Modena, 5 novembre 2024

“Applicazioni della Spettrometria di Massa con campionamento LASER nelle Geoscienze”

Alberto Zanetti

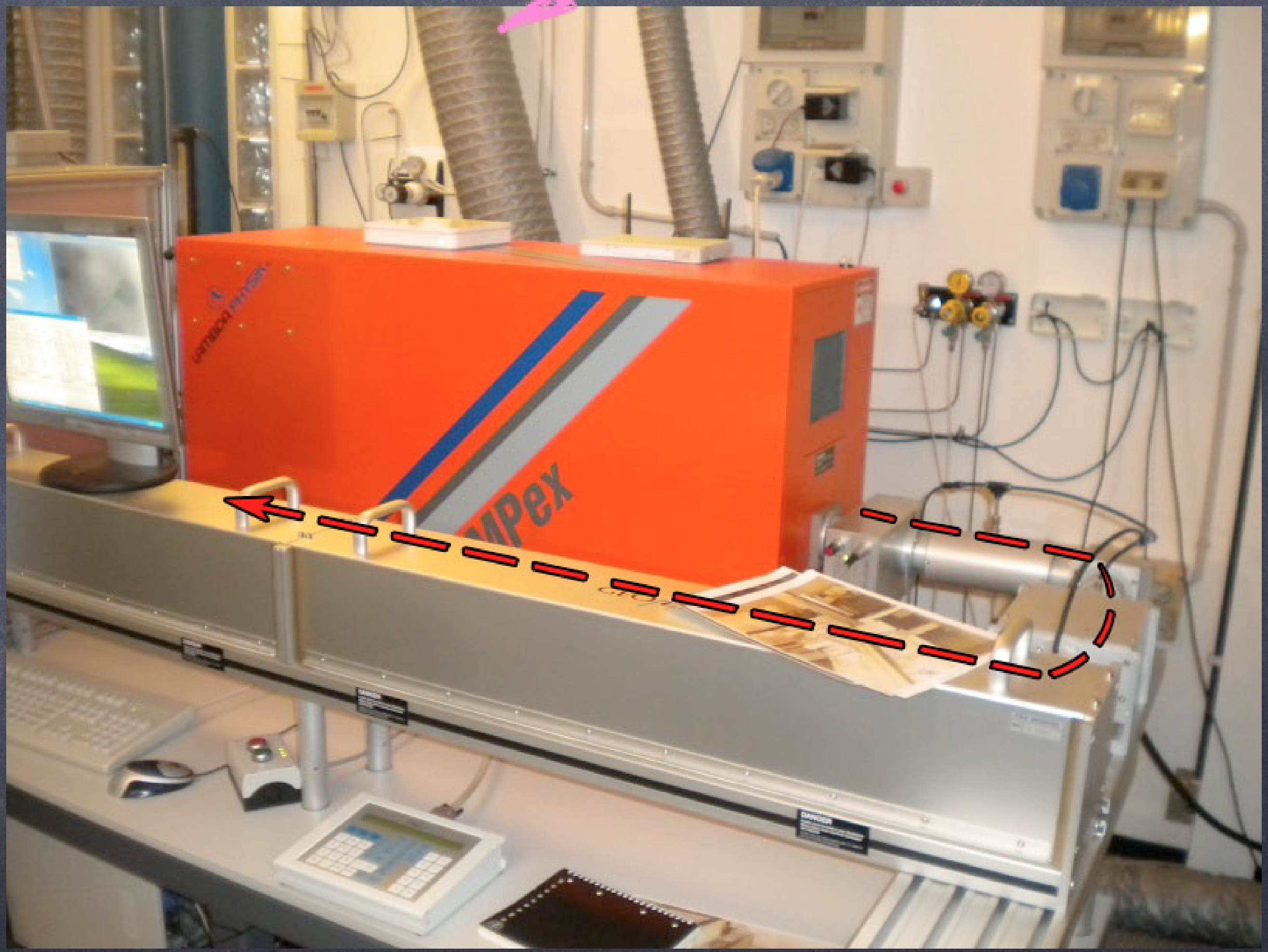
Consiglio Nazionale delle Ricerche
Istituto di Geoscienze e Georisorse – Pavia

- Outline

- - Principles of LA-ICP-MS technique
- - Trace Element analysis
- - U-Th-Pb geochronology

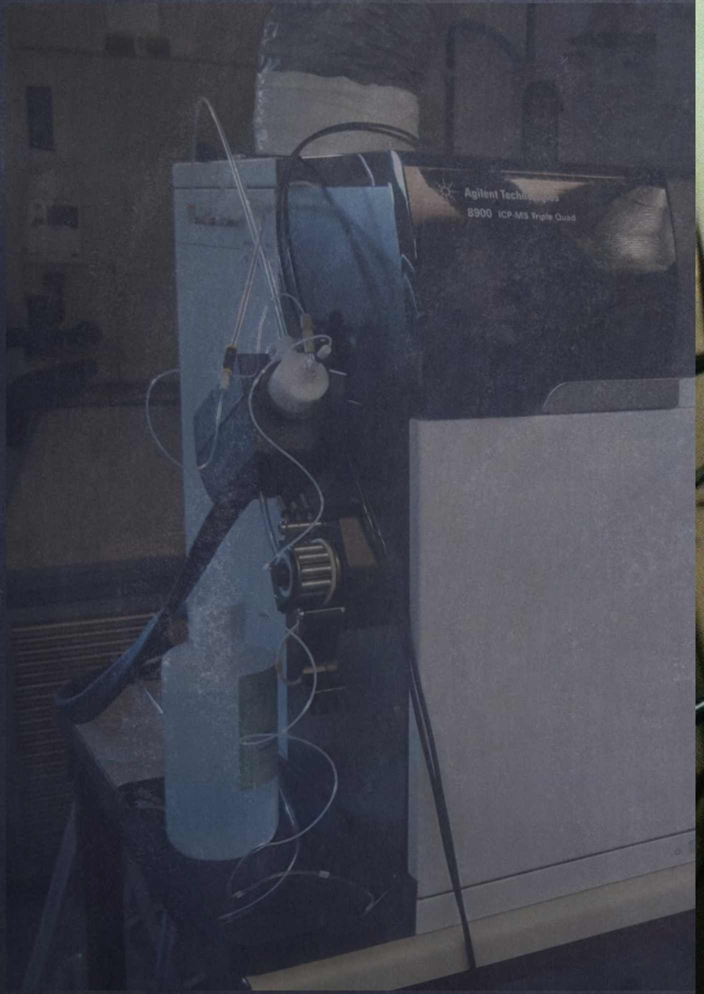
LA + ICP + MS

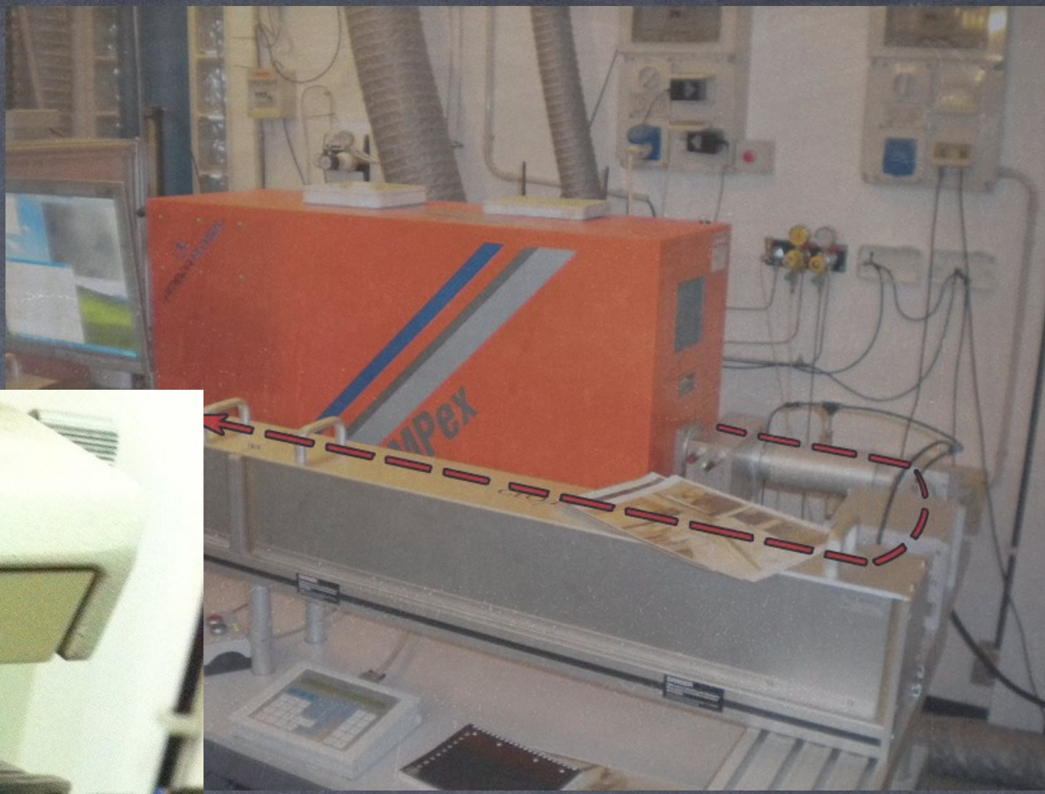
8900 QQQ (Agilent)

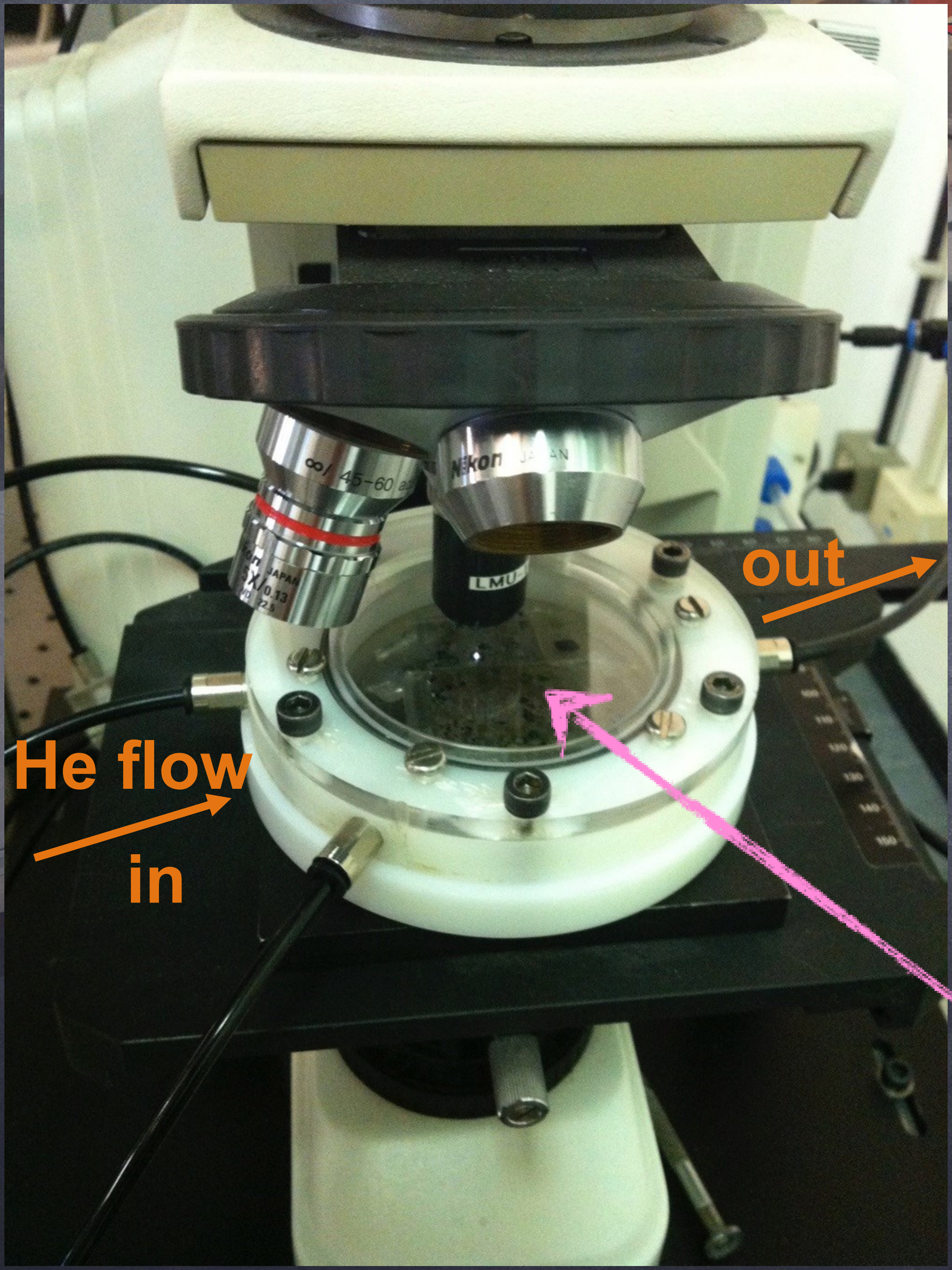


Excimer Laser 193nm ArF (GeoLas 102, Microlas)

LA + ICP + MS







Nd:YAG laser

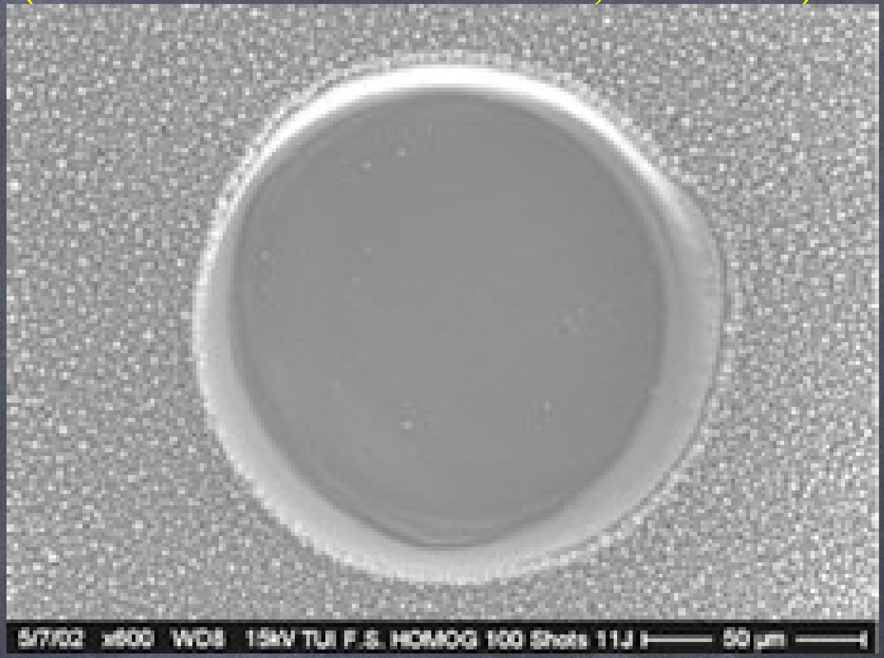
Ablation cell

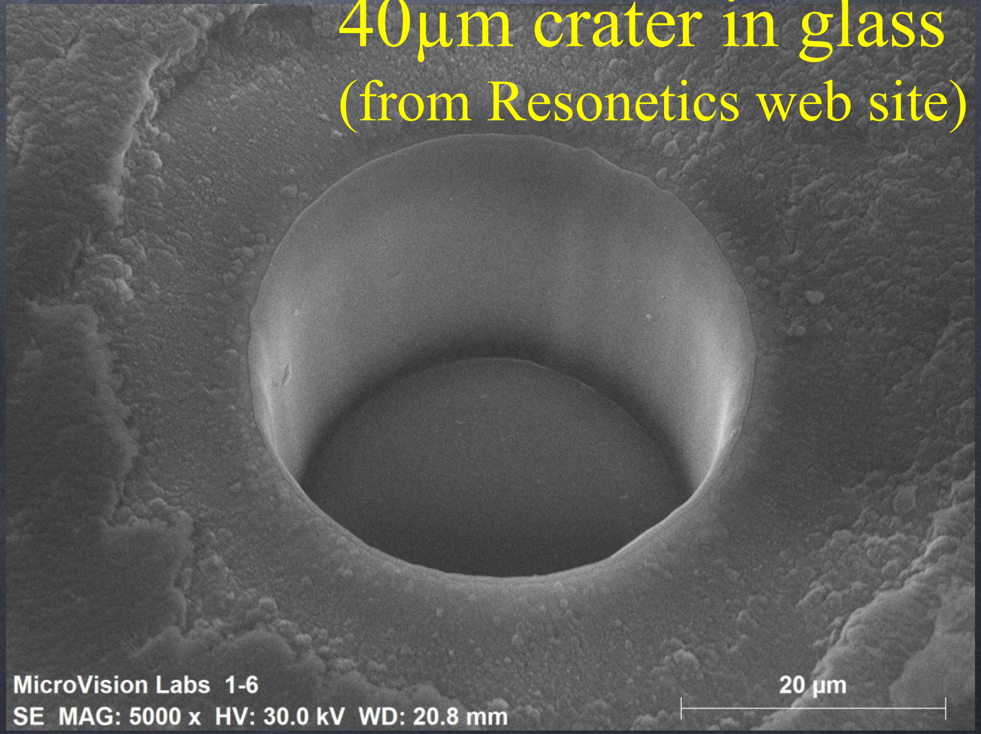
LA-ICP-MS approaches

"In situ": isotopic analysis of small cylindrical volumes (5-100μm diameter)

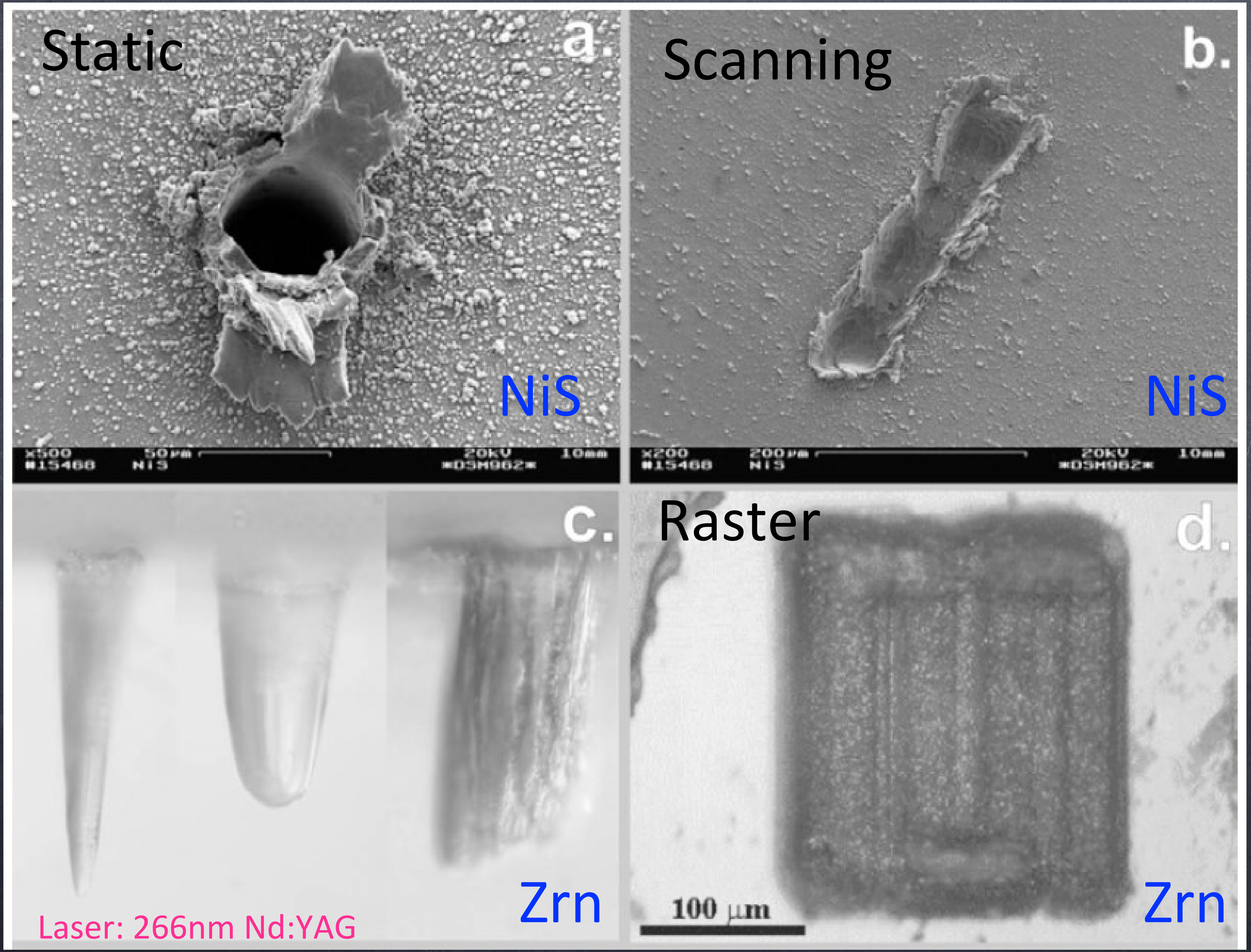
Mineral/solid material **separates** or directly on ordinary **thin sections**

100μm crater in fused silica
(from Coherent web site, 193 nm)

