Conference on
Exploration and Exploitation
of Critical Raw Materials

Perspectives of phosphorites deposits as REE resources

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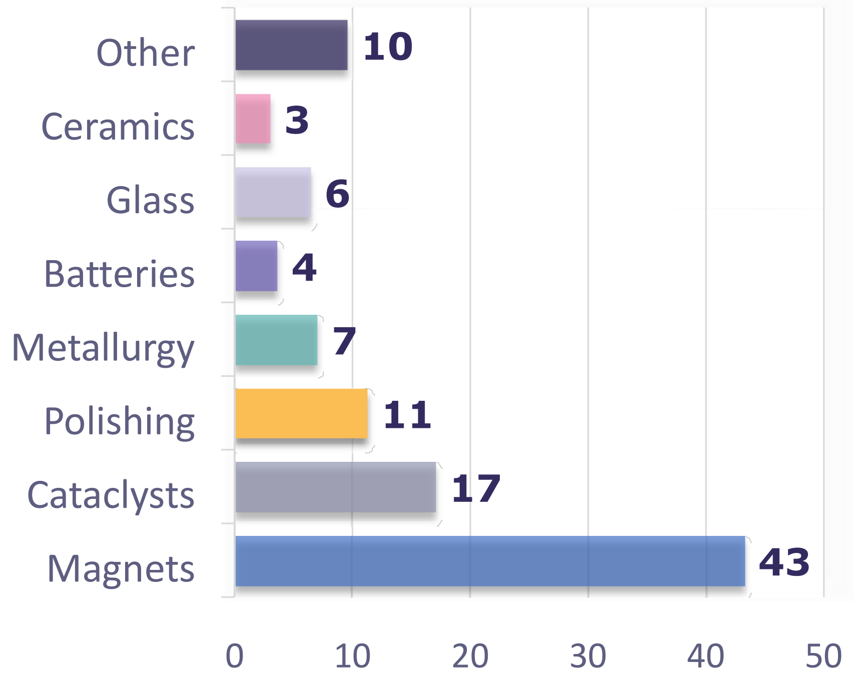
TAL TECH

REE challenge in EU

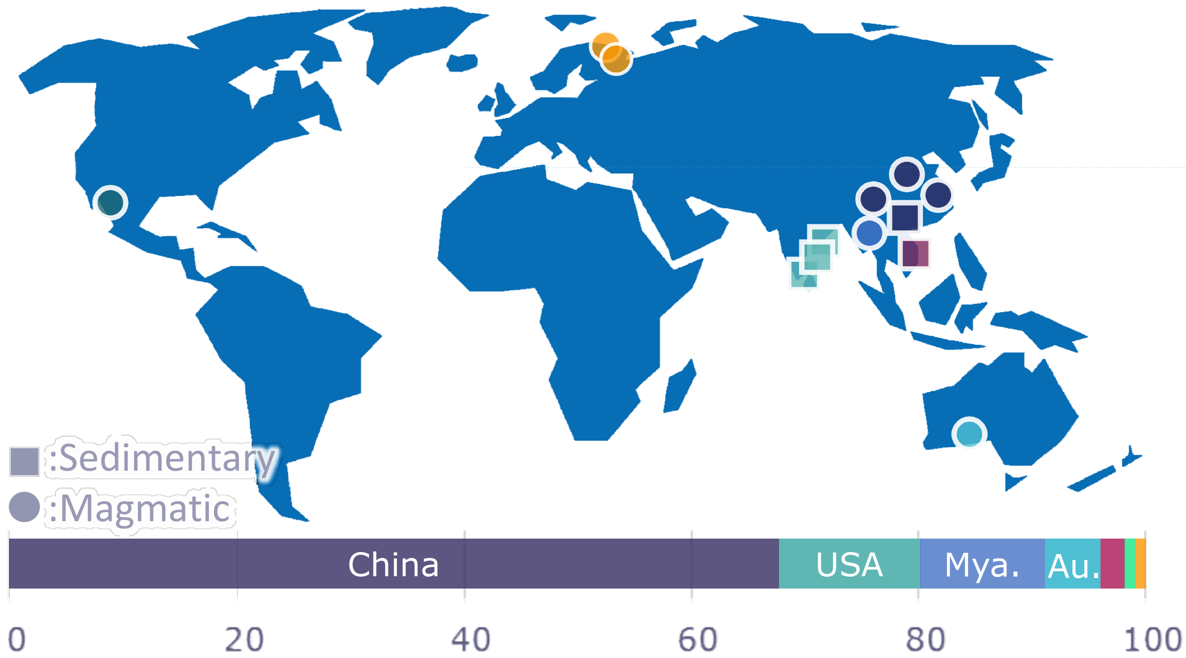
15 Lanthanides, plus Y and Sc

CRM for the energy transition, high supply risk for EU

Global REEs consumption per sector (%)



Exploited REE deposits and 2023 production shares



Depletion of high-quality deposits | Resource scarcity and availability

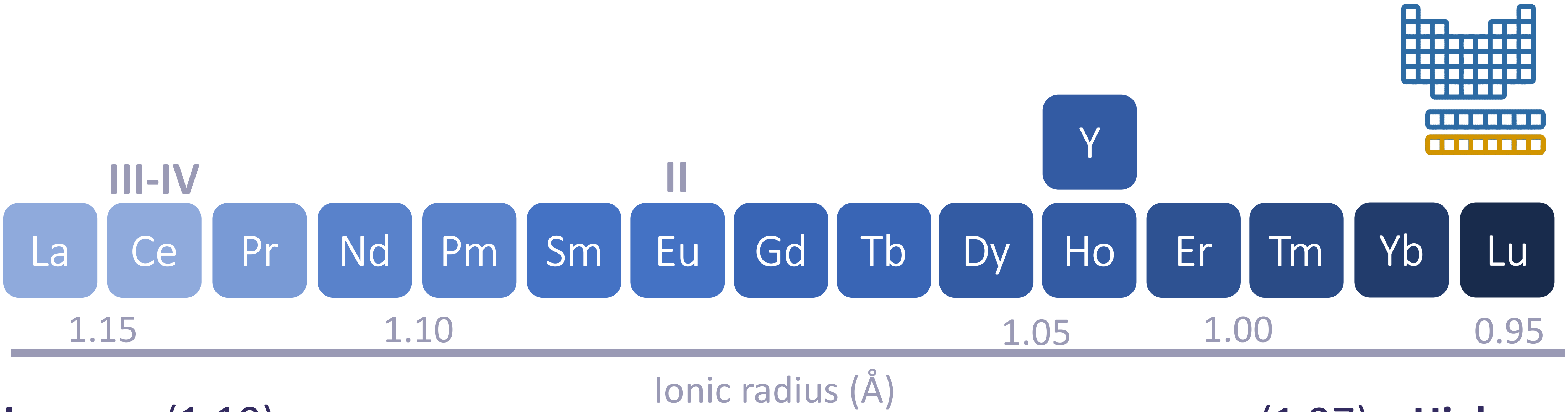
Raising interest in phosphorites ores as REE sources

