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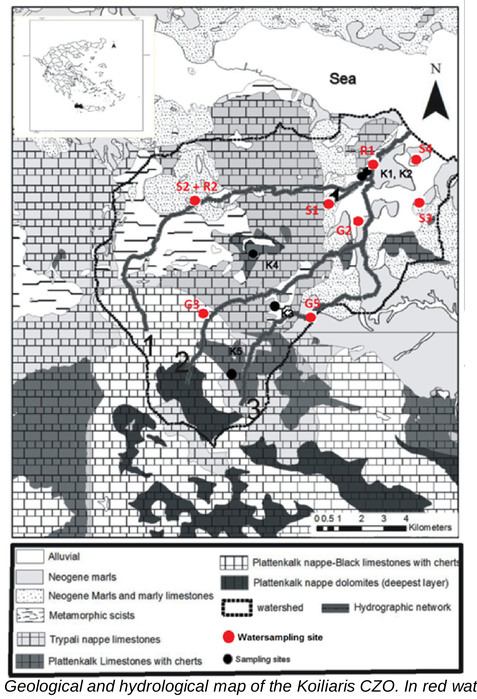
REE profiles in continuous leach ICP-MS (CL-ICP-MS) experiments in soil linked to REE profiles in surface water in the Koiliaris River Critical Zone Observatory (CZO), Crete, Greece.

Site description

The Koiliaris River CZO watershed:
- situated 25 km east from the city of Chania, Crete, Greece;
- total surface area 130 km^2;
- total length of 36 km;
- maximum altitude difference of 2120 m.



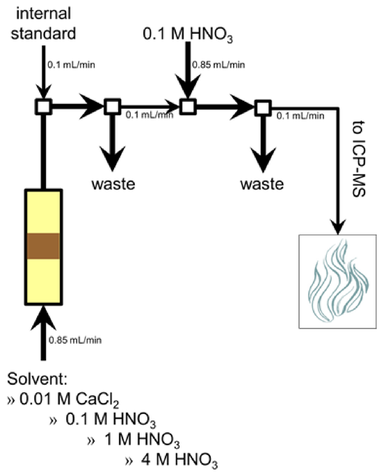
Geological and hydrological map of the Koiliaris CZO. In red water sampling locations, in black the soil sampling locations (K1 –K5). The selection of the sites was based on variability in bedrock (limestone, metamorphic and alluvial sediments) and current land use (grape farming, olive trees).

Higher altitudes in the south: Plattenkalke nappe (K4&K5) topped by Trypali nappe (K3), bedded and recrystallised brecciated limestones containing large karstic sinkholes. Tripaly nappe topped by Western Crete phyllites (quartz and micaceous minerals).

Lower altitudes: Dominated by neogene marls and marly limestones and recent alluvial sand and conglomerate deposits (K1& K2).

Hydrology
- spring outflow (rain + snow melt) at limestone- fluvial sediment boundaries (elev. <200 m), draught in summer;
- (largely) dry rivers through the limestone nappes;
- 1 ephemeral river on the top of the phyllites;
- Stylos spring (S1) is main water supply for (G2& R1), other tributaries mainly in karstic areas and limited flow.

Method



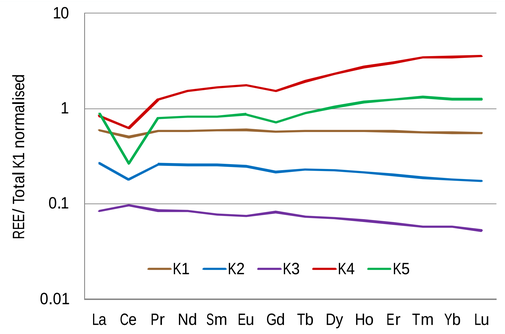
Solvent:
» 0.01 M $CaCl_2$
» 0.1 M HNO_3
» 1 M HNO_3
» 4 M HNO_3

Experimental setup for continuous leach extractions.

- 5 soil samples subjected to on-line continuous leach ICP-MS (for more details on the method used: EGU2014-14923);
- Water samples collected at 9 locations in spring, summer and autumn.

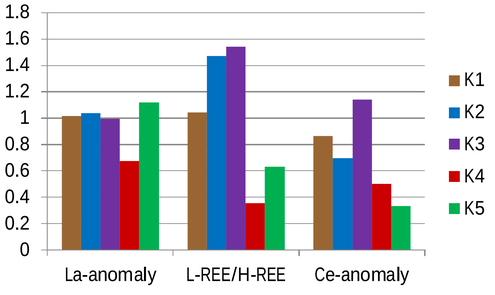
Aim: To investigate if the REE-concentrations in continuous leach extracts could be used to investigate the provenance of spring and surface waters in the Koiliaris River Critical Zone Observatory.

Results



REE pattern of the different locations (K1-K5) in 1 M HNO_3. normalised to total leached amount for K1. Normalisation elucidates the differences between locations.

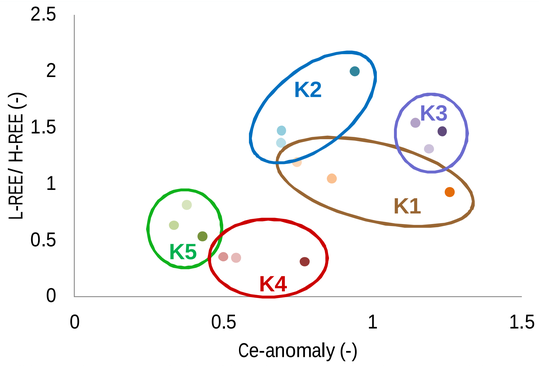
- Majority of REE is extracted during the 1 M HNO_3 step and therefore associated with clay particles;
- REE patterns between extraction steps show minor variations, except for location K1;
- La-anomaly is predominantly present in the 0.1 M HNO_3 step (carbonates).



Differences in REE-patterns between the 5 sampled locations in 1 M HNO_3

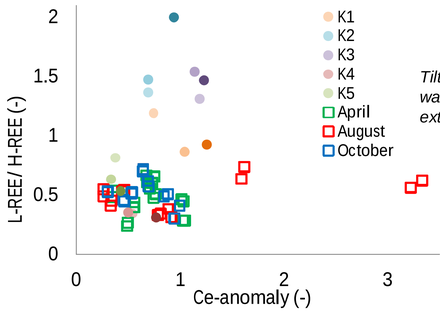
There are large differences observed between the different sample locations:
- Tilting (L-REE/H-REE) of the REE-patterns ($2*Pr_n / (Yb_n + Lu_n)$);
- Cerium anomalies (Ce_n / Pr_n);
- La-anomalies (La_n / Pr_n).

By combining these characteristics and assuming conservative behaviour they can be used for tracing the source of the surface water.



Tilting and Ce-anomaly for all locations and extraction steps. Lightest colours for 0.1 M HNO_3, darkest colours for 4 M HNO_3.

- Combination Ce-anomaly and tilting makes it possible to distinguish the 5 sites;
- Variability of the different extraction steps is relatively small at the locations K3, K4 and K5 and large at the K1 and K2. K1 and K2 consist of alluvial deposited material and therefor mixture of surrounding areas, K3-K5 are more uniform sampling areas.



Tilting versus Ce-anomaly for the water samples compared to the extracts.

- K4 and K5 mainly determine the REE-pattern in the water samples;
- During the dry period the Ce-anomaly cannot be regarded a conservative tracer.

Preliminary conclusions

- Online sequential extractions are an interesting technique for direct linkage of mineralogy (major elements) and trace elements.

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