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# Rare earth and other trace and major elemental distribution in a pedogenic calcrete profile (Slimene, NE Tunisia)

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#### ABSTRACT

A calcrete profile developed on the top of a calcareous consolidated dune located in a coastal area of NE Tunisia (semi-arid climate) was studied with the aim to investigate the behavior of the chemical elements (rare earth elements—REE—and other trace and major elements) during the processes associated with calcrete formation, particularly dissolution and precipitation of carbonates in the vadose zone. The profile shows a vertical sequence, with clear zonations from the surface downwards: a reddish soil at the land surface, a nodular horizon, a laminar-structured level, and the consolidated old dune. Chemical and mineralogical analyses of samples from all levels were performed by neutron activation analysis and X-ray diffraction (bulk samples and <2 µm fraction). Detailed studies of iron speciation and iron minerals were done by Mössbauer spectroscopy. Microfauna, mineralogical and chemical variations in the Slimene weathering profile point to a long term aerial exposure of the old dune in a semi-arid carbonated environment leading to the development of a pedogenic calcrete profile. The mineralogical variations with depth indicate carbonate dissolution at the surface and downward leaching of calcium. Secondary carbonates overgrow primary ones and precipitate as coating or concretions below. Minerals found in the upper levels correspond to original materials of the old dune and also weathering phases and atmospheric inputs. Phyllosilicates decrease while calcite and K-feldspars increase with depth. Kaolinite was the only clay mineral found in the old dune. Illite and chlorite were also found in all samples with calcrete. Authigenic smectite formation occurs above the laminar-structured calcrete due to restricted drainage conditions. The most significant chemical variations associated with the calcrete formation are (i) enrichment of Co, U, Br, and REE in calcrete; (ii) depletion of middle REE in the upper levels, particularly Eu, and enrichment of middle REE and heavy REE in calcrete; and (iii) Hf, Zr, Cr, Th, Cs, Ta, Ga, Rb, and K appear to be retained in the upper levels, where calcite has been dissolved. Here iron is more reduced. Fe<sup>3+</sup> occurs in iron oxides (goethite and hematite), and clay minerals. The ratio goethite/hematite appears to increase down the profile; and  $Fe^{2+}$  is mainly present in clay minerals. © 2011 Elsevier B.V. All rights reserved.

#### 1. Introduction

Calcretes occur in arid and semi-arid regions, and are near surface, terrestrial, accumulations of fine-grained low magnesium calcium carbonate, having formed within the meteoric vadose zone by pedogenetic alteration and replacement of the host material. Calcrete occurs in a variety of forms from powdery to nodular to highly indurated. Biological influences are commonly found. In fact, the evaporation of the soil solution or the biological influence induces the precipitation of pedogenetic carbonates at or near the soil surface (Bellanca and Neri, 1993; Blümel, 1982; Milnes, 1992; Paquet and Ruellan, 1997; Phillips et al., 1987; Salomon and Pomel, 1997).

Carbonates dissolve upon rainfall until secondary precipitation by increased pH and  $pCO_2$  levels. In general the secondary carbonates overgrow primary ones and precipitate as coating or concretions or may form cemented horizons (Arakaki and Mucci, 1995; Bellanca and Neri, 1993; Reheis et al., 1992; Shankar and Achyuthan, 2007; West et al., 1988). Several studies including the distribution of rare earth elements (REE) and other trace and major elements associated with calcretes in present-day and paleoenvironments have been reported (Compton et al., 2003; Grevenitz, 2006; Kamppunzu et al., 2007; Mumm and Reith, 2007; Ramakríshnan and Tiwari, 1998; Singh et al., 2009; Wagner et al., 2010; Young and Caldwell, 2009).

