# Weathering processes and formation of red polygenetic soils and paleosols on hard carbonate rocks: a multi-proxy approach (Northern Adriatic, Croatia)

**Goran Durn**

University of Zagreb, Croatia

WIANLab

Hrvatska zaklada za znanost

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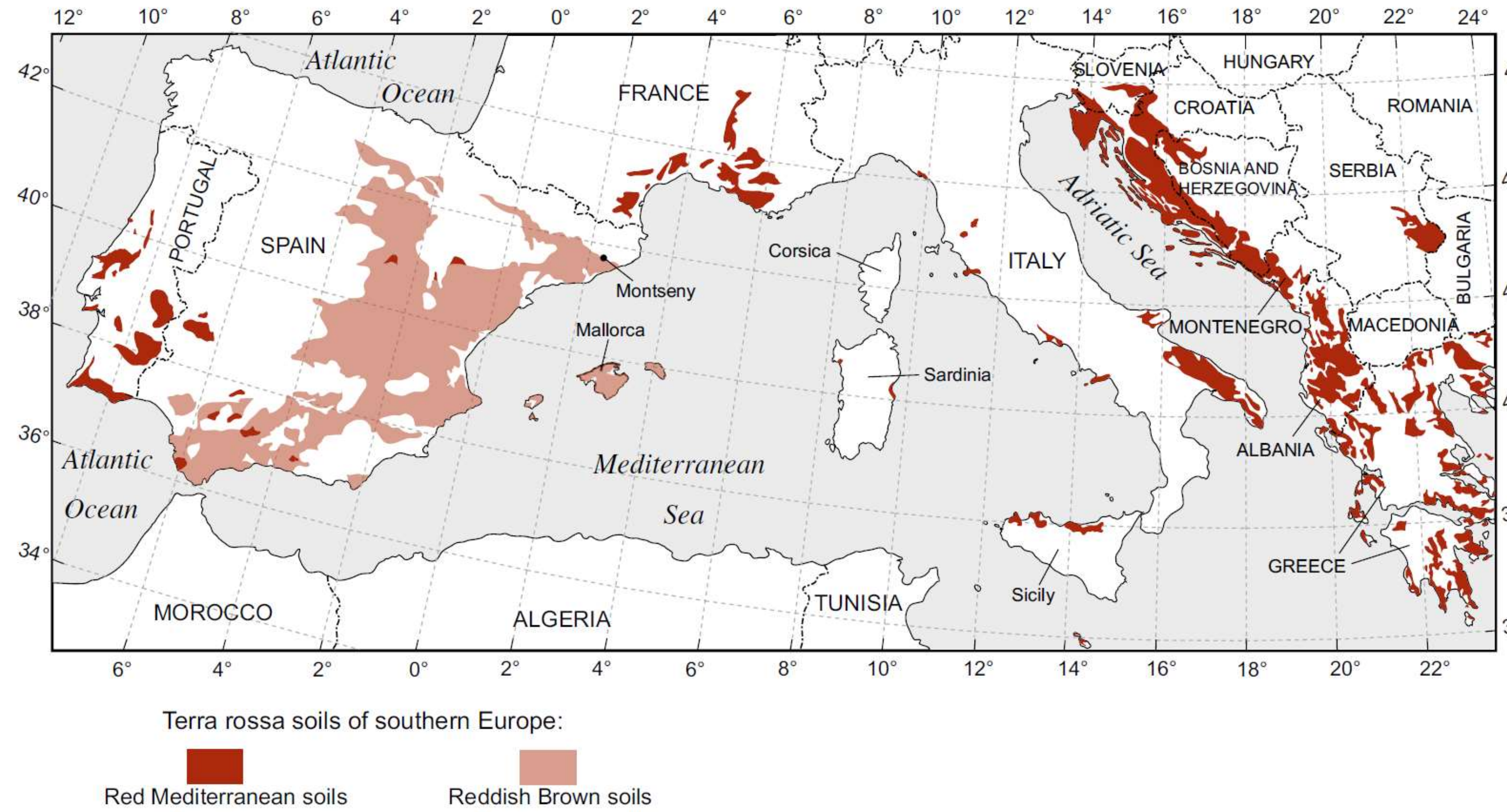
# Map of southern Europe showing the distribution of Red Mediterranean and Reddish Brown soils (from Muhs et al. 2010)



- Red Mediterranean soils and Reddish Brown soils occur in many Mediterrannean countries especially along continental shores and islands.
- When situated on hard carbonate substrates (limestone and dolomite) this soils are called ”terra rossa”.
- They have sharp contacts with the underlying limestone or dolomite and often fill solution cavities within the carbonate bedrock. They have highly variable thicknesses, depending on landscape position, with thicker soils typically found in low-lying portions of the landscape.

- Terra rossa is a generic term that refers to a soil formed in a Mediterranean climate, has a red color, is well structured, has a high content of Fe - oxides strongly associated with clay minerals (major soil-forming processes are rubefaction and illuviation).
- In the WRB classification system, terra rossa soils can be classified as Cambisols, Luvisols, Nitisols and Leptosols.
- Since they fall under a number of new soil taxa, soil classification systems have eliminated terra rossa soils as a distinct unit.
- The term is commonly used by pedologists, geologists, archeologists, geomorphologists, and sedimentologists in the Mediterranean region and in areas with continuosly humid climates in the Western Hemisphere (e.g., southern Australia, Caribbean, Indiana, Wisconsin).

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# Formation, dispersion and accumulation of terra rossa on the Cayman Islands

BRIAN JONES
*Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, Alberta, T6G 2E3, Canada (E-mail: brian.jones@ualberta.ca)*

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## ABSTRACT

Unconsolidated and lithified terra rossa fills surface depressions, joints, fractures and cavities throughout the karst landscapes on the Cayman Islands. The terra rossa is formed from kaolinite, halloysite, vermiculite, hydrotalcite, böhmite, gibbsite, goethite, hematite, anatase, quartz, calcite, dolomite, halite and X-ray amorphous material. Locally, phosphate derived from bird guano and biofragments is present. Lithified terra rossa is characterized by numerous generations of fractures that are lined with clay and filled with multiple phases of calcite cement. There are no obvious geographic or stratigraphic differences between the terra rossa found on the three islands. A residual origin for the terra rossa is unlikely given that the Oligocene to Pleistocene limestone/dolostone bedrock contains <1% non-carbonate material. Detrital sediments cannot be the source because none developed on these islands, given that they are surrounded by deep oceanic waters. The terra rossa probably originated largely from wind-blown volcanic dust or Saharan dust. Various geochemical ratios and rare earth element profiles indicate that that the Cayman terra rossa has a strong affinity to Saharan dust that is frequently blown into the Caribbean region each year. The Cayman terra rossa is characterized by $SiO_2/Al_2O_3$ ratios (<1.1) that are significantly lower than those associated with terra rossa on other islands, such as Jamaica and Barbados. The low $SiO_2/Al_2O_3$ ratios of the Cayman terra rossa is due, at least in part, to the fact that quartz is rare to absent. X-ray amorphous material is a common component in many of the Cayman samples. Although difficult to date precisely, the formation of terra rossa on the Cayman Islands appears to have been an ongoing process for at least the last 5 Myr. This time frame is consistent with the origin of the Sahara Desert that came into existence with aridification of North Africa about 5 Ma.

**Keywords** Cayman Islands, rare earth elements, stable isotopes, terra rossa.

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# Soil-sediment-configurations on slopes of Central and Western Crete (Greece) and their implications for late Holocene morphodynamics and pedogenesis – A conceptual approach

Fabian Kirsten [a,*], Jürgen Heinrich [b]

[a] Freie Universität Berlin, Department of Earth Sciences, Physical Geography, Malteserstraße 74-100, Haus H, 12249 Berlin, Germany
[b] Universität Leipzig, Institute for Geography, Johannisallee 19a, 04103 Leipzig, Germany

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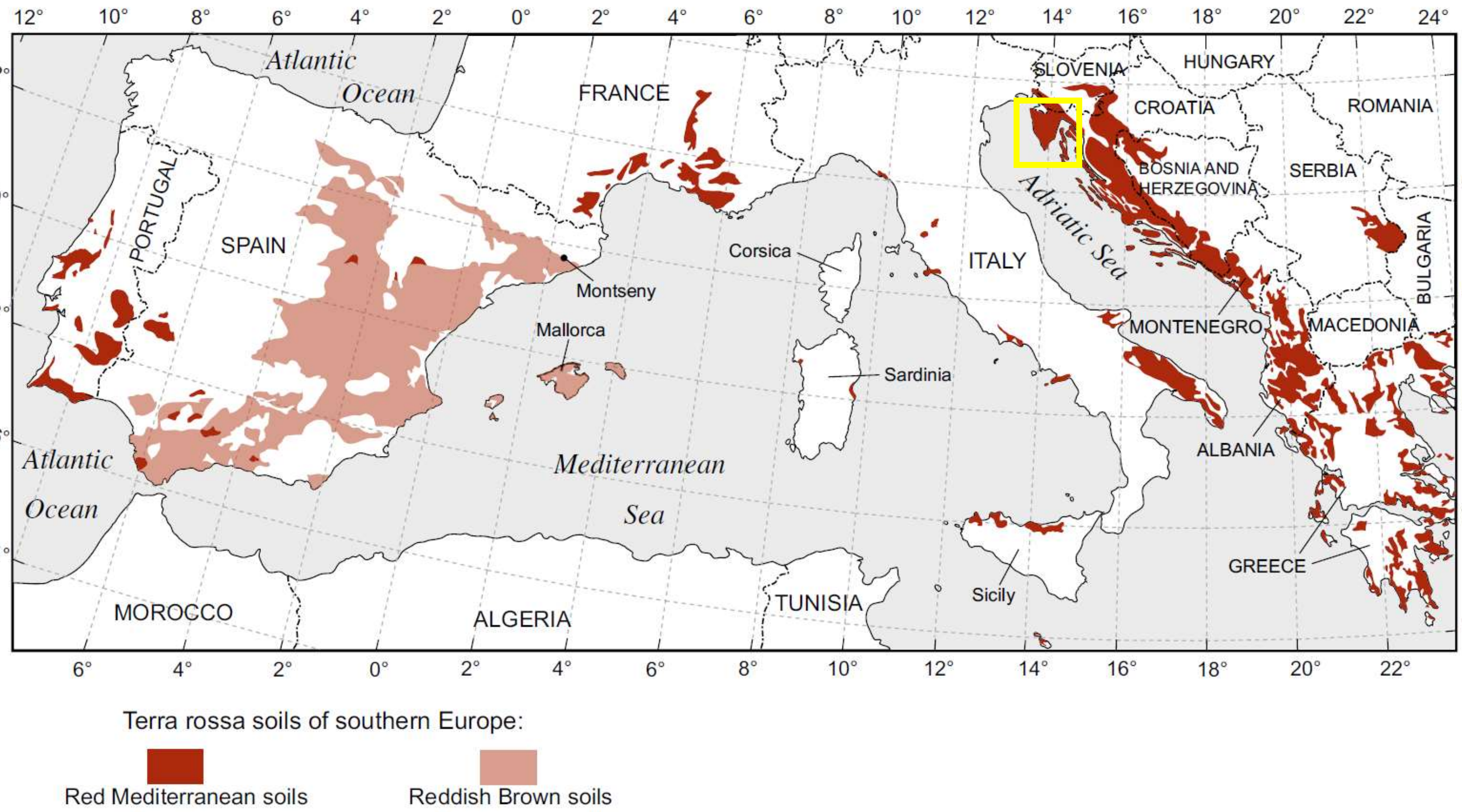
ABSTRACT

Geomorphological processes and soil formation in slope positions within the Mediterranean area have been in the focus of research for a long time. Many of the surface-near soil-sediment-configurations in the Mediterranean area have been termed soils and have been interpreted as typical (zonal) Mediterranean reddish-brown soils (RMS) of Terra Rossa type associated with clay illuviation as main pedological process. However, there has been an extensive scientific debate which (late) Holocene geomorphological and pedological processes in fact dominate current soil-sediment-configurations, especially before the background of a long-lasting history of intense human land use impacts.

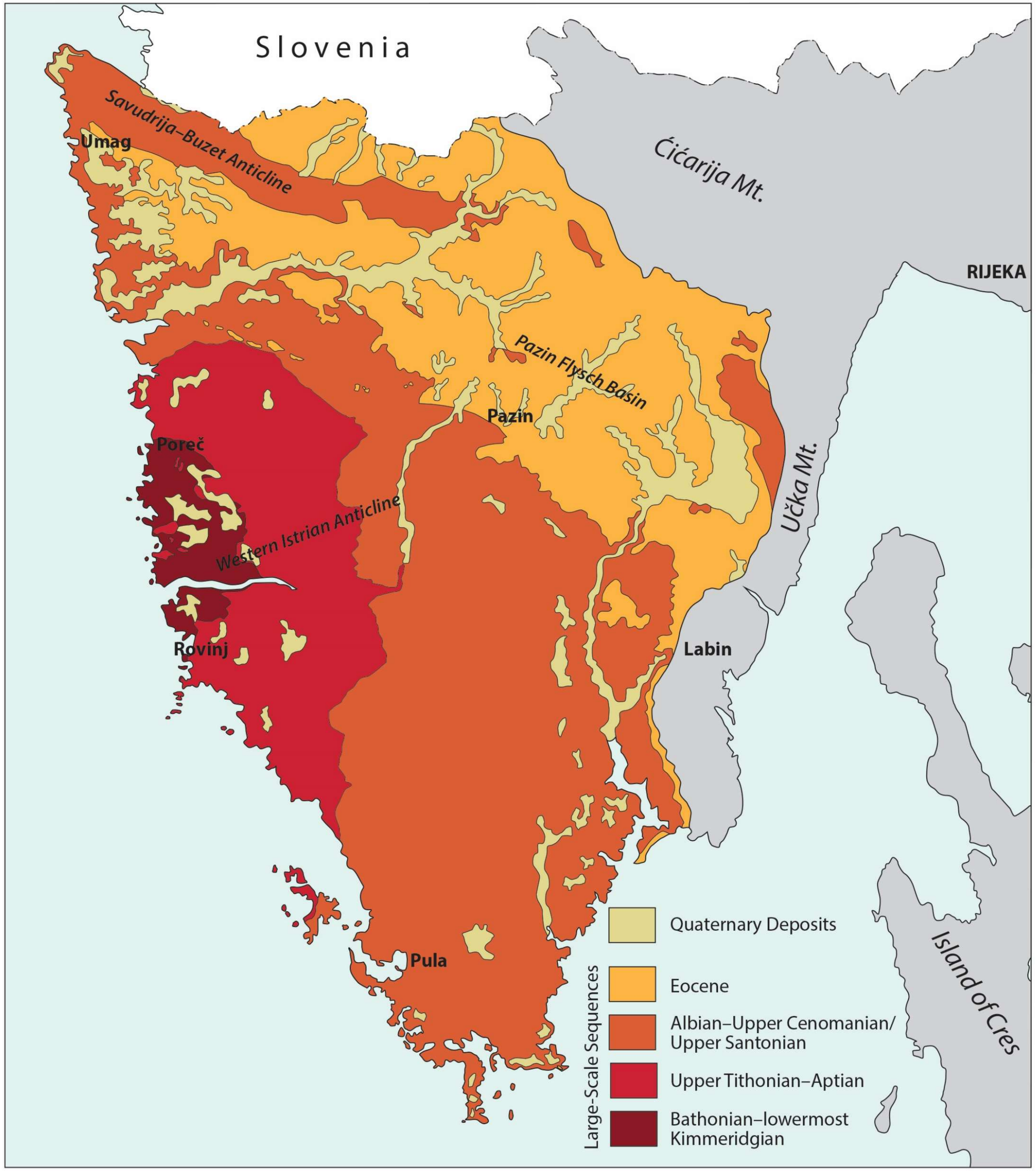
In the present study, we present field evidence as well as analytical data for a number of representative soil-sediment-profiles located in a variety of geological, geomorphological and climatic settings in central and western Crete (Greece). We have grouped the profiles in three schematic geomorphological categories in order to provide a geomorphological instead of a pedological context for their interpretation and comparison. Based on geochemical, mineralogical, geophysical and micromorphological evidence we could show that in most of the studied profiles, (late) Holocene pedogenesis is comparatively weak, except for bioturbation in combination with surprisingly high TOC-contents. Discontinuities within profiles are the result of geomorphological processes and the corresponding deposition of clearly distinguishable parent materials (substrates) rather than pedologic processes resulting in the in-situ differentiation of soil horizons. Furthermore, characteristic and ubiquitous peaks in grain size distribution within the clay and silt grain size fractions could be identified and are most likely related to long-range dust inputs. Whether the weak degree of recent pedogenesis is due to the long-lasting history of intense land use or rather due to the (naturally) high intensity of geomorphological processes and sediment relocation remains one of the main open questions raised by the results of this study.

