Geochemistry, mineralogy and micropaleontoly of a pedogenic calcrete profile (Slimene, NE Tunisia)

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Abstract

A calcrete profile developed on the top of a calcareous consolidated dune in a coastal area of NE Tunisia (semi-arid climate) was studied focussing on: (i) geochemistry of rare earth elements (REE) and other trace and major elements during the processes associated with calcrete formation, and (ii) mineralogy of the different horizons of the profile. The profile shows a vertical sequence: surface horizon, sub-surface horizon, lithoclast-rich horizon, laminar-structured level, and the old dune. Chemical and mineralogical analyses were performed by neutron activation analysis and X-ray diffraction (whole samples and clay fraction).
The calcrete is mainly composed of quartz, calcite and K-feldspar. Phyllosilicates were also found in the other levels. Hematite was only detected in surface levels. The clay minerals present are kaolinite, illite and chlorite. Smectite also occurs in the matrix of the nodular horizon. The microfauna identified is the one commonly found in dunes close to the sea (terrestrial environment). Co, U, Br and heavy REE enrichment occur in the evaporite carbonate rich levels, while the light REE, Hf, Zr, Cr, Th, Cs, Ta, Ga, Rb, and K appear to be retained in the upper levels.

Key Words

Soil, calcrete, semi-arid environment, geochemistry, mineralogy, microfauna

Introduction

Calcretes occur in the semi-arid and arid regions, and are accumulations of fine-grained low magnesium calcite having formed within the meteoric vadose zone, facilitated by loss of H_2O and CO_2, by pedogenic alteration and replacement of the host material. Biological influences are commonly found.
Detailed chemical and mineralogical studies of soils and sediments of the semi-arid area of the El Melah coastal lagoon (NE Tunisia) with a closing evolution dynamic have been done. Among the different mineral phases found, carbonates appear to play an important role on the trace elements distribution in the surface environments under a semi-arid climate (Ruiz, 2006; Prudêncio *et al.*, 2007; 2010). In this work a mineralogical, chemical and micropaleontological study of a calcrete profile developed on the top of a calcareous consolidated dune located near Slimene, in the central area of the El Melah lagoon, is done. The evaluation of the redistribution of chemical elements during the weathering processes associated with calcrete formation, particularly the dissolution of carbonates and precipitation in the vadose zone, is a major goal.

Methods

Sample collection

The sampling location, the profile and the sampled levels are shown in Figure 1, where a vertical sequence, with clear zonations from the surface downwards can be seen: (1) a reddish modern soil at the land surface, appr. 50 cm thick, (2) a lithoclast-rich horizon (1m thick). The clasts are subrounded to stellate in shape due to dissolution, in a terrigenous yellowish matrix, (3) a laminar structured calcrete up to 30 cm thick, and (4) the consolidated dune. The samples reference and description are given in Table 1.
Samples were sieved into <2mm and grounded. Nodules and laminar calcrete were finely ground. The <2µm fraction was obtained by wet sieving and sedimentation according to Stokes law.

Analytical Methods

Chemical and mineralogical analyses of samples from all levels were performed by neutron activation analysis and X-ray diffraction (bulk samples and clay fraction). Chemical contents of Na, K, Mn, Fe, Sc, Cr, Co, Zn, Ga, As, Br, Rb, Zr, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Dy, Yb, Lu, Hf, Ta, Th, and U were obtained. Relative precision and accuracy are, in general, to within 5% (Gouveia and Prudêncio, 2000). Iron detailed studies were done by Mössbauer spectroscopy. A micropaleontological study of all levels, with the taxonomical determination of ostracode species was performed. For this purpose, a fixed quantity (15 g dry weight) was sieved through a 63µm mesh. If possible, 500 individuals were picked from each sample, with an extrapolation to the whole sample. This number exceeds clearly the number of individuals (300) required for the statistical analysis of the ostracode assemblages (e.g., Ruiz *et al.*, 1997).