REE properties and abundances

Common elements, yet rarely in *minable concentrations*: do not 'fit' in silicates

Average concentrations of ∑REE 85-299 ppm in the continental crust (*Cu 27 ppm*)

Large ionic raddi (1Å), 3+ oxygenation state, electronegativity similar to Ca, Na, Sr



Lower χ (1.10)

(1.27) **χ Higher**

LREE (La-Nd) are the most abundant, while HREE (Eu-Lu) are found below 1ppm

REE properties and abundances

Common elements, yet rarely in *minable concentrations*: do not 'fit' in silicates

Production driven by bastnaesite and monazite concentrates

Major REE bearing minerals

Bastnaesite

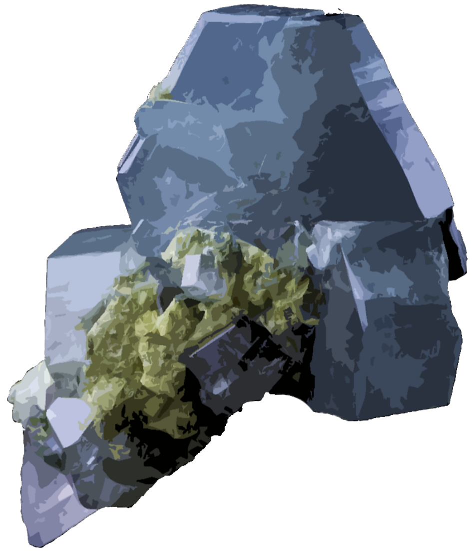
$(La,Ce)CO_3F$

Monazite

$(Ce,La,Th)PO_4$

Xenotime

YPO_4

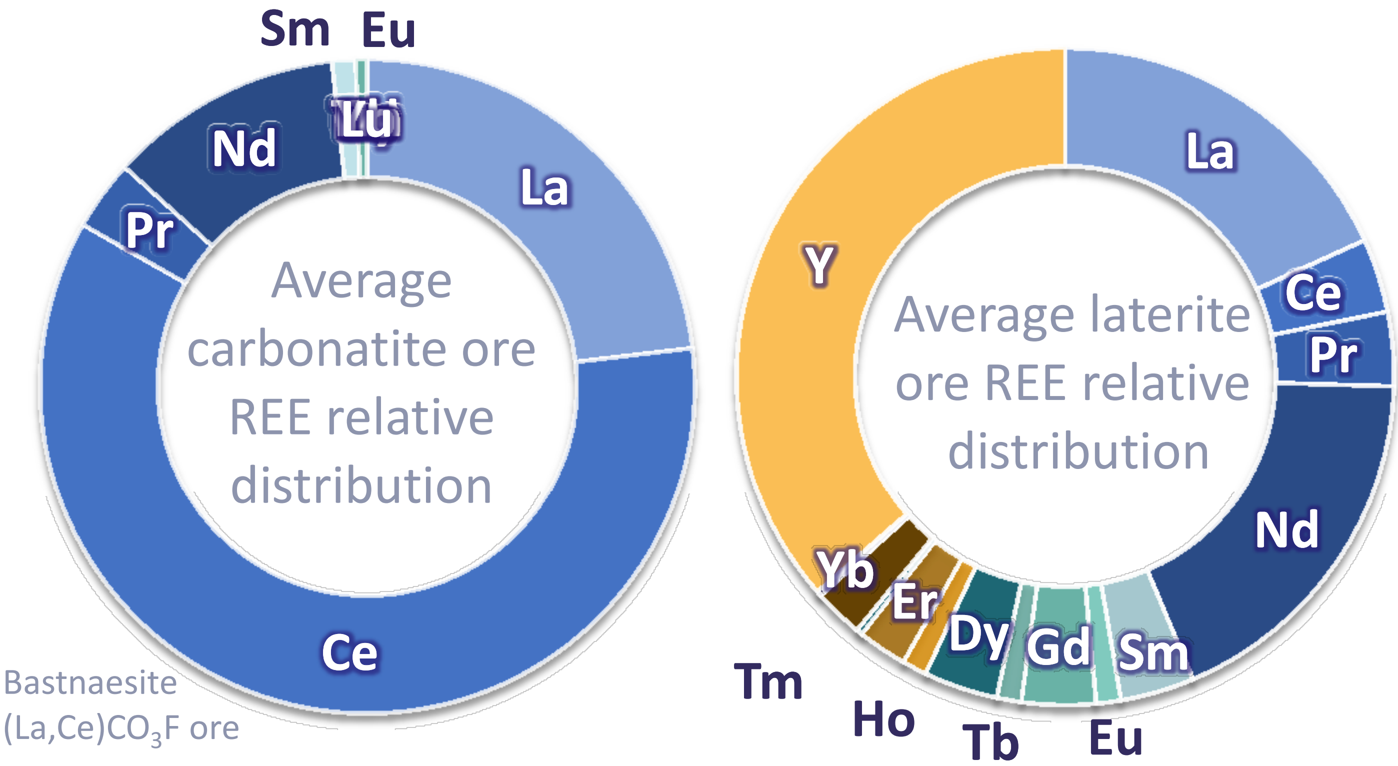


Apatite

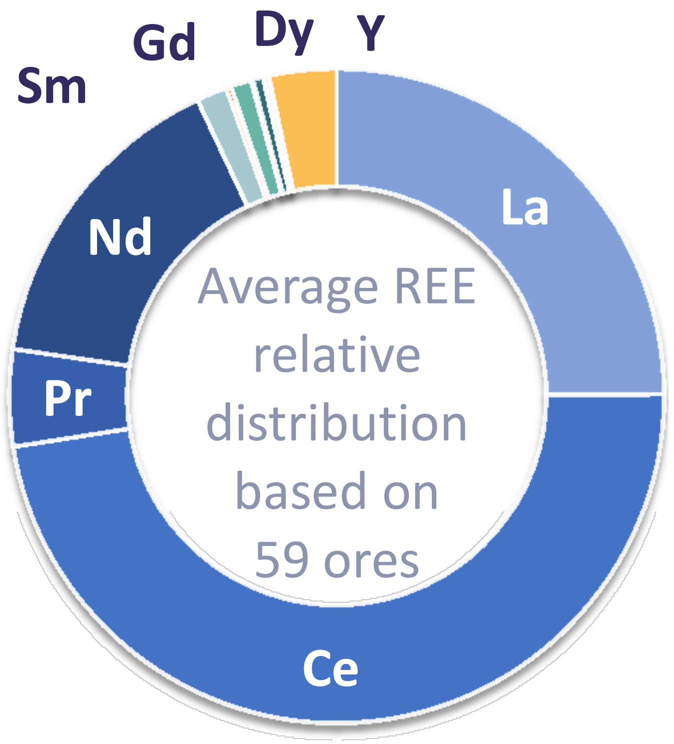
$(Ca,REE)_5(PO_4)_3(OH,Cl,F)$

Most common phases in carbonatites & placers

REE properties and abundances



