

## DEFENS kick-off meeting

January 27th, 2026 - Campus di Chieti - Sala Multimediale del Rettorato

# ***RARE EARTH ELEMENTS (REE) GEOCHEMISTRY IN SEDIMENTARY ROCKS***

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# Rare Earth Elements - REE

- They are the most **widely used** group of trace elements in geochemistry for igneous, metamorphic, and sedimentary systems.

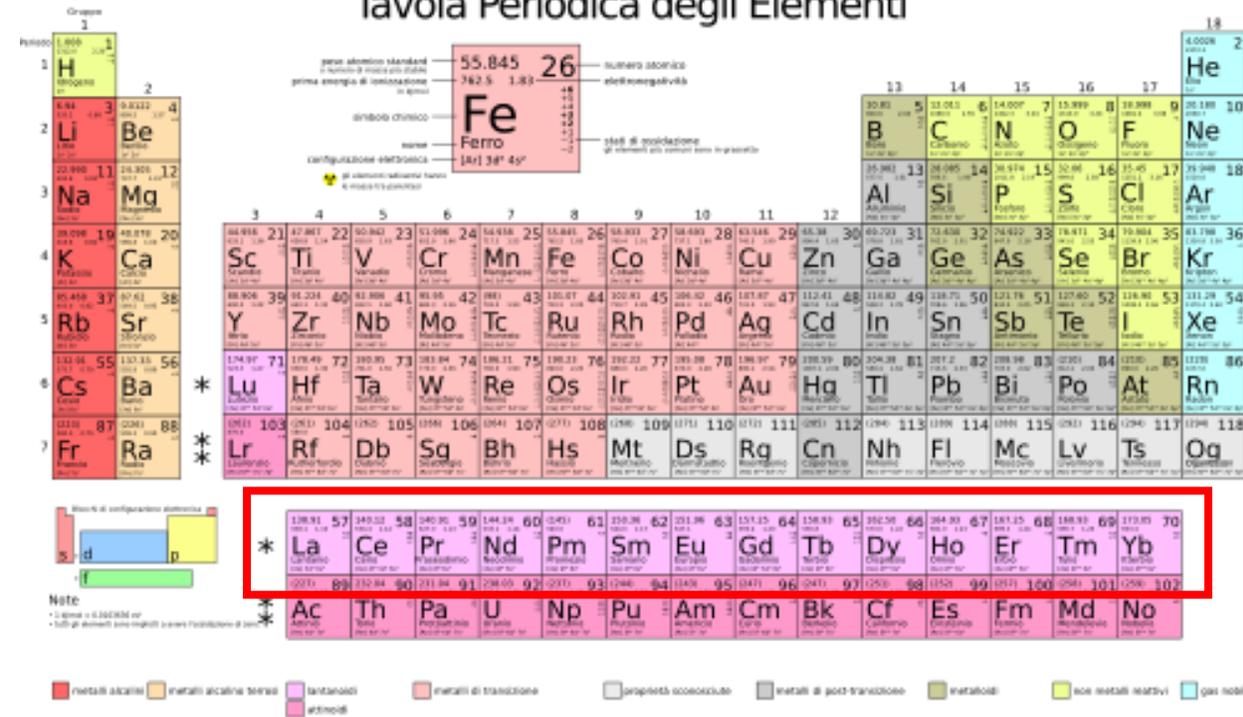
| Z  | element      | symbol | charge |       |    |
|----|--------------|--------|--------|-------|----|
|    |              |        | +2     | +3    | +4 |
| 57 | Lanthanum    | La     |        | 103.2 |    |
| 58 | Cerium       | Ce     |        | 102   | 87 |
| 59 | Praseodymium | Pr     |        | 99    | 85 |
| 60 | Neodymium    | Nd     | 1298   | 98.3  |    |
| 61 | Promethium*  | Pm     |        | 97    |    |
| 62 | Samarium     | Sm     | 1224   | 95.8  |    |
| 63 | Europium     | Eu     | 117    | 94.7  |    |
| 64 | Gadolinium   | Gd     |        | 93.8  |    |
| 65 | Terbium      | Tb     |        | 92.3  | 76 |
| 66 | Dysprosium   | Dy     | 107    | 91.2  |    |
| 67 | Holmium      | Ho     |        | 90.1  |    |
| 68 | Erbium       | Er     |        | 89    |    |
| 69 | Thulium      | Tm     | 103    | 88    |    |
| 70 | Ytterbium    | Yb     | 102    | 86.8  |    |
| 71 | Lutetium     | Lu     |        | 86.1  |    |

1 Å = 100 pm (picometres)