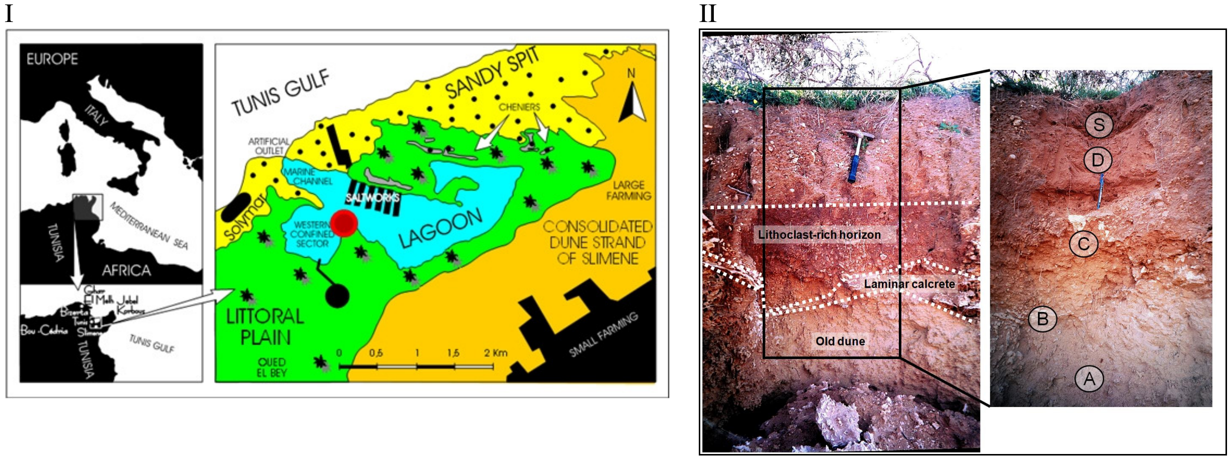

Figure 1. I) El Melah lagoon area: location of the calcrete profile (red circle); II) The pedogenic calcrete profile before (left) and after (right) cleaning and sampling with the identification of the sampled levels. A- old dune; B- laminar-structured level; C- lithoclast-rich horizon; D - sub-surface horizon (25-50 cm depth); and S – surface horizon (0-25cm depth).

Results

Quartz, calcite and feldspars are present in the whole samples of all levels (Table 1). The calcrete is mainly composed of quartz, calcite and K-feldspar. Phyllosilicates and plagioclase also occur in the other levels. Hematite is present in the surface, sub-surface and in the terrigenous matrix of level C, explaining the reddish colour of these levels (see Figure 1). The clay minerals present are kaolinite, illite and chlorite. Smectite also occurs in the terrigenous matrix of the lithoclasts-rich horizon (C) above the laminar structure. Goethite is the dominant iron oxide in the clay fraction. Calcite and gypsum are also found in the clay fraction of the surface and sub-surface levels (S and D).

Table 1. Sample reference, description, and mineral composition (whole sample and <2µm fraction). Qz-quartz, Ca-calcite, Phyl-phyllosilicates, KFs-K-feldspar, Plg-plagioclase, Hem-hematite; K-kaolinite, I-illite, C-chlorite, Sm-smectite; G-goethite; Gy-gypsum. (*) after decarbonation

Sample	Description	Whole sample	Clay fraction
S	Surface (0-25cm)	Qz, Ca, Plg, Phyl, Hem	K, I, C, Ca, Qz, Gy
D	Sub-surface (25-50 cm)	Qz, Ca, Phyl, KFs, Plg, Hem	K, I, C, Ca, Qz, Gy
C	Terrigenous matrix of level C	Qz, Ca, Phyl, KFs, Plg, Hem	K, I, C, Sm, Qz
CN	Nodules of level C (45% carbonates)	Qz, Ca, KFs	I, K, C, Qz, G (*)
B	Laminar calcrete (50% carbonates)	Qz, Ca, KFs	I, K, C, Qz, G (*)
A	Old dune (parent rock)	Qz, Ca, KFs, Plg, Phyl	

