Differences in the behaviour of trace and rare- earth elements in oxidizing and reducing soil environments: Case study of Terra Rossa soils and Cretaceous palaeosols from the Istrian peninsula, Croatia [Prezentacija]

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Differences in the behaviour of trace and rare-earth elements in oxidizing and reducing soil environments: Case study of Terra Rossa soils and Cretaceous palaeosols from the Istrian peninsula, Croatia

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This work has been fully supported by Croatian Science Foundation under the project no. IP-2019-04-8054 – WIANLab („Western Istrian Anticline as an ideal natural laboratory for the study of the regional unconformities in carbonate rocks“)

Introduction

- Differences in trace-element mobility between terra rossa and Cretaceous palaeosols
- Reducing and oxidizing soil environments during karst pedogenesis
- Emphasis on rare earth elements (REEs) mobility

Study area

- Succesion of the Western Istrian anticline can be divided into four mega-sequences separated by long lasting emersions:
    - First mega-sequence (Early Bathonian - Early Kimmeridgian)
    - First emersion (Early Kimmeridgian – Late Tithonian)
    - Second mega-sequence (Late Tithonian - Early/Late Aptian)
    - Second emersion (Early/Late Aptian – Late Albian)
    - Third mega-sequence (Late Albian - Late Santonian)
    - Third emersion (Late Santonian – Lower Eocene)
    - Fourth mega-sequence (Lower Eocene – Upper Eocene)
    - Fourth emersion (? - recent)