Average REE distribution in main ore types



Average REE distrib. for advanced stage REE deposits

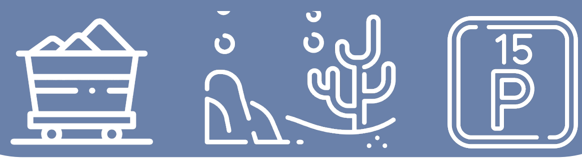
- LREE (La, Ce) dominate current REE market resource
- Growing need for **Pr**, **Nd**, **Dy**, **Eu** and **Y** for green technologies: **Need for alternative sources**

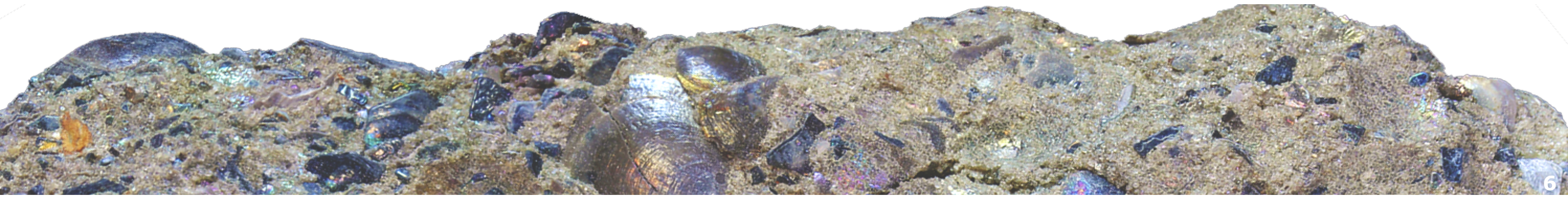
REE unconventional sources

Recycling of industrial waste, lack of cost-effective methods and low REE contents

Polymetallic REE sources, as co or by-products

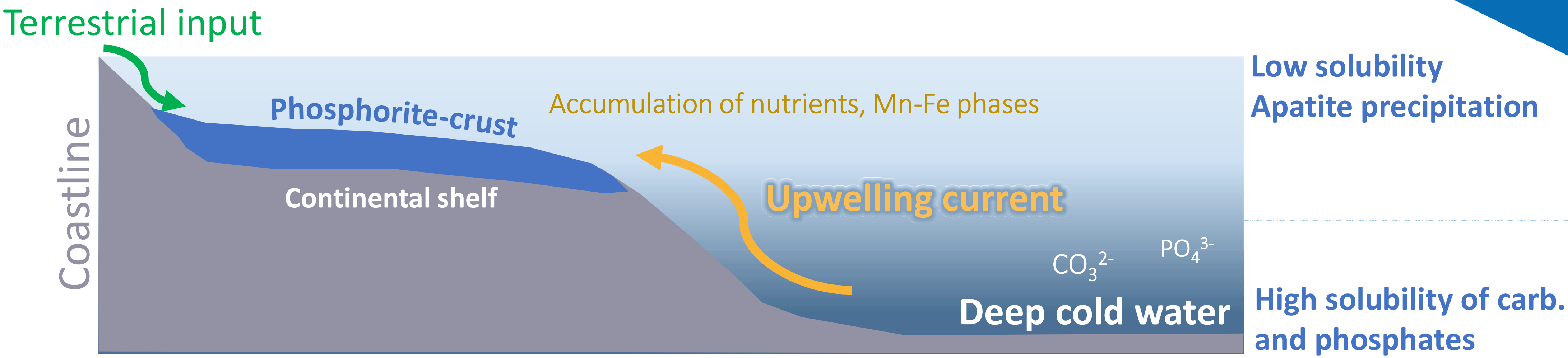
Valorised resources	Raw resources
Waste rocks from mines	Coals
Red muds	Ocean bottom sediments
E-Waste	Geothermal brines
Magnets	Phosphorites





Phosphorites genesis and REE

Classical genesis process – First steps



Precipitation of phosphorites through upwelling current

Upwelling of cold PO_4^{3-} rich-water in shallow setting | Burial of OM and microbial degradation

