



# RARE EARTH ELEMENTS (REE) IN GROUNDWATER IN THE ARCHEOLOGICAL SITE OF CUMAE (PHLEGRAEAN FIELDS, SOUTHERN ITALY)



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## 1. Introduction

The rare-earth elements (REE) and combined yttrium (YREE) elements are ubiquitous with stable and long-lived isotopes; they have been used to trace some geological processes as weathering processes and water-rock interaction.

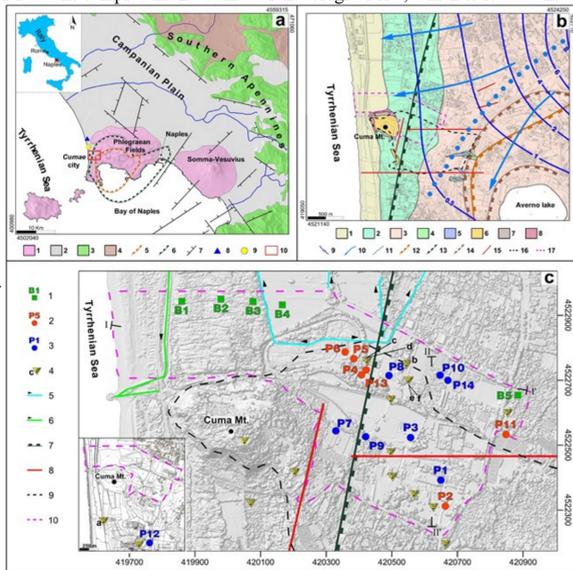
REE were determined on groundwaters collected of 14 wells sampled in the Cumae archaeological site, which is located in the coastal north-western sector of the volcanic district of Phlegraean Fields (Southern Italy)[1]

Fig.1. Location of study area

- a) Geological map of the Campanian Plain. 1) Quaternary epiclastic deposits; 2) Quaternary volcanic deposits; 3) Apennine platform carbonates; 4) Miocene deposits; 5) NYT caldera boundary; 6) CI caldera boundary; 7) Normal fault; 8) Licola pluviometric station; 9) Licola draining station; 10) Study area.

- b) Hydrogeological map of the western sector of Phlegraean Fields volcanic system. 1) Eolic deposits; 2) Pyroclastic-fluvio-palustrine deposits; 3) Pyroclastic deposits; 4) Baia's tuffs; 5) Gauro's eruption deposits; 6) Neapolitan Yellow Tuff; 7) Museum Breccia; 8) Mt. Cuma's lavas; 9) Groundwater contour line (m a.s.l.); 10) Groundwater flow direction; 11) Groundwater divide; 12) NYT caldera boundary; 13) CI caldera boundary; 14) Buried caldera boundary; 15) Normal fault; 16) Cumae archaeological park; 17) Study area.

- c) Groundwater, soil, and air sampling network. 1) Borehole; 2) Sampling point of shallow groundwater, soil, and air; 3) Sampling point of deep groundwater, soil, and air; 4) Archaeological site; 5) Groundwater draining channel; 6) Wastewater channel; 7) CI caldera boundary; 8) Normal fault; 9) Cumae archaeological park; 10) Study area.



## 2. Origin and uses of rare earth elements (REE)

Rare earth elements (REE) are mainly divided into light and heavy rare earth elements (LREE and HREE, respectively). The LREEs are defined as the lanthanide elements from lanthanum through to samarium (La, Ce, Pr, Nd, Sm) and the HREEs as the lanthanide elements from europium through to lutetium and yttrium (Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y). Yttrium is often grouped with the HREE due to its similar properties [2] (REEY). REEYs are geochemically classified into three groups: the light rare earth elements (LREE- La, Ce, Pr, Nd and Sm), middle rare earth elements (MREE: Eu, Gd, Tb, Dy and Y) and heavy rare earth elements (HREE: Ho, Er, Tm, Yb, Lu) [3].

The extended use of REEYs is linked to their magnetic, catalytic and optical properties. Their main uses are in the automotive, telecom and electronic sectors, as well as aerospace, defence, and renewable energy. Their demand in recent years has continued to increase with the global production of REEs reaching 210,000 tonnes in 2019. REEY are contained in such low concentrations. REEY values measured at the P1-P14 sites are included in the ranges shown in Table 1.