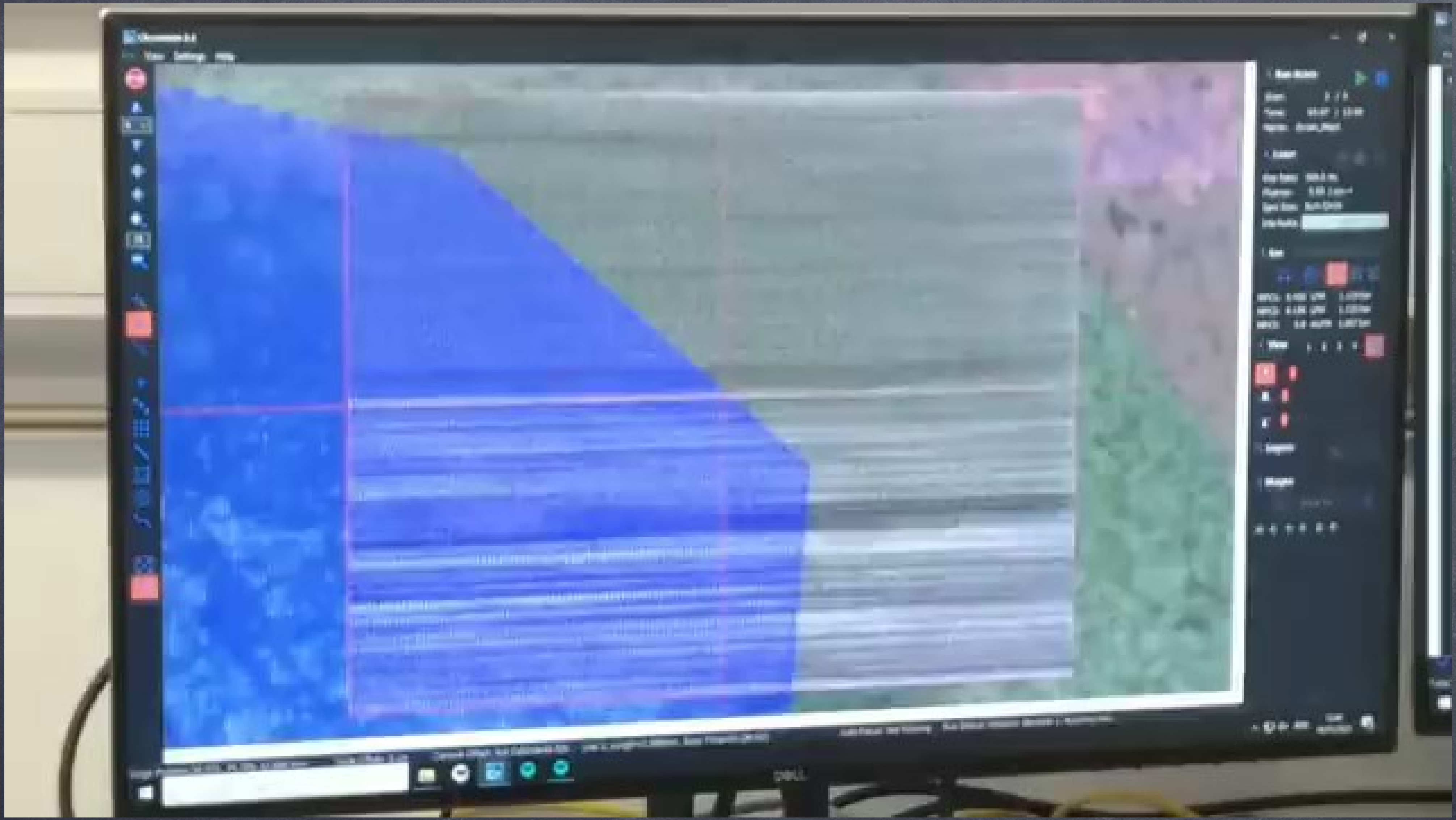




Ablation protocols



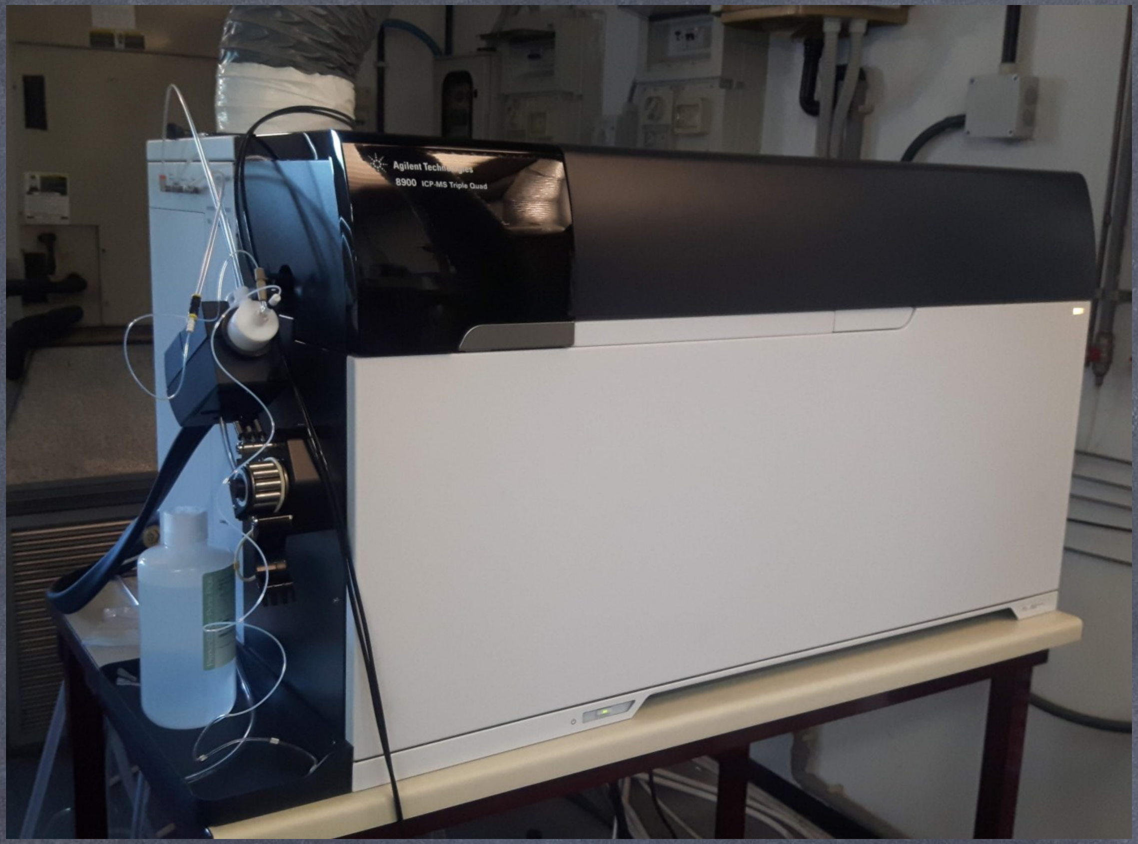
Jan Kosler (2008) in:
Laser Ablation ICP-MS in the Earth Sciences: Current Practices and Outstanding Issues



Analisi raster di zircone con Excimer LASER (193 nm).
Spot 5 µm, 200 KHz

(Irydia, Teledyne, Spot da 1 µm, 1 MHz)

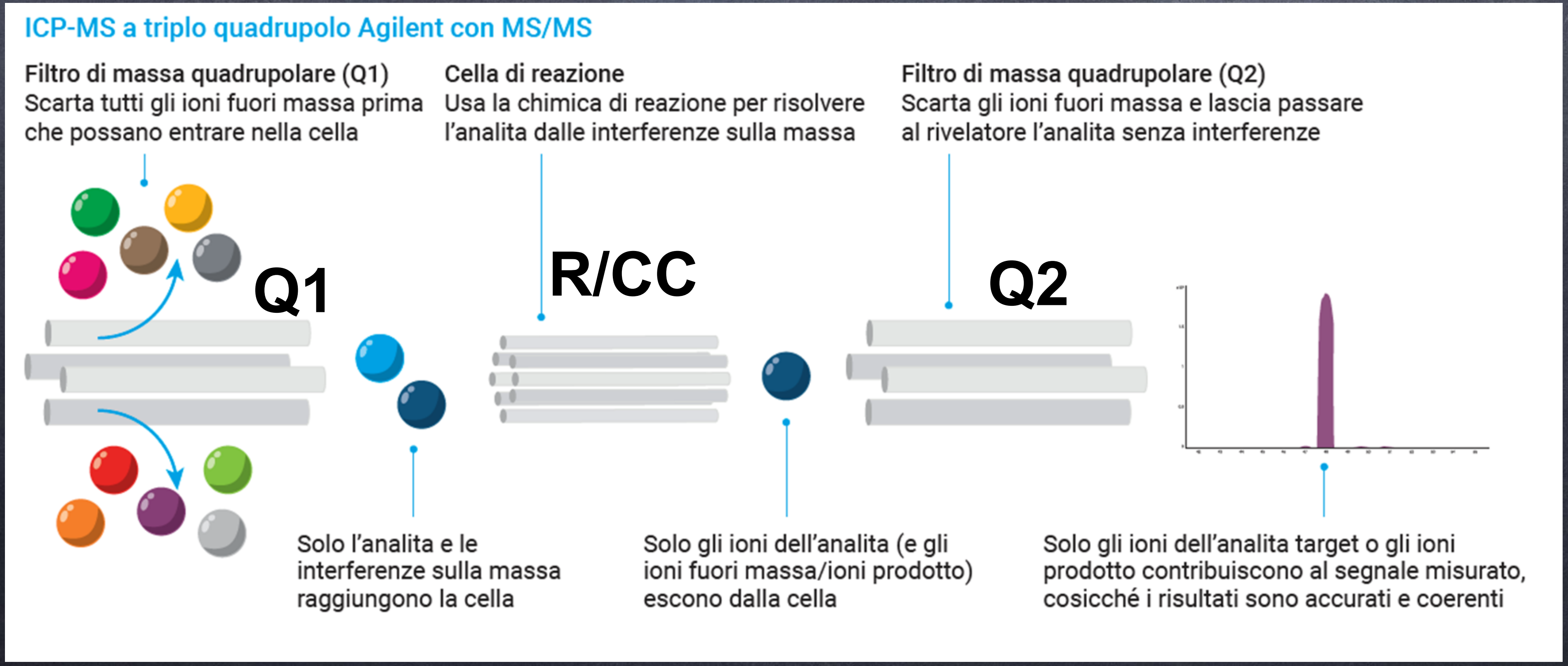
Q-and-QQQ-ICP-MS



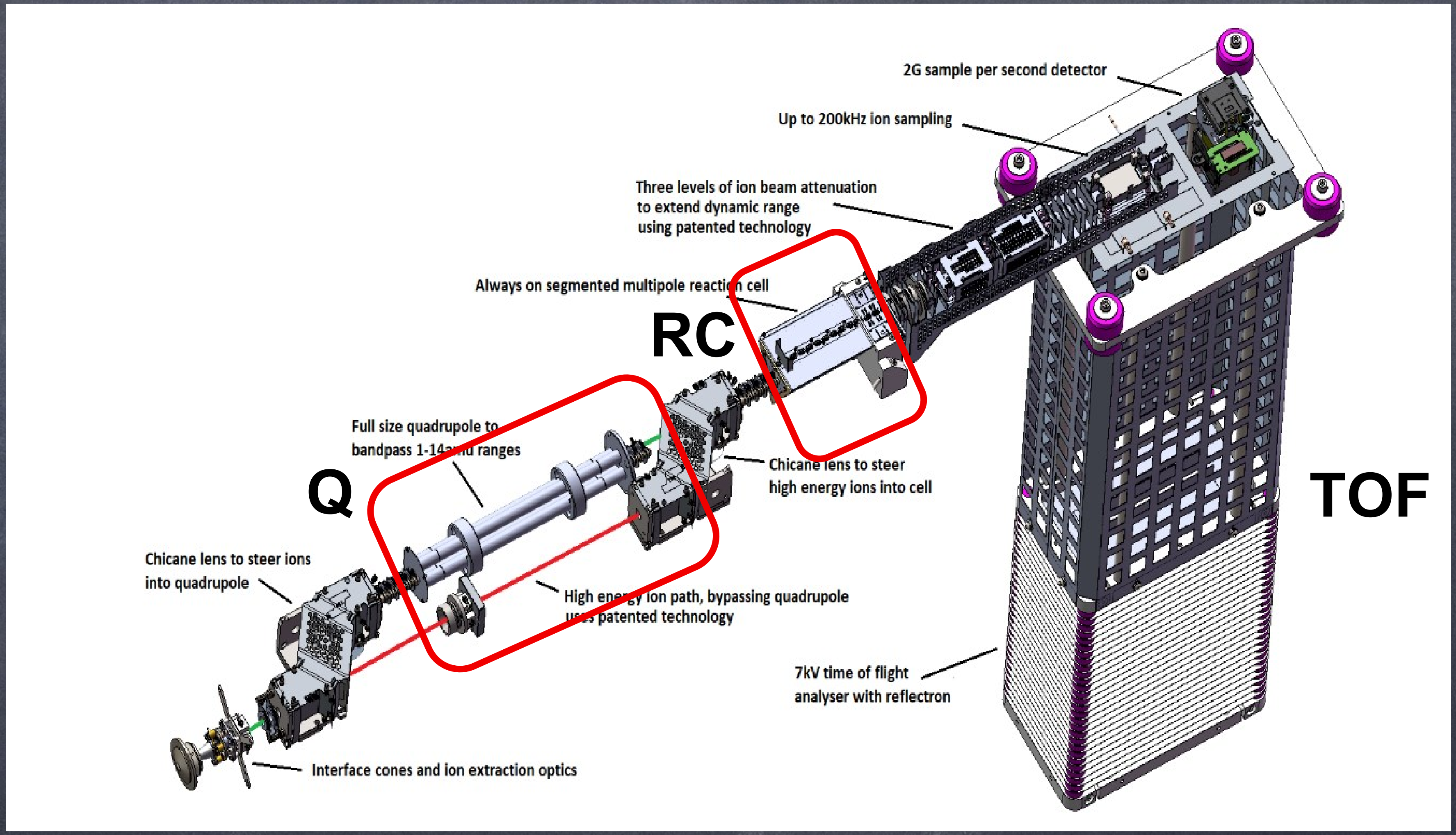
Agilent Series 8900 QQQ

Quadrupolo (Q)

Reaction/Collison Cell (R/CC) = rimozione inteferenze isobariche



ICP-MS-TOF



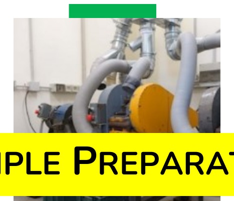
- scansione velocissima dello spettro in massa a partire da una soglia con acquisizione di tutte le masse

ICP-MS a Settore Magnetico

Giornate di confronto sulla Paleoclimatologia in Italia

Istituto di Geoscienze e Georisorse (IGG) - Pisa

Multi Collector ICP Mass Spectrometry Laboratory



Sample Preparation

Sample Weighting

Sample Digestion

Chemical Separation

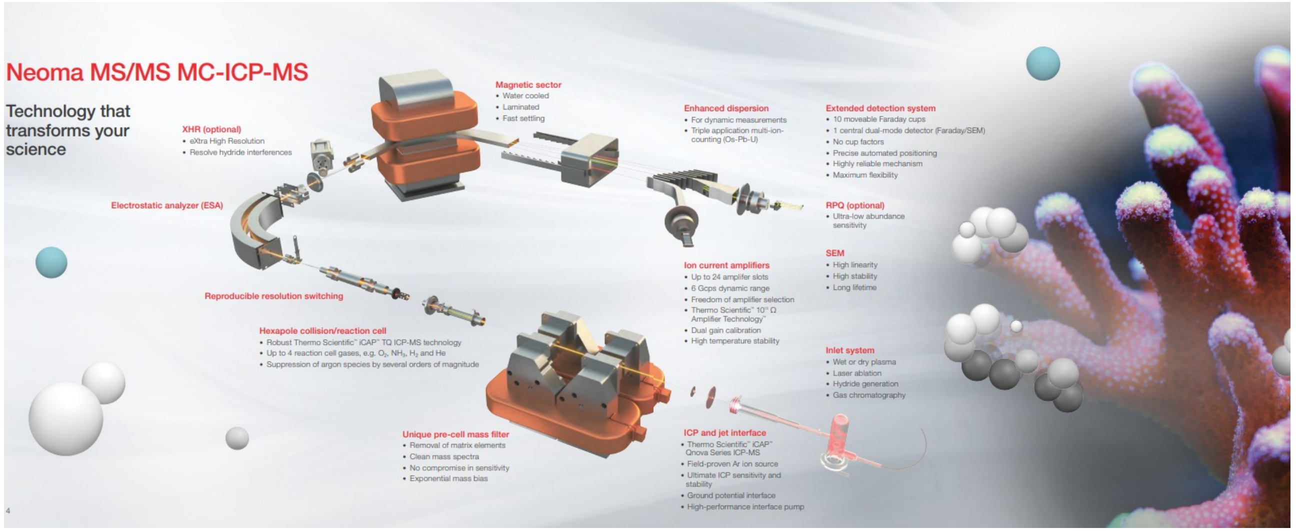
Measurements

In Situ Analyses

Interference Separation

Thermo Scientific NEOMA

MS/MS MC-ICP-MS



11 Faraday Cup mobile detector array

10^{13} Ω Amplifer Technology

Highest sensitivity and stability

Superior Vacuum System

Extra High Resolution (XHR) increasing the resolving power

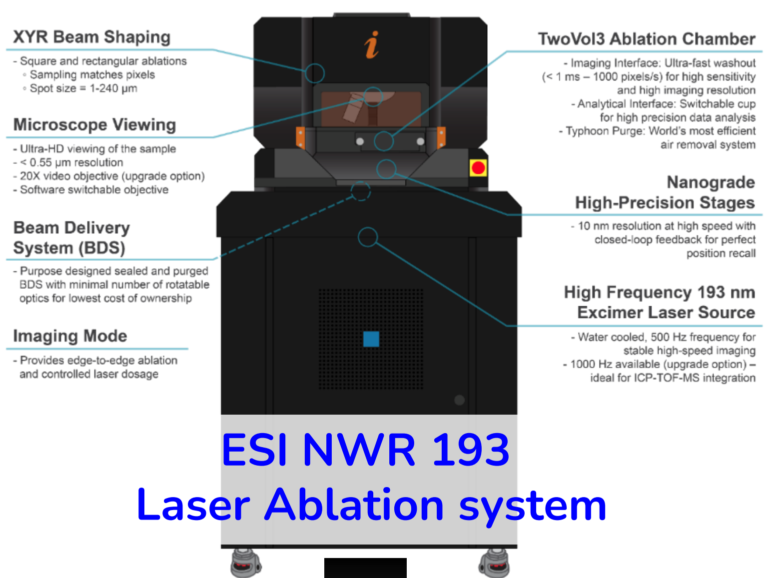
Retarding Potential Quadrupole (RPQ) improving abundance sensitivity

ICP-MC-MS

ISTITUTO DI GEOSCIENZE E GEORISORSE (IGG)

NEPTUNE-NEOMA LABORATORY

IN SITU ANALYSES

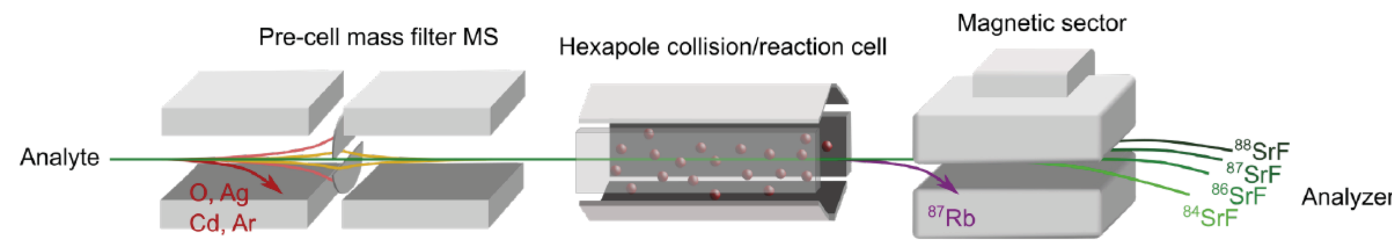


ESI NWR 193
Laser Ablation system

MINIMAL SAMPLE PREPARATION

SAMPLE CONTAMINATION REDUCTION

MS/MS TECHNOLOGY



FILTER	REACTION	SEPARATION
REMOTION OF SAMPLE MATRIX	EFFECTIVE INTERFERENCE REMOVAL	ROBUST ISOTOPE SEPARATION AND DETECTION
NON-ISOBARIC INTERFERENCE REMOVAL	DIFFERENT REACTIVE GASES	SIMULTANEOUS MEASUREMENT OF ALL ISOTOPES OF INTEREST
MAGNETIC SECTOR TECHNOLOGY		LOW TO HIGH RESOLUTION MODE

CNR igg

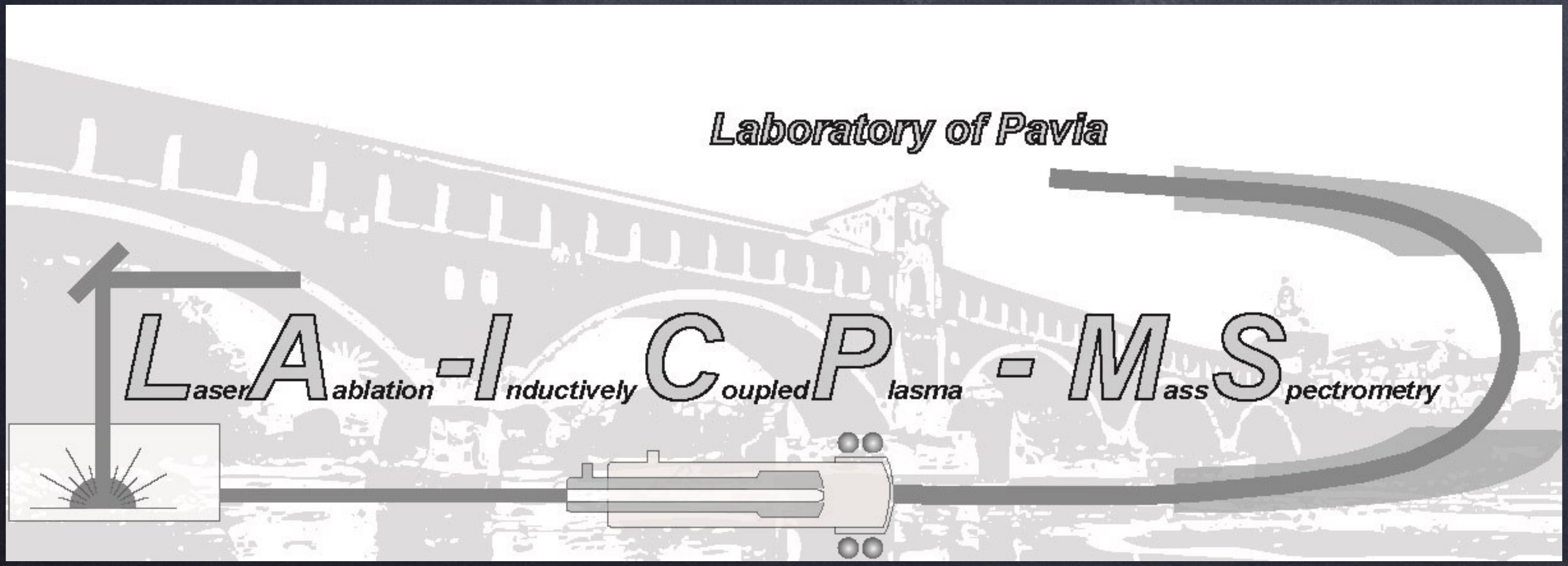
ITINERIS

LA-ICP-MS analysis:

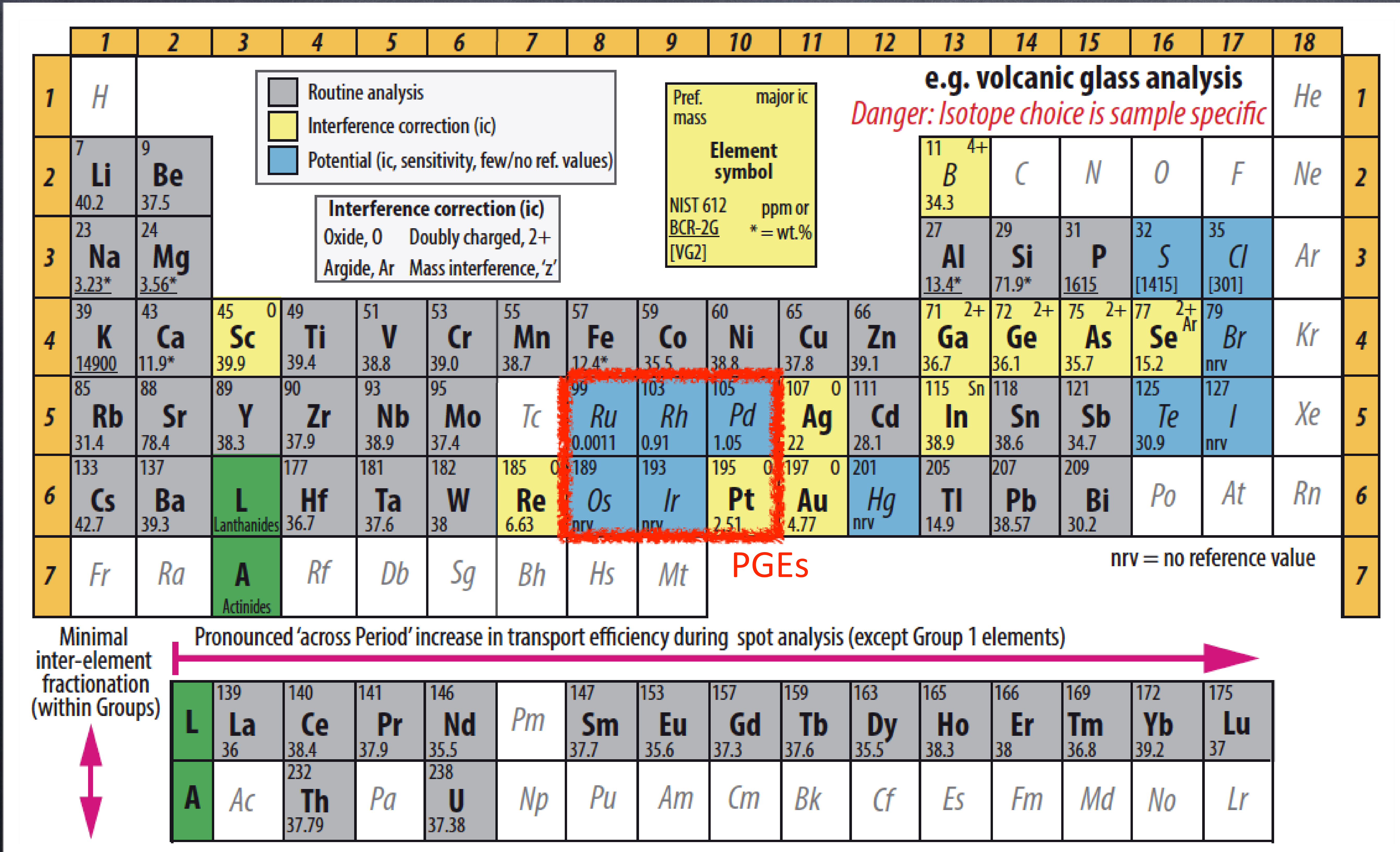
– what we can do!