- Terra rossa is considered by various researchers as:
  - polycyclic soil,
  - polygenetic soil,
  - relict soil,
  - paleosol,
  - vetusol,
  - semi-lithified and lithified terra rossa soil,
  - soil-sediment,
  - pedosediment,
  - pedo-sedimentary complex,
  - sediment
- Most authors agree terra rossa soil (and Red Mediterranean soils in general) formed discontinuously during the Quaternary (periods of environmental stability - interglacials).
- Many questions related to the origin and provenance of these red soil-sediments are still unresolved.

# Map of southern Europe showing the distribution of Red Mediterranean and Reddish Brown soils (from Muhs et al. 2010)

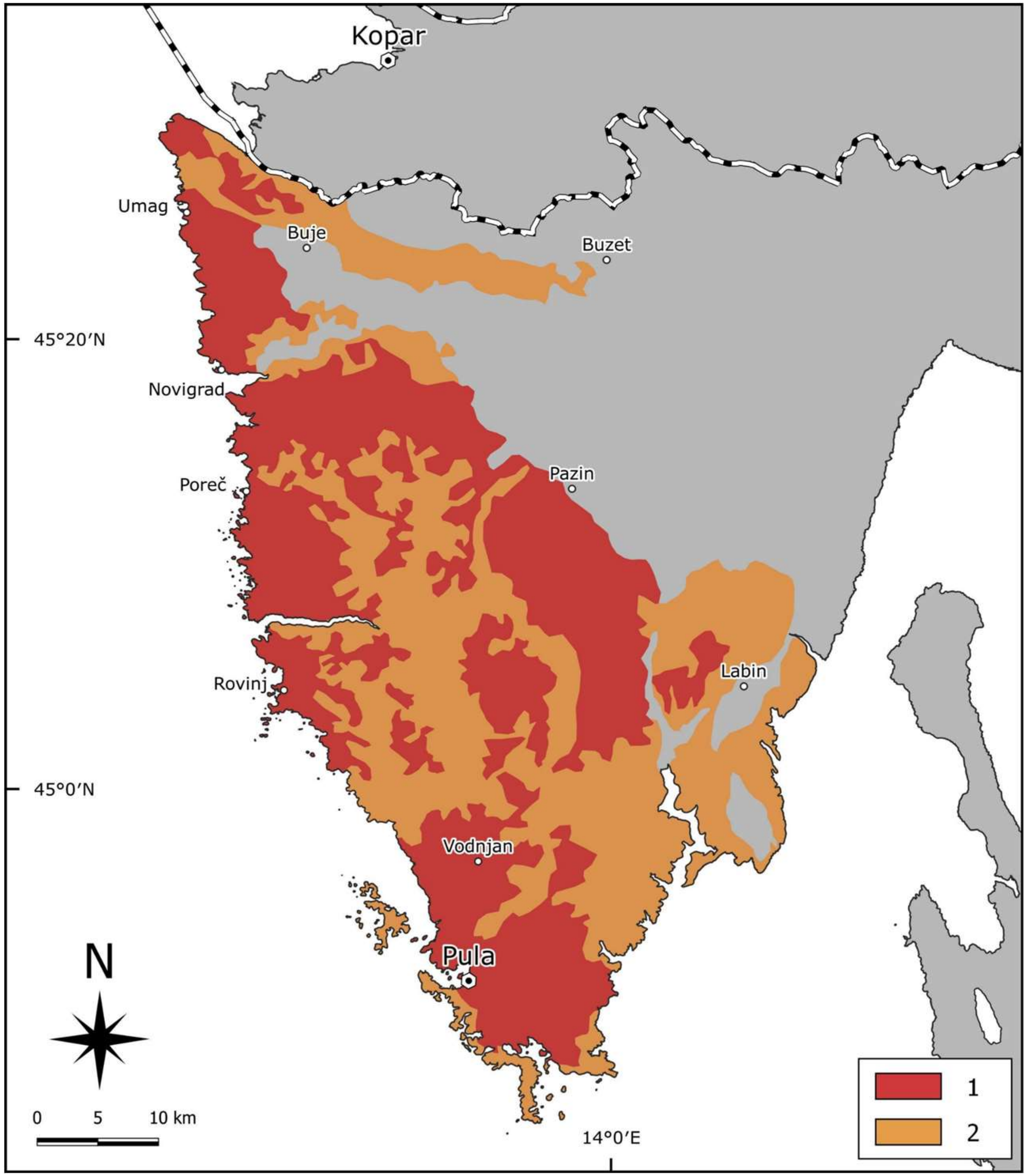


# Schematic map of the NW part of the Adriatic carbonate platform (AdCP)




- succession of carbonate deposits more than 2000 m thick
- consists of four mega-sequences separated by long-lasting emersions (subaerial unconformities)
- the succesions of the three oldest mega-sequences consist exclusively of carbonate rocks while the fourth (Eocene) mega-sequence begins with the deposition of foraminiferal limestones and ends with flysch deposition
- Upper Eocene-Recent unconformity was of a very long duration resulting in stratigraphic hiatus of approximately 35 Ma
- the final emergence of the Istrian peninsula was triggered by the collision of the Adriatic microplate with Eurasia
- terra rossa soils mark the subaerial unconformity of the fourth large-scale mega-sequence
- unconformity is also accompanied by various sediments (e.g. Upper Pleistocene loess)

# Terra rossa soils in the NW part of the AdCP (modified after FAO-UNESCO Soil Map of Croatia, Bogunović et al., 1998)




- ❖ Terra rossa soils in the NW part of the Adriatic carbonate platform are almost exclusively Chromic Luvisols (1) and Chromic Cambisols (2)

# Research questions

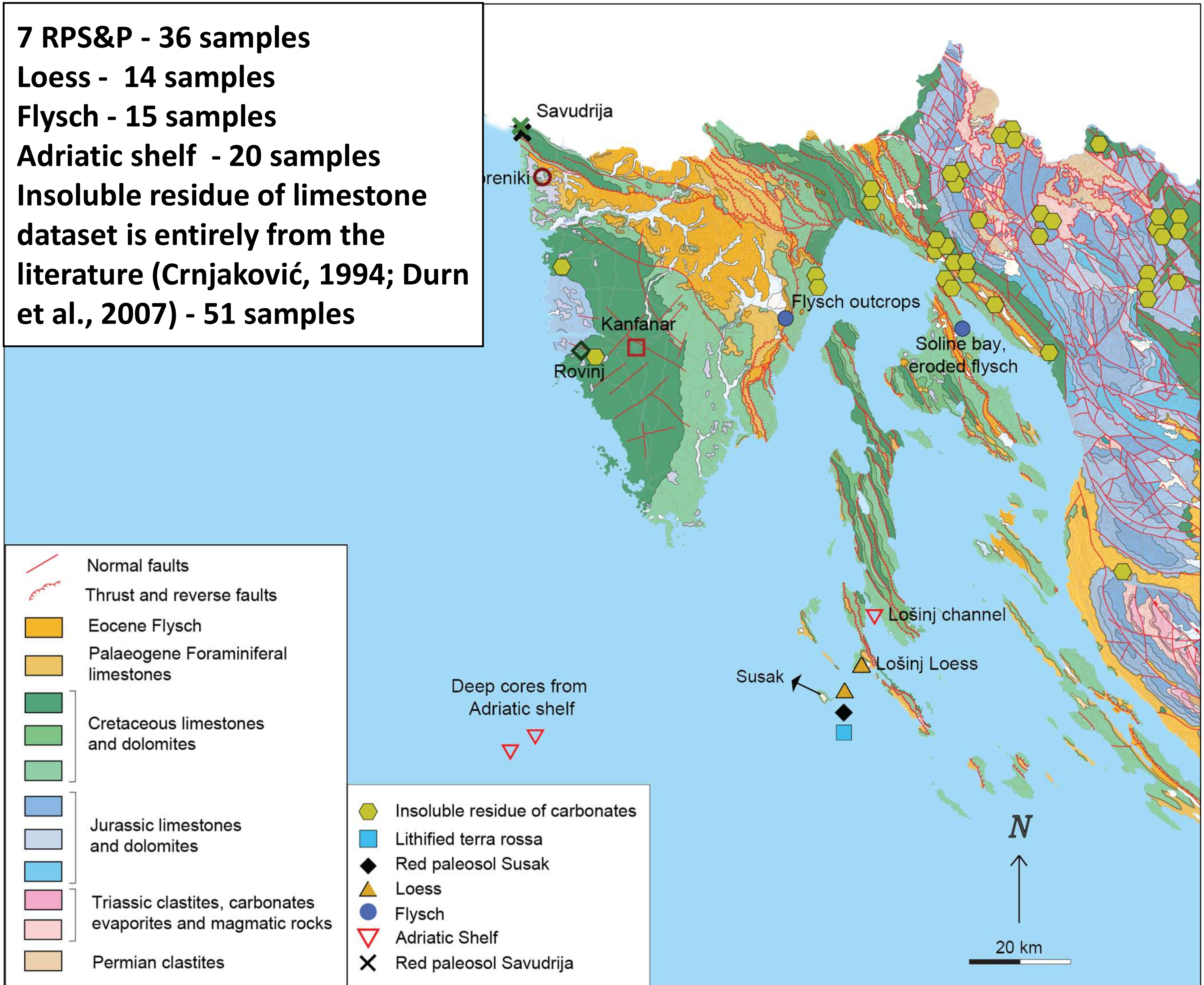
- Are terra rossa soils, polygenetic soils, paleosols, soil-sediments, pedosediments, sediments…?
- What is the provenance of parent material for terra rossa soils?
- When and how they formed?
- Why terra rossa soils are most pronounced on the eastern Adriatic coast on a global scale?

# Content

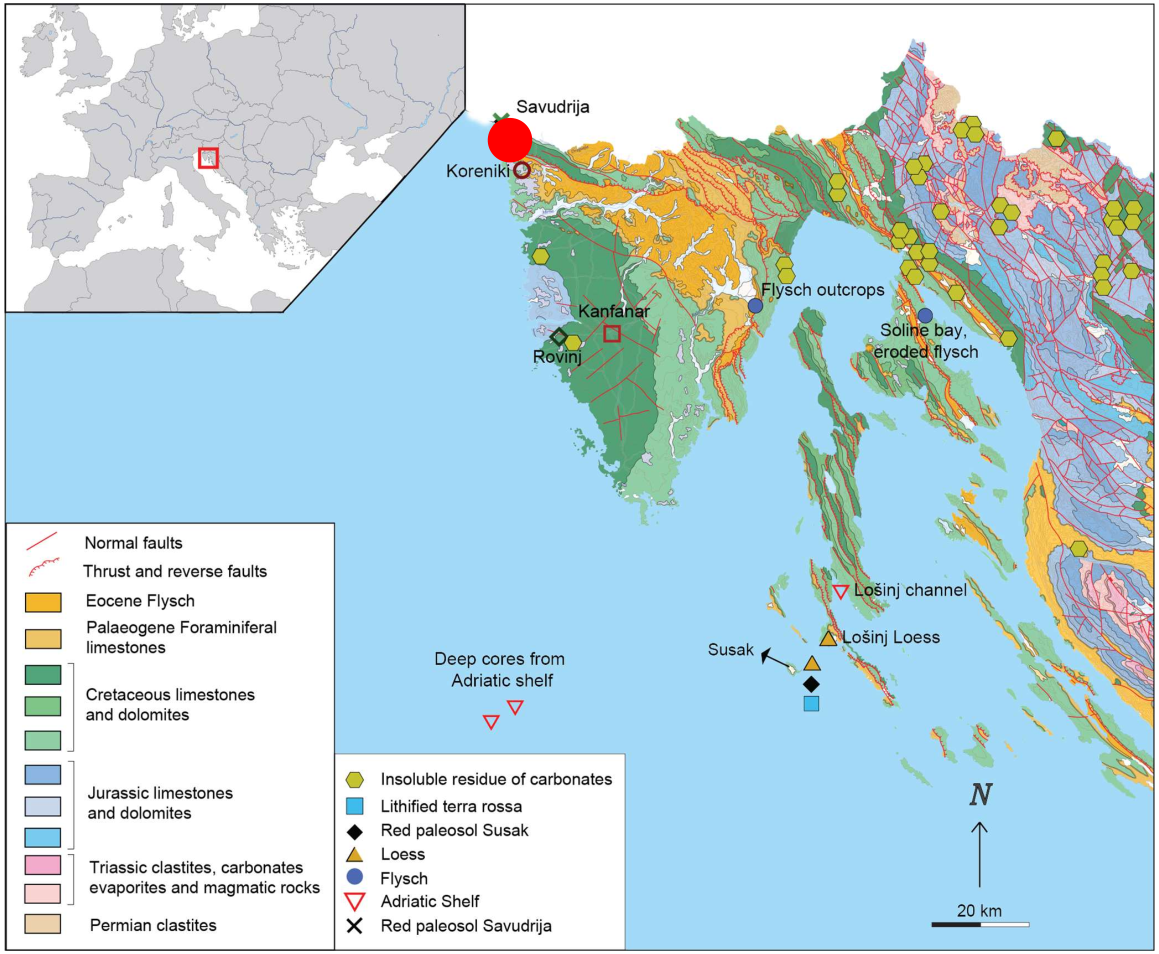
- Materials and methods
- Multy-proxy approach
- Coherent provenance analysis based on heavy mineral assemblages
- Weathering processes and formation of terra rossa soils on hard carbonate rocks
- Conclusions