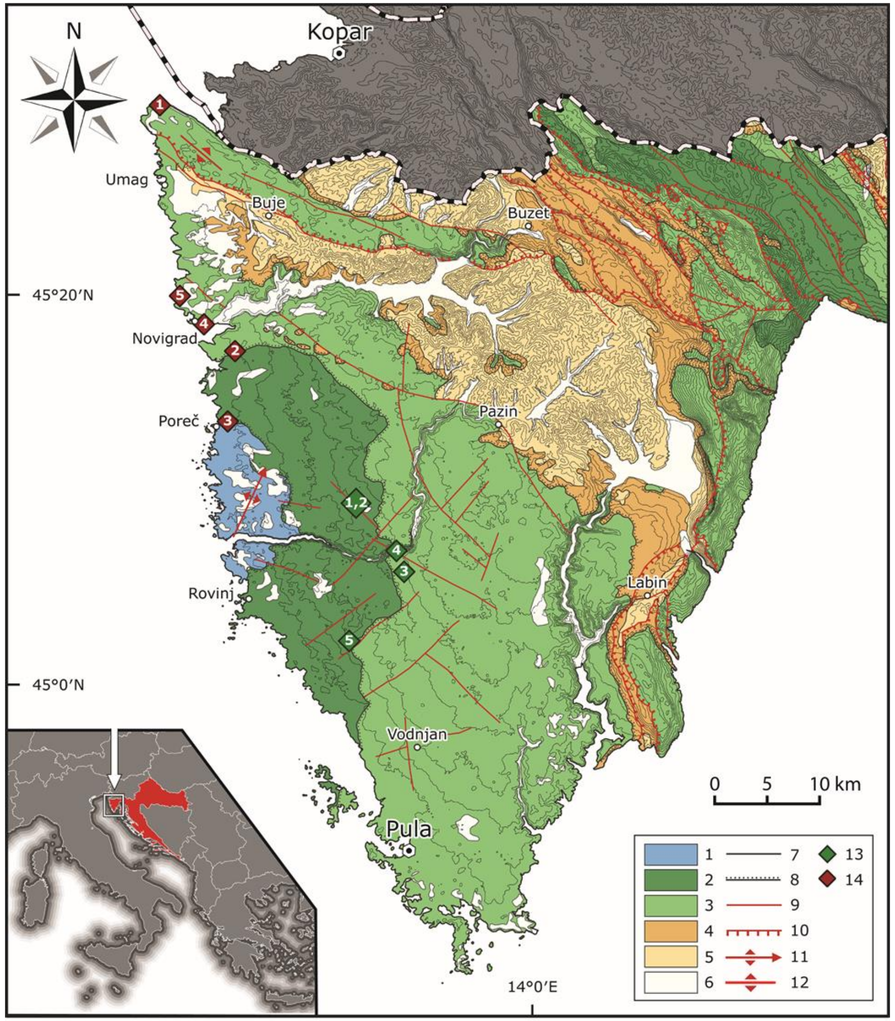


Figure 1. Geological map of Istrian peninsula, outlining the large-scale megasequences and major faults, modified after: Velić et al. (1995) and Basic geological map of Croatia, 1:300,000; 1 - Jurassic, 2 – Lower Cretaceous, 3 - Upper Cretaceous, 4 - Lower Eocene, 5 - Middle to Upper Eocene, 6 - Quaternary, 7 – normal geological boundary, 8 - erosional geological boundary, 9 - normal fault, 10 - reverse fault,11 – Western Istrian anticline, 12 – Savudrija-Buzet anticline, 13 – sampling sites of Cretaceous palaeosols, 14 – sampling sites of terra rossa.

Terra rossa

- Formed during the final emergence of the Istrian peninsula
- Polygenetic relict soils
- Parent material derived mainly from insoluble carbonate residue, aeolian dust, flysch sediments, and sporadically from tephra and bauxite material
- Composed from thin A horizon and a thick B horizon
- Characteristic red colour of the B horizon – reflects rubification
- Oxidizing pedoenvironment

Figure 2. *Terra rossa soils on the outcrop*

Cretaceous palaeosols

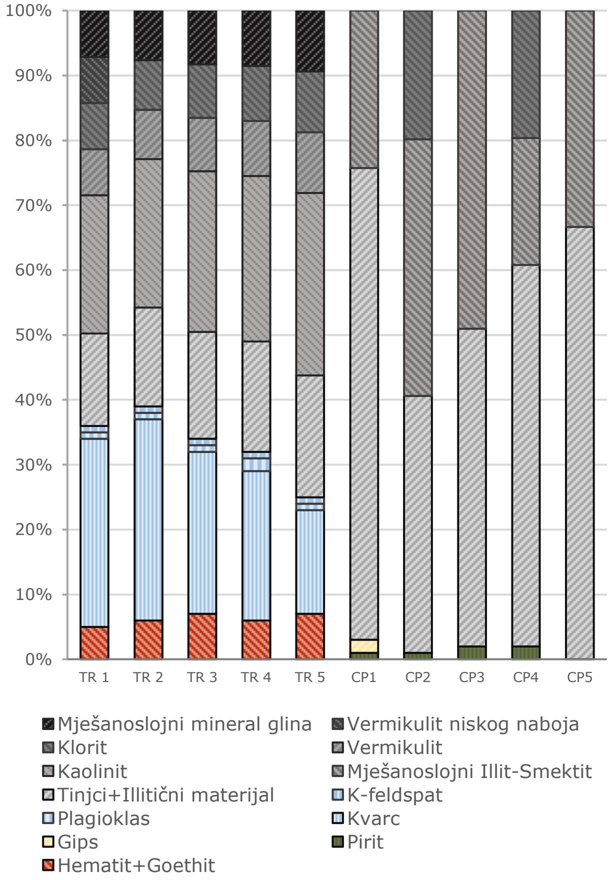
- Formed during the emeregence of the Western istrian anticline during the early/late Aptian to late Albian
- Truncated wetland palaeosols composed only from B horizon and sometimes C horizon
- Root remains, nodular pedofeatures, burrows and channels filled with pyrite framboids
- Parent material derived from insoluble carbonate residue and volcanic material deposited in coastal wetlands
- Reducing pedoenvironment