Trace element
(<1000 ppm/ 0.01 wt%)

U-(Th)-Pb
Geochronology



LA-ICP-MS Trace element



LA-ICP-MS Trace element

Main application

Silicates: Olivine, Amphibole, Pyroxene, Garnet, Mica, Plagioclase, epidote, titanite..

Oxides: chromite, rutile, corundum

Phosphate (e.g. Monazite)

Sulfides (e.g. Pyrite) & Sulfates (e.g.Anhydrite CaSo4)

Petrology

Carbonates: calcite and dolomite

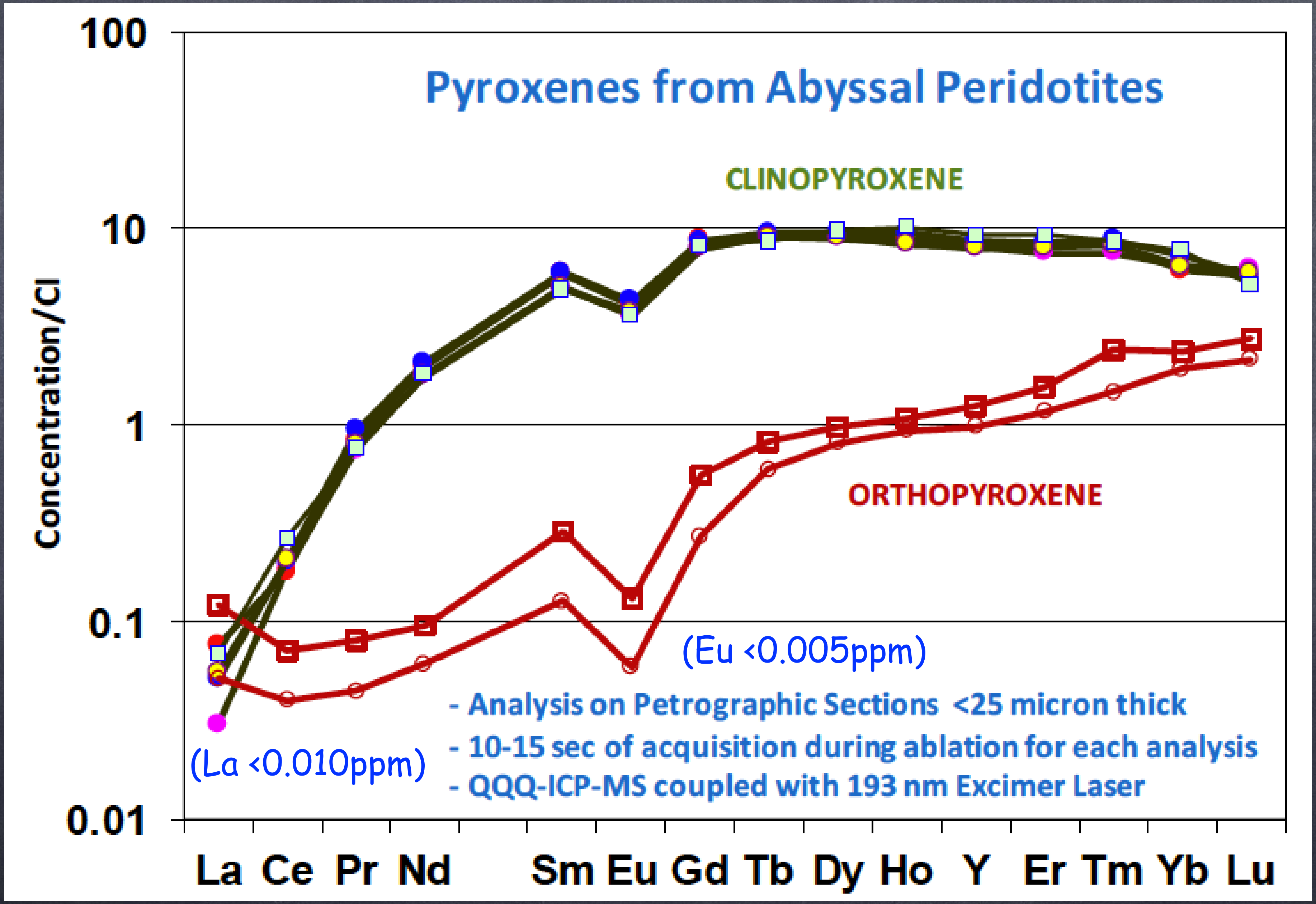
Biology

Glasses

Archaeometry

LA-ICP-MS Trace element

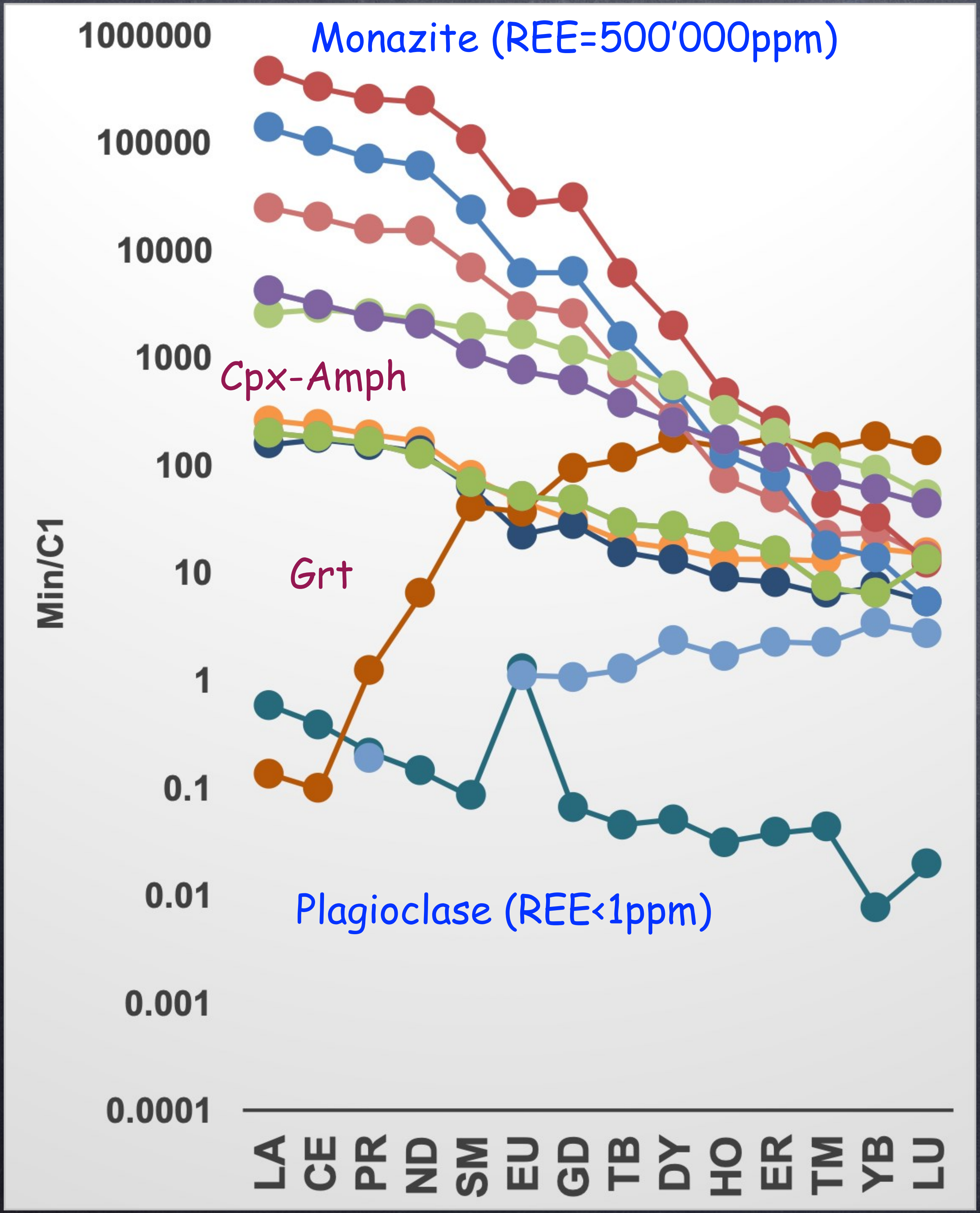
Petrology….

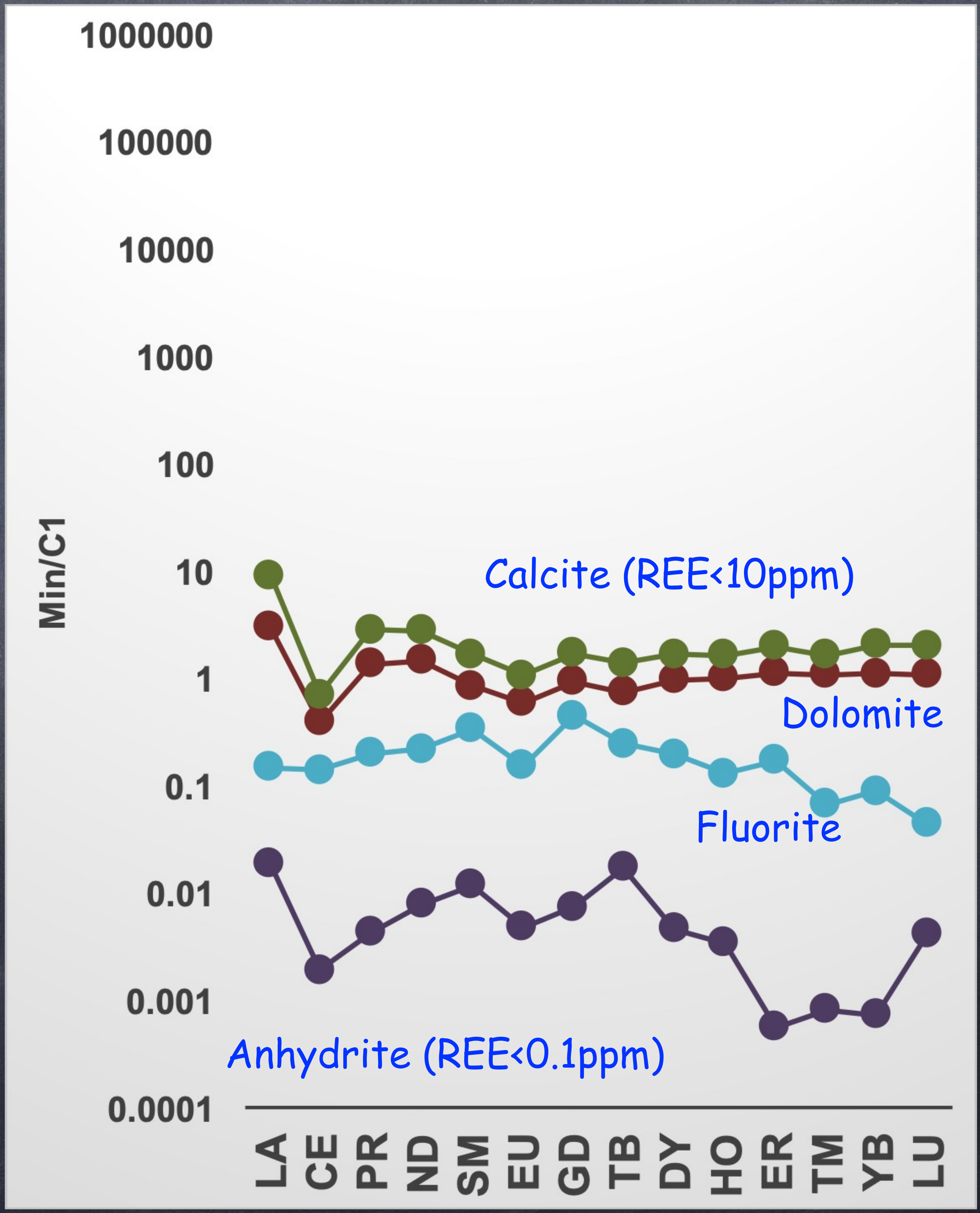


Trace element composition normalised to Chondrite CI (Primitive Meteorites)

LA-ICP-MS Trace element

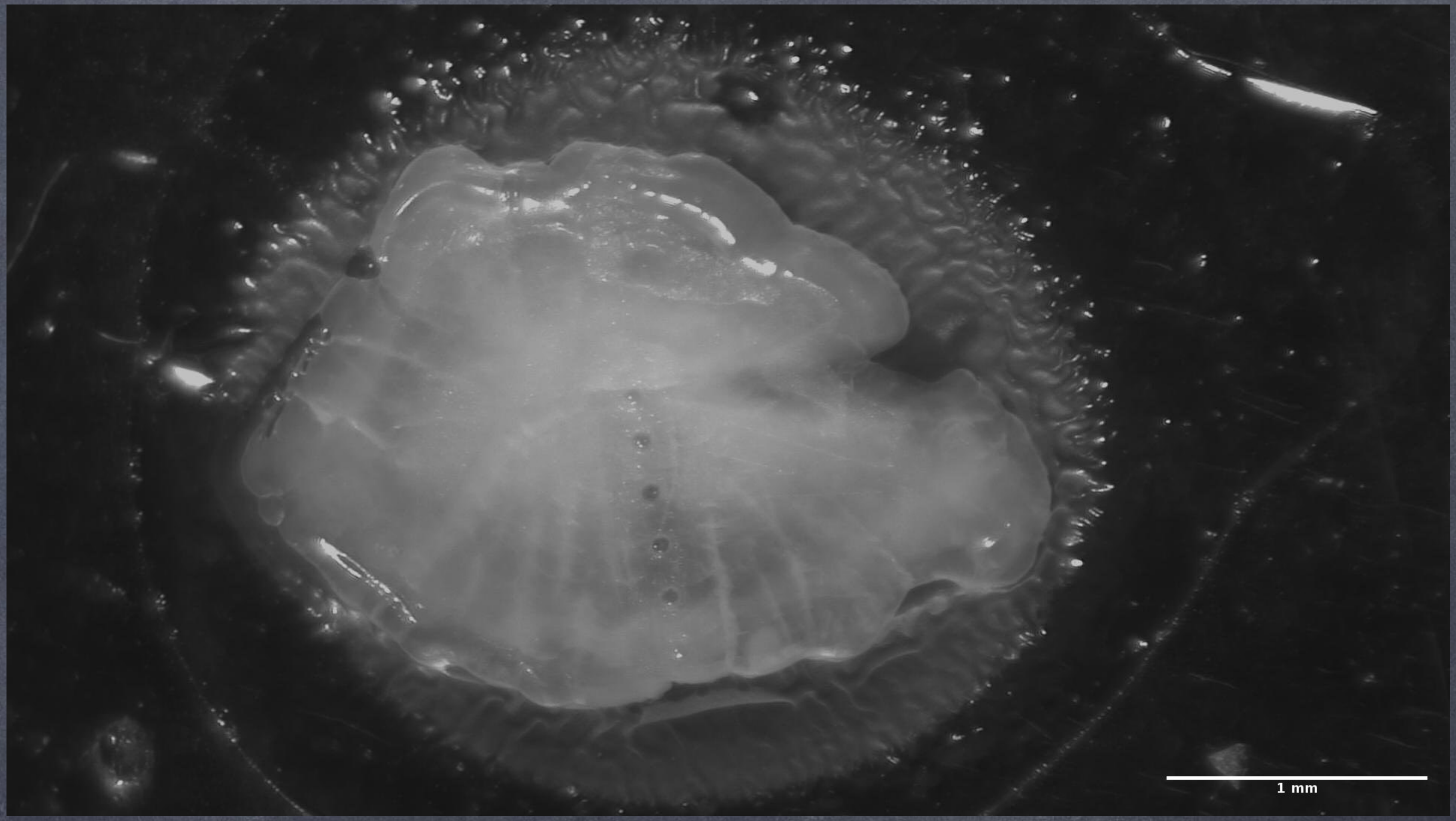
Petrology....





LA-ICP-MS Trace element

Biology: chemical profiles of carbonate growth



Lithothamnion corallioides
(Alghe rosse calcaree)

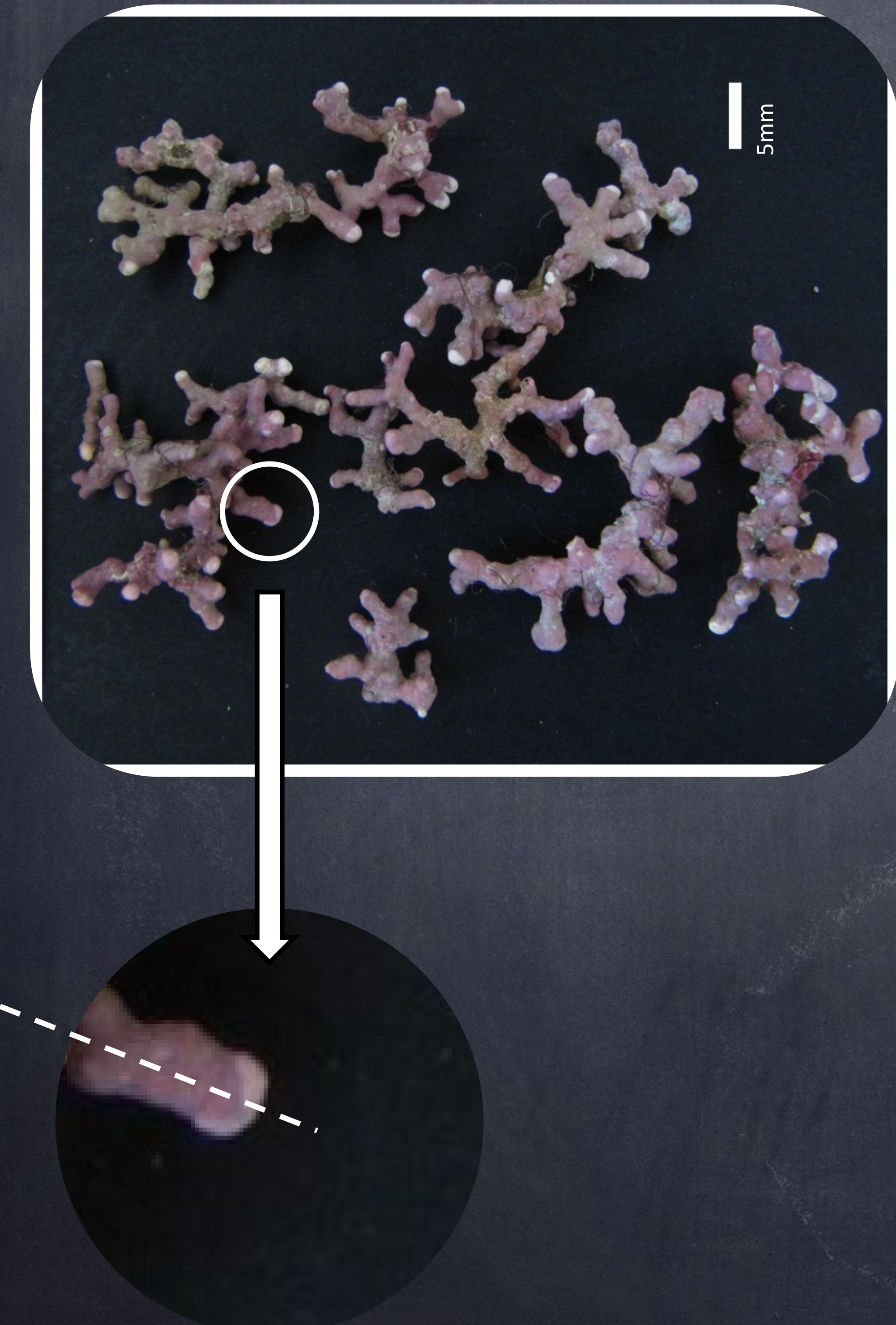
Mullet Otolith
(Otolite di triglia)