Ionic radius

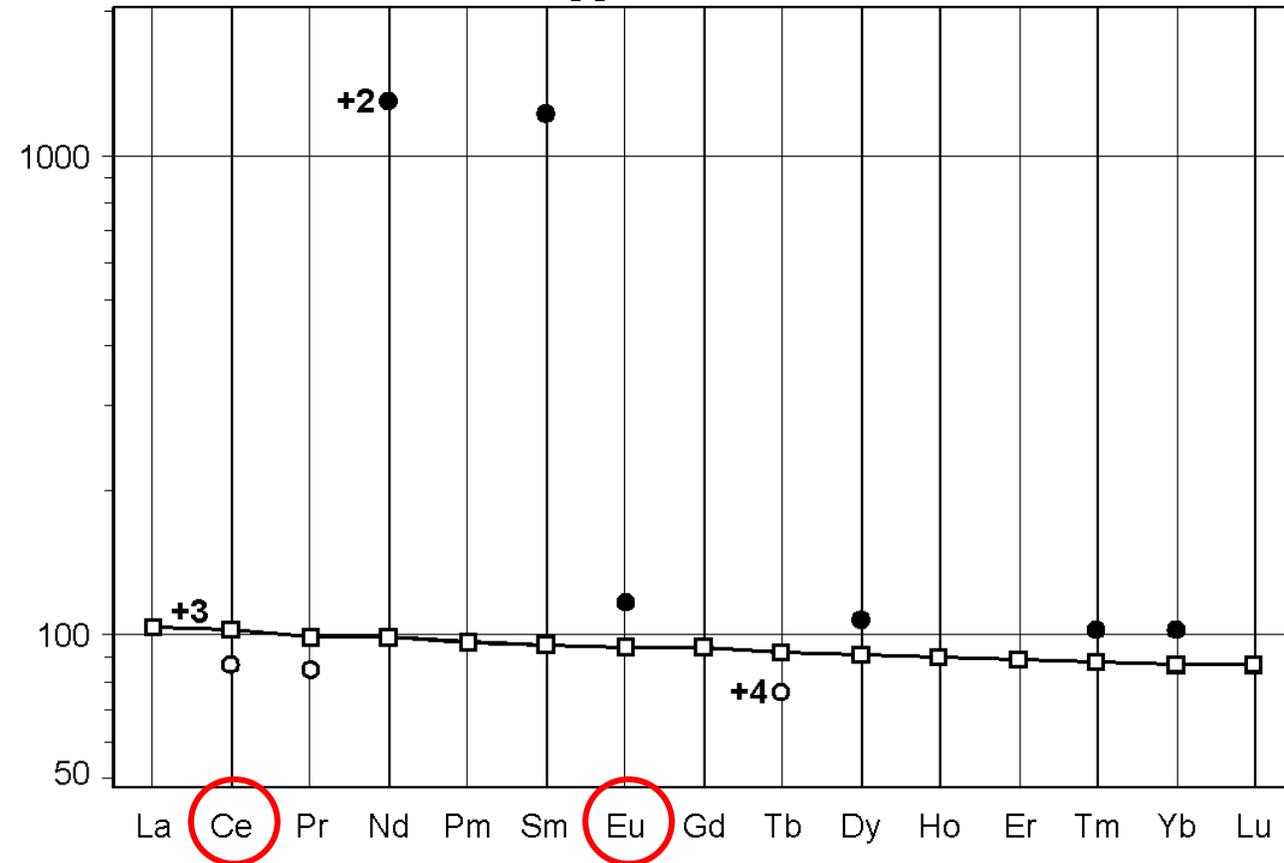
\* synthetic

Tavola Periodica degli Elementi



- REEs are **metals** with atomic numbers from 57 to 71, from La to Lu. In some cases, **Y**, having an ionic radius similar to Ho, is included in the REE group.
- Generally, REEs with a lower atomic number are called Light REEs (LREEs), those with an intermediate Z are called Medium REEs (MREEs), while REEs with a higher Z are called Heavy REEs (HREEs).
- REEs have **similar chemical and physical properties** because they are all elements with stable 3+ ions and similar radii.

# Rare Earth Elements - REE



Small differences in ionic radii determine slightly different ionic potentials (charge/ionic radius), which cause a natural (and predictable) fractionation of the REE ions relative to one another.

However, environmental/geological processes that can modify the oxidation state of REE can change the mobility of these elements. It leads to an anomalous distribution of some RE elements in the rocks.

For instance,

Cerium (Ce): Oxidizing conditions

$\text{Ce}^{3+} \rightarrow \text{Ce}^{4+}$ , and Ce precipitates as  $\text{CeO}_2$ , creating negative Ce anomalies in water and often in sediments, while retaining it in topsoils.

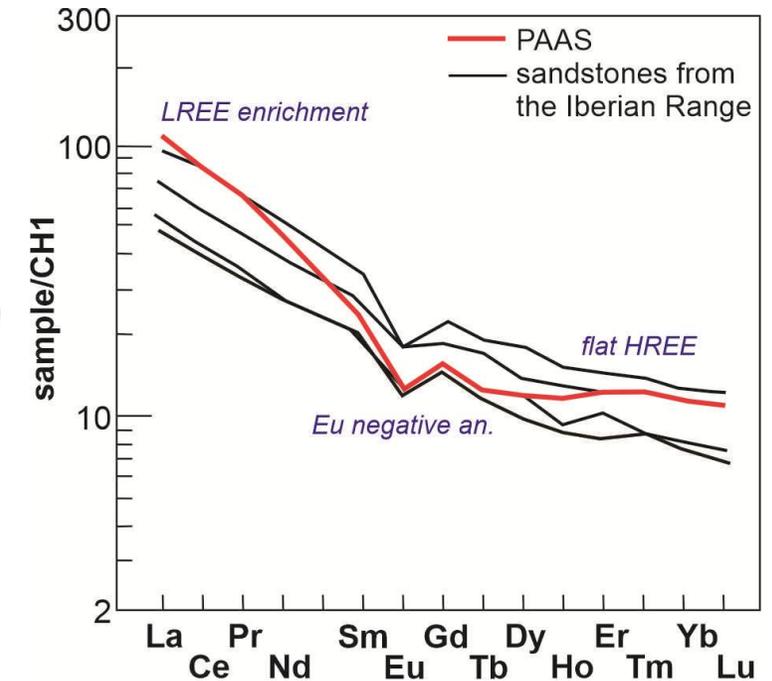
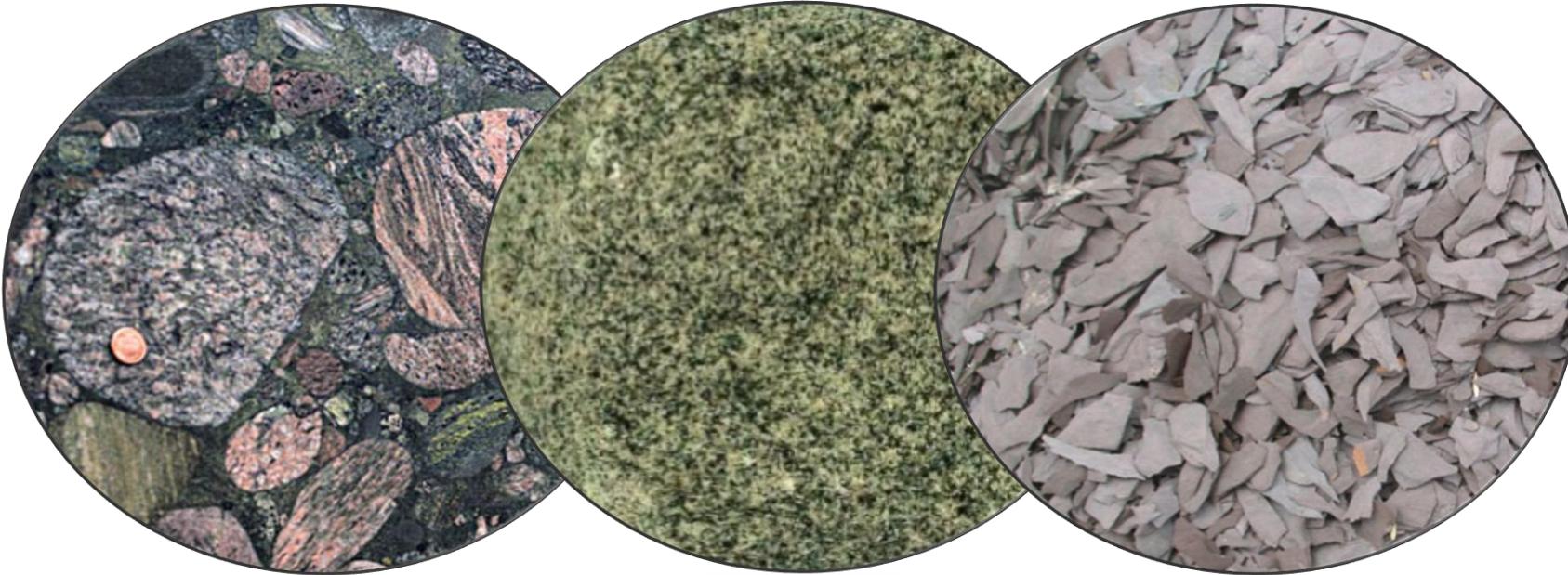
Europium (Eu): Reducing condition (low  $f\text{O}_2$ )