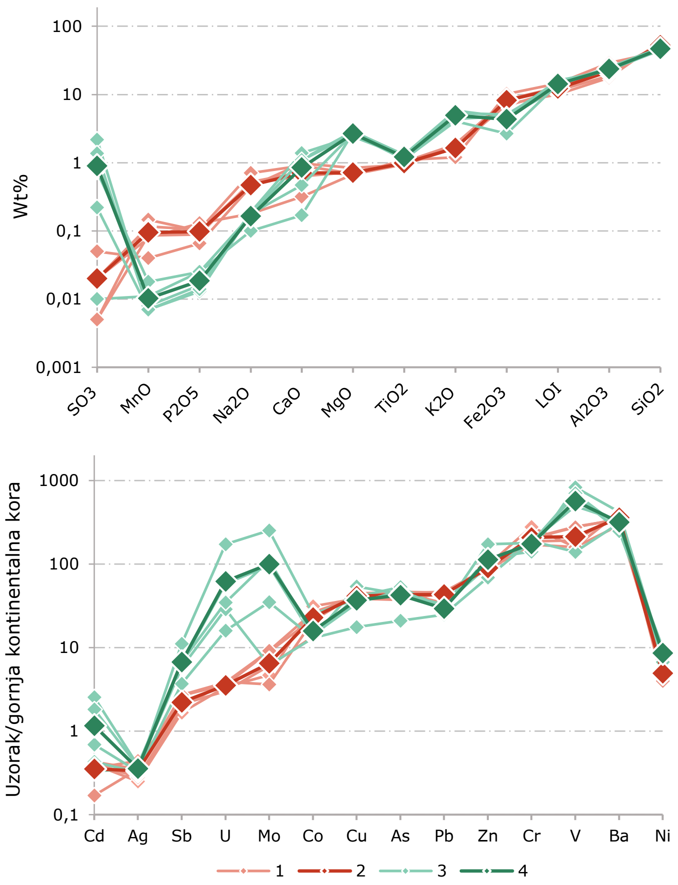
Figure 3. *Cretaceous palaeosols on the outcrop*

Methodology

- Five samples collected from both Cretaceous palaeosols and Terra rossa
- X-ray diffraction (XRD) on bulk and <2-µm samples
- X-ray diffraction and clay mineral analysis on oriented <2-µm samples
- Amount of major oxides, trace and rare earth elements was determined using XRF and ICP-MS
- Tessier seuquential extraction was used to determine the amount of certain trace elements in:
  - The exchangeable fraction (I)
  - The acid soluble fraction (II)
  - The reducible fraction (III)
  - The oxidizable fraction (IV)
  - The residual fraction (V)
- After each extraction step Ba, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, V, and Zn were determined using ICP-OES
- REEs were determined after each extraction step using ICP-MS
- REE values were normalized to the upper continental crust values (Taylor and McLennan, 1985)
- Yb/La ratio, Cerium and Europium anomalies were calculated for all Terra rossa and Cretaceous palaeosol samples after normalizing
- Correlation matrices for REEs were constructed

Mineralogy, major and trace elements





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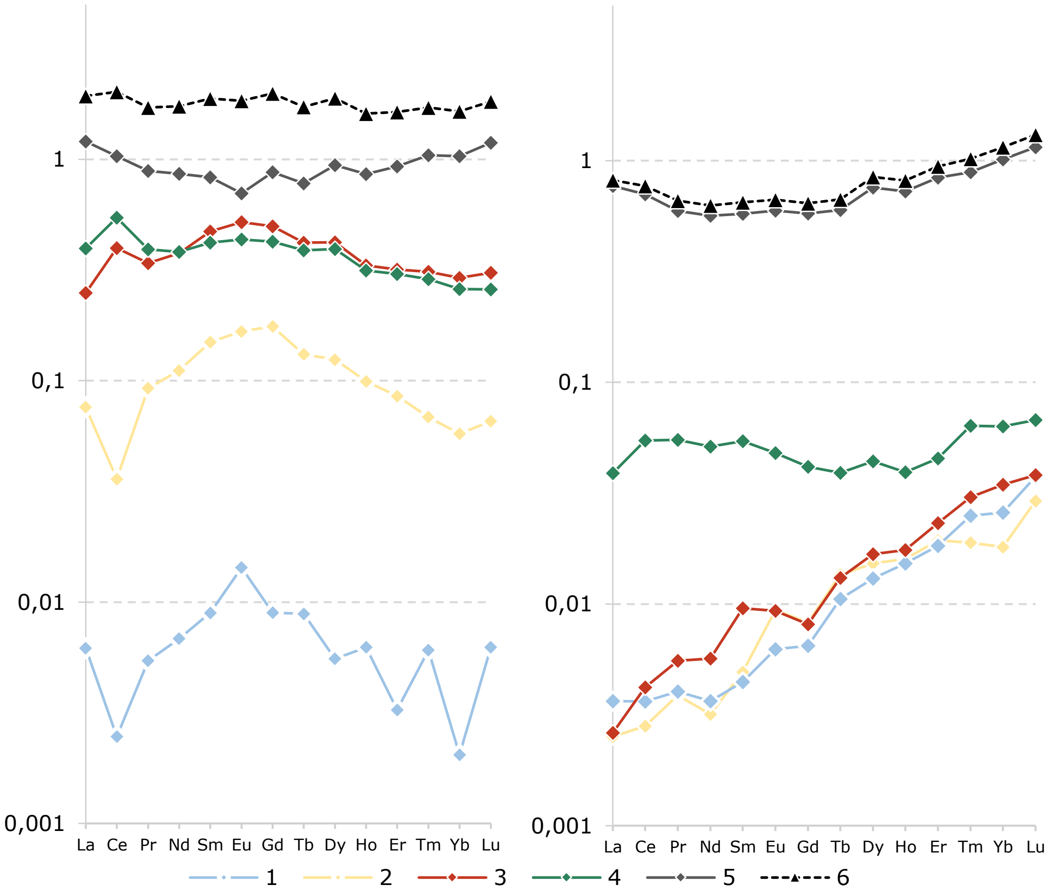

