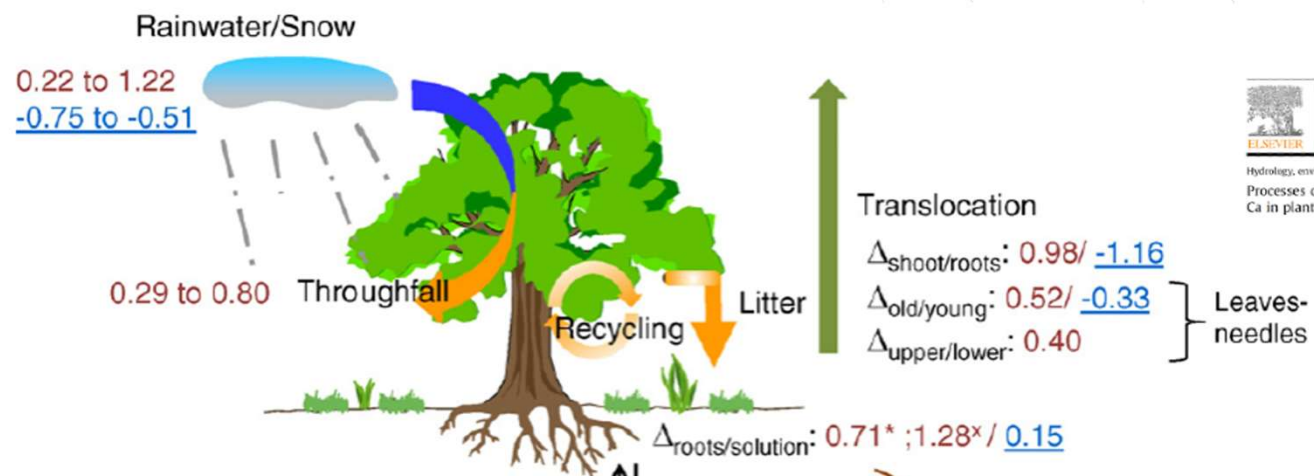


Isotopes to deciphering Critical Zone's processes: the multi-isotope toolbox (Chemical Geology, Vol 445, 2016)

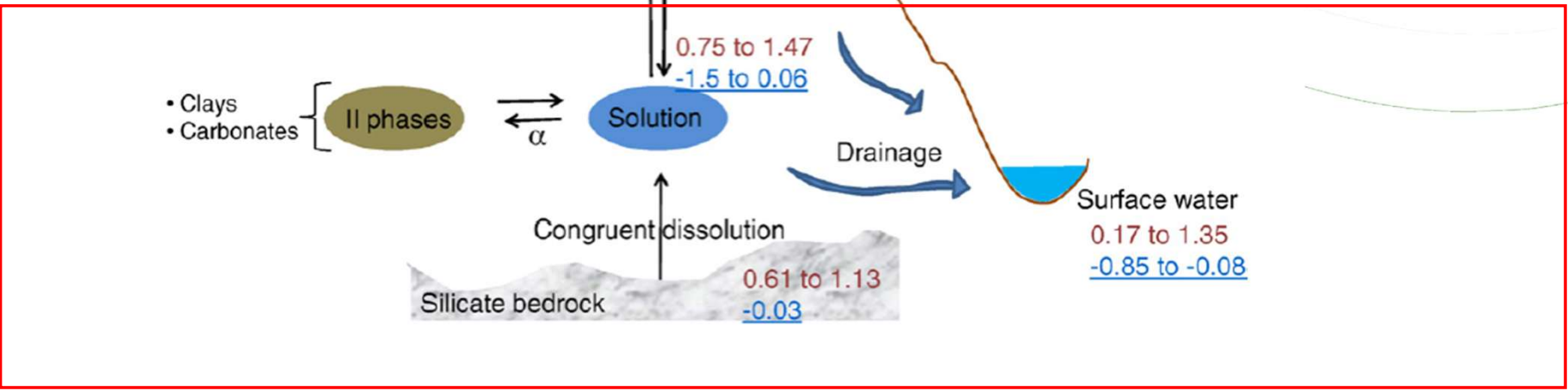
- Li isotopes: ideal tracer for continental weathering (not affected by phytoplankton or plants grow)
- Mg: ideal to trace the origin of dolostone and weathering
- Cu and Zn isotopes: contrasting behaviour. Preferential release of the heavy isotopes into fluids during weathering of chert and shales (global cycling of Cu and Zn into the ocean), not observed for Zn in basal and granitoid environment
- Mo isotopes: Influx from a combination of precipitation, volcanic fog, anthropogenic inputs as well as Mo-organic matter interactions
- Uranium-series: tracer of residence time and mixing of different water sources
- Sr and Ca isotopes: interaction between slower chemical weathering processes and more rapid, biologically driven cycling between soil and biomass

Synthesizing multiple isotope proxies to elucidate Critical Zone's processes across timescales in a temperate forested landscape. **Sullivan et al., 2016**





Geochemistry



Isotope investigations

Understanding the isotope fractionation mechanisms during Earth surface processes is the prerequisite for using isotopes in Environmental, Hydrological and Critical Zone studies

Only a very precise determination of isotopic compositions allows quantification of isotopic fractionations in nature

This was not possible in the past due to the lack of analytical techniques

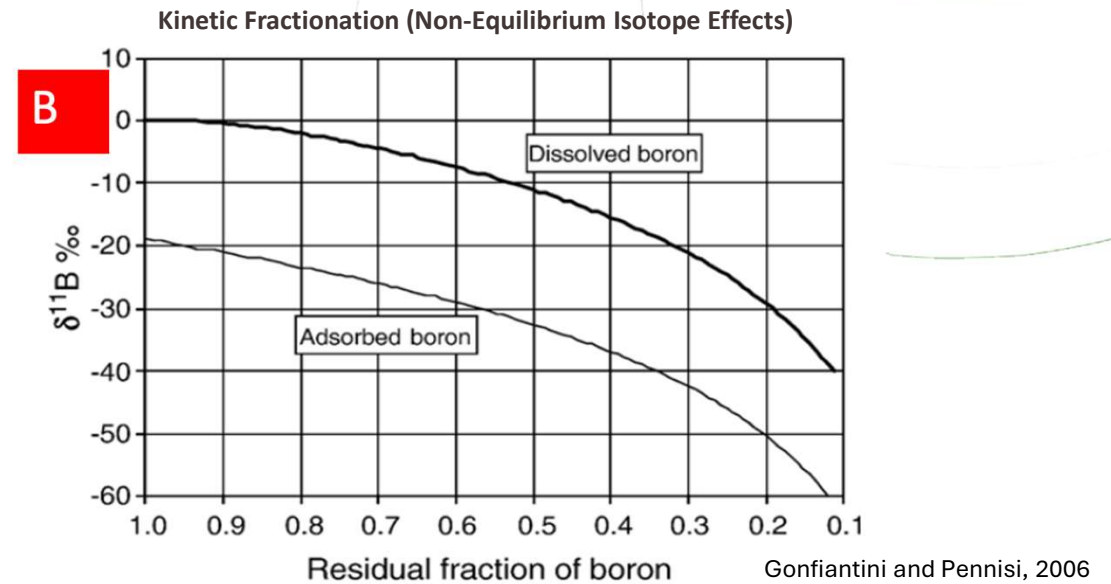
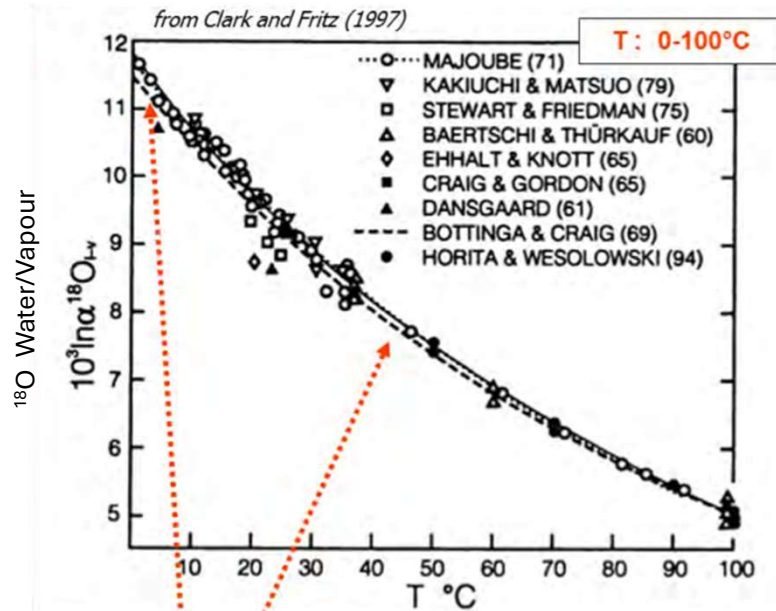
Teng & Ma, Chemical Geology 2016

Research questions cover different space and time scales

Most isotopic fractionations recognized in nature take place near the Earth's surface

Isotopic fractionation occurs in any thermodynamic reaction due to difference in the rates of reaction for different molecular species. The result is disproportionate concentration of one isotope over the other on one side of the reaction

Isotopic fractionation being more significant in low-temperature environments, most isotopic fractionations recognized in nature take place near the Earth's surface



Isotopic systematics of B, Sr and Li

$\delta^{11}\text{B}\text{‰}$

$$\delta^{11}\text{B} = \left[\frac{(^{11}\text{B}/^{10}\text{B})_{\text{sample}}}{(^{11}\text{B}/^{10}\text{B})_{\text{standard}}} - 1 \right] \times 1000$$

B:	¹¹ B	¹⁰ B	Stable
	81.02. %	18.98%	

The relatively light Li (⁶Li and ⁷Li) and B (¹⁰B and ¹¹B) isotopes have a 17% and 10% mass difference, respectively and undergo significant stable isotope fractionation

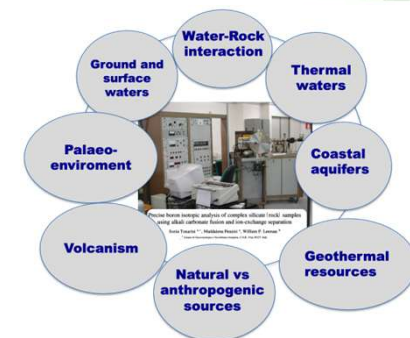
In contrast, the heavy isotopes ⁸⁷Sr and ⁸⁶Sr have a 1.1% mass difference and do not exhibit detectable mass fractionation

$^{87}\text{Sr}/^{86}\text{Sr}$

Sr:	⁸⁸ Sr	⁸⁶ Sr	⁸⁷ Sr	⁸⁴ Sr	Radiogenic
	82.56%	9.86%	7.02%	0.56%	

$\delta^7\text{Li}\text{‰}$

Li:	⁷ Li	⁶ Li	Stable
	92.48%	7.52%	

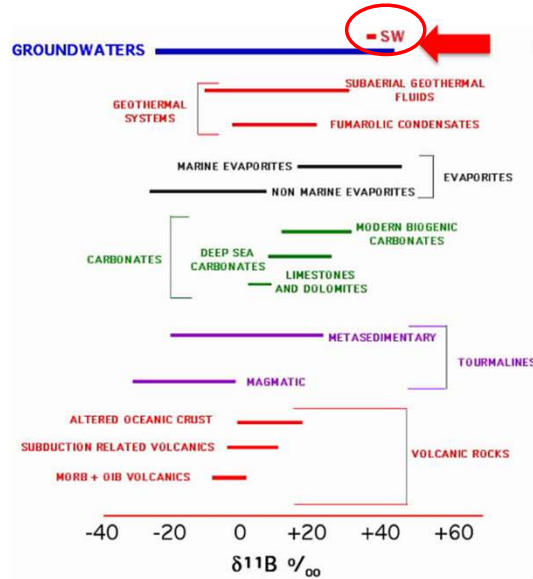


Boron Isotopic systematic

"Because boron is highly soluble in aqueous fluids, its geochemistry depends (and potentially tracks) the roles of such fluids in the mantle, lithosphere, and hydrosphere"

Leeman & Sisson, 2006

$$\delta^{11}\text{B} = \left[\frac{(^{11}\text{B}/^{10}\text{B})_{\text{sample}}}{(^{11}\text{B}/^{10}\text{B})_{\text{standard}}} - 1 \right] \times 1000$$



Boron reservoirs

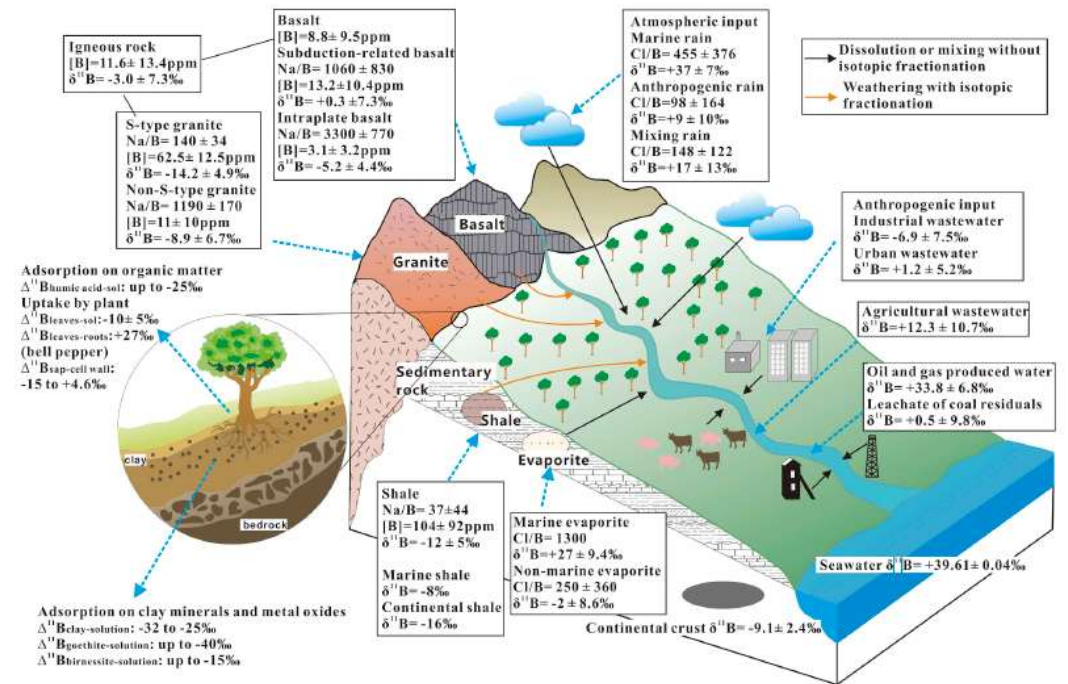


Fig. 1. Schematic of the main sources of B input into rivers and B isotopic fractionation in regolith. The uncertainty of $\delta^{11}\text{B}$ values in each reservoir is expressed as one standard deviation (1SD). The estimated $\delta^{11}\text{B}$ values of seawater and the continental crust are from Foster et al. (2010) and Marschall et al. (2017), respectively. For atmospheric inputs, see Section 2.1; for evaporites, see Section 2.3; for igneous rocks, see Section 2.4.1 (for granites, see Section 2.4.1.1 and for basalts, see Section 2.4.1.2); for shales, see Section 2.4.2; for anthropogenic inputs, see Section 2.5; and for adsorption and plant uptake, see Section 3.2.2.