Table 1. Concentration ranges of REEY elements measured in the P1-P14 sites.

REEY concentration ranges (µg/L)														
La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
0.01-1.60	0.01-1.55	0.01-0.15	0.01-0.60	0.01-0.10	0.005-0.02	0.005-0.07	0.005-0.02	0.005-0.06	0.005-0.02	0.01-0.05	0.01-0.02	0.005-0.04	0.005-0.06	0.02-0.45

REEY behavior is better presented if the content values are "normalized" (is denoted by the chemical symbol with the subscript n (Lan, Prn, ecc.) and reported as a relative abundance plot [4]. This means that the REE concentrations found in the sample  $[(REEY)_{SAMPLE}]$  are divided by the concentration of the same REE element contained in a reference material  $[(REEY)_{PAAS}]$ . Most popular reference samples include the PAAS (Post-Archean Australian Shales) of Taylor and McLennan [4]:

$$REEY_n = \frac{[(REEY)_{SAMPLE}]}{[(REEY)_{PAAS}]}$$

There are mainly two advantages of this method. The first is that the abundance variation between REEs of even and odd atomic numbers is eliminated. The second, even more important, advantage is the real possibility of perceiving any fractionation that has occurred among the REEYs in the sample. Hence, the abundance peaks (positive or negative) in the "normalized" REEY pattern reflect the geochemical history of the sample. The aqueous geochemistry of REEYs is mainly influenced by their high charge and the ensuing high ionic potential. Since the REEYs normally show a very coherent behavior, any shift from the expected distribution pattern can also help to understand the processes involved in the geochemical evolution of an aqueous system.

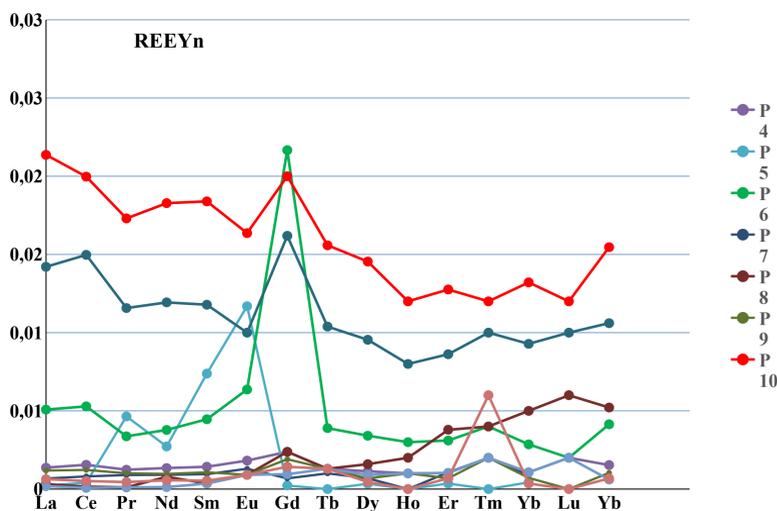


Fig.2. Rare earth element (REEYn) diagram normalized to Post-Archean Australian Shales (PAAS) for groundwaters collected in the Cumae archaeological sites.

Table 1. REEY concentrations (mg/kg) in Post-Archean Australian Shales (PAAS)[4].

Post-Archean Australian Shales (PAAS) (mg/kg)														
La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
38	80	8,9	32	5,6	1,1	4,2	0,77	4,4	1,0	2,9	0,5	2,8	0,5	28

## 3. Variation of REEY concentrations with the depth of the sites

Measurements of the REEY concentration as a function of depth indicate an enrichment of groundwater with depth (Fig. 3, Fig. 4)

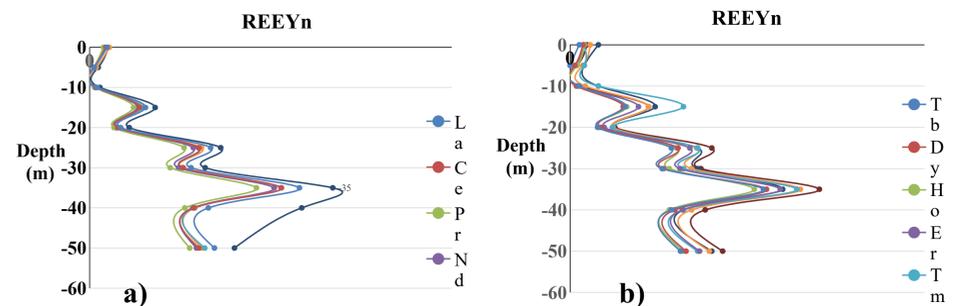


Fig.3. Vertical profiles of REEYn as a function of depth (in meter) for two wells: P3 (a) and P9 (b).