In collaboration with Marco Stagioni (UniBo)

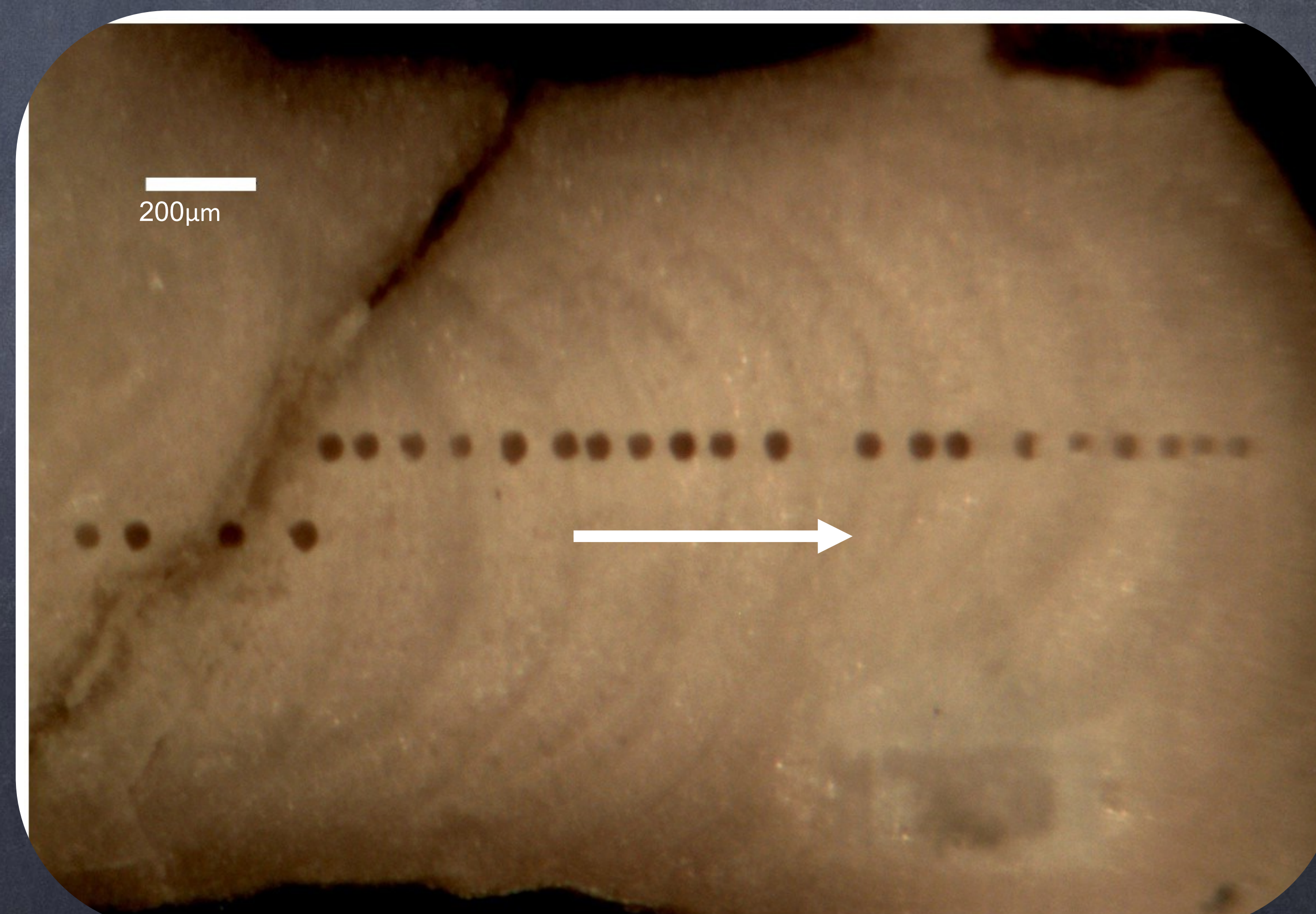
In collaboration with Prof. Basso Daniela Maria (UniMiB) and co-authors
Piazza et al. 2021

LA-ICP-MS Trace element

Lithothamnion corallioides
(Alghe rosse calcaree)



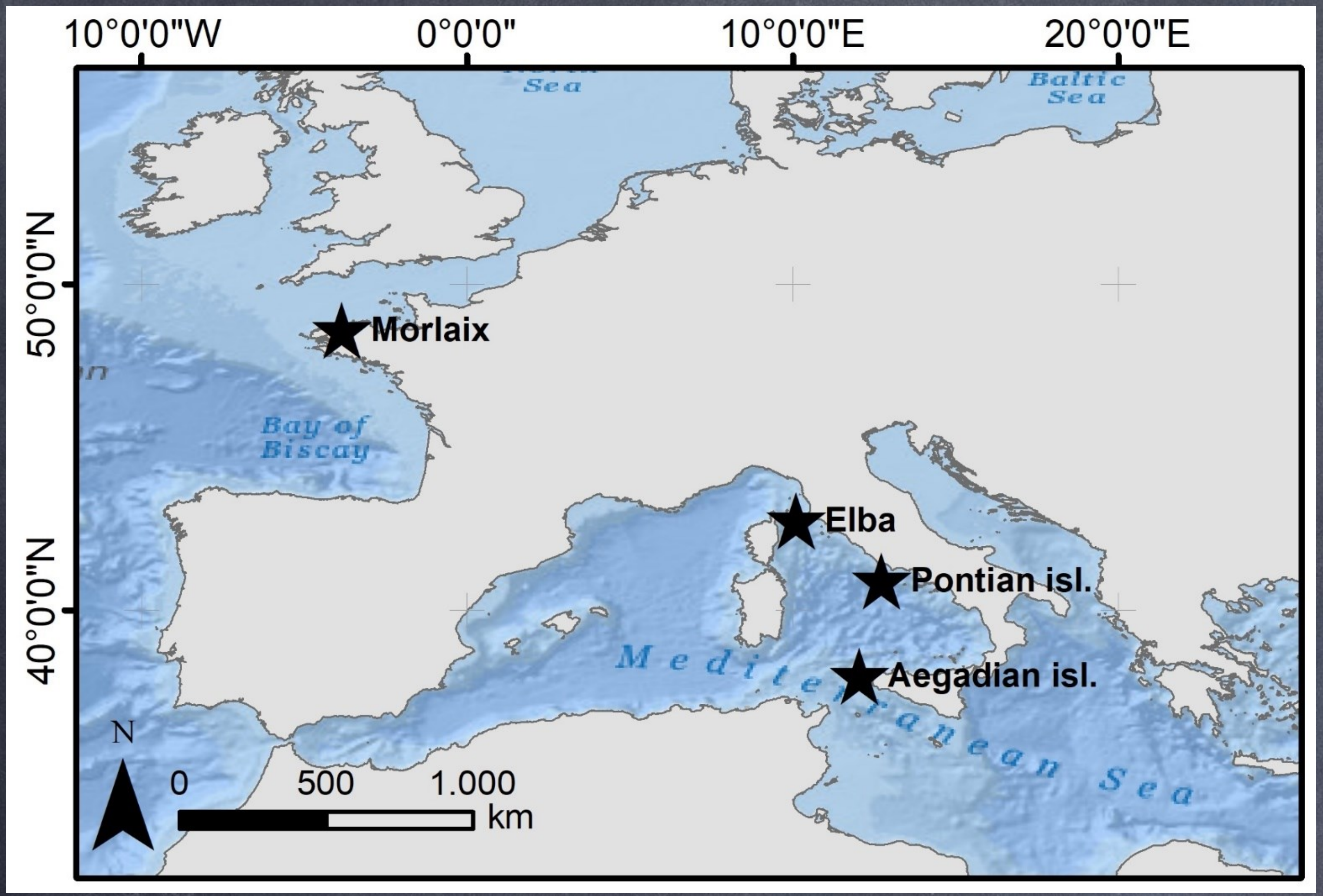
LA-ICP-MS was performed on longitudinal sections of the calcareous red algae *Lithothamnion corallioides*, following the growth direction



In collaboration with Prof. Basso Daniela Maria (UniMiB) and co-authors
May 2019

LA-ICP-MS Trace element

Lithothamnion corallioides
(Alghe rosse calcaree)

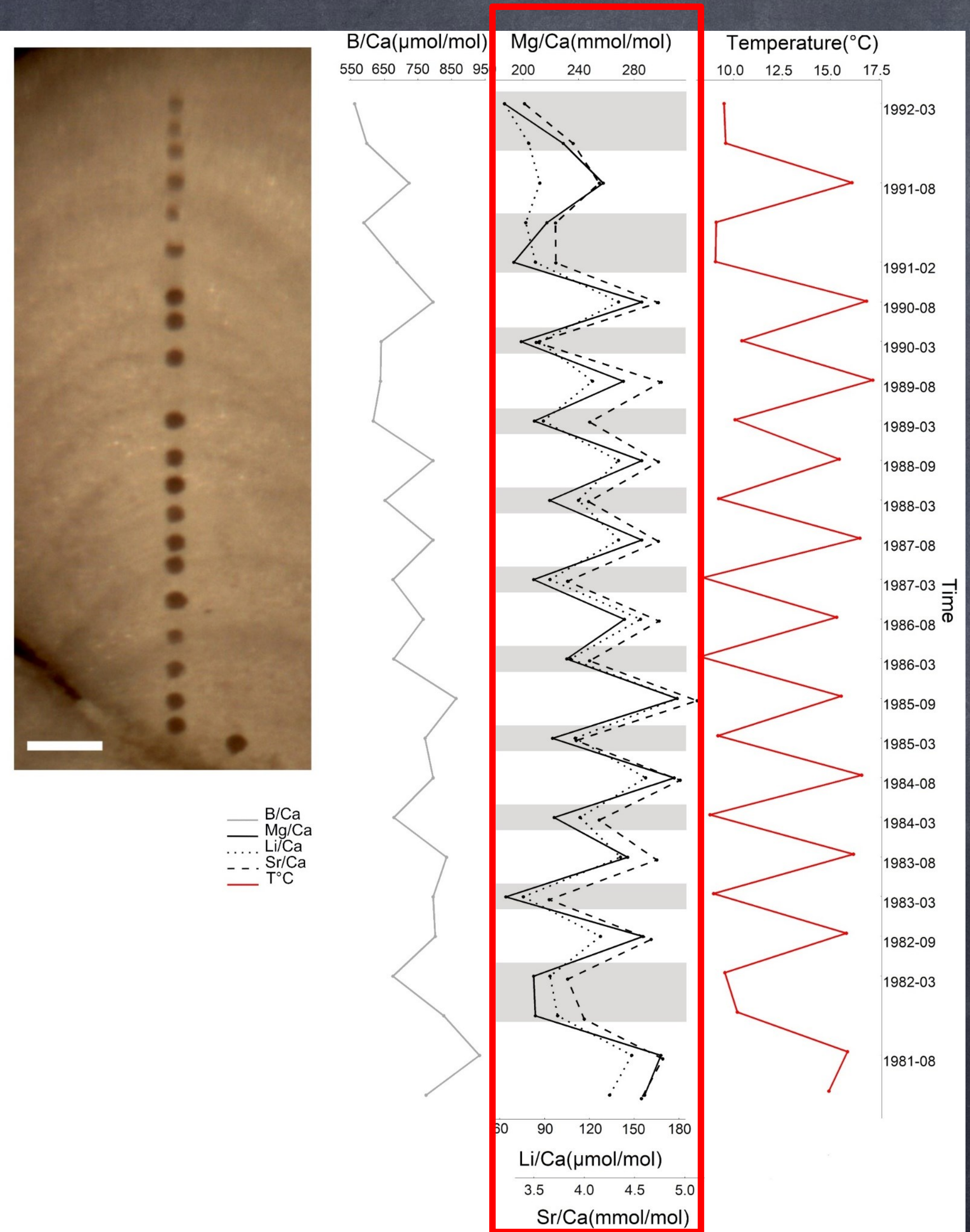


356.0 μmol/mol < B/Ca < 954.1 μmol/mol
171.7 mmol/mol < Mg/Ca < 311.2 mmol/mol
53.8 μmol/mol < Li/Ca < 178.5 μmol/mol
2.9 mmol/mol < Sr/Ca < 5.1 mmol/mol

Sampling site	**B/Ca (μmol/mol)**		**Mg/Ca (mmol/mol)**		**Li/Ca (μmol/mol)**		**Sr/Ca (mmol/mol)**		**Mg/Li (mol/mmol)**	
	mean	st. dev.	mean	st. dev.	mean	st. dev.	mean	st. dev.	mean	st. dev.
Aegadian Isl.	610.8	63.9	224.9	30.3	81.9	18.4	3.7	0.4	2.8	0.5
Elba	757.7	75.5	223.4	26.4	85.2	14.3	3.6	0.4	2.7	0.3
Pontian Isl.	462.8	49.2	216.1	21.9	79.6	14.6	3.3	0.3	2.8	0.4
Morlaix	726.9	102.8	239.5	41.2	113.1	32.9	4.1	0.5	2.2	0.4
total	**661.9**	**138.9**	**225.3**	**30.4**	**89.0**	**23.3**	**3.7**	**0.5**	**2.6**	**0.4**

Piazza, G., Bracchi, V. A., Langone, A., Meroni, A. N., and Basso, D.: Growth rate rather than temperature affects the B / Ca ratio in the calcareous red alga *Lithothamnion corallioides*, Biogeosciences Discuss. [preprint], https://doi.org/10.5194/bg-2021-21, in review, 2021.

LA-ICP-MS Trace element



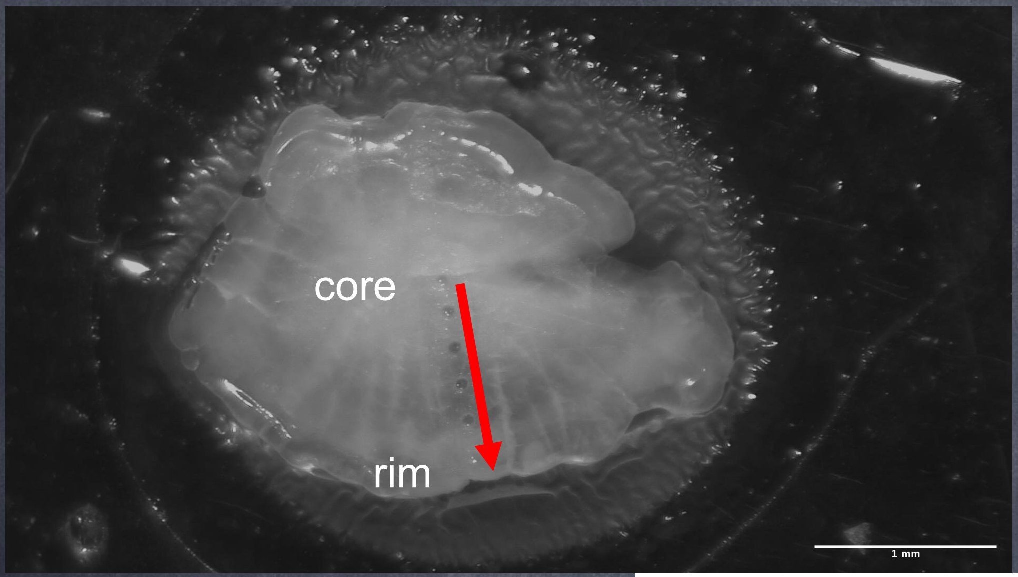
Lithothamnion corallioides
(Alghe rosse calcaree)

Dark bands correspond to winter growth,
Light bands correspond to summer growth.

Mg, Li, Sr/Ca show cyclic variations corresponding to the seasonal fluctuation in seawater temperature.

B/Ca lack of a significant temperature influence.

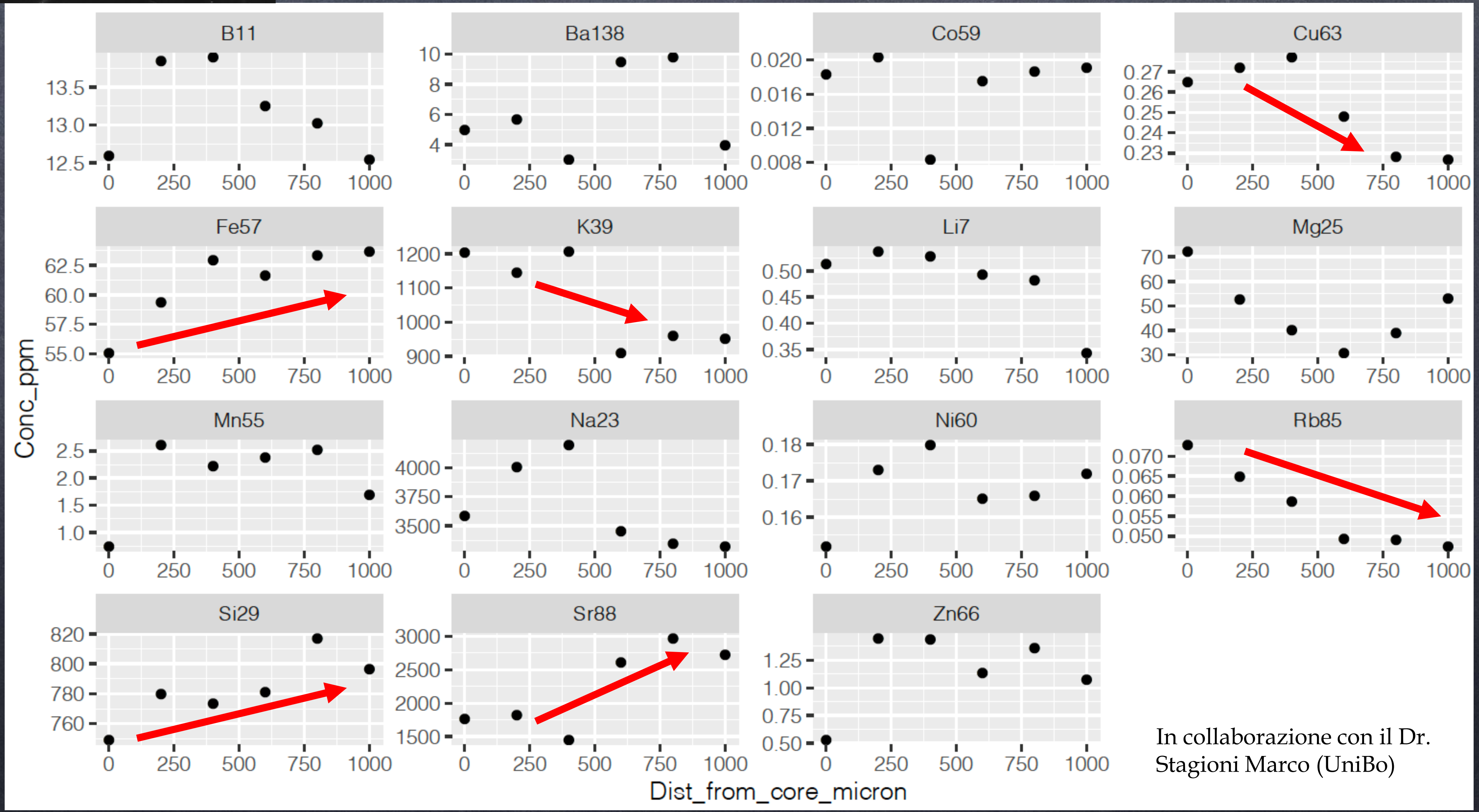
LA-ICP-MS Trace element



LA-ICP-MS was performed on mullet otholith

Core => larva => pelagic conditions

Rim => 1 year old => deep water conditions

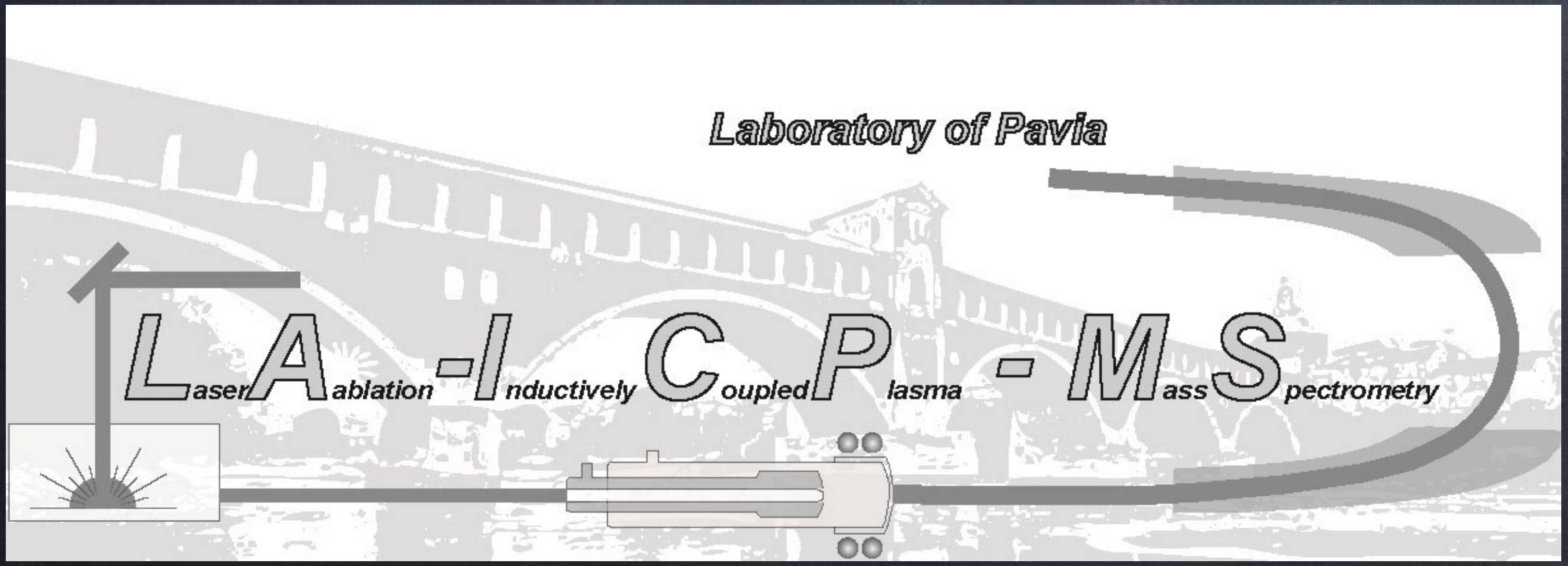


In collaborazione con il Dr.
Stagioni Marco (UniBo)

LA-ICP-MS analyses:

- what we can do!