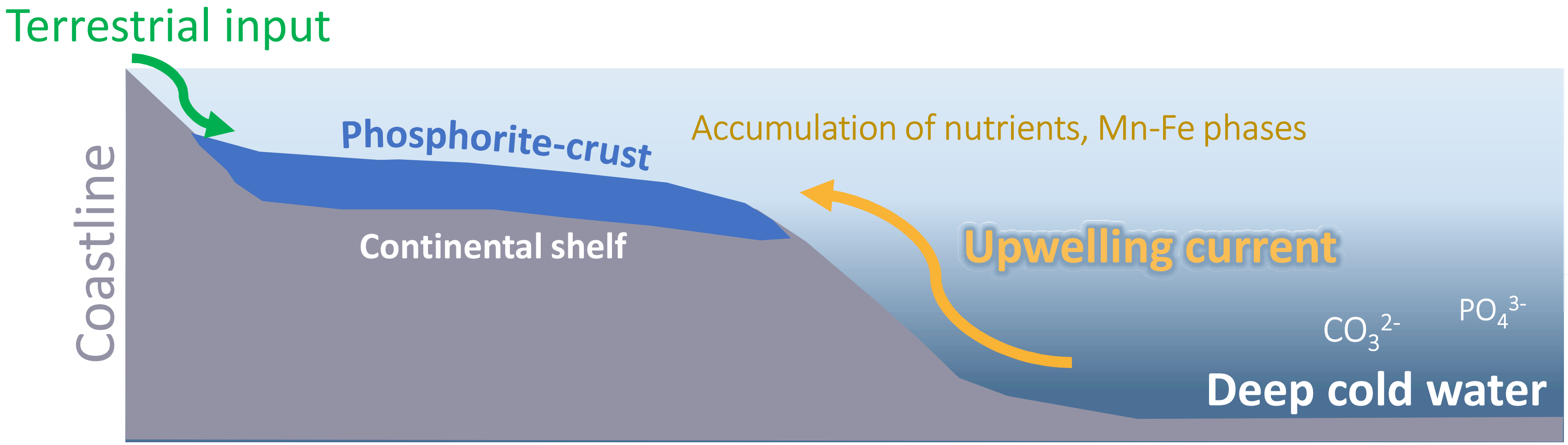
Precipitation of hydroxyapatite ($Ca_5(PO_4)_3OH$), initially with low REE contents

Dissolution precursors carriers' phases (Mn-Fe-hydroxides, Ca-phophates): **REE release**

REE enrichement occures during the diagenesis

Phosphorites genesis and REE

Classical genesis process – First steps



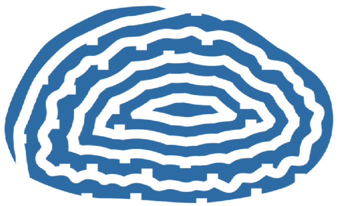
Low solubility
Apatite precipitation

High solubility of carb. and phosphates

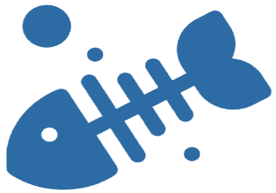
Precipitation of phosphorites through upwelling current