# MATERIALS AND METHODS

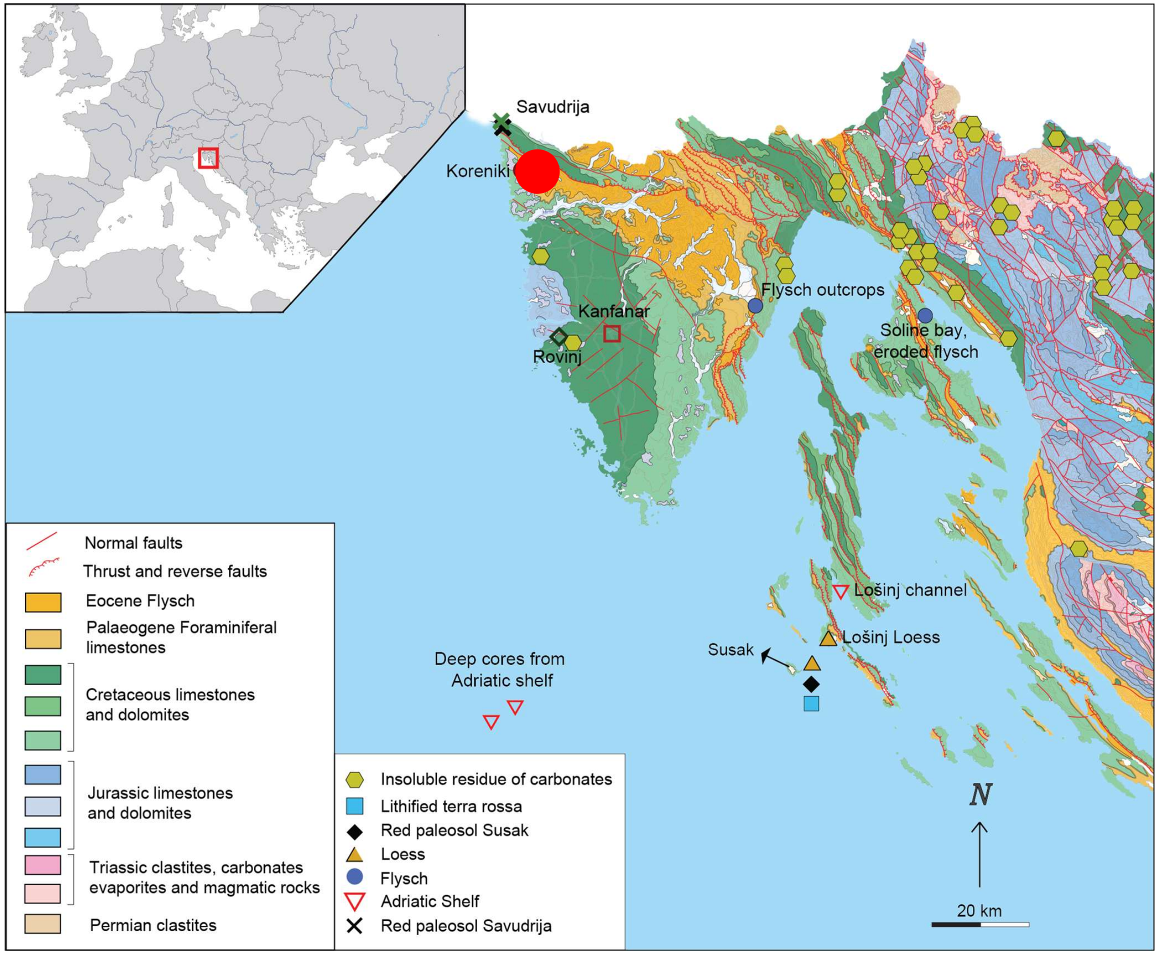
**7 RPS&P - 36 samples**
**Loess - 14 samples**
**Flysch - 15 samples**
**Adriatic shelf - 20 samples**
**Insoluble residue of limestone dataset is entirely from the literature (Crnjaković, 1994; Durn et al., 2007) - 51 samples**