The El Melah lagoon is a coastal, exoreic lagoon (200 ha) located near the Slimene town (NE Tunisia) under a semi-arid, Mediterranean climate. This lagoon is elongated in a W–E direction and presents an artificial connection with the Tunis Gulf, crossing a littoral dune strand (Fig. 1-I). Four main geomorphologic units may be distinguished: a)



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Fig. 1. I) El Melah lagoon area: location of the calcrete profile (square); 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–nodular horizon; D–sub-surface horizon (25–50 cm depth); and S–surface horizon (0–25 cm depth).

the littoral dune strand, with a small mean height (5 m); b) El Melah lagoon, with permanent waters; c) the littoral plain, formed by old dunes and marshes; and d) the consolidated dune strand of Slimene, extending from Borj-Cédria (western sector) to Jebel Korbous (northeastern sector). Both this scenario, drawn by a multidisciplinary analysis of the El Melah lagoon coastal environment, and the recent (1948–1996) evolution observed by aerial photos, strongly suggest a future evolution towards a sabkha (Prudêncio et al., 2007; Ruiz et al., 2006), i.e., a coastal flat area between a desert and an ocean, characterized by a crusty surface consisting of evaporite-salt, tidalflood and eolian deposits. 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 (Prudêncio et al. 2007, 2010a, Ruiz et al., 2006).

In this study we investigated the geochemistry, mineralogy and micropaleontology of a weathering profile. The profile has developed on the top of a small hill formed by a calcareous consolidated dune, where pedogenic calcretes occur as discrete horizons (both nodular and laminar-structured). This profile is located in the central part of the El Melah lagoon area where a small hill of the consolidated dune strand of Slimene occurs. The use of the term "pedogenic calcrete profile" in this work refers to a set of related calcic horizons within the soil profile, as well as the bottom of the profile (old dune) and the superficial levels. Surface and sub-surface soils of this profile were included in a previous study (Prudêncio et al., 2010a). Preliminary results of this Slimene profile were already presented by Prudêncio et al. (2010b). Chemical and mineralogical analyses of samples from all levels of the profile (bulk samples and  $<2\,\mu m$  fraction) were performed by instrumental neutron activation analysis and X-ray diffraction. The chemical contents of Na, K, Mn, Fe, Sc, Cr, Co, Zn, Ga, As, Br, Rb, Zr, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Dy, Tb, Yb, Lu, Hf, Ta, Th and U, were obtained. Detailed iron studies were done by Mössbauer spectroscopy.

Special attention is paid to the REE behavior in this semi-arid environment. Besides REE, the behavior of all the other elements obtained by INAA is also discussed. According to Ramakríshnan and Tiwari (1998), REE can be fractionated and mobilized within the calcrete profiles developed under semi-arid conditions in the Thar Desert, India. The variation in REE concentrations of soil profiles and evaporite salt pan sediments from a small granite catchment in a semi-arid climate (South Africa) was studied by Compton et al. (2003). They found that the light REE (LREE) are generally retained by clayey and amorphous Fe-oxide-rich soils and sediments, whereas heavy REE (HREE) are retained by precipitation of soil and pan carbonates. Prudêncio (1993) already found that an enrichment of the HREE relative to the LREE occurs in meteoric secondary calcites filling vacuoles and fissures when compared with the surrounding basaltic rocks from the Lisbon Volcanic Complex (Portugal), and particularly in Budens basalt from Algarve (south of Portugal) where a higher aridity index exists. Besides a positive Eu anomaly and a negative Ce anomaly were also found, explained by the incorporation of  $Eu^{2+}$  in calcite after the breakdown of primary minerals like feldspars, and the retention of Ce<sup>4+</sup> after the oxidation of Ce<sup>3+</sup> released by primary hosts like apatite, and before the calcite precipitation. An enrichment of REE, with a particular strong concentration of middle REE (MREE), was also found in a resistant carbonate-rich zone (cornstone) on the Dalradian paleosurface, explained as a result of leaching from the country rocks by groundwater, followed by evaporate concentration (Young and Caldwell, 2009).

The objectives of this paper were to investigate: (1) the chemical and mineralogical characterizations of the several horizons of the calcrete profile developed on a coastal old dune of NE Tunisia, Slimene; and (2) the redistribution of REE and other trace and major elements, during the superficial processes associated with calcrete formation, particularly dissolution of carbonates and precipitation in the vadose zone in this semi-arid environment.