U-(Th)-Pb Geochronology



U-(Th)-Pb Geochronology

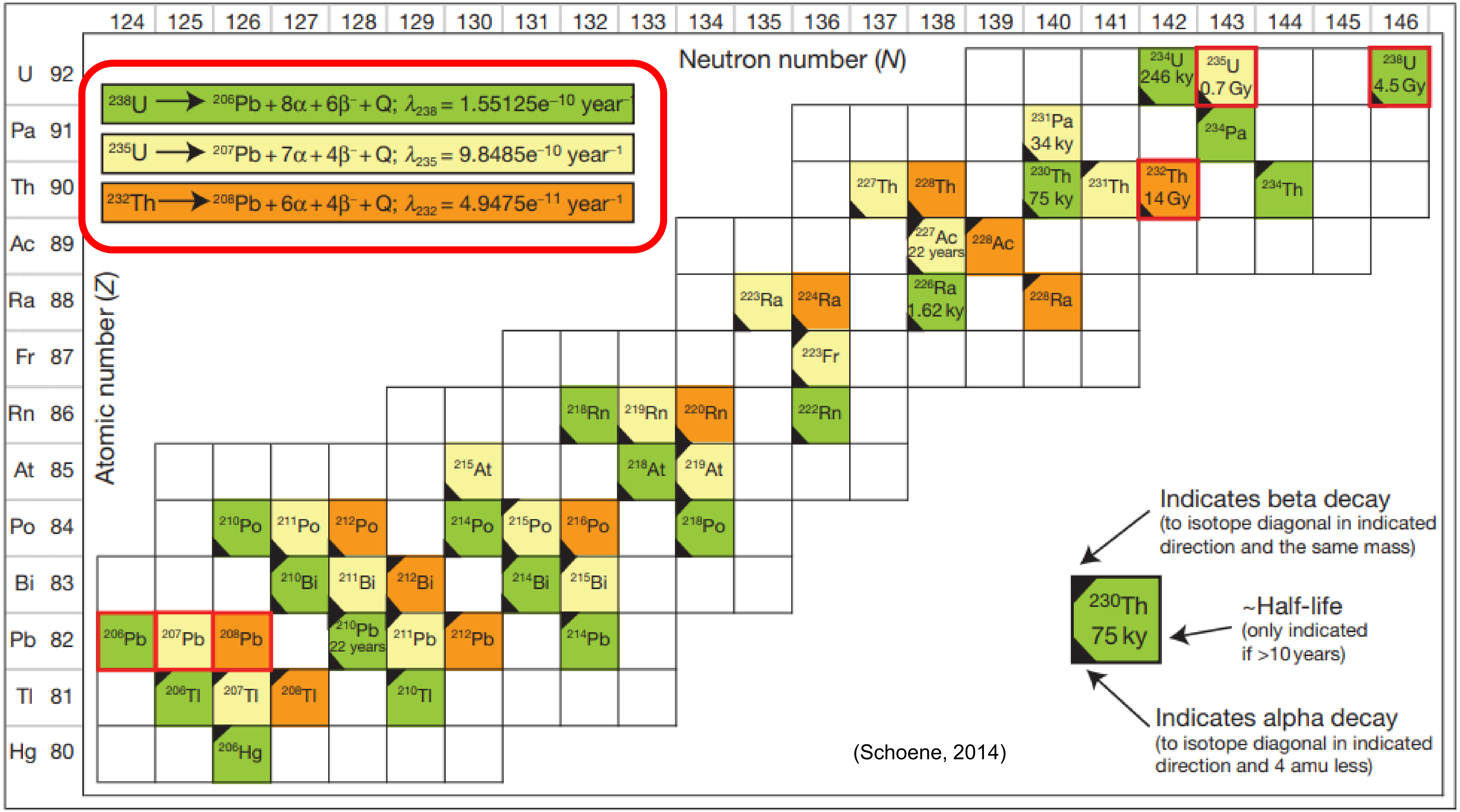
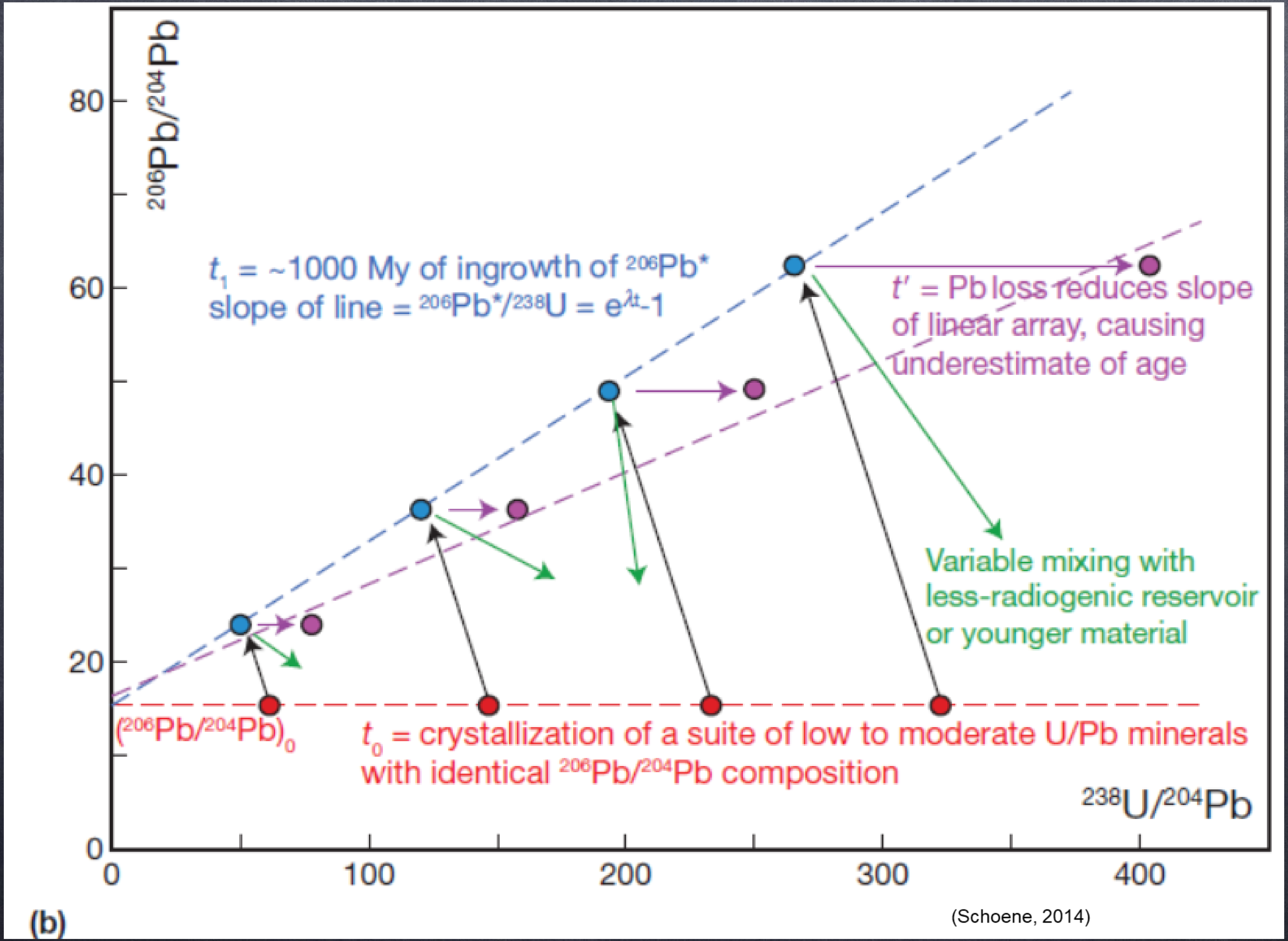


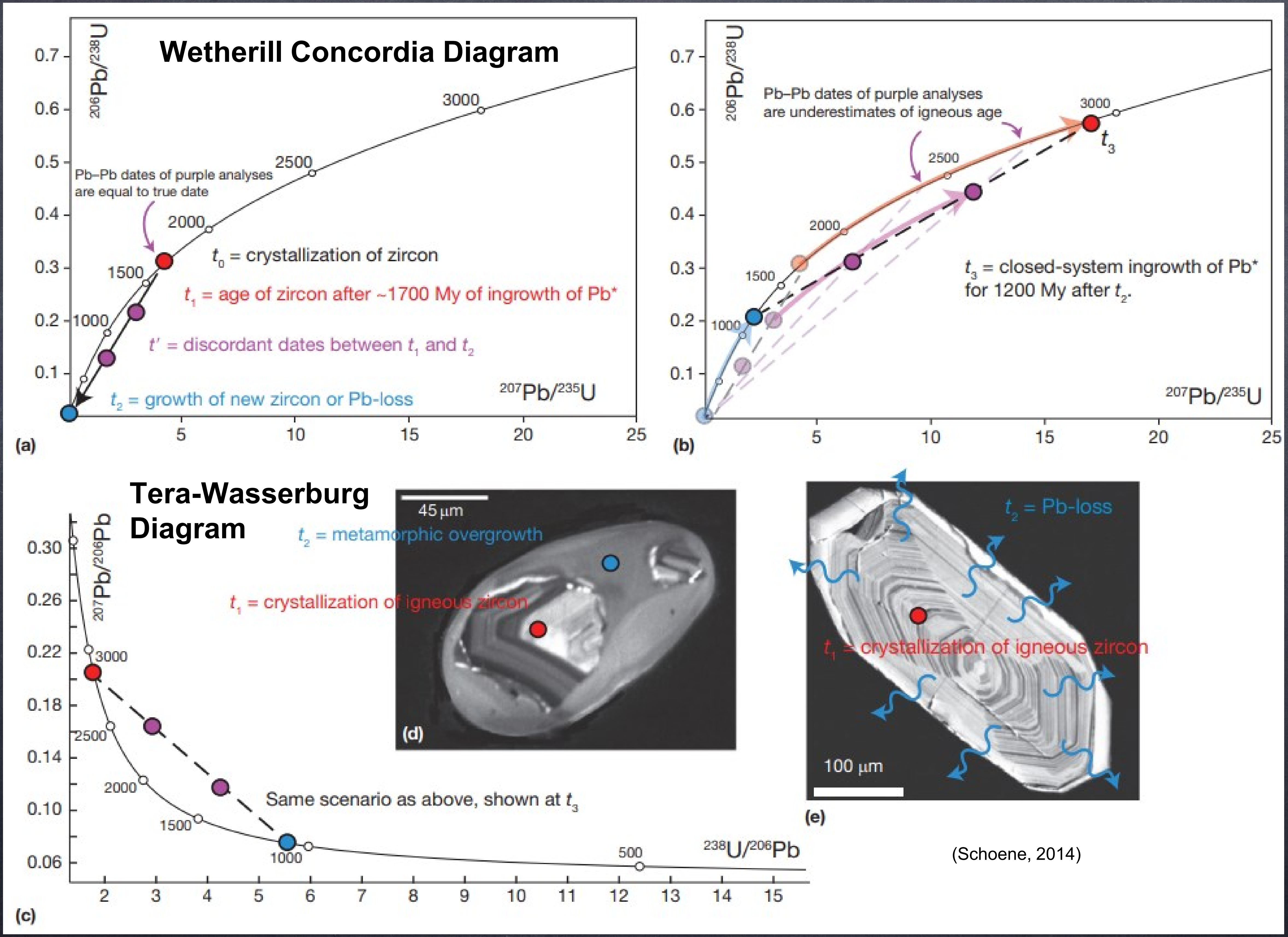
Figure 2 An illustration of the U–Th–Pb decay chains. Each isotope occurring in a given decay chain is color-coded to its parent isotope, which are outlined in red, as are the stable daughter isotopes of Pb. See inset for description of symbols used in each box. α is an alpha particle, β is a beta particle, and Q is energy released during the decay.

U-(Th)-Pb Geochronology



(Schoene, 2014)

U-(Th)-Pb Geochronology



(Schoene, 2014)

Common minerals used for U-Pb dating

Igg-Pv

Zircon: $ZrSiO_4$

Monazite: (LREE)PO_4

Rutile (TiO_2)

Titanite ($CaTiSiO_5$)

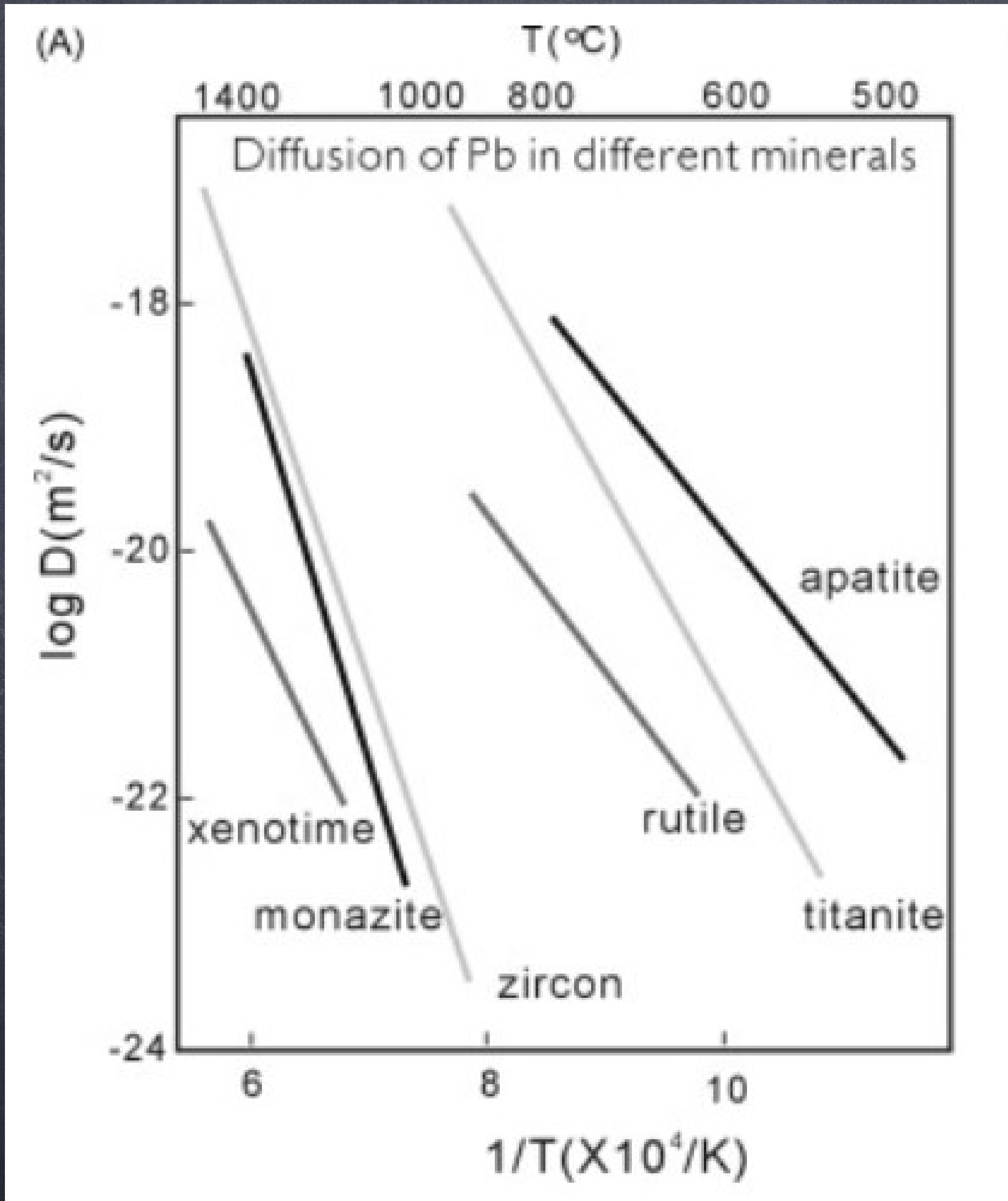
Allanite

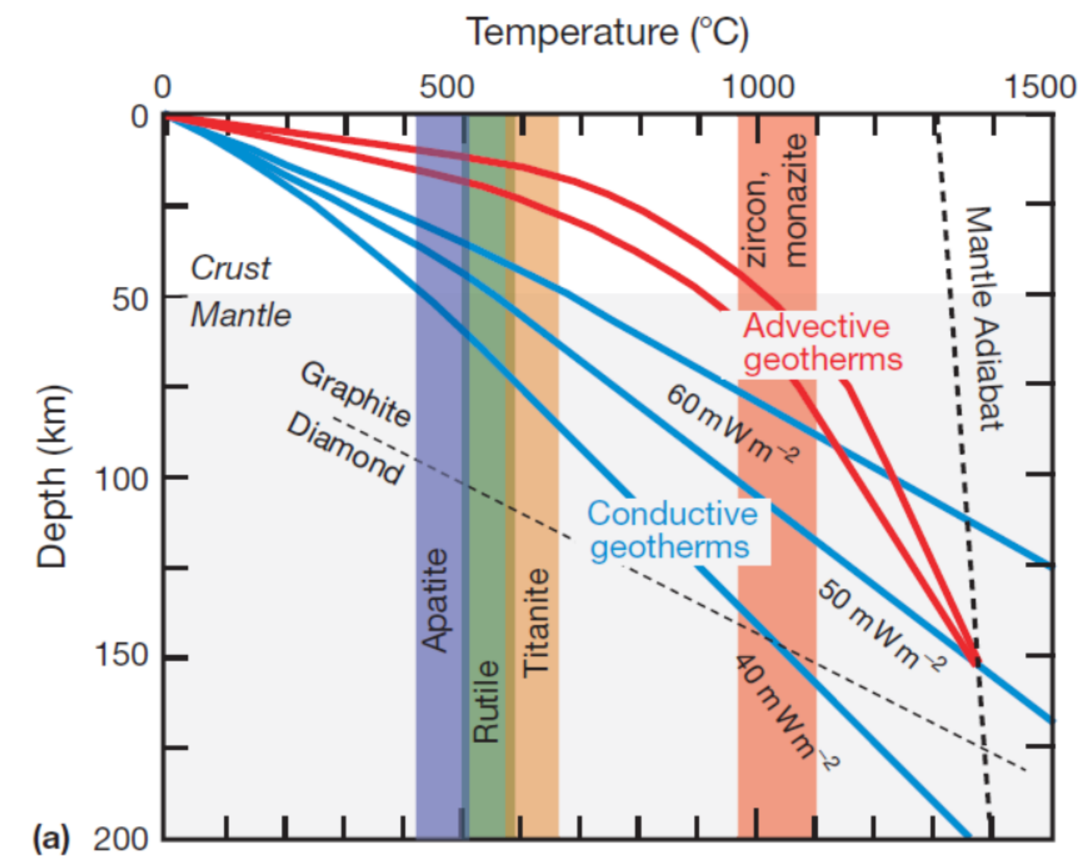
Ca(REE,Ca)Al_2(Fe^{++},Fe^{+++})(SiO_4)(Si_2O_7)O(OH)

Th between 0.05 and 3 wt.% and U between 10 and 3000 ppm

prime target for U–Pb and Th–Pb geochronology

U-(Th)-Pb Geochronology





(Schoene, 2014)

Cherniak DJ (2010) Diffusion in accessory minerals: Zircon, Titanite, Apatite, Monazite and Xenotime. *Reviews in Mineralogy & Geochemistry* 72: 827–869.

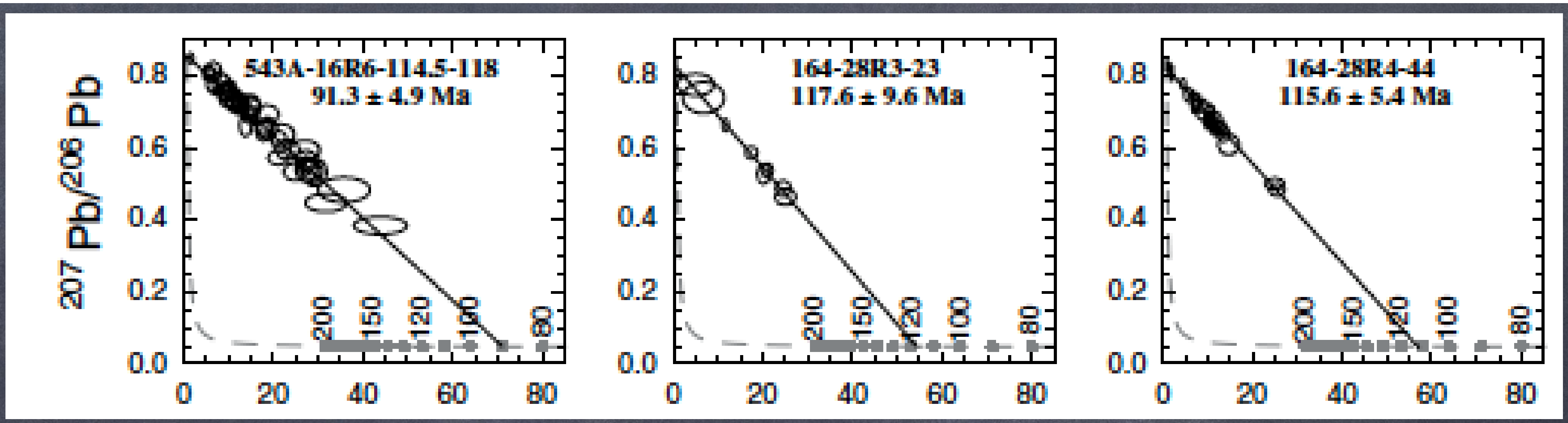
…. calcite U-Pb dating

Calcite
($CaCO_3$)

Early hydrothermal carbon uptake by the upper oceanic crust: Insight from in situ U-Pb dating

Geology, 2016

Laurence A. Coogan[1]*, Randall R. Parrish[2,3], and Nick M.W. Roberts[3]



3% 2sigma error

U ranges from 13 to 2400 ppm!!!!