Most common occurrences

P concretions



Mineralised debris



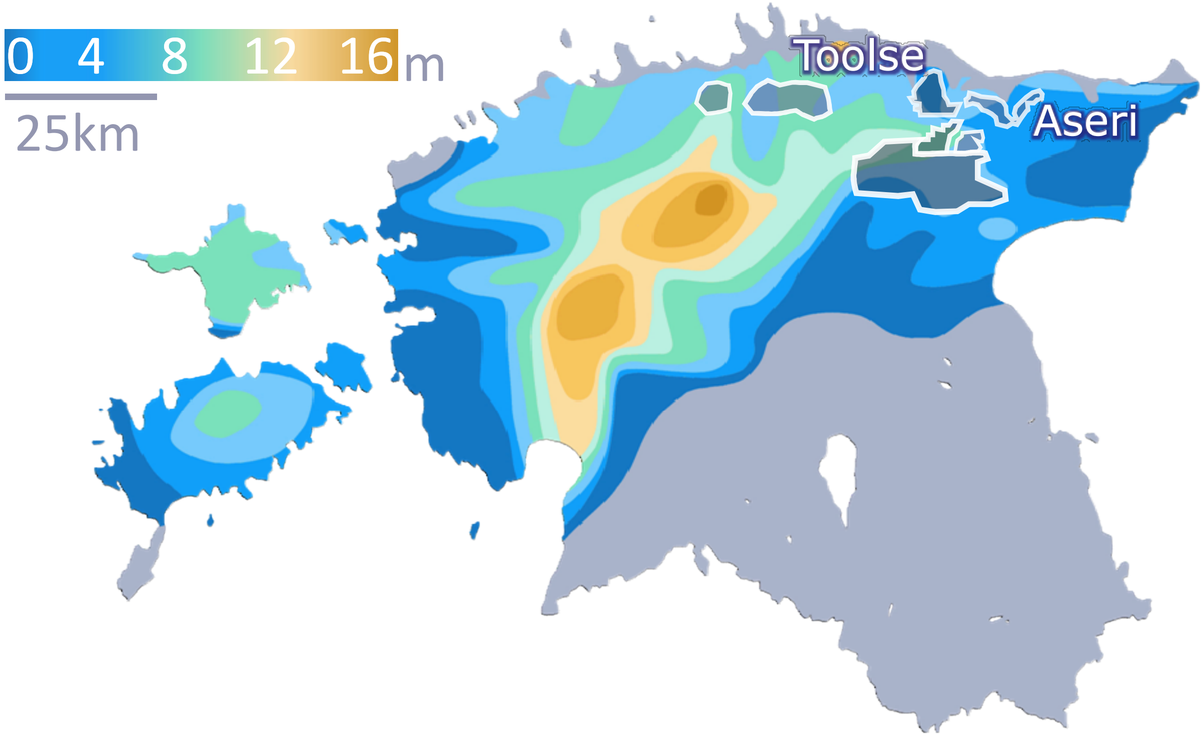
Coquina

Namibia
Estonia

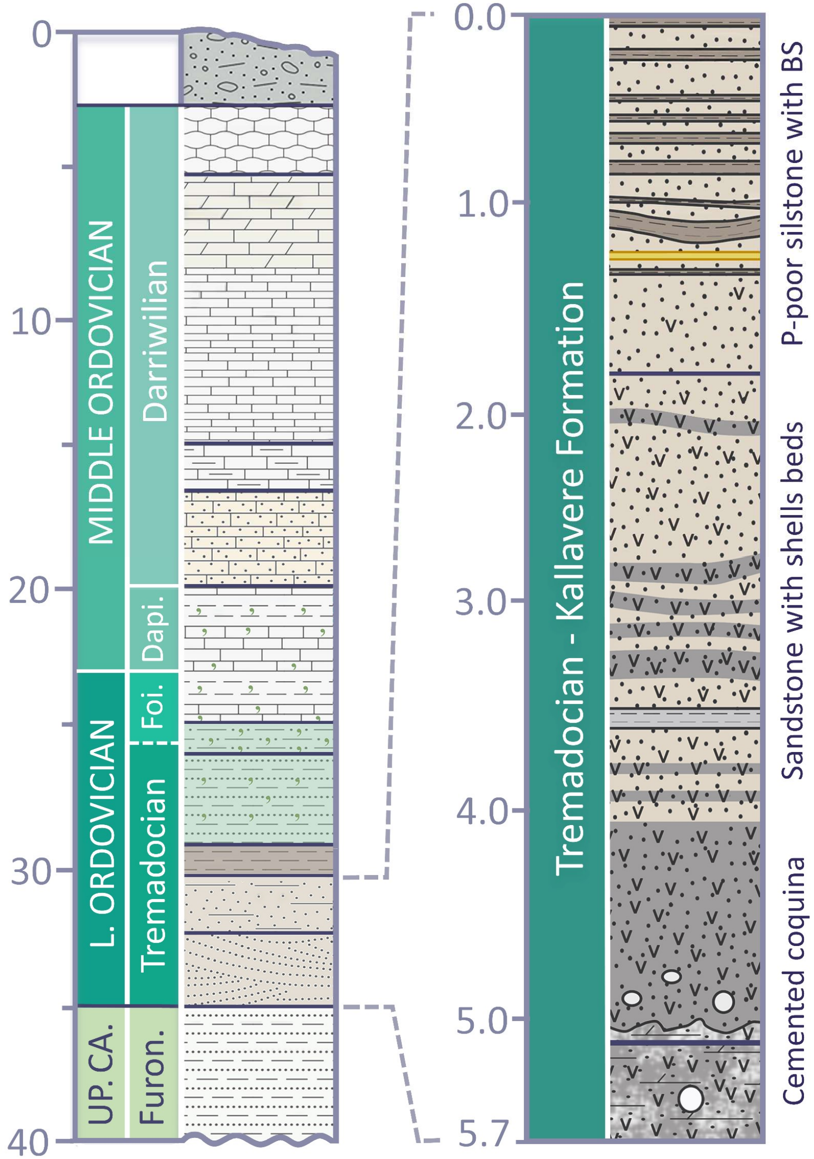
Uncommon REE mineralisations to assess and investigate

Baltic phosphorites

Thickness of the phosphorite formation and targeted ores



Cross section of the Toolse deposit



- Estonian phosphorites are one of the main opportunities for REE and P in the EU
- Average REE grade: 600 ±200ppm with 27% apatite. Up to 1300ppm and 60% apatite. $\pm 3^{12}$ t resources

Baltic phosphorites

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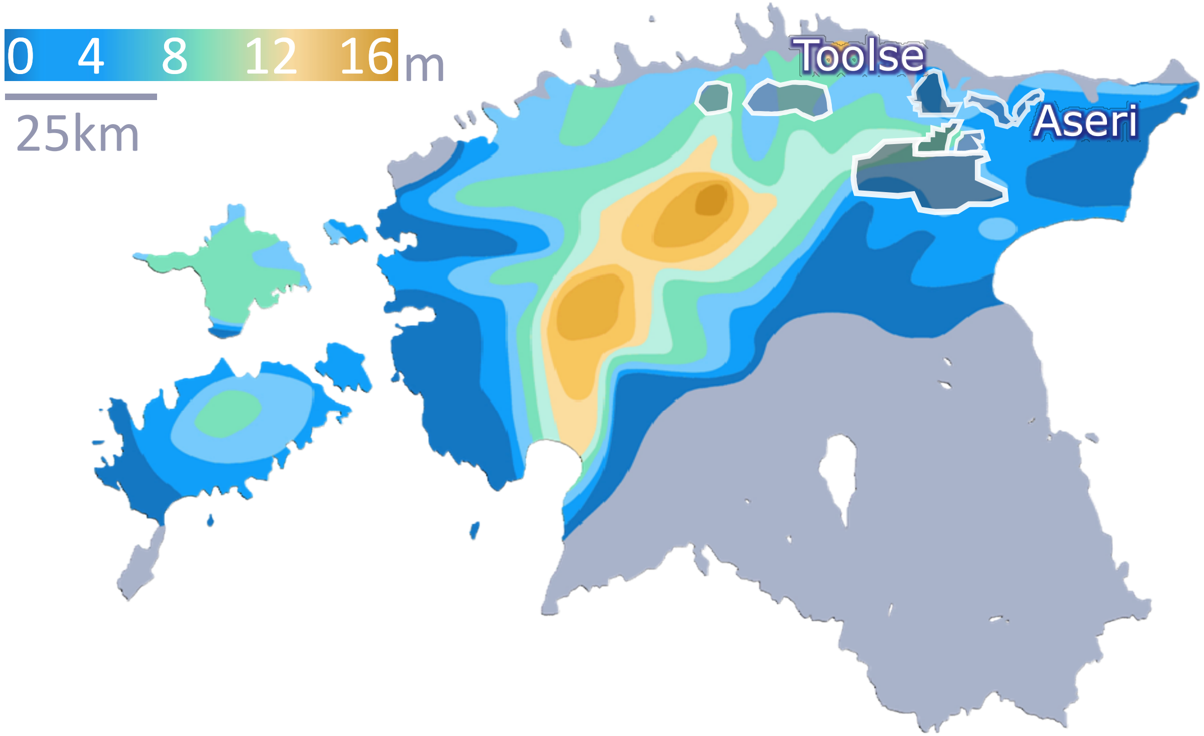

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Drill core from Aseri deposit

Baltic phosphorites

Placer-like ores, highly variable

- Diagenetic REE enrichement
- Mineralisation carried by CAF-apatite, authigenic recrystallisation of brachiopod' shells.
- Important textural and elemental variations on shell and carbonates