$\text{Eu}^{+3} \rightarrow \text{Eu}^{+2}$  and Eu is incorporated more efficiently into silicate minerals, producing Eu fractionation (removal) with respect to the other REEs

# REE Behavior in Sedimentary Rocks



**Siliciclastic sedimentary rocks** (Rock fragments and/or crystal grains and/or clay minerals)



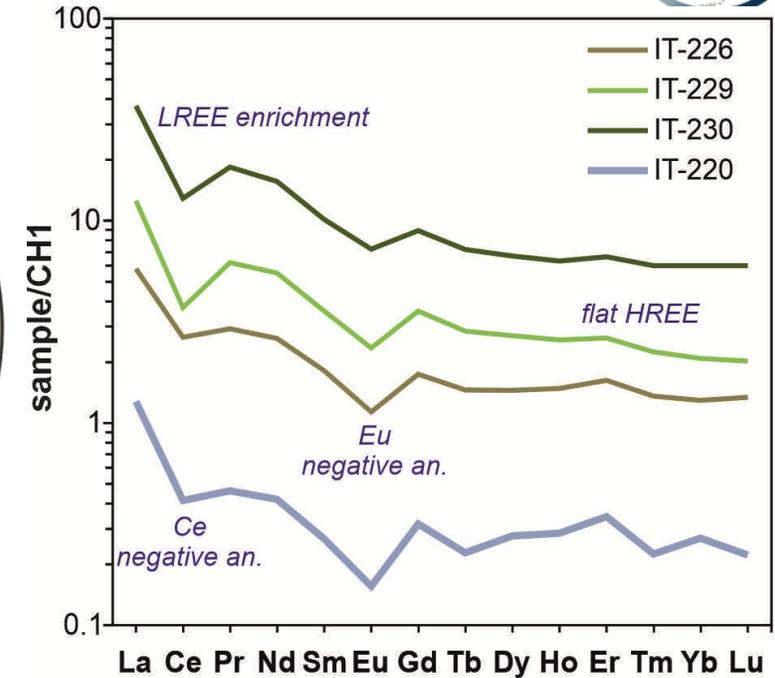
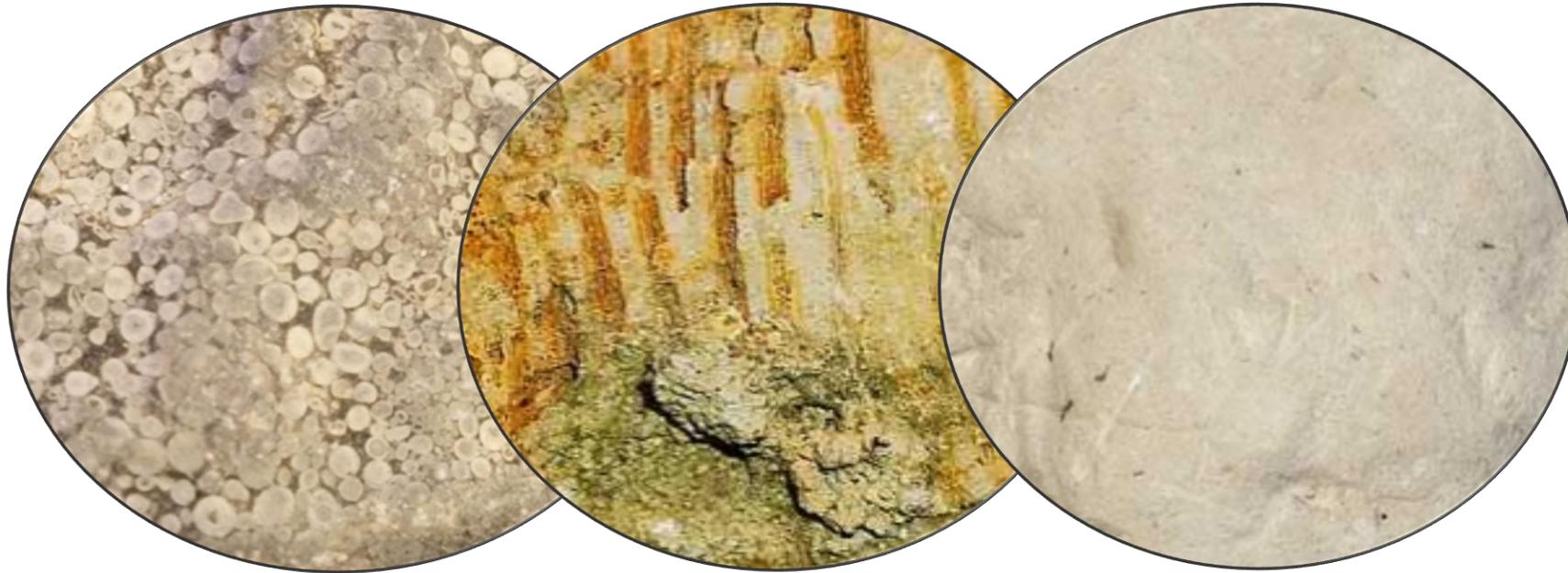
Rare Earth Element (REE) contents in siliciclastic rocks are primarily controlled by provenance, transport, and sorting, ***mirroring their source composition*** (in general, Upper Crust like PAAS = Post Archean Australian Shales). Due to the variability of weathered rocks, the REE contents in siliciclastic rocks are very variable.