#### 2. Materials and methods

The vertical sequence of the Slimene profile with sampled levels shows clear zonations from the top to the bottom (Fig. 1-II): a reddish-brown modern soil at the land surface, appr. 25 cm thick (S); a sub-surface reddish horizon at 25–50 cm depth (D); a nodular horizon up to 1 m thick (C) comprising subrounded calcrete clasts in a terrigenous yellowish matrix; a laminar-structured calcrete up to 30 cm thick (B); and the consolidated dune (A). The samples reference and description are given in Table 1.

Samples were sieved into fractions  ${<}2$  mm and ground. Nodules and laminar calcrete were finely ground. The  ${<}2\,\mu m$  fraction was obtained by wet sieving and sedimentation according to Stokes law.

Total amounts 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 determined by instrumental neutron activation analysis (INAA). Relative precision and accuracy were in general less than 5%, and

#### Table 1

Sample reference, description, and mineral composition of the pedogenic calcrete profile of Slimene (NE Tunisia) (semi-quantification in% for the whole sample; and minerals present in the <2  $\mu$ m 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						${<}2\mu m$ fraction
		Qz	Phyl	Plg	KFs	Ca	Hem	
S	Surface (0–25 cm)	68	16	3	-	12	<1	K, I, C, Ca, Qz, Gy
D	Sub-surface (25-50 cm)	70	10	<1	2	17	<1	K, I, C, Ca, Qz, Gy
С	Terrigenous matrix of level C	46	8	<1	7	38	<1	K, I, C, Sm, Qz
CN	Nodules of level C	39	-	-	<1	60	-	I, K, C, Qz, G (*)
В	Laminar calcrete	44	-	-	1	55	-	I, K, C, Qz, G (*)
A	Old dune (parent rock)	49	-	<1	2	48	-	K, Ca, Qz

occasionally less than 10%. For INAA, aliquots of about 1 g of samples were then dried in an oven at 110 °C for 24 h and stored in a desiccator until the samples could be weighed for irradiation. The same procedure was carried out for soils GSS-4 and GSS-5 from the Institute of Geophysical and Geochemical Prospecting (IGGE) as reference materials. The reference values were taken from data tabulated by Govindaraju (1994).

The powdered samples and standards were prepared by weighing 200–300 mg of powder into cleaned high-density polyethylene vials. Irradiations were performed in the core grid of the Portuguese Research Reactor at a thermal flux of  $3.34 \times 10^{12}$  n cm<sup>-2</sup>s<sup>-1</sup>;  $\phi_{epi}/\phi_{th} = 1.4\%$ ;  $\phi_{th}/\phi_{fast} = 12.1$ . Two  $\gamma$ -ray spectrometers were used: (1) one consisting of a 150 cm<sup>3</sup> coaxial Ge detector connected through a Canberra 2020 amplifier to an Accuspec B (Canberra) multichannel analyser. This system had a FWHM of 1.9 keV at 1.33 MeV; and (2) the other consisting of a low energy photon detector (LEPD) connected through a Canberra 2020 amplifier to an Accuspec B (Canberra) multichannel analyser. This system had a FWHM of 300 eV at 5.9 keV and of 550 eV at 122 keV.

The spectra were processed by using the programs GELI and DAISY, adapted respectively from GELIAN and OLIVE programs (Op de Beek, 1972, 1974). Corrections for the spectral interference from uranium fission products in the determination of barium, rare earths and zirconium were done (Gouveia et al., 1987; Martinho et al., 1991). More details of the analytical method were published elsewhere (Gouveia and Prudêncio, 2000; Prudêncio et al., 1986).

Mineralogical analysis of the whole sample was performed by X-ray diffraction (XRD) of non-oriented aggregate powders using a Philips diffractometer, CuK $\alpha$  radiation at 45 kV and 40 mA, a step size of 1° 2 $\theta$ /min from 2 to 70° 2 $\theta$ . For the semi-quantification of the clay minerals oriented aggregates were prepared and submitted to the following treatments: air drying, ethylene glycol solvation, and heating (550 °C), before analysis, using the same apparatus from 2 to 30° 2 $\theta$ . Mineral proportions were determined by semi-quantitative XRD diagnosis of peak areas, according to procedures proposed by Schultz (1964) and Rocha (1993).