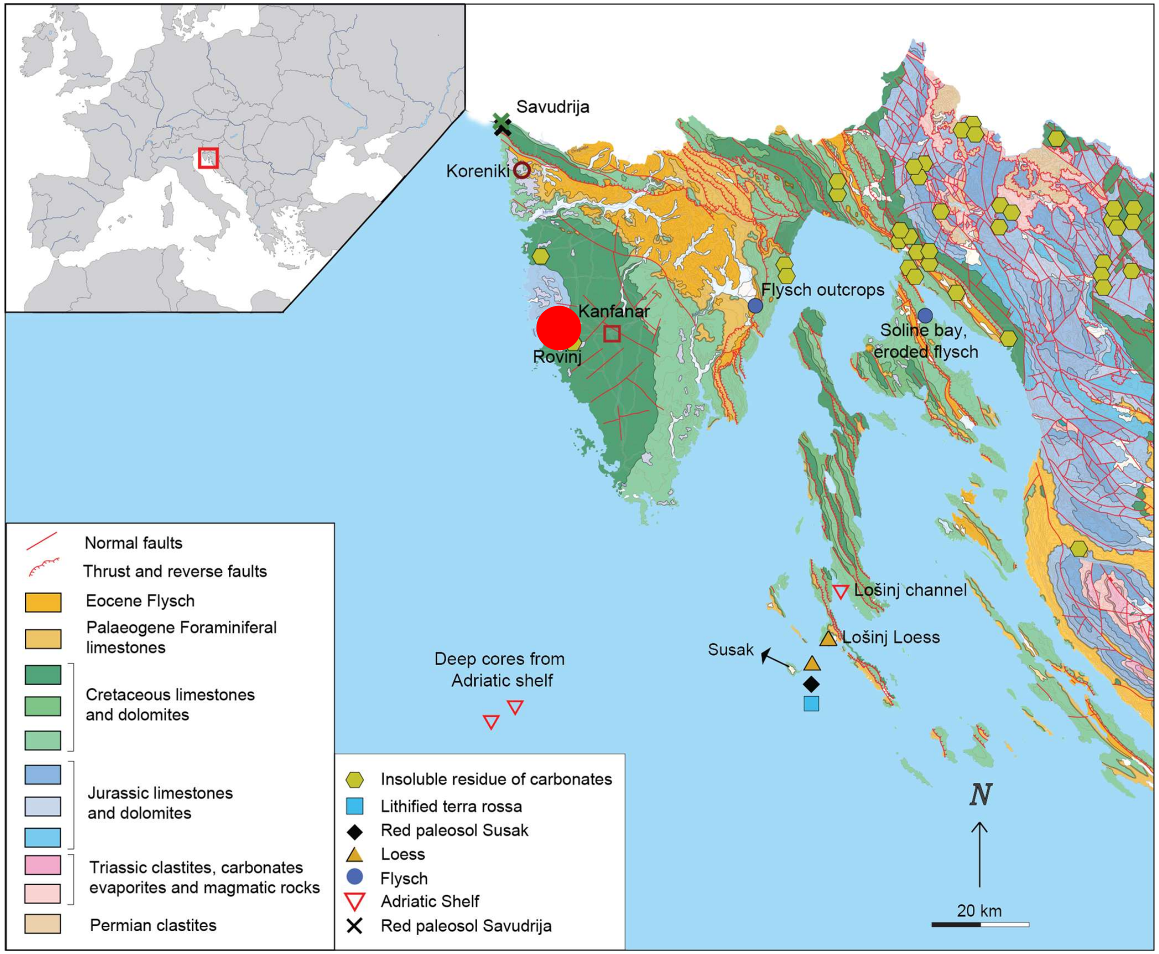
# Red paleosol Savudrija



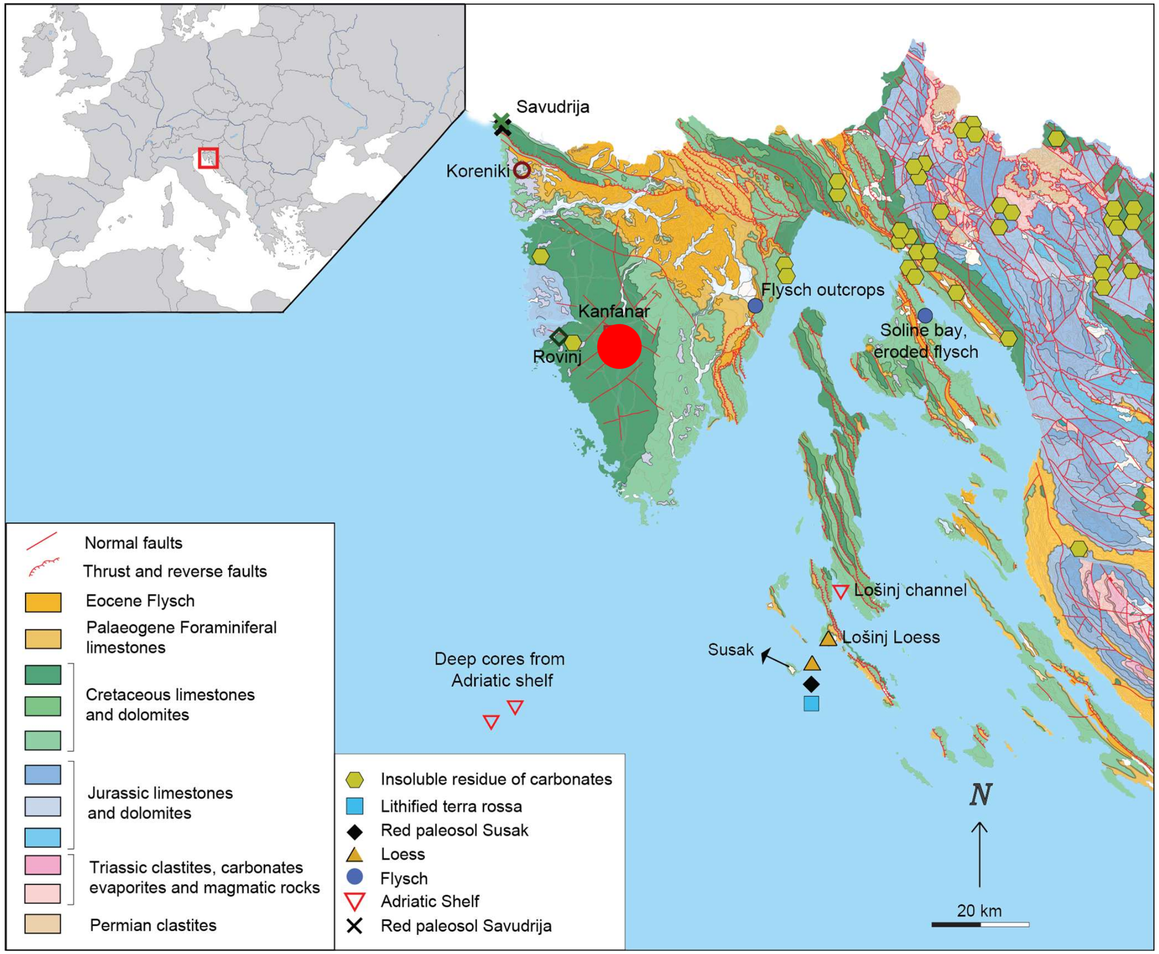

# Red polygenetic soil Koreniki



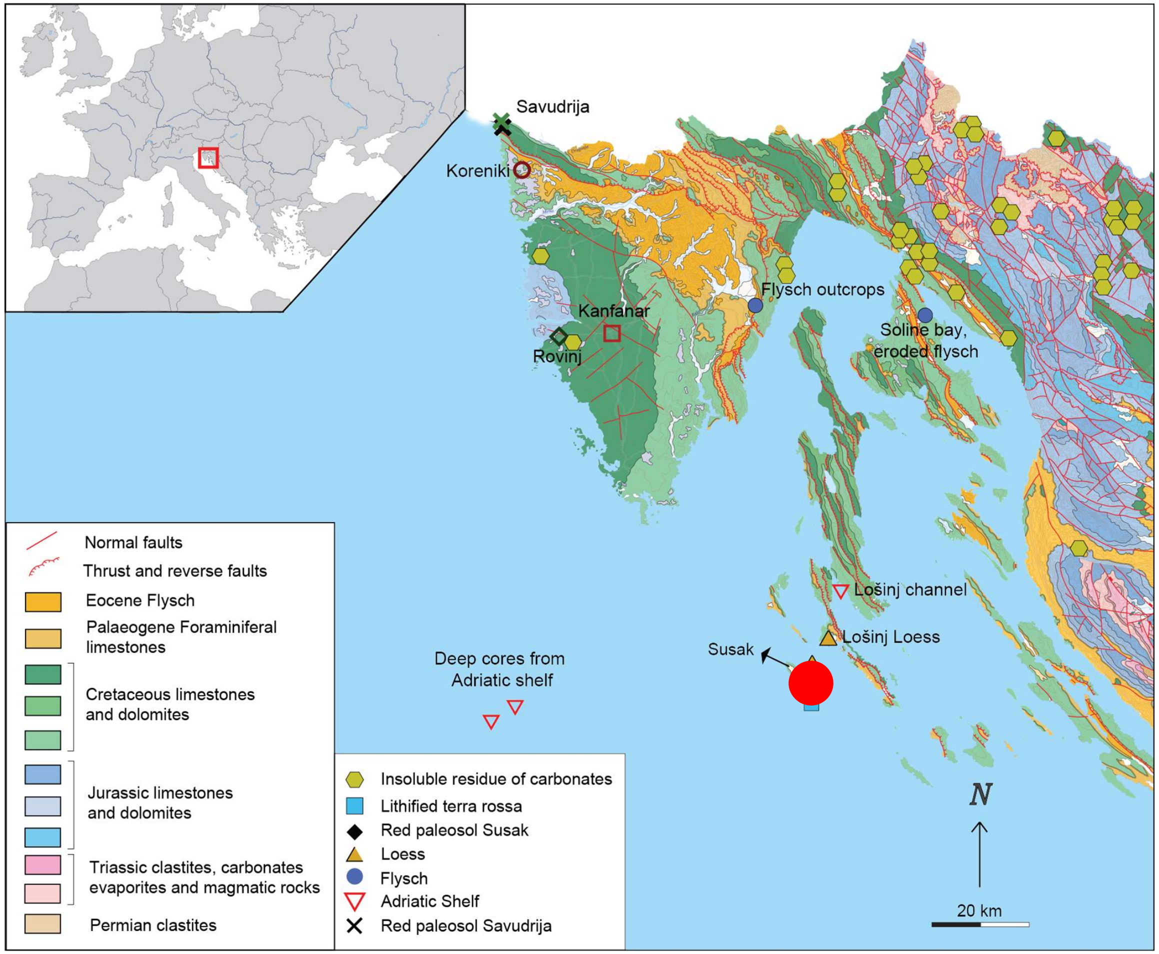

# Red polygenetic soil Rovinj



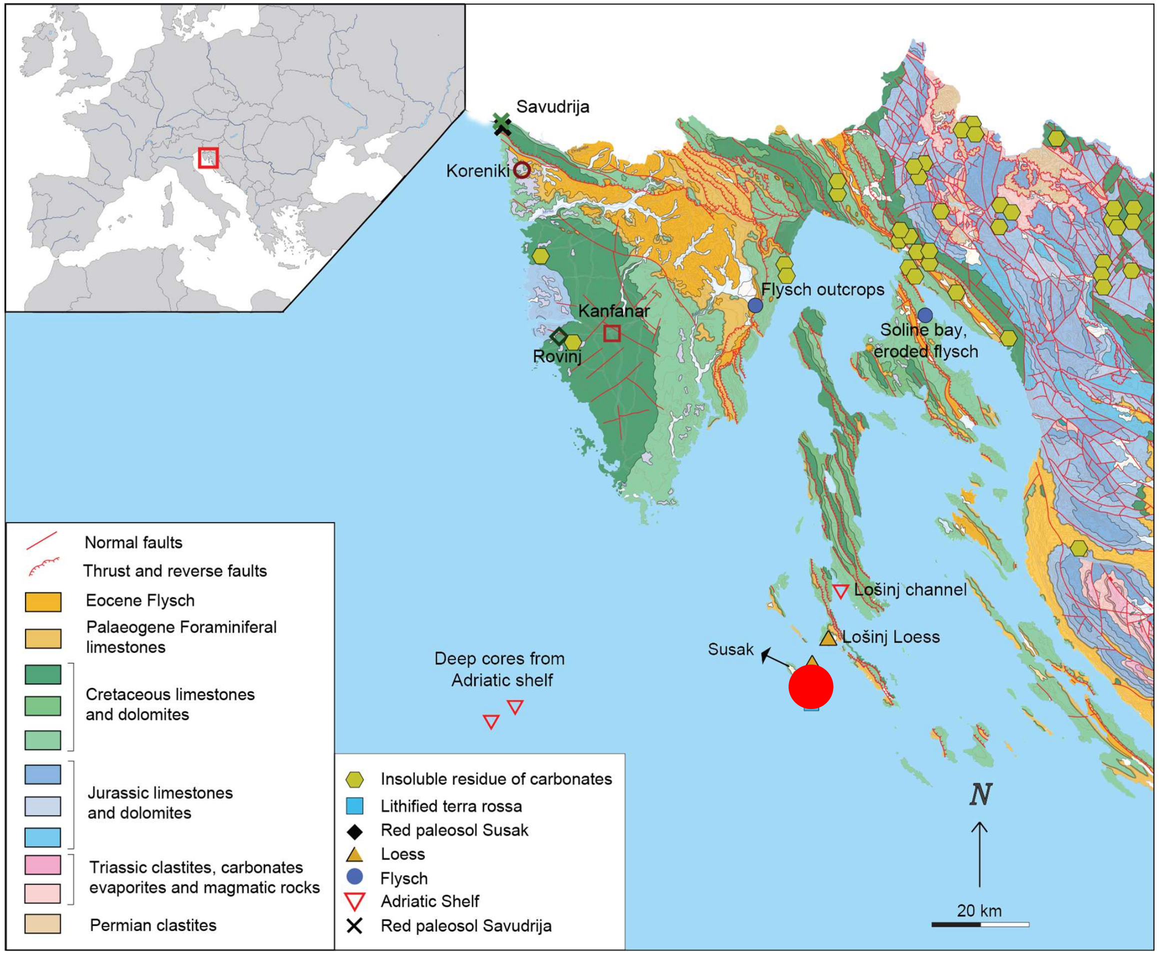

# Red polygenetic soil Kanfanar



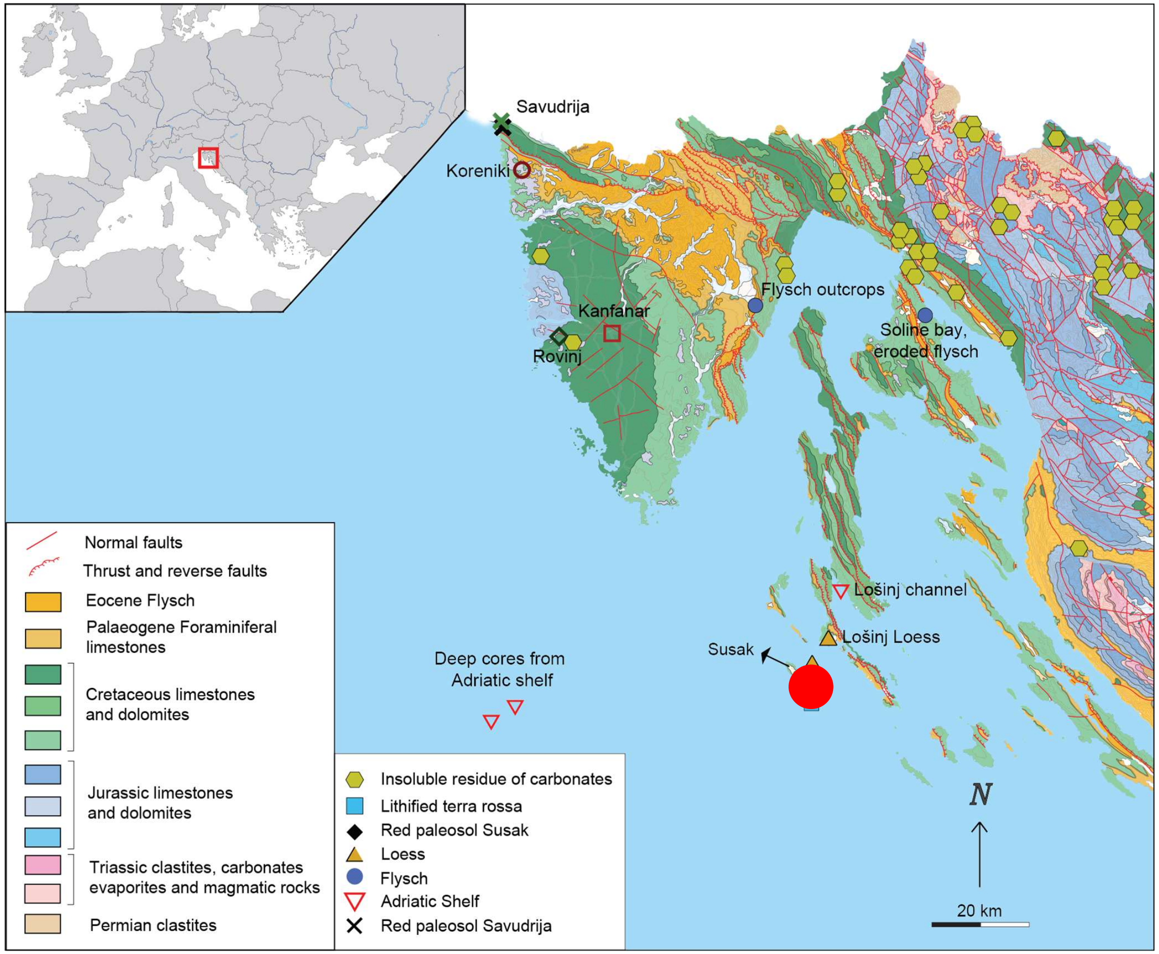

# Red paleosol Susak

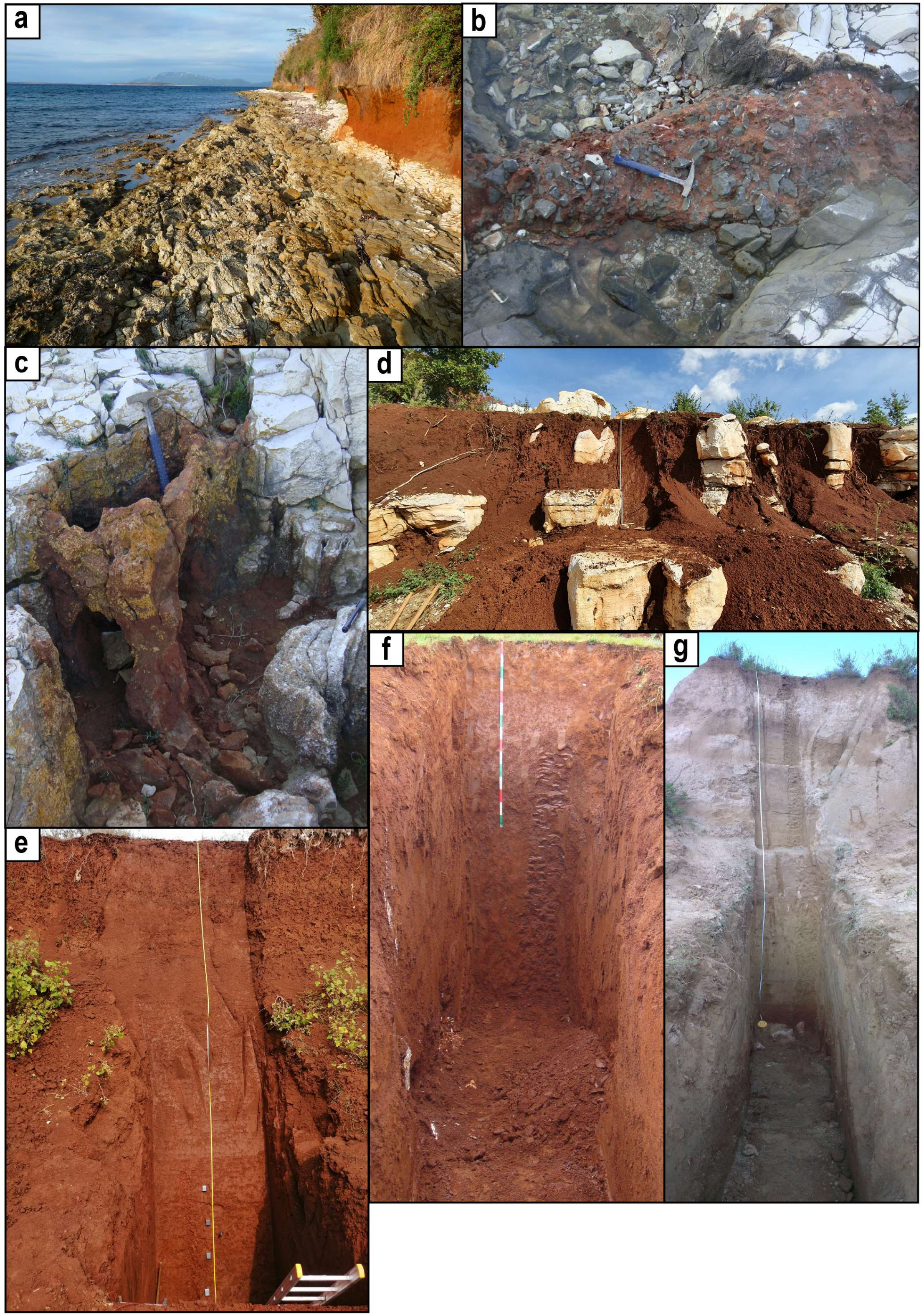



# Red lithified paleosol 1 Susak




# Red lithified paleosol 2 Susak





a
b
c
d
e
f
g

# MULTY-PROXY APPROACH

# Multy-proxy approach

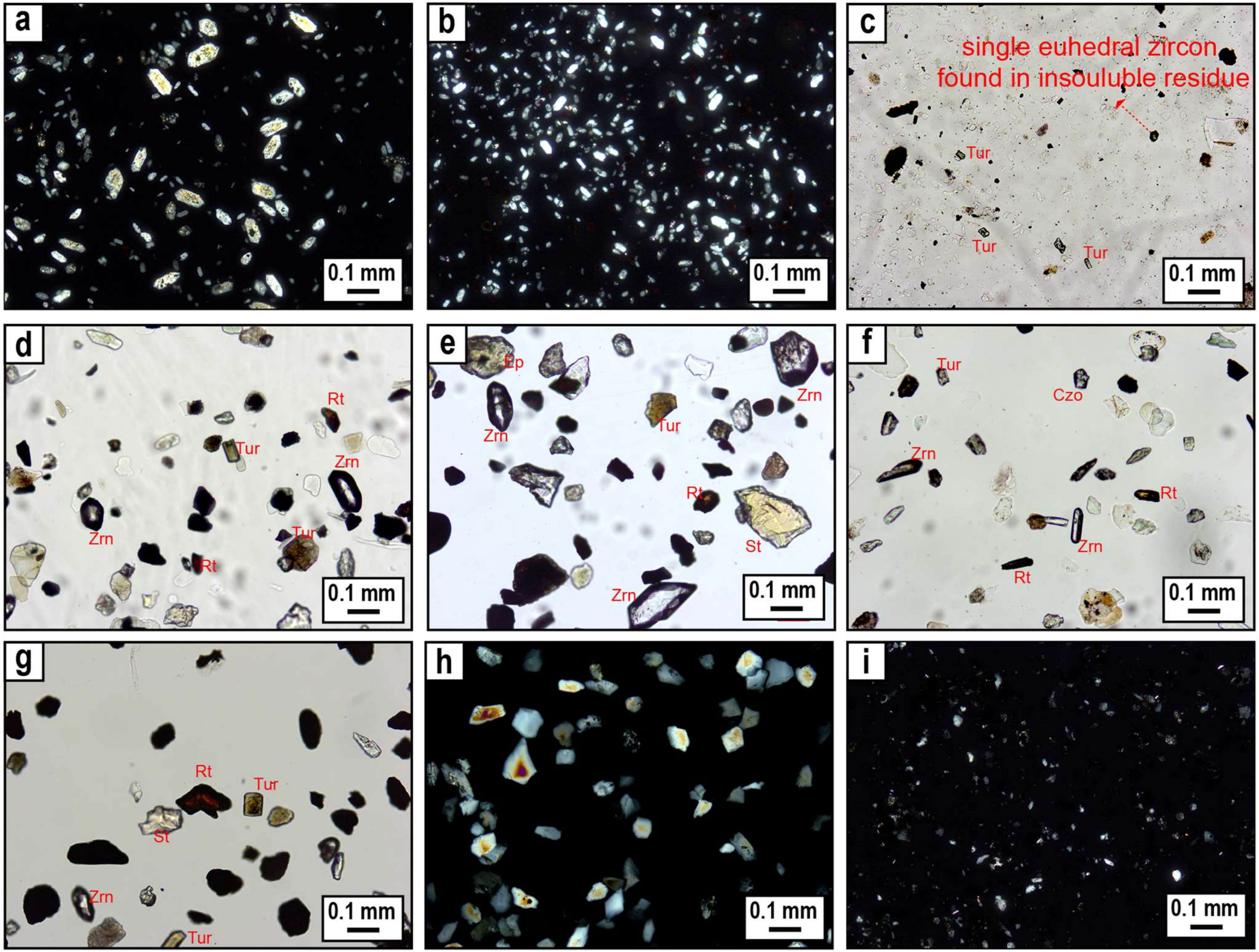
- The value of any multi-proxy study clearly rests on the reliability of the proxies used
  - heavy mineral assemblage (32-125 µm fraction)
  - $Fe_d/Fe_t$
  - Al/Si
  - inherited and pedogenic clay minerals