440

Mao et al., 2019

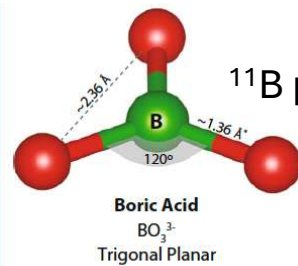
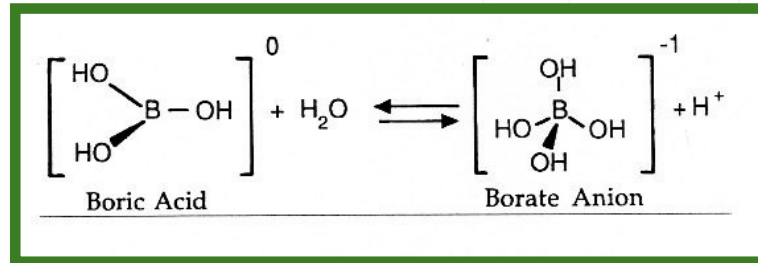
De Hoog and Savov, 2018

Boron: isotopes fractionation in water

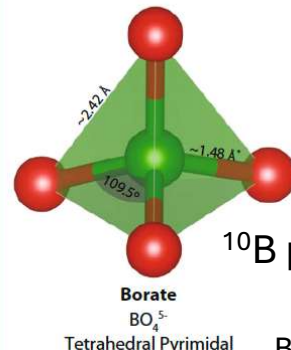
There is a broad agreement that the boron isotopic composition of groundwater is controlled both by the host bedrock mineralogy and processes fractionating boron isotopes, mainly due to sorption

In fluids and rocks, boron is always bound to oxygen

In fluids, the distribution of $B(OH)_3$ and $B(OH)_4^-$ species is controlled by mainly the pH



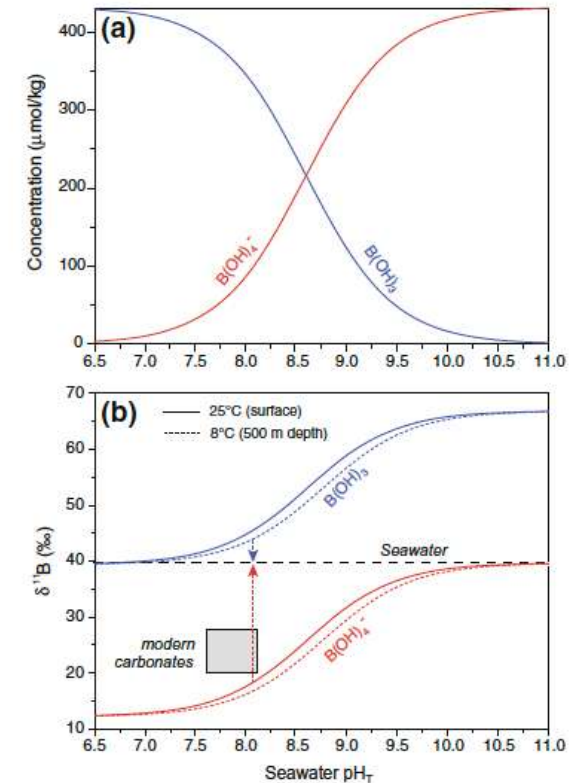
^{11}B preferentially enters trigonal sites



^{10}B preferentially enters tetrahedral sites

Branson, 2018

Large fractionation due large mass difference between ^{10}B - ^{11}B



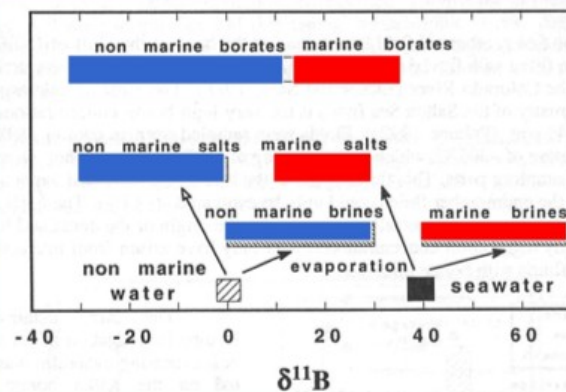
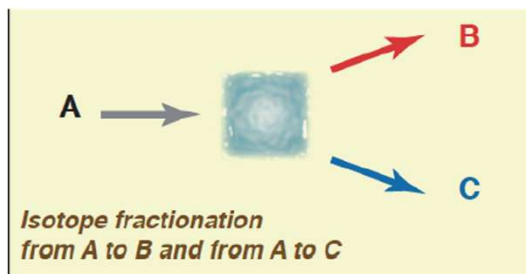
Malcolm et al, 2018

$\alpha = 0.981$ (19‰)

Principle of B-isotope fractionation

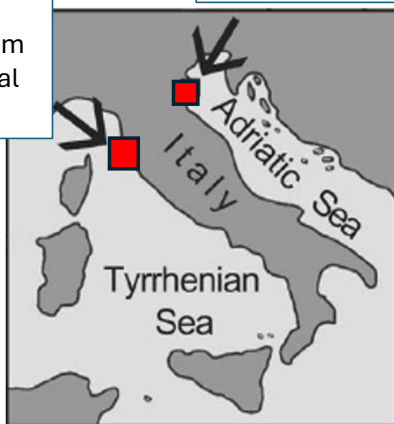
Isotope fractionation

evaporation/condensation
 sorption/desorption,
 mineral precipitation,..

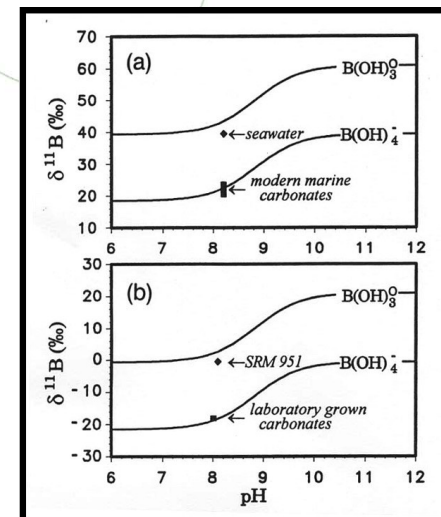


Val di Cornia
 B-rich
 waters from
 geothermal
 fluids

Marine Coastal
 Lagoon, Ravenna



Core / sample / palaeoenvironment / analyzed taxon	δ ¹¹ B	permil rsd
sample at -19.60 m core depth: lagoon with high freshwater influx		
analyzed taxon: <i>Cerastoderma glaucum</i>	-14.1	0.50
<i>C. glaucum</i> (analyses repeated)	-12.6	0.62
sample at -20.60 m core depth: lagoon with low freshwater influx		
analyzed taxon: <i>Cerastoderma glaucum</i>	-9.1	0.60
<i>C. glaucum</i> (analyses repeated)	-9.2	0.60
<i>C. glaucum</i> (analyses repeated)	-10.4	0.37
analyzed taxon: <i>Cerithium vulgatum</i>	-19.6	0.43
<i>C. vulgatum</i> (analyses repeated)	-20.0	0.65
sample at -174.80 m core depth: lagoon with high freshwater influx		
analyzed taxon: <i>Cerastoderma glaucum</i>	5.0	0.52
<i>C. glaucum</i> (analyses repeated)		
analyzed taxon: <i>Bitium reticulatum</i>	1.3	0.44
sample at -174.90 m core depth: lagoon with high freshwater influx		
analyzed taxon: <i>Cerastoderma glaucum</i>	13.1	0.44
<i>C. glaucum</i> (analyses repeated)	13.4	1.02



Principle of B-isotope fractionation

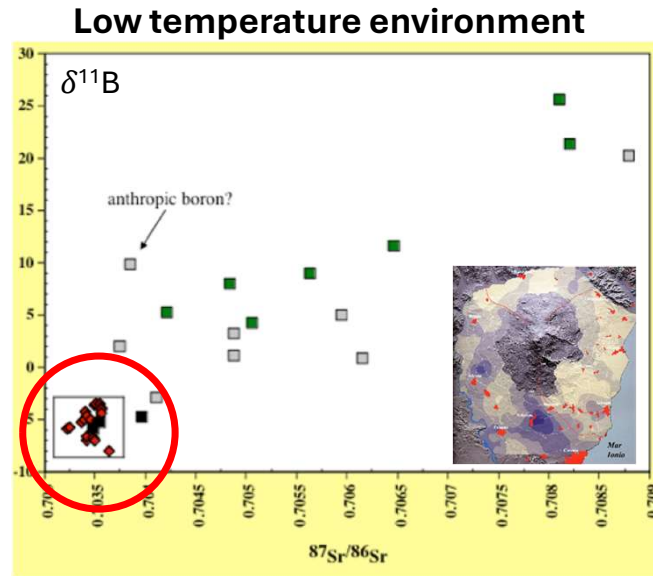
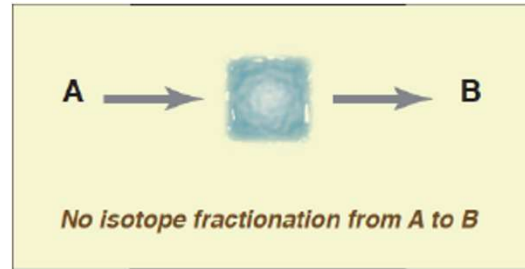
Isotope fractionation

processes:
 evaporation/condensation
 sorption/desorption,
 mineral precipitation,

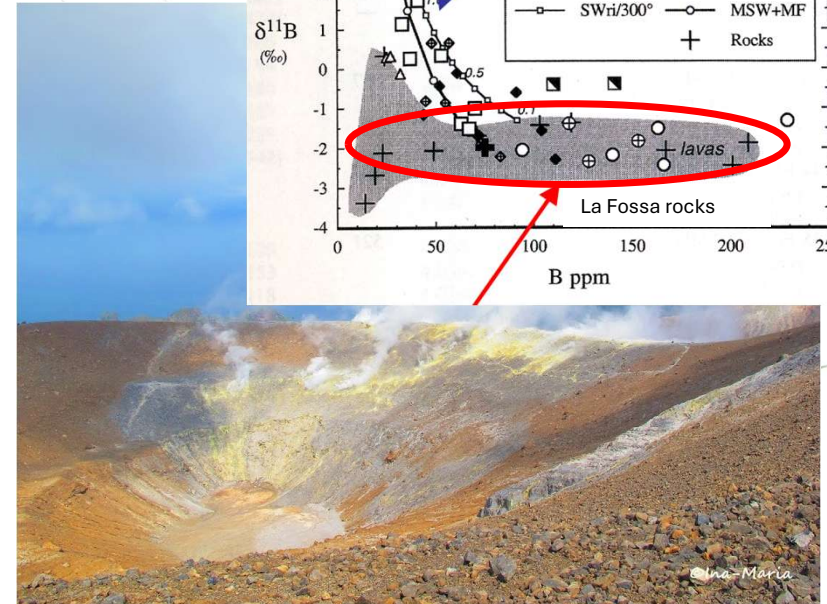
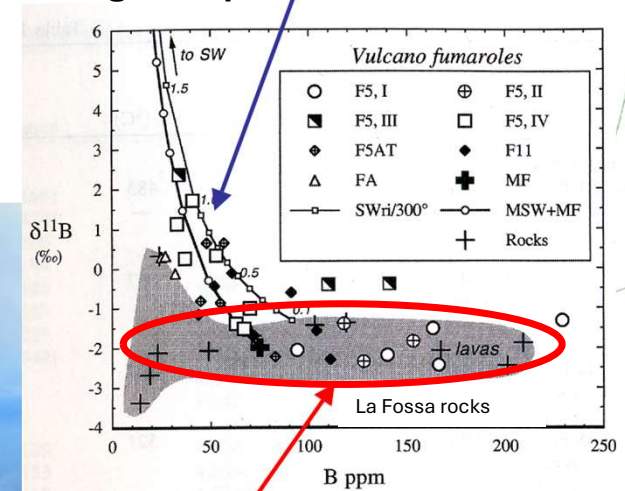
footprinting

Rocks, waters, contaminants, ect
 Lack of fractionation during given processes (biological or other)

Etnean's basalts
 $\delta^{11}\text{B} = -5$ permil
 $^{87}\text{Sr}/^{86}\text{Sr} = 0.7033$



High temperature environment



Research questions: the different space and time scales



🌐 Dissolved boron budget from global riverine input

🌐 Wide range of values of $\delta^{11}\text{B}$, due to variable lithogenic (silicate and evaporite), atmospheric, and anthropogenic inputs

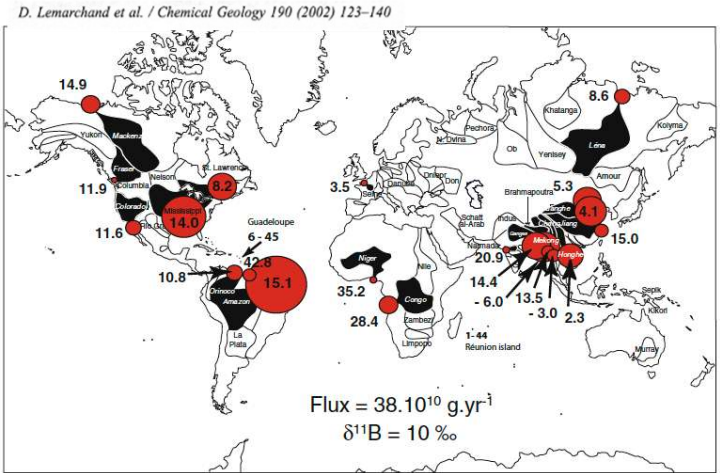
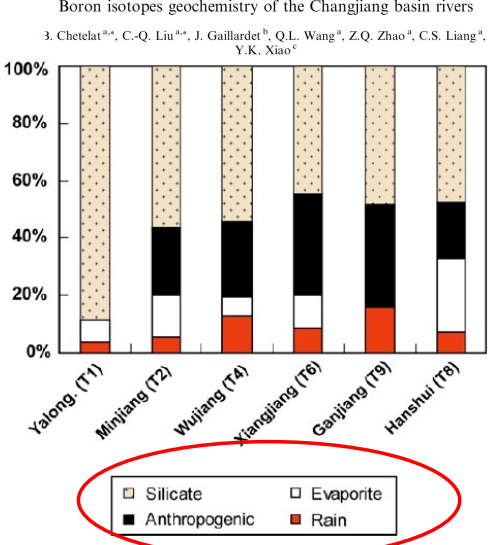


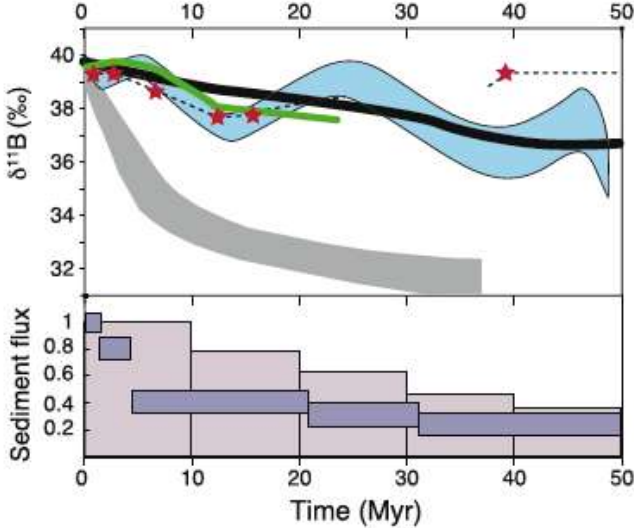
Fig. 7.11 Global riverine input of boron to the ocean. Database from Lemarchand et al. (2000) and Spivack et al. (1987) updated by more recent studies of Lemarchand and Gaillardet (2006), Chetelat et al. (2009), Louvat et al. (2011, 2014) for Lesser Antilles and Réunion Islands. Note the ^{11}B enrichment in tropical surface waters