Figure 8. Spider diagram of REEs values in each extration step and bulk sample from Terra rossa and Cretaceous palaeosols; 1 – exchangeable, 2 – acid-soluble, 3 – reducible, 4 – oxidizable and 5 – residual fraction, 6 – Bulk sample

Rare earth elements

- Terra rossa:
  - Average amount of REE is 280mg/kg
  - 2.5 times more total REE content than in Cretaceous palaeosols
  - More REE sinks than in Cretaceous palaeosols
  - MREE enrichment in the I, II, III and IV fraction
  - Ce anomalies

- Cretaceous palaeosols:
  - Average amount of REE is 110mg/kg
  - Residual fraction is the main REE sink
  - HREE enrichment in the I, II , III and V fraction
  - LREE enrichment in the IV fraction

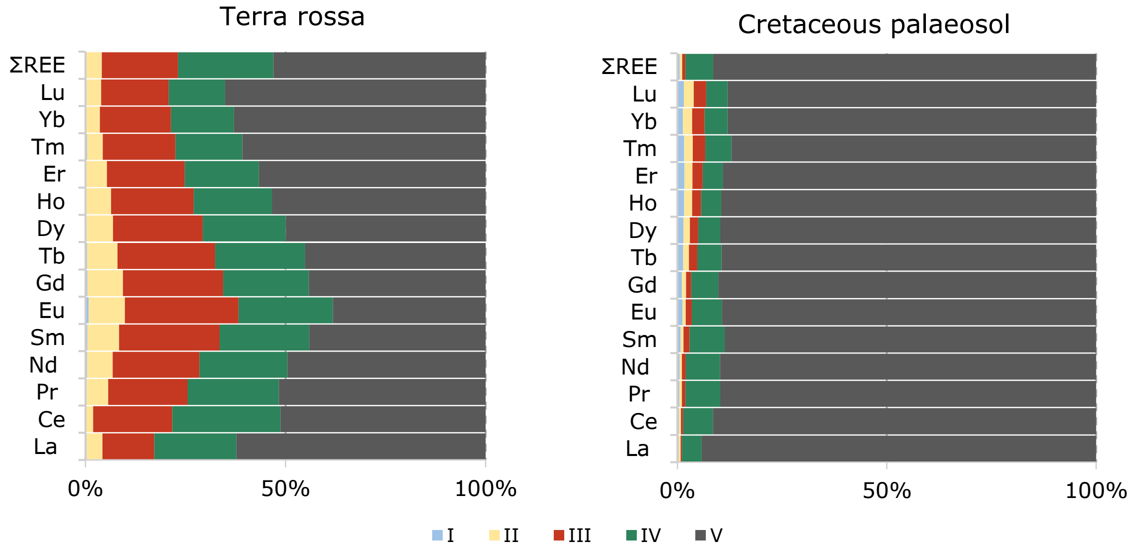

Figure 7. sequential extraction values for REEs in Terra rossa and Cretaceous palaeosols; I – exchangeable, II – acid-soluble, III – reducible, IV – oxidizable and V – residual fraction