Mössbauer spectra were collected at room temperature and at 10 K in transmission mode using a conventional constant-acceleration spectrometer and a 25 mCi <sup>57</sup>Co source in a Rh matrix. The velocity scale was calibrated using  $\alpha$ -Fe foil. The absorbers were obtained by pressing the powdered samples (5 mg of natural Fe/cm<sup>2</sup>) into perspex holders. In order to avoid texture effects, the radiation was allowed to pass through the absorbers at an angle of 54.7° to the packing direction (Ericsson and Wäppling, 1976). Low-temperature spectra were collected using a liquid-helium flow cryostat. The spectra were fitted to Lorentzian lines using a non-linear least-squares method (Waerenborgh et al., 1990); isomer shifts, IS, are given relative to

metallic  $\alpha$ -Fe at room temperature. The relative areas and line widths of each peak in a quadrupole doublet were constrained to remain equal during the refinement procedure, as expected for samples with no texture effects.

A micropaleontology study of the several samples of the profile was done, with the taxonomical determination of ostracode species. For this purpose, a fixed quantity (15 g dry weight) was sieved through a 63 µm mesh. If possible, 500 individuals were picked from each sample, with an extrapolation to the whole sample. This number clearly exceeds the required number of individuals (300) for the statistical analysis of the ostracode assemblages (e.g., Ruiz et al., 1997).

# 3. Results

#### 3.1. Ecology

Microfauna 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)microfauna is limited to very rare specimens of marine foraminifers (Ammonia beccarii); (iii) laminar-structure (level B)-microfauna is covered by a coarse calcareous sheet that hinders the taxonomical determination of numerous specimens. Nevertheless, all individuals belong to marine species of foraminifers (A. 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 (A. beccarii, Ammonia tepida, Quinqueloculina spp.), and rounded fragments of spines of echinoderms, briozoos remains and undifferentiated fragments of bivalves were found. These results point to a long term aerial exposure of the old dune.

# 3.2. Mineralogy

Concerning the mineralogical composition obtained by XRD, the old dune (parent rock) is mainly composed of calcite and quartz in similar amounts. Small amounts of K-feldspars and traces of plagioclase were also found (Table 1). In the nodular and laminar calcrete calcite/quartz ratios are 1.54 and 1.25, respectively. Feldspars and phyllosilicates are found in the terrigenous matrix of the nodular calcrete horizon, together with a lower amount of calcite relative to the original material. Calcite increases while phyllosilicates decrease towards the bottom of the profile. While larger amounts of plagioclase occur at the surface, K-feldspars are absent and increase with depth. The reddish color of upper levels is explained by an ubiquitous presence of hematite.

Kaolinite is the solely clay mineral in the old dune while illite and chlorite also occur in any other place, including calcrete. Furthermore smectite occurs in the terrigenous matrix of the nodular horizon (C). Goethite was identified in calcrete samples. Calcite and gypsum are found in surface and sub-surface horizons (S and D).

#### 3.3. Geochemistry

The elemental composition obtained for the whole samples of all levels of the weathering profile (S, D, C, CN, B and A), and the respective  $<2 \mu m$  fractions for samples S, D, C and A are given in Table 2.

Variations with depth of the chemical contents in the whole sample showed that upper levels (S and D, see Fig. 1) have higher contents of the elements studied (Table 2). Exceptions were found for: (i) Co in the laminar calcrete (sample B), (ii) As in the terrigenous matrix of the nodular horizon (sample C) and in the old dune (sample A), (iii) Br in the terrigenous matrix of the nodular horizon (sample C) and solve the sample A).

## Table 2

Chemical results obtained by INAA of the whole sample and <2 µm fraction of the different levels of the pedogenic calcrete profile of Slimene (NE Tunisia). Major elements are expressed in% oxide and trace elements in µg/g.