Carbonate input is negligible

CALCULATED COUPLING WATER CHEMISTRY & B- ISOTOPES

SECULAR VARIATION OF $\delta^{11}\text{B}$ IN SW

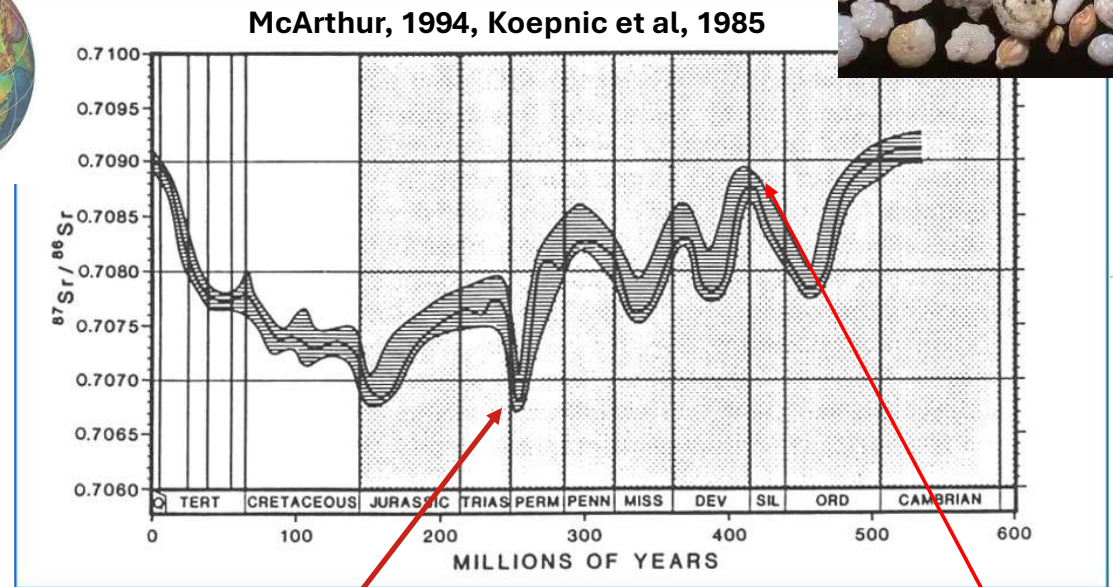
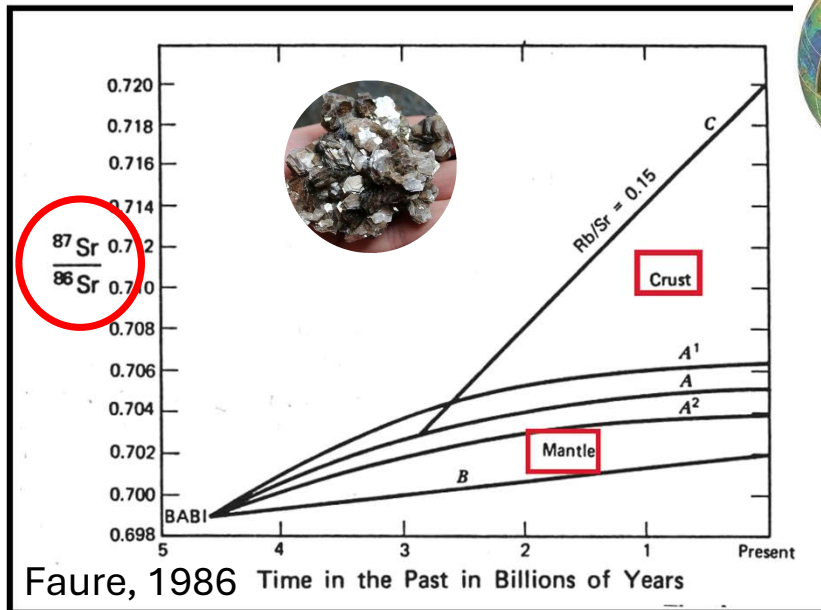
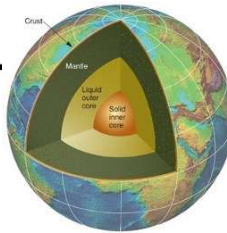
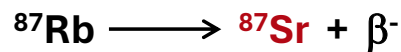


Gaillardet and Lemarchand, 2018

Strontium: isotope variation in geological reservoirs

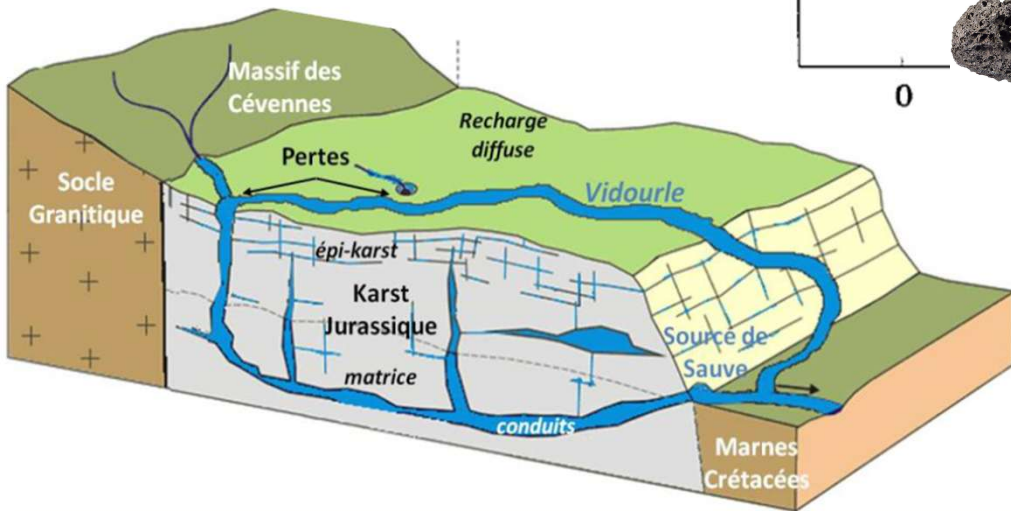
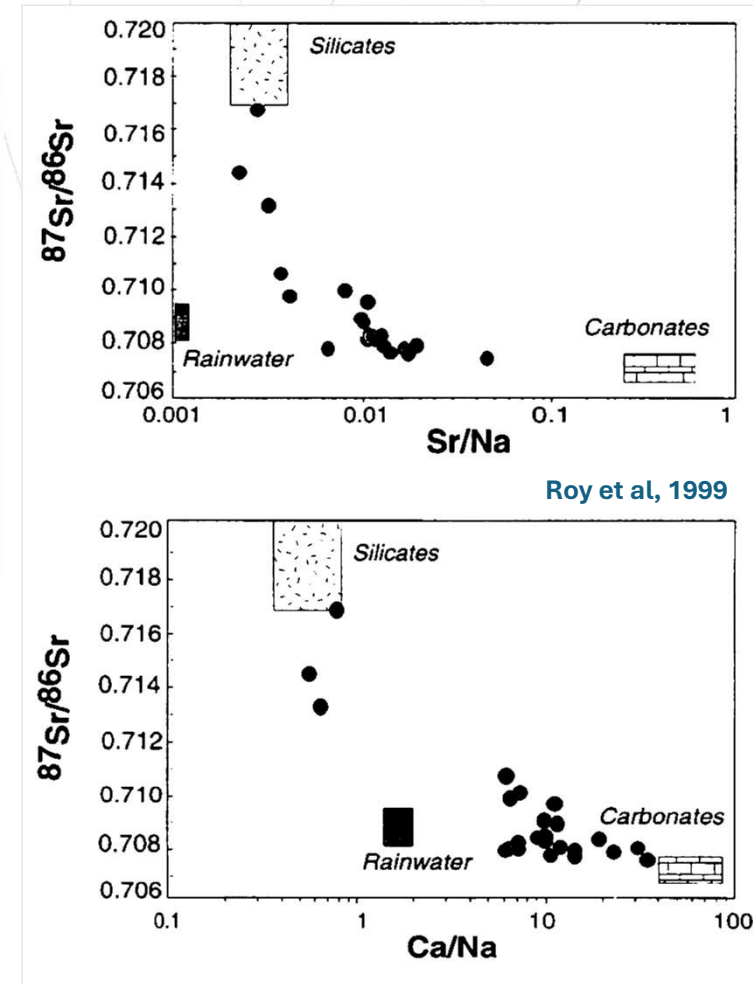
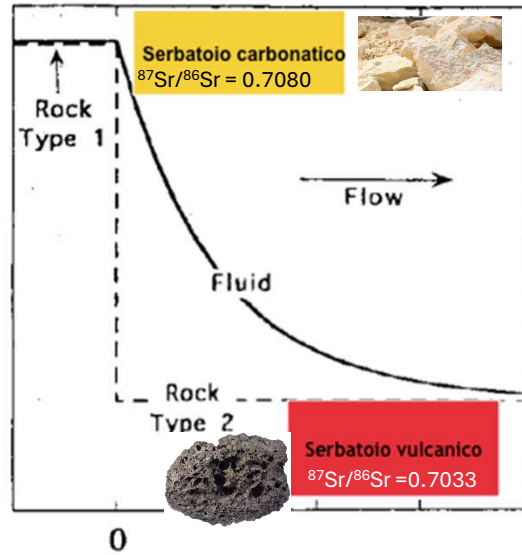
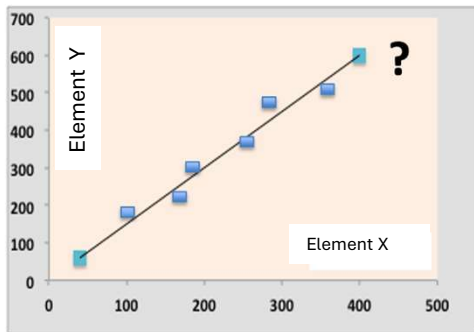


Strontium (Sr) is an ever-present trace element within rocks, water, soil and plants. It has four naturally occurring isotopes, ^{84}Sr , ^{86}Sr , ^{87}Sr , and ^{88}Sr , where ^{87}Sr is a radiogenic product of ^{87}Rb through beta decay with a half-life of **48.8 billion years**



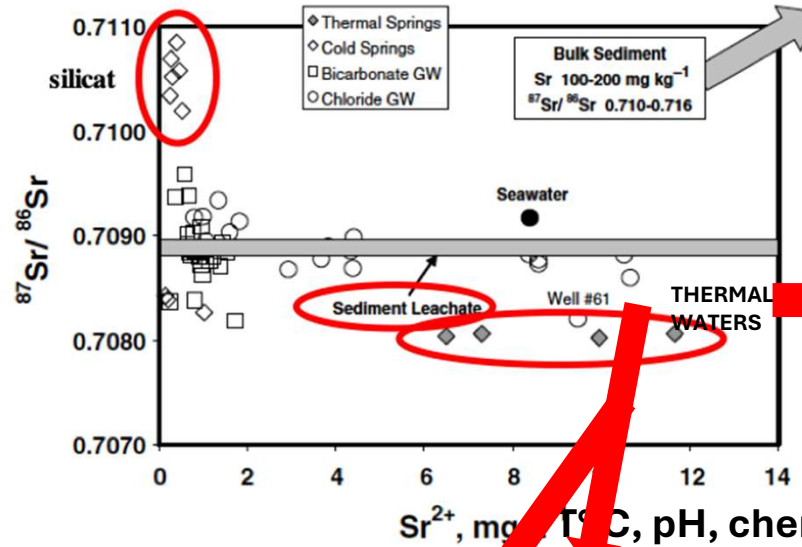
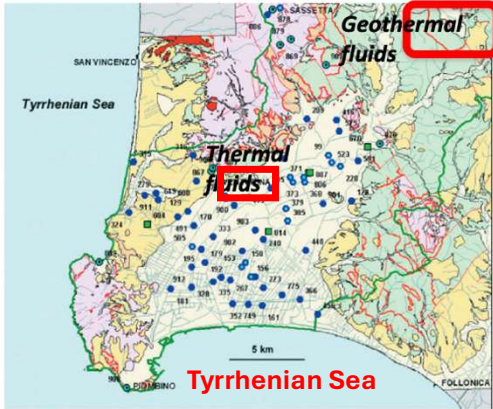
Oceanic ridge $^{87}\text{Sr}/^{86}\text{Sr} \sim 0.703$ Continental crust (rivers)

Using water chemistry and Sr-isotopes to determine the Sr source/s and mixing processes in groundwater

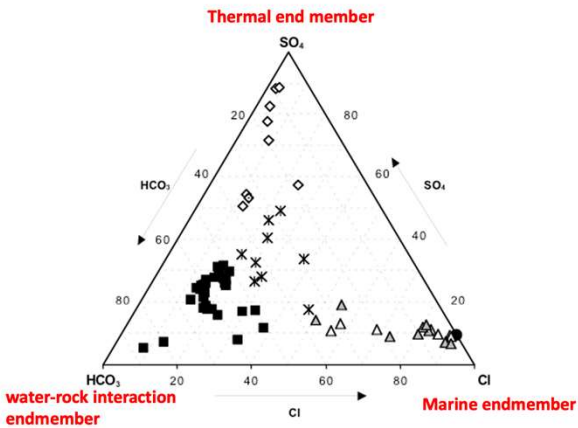


Contribution of DEEP SOURCES to the shallow environment

discharge of thermal springs induced by «piston effect» during high-rain periods



Sr²⁺, mg kg⁻¹, T°C, pH, chemistry, redox state, bacteria...