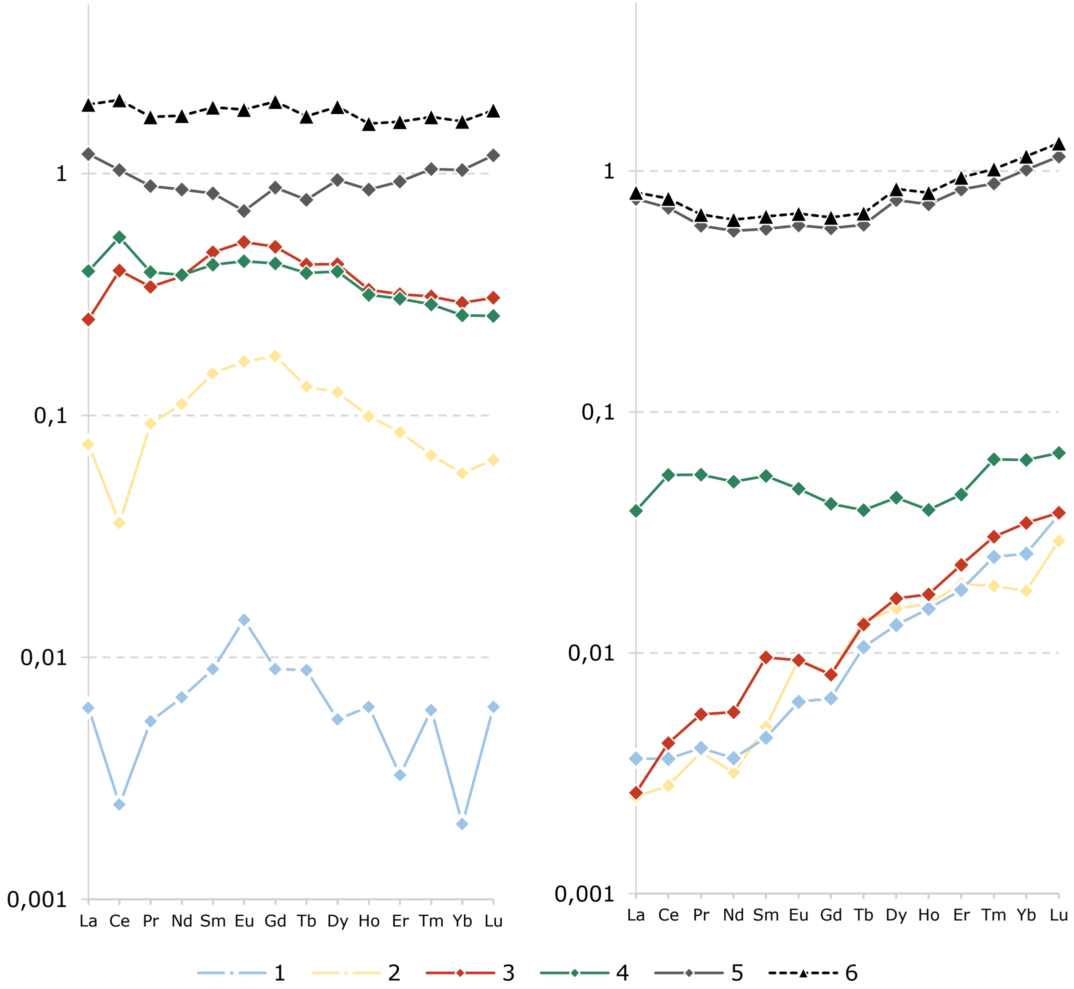

Figure 8. Spider diagram of REEs values in each extration step and bulk sample from Terra rossa and Cretaceous palaeosols; 1 – exchangeable, 2 – acid-soluble, 3 – reducible, 4 – oxidizable and 5 – residual fraction, 6 – Bulk sample

Rare earth elements

__Table 1.__ Cerium and Europium anomalies in each sequential extraction step and bulk sample; ; I – exchangeable, II – acid-soluble, III – reducible, IV – oxidizable and V – residual fraction