- Additional tools
  - light mineral assemblage (32-125 µm fraction)
  - bulk mineralogy
  - physical/chemical properties
  - micromorphology (thin sections + SEM)
  - geochemistry
  - chronological tools

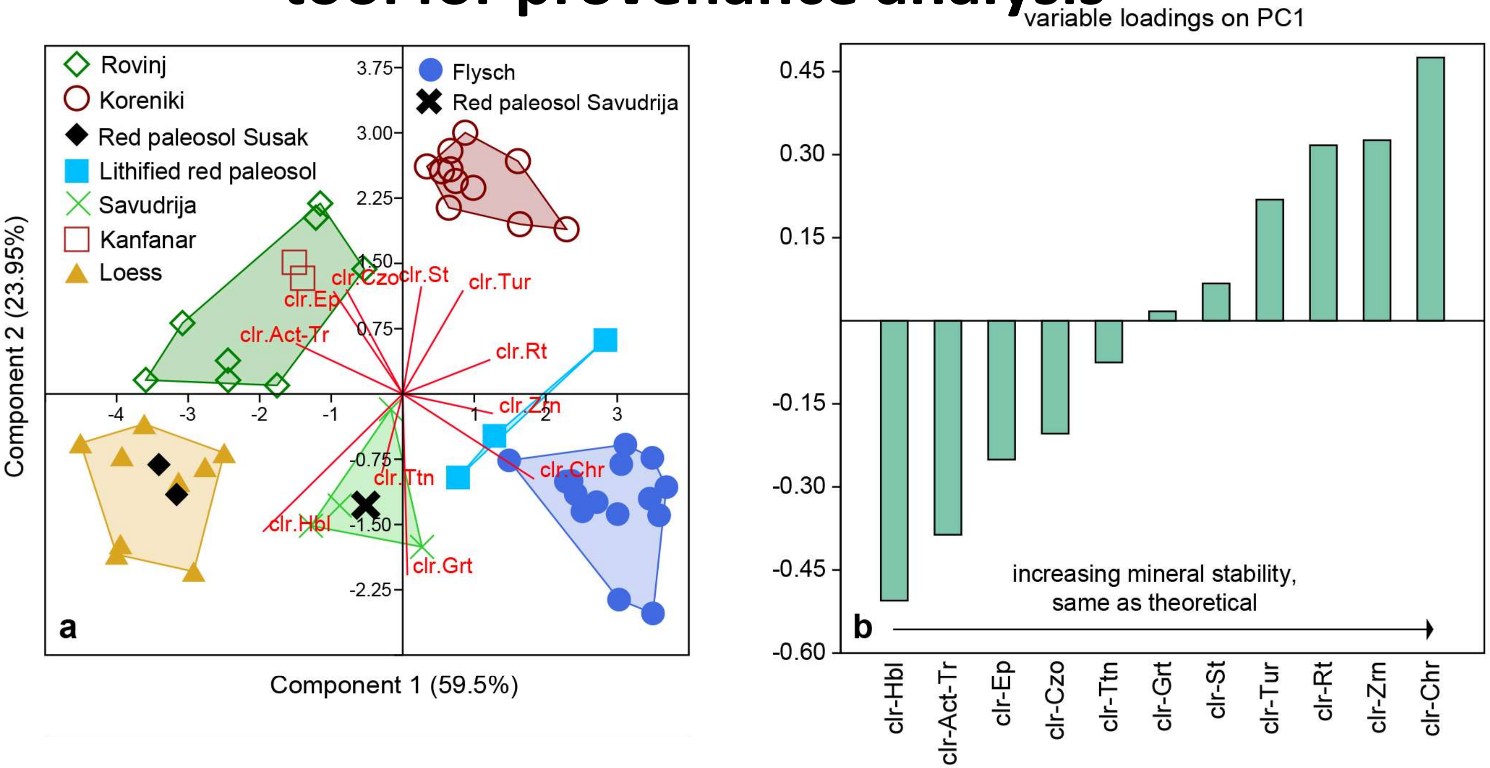
- WRB classification

# COHERENT PROVENANCE ANALYSIS BASED ON HEAVY MINERAL ASSEMBLAGES

# Microphotographs of mineral associations



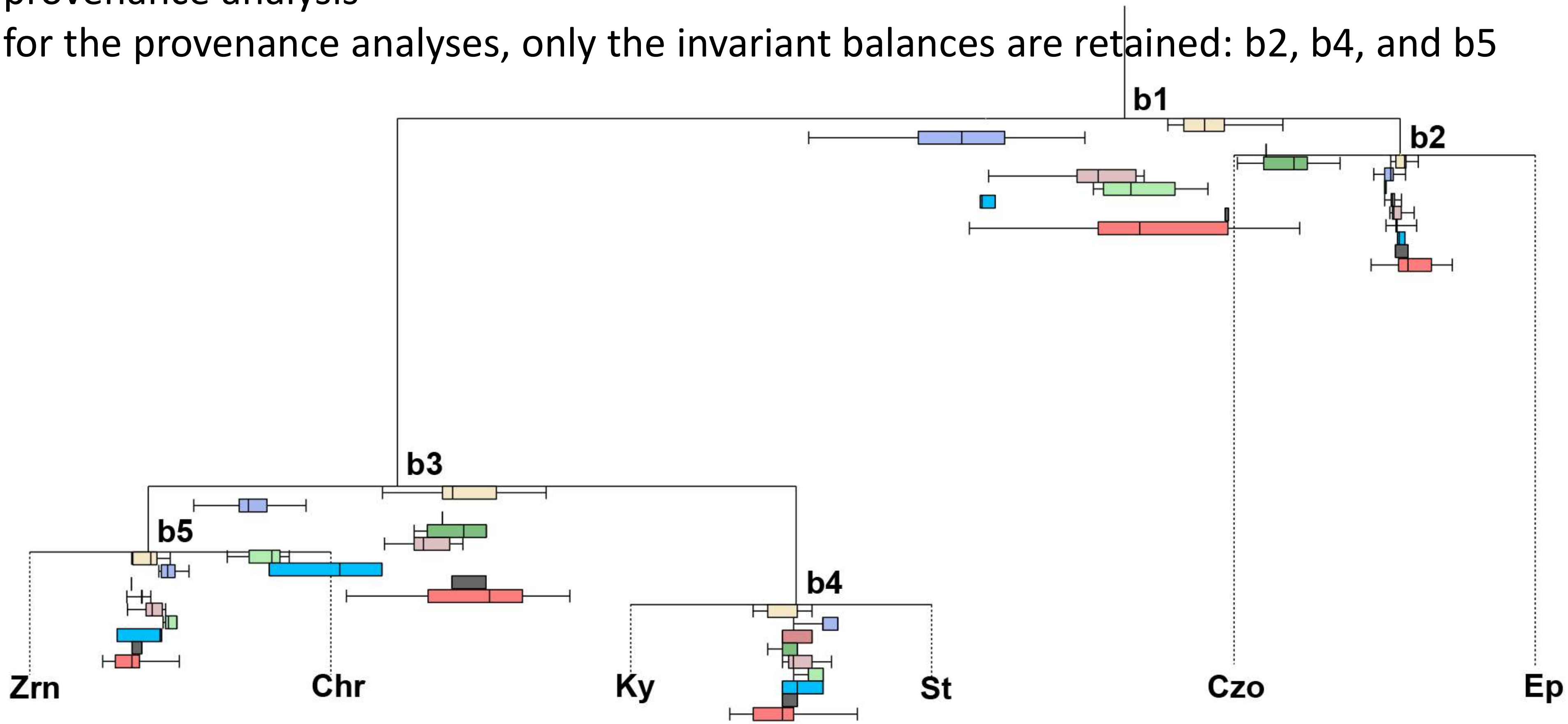
# Compositional biplot: Weathering and hydraulic sorting of minerals make absolute concentrations of heavy minerals an inappropriate tool for provenance analysis




- least stable mineral associations are loess samples, followed by soil profiles from Kanfanar and Rovinj, the most mineralogically stable soil profile is Koreniki, while flysch and lithified red palaeosol has the most stable mineral association overall
- Savudrija loess section does not follow this pattern
- less stable minerals have negative loadings on the PC1, while ultra-stable ones have positive loadings
- the variation in the CB can be attributed almost entirely to selective weathering of minerals
- compensation for weathering effects is mandatory before a conclusion on provenance can be made (transport/weathering invariant variables should be applied)

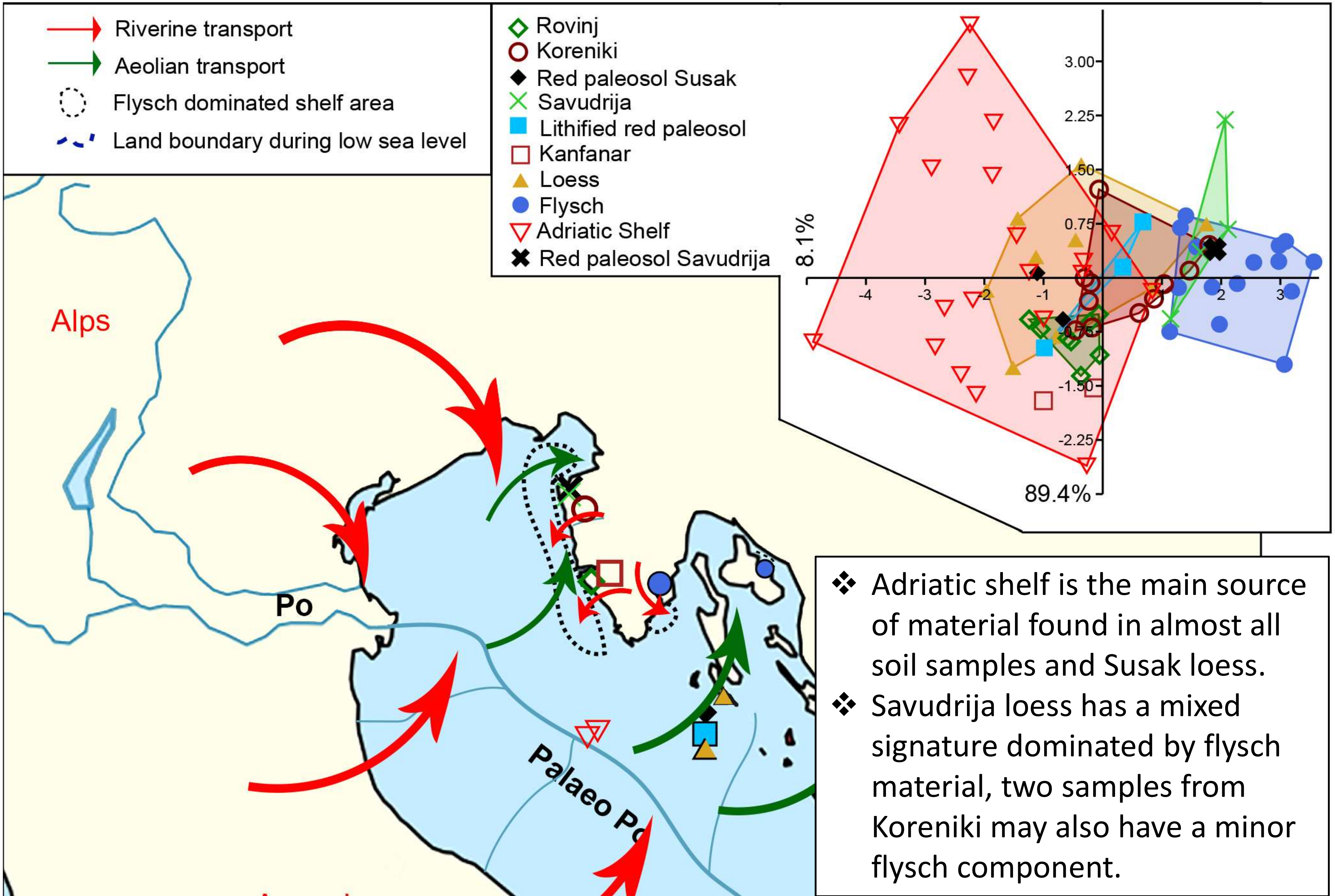
# Categorized balance - dendrogram

- for the invariant balances, it is essential to establish ratios of minerals with similar properties
- epidote, clinozosite, kyanite, staurolite, chrom spinel and zircon were selected for provenance analysis
- provenance-related variables are constructed using the minerals retained for the provenance analysis
- for the provenance analyses, only the invariant balances are retained: b2, b4, and b5