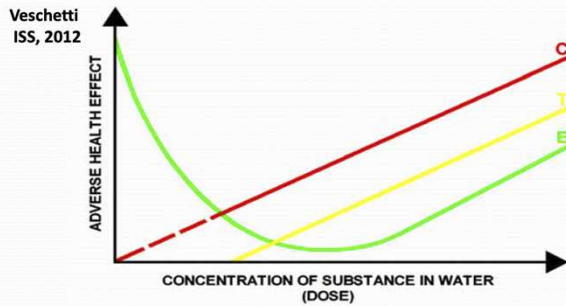


ISOTOPE GEOLOGY vs CROPS

- Understanding the mechanism that control element transfers between vegetation and soil is fundamental to constrain the biological cycle of the nutrients and therefore limiting the use of fertilizer (boron) and maintaining favorable conditions for plant growth



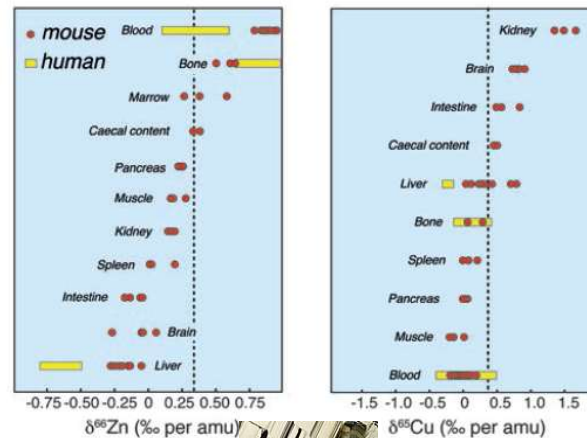
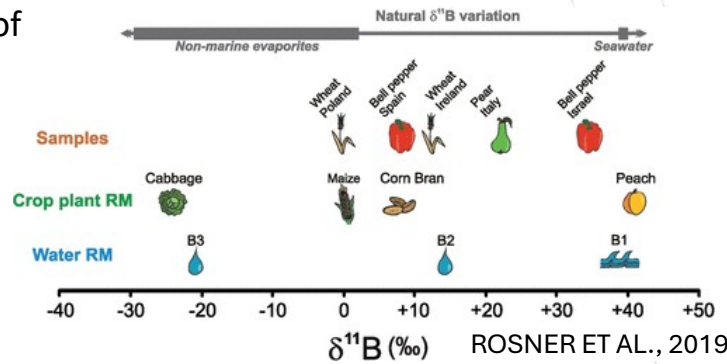
Paracelsus 1493 - 1541



C= Carcinogenic substances (with no threshold effect)

T= Toxic substances (with threshold effect)

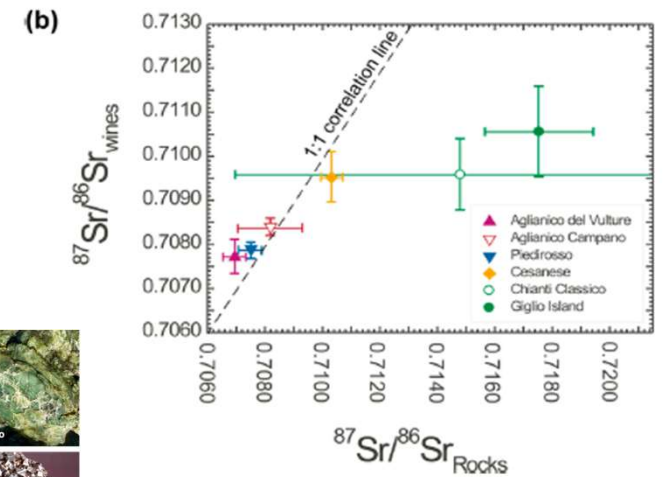
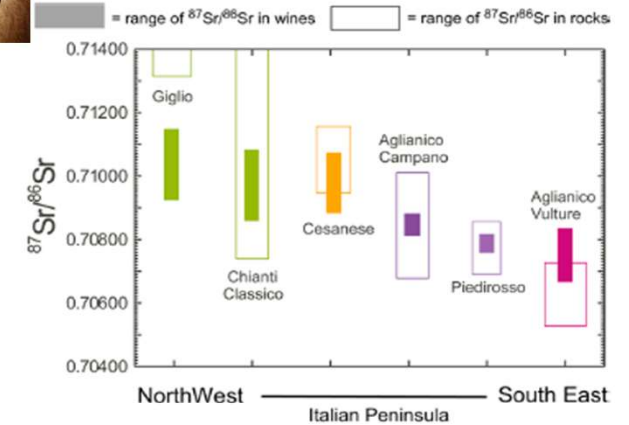
E = Essential substances (nutrients)



Albarede et al., 2016

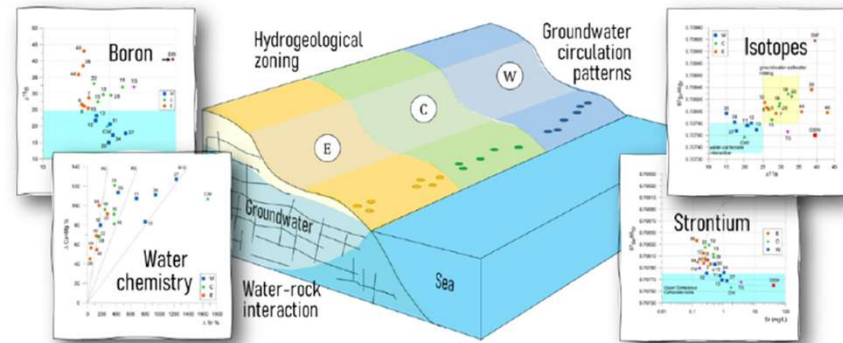


Ni, Cr, As, Thallium in barite-pyrite-iron oxide deposit

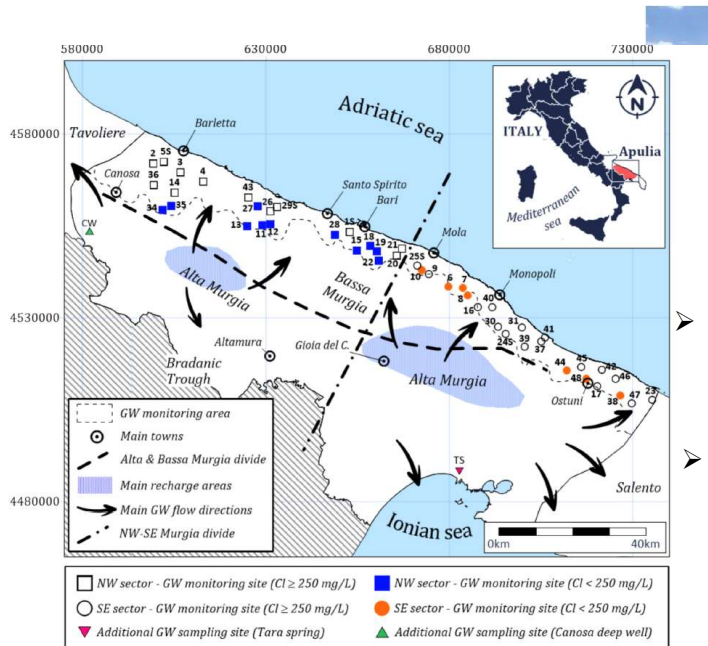


Evaluating complex groundwater circulation patterns, hydrogeological zoning, and water-rock interaction

- Murgia, Apulia karst aquifer
- The chemical & multi-isotopic approach (O, H, B, Sr)
- Establishing the origin of the water molecule, define water/rock interaction, and the sources of salinity (present or fossil sea water)



Salvadori et al., 2024



O, H: Identification of recharge zones

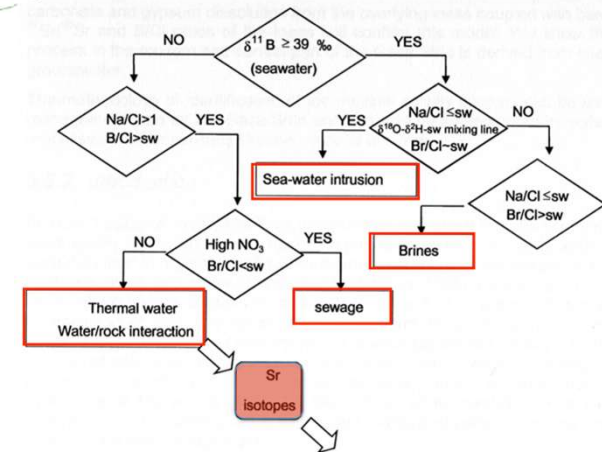
¹ H	² H	¹⁶ O	¹⁷ O	¹⁸ O
1.00794	2.0141	15.9949	16.9991	17.9991
99.985%	0.015%	99.76%	0.04%	0.20%

B, Sr: Water/Rock interaction (lithotype identification, adsorption processes, desorption)

⁸⁴ Sr	⁸⁶ Sr	⁸⁷ Sr	⁸⁸ Sr
83.9134	85.9093	86.9089	87.9056
0.56%	9.86%	7.00%	82.58%

B, Sr: Origin of salinization (present day vs fossil)

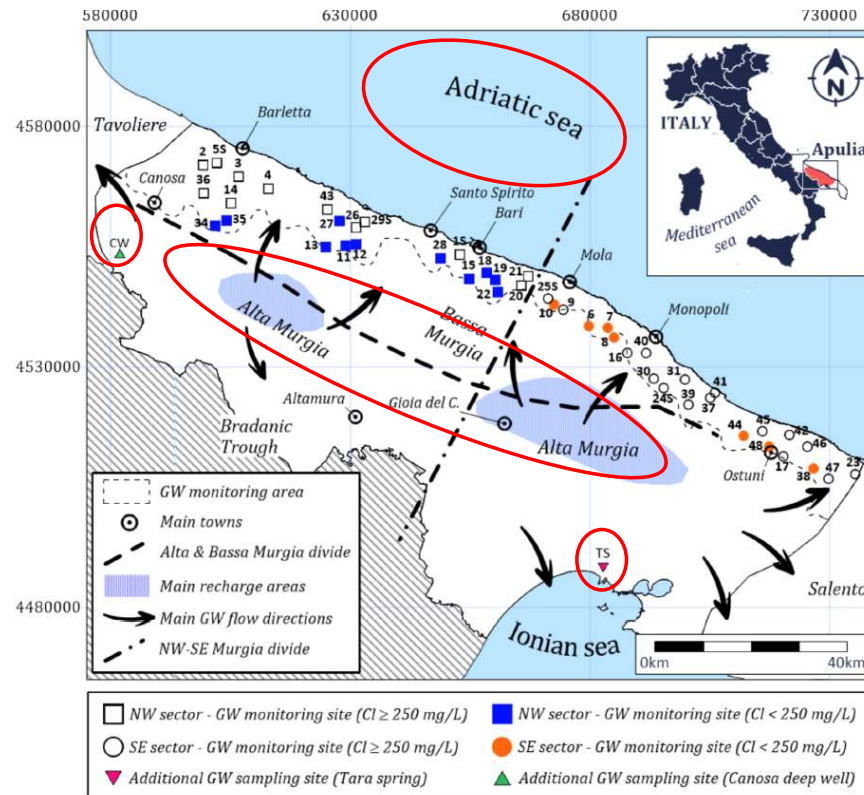
¹⁰ B	¹¹ B
10.0129	11.0093
19.9%	80.1%



Chemical and multi-isotopic investigation in hydrology: The Murgia example



- Sampling site selection
- Sampling
- Chemical analyses
- Isotopic analyses
- Conceptual model



Evaluating complex groundwater circulation patterns, hydrogeological zoning, and water-rock interaction

Coupling water chemistry, water isotopes, water and hydrogeology

Identification of water reservoirs and circulation patterns

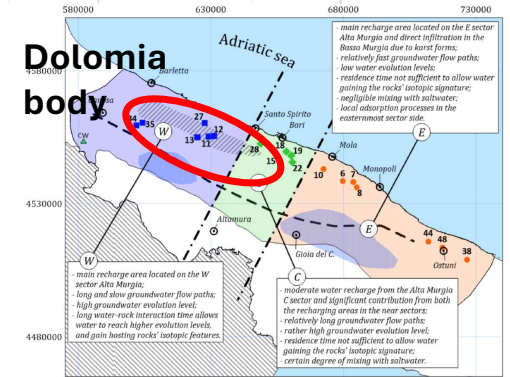
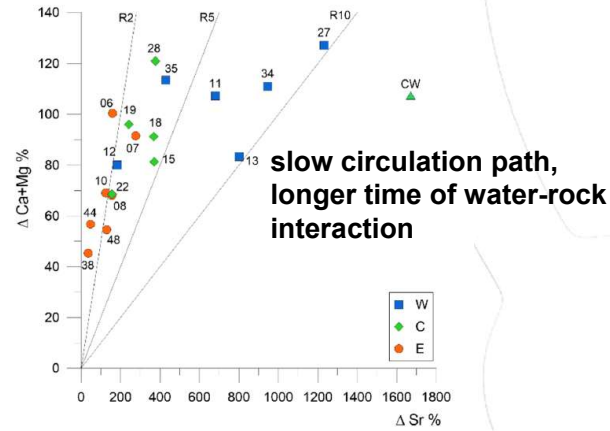
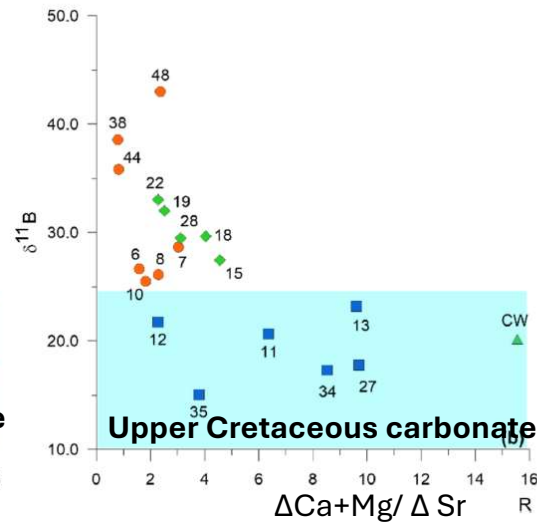
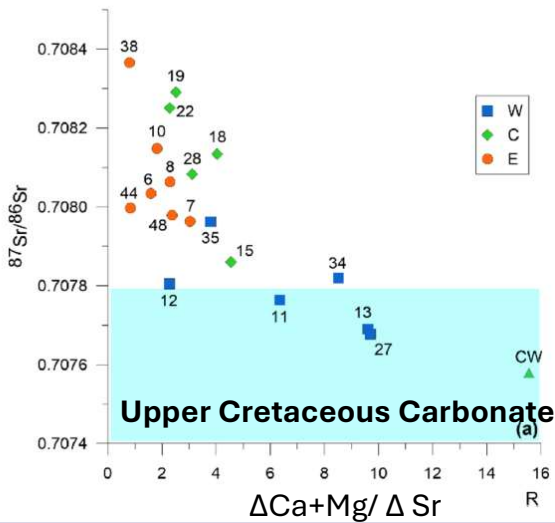


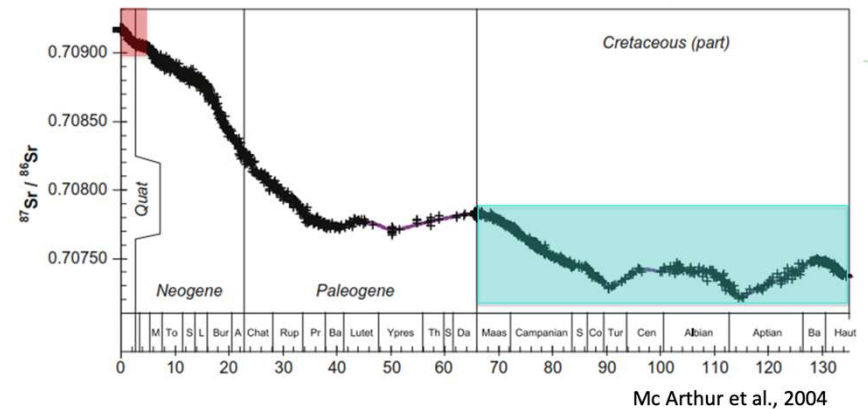
Fig. 12. Sketched conceptual model of the groundwaters circulation in the Adriatic Murgia aquifer showing the areas with different hydrogeological features.