**Sedimentary Environment:** REE signatures can be modified by diagenetic processes, with Fe-Mn oxyhydroxides in oxidizing conditions potentially creating positive Ce anomalies or influencing MREE enrichment.

**Clay Concentration:** Fine-grained clay-sized fractions often act as the primary sink for REEs in sedimentary rocks.

# REE Behavior in Sedimentary Rocks

Carbonate sedimentary rocks (minerals based on the  $\text{CO}_3^{2-}$  ion)



Rare Earth Element (REE) contents in limestones represent **paleo-seawater chemistry**: marine carbonates, such as aragonite and calcite, inherit REE patterns directly from sea or pore water. Due to the low REE solubility in water, the REE content in carbonates is relatively low.

**Diagenetic Alteration:** Post-depositional processes (diagenesis) can alter primary REE signatures

## Environmental Proxies:

- **Oxygenation:** negative Ce anomalies indicate oxygenated conditions;
- **pH Indicator:** REE concentrations, specifically variation of HREE/LREE ratio, are a proxy for ancient seawater pH;
- **Terrigenous Input:** a lowering in Y/Ho ratios indicates higher terrigenous, or land-derived, input.



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## Journal of Asian Earth Sciences: X

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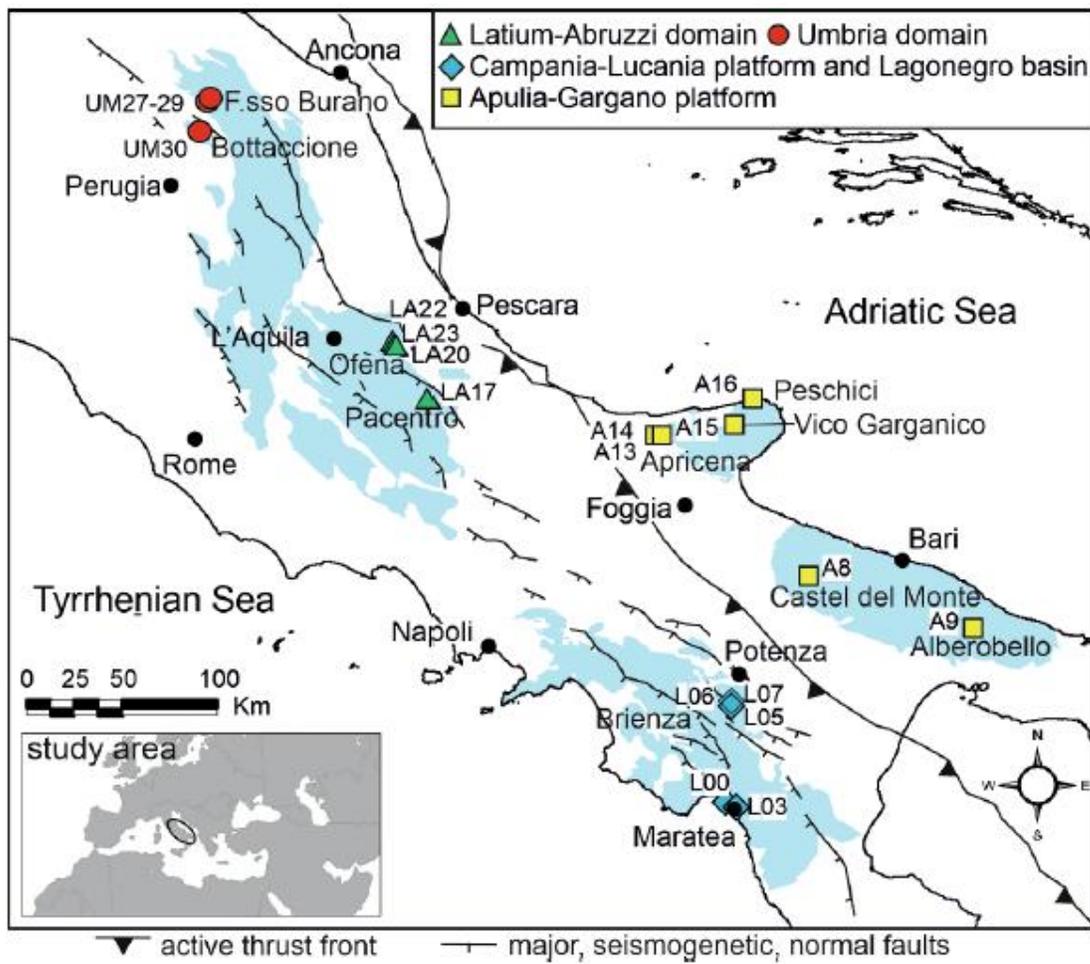