	Whole sample							<2 µm fraction				
	S	D	С	CN	В	А	S	D	С	А		
Na <sub>2</sub> O	0.130	0.130	0.130	0.0645	0.0770	0.0880	0.217	0.194	0.130	0.110		
K <sub>2</sub> O	0.600	0.550	0.390	0.208	0.180	0.220	2.79	2.37	1.04	0.224		
MnO	0.0236	0.0210	0.0134	0.0143	0.0097	0.0151	0.135	0.0866	0.0382	0.029		
Fe <sub>2</sub> O <sub>3</sub> T	1.52	1.52	1.28	0.722	0.670	0.900	9.79	9.53	4.49	1.37		
Sc	3.35	3.33	2.82	1.62	1.52	1.94	22.9	23.0	9.97	2.28		
Cr	20.4	20.6	17.1	8.82	9.04	8.64	129	130	65.6	17.9		
Со	3.56	3.76	3.13	2.24	5.12	2.24	25.3	20.6	12.2	8.01		
Zn	24.6	22.6	21.0	18.2	12.1	15.6	192	166	93.7	73.8		
Ga	3.18	3.04	3.02	0.587	0.840	0.640	24.6	24.3	11.9	2.70		
As	9.46	9.68	9.92	7.84	7.42	10.4	55.7	60.2	28.0	18.9		
Br	11.0	13.4	21.5	7.48	24.2	9.00	50.5	62.6	58.9	32.0		
Rb	18.7	18.4	12.6	5.16	5.30	6.50	113	100	44.3	8.82		
Zr	79.0	100.8	56.6	34.2	38.8	34.0	155	148	61.0	22.0		
Sb	0.310	0.220	0.290	0.193	0.190	0.200	1.56	1.43	0.604	0.367		
Cs	0.98	1.02	0.85	0.266	0.28	0.37	7.60	7.65	4.03	0.888		
Ba	88.4	86.3	71.2	53.7	47.7	59.9	226	240	96.5	99.5		
La	10.7	10.6	8.51	5.10	4.63	5.57	59.0	51.3	23.3	7.37		
Ce	21.2	20.9	16.7	10.1	9.60	11.2	124	98.5	45.9	18.4		
Nd	10.6	10.3	8.26	5.36	5.17	6.39	58.3	51.5	23.2	8.50		
Sm	1.92	1.89	1.61	1.13	0.980	1.20	10.8	9.41	4.39	1.84		
Eu	0.41	0.43	0.36	0.258	0.23	0.29	2.40	2.19	0.969	0.422		
Tb	0.280	0.290	0.230	0.150	0.134	0.165	1.38	1.19	0.552	0.212		
Dy	1.55	1.62	1.32	0.920	0.792	0.99	8.37	7.95	3.68	1.52		
Yb	0.713	0.700	0.630	0.394	0.342	0.411	4.19	3.67	1.65	0.536		
Lu	0.110	0.110	0.0970	0.0579	0.0500	0.0600	0.548	0.533	0.243	0.0865		
Hf	2.46	2.79	1.57	0.909	1.16	1.03	3.76	3.37	1.45	0.530		
Ta	0.300	0.260	0.190	0.0965	0.0720	0.0820	1.65	1.35	0.661	0.0981		
Th	2.33	2.26	1.90	0.865	0.81	1.01	14.5	12.6	5.84	1.63		
U	0.490	0.380	0.480	0.359	0.350	0.270	1.88	1.55	1.00	0.321		

C), and in the laminar calcrete (sample B), and (iv) Sb and U in the terrigenous matrix of the nodular horizon (sample C). Compared with the old dune (A), calcrete (both nodular and laminar-structured) shows lower contents of Na, Fe, Sc, As, Ba, REE and Th, and higher contents of U. The laminar calcrete has also higher contents of Co and Br, and lower contents of Ba than the original material; and the nodular calcrete presents higher Zn concentration.

The REE patterns of the whole samples relative to chondrites are shown in Fig. 2 (chondrites values of Anders and Grevesse, 1989,





Fig. 2. Chondrite-normalized REE patterns of the whole samples of the Slimene pedogenic calcrete profile (chondrites values of Anders and Grevesse, 1989, multiplied by 1.36, obtained by Korotev, 1996a,b). A–old dune; B–laminar-structured level; C–nodular horizon; CN–carbonated nodules of level C; D–sub-surface horizon (25–50 cm depth); and S–surface horizon (0–25 cm depth).