M. Salvadori et al.



Shallow aquifer

Deep carbonatic aquifer



Evolution in time of IGG-CNR's Thermal ionization MS lab

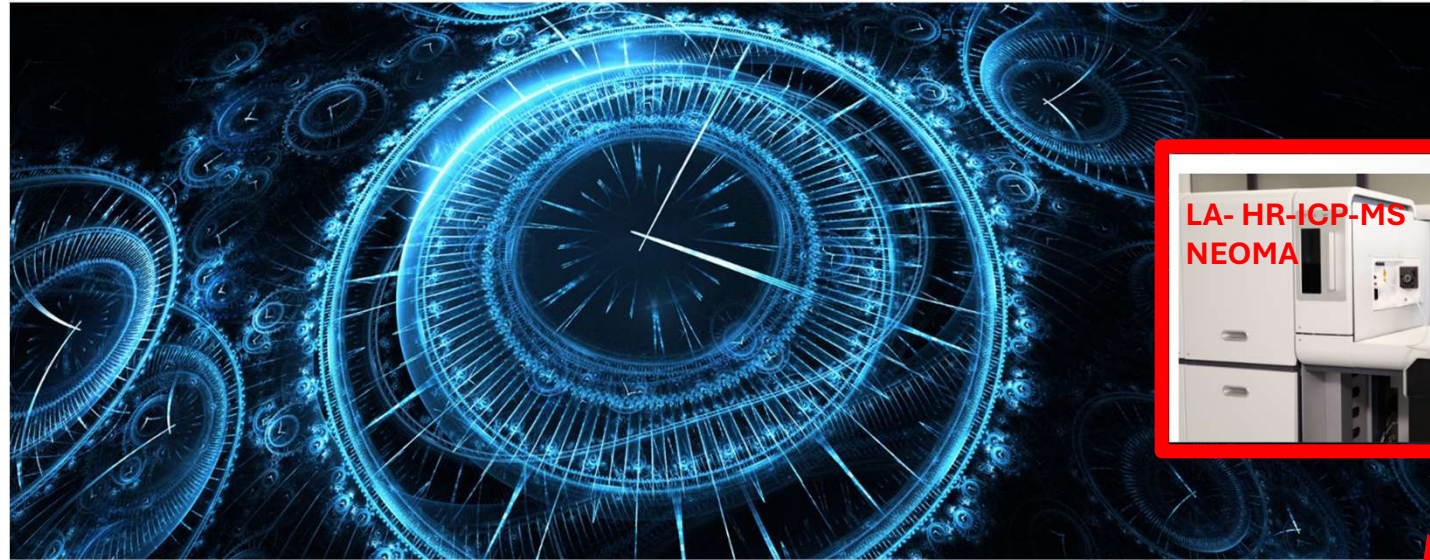
1970 – 1981

Monocollettor
thermal ionization
sourced

1991 Multicollector
Thermo ionization
sourced

2017 Multicollector
plasma sourced
NEPTUNE PLUS™

2025 Multicollector
plasma-sourced
with Laser Ablation
NEOMA™



2025

✓ From rock and minerals, to fluids and environmental matrices

✓ From ppm to ppb to laser ablation

TH5



1970

VG 54E



1981

Finnigan MAT 262



1991

**NEPTUNE PLUS
Thermo Fisher**



2017

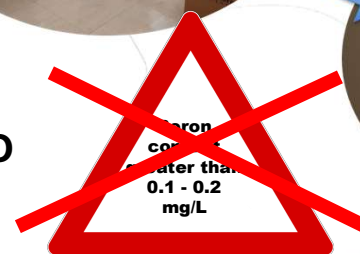
Multi-collector Plasma Sourced Mass Spectrometry

MC-ICP-MS NEPTUNE PLUS™

MC-ICP-MS Neptune Plus™ lab



FROM
ppm TO
ppb



Iron
concentration
water than
0.1 - 0.2
mg/L

Clean Room 100 – 100 class

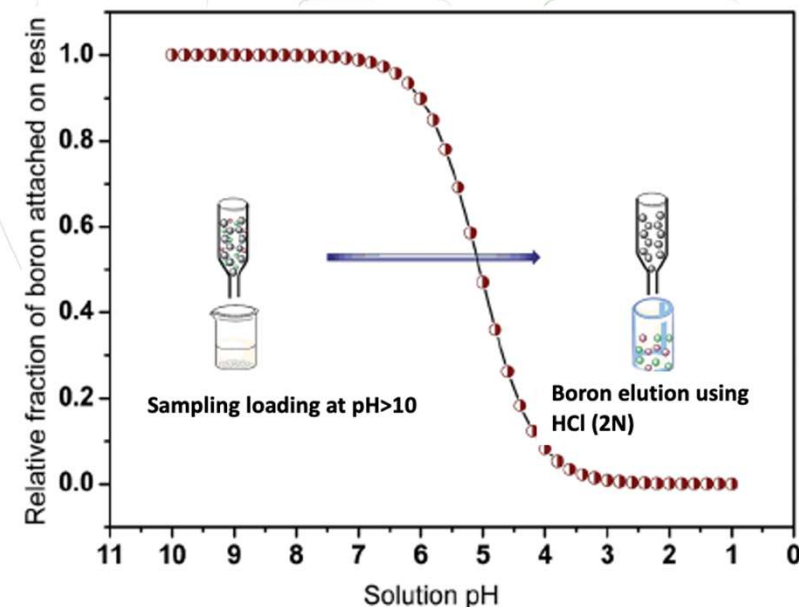


Clean Room and Ion Exchange Procedures

- element separation from the matrix
- resins and reagents are specific for each isotopic systematic



Boron procedure:
Specific ion-exchange resin (Amberlite)
 TONARINI ET AL 1997

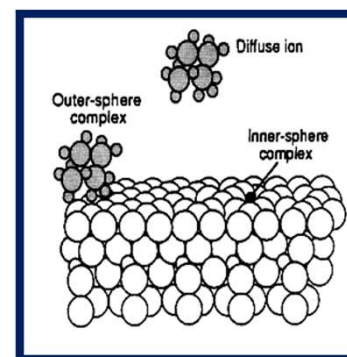


laboratory mimics the natural system

Adsorption on clays

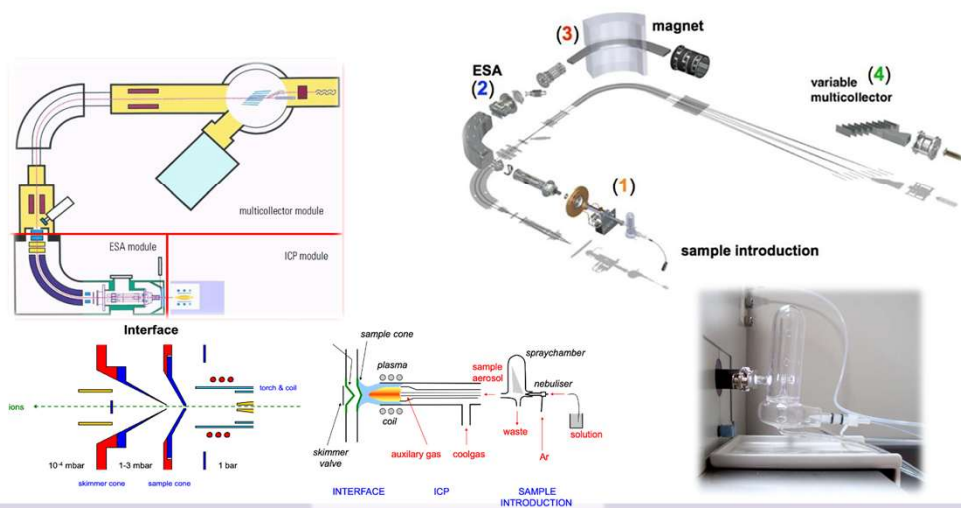
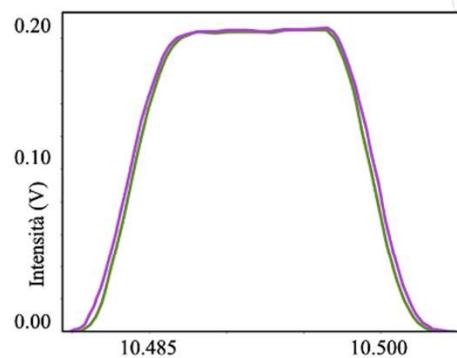
Palmer et al., 1987; Spivack et al, 1987; You et al., 1995

$$\frac{\Delta(\delta^{11}\text{B}/^{10}\text{B})_{\text{ads}}}{(\delta^{11}\text{B}/^{10}\text{B})_{\text{sol}}} = \sim -25\text{‰}$$



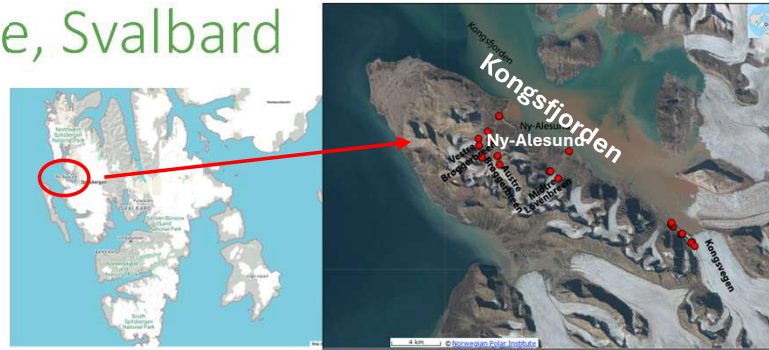
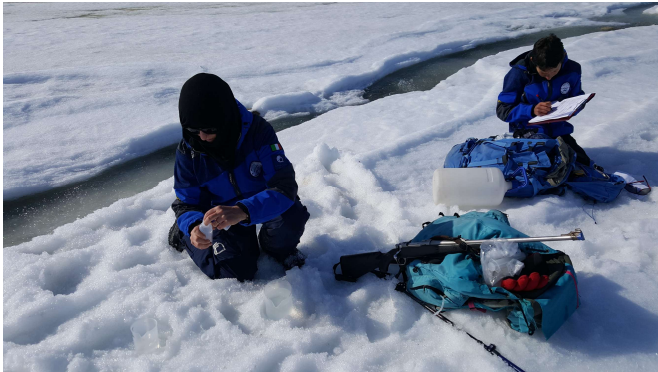
The advantages of using MC-ICP-MS in Earth Science & Environmental studies

- 🌐 Analysis of metals and metalloids
- 🌐 High Precision and Accuracy (10^{13} Ω amplifiers; International Standards; Bracketing)
- 🌐 High number of samples analyzed H24



Environmental isotopes: the challenge to investigate B-low environments

The ARTIC glacial drainage, Svalbard



🌐 A first attempt to determine the isotopic signature of Sr and B (**ppb level**) in glacial drainages was done using the MC-ICP-MS Neptune Plus™ installed at IGG Pisa to investigate the origin of these solutes

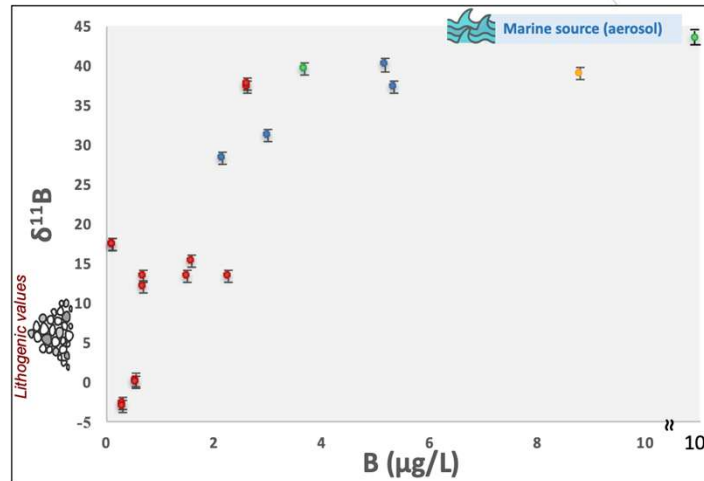
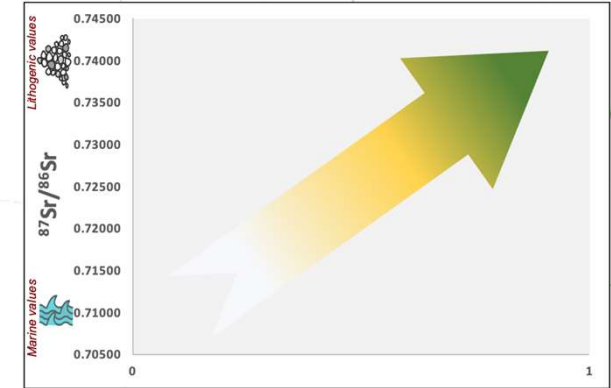
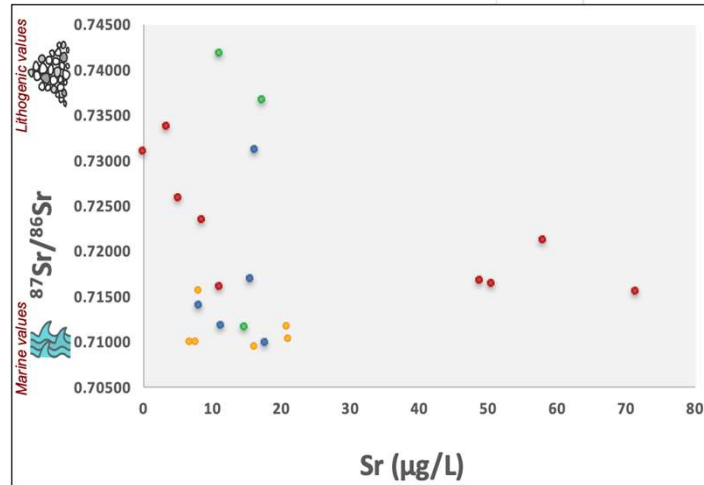
🌐 $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and $\delta^{11}\text{B}$ data were determined in surface waters sampled in the Kongsfjorden area, where a network of glacio-drainage system develops and remains active in the June-September period, as a consequence of glacier melting



The challenge to investigate low-B (ppb level) environment: The ARTIC glacial drainage, Svalbard

High values of $^{87}\text{Sr}/^{86}\text{Sr}$ (i.e. ^{87}Sr from rich **silicate minerals**) are evidenced in the **low salinity** waters (electrical conductivity < 50 $\mu\text{S}/\text{cm}$)

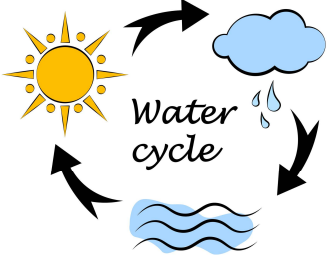
$\delta^{11}\text{B}$ values close to or equal to the marine signature of +40‰ indicate a significant **marine atmospheric source**



increase in thaw depth

Salvadori et al., SSC conference, 2021

The challenge to investigate low-B environments: the meteoric precipitation

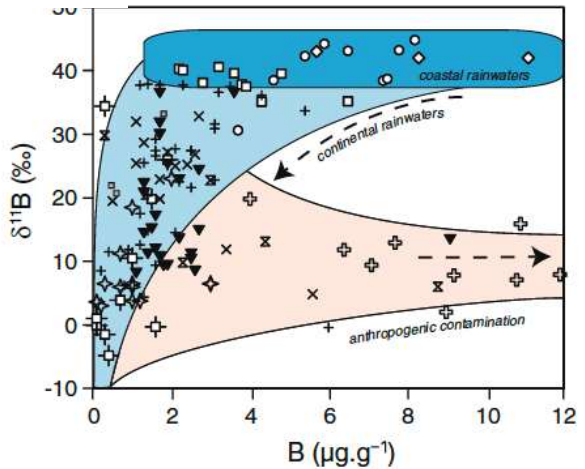


🌐 Boron in the atmosphere an meteoric precipitations

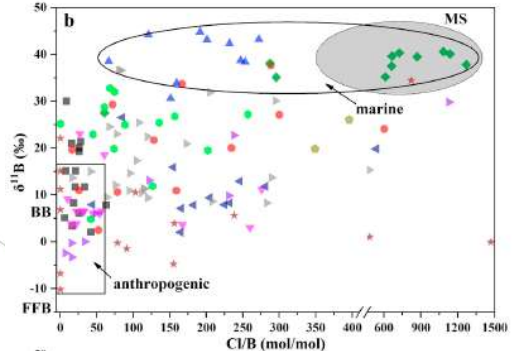
- Temperature dependant
- Gaseous boric acid = primary form in the atmosphere (vs particulate)
- Sea salt particles source of gaseous boric acid as they dehydrates
- Residence time