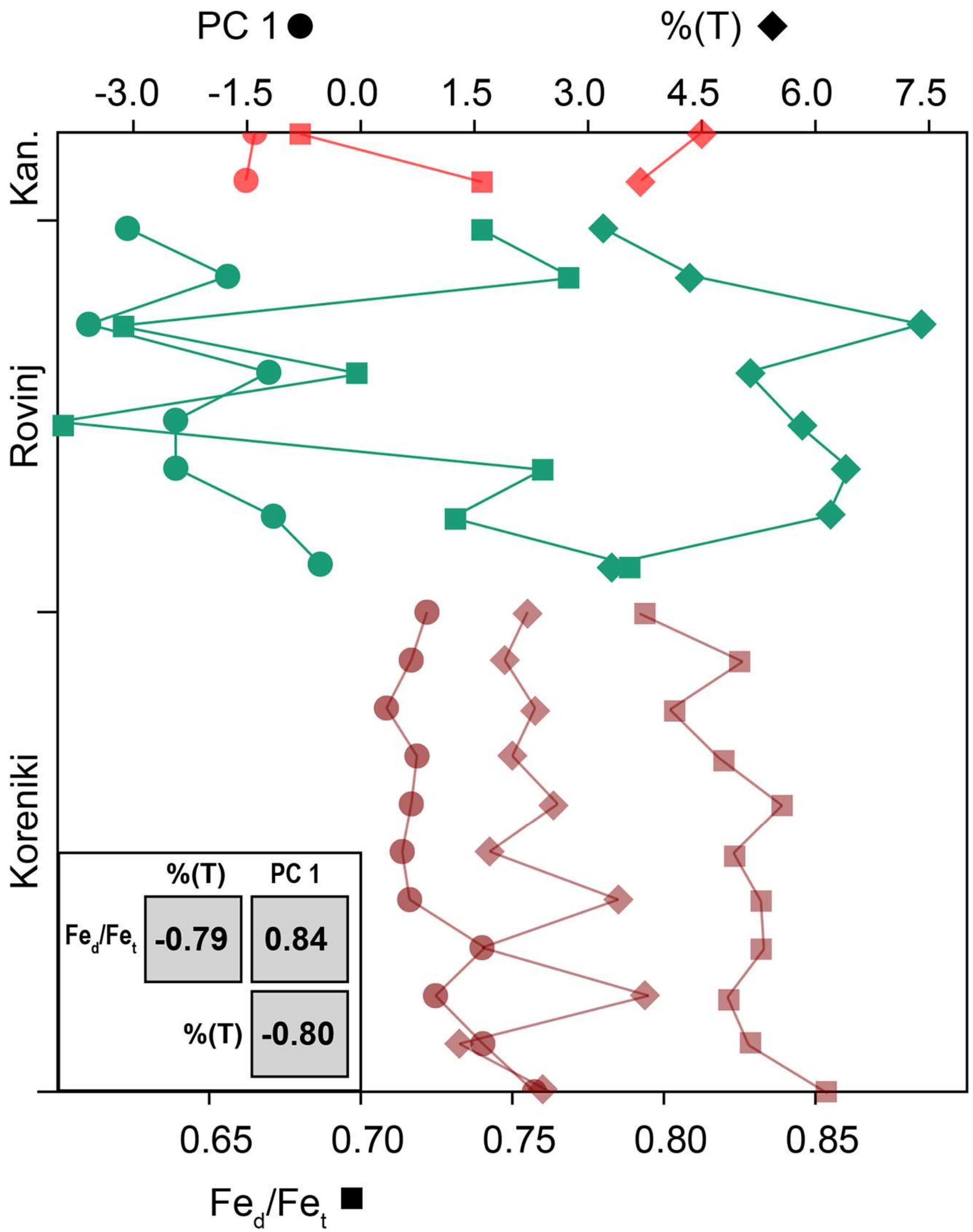

| balance | Ky | St | Ep | Czo | Zrn | Chr | A | B |
|---|---|---|---|---|---|---|---|---|
| b1 | -1 | -1 | 1 | 1 | -1 | -1 | | + |
| b2 | 0 | 0 | 1 | -1 | 0 | 0 | + | |
| b3 | 1 | 1 | 0 | 0 | -1 | -1 | | + |
| b4 | -1 | 1 | 0 | 0 | 0 | 0 | + | |
| b5 | 0 | 0 | 0 | 0 | -1 | 1 | + | |

# Reconstruction of sediment pathways based on linear discrimination analysis (LDA) of heavy mineral data



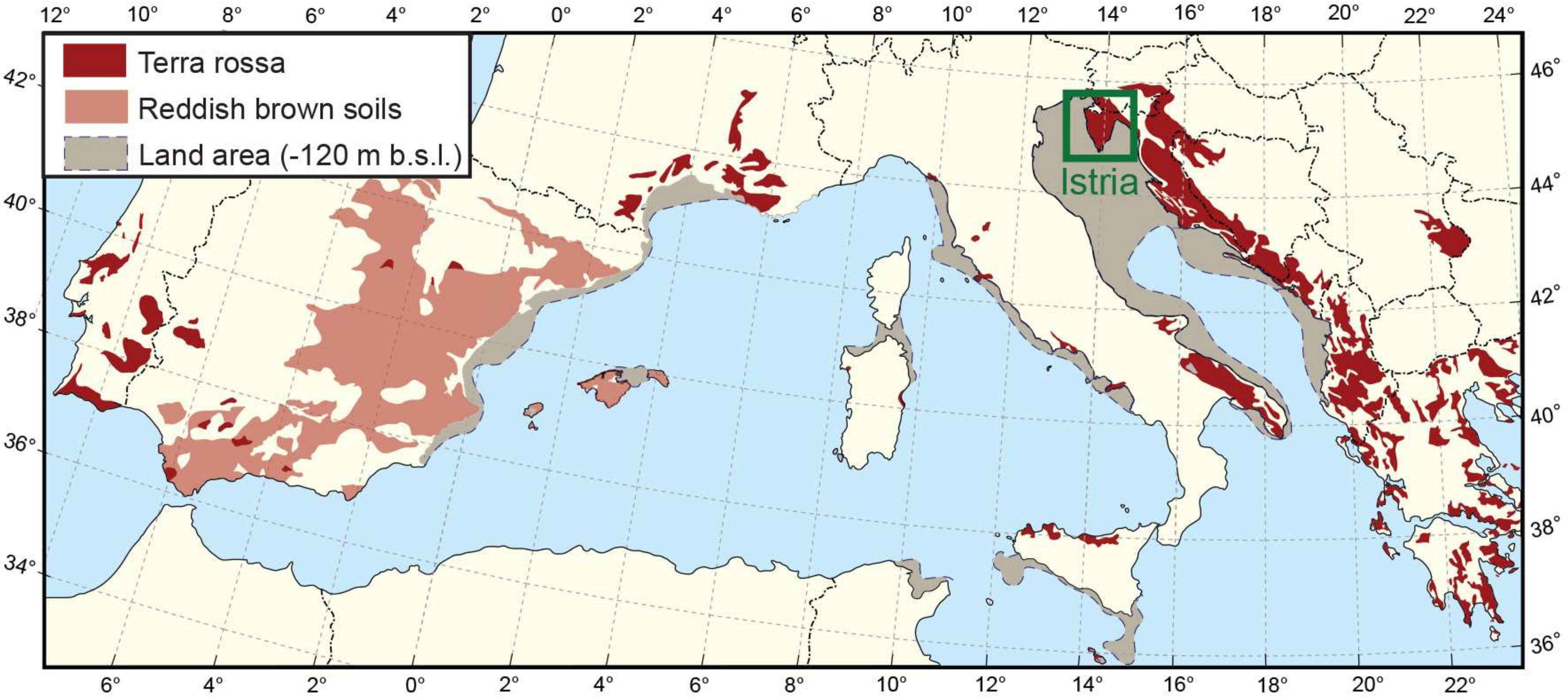

- ❖ Adriatic shelf is the main source of material found in almost all soil samples and Susak loess.
- ❖ Savudrija loess has a mixed signature dominated by flysch material, two samples from Koreniki may also have a minor flysch component.

# The relationship between mineral weathering (PC1 from the compositional biplot), $Fe_d/Fe_t$ ratio and total heavy mineral (HM) abundances (%T)



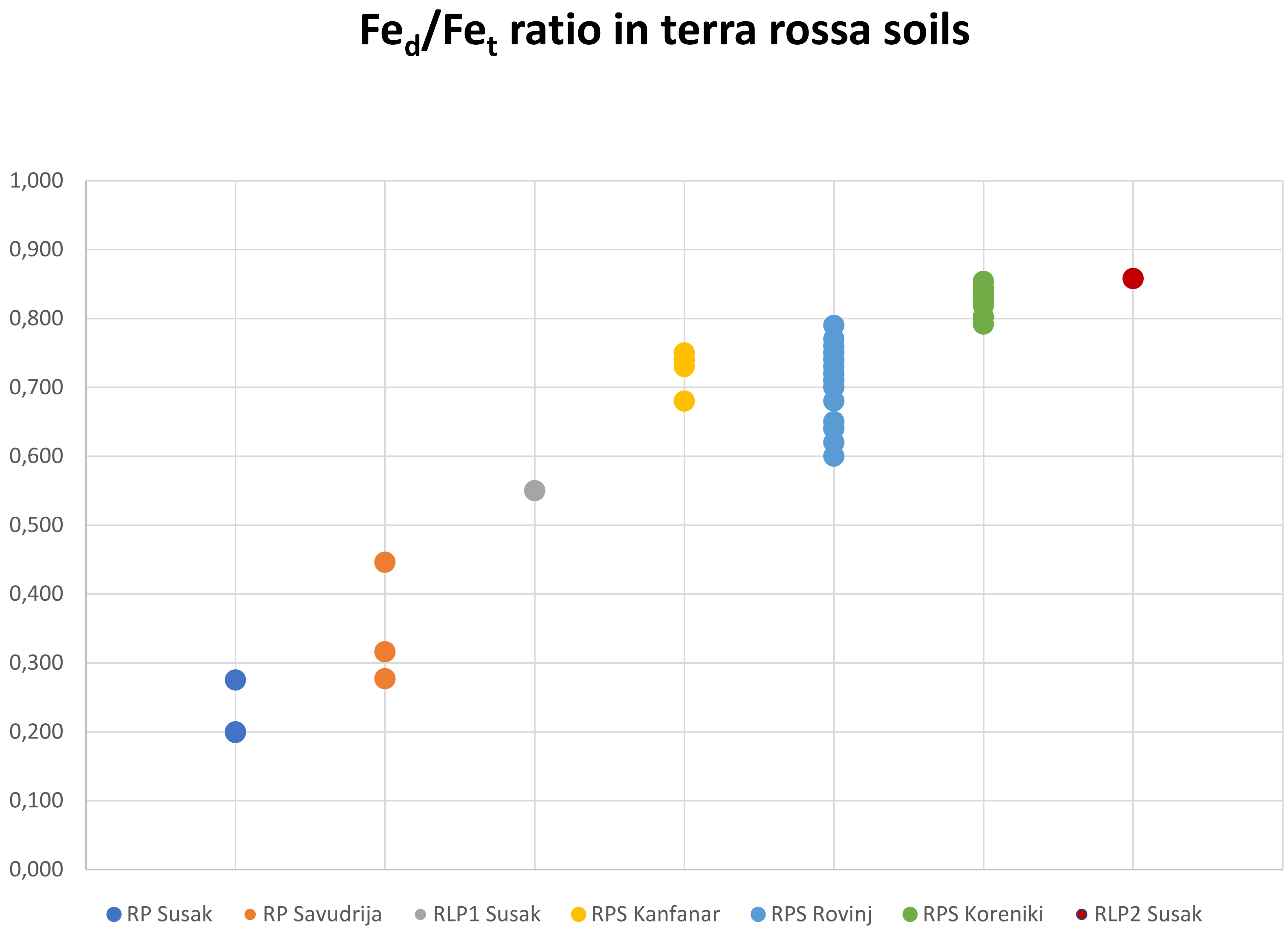

- ❖ allochthonous material serves as a parent material for the authigenic soil minerals
- ❖ as weathering based on the HM associations increases, the $Fe_d/Fe_t$ ratio increases while %T decreases

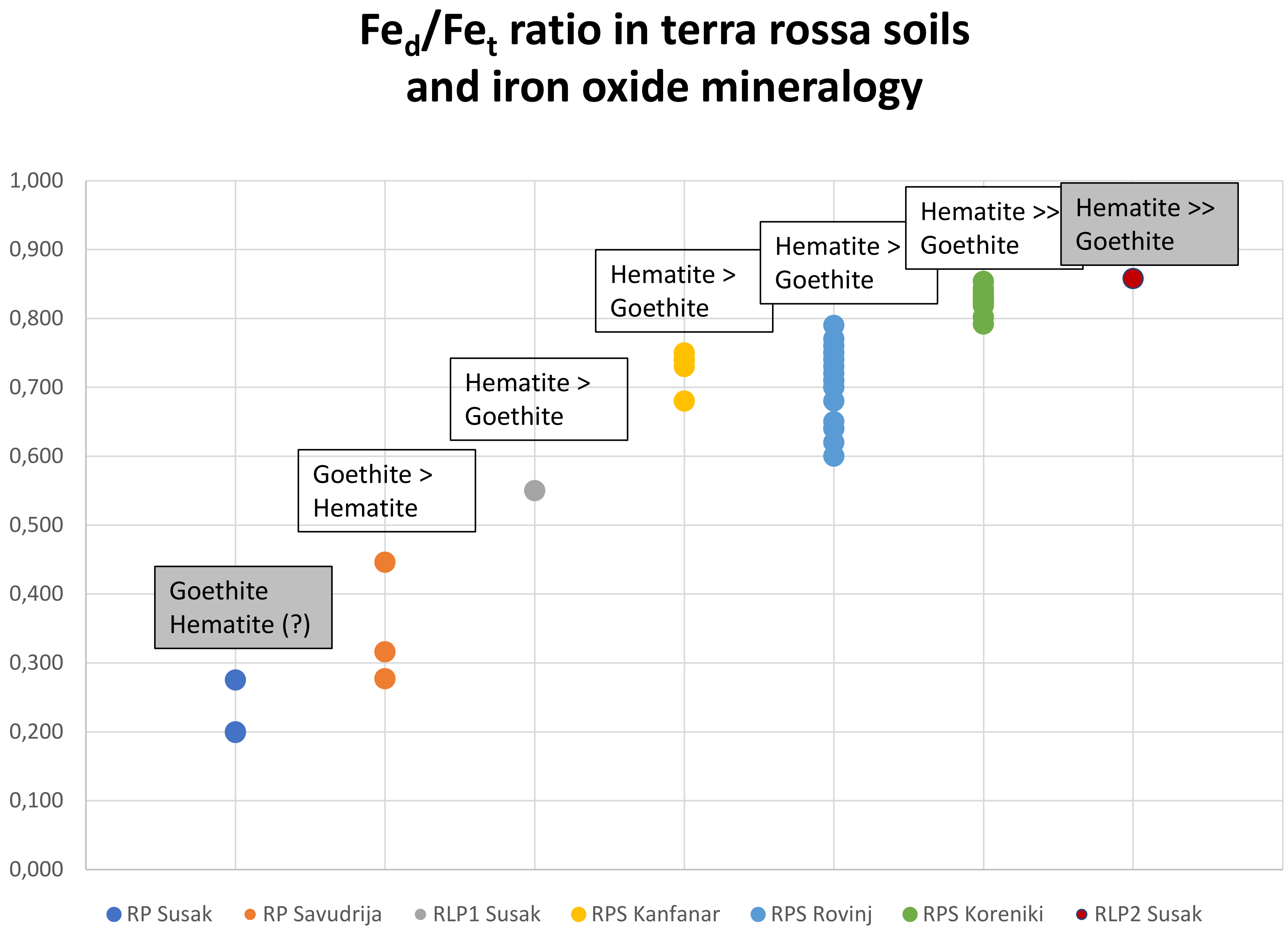
# Map of southern Europe showing the distribution of Red Mediterranean and Reddish Brown soils (from Muhs et al. 2010), and surface shelf during the low sea levels