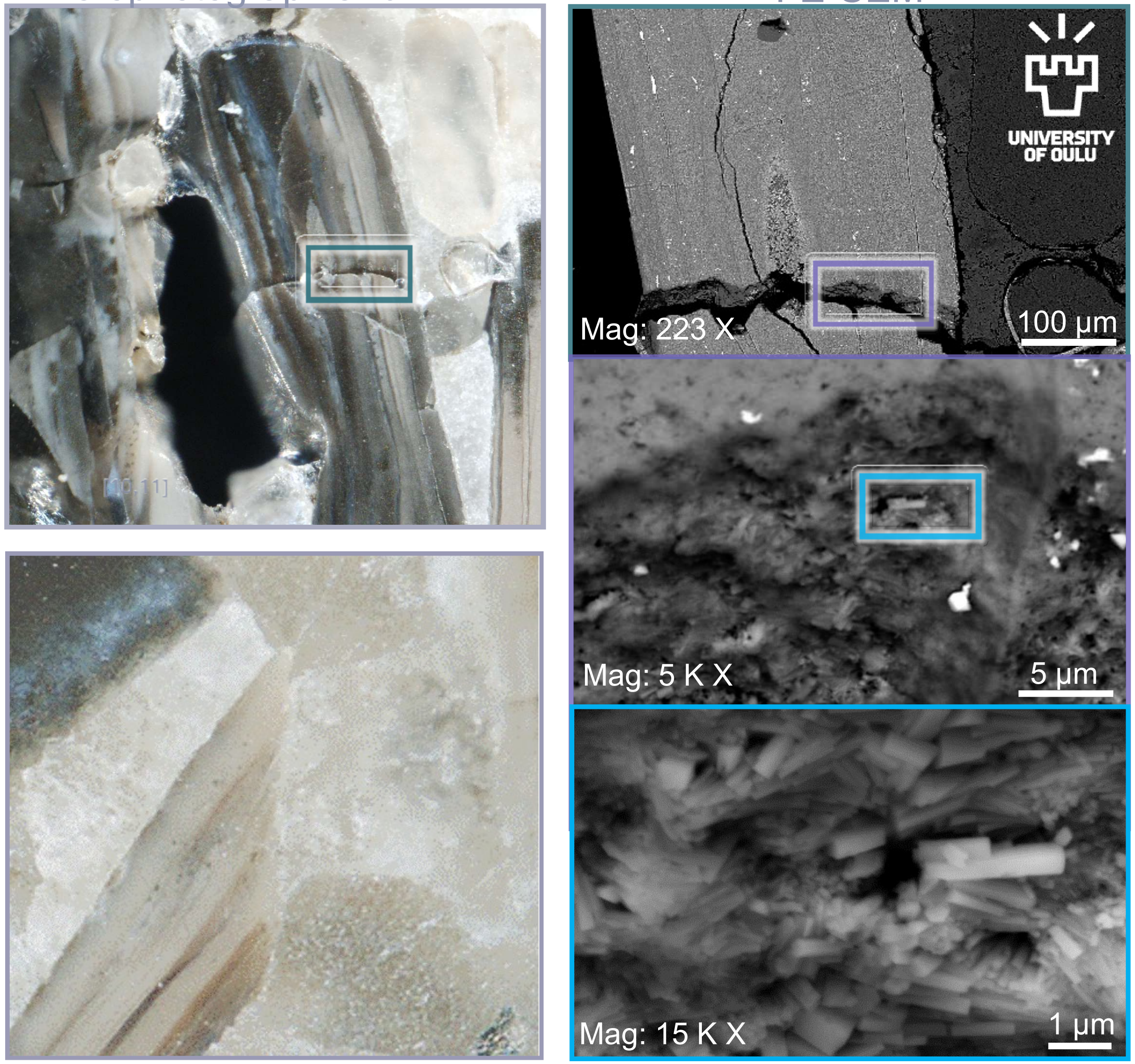
Need for REE in-situ analyses

✓ **REE distribution**
✓ **Apatite predictability**
✓ **Ore processing**

Microtextures

Microphotograph and EPMA

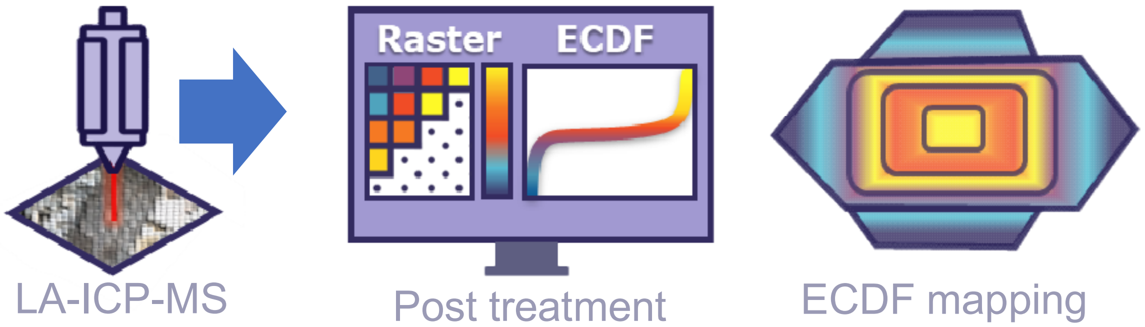
FE-SEM



REE with LA-ICP-MS imaging

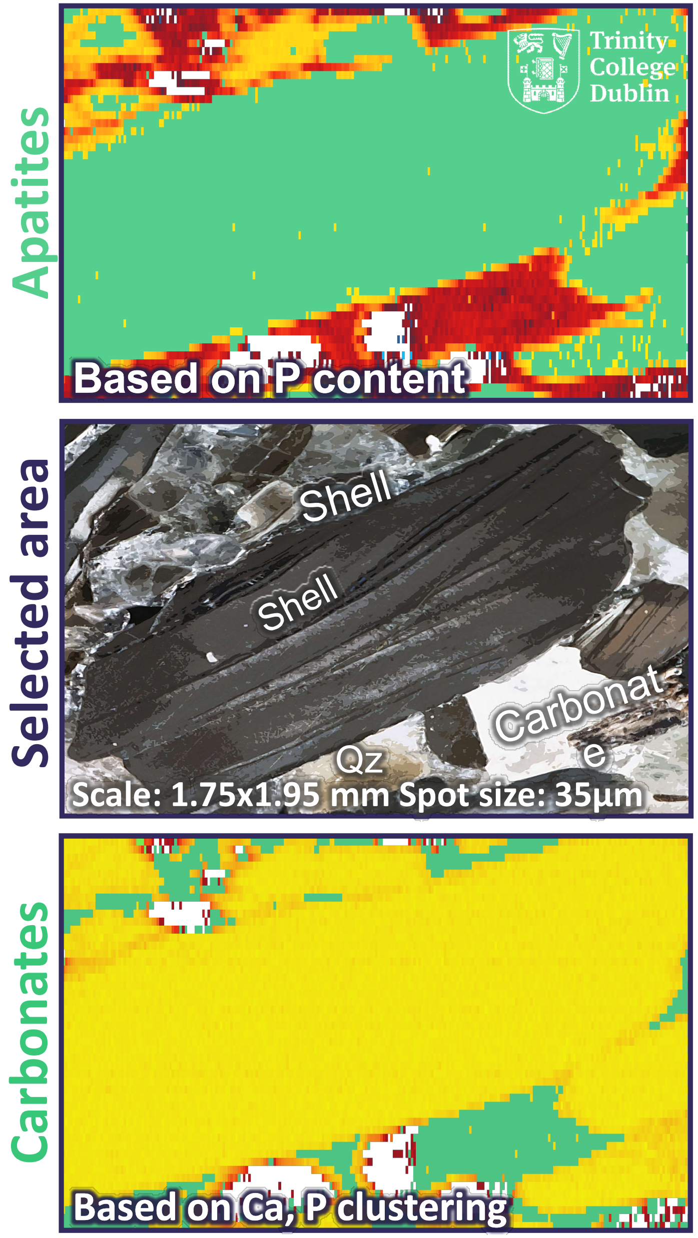
New tool for low REE semi-quantification

- Method based on laser-ablation rasters combined into distribution maps. Allow automated mineralogy like process for low grade contents



- Identification and discrimination of mineral phases by integrating semiquantitative data.

- Pixels are divided into groups 'steps' applying an eCDF, and data are then sorted through values of a selected channel in ascending order.