❖ The B content in rain from 1500 to 4500 times less than sea water

❖ Rains from oceanic islands and coastal area have B content on average higher than those from inland continental/areas



Gaillardet and Lemarchand, 2018



Mao et al., 2019

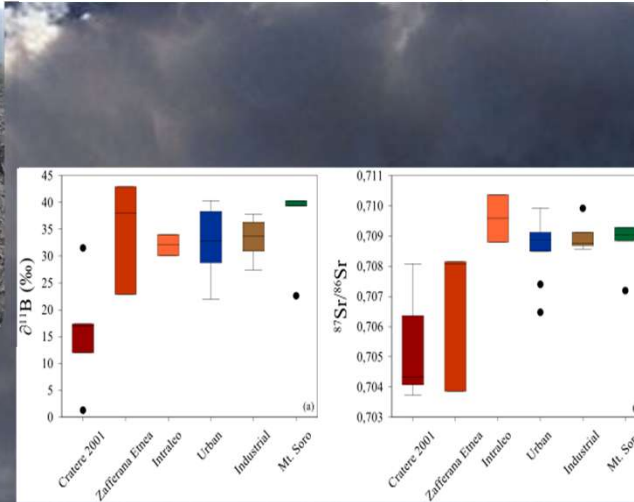
Coastal, Continental, and Anthropogenic signature of rainwater

Anthropogenic sources of B: g/yr	
Fly ash and fuel oil:	12×10^{10}
Wood fuel:	5×10^{10}
Agriculture burning:	36×10^{10}

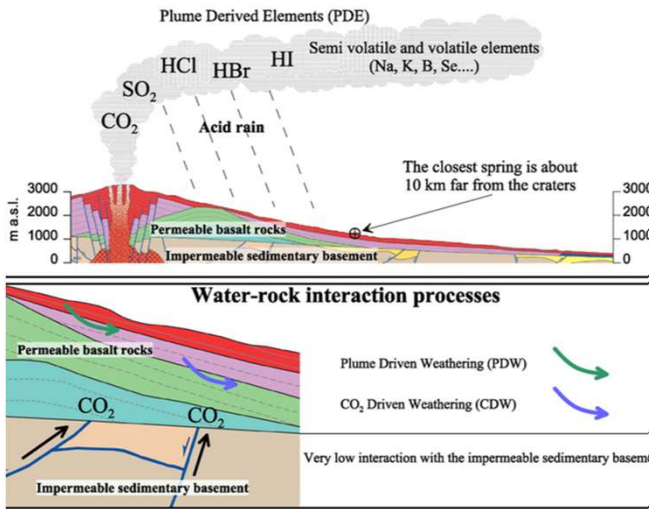
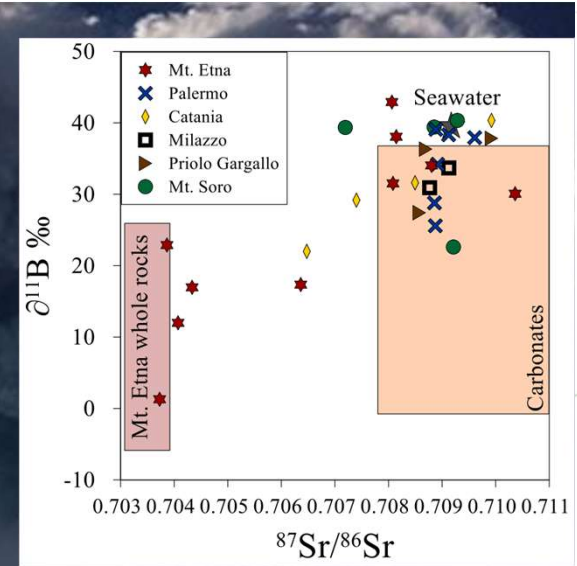
Park and Schlesinger, 2002

The challenge to investigate meteoric precipitations: Mt Etna

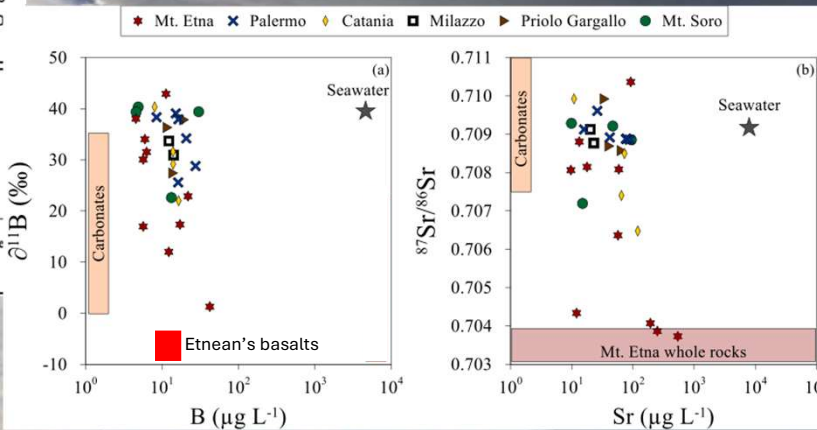
A persistent volcanic plume supplies volcanogenic elements through rainfall and dry deposition with implication on water, soil, and vegetation



Brugnone, et al., in preparation; Brugnone PhD, University of Palermo

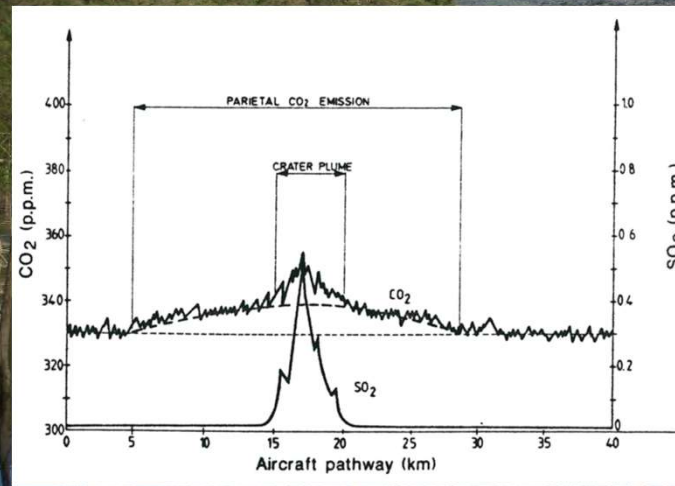
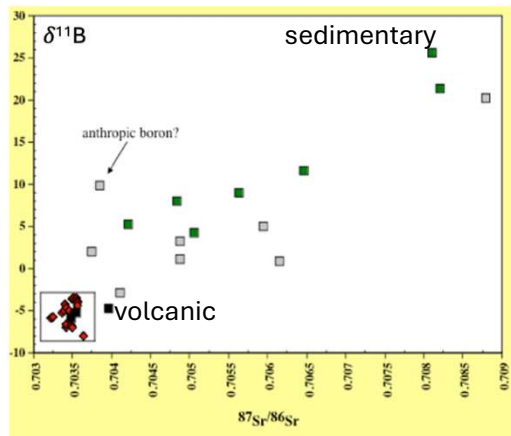
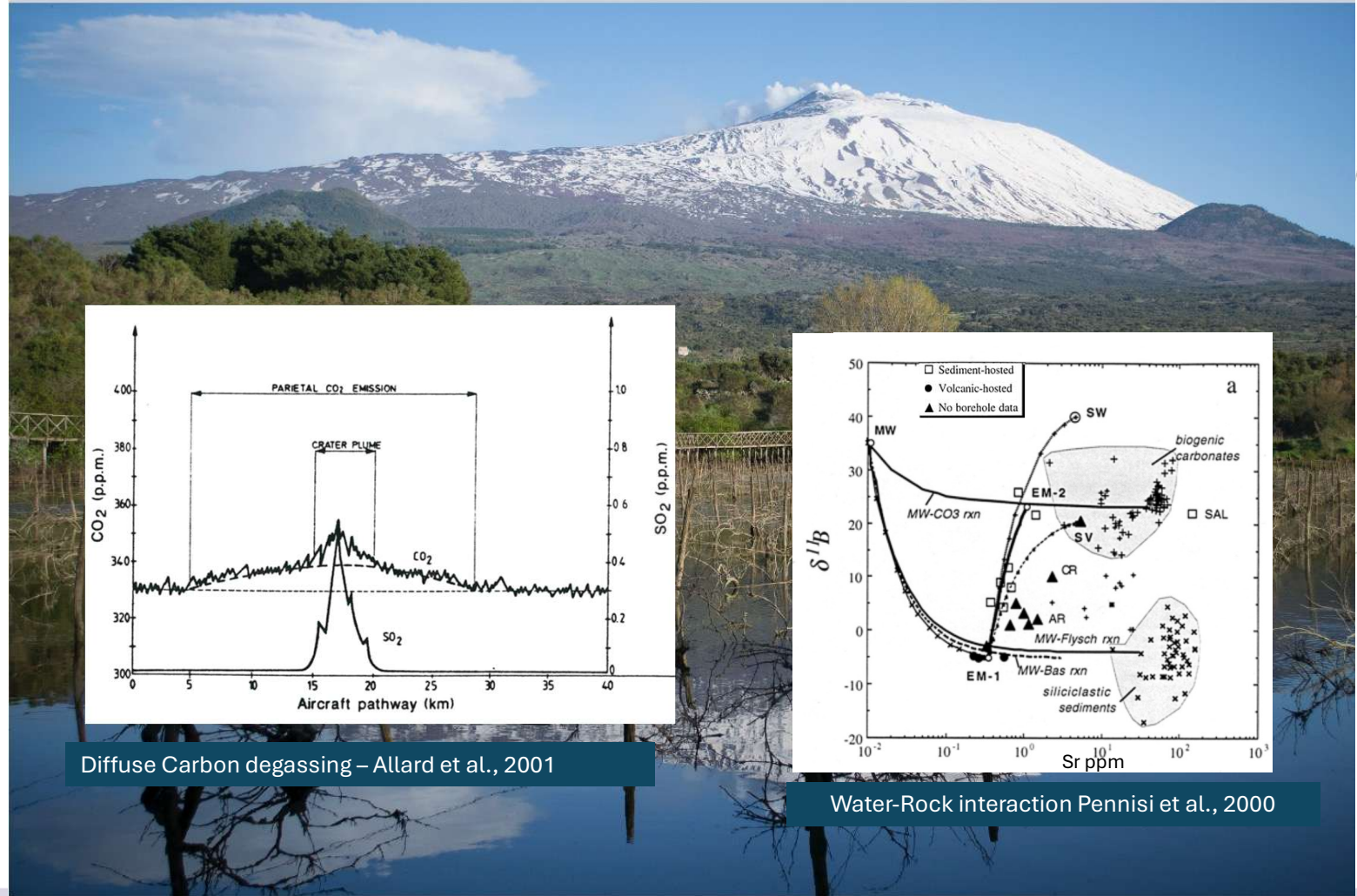


Liotta et al., 2016

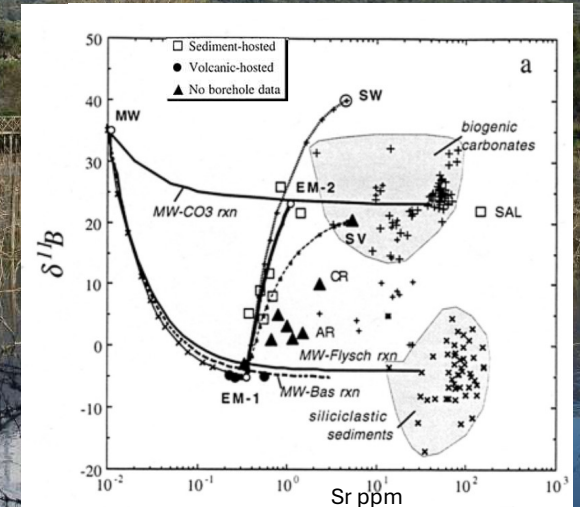


The challenge to investigate low-B environments : Mt Etna ecosystem

- Elemental sources in meteoric precipitations
- Water-rock interaction processes
- Rock-derived chemicals and biota



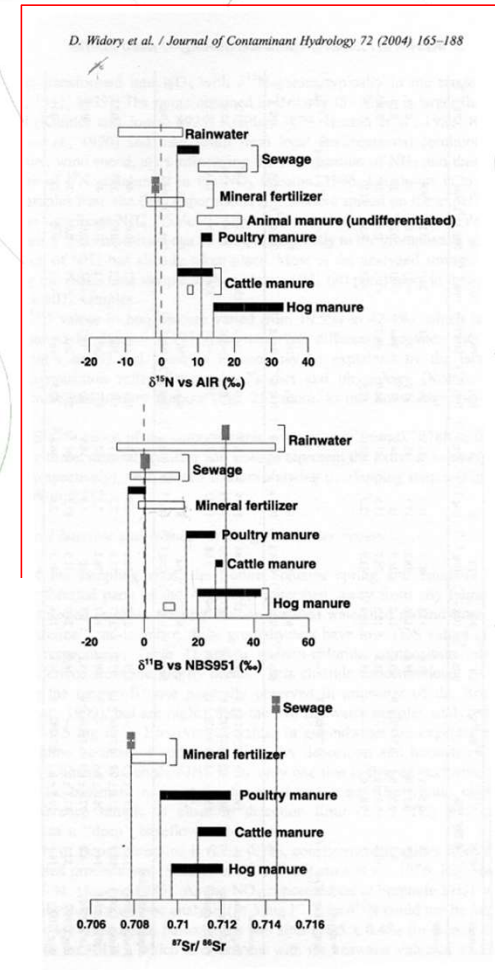
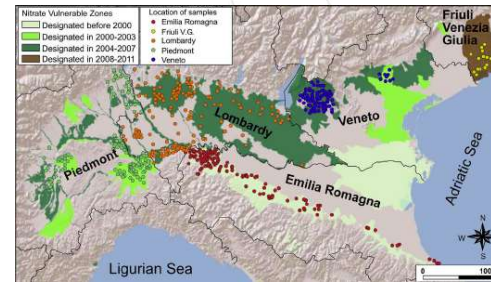
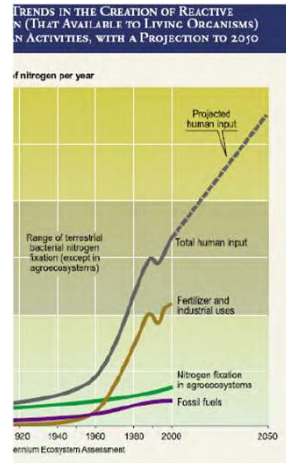
Diffuse Carbon degassing – Allard et al., 2001



Water-Rock interaction Pennisi et al., 2000

The challenge to trace nitrate pollution in water: the co-tracers $\delta^{15}\text{N}$ & $\delta^{11}\text{B}$

- Nitrogen is biologically modified by nitrification and denitrification processes, which cause isotopic fractionation of nitrate
- Combined use of B and N isotopes is used to trace the origin of nitrate in polluted waters
- Regulations; excess from fertilizers; livestock and civil effluents
- Sr isotopes provide an additional constraint for pollutant identification



Advantages and disadvantages of Nitrate and Borate isotopes

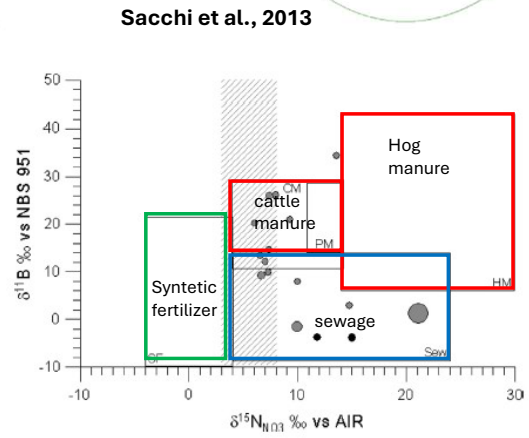
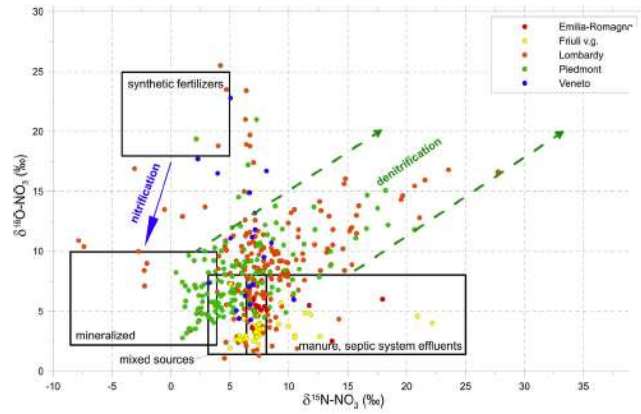
$\delta^{15}\text{N}$ NO_3^- intrinsic molecule

- Useful for determining mixing processes.
- Isotopic fractionation by natural denitrification.