**Fig. 3.** REE patterns of the whole samples relative to the parent rock (old dune) of the Slimene pedogenic calcrete profile (see titles in Fig. 2).

with slightly higher contents. There is a general decrease of the negative Eu anomaly degree from the top to the bottom. The differences found are enhanced in Fig. 3 where samples are compared with the old dune: (i) higher contents of all REE in samples S, D and C; (ii) lower contents in calcrete; (iii) lower MREE/LREE and HREE/LREE ratios in the upper levels (S,D); (iv) the terrigenous matrix of the nodular horizon (C) presents a higher HREE/LREE ratio than in upper levels; and (v) higher MREE/LREE and HREE/LREE ratios are found in calcrete samples, particularly in the nodular one (CN). In Fig. 4 the variations with depth of several REE parameters are shown. From the top of the profile to the bottom there is: (a) a decrease of the LREE relative to the HREE and also of the LREE relative to the MREE. The nodular calcrete has the lower (La/Yb)<sub>ch</sub> and (La/Sm)<sub>ch</sub> ratios; (b) a decrease of the negative Eu anomaly indicating a preferential loss of Eu in the upper levels and preferential retention below; (c) a general increase of the negative Ce anomaly degree, except the laminar calcrete where the highest Ce/Ce\* was found.

In order to evaluate the enrichment and depletions with depth of the elements, their absolute concentrations were normalized to Sc (conservative element, Dias and Prudêncio, 2008). This procedure clearly showed that significantly higher element/Sc values were found for: (i) U, MREE and HREE in both nodular and laminar calcrete; (ii) Co and Br in the laminar-structured; and (iii) Zn in the nodular one. The extent of variation by using chemical elements normalized to Sc has been estimated considering the old dune (A) as the reference sample (Enrichment factor  $x = [X/Sc]_{sample}/[X/Sc]_A$ ) (Figs. 5 and 6). Significant enrichments factors (EF) were found for Co and Br in the laminar



**Fig. 5.** Sc-normalized values of chemical elements of the whole samples relative to the parent rock (old dune) of the Slimene pedogenic calcrete profile (refer to Fig. 2 for abbreviations).

calcrete and Ga in the surface and sub-surface levels, as well as in the terrigenous matrix of the nodular horizon (EF>2.5). Enrichments of K, Cr, Ga, Zr, Hf, and Ta were found in all samples/levels of the profile. Thorium is more enriched in the upper levels (not in the calcrete) and



Fig. 4. Changes in REE ratios with depth in the Slimene pedogenic calcrete profile (refer to Fig. 2 for abbreviations).



**Fig. 6.** Sc-normalized values of REE of the whole samples relative to the parent rock (old dune) of the Slimene pedogenic calcrete profile (refer to Fig.2 for abbreviations).

uranium is enriched in the calcrete. Rubidium and cesium are enriched in the upper levels (S, D and C). A general depletion in Fe and As also occurs. Concerning the REE (Fig. 6) a depletion of the MREE, particularly Eu, in the surface level and also in the sub-surface and terrigenous matrix of the nodular horizon occurs, along with a relative enrichment in the calcrete. Also a more significant enrichment of the HREE occurs in the calcrete, whereas LREE (particularly La and Ce) are more enriched in the surface and sub-surface levels (S and D). Neodymium reveals a behavior more similar to other MREE than to La and Ce.

The elements studied are in general concentrated in the  $<2 \mu m$  fraction of samples S, D, C and A, when compared with the respective whole sample (Fig. 7). However some differences were found: (i) the upper levels (S and D) present a similar geochemical pattern, with more than 4x the contents found in the whole sample, except for Na, Zr, Ba and Hf. Nevertheless these elements are more concentrated than in the whole sample; (ii) the terrigenous matrix of the nodular horizon (sample C) has a similar pattern, but with a generally smaller degree of concentration; (iii) the  $<2 \mu m$  fraction of the old dune (parent rock) presents a different pattern (Fig. 7) with less pronounced K enrichment, and Co, Zn, Ga, and Br are the most concentrated elements (~4×); Zr and Hf contents are lower than in the whole sample. Concerning the REE the whole sample-normalized patterns (Fig. 8) show that (i) REE are concentrated in the clay



Fig. 7. The ratio of elemental composition in the clay fraction versus the composition of the whole soil in the Slimene pedogenic calcrete profile (refer to Fig. 2 for abbreviations).