### Elemental abundances and isotopic composition of Italian limestones: Glimpses into the evolution of the Tethys

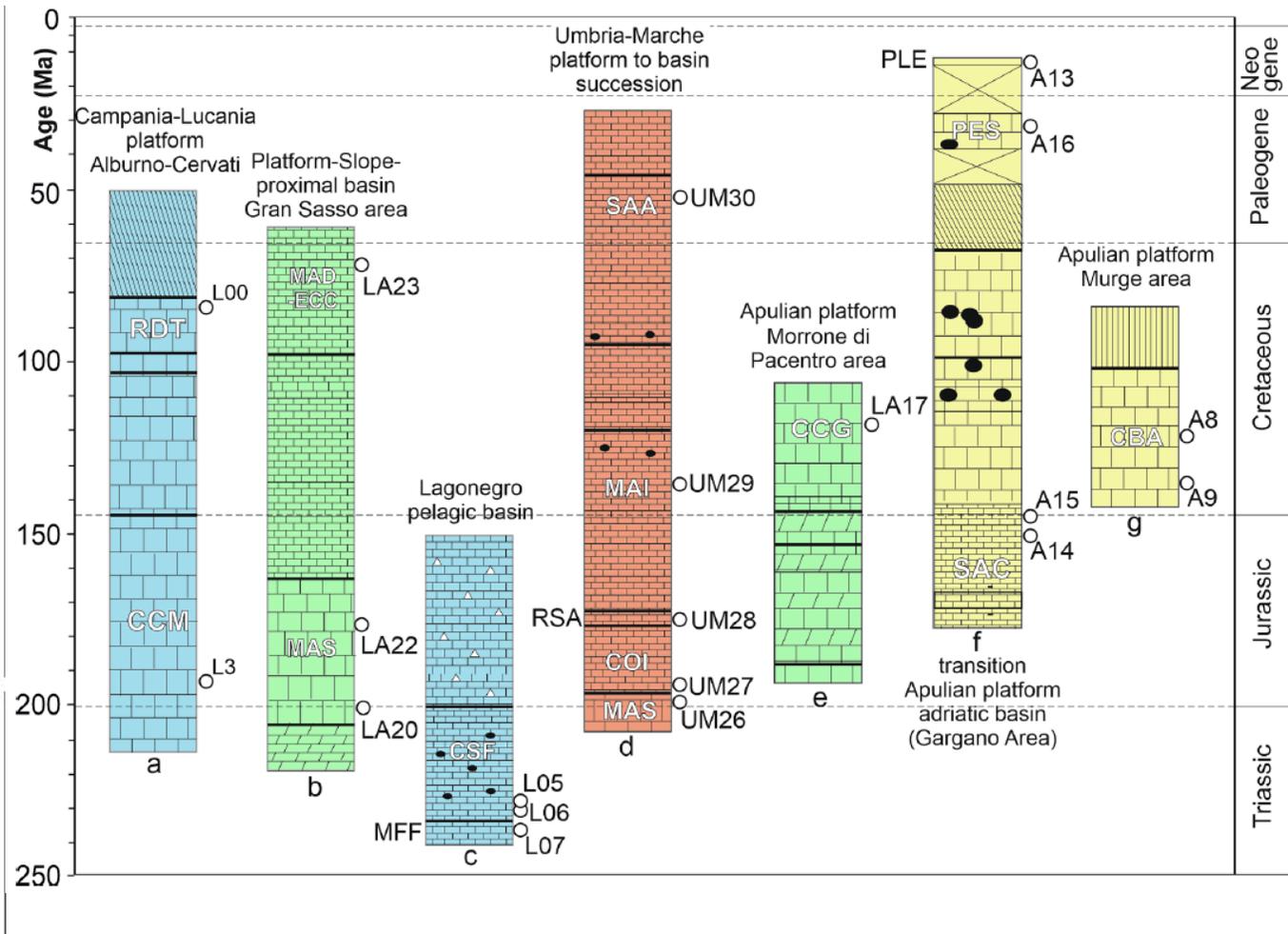
Gianluigi Rosatelli <sup>a,\*</sup>, Francesca Castorina <sup>b,c</sup>, Ada Consalvo <sup>a</sup>, Francesco Brozzetti <sup>a</sup>,  
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# ***REE+Y in Italian limestones***





Map showing the Tethyan (**Triassic-Miocene, light blu**) sedimentation domains in the Central-Southern Apennines and sampling localities. Sampling sites: Maratea and Brienza for Lagonegro platform/basin; Alberobello, Castel del Monte, Apricena, Vico Garganico, Peschici, for Apulian Garganic platform; Pacentro and Ofena for Lazio-Abruzzi sequence and F.sso Burano and Bottaccione for Umbria-Marche sequence.