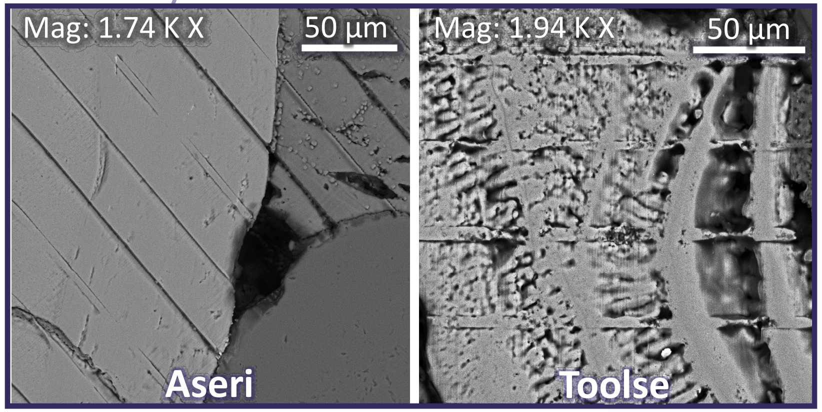


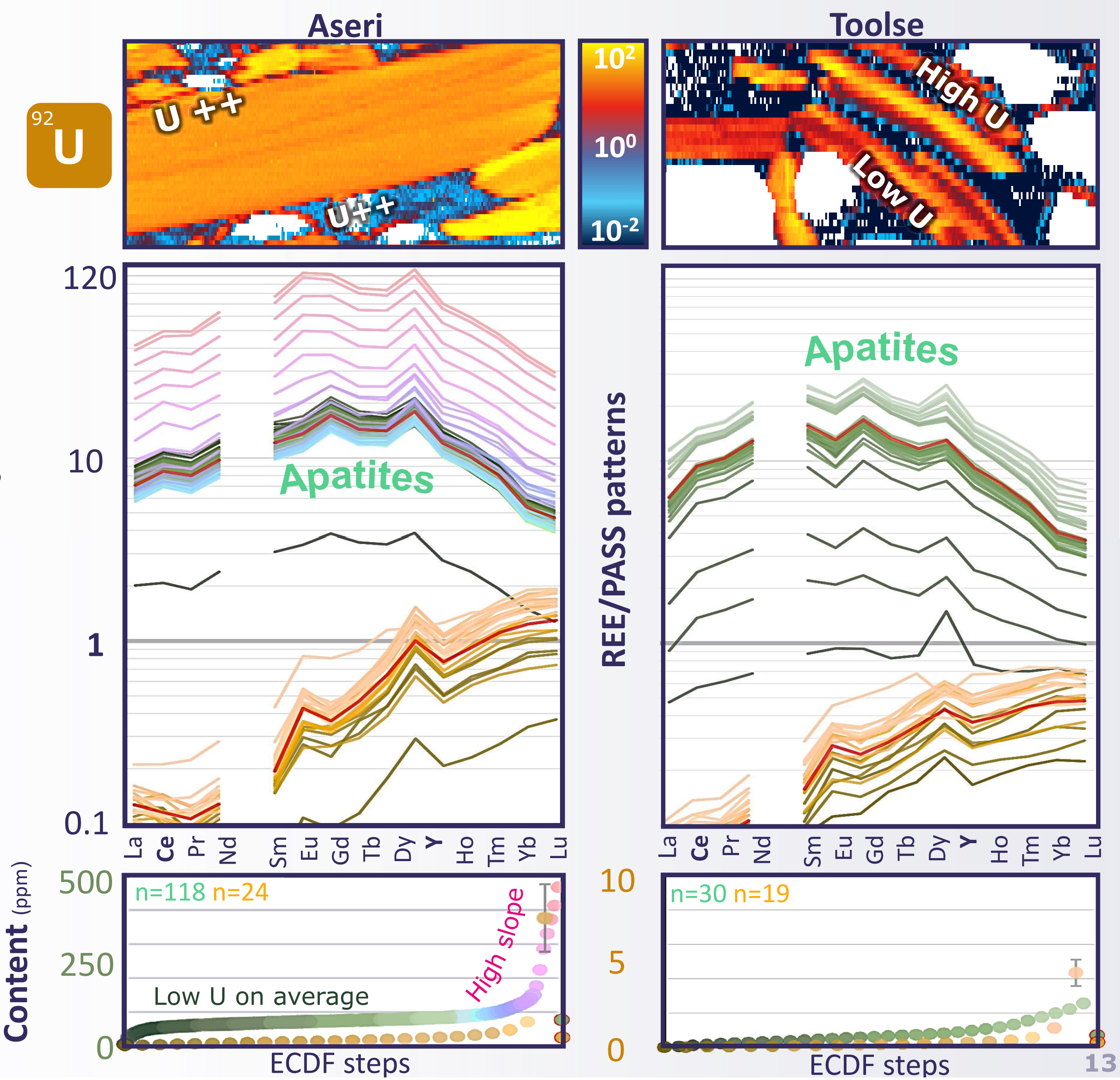
REE investigation

REE trends following U content in apatites and carbonates

- General homogenous REE trends
- Variations of diagenetic overprint: early to advanced, ⬆redox conditions
- Influence on apatite recrystallisation and textures

Recrystallised | Pristine-like texture



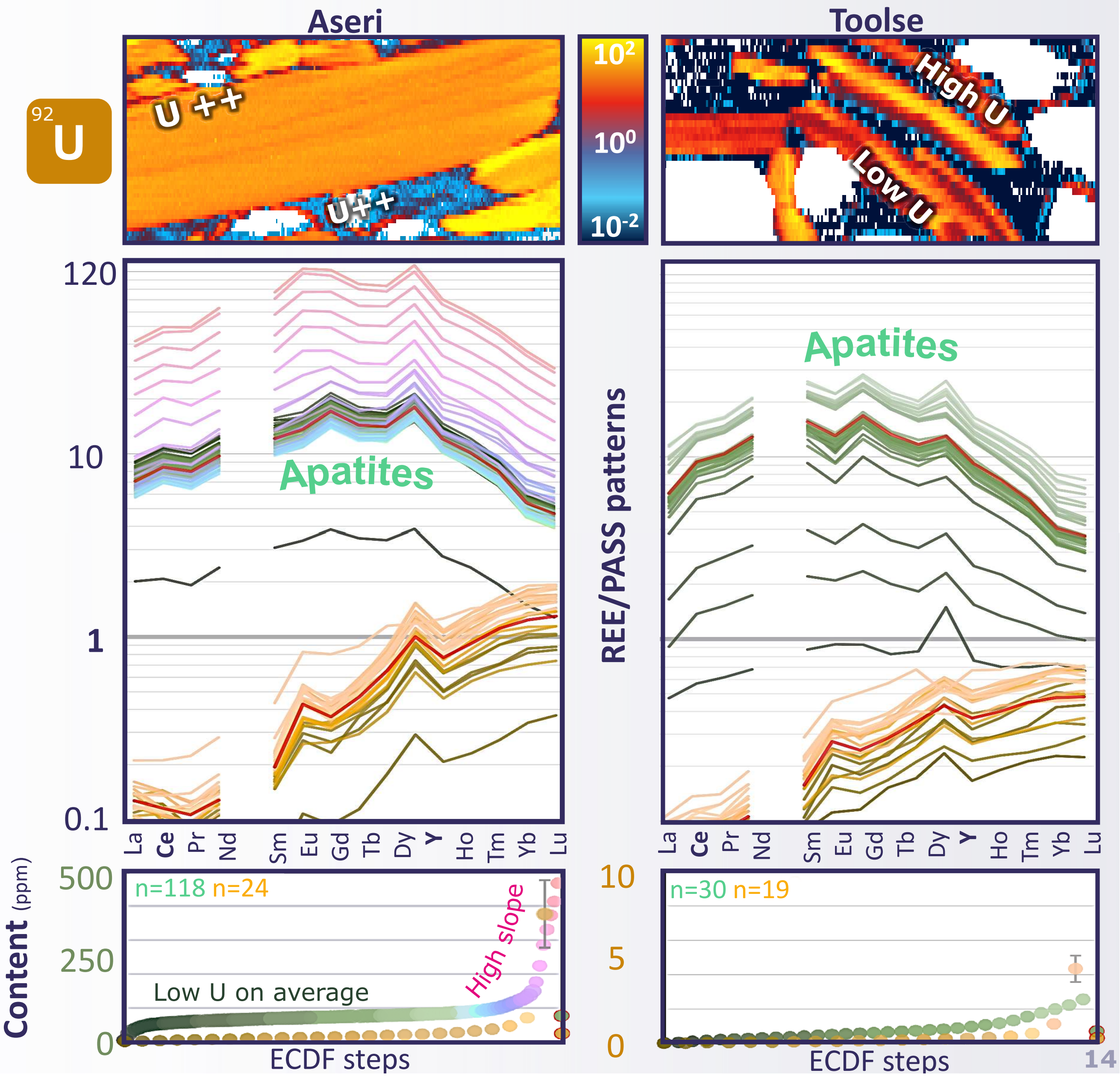


REE investigation

REE trends following U content in apatites and carbonates

- Specific REE enrichment on edges of altered shell fragments
- REE content up to 121-folds in Aseri: late alteration uptake
- Euxinic settings, lithogenic input

Altered edges and fragments (fines)



Conclusion & Perspectives

Phosphorites are highly variable deposits but tend to homogenise locally during diagenesis

Estonian phosphorites are promising low-grade REE ore (1500-2000ppm), highly enriched fraction on shell edges (3000-8000ppm)

Necessity of minimising fines loss for maximal REE recovery

To be further explored

- Reconciliation between whole-rock and LA-ICP-MS data
- LA-ICP-MS mapping application to concentrates & other apatite REE ores
- Beneficiation process

EGT-TWINN

crm

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THANK YOU FOR YOUR ATTENTION

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Republic of Estonia
Geological Survey

University of Oulu

Trinity College Dublin