Microfaune commonly found in dunes close to the sea was observed in the studied profile: (i) surface levels (S and D) - gastropods (terrestrial environment); (ii) carbonated nodules (CN of level C) - microfaune is almost absent, with the presence of very rare specimens of marine foraminifers (*Ammonia beccarii*); (iii) laminar-structure (level B) - microfaune is covered by a coarse calcareous sheet that impedes the taxonomical determination of numerous specimens. Nevertheless, all individuals belong to marine species of foraminifers (*Ammonia beccarii, Elphidium crispum, Quinqueloculina spp*.), ostracods (*Bairdia mediterranea, Cytheretta adriatica*), spines of echinoderms and undifferentiated fragments of bivalves; and (iv) old dune (level A - eolian deposits close to the sea) - dune sands partially composed of marine provenance where fragments of marine species of very scarce ostracods (*Pontocythere elongata*), foraminifers (*Ammonia beccarii, Ammonia tepida, Quinqueloculina spp*.), and rounded fragments of spines of echinoderms, briozoos remains and undifferentiated fragments of bivalves were found.

The in depth chemical variation, normalized to Sc (conservative element) correlations are shown in the tree-clustering (Figure 2). Among the elements studied, Br, Co, U heavy REE, Na, and Sb are the most enriched in the calcrete (B, CN). Concerning Co, U and Br the in depth variations (Figure 3) may be explained as follows: calcite precipitation requires high pH values (often >9), favouring the uptake of Co^{2+} in calcite; in carbonated groundwater U is transported as extremely soluble uranyl dicarbonate and tricarbonate complex ions. Removal of CO_2, while making $CaCO_3$ less soluble, increases pH. Evaporite or common-ion precipitation of carbonate results in eventual precipitation of carnotite along with carbonate; Br/Sc distribution suggests a biological role in carbonate precipitation. In the surface horizons an enrichment of the following elements is observed: light REE, Hf, Zr, Cr, Th, Cs, Ga, Rb, Ta, and K.
The investigation of the iron crystalchemistry in levels S, D and C by Mössbauer spectroscopy showed that: (a) Fe is more reduced in the upper level (9%) than in levels D and C (4%); (b) Fe^{3+} occurs in iron oxides - goethite and hematite, and clay minerals. The ratio goethite/hematite appears to increase downwards along the profile; and (c) Fe^{2+} is mainly present in clay minerals.

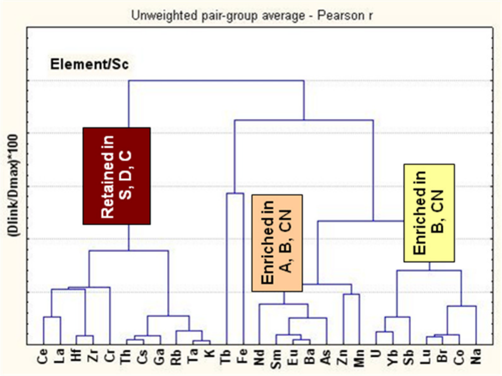

Figure 2. Tree-clustering showing the correlation among variables (element/Sc).

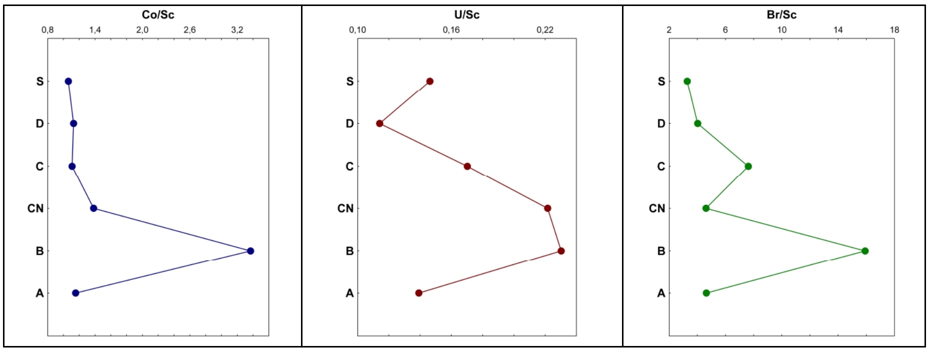

Figure 3. In depth profiles of Co/Sc, U/Sc, and Br/Sc ratios.

The clay fraction is in general enriched relative to the whole sample in the elements studied, but Hf and Zr (Figure 4). Surface levels (S and D) present similar geochemical patterns. The old dune (A) presents a different pattern compared to the terrigenous matrix of level C. REE are concentrated in the clay fraction, increasing upwards; a positive Ce anomaly was found in the old dune and in superficial level relative to the whole sample (see Figure 5III).