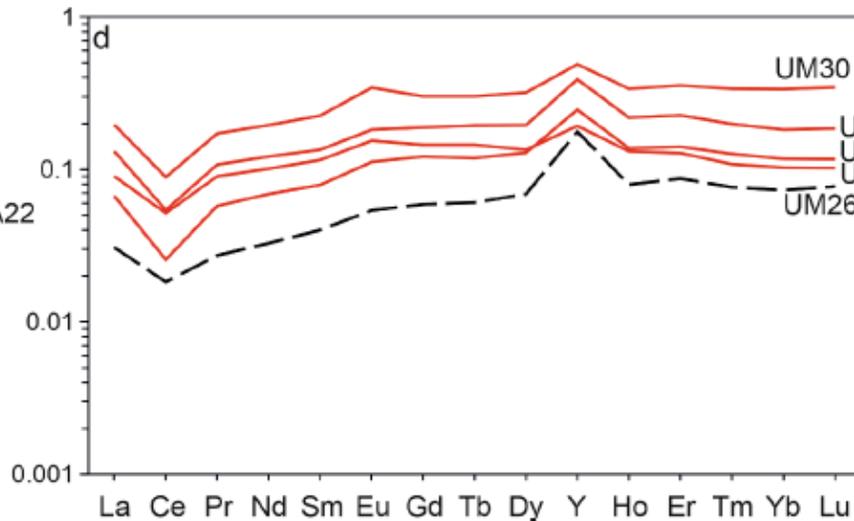
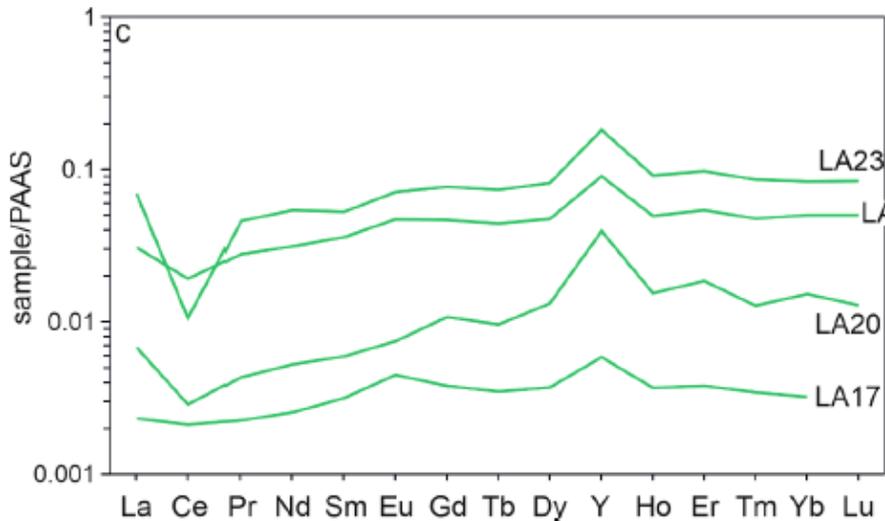
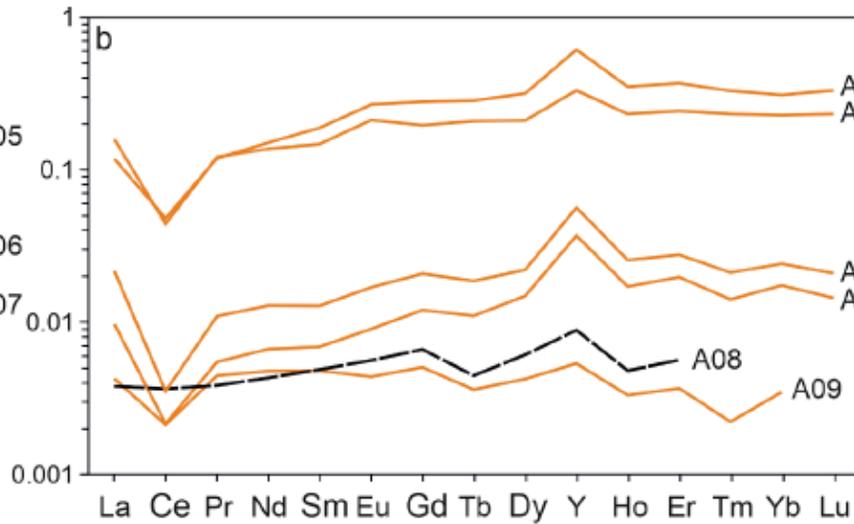
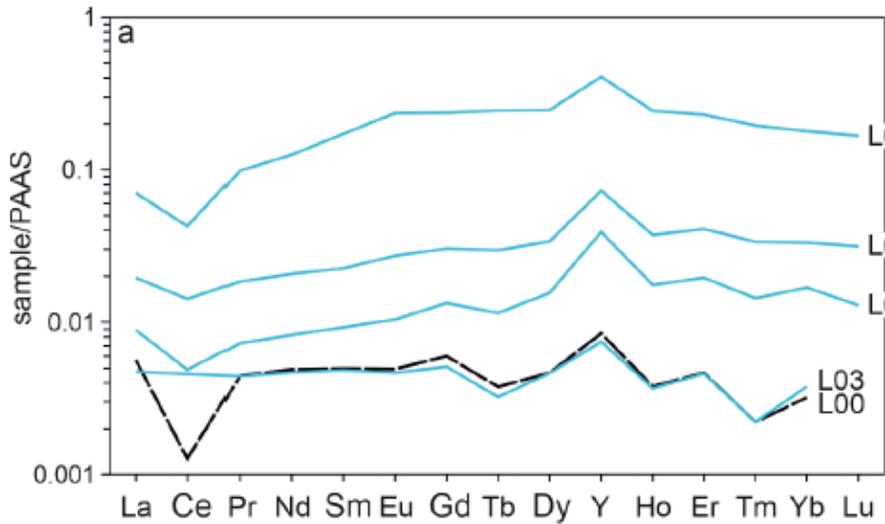
Stratigraphic schemes are representative of the different paleogeographic domains recognized in the central-southern Apennines. The length of the columns is related to the time-extent of each succession (reported in Ma on the vertical axis) and not to their actual thickness (i.e. not to scale).