14% 2sigma error

…. calcite U-Pb dating

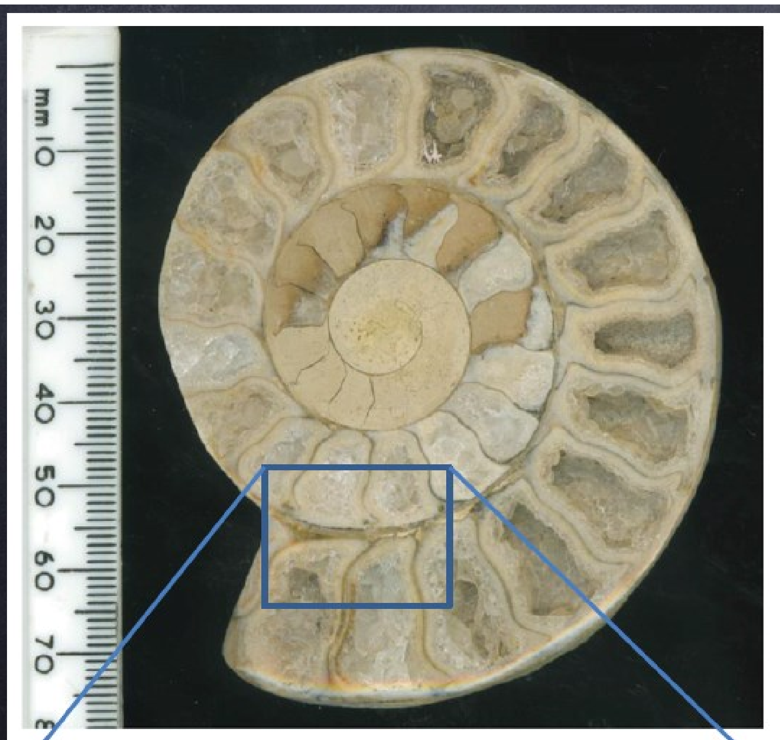
Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

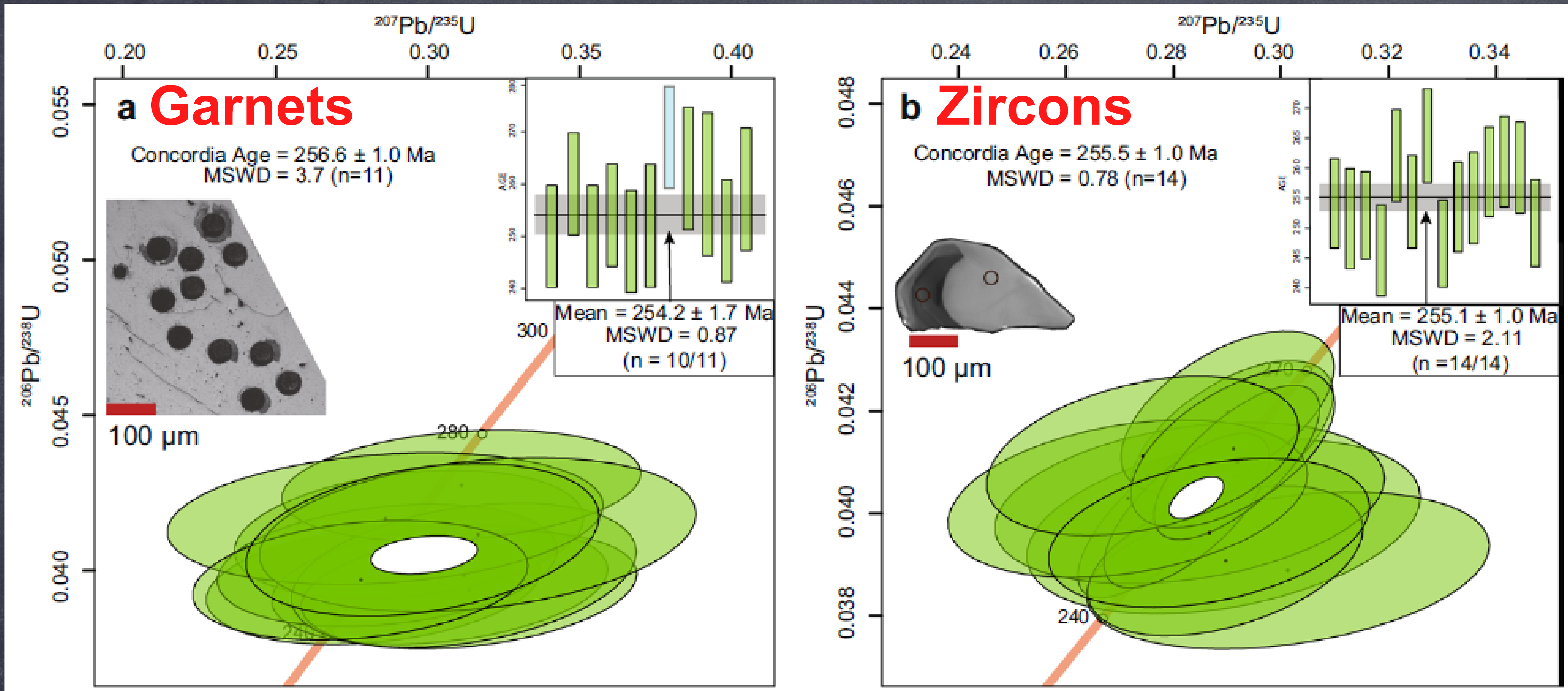
U–Pb dating of cements in Mesozoic ammonites

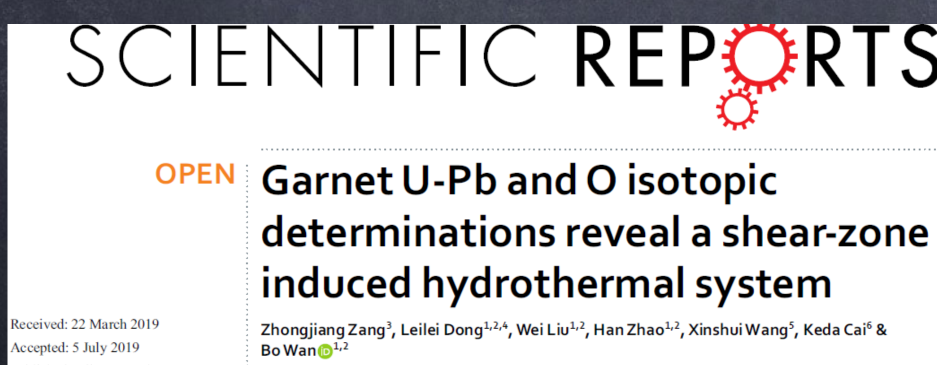
Q. Li [a,*], R.R. Parrish [b,c], M.S.A. Horstwood [c], J.M. McArthur [a]



U ranges from 0.47 to 5.3ppm!!!!

U-Pb dating: Garnet vs. Zircon



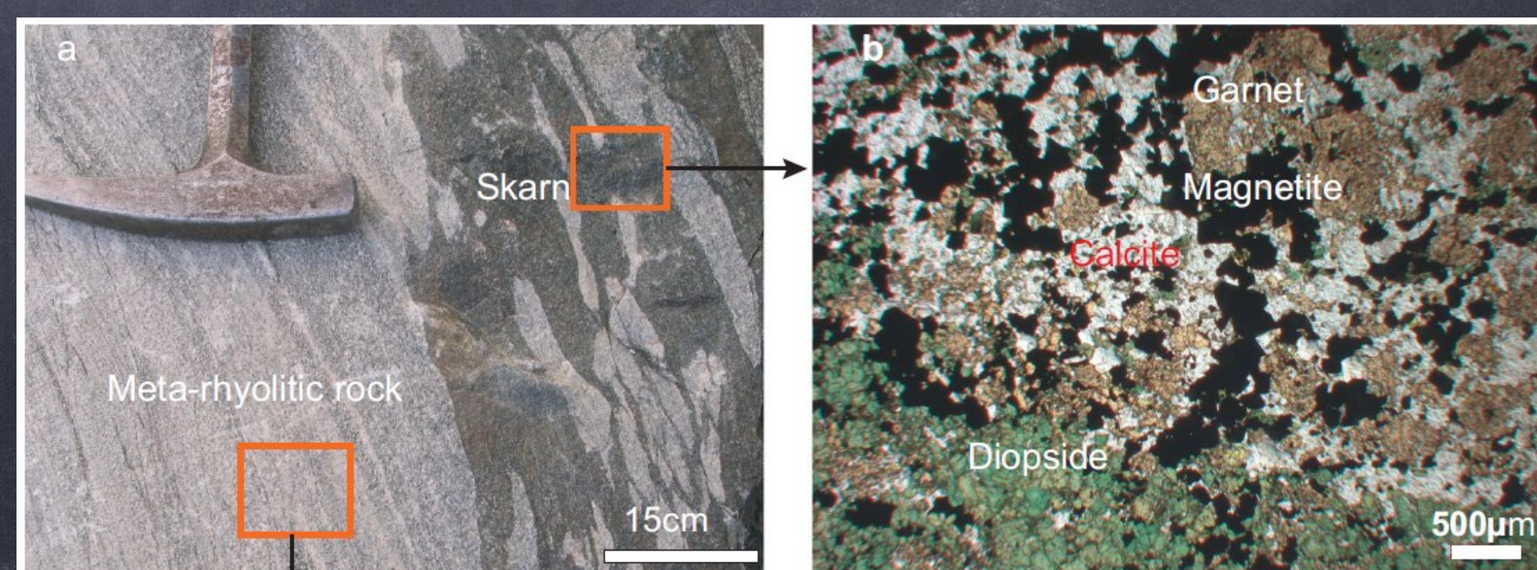

SCIENTIFIC REPORTS

OPEN

Garnet U-Pb and O isotopic determinations reveal a shear-zone induced hydrothermal system

Received: 22 March 2019
Accepted: 5 July 2019
Published online: 17 July 2019

Zhongjiang Zang[3], Leilei Dong[1,2,4], Wei Liu[1,2], Han Zhao[1,2], Xinshui Wang[5], Keda Cai[6] & Bo Wan[1,2]



Andradite:

$Ca_3Fe^{3+}{}_3Si_3O_{12}$

minerals

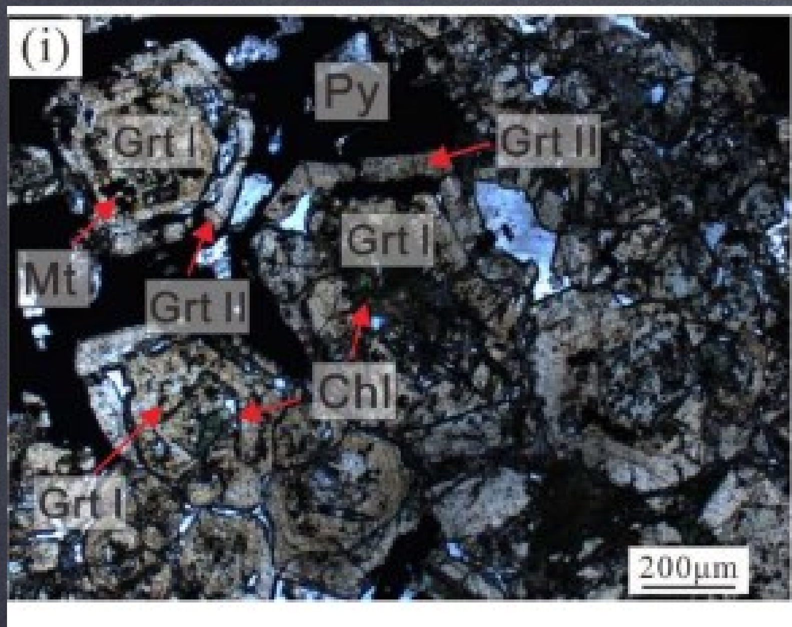
MDPI

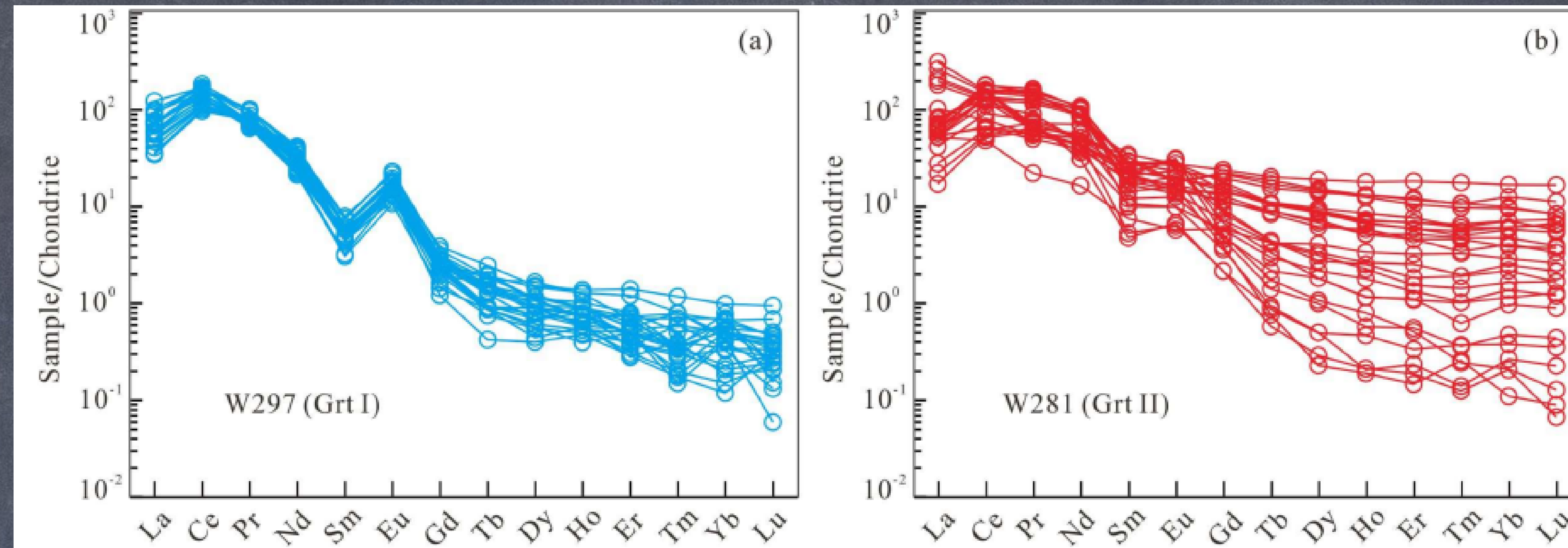
Article

U-Pb Geochronology and Geochemistry of U-Rich Garnet from the Giant Beiya Gold-Polymetallic Deposit in SW China: Constraints on Skarn Mineralization Process

Yu Fu [1,2], Xiaoming Sun [1,2,3,*], Dengfeng Li [1,2] and Hai Lin [2,3]

U-Pb dating & Traces: Garnet





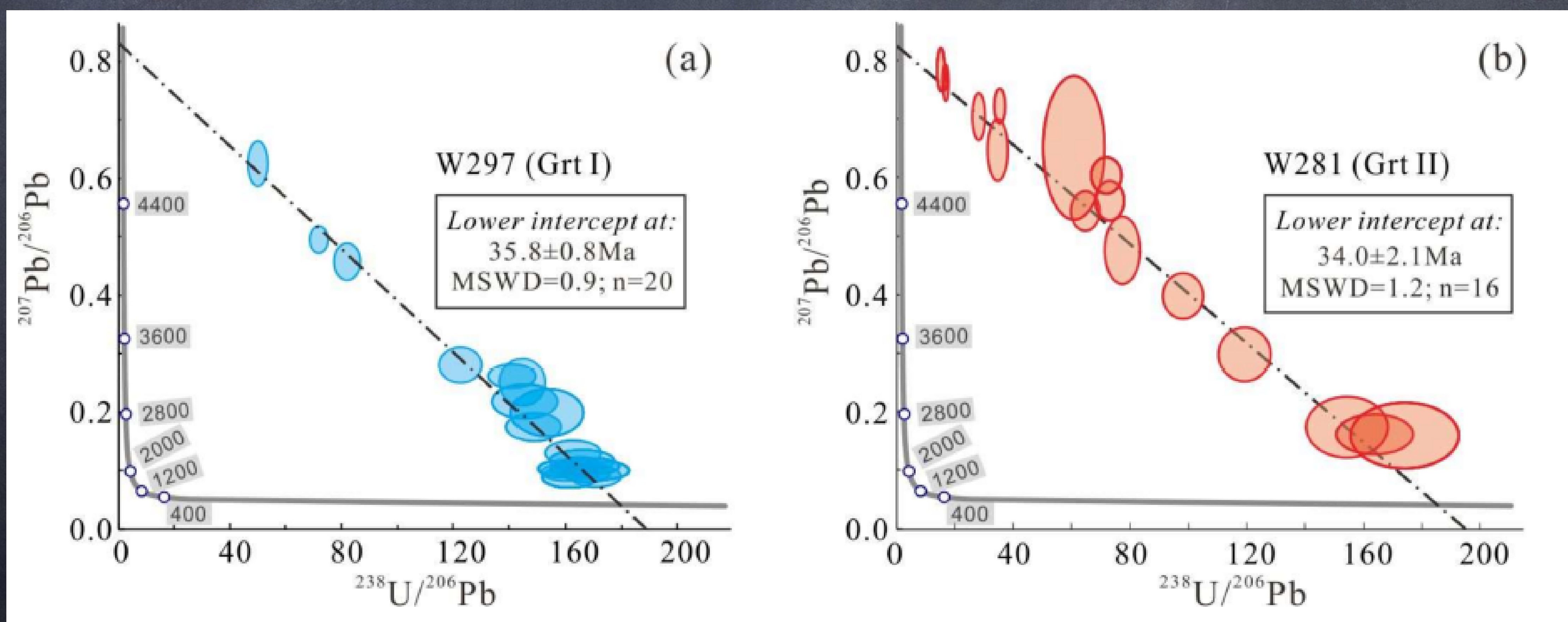


Figure 7. Tera–Wasserburg diagram for the Beiya garnet: (**a**) W281, (**b**) W297.

U-Pb dating: Mantle Garnet

Uranium–lead geochronology applied to pyrope garnet with very low concentrations of uranium

Gary J O'Sullivan[1], Brendan C Hoare[2], Chris Mark[1,*], Foteini Drakou[3] and Emma L Tomlinson[3]

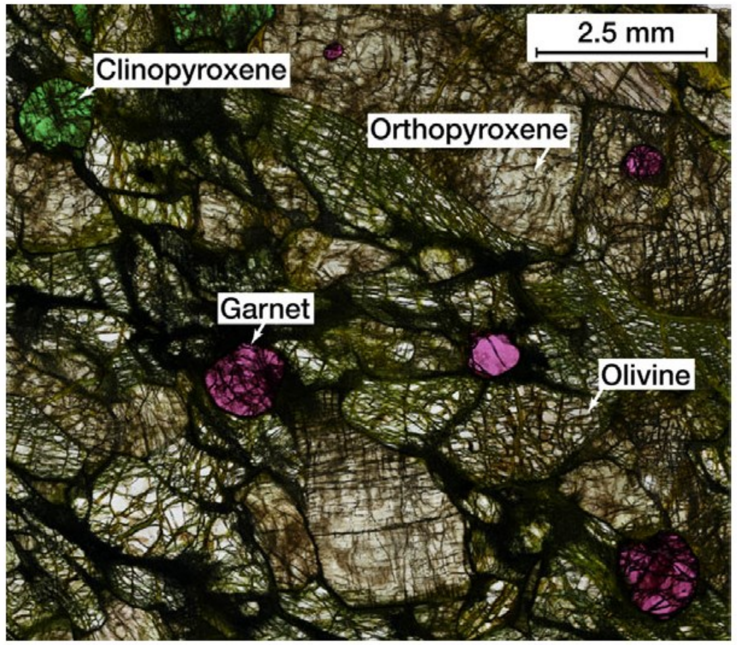


Fig. 2. (Colour online) Transmitted light image of a thick section of coarse-grained lherzolite from Bultfontein (sample CLA-13). Garnet are magenta in colour.

U = 20-85 ng/g
No Pb comune

ca. 85 Ma

Coincidente con età magmatismo

Piropo: $Mg_3Al_3Si_3O_{12}$

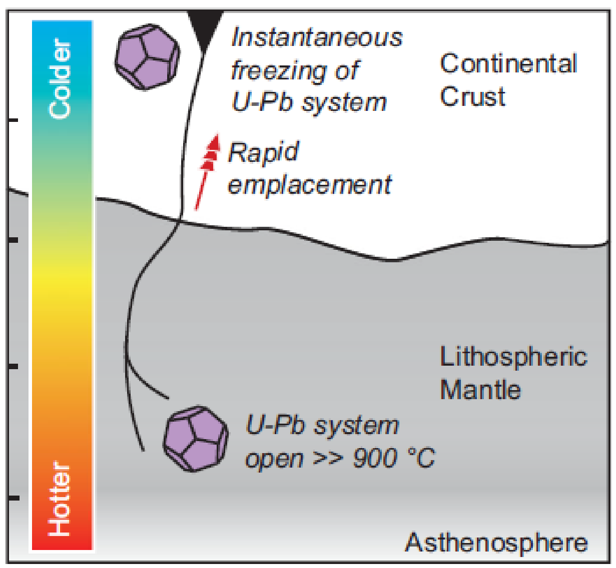


Fig. 5. (Colour online) Conceptual model of the behaviour of the U–Pb system in pyrope-rich garnet from sampled xenoliths. Garnet sampled from very high temperatures, as in this study, will reflect emplacement. Garnet yielding lower equilibration temperatures or encapsulated in diamond (none in this study) might retain ancient information.

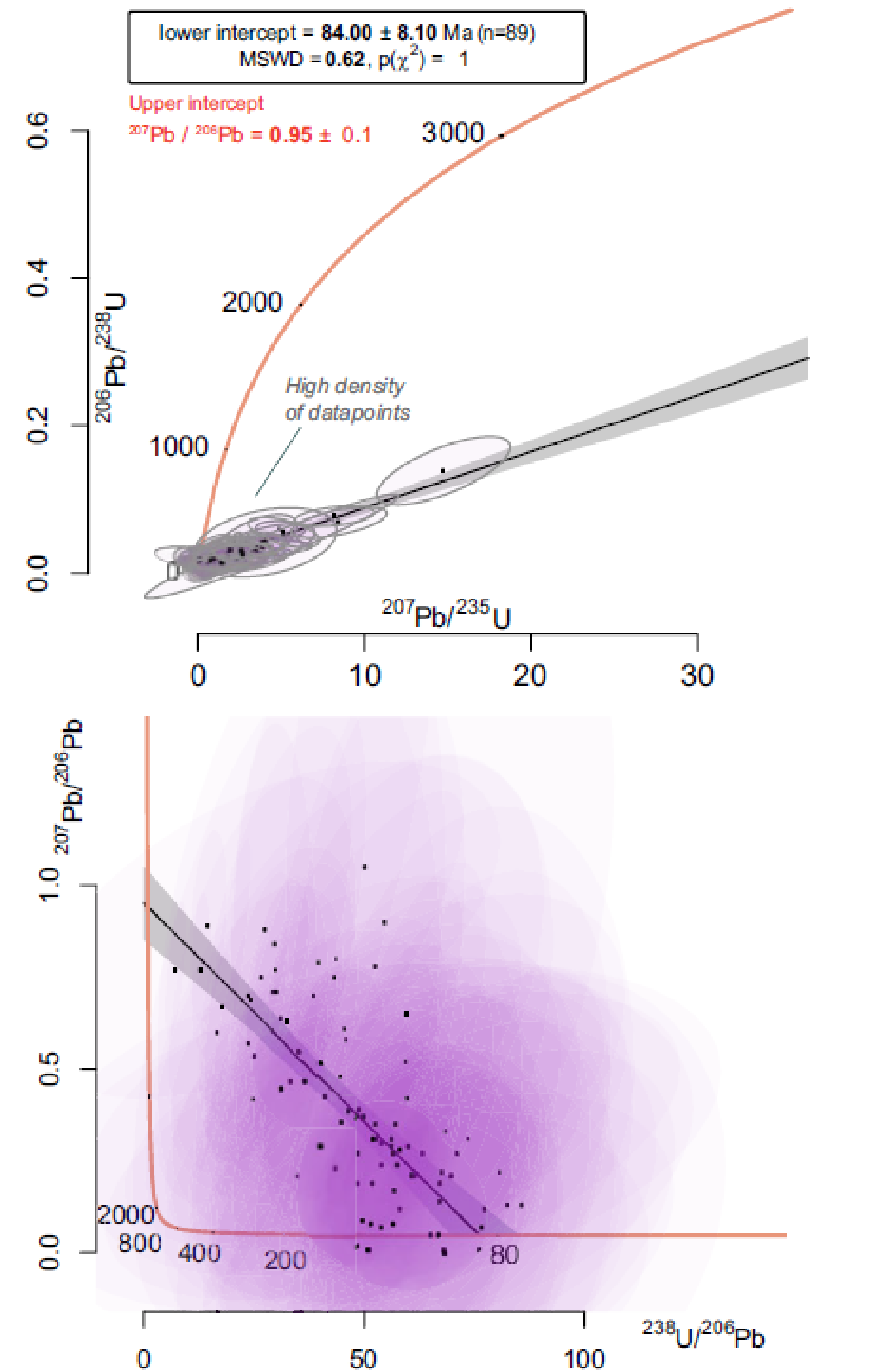


Fig. 4. (Colour online) $^{207}Pb/^{206}Pb$ vs $^{206}Pb/^{238}U$ garnet U–Pb discordia age of Bultfontein xenolith garnet. Age calculations employed the independently measured $^{207}Pb/^{206}Pb$ and $^{206}Pb/^{238}U$ ratios, but are here presented both in a Tera–Wasserburg diagram and transformed for display on Wetherill concordia for comparison. Ellipses are plotted at 2σ. In the Tera–Wasserburg diagram, ellipses are plotted with low transparency to show regions of greatest data density.