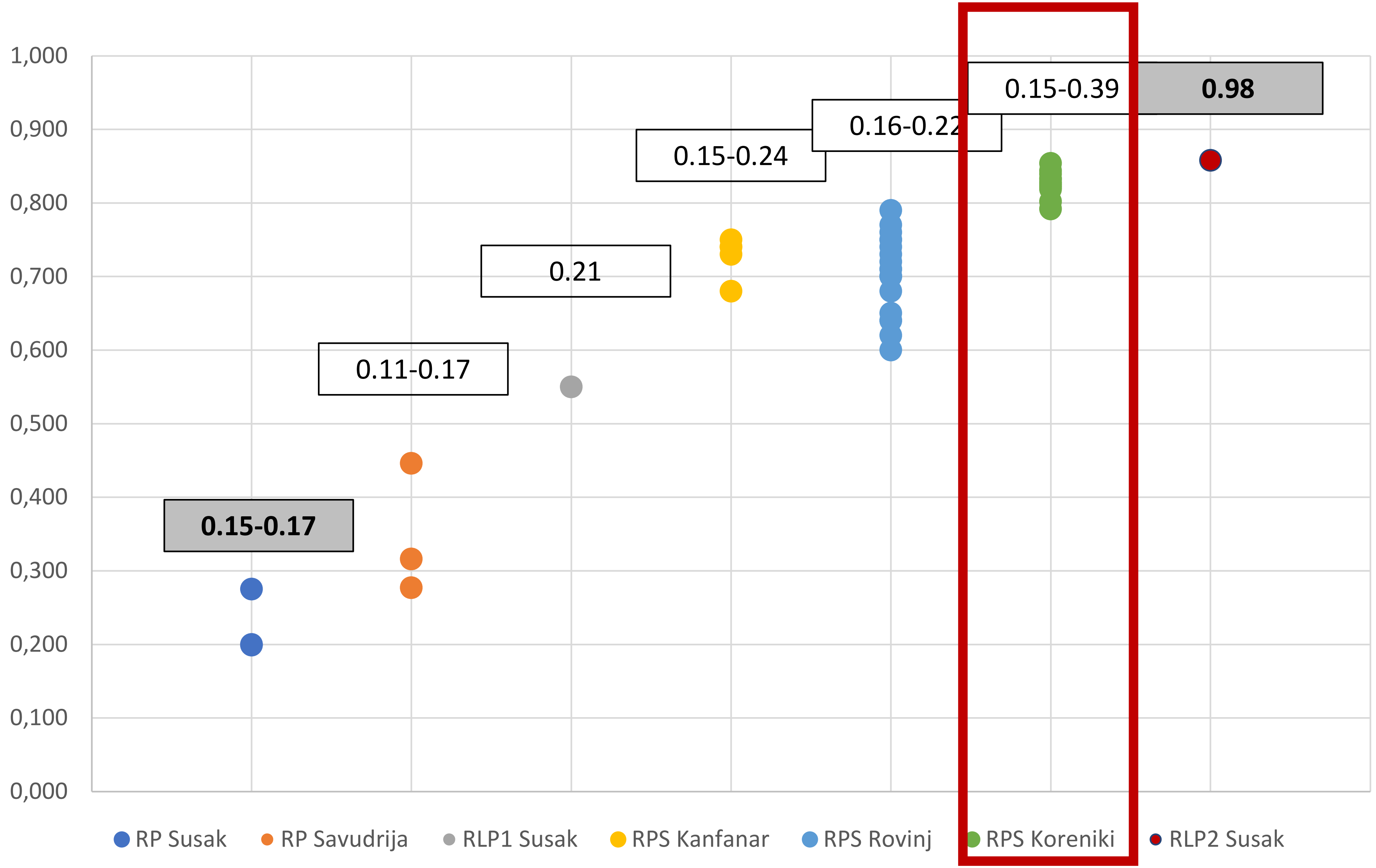

- It is evident that large occurrences of terra rossa soils on the eastern Adriatic coast are associated with the large shelf area that provided siliclastic material for soil formation

# WEATHERING PROCESSES AND FORMATION OF RED POLYGENETIC SOILS AND PALEOSOLS ON HARD CARBONATE ROCKS

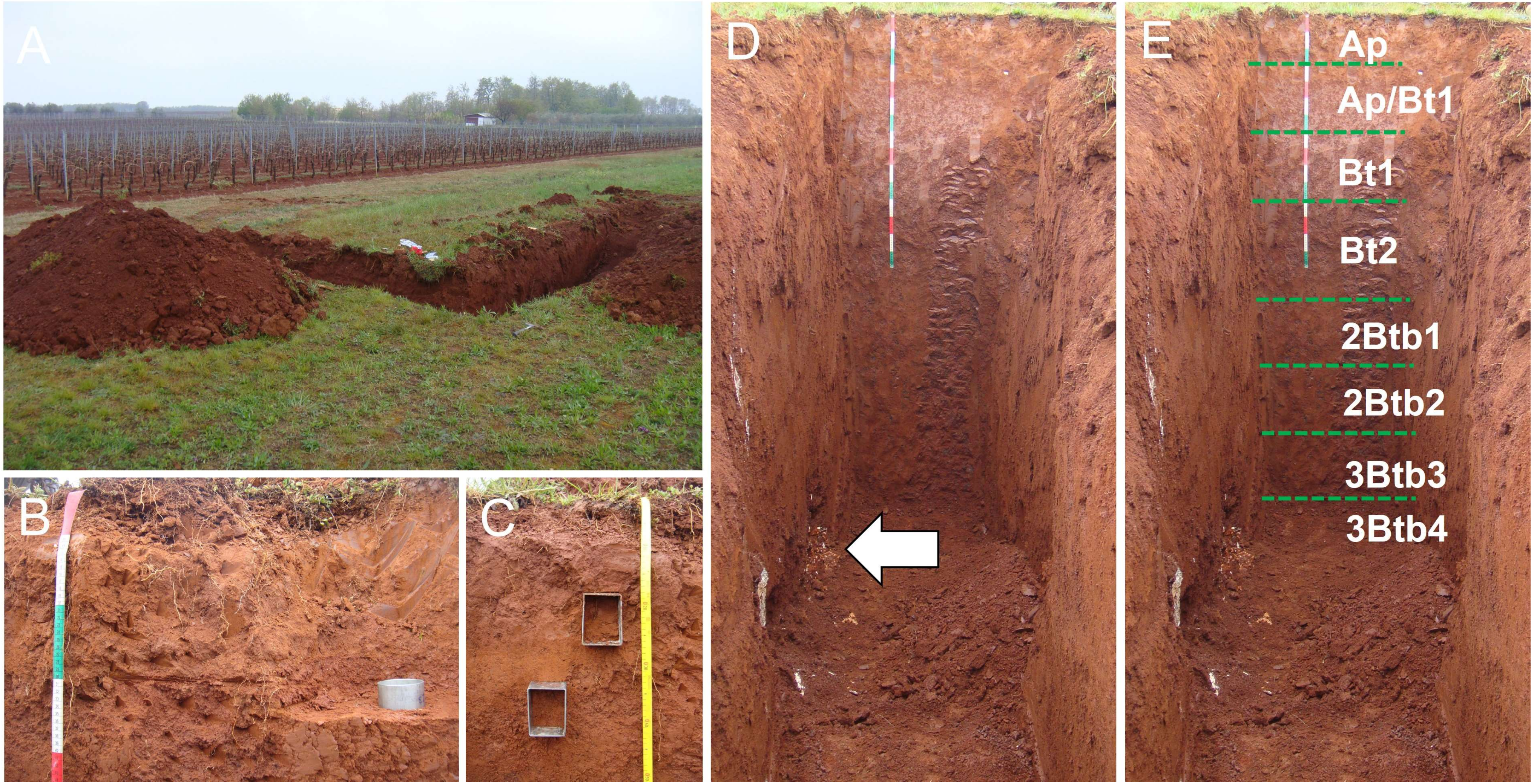

Fed/Fet ratio in terra rossa soils
1,000
0,900
0,800
0,700
0,600
0,500
0,400
0,300
0,200
0,100
0,000
RP Susak
RP Savudrija
RLP1 Susak
RPS Kanfanar
RPS Rovinj
RPS Koreniki
RLP2 Susak


Fe_d/Fe_t ratio in terra rossa soils
and iron oxide mineralogy
1,000
0,900
0,800
0,700
0,600
0,500
0,400
0,300
0,200
0,100
0,000
Goethite
Hematite (?)
Goethite >
Hematite
Hematite >
Goethite
Hematite >
Goethite
Hematite >
Goethite
Hematite >>
Goethite
Hematite >>
Goethite
RP Susak
RP Savudrija
RLP1 Susak
RPS Kanfanar
RPS Rovinj
RPS Koreniki
RLP2 Susak

# $Fe_d/Fe_t$ ratio in terra rossa soils and range of Al/Si ratio



# RPS Koreniki




a) RPS located in a vineyard at Koreniki (west coast of the Istrian peninsula, Croatia); b) Sampling of undisturbed soil from Ap/Bt1 horizon using 100 $cm^3$ core. c) Positions of Kubiena boxes in Ap and Ap/Bt1 horizons. d) Cleaned soil profile situated on a Lower Eocene limestone (see white arrow); e) Soil profile with Ap, Ap/Bt1, Bt1, Bt2, 2Btb1, 2Btb2, 3Btb3 and 3Btb4 horizons.

# Selected geochemical properties of the RPS Koreniki

| Soil horizon | Depth (cm) | Al/Si | Ba/Sr | CIA | (K+Na)/Al | La/Ce | Sm/Nd | Ti/Al | $Fe_t$ % | $Fe_d$ % | $Fe_d/Fe_t$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Ap | 0-30 | 0.15 | 5.28 | 85.26 | 0.14 | 0.463 | 0.185 | 0.08 | 4.61 | 3.65 | 0.79 |
| Ap/Bt1 | 30-70 | 0.23 | 5.82 | 87.67 | 0.11 | 0.476 | 0.193 | 0.06 | 5.85 | 4.76 | 0.81 |
| Bt1 | 70-110 | 0.23 | 5.62 | 87.81 | 0.10 | 0.475 | 0.186 | 0.06 | 5.87 | 4.87 | 0.83 |
| Bt2 | 110-170 | 0.23 | 5.50 | 88.66 | 0.09 | 0.419 | 0.188 | 0.06 | 6.08 | 4.99 | 0.82 |
| 2Btb1 | 170-200 | 0.27 | 5.81 | 90.30 | 0.08 | 0.416 | 0.177 | 0.05 | 6.47 | 5.39 | 0.83 |
| 2Btb2 | 200-230 | 0.32 | 5.67 | 91.19 | 0.07 | 0.433 | 0.191 | 0.05 | 6.92 | 5.68 | 0.82 |
| 3Btb3 | 230-260 | 0.34 | 5.53 | 91.59 | 0.06 | 0.430 | 0.190 | 0.05 | 7.01 | 5.81 | 0.83 |
| 3Btb4 | 260-300 | 0.39 | 6.10 | 92.00 | 0.05 | 0.519 | 0.190 | 0.05 | 7.29 | 6.19 | 0.85 |

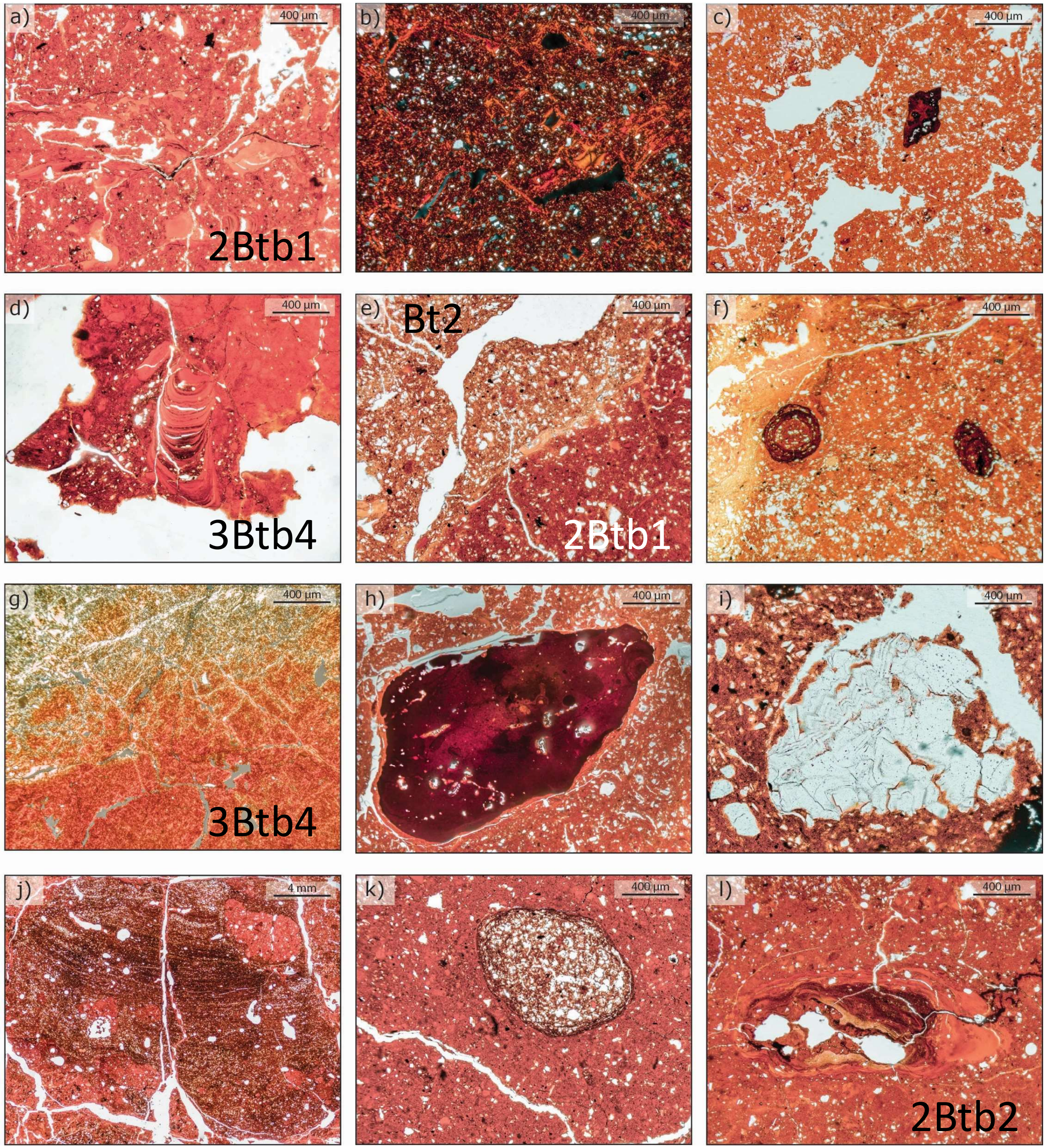
CIA=Chemical Index of Alteration calculated as Al ∗ 100 / (Al+Ca+K+Na)

$Fe_t$ =total iron ($Fe_2O_3$). $Fe_d$ = iron extracted with Na–dithionite–citrate bicarbonate.