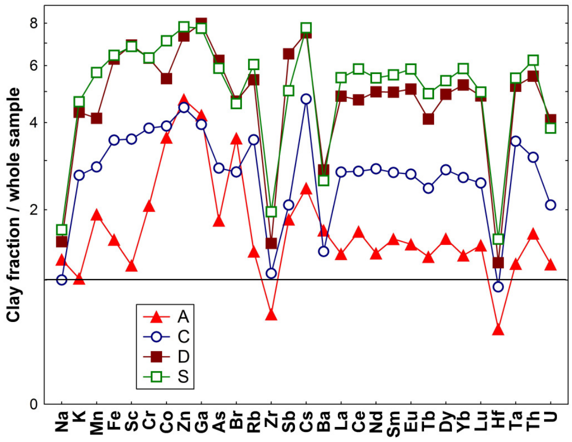

Figure 4. Chemical contents of the clay fraction relative to the respective whole sample.

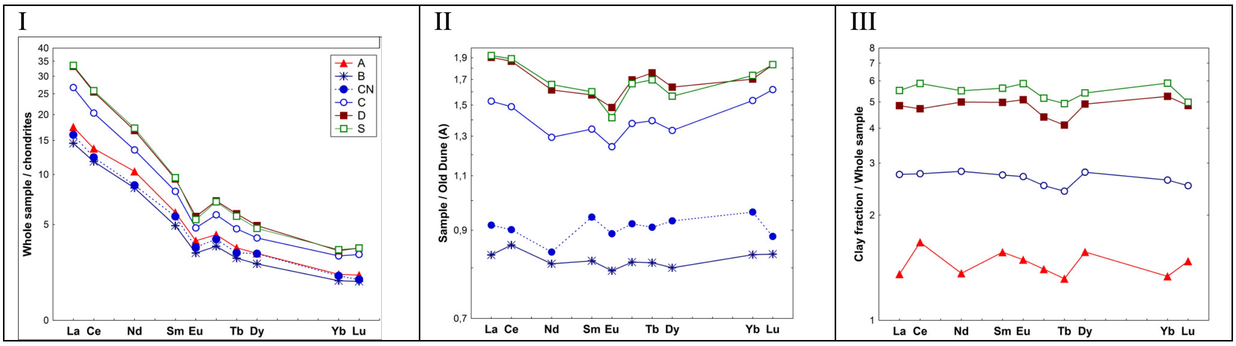

Figure 5. REE patterns: I- whole sample relative to chondrites; II- whole sample relative to sample A (parent rock); and III- clay fraction relative to the respective whole sample.

The enrichment of REE in the upper levels relative to the old dune (Figure 5II) may correspond to (i) sorption into clay minerals and iron oxides in the case of the LREE, and (ii) precipitation of pedogenic calcite in the case of the HREE as already found by Compton *et al*., 2003 in soil profiles and evaporate salt pan sediments from a small granite catchment in a semi-arid climate (South Africa). The MREE are enriched in the old dune, and in the nodular and laminar calcrete. A lower negative Eu anomaly occurs in the carbonates rich levels pointing to its uptake by calcite and evaporite carbonates after the breakdown of feldspars.

Conclusion

The results obtained by studying a calcrete profile, where a reddish soil was derived by weathering of a calcareous consolidated dune under a semi-arid environment point to: (i) similar mineralogical association down to the laminar-structure level, except for the presence of smectite in the terrigenous matrix of the nodular level above the laminar structure, indicating restricted drainage conditions. The presence of hematite in the upper levels indicates more oxidizing conditions; (ii) among the chemical elements studied an enrichment of Br in the calcrete was found, suggesting an important biological role in the carbonates precipitation. Co and U uptake and an enrichment of the heavy REE relative to the light REE are also observed in the calcrete; (iii) a higher fractionation of the REE in the superficial levels was found, which may be explained by the incorporation of the light REE in clay minerals and iron oxides, as well as the migration downwards of the heavy REE due to carbonates dissolution.

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