**Fig. 8.** REE patterns of the clay fraction relative to the respective whole sample of the Slimene pedogenic calcrete profile (see titles in Fig. 7).

fraction, decreasing with depth; (ii) there is a small positive Ce anomaly in the upper level (S) and a small negative Ce anomaly in the sub-surface (D); and (iii) a positive Ce anomaly exists in the  $<\!2\,\mu m$  fraction of the old dune.

# 3.4. Iron crystal chemistry in samples S, D and C

The variation with depth of the total iron content and the Fe/Sc ratio are shown in Fig. 9. The calcrete has the lowest Fe values. Higher contents of iron were found in the upper levels—S, D and C (Table 2). After Sc normalizing, subtle differences were found in these levels of the profile. Fe/Sc ratio increases with depth from S to D, and decreases down to the terrigenous matrix of the nodular horizon. The Fe content of the clay fraction follows the same trend observed for the whole samples. This is not surprising since the difference in mineral composition between whole samples and the corresponding clay fractions (Table 1) is essentially due to the presence of large quartz and feldspar grains, phases which only contain trace amounts of Fe.

Mössbauer spectra were obtained for the clay fraction of the Ferichest S, D and C samples. These spectra are typical of soil samples. The spectra taken at room temperature consist of three resolved absorption peaks (Fig. 10) which may be fitted by two quadrupole doublets with parameters typical of high-spin Fe<sup>3+</sup> and Fe<sup>2+</sup>. The doublet with lower isomer shift, IS, and quadrupole splitting, QS, is due to Fe<sup>3+</sup> incorporated in the structure of silicates and of fine-particle Fe<sup>3+</sup> oxide/hydroxides that have superparamagnetic behavior at room temperature. The doublet with higher IS and QS is attributed to Fe<sup>2+</sup> incorporated in the structure of phyllosilicates. In the present spectra there is no evidence of a quadrupole doublet with parameters typical of Fe<sup>2+</sup> in carbonates as observed in soil samples from the same area (Prudêncio et al., 2010a).

Low-temperature spectra (Fig. 10 and Table 3) confirm that a significant fraction of the Fe<sup>3+</sup> is incorporated in small particle size Fe oxide/hydroxides that have a superparamagnetic behavior at room temperature. Characteristic magnetic interactions of hematite and goethite (Vandenberghe et al., 2000) may be observed in the spectra taken at 10 K. The remaining contributions to the spectra are fully consistent with room temperature data.

In summary, the investigation of the iron crystal chemistry 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<sup>3+</sup> occurs in iron oxides (goethite and hematite), and clay minerals. The ratio goethite/hematite appears to increase with depth; and (c) Fe<sup>2+</sup> is mainly present in clay minerals.



Fig. 9. Changes in Fe<sub>2</sub>O<sub>3</sub> with depth (absolute contents and Sc-normalized) in the weathering profile of Slimene (NE Tunisia). See Table 1 for references (sample C is plotted above the nodular calcrete for comparative reasons with the laminar calcrete).

#### 4. Discussion and conclusions

The micropaleontological results obtained for the several levels of the weathering profile confirm that the old dune has been emerged for a long period of time within the El Melah lagoon area. Marine species fragments are found in the old dune. Furthermore broken parts of marine foraminifera specimens are still present in the nodular and laminar calcrete, preserved in some cases by coarse calcareous material. In the upper levels (S and D), the absence of marine species fragments certainly reflects dissolution, and terrestrial species (gastropodes) dominate.

The mineralogical variations found with depth in the studied profile indicate carbonate dissolution at the surface and downward leaching of calcium. Secondary carbonates then precipitate deeper where pH and  $pCO_2$  increase and carbonate saturation is reached. Secondary carbonates overgrow primary ones and precipitate as coating or concretions in the nodular horizon forming laminar



**Fig. 10.** Mössbauer spectra taken at different temperatures of the clay fraction of D sample. The lines over the experimental points are the sum of quadrupole doublets, and at 10 K of sextets, shown slightly shifted for clarity. The estimated parameters are collected in Table 3.

structures below. Minerals found in the upper levels correspond to original materials of the old dune and also weathering phases and atmospheric inputs. Authigenic smectite formation occurs above the laminar-structured calcrete due to restricted drainage conditions.