Exploring the limits of in-situ U-Pb dating of metamorphic garnet

Aratz Beranoaguirre[1,2], Leo J. Millonig[2], Qiao Shu[3], Richard Albert[2], Horst R. Marschall[2], Jose Ignacio Gil Ibarguchi[4], and Axel Gerdes[2]

Recent advances in analytical techniques and instrumentation allow for the analysis of increasingly smaller sample volumes and lower concentrations. This development significantly expands the possibilities of in-situ geochronology, *e.g.*, LA-MC-ICPMS. Minerals with low U (and Pb) contents such as garnet become the target of in-situ U-Pb geochronology since ages can potentially be obtained from single (sub-)mm-sized garnet grains in thin sections. In this contribution, we explore the current limits of in-situ U-Pb geochronology: what are the minimum concentrations from which an accurate and precise U-Pb age can be obtained?

For that purpose, we have analysed garnets from three different localities that were unsuccessfully analysed in the past using a single-collector sector-field Element XR instrument at FIERCE. These garnets have been re-analysed at FIERCE using a Neptune Plus MC-ICPMS coupled to a RESOLution-LR ArF Excimer laser. The analyses were performed in static mode measuring the masses ^{206}Pb and ^{207}Pb with Secondary Electron Multiplier (SEM) and ^{202}Hg, ^{204}Pb and ^{238}U with the Multiple Ion Counters (MIC). With a spot diameter of 193 µm (round) and a fluence of 2 J/cm^2 at 15 Hz, ca. 18 µm pit depth was ablated in 18s analysis time, resulting in a total of 2 µg of ablated material. This is more than 2,000 times less material compared to conventional isotope dilution analyses and 3,000 times less U than for a typical LA-ICPMS zircon analysis (20 µm spot). Although the analysed garnets typically have U contents below 10 ng/g, about 15–30 spots are commonly sufficient to define a regression line in the Tera-Wasserburg diagram, yielding a precision of typically <3 % for the lower intercept age. Challenges and details of the method will be discussed using samples of metamorphic garnet from Kaapvaal craton granulites and Eastern and Western Variscan eclogites.

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- ..with 10 ng/g about 15-30 spots give precision <3%
- This guy is doing U-Pb dating in orthopyroxene…pers. comm

Laser Ablation Split Stream (LASSS) for Zircon Petrochronology

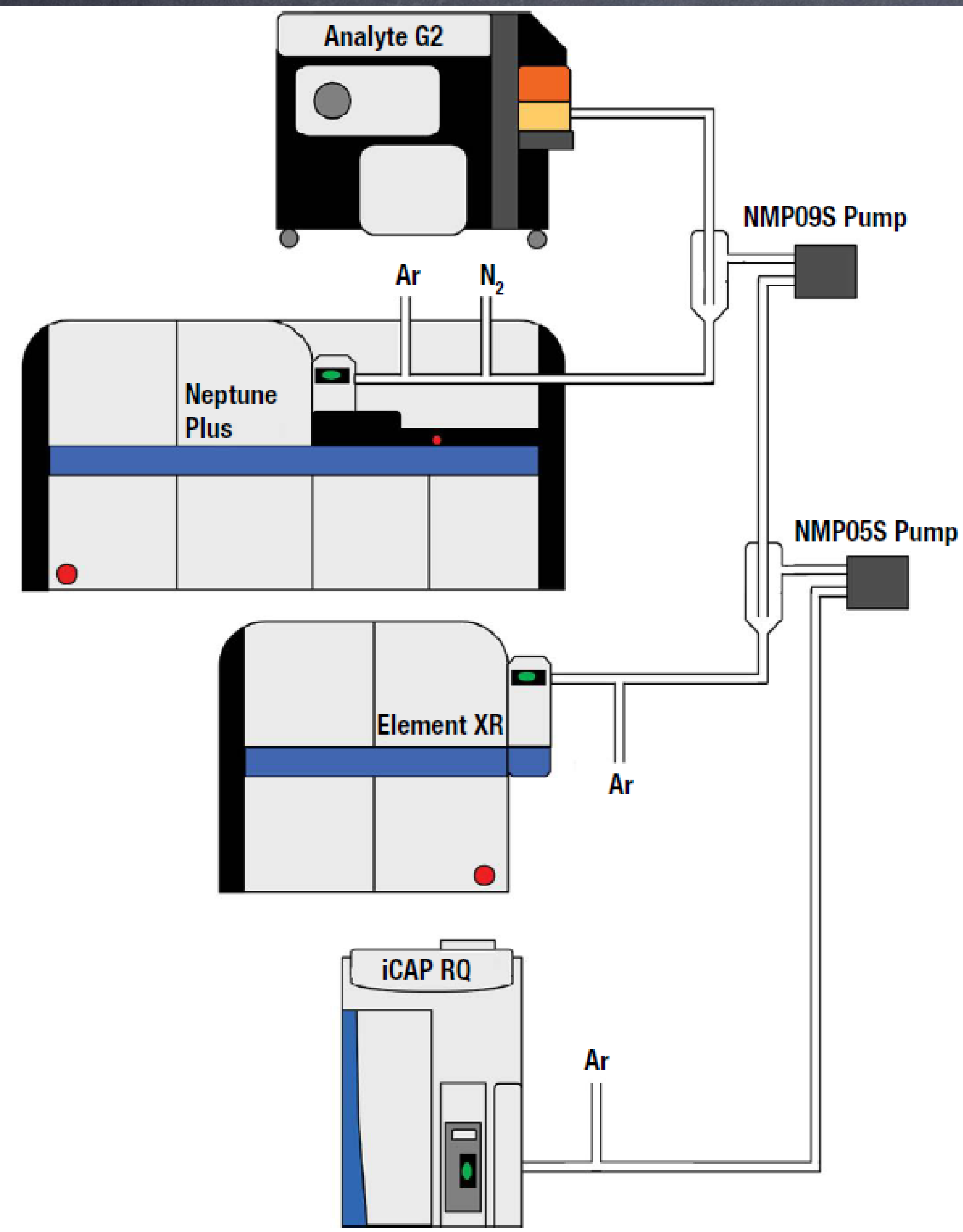


Figure 1. Schematic of LASS to three ICP-MS systems. Approx. 50% of the laser aerosol output was extracted from the primary MC-ICP-MS channel to SF-ICP-MS. Approx. 30% of the SF-ICP-MS channel was extracted to Q-ICP-MS.

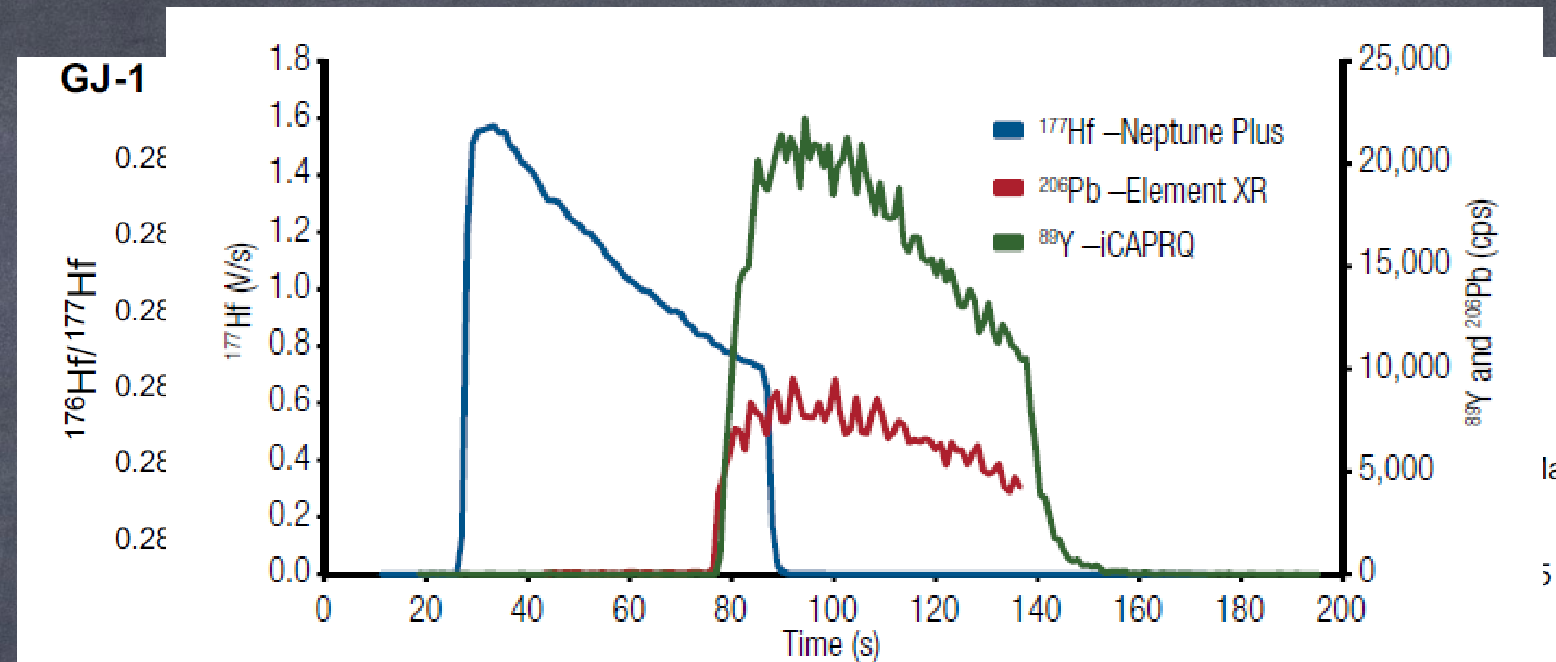


Figure 2. Signal traces for spot ablation of 91500 zircon, LASS to three ICP-MS. Integration times ≈ 1 s. ^{177}Hf (MC-ICP-MS), responded faster than ^{206}Pb (SF-ICP-MS) and ^{89}Y (Q-ICP-MS), reflecting the relative distances from the laser ablation cell.

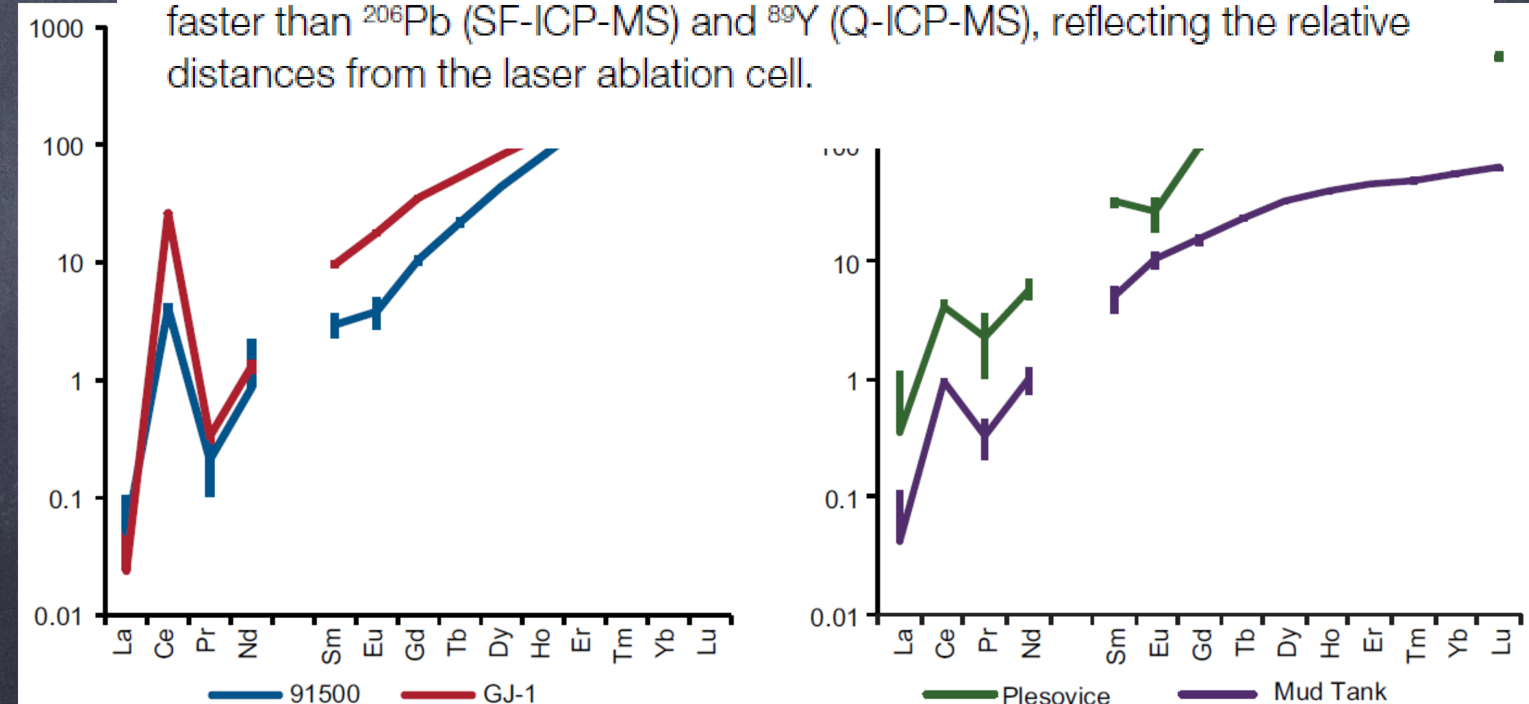
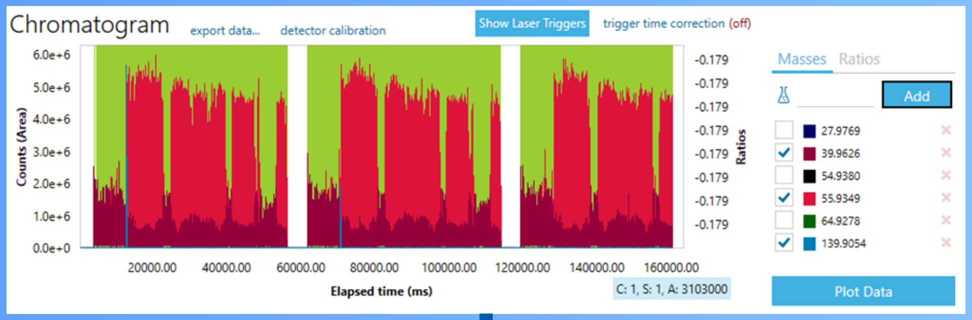


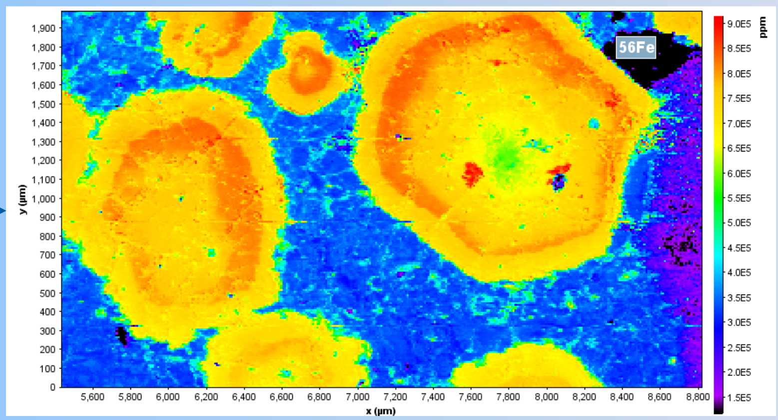
Figure 6. Chondrite-normalized REE concentrations[11] (error bars = SD) determined in the four reference zircons on the iCAP RQ ICP-MS in the LASS configuration.

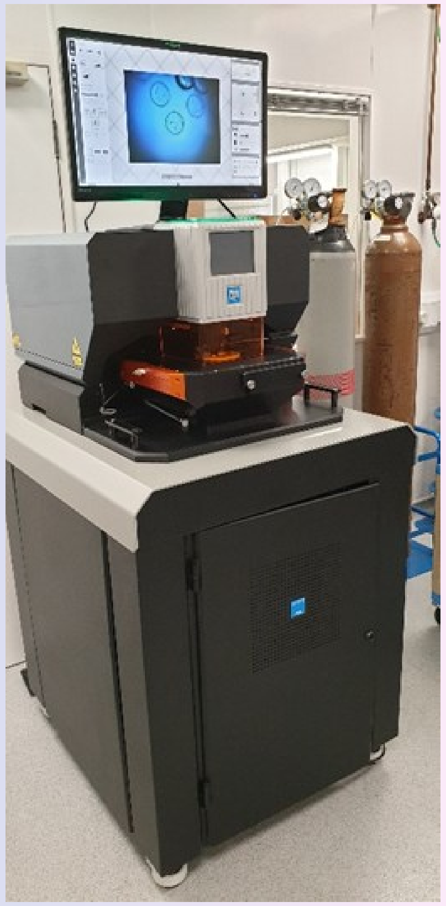
ICP-MS-TOF

ICP-MS Imaging

- 2D elemental map oftentimes used for biological or geological samples
- Instrumental setup: Laser ablation – ICP-MS
  - Sample is shot at with a laser (typically 5-50 µm in size).
  - The generated aerosol is carried to the ICP for analysis
- Modern laser ablation systems can generate separate aerosol clouds every few milliseconds





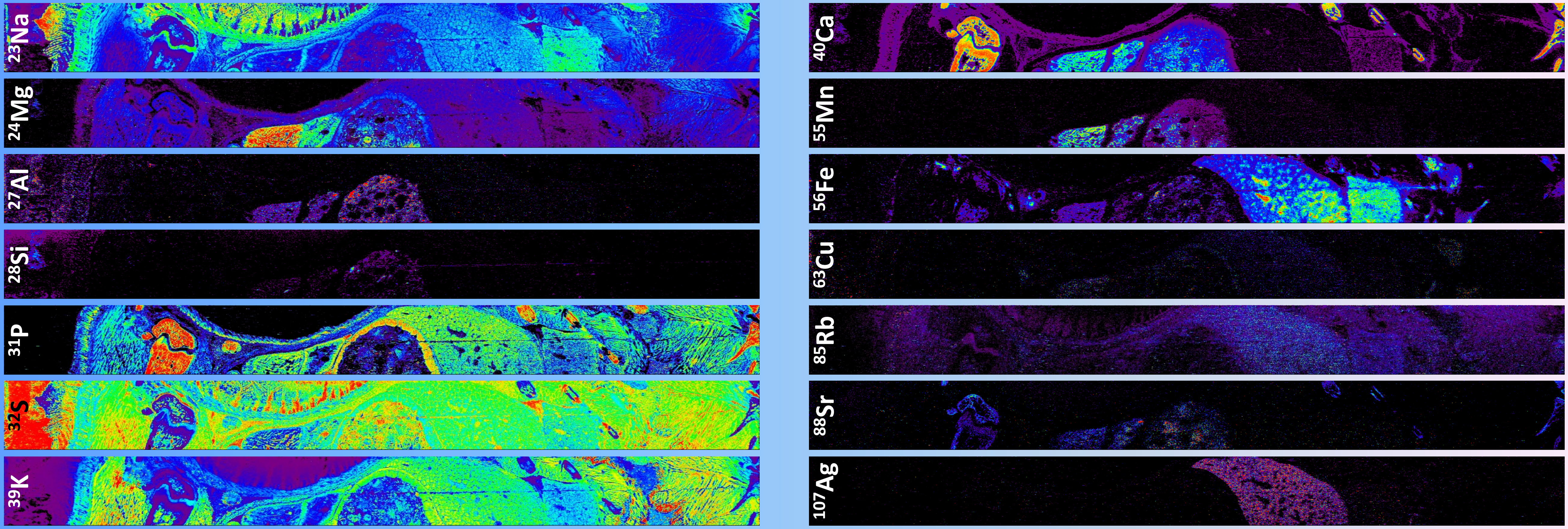


- Combining the coordinates of the laser shot and the intensities results in 2D elemental distribution map
- Pixels can only be resolved if every laser shot is discriminated