$\delta^{11}\text{B}$ Co-migrant of the NO_3^- molecule

- Useful for determining mixing processes.
- Not affected by natural denitrification.
- Isotopic fractionation by adsorption/desorption on clay minerals

From Dave Widory



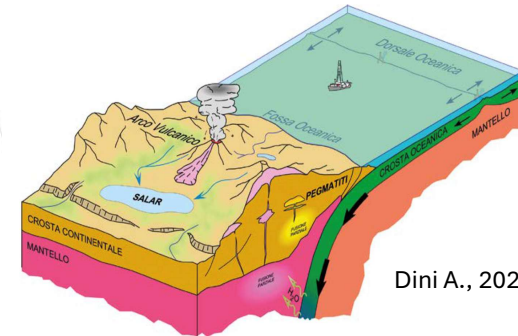
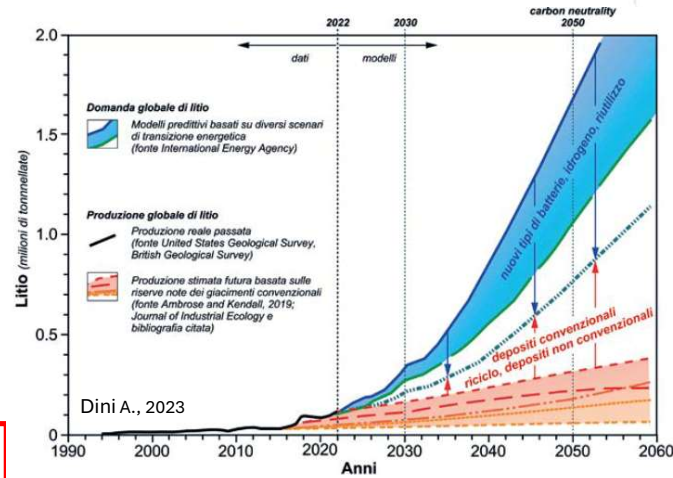
PNRR ITINERIS: Origin and Evolution of a potential unconventional Lithium resource



- Lithium demand is estimated to increase by 12 fold by 2030, and 21 fold by 2050 in EU (89 fold worldwide by 2050)



From 2020 in the list of **Critical Raw Material**
 2023 → Critical and **Strategic** RM
 2024 → **European Critical Raw Materials Act**



Schema semplificato di una zona di subduzione con formazione di apparati vulcanici in superficie e di complessi granitico-pegmatitici in profondità, a cui sono associati i principali giacimenti di litio del pianeta.



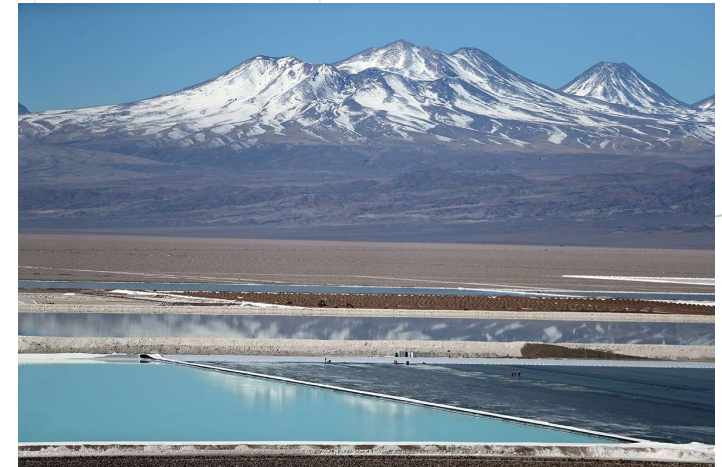
Li-rich claystone



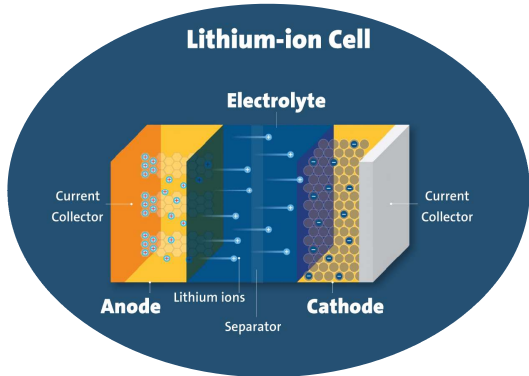
Spodumene
 $\text{LiAl}(\text{SiO}_3)_2$

Li-Sources: granite and pegmatites with high spodumene ($\text{LiAlSi}_2\text{O}_6$) content

Continental brine deposits in evaporative basins, Li-rich volcanic rocks



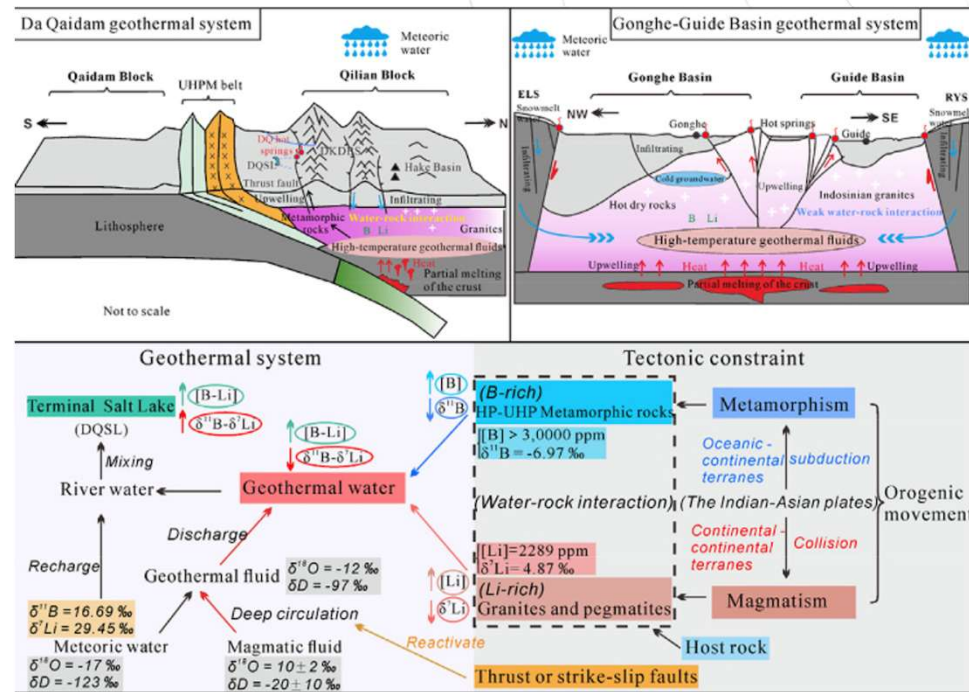
50-70% of known world lithium reserves, the Salar de Uyuni in Bolivia is the world's largest lithium deposit
<https://www.geologyforinvestors.com/brine-lithium-deposits/>



Isotopes in Li and B-rich geothermal fluids

The concentrations of B and Li are unusually high in geothermal waters and the total resource reserves are even significantly higher than that in the terminal salt lakes, (Han et al., 2024)

- B-rich metamorphic rocks and Li-bearing pegmatites create differential B-Li contents
- B- $\delta^{11}\text{B}$ and Li- $\delta^7\text{Li}$ of meteoric water and host rocks constrain B-Li cycling
- Deep circulation reactivated by thrust or strike-slip faults formed geothermal water

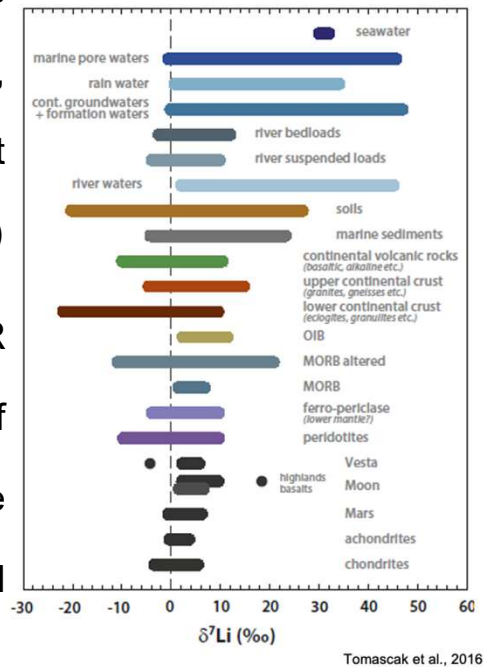


Han et al., 2024

PNRR ITINERIS: Set-up of the analytical procedure for the analysis of Li isotopes in rocks and fluids (PhD M. Salvadori: DST Pisa, IGG-CNR)



- 🌐 **Large fractionation** due large mass difference between ^6Li - ^7Li , determined by bonding environment (coordination number, distance Li-O)
- 🌐 At IGG-CNR, Pisa (PhD PNRR ITINERIS) is ongoing the set up of the analytical procedure for the measure of $^7\text{Li}/^6\text{Li}$ in **solid and liquid geologic matrices**
- 🌐 Intercalibration with **BRGM**, Orleans



CHEMICAL PURIFICATION PROCEDURE Cleanroom IGG-CNR

Single-pass purification

AGMP-50 100-200 resin

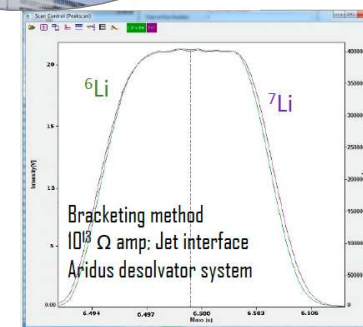
High aspect ratio columns



MC-ICP-MS
Neptune Plus

MASS SPECTROMETRY ANALYSIS

Bracketing method
NIST SRM 8545 L-SVEC



$10^{13} \Omega$ amplifier
Jet interface and jet cones
Aridus desolvator system

PNRR ITINERIS: Set-up of the analytical procedure for the analysis of Li isotope in rocks and fluids (PhD ITINERIS, M. Salvadori)



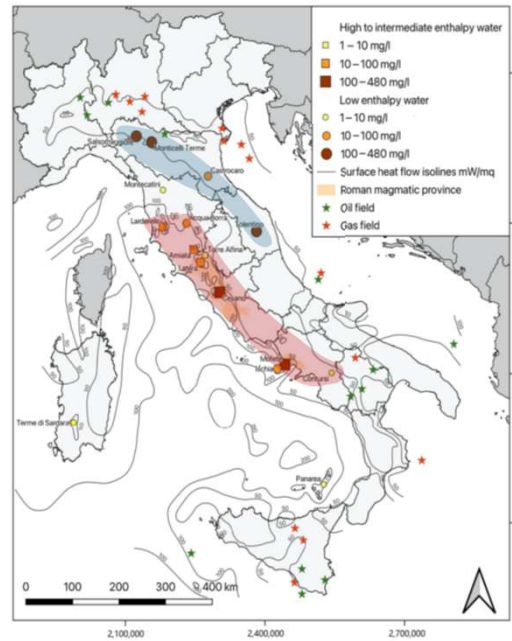
LI-RICH FLUIDS IN ITALY:

- High-to-mid enthalpy geothermal fluids in the peri-Tyrrhenian volcanic-geothermal zone
- Low-enthalpy Li-rich fluids (up to 200 ppm) occurring in several areas along sedimentary sequences in the Apennines margin

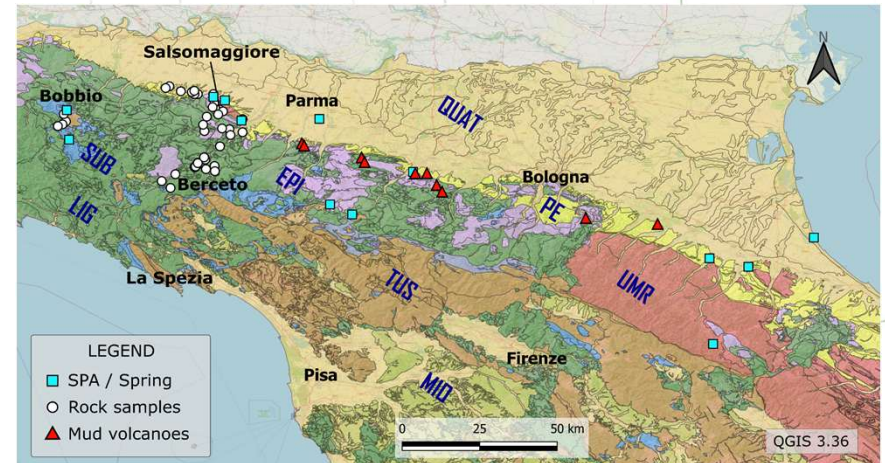
Scientific goals:

- processes controlling Li-enrichment in rocks

- water/rock interaction processes controlling Li-enrichment in waters



Dini et al, 2023



- 48 rock and water samples including mud volcanoes:

Identification Li-enriched rocks

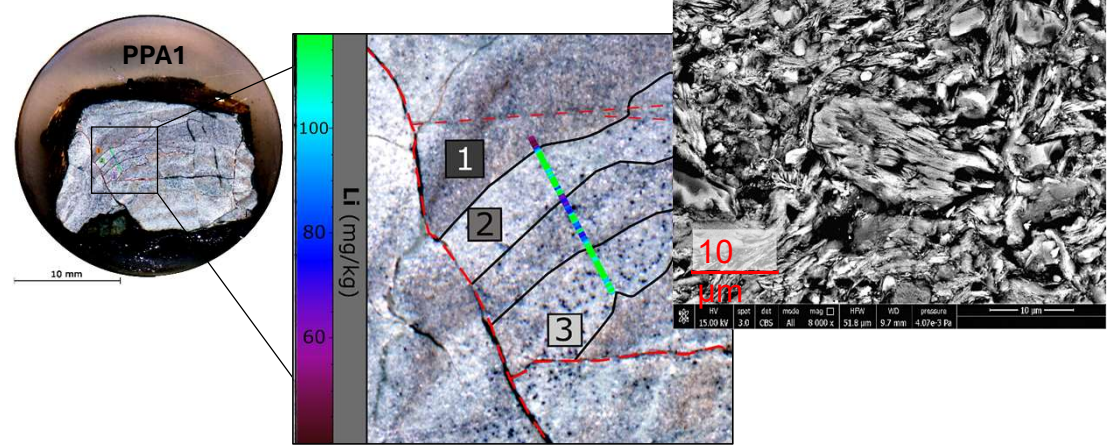
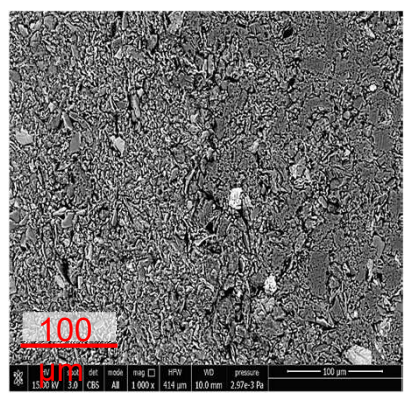
Identification of water-rock interaction using chemistry and a multi-isotope approach

PNRR ITINERIS: Li isotopes in rocks: the challenge using NEOMA and FSEM (PhD ITINERIS, M. Salvadori)



- Mineralogic zonation to study **Li variability** and its association with other elements
- Heterogeneous Li distribution observed at the macroscale is attested also at the microscale
- Constraining the sources of Lithium and its enrichment in water**

FEG-SEM BSE image



NEW PNRR ITINERIS INSTRUMENTS INSTALLED AT IGG-CNR PISA

LA-MC-ICP-MS: Neoma MC-ICP-MS/MS + NWR193 LA

- In-situ B*
- In situ isotopic analyses**
- Laser Conditions**
- 6 J/cm² Fluence
 - 13 Hz repetition rate
 - 100 µm circle spot size
 - Jet Interface
 - 0.750 L/min He
 - 4 mL/min N₂

- Reference Materials**
- NIST SRM610
 - JCt-1
 - JCp-1



Field emission scanning electron microscope (FE-SEM)

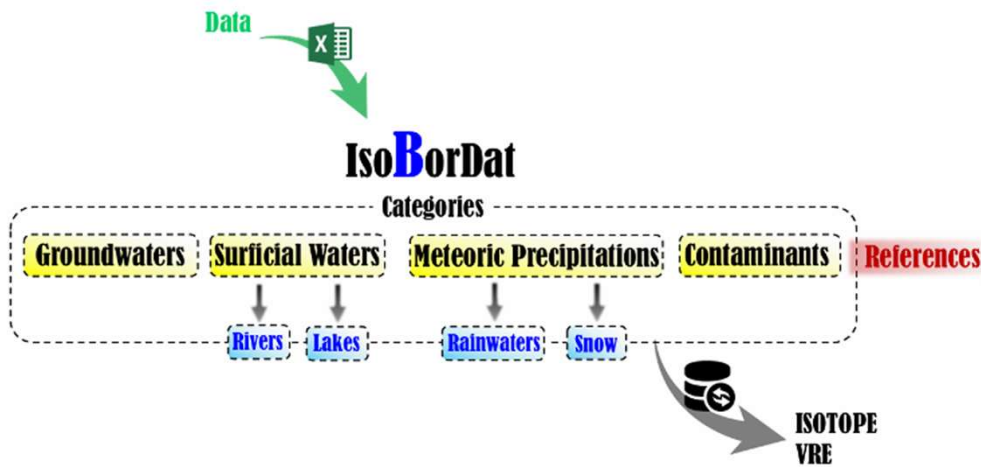


High-resolution imaging and characterization

Identify phases and analyze texture in 2D and 3D

ISOBORDAT: an online database on boron isotopes in hydrology

<http://isobordat.igg.cnr.it>



ISOBORDAT aims to be as interactive as possible, and calls to cooperation of the whole boron isotope community.

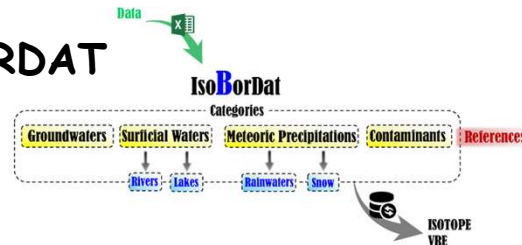
The database helps boron isotope hydrologists and geochemists by speeding up the research of, and the comparison with, data already existing in the scientific literature

The screenshot shows the IsoBorDat website homepage. The header includes the site name 'IsoBorDat' and a language selector for 'English'. Below the header is a navigation menu with categories: CONTAMINANTS, GROUNDWATERS, RAINWATERS, RIVERS, LAKES, REFERENCES, and DOWNLOADS. The main content area features a large banner with the text 'WELCOME TO ISOBORDAT' and a sub-link 'Home » WELCOME TO ISOBORDAT'. Below the banner, the text reads: 'By IGG-CNR, Pisa, Italy'. The main body of the page contains the following text: 'The site is addressed to all are interested in hydrogeochemistry and can have in boron isotopes a tool to investigate the origin of salinity, and the sources of pollution in surface and groundwaters. Bibliography is a benchmark of extreme importance to fully understand the application of $\delta^{11}\text{B}$. The data base consists of 6 items: 1) bibliography, which contains references to papers dealing with boron isotopes and five categories: 1) rainwater 2) lakes 3) rivers 4) groundwaters 5) contaminants that report analytical data on B content and $\delta^{11}\text{B}$, together with the study site and environmental context, the name of first author, the year of publication and the number corresponding to the full reference. This site aims to be as interactive as possible and will be developed taking into account the information and suggestions that come. Enjoy boron and its isotopes... Daniela Andreani, Alessandra Adorni-Braccesi, Maddalena Pennisi* (data collection) Lorenzo Gori (webmaster) *corresponding author: m.pennisi@igg.cnr.it Cite as: ISOBORDAT: an on line database on boron isotopes. Pennisi M., Adorni-Braccesi A., Andreani D., Gori L., Sciuto P.F., Gonfiantini R.

ISOBORDAT meets ITINERIS: the Isotope Database VRE 8.9



INPUT:
ISOBORDAT



OUTPUT:
ITINERIS –
Isotope Database
VRE 8.9



Di Giuseppe, Perrone, Gennaio 2025

Mixing Modelling

Data Plotting

Binary Diagrams

Ternary Diagrams

Normalised Spider Diagrams

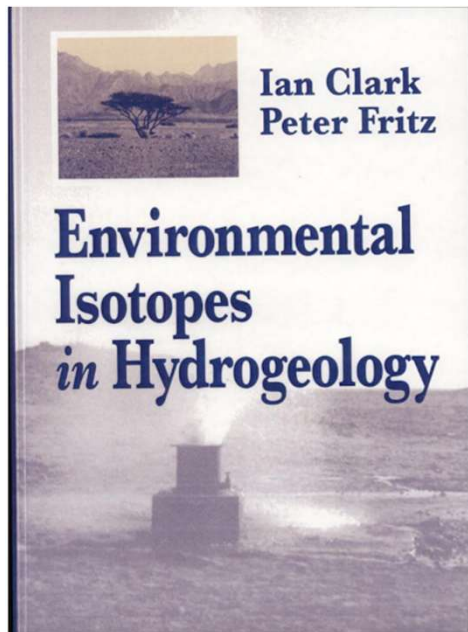
Schoeller-Berkaloff Diagrams



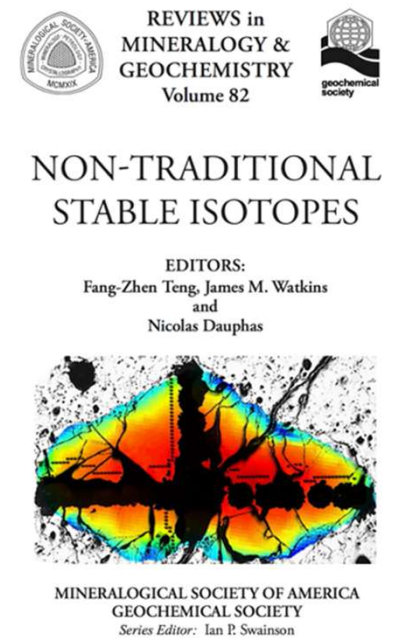
For those who would like to explore isotopes in earth and environmental studies further...



🌐 Isotopes to deciphering Critical Zone's processes: the multi-isotope toolbox
Chemical Geology, Vol 445, 2016



1998

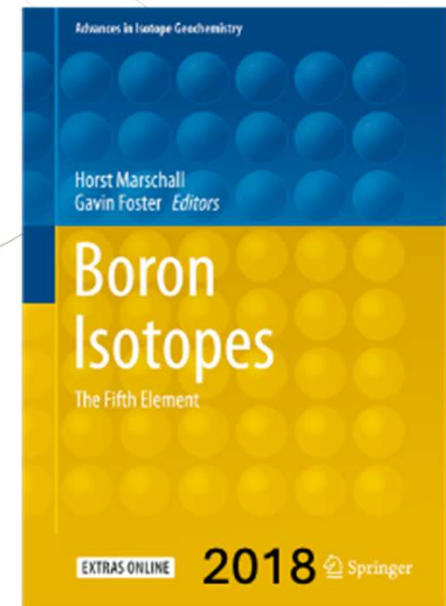


2017

2004

ISSN 1529-6466

1996



2018



THANKS!



IR0000032 – ITINERIS, Italian Integrated Environmental Research Infrastructures System
(D.D. n. 130/2022 - CUP B53C22002150006) Funded by EU - Next Generation EU PNRR-
Mission 4 "Education and Research" - Component 2: "From research to business" - Investment
3.1: "Fund for the realisation of an integrated system of research and innovation infrastructures"



PERIODIC TABLE OF THE ELEMENTS

<http://www.periodni.com>

PERIOD	GROUP																18				
	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18		
	IA	IIA		IIIB	IVB	VB	VIB	VII B	VIII B	IX			X	XIB	XIIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1	1.0079 H HYDROGEN																				
2	3 6.941 Li LITHIUM	4 9.0122 Be BERYLLIUM																			
3	11 22.990 Na SODIUM	12 24.305 Mg MAGNESIUM																			
4	19 39.098 K POTASSIUM	20 40.078 Ca CALCIUM	21 44.956 Sc SCANDIUM	22 47.867 Ti TITANIUM	23 50.942 V VANADIUM	24 51.996 Cr CHROMIUM	25 54.938 Mn MANGANESE	26 55.845 Fe IRON	27 58.933 Co COBALT	28 58.693 Ni NICKEL	29 63.546 Cu COPPER	30 65.38 Zn ZINC	31 69.723 Ga GALLIUM	32 72.64 Ge GERMANIUM	33 74.922 As ARSENIC	34 78.96 Se SELENIUM	35 79.904 Br BROMINE	36 83.798 Kr KRYPTON			
5	37 85.468 Rb RUBIDIUM	38 87.62 Sr STRONTIUM	39 88.906 Y YTTRIUM	40 91.224 Zr ZIRCONIUM	41 92.906 Nb NIOBIUM	42 95.96 Mo MOLYBDENUM	43 (98) Tc TECHNETIUM	44 101.07 Ru RUTHENIUM	45 102.91 Rh RHODIUM	46 106.42 Pd PALLADIUM	47 107.87 Ag SILVER	48 112.41 Cd CADMIUM	49 114.82 In INDIUM	50 118.71 Sn TIN	51 121.76 Sb ANTIMONY	52 127.60 Te TELLURIUM	53 126.90 I IODINE	54 131.29 Xe XENON			
6	55 132.91 Cs CAESIUM	56 137.33 Ba BARIUM	57-71 La-Lu Lanthanide	72 178.49 Hf HAFNIUM	73 180.95 Ta TANTALUM	74 183.84 W TUNGSTEN	75 186.21 Re RHENIUM	76 190.23 Os OSMIUM	77 192.22 Ir IRIDIUM	78 195.08 Pt PLATINUM	79 196.97 Au GOLD	80 200.59 Hg MERCURY	81 204.38 Tl THALLIUM	82 207.2 Pb LEAD	83 208.98 Bi BISMUTH	84 (209) Po POLONIUM	85 (210) At ASTATINE	86 (222) Rn RADON			
7	87 (223) Fr FRANCIUM	88 (226) Ra RADIUM	89-103 Ac-Lr Actinide	104 (267) Rf RUTHERFORDIUM	105 (268) Db DUBNIUM	106 (271) Sg SEABORGIUM	107 (272) Bh BOHRIUM	108 (277) Hs HASSIUM	109 (276) Mt MEITNERIUM	110 (281) Ds DARMSTADIUM	111 (280) Rg ROENTGENIUM	112 (285) Cn COPERNICIUM	113 (...) Uut UNUNTRIUM	114 (287) Fl FLEROVIUM	115 (...) Uup UNUNPENTIUM	116 (291) Lv LIVERMORIUM	117 (...) Uus UNUNSEPTIUM	118 (...) Uuo UNUNOCTIUM			

RELATIVE ATOMIC MASS (1)

GROUP IUPAC GROUP CAS

ATOMIC NUMBER SYMBOL ELEMENT NAME

B
BORON

- Metal
- Semimetal
- Nonmetal
- Alkali metal
- Alkaline earth metal
- Transition metals
- Lanthanide
- Actinide
- Chalcogens element
- Halogens element
- Noble gas

STANDARD STATE (25 °C; 101 kPa)

Ne - gas Fe - solid
Hg - liquid Tc - synthetic

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(1) Pure Appl. Chem., 81, No. 11, 2131-2156 (2009)
Relative atomic masses are expressed with five significant figures. For elements that have no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived isotope of the element. However three such elements (Tl, Pa and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.

LANTHANIDE														
57 138.91 La LANTHANUM	58 140.12 Ce CERIUM	59 140.91 Pr PRASEODYMIUM	60 144.24 Nd NEODYMIUM	61 (145) Pm PROMETHIUM	62 150.36 Sm SAMARIUM	63 151.96 Eu EUROPIUM	64 157.25 Gd GADOLINIUM	65 158.93 Tb TERBIUM	66 162.50 Dy DYSPROSIUM	67 164.93 Ho HOLMIUM	68 167.26 Er ERBIUM	69 168.93 Tm THULIUM	70 173.05 Yb YTTTERBIUM	71 174.97 Lu LUTETIUM
ACTINIDE														
89 (227) Ac ACTINIUM	90 232.04 Th THORIUM	91 231.04 Pa PROTACTINIUM	92 238.03 U URANIUM	93 (237) Np NEPTUNIUM	94 (244) Pu PLUTONIUM	95 (243) Am AMERICIUM	96 (247) Cm CURIUM	97 (247) Bk BERKELIUM	98 (251) Cf CALIFORNIUM	99 (252) Es EINSTEINIUM	100 (257) Fm FERMIUM	101 (258) Md MENDELEVIUM	102 (259) No NOBELIUM	103 (262) Lr LAWRENCIUM