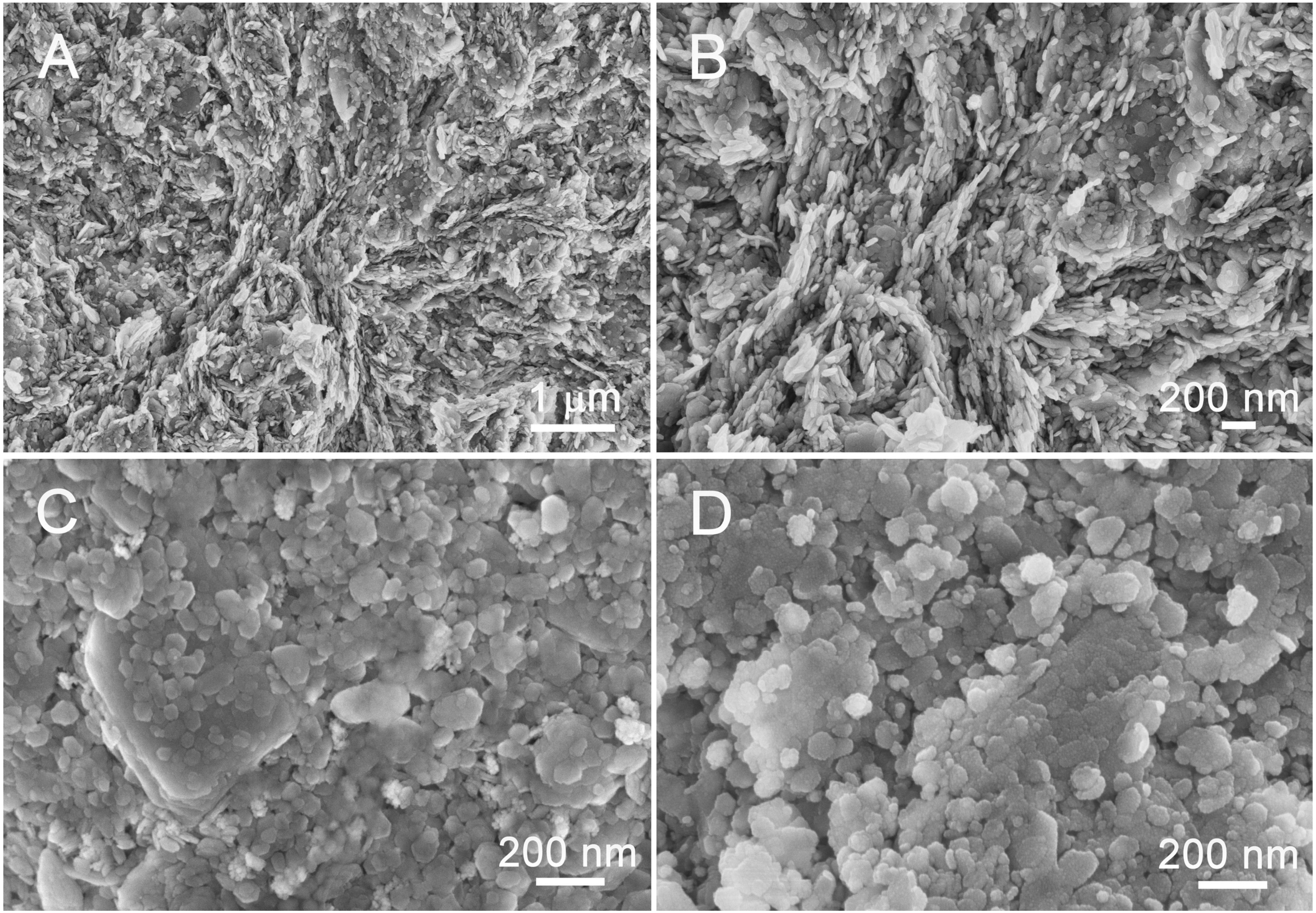
# Mineral composition of the <2 µm fraction of the RPS Koreniki

| Soil horizon | Illite | Kaolinite | Chlorite | Mixed layer clay mineral |
|---|---|---|---|---|
| Ap | 24 | 76 | - | tr |
| Ap/Bt1 | 24 | 76 | - | tr |
| Bt1 | 23 | 77 | - | tr |
| Bt2 | 20 | 80 | - | tr |
| 2Btb1 | 15 | 85 | - | tr |
| 2Btb2 | 14 | 86 | - | tr |
| 3Btb3 | 10 | 90 | - | tr |
| 3Btb4 | 8 | 92 | tr | tr |

# Photomicrographs of the RPS Koreniki



# FE-SEM photomicrographs of soil microaggregates in the 3Btb3 horizon

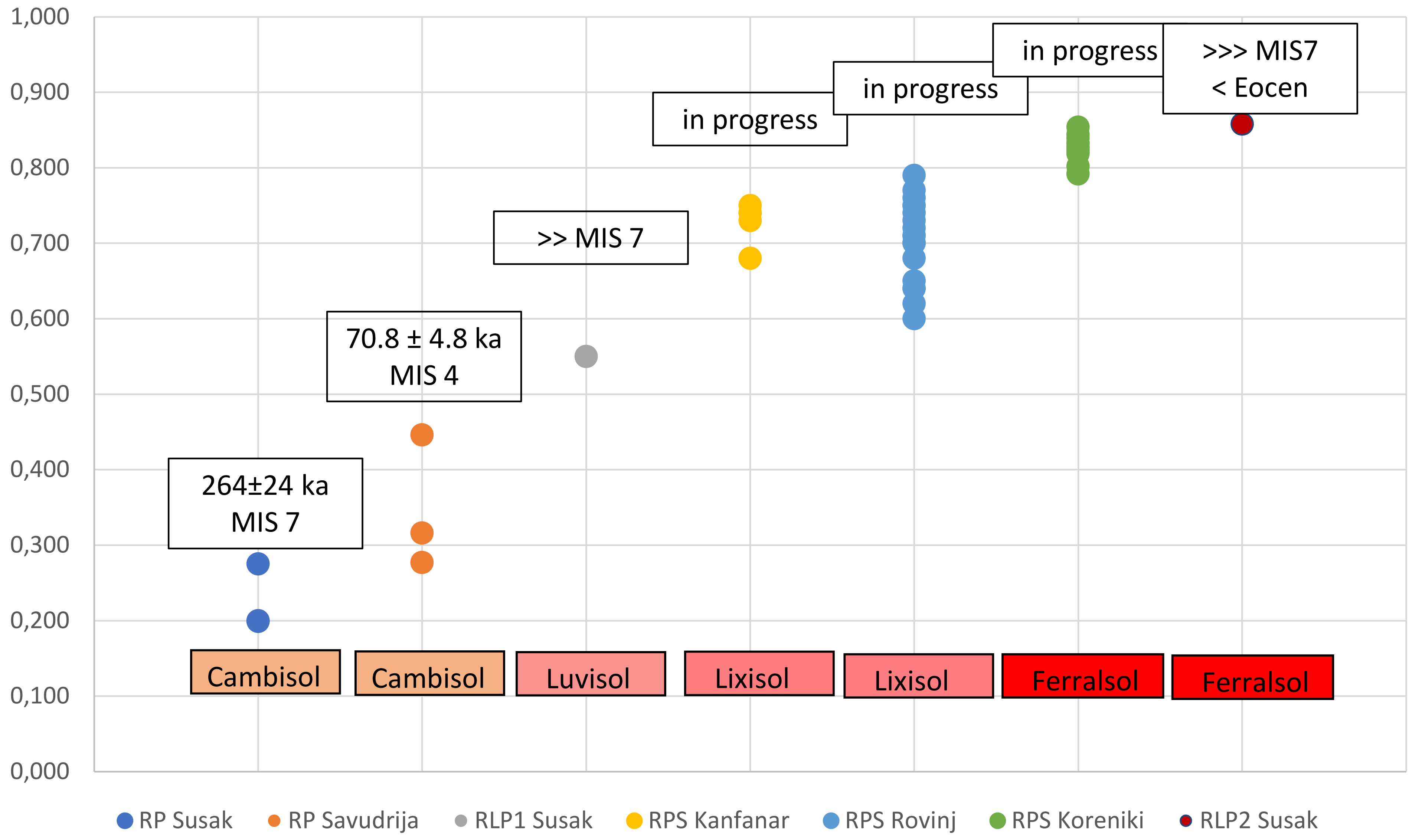


| Locality | $Fe_d/Fe_t$ (range) | Fe oxide mineralogy | Al/Si (range) | Inherited and pedogenic clay minerals | WRB classification | Age (ka) |
|---|---|---|---|---|---|---|
| RP Susak | **0.20-0.28** | Goethite Hematite (?) | 0.15-0.17 | Main: Sm, Ill Subordinate:Chl, Chl–Ver, $Kln_D$, Kln | **Hypereutric Chromic Cambisol (Episiltic, Endoloamic)** | 264±24 MIS 7 |
| RP Savudrija | **0.32-0.45** | Goethite> Hematite | 0.11-0.17 | Main: Sm, Ill, Ver Subordinate: Chl–Ver, $Kln_D$, Kln | Chromic Cambisol | 70.8 ± ±4.8, MIS 4* |
| RLP 1 Susak | **0.55** | Hematite> Goethite | 0.21 | Main: Kln, Chl–Ver Subordinate: Ill, $Kln_D$ | Chromic Luvisol | >> MIS 7 |
| RPS Kanfanar | **0.68-0.74** | Hematite> Goethite | 0.15-0.24 | Main: Kln, Ill Subordinate: Chl–Ver, $Kln_D$ | Rhodic Lixisol | dating in progress |
| RPS Rovinj | **0.62-0.79** | Hematite> Goethite | 0.16-0.22 | Main: Kln, Ill Subordinate: Chl–Ver, $Kln_D$ | Rhodic Lixisol | dating in progress |
| RPS Koreniki | **0.79-0.85** | Hematite>> Goethite | 0.15-0.39 | Main: Kln, Subordinate: Ill, $Kln_D$, MLM | **Lixic Rhodic Ferralsol (Clayic, Hypereutric, Raptic)** | dating in progress |
| RLP 2 Susak | **0.86** | Hematite>> Goethite (Magnetite) | 0.98 | Main: Kln, $Kln_D$ (Gib, Boe) | Ferralsol | >>> MIS7 < Eocen |

# Sampling of RLP2 Susak for paleomagnetiuc measurements

❖ the extremely viscous behaviour of the samples studied hindered the acquisition of a stable remanent magnetisation.

## $Fe_d/Fe_t$ ratio in red polygenetic soils and paleosols, age of formation and classification according to the WRB



# Conclusions

# Conclusions

- The provenance of the allochthonous soil components showed that they originated from the Adriatic shelf, with two different signatures, Alpine/Apennine for all soil profiles except Savudrija, where Eocene flysch, also windblown from the shelf, was a dominant source, and Koreniki, where two samples with probably lower flysch contribution were found.
- The degree of mineral weathering, which correlates with the $Fe_d/Fe_t$ and the portion of heavy minerals, shows that this allochthonous component is a parent material of the soils and not an impurity.
- The origin and formation of the parent material are linked to sea level oscillations, so that during periods of low sea level, material is windblown from the shelf onto the land, while during periods of high sea level, soils were formed. This could be traced far back into the Cenozoic.
- The abundance of RMS soils on the eastern Adriatic coast can be attributed to a large shelf area that supplied the carbonate platform with siliciclastic material from the Alps.
- Formation of RMS in the Eastern Adriatic is a recurrent process, i.e., RMS may have formed repeatedly in a specific and favourable soil environment on hard carbonate rocks since the Eocene. Possible favourable periods for soil formation include the Quaternary interglacials, the mid-Piacenzian Warm Period (Pliocene) and the Miocene Climatic Optimum.

# Conclusions

- Some RMS, previously classified as e.g. Cambisols or Luvisols, might actually be Ferralsols or other tropical soils (e.g. Lixisols), in which relict properties are preserved in the present climate.
- The finding of a Ferralsol in the study area indicates the old age of the surface of the karst depression and provides the first data on the burial history of the southwestern Istrian planation surface.
- Fine clay dominated by pedogenic kaolinite is the main component of illuviated clay in the form of coatings and infillings in both Lixisols and Ferralsols.
- The prevalence of kaolinite and hematite in Lixisols and Ferralsols and the absence of chlorite and, in case of Ferralsols, intermediate clay minerals formed by the destabilization of chlorite (e.g. chlorite-vermiculite mixed layer mineral and vermiculite) in the clay fraction may indicate that chlorite (along with feldspar, mica, and illite) was one of the main precursors for the formation of authigenic kaolinite and the main source for the formation of iron oxides.

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