		CP1	CP2	CP3	CP4	CP5	TR1	TR2	TR3	TR4	TR5
Residual fraction	Eu*	1.11	1.22	0.89	1	0.94	1.06	0.85	0.85	0.78	0.79
	Ce*	1.2	1.07	1.25	1.08	1.09	1.27	1.19	1.07	1.1	1.04

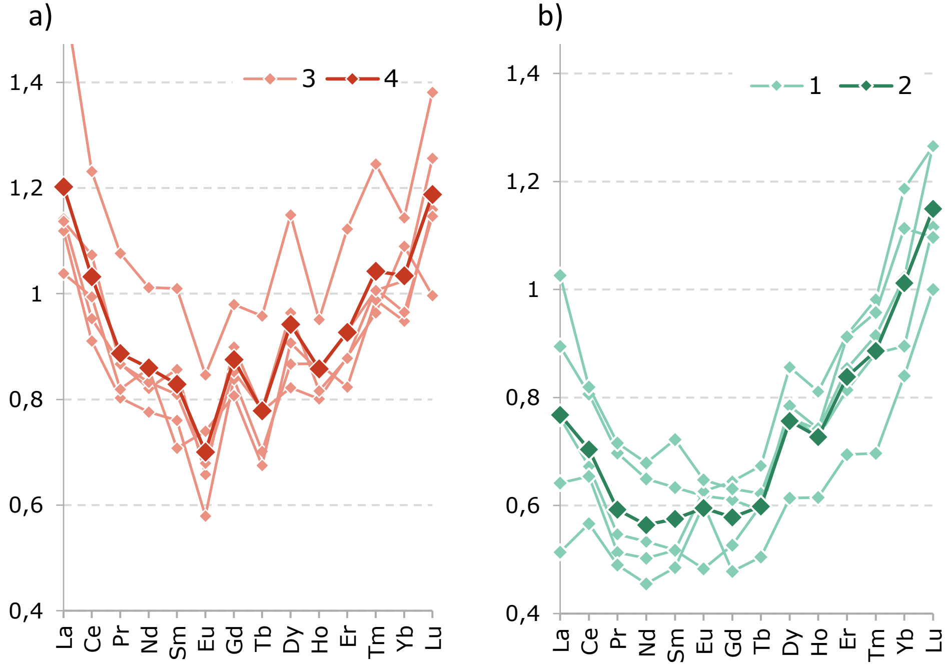

__Figure 9.__ a) Residual fraction of Terra rossa, b) residual fraction of Cretaceous palaeosols; 1 – Terra rossa samples, 2 – mean Terra rossa values, 3 – Cretaceous palaeosol samples, 4 – mean Cretaceous palaeosol values

- Positive Cerium anomalies in residual fraction from both Terra rossa and Cretaceous palaeosols
- Positive Cerium anomaly – achieved in oxidizing pedoenvironment through oxidation on manganese oxides (Braun et al., 1998; Coelho and Vidal-Torrado, 2000; Ohta and Kawabe, 2001)

- Differences in the correlation of REEs
- LREE elements negatively correlated with Yb/La ratio in Cretaceous palaeosols – suggests they were leached

- (LREE/HREE)ucc values lowest in Cretaceous palaeosol samples with Sr/Ba higher than 0.2
- Sediments with Sr/Ba higher than 0.2 formed in marine to brackish environments (Wei & Algeo, 2020)
- HREEs are more easily adsorbed and retained in clays than LREE in high ionic strength solutions (Cheng et al., 2012; Hao et al., 2019)

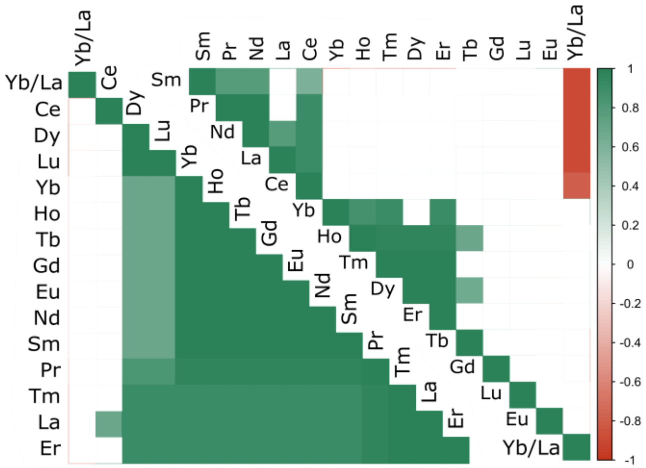

__Figure 10.__ Correlation matrices of REEs and Yb/La for Terra rossa (lower correlation matrix) and Cretaceous palaeosols (upper correlation matrix