## 4. Correlation between REEY and chemical composition of groundwaters

Variations of REE patterns normalized to PAAS can be correlated with different types of waters. While waters from gneisses always display  $Lan/Gdn > 1$ , waters from granites have  $Lan/Gdn < 1$ . The majority of the samples are relatively depleted in light REE (LREE), resulting in a  $Lan/Gdn$  ratio  $< 1$ . Heavy REE (HREE) are depleted compared to middle REE ( $Ybnorm/Gdnorm < 1$ ) for the majority of the sample.

Europium anomalies and cerium anomalies are expressed by:

$$(Eu/Eu^*) = \frac{Eu_n / (Sm \times Gd)^{0.5}}{1.1}$$

$$(Ce/Ce^*) = \frac{Ce_n / (Lan \times Prm)^{0.5}}{1.2}$$

The data indicate the presence of few values below the average, while the majority of groundwater show values in the average, for both parameters,  $(Eu/Eu^*)$  and  $(Ce/Ce^*)$ .

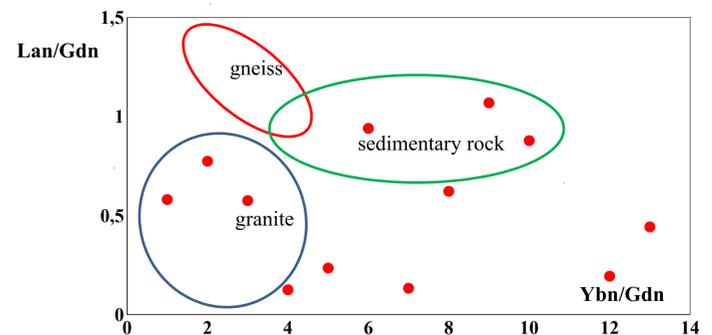


Fig.4. Lan/Gdn in function of Ybn/Gdn of groundwater samples, from different host rocks (gneiss, granite, and sedimentary rock).

There is a correlation between the total concentration of REEY and the content of Fe and Mn. Studies reported in the literature show that this effect depends on the presence of Fe and Mn oxides in suspension which adsorb the REEY elements

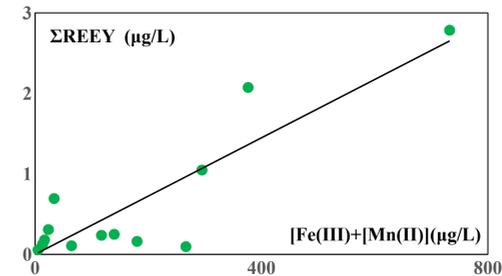


Fig.5. REEY total concentrations ( $\Sigma REEY$ ) in function of  $[Fe(III)+Mn(II)](\mu g/L)$  of groundwater samples ( $y=0,0036x$ ,  $r^2=0,854$ ).

Stability constants indicate that the strongest complexes formed by the trivalent REEYs occur with hydroxide, fluoride, sulfate, carbonate and phosphate, while chloride and nitrate complexes are unlikely to be of importance in natural waters. The data collected show no correlation between the concentrations of the aforementioned anions and that of the REEYs, establishing that the effect of complexation is negligible on the dissolution of the REEY elements.

## 5. Experimental

Before groundwater sampling, a sufficient volume of groundwater was purged by flushing the borehole to eliminate initial fluid in the borehole. The groundwater was immediately acidified by high-purity 60 wt.%  $HNO_3$  so that they contained 1.2 wt.%  $HNO_3$  to lower the pH and preserve for REEY analysis. Chemical analyses to determine major elements were performed by ion chromatography (Dionex, ICS-1000) and inductively coupled plasma mass spectrometry (Agilent 7700x ICP-MS model, Agilent Technologies, USA). The LOD ranged from 0.05 ng/L to 0.5 ng/L

## 6. References

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