# Rare Earth Elements concentration in limestones

| ppm                     | Lagonegro basin |      |       |      |      | Apulian platform |      |      |      |      |       | Lazio-Abruzzo |      |      |      | Umbria-Marche |       |       |       |       |
|-------------------------|-----------------|------|-------|------|------|------------------|------|------|------|------|-------|---------------|------|------|------|---------------|-------|-------|-------|-------|
|                         | L00             | L03  | L05   | L06  | L07  | A13              | A16  | A09  | A08  | A15  | A14   | LA23          | LA17 | LA22 | LA20 | UM26          | UM27  | UM28  | UM29  | UM30  |
| La                      | 0.25            | 0.21 | 3.14  | 0.87 | 0.40 | 5.24             | 0.43 | 0.19 | 0.17 | 0.96 | 7.06  | 3.09          | 0.10 | 1.37 | 0.30 | 1.37          | 5.89  | 4.04  | 2.98  | 8.75  |
| Ce                      | 0.11            | 0.40 | 3.76  | 1.25 | 0.43 | 4.25             | 0.19 | 0.19 | 0.32 | 0.31 | 3.90  | 0.93          | 0.19 | 1.69 | 0.25 | 1.62          | 4.80  | 4.57  | 2.27  | 7.88  |
| Pr                      | 0.05            | 0.04 | 1.00  | 0.19 | 0.07 | 1.21             | 0.06 | 0.05 | 0.04 | 0.11 | 1.23  | 0.46          | 0.02 | 0.28 | 0.04 | 0.28          | 1.09  | 0.92  | 0.59  | 1.75  |
| Nd                      | 0.18            | 0.18 | 4.67  | 0.77 | 0.31 | 5.60             | 0.25 | 0.18 | 0.16 | 0.48 | 5.11  | 2.01          | 0.09 | 1.16 | 0.20 | 1.22          | 4.55  | 3.79  | 2.58  | 7.30  |
| Sm                      | 0.03            | 0.03 | 1.18  | 0.16 | 0.06 | 1.29             | 0.05 | 0.03 | 0.03 | 0.09 | 1.01  | 0.36          | 0.02 | 0.25 | 0.04 | 0.28          | 0.93  | 0.80  | 0.55  | 1.55  |
| Eu                      | 0.01            | 0.01 | 0.29  | 0.03 | 0.01 | 0.33             | 0.01 | 0.01 | 0.01 | 0.02 | 0.26  | 0.09          | 0.01 | 0.06 | 0.01 | 0.07          | 0.22  | 0.19  | 0.14  | 0.42  |
| Gd                      | 0.04            | 0.03 | 1.43  | 0.18 | 0.08 | 1.68             | 0.07 | 0.03 | 0.04 | 0.13 | 1.18  | 0.46          | 0.02 | 0.28 | 0.06 | 0.36          | 1.14  | 0.88  | 0.73  | 1.83  |
| Tb                      | 0.00            | 0.00 | 0.22  | 0.03 | 0.01 | 0.25             | 0.01 | 0.00 | 0.00 | 0.02 | 0.19  | 0.07          | 0.00 | 0.04 | 0.01 | 0.05          | 0.17  | 0.13  | 0.11  | 0.27  |
| Dy                      | 0.02            | 0.02 | 1.31  | 0.18 | 0.08 | 1.68             | 0.08 | 0.02 | 0.03 | 0.12 | 1.12  | 0.43          | 0.02 | 0.25 | 0.07 | 0.37          | 1.04  | 0.72  | 0.69  | 1.70  |
| Y                       | 0.23            | 0.20 | 11.11 | 1.99 | 1.07 | 16.74            | 1.01 | 0.15 | 0.24 | 1.54 | 9.06  | 4.94          | 0.16 | 2.45 | 1.07 | 4.84          | 10.68 | 5.29  | 6.75  | 13.43 |
| Ho                      | 0.00            | 0.00 | 0.26  | 0.04 | 0.02 | 0.37             | 0.02 | 0.00 | 0.01 | 0.03 | 0.24  | 0.10          | 0.00 | 0.05 | 0.02 | 0.08          | 0.23  | 0.14  | 0.15  | 0.36  |
| Er                      | 0.01            | 0.01 | 0.71  | 0.13 | 0.06 | 1.14             | 0.06 | 0.01 | 0.02 | 0.08 | 0.75  | 0.30          | 0.01 | 0.17 | 0.06 | 0.27          | 0.70  | 0.39  | 0.43  | 1.10  |
| Tm                      | 0.00            | 0.00 | 0.09  | 0.02 | 0.01 | 0.15             | 0.01 | 0.00 |      | 0.01 | 0.10  | 0.04          | 0.00 | 0.02 | 0.01 | 0.03          | 0.09  | 0.05  | 0.06  | 0.15  |
| Yb                      | 0.01            | 0.01 | 0.54  | 0.10 | 0.05 | 0.93             | 0.05 | 0.01 | 0.01 | 0.07 | 0.69  | 0.25          | 0.01 | 0.15 | 0.05 | 0.22          | 0.55  | 0.31  | 0.35  | 1.02  |
| Lu                      |                 |      | 0.07  | 0.01 | 0.01 | 0.15             | 0.01 |      |      | 0.01 | 0.10  | 0.04          |      | 0.02 | 0.01 | 0.03          | 0.08  | 0.04  | 0.05  | 0.15  |
| $\Sigma_{\text{REE}}$   | 0.73            | 0.96 | 18.67 | 3.96 | 1.60 | 24.25            | 1.29 | 0.72 | 0.85 | 2.43 | 22.94 | 8.62          | 0.51 | 5.79 | 1.12 | 6.25          | 21.48 | 16.96 | 11.67 | 34.22 |
| $\Sigma_{\text{REE+Y}}$ | 0.96            | 1.17 | 29.78 | 5.95 | 2.67 | 40.99            | 2.30 | 0.87 | 1.09 | 3.98 | 32.00 | 13.56         | 0.67 | 8.24 | 2.19 | 11.10         | 32.17 | 22.24 | 18.41 | 47.65 |