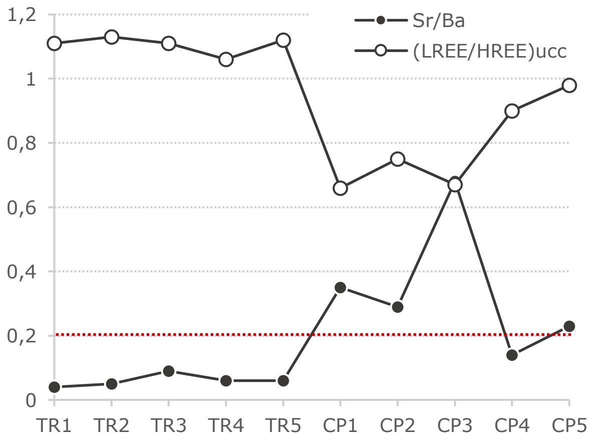

__Figure 11.__ Values of Sr/Ba and (LREE/HREE)$_{ucc}$

Conclusions

- Visible differences in trace and rare earth elements behaviour between Terra rossa and Cretaceous palaeosols

- Terra rossa enriched Mn and Fe – **presence of ferromanganese oxides**
- Cretaceous palaesols are enriched in Sb, Cd, V and especially U and Mo - **euxinic conditions**

- Terra rossa enriched in REEs compared to Cretaceous palaeosols
- LREEs and MREEs leached in Cretaceous palaeosols during redox/water table fluctuations – **dissolution of ferromanganese oxides**
- HREEs enriched in Cretaceous palaeosols – **marine to brackish pore waters**
- Terra rossa enriched in MREEs in the reducible and oxidizable fractions – **presence of ferromanganese oxides and organic matter**
- Positive Cerium anomalies in residual fraction in both materials – **present or past presence of ferromanganese oxides**
- Terra rossa has almost twice as much REEs as Cretaceous palaeosols – **this difference is entirely pedogenetic**

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Chemosphere 283 (2021) 131286

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Differences in the behaviour of trace and rare-earth elements in oxidizing and reducing soil environments: Case study of Terra Rossa soils and Cretaceous palaeosols from the Istrian peninsula, Croatia

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A R T I C L E I N F O

Handling Editor: Lena Q. Ma

Keywords:
Redox conditions in karst soils
REE/Trace elements characteristics
Terra rossa
Wetland palaeosols
Istrian peninsula

A B S T R A C T

This study compares the differences between the distribution of trace elements and rare-earth elements (REEs) formed under reducing and oxidizing soil conditions during pedogenesis on carbonate bedrock. Terra rossa (TR) soils, representing pedogenesis under oxic conditions, and Cretaceous palaeosols (CP), representing pedogenesis under reducing conditions, were sampled on the Istrian peninsula. They were studied by ICP-MS, ICP-OES, XRF, XRD, sequential extraction and statistical analyses. The differences in trace-element behaviour between the TR and CP stem from different redox conditions, but the most remarkable difference was observed in the behaviour of the REEs. Statistical analyses revealed that in TR soils all the REEs showed a very positive correlation, while in CPs the light REEs and heavy REEs showed an internal, very positive correlation. TR soils have almost twice as much REEs as CPs. This difference is pedogenetic, as both materials have a very similar amount of REEs in the residual fraction. While TR soils have the same amount of REEs in fractions other than the residual fraction, CPs have almost no REEs in these fractions. Different REE patterns obtained from sequential extraction, such as a middle-REE enrichment and a positive Ce anomaly in TR soils and light-REE depletion, heavy-REE enrichment, positive Ce and Eu anomalies in CPs, contributed to an understanding of the redox and pedogenetic processes. This study successfully emphasized the influence of different redox conditions on the behaviour of trace and rare-earth elements during pedogenesis on a carbonate bedrock and the ability of the REEs to track pedogenetic processes.

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