ICP-MS-TOF

Multi-element imaging

- Elemental maps of the entire periodic table
  - *Thin section of entire mouse*

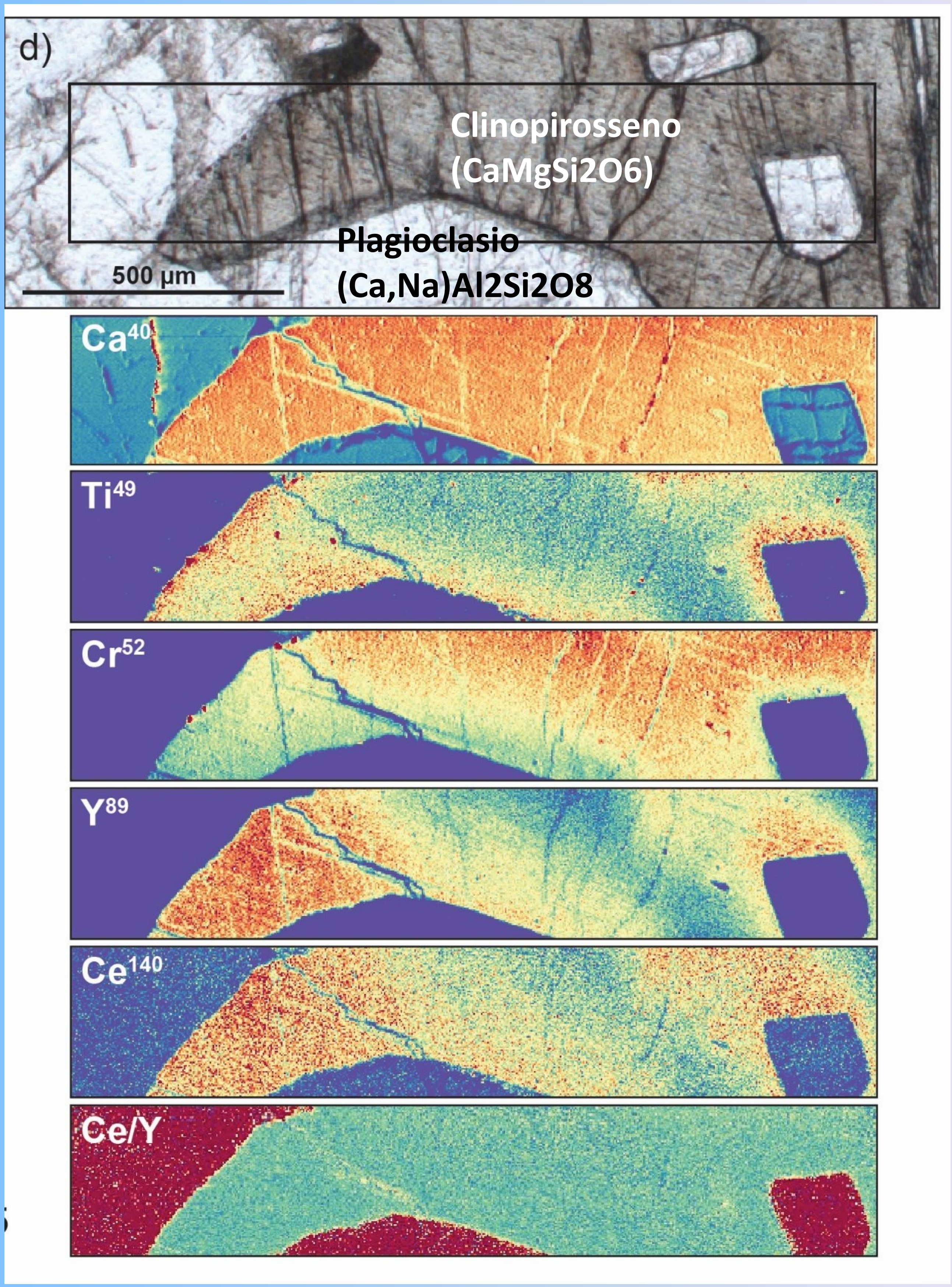


ICP-MS-TOF

Gabbro oceanico da Hess Deep, che rappresentano i cumulati più impoveriti in Terre Rare di ambiente oceanico

Basch et al. (2024)
Journal of Petrology

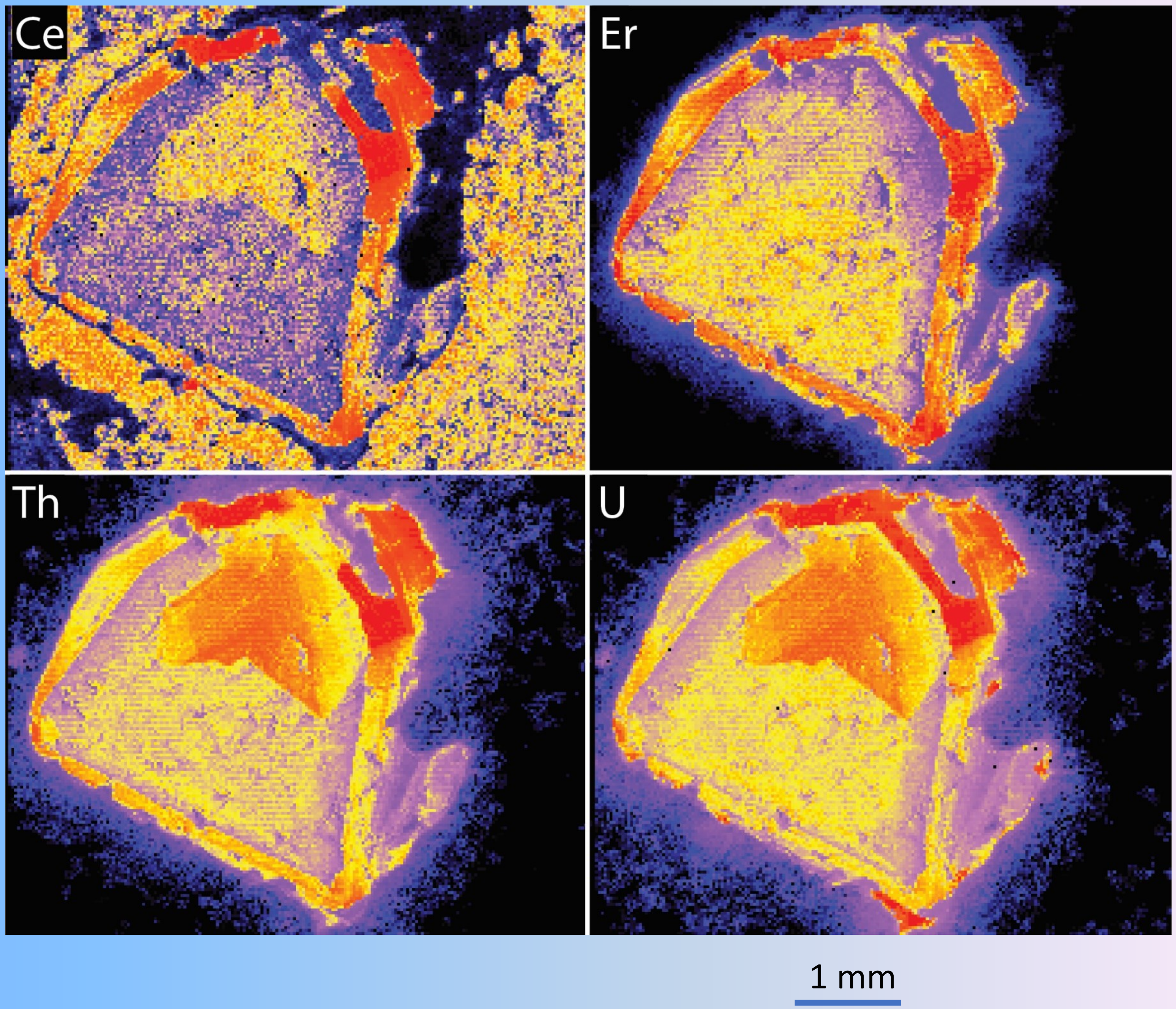
ArF Excimer ESI + Vitesse (Nu)



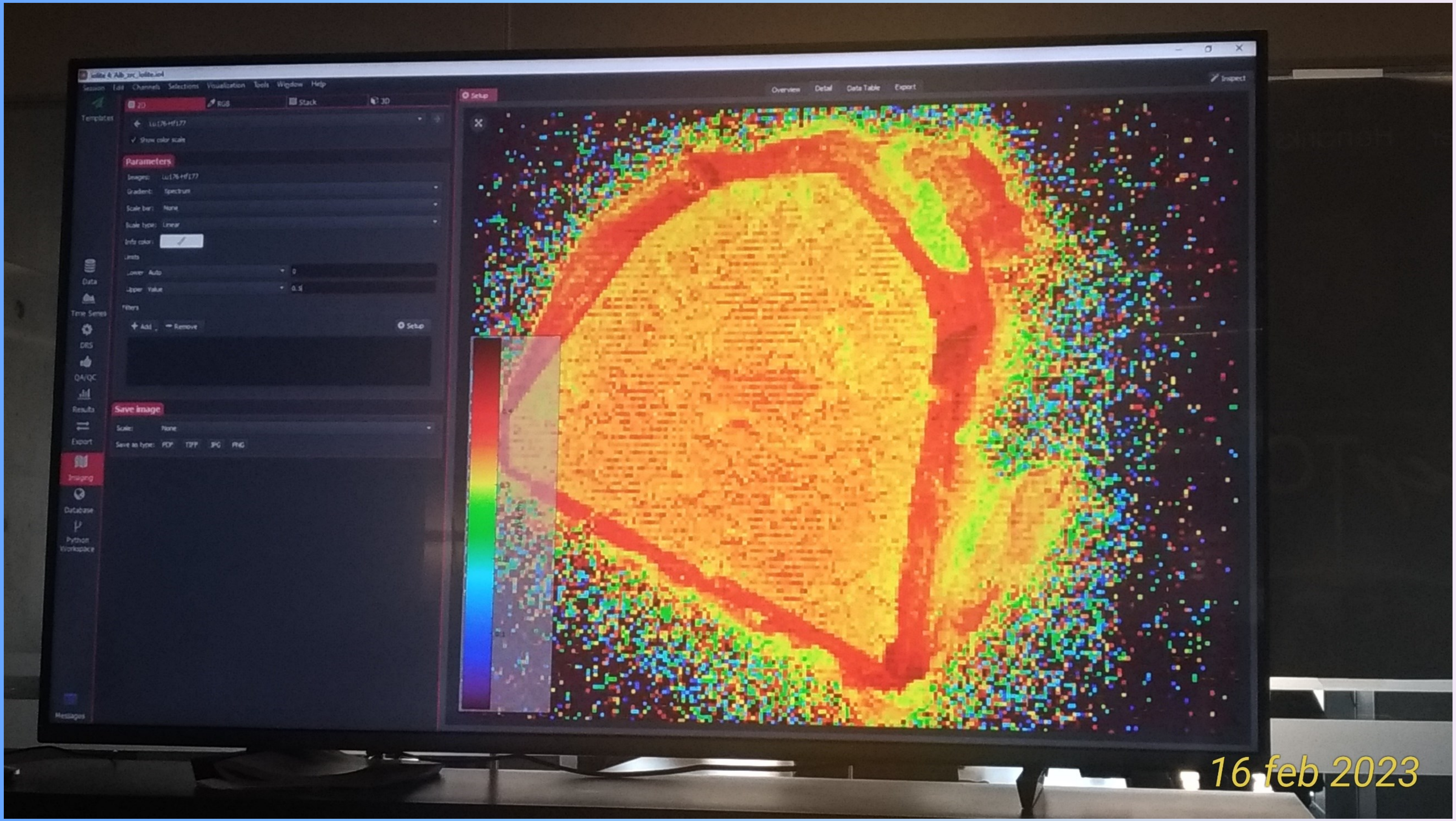
ICP-MS-TOF

Elementi in tracce in Zircone Magmatico

ArF Excimer ESI + TofWerk



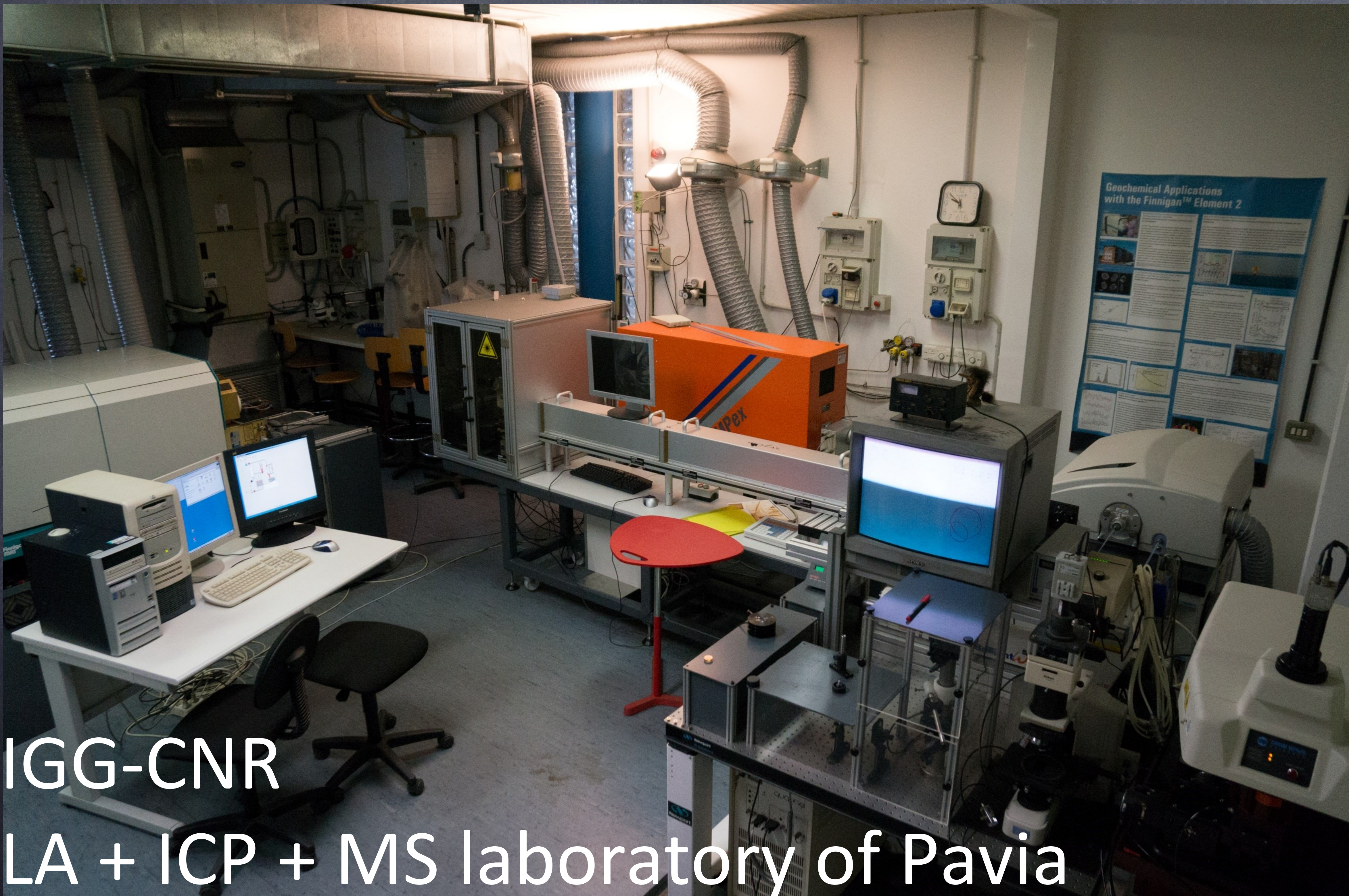
ICP-MS-TOF



1 mm

Rapporto isotopico Lu^{176}/Hf^{177} in Zircone magmatico

Grazie



IGG-CNR

LA + ICP + MS laboratory of Pavia

Giornate di confronto sulla Paleoclimatologia in Italia

Istituto di Geoscienze e Georisorse (IGG)

Neptune-Neoma Laboratory

Lab Head: Dr Samuele Agostini

 +  + 

At Present

Rb-Sr
- Tracing Mixing of Global Reservoirs
- High-T Processes
- Water-Rocks Weathering
- Dating Carbonate Successions
- Oceanic Water Mixing

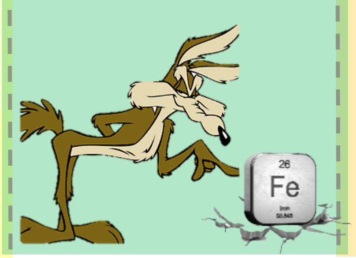
Sm-Nd
- Isotope Marine Signature and Palaeoceanographic Variations
- Mantle and Crust-derived Igneous Crust Discrimination

Pb-U-Th
- Evolution of Solar System
- Formation of Earth Crust
- Ore-Forming Material Sources
- Geochronometer
- Geogenic or Anthropogenic Pollution

B
- Mixing and Tracing Processes
- Continental Weathering
- Ancient Marine pH Reconstruction
- Magmatic Activity
- Water-Rocks Weathering
- Geogenic or Anthropogenic Pollution
- Ore-Forming Processes

New Systematic

Fe
- Metal Source
- Hydrothermal Circulation
- Ore-Forming Processes
- Critical Zone Studies
- High-T Processes
- Human Health



In Progress

Li
- Li-Rich Geothermal Fluids
- High-T Processes
- Water-Rock Interactions

In Program

- U-Th Dating of Speleothems
- In situ B Isotopes on Carbonate Samples
- In Situ Rb-Sr Dating
- Mg Systematics
- Zn-Cu Systematics
- Ca Systematics

CNR igg

ITINERIS

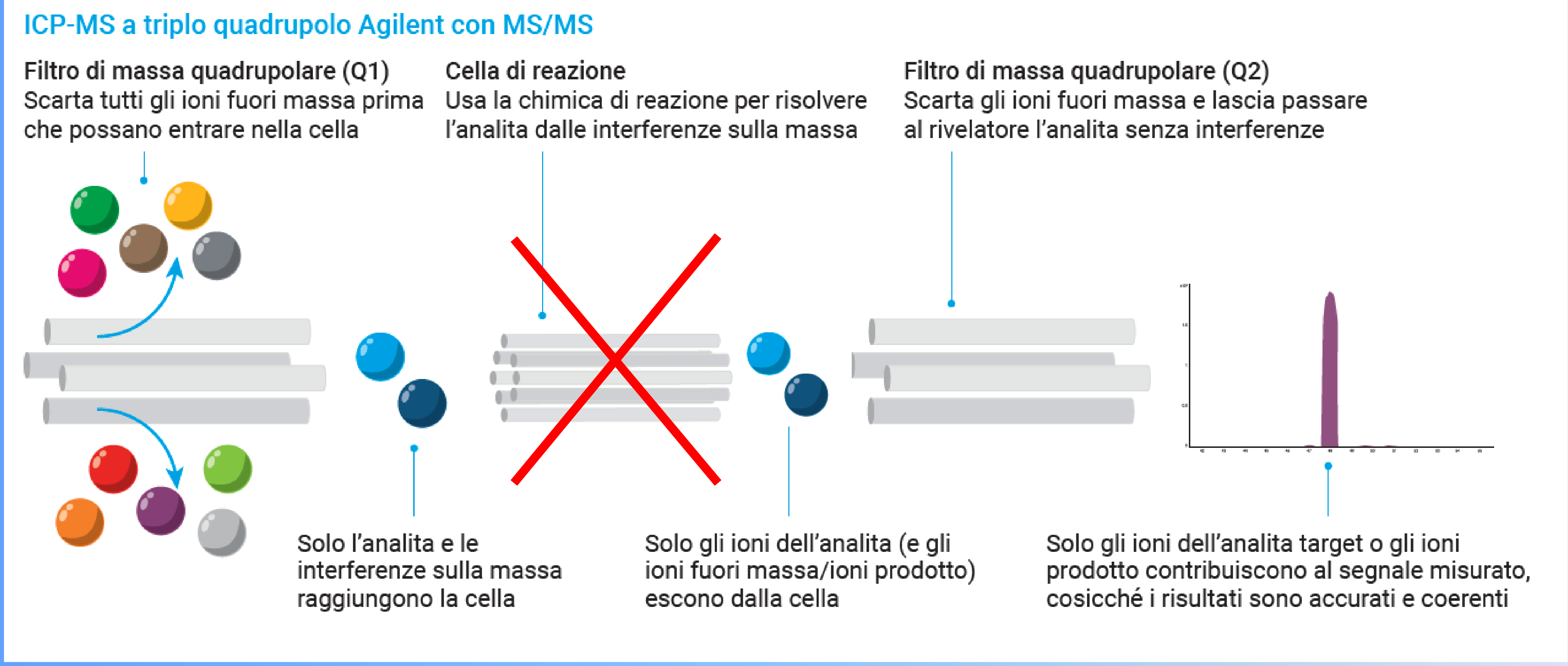
Cella porta campioni fast-washout del sistema LASER

Da ablazione a analisi pochi ms

Analisi di qualunque matrice solida, geo e bio

LA-ICP-MS Trace element

No gas MS/MS mode



MS/MS improves the accuracy and confidence, reduce the oxides

…. to correct isobaric interference

Titanite

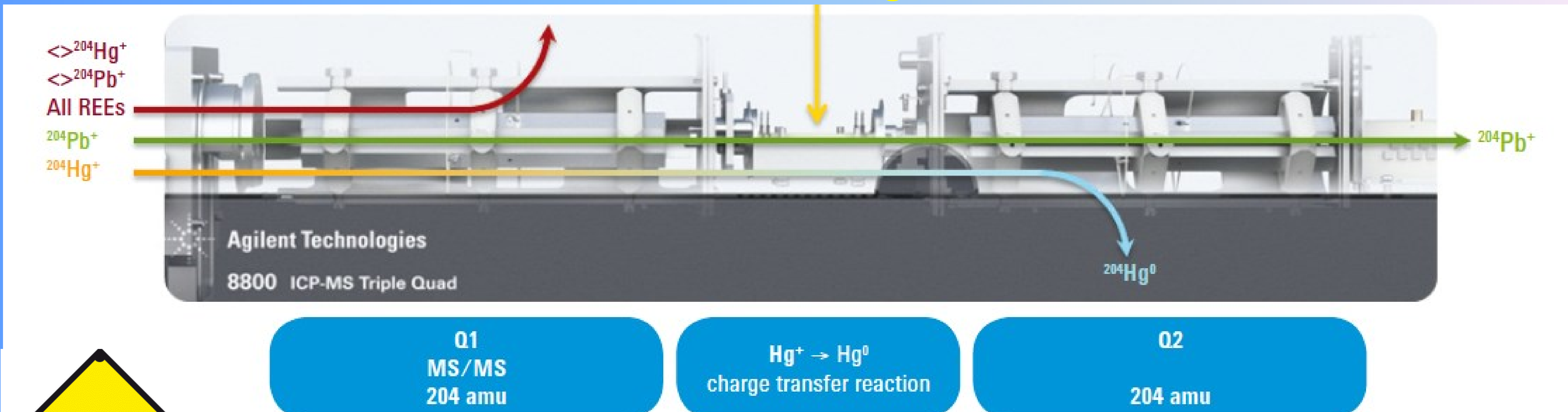
Allanite

contain Hg =>

^{204}Hg-^{204}Pb isobaric interference

Lead isotope analysis: Removal of ^{204}Hg isobaric interference from ^{204}Pb using ICP-QQQ in MS/MS mode

NH3 reaction gas



atic representation of MS/MS reaction mode for Hg interference removal . Q1 is set to *m/z* 204 rejecting all ions at masses other than 204 amu

Glenn Woods (Agilent)

QQQ: what we would like to do

Rb-Sr dating

(NO2 in reaction cell)

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Earth and Planetary Science

15th Water-Rock Interaction International Symposium, WRI-15

In situ Rb-Sr dating of fine-grained vein mineralizations using LA-ICP-MS

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