Sum of REE may vary of 3 orders of magnitude

Very low concentrations sometime below instrumental detection limits

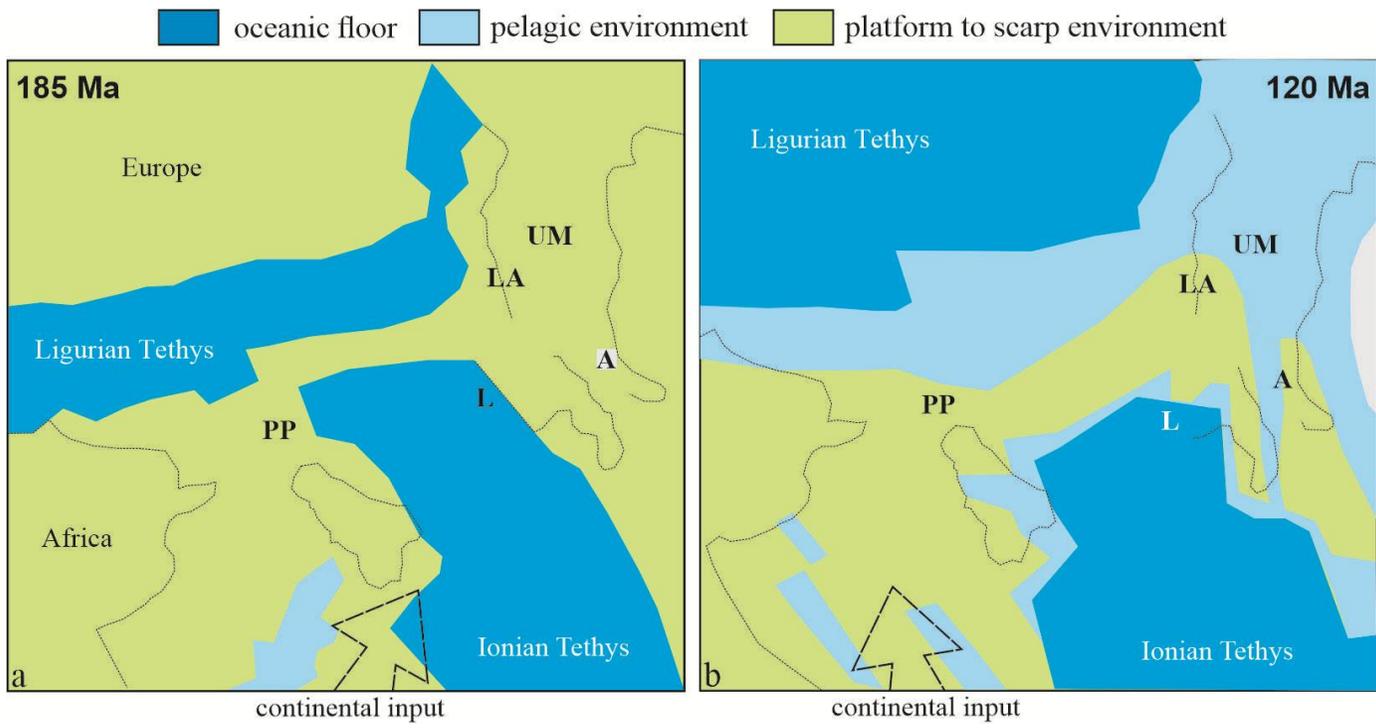
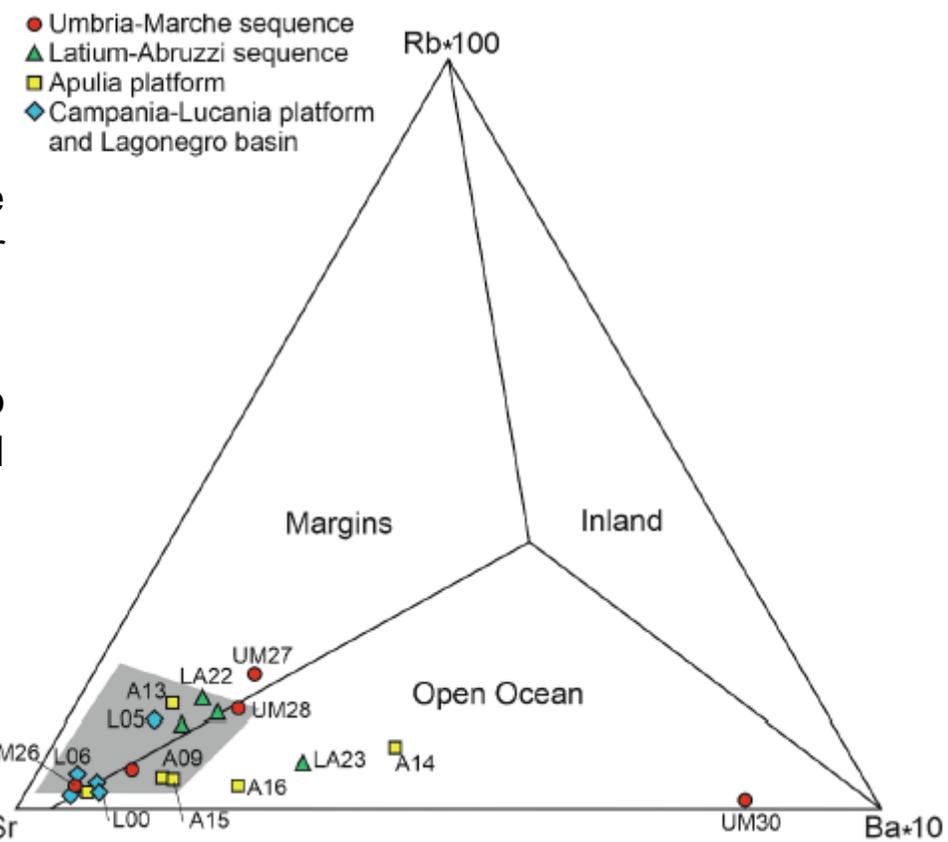


- The REE+Y<sub>PAAS</sub> patterns for the limestones display an overall progressive enrichment of heavy REE (HREE) over middle REE (MREE) and light REE (LREE).
- The relative enrichment of HREE over LREE observed is typical of “seawater-like” patterns and is related to REE bound to CO<sub>3</sub><sup>2-</sup>. There is negligible input from hydrothermal fluids or terrigenous detrital materials.
- Common features include the negative Ce anomaly, only a few samples showing an Eu positive anomaly.

REE+Y concentrations normalized to PAAS (Pourmand et al., 2012); a) southern section: Lagonegro basin; b) southern section: Apulian platform; c) central section; Lazio-Abruzzo sequence; d) northern section: Umbria-Marche sequence.

Considering the distribution of other trace elements (Sr, Rb, Ba), the depth of the depositional environment was responsible for the REE+Y budget in seawater and in limestone.

It is also interesting that the data from the Italian Tethys limestones fall close to those of the *meso*-Tethyan oceanic plateaux in Tibet (Zhang et al., 2017), and suggest a geographical link between the two basins.



Schematic paleogeographic reconstruction of the central Mediterranean area during: a) Toarcian, **Lower Jurassic** (185 Ma); b) Aptian, **Lower Cretaceous** (120 Ma). UM = Umbria-Marche limestone series, LA = Lazio.Abruzzo limestone series; A = Apulian platform, L = Lagonegro basin; PP = Panormide Platform. Redraw after Stampfli and Borel (2002); Zarccone et al. (2010); Tavani et al. (2013); Vitale et al. (2017).

## Development research opportunities within DEFENS:

1. Evaluation of the geochemical behaviour of other trace elements in the fault escarpment: for instance, mobile elements like Ba, Rb, Sr vs immobile elements Cr, Ni, V, Ti;
2. Assessment of the role of Fe-Mn oxydes and Phosphates on the REE mobility along the interface soil-fault surface and within the soil;
3. Improving analytical capacities;