Despite the low total uranium contents found in the Slimene weathering profile, it is possible to conclude that uranium is enriched in the calcrete showing a behavior similar to that reported for Australian, Namibia and South Africa arid zones (Carlisle, 1983). The total uranium contents variation with depth (Fig. 11) may be explained as follows: in carbonated water U is transported as the extremely soluble uranyl dicarbonate and tricarbonate complex ions. Removal of CO<sub>2</sub> decreases the solubility of CaCO<sub>3</sub> and increases pH. Evaporite formation or co-precipitation of carbonate with uranium vanadate may result in precipitation of carnotite along with carbonates in calcrete. The occurrence of trace amounts of uranyl in natural calcite has posed a long-standing problem in crystal chemistry because of speculation that the size and shape of the uranyl ion may preclude its incorporation in a stable lattice position in calcite. This also defines an important environmental problem because of its bearing on the transport and sequestration of uranyl released from nuclear facilities and uranium mining operations. The results obtained by Kelly et al. (2003) indicate substitution of uranyl for a calcium and two adjacent carbonate ions in calcite. These new data imply that uranyl has a stable lattice position in natural calcite, indicating that it may be reliably sequestered in calcite over long time scales. Thus even carnotite does not precipitate along with carbonates in Slimene calcrete, uranyl may have been incorporated in secondary calcite of both nodular and laminar-strucured calcrete explaining the enrichment.

The variations with depth of Co and Br in calcrete (Fig. 11) may be explained as follows: calcite precipitation requires high pH values (often >9), favoring the uptake of  $Co^{2+}$  in calcite (Cheng et al., 2000; Xu et al., 1996); Br/Sc distribution suggests a biological role in carbonate precipitation.

A general enrichment of Fe and As from the top to the bottom of the profile also occurs. Zinc also generally increases except in the nodular calcrete, where a significant enrichment occurs which may be explained by (i) a first retention of Zn by authigenic smectite formed in the level C, as already found by Marques (2007); and (ii) then fixed in the calcrete nodules.

The downward depletion of K, Rb and Cs is certainly related to the higher proportion of phyllosilicates, and also of feldspars in the terrigenous materials (S, D and C). It should be noted that the increase of these elements and minerals is due to a decrease in calcite

Table 3

Estimated parameters from the Mössbauer spectra of the clay fraction of samples of the pedogenic calcrete profile of Slimene (NE Tunisia), taken at different temperatures T.

Sample	Depth (cm)	Т		IS, mm/s	QS, ε, mm/s	B <sub>hf</sub> , tesla	Γ, mm/s	Ι
S	0-25	295 K	Fe <sup>3+</sup>	0.36	0.61	-	0.55	91%
			Fe <sup>2+</sup> clay minerals	1.12	2.73		0.39	9%
D	25-50	295 K	Fe <sup>3+</sup>	0.35	0.61	-	0.51	96%
			Fe <sup>2+</sup> clay minerals	1.11	2.71	-	0.28	4%
	25-50	10 K	Fe <sup>3+</sup>	0.48	0.64	-	0.64	45%
			Fe <sup>2+</sup> clay minerals	1.27	2.95	-	0.30	4%
			hematite	0.50	-0.21	53.3	0.28	6%
			goethite	0.48	-0.26	48.9	0.47	45%
С	50-75	295 K	Fe <sup>3+</sup>	0.36	0.60	-	0.53	95%
			Fe <sup>2+</sup> clay minerals	1.11	2.71	-	0.27	5%
	50-75	10 K	Fe <sup>3+</sup>	0.47	0.66	-	0.70	41%
			Fe <sup>2+</sup> clay minerals	1.23	2.98	-	0.31	3%
			hematite	0.49	-0.21	53.0	0.30	3%
			goethite	0.50	-0.26	48.3	0.76	53%

IS (mm/s) isomer shift relative to metallic α-Fe at 295 K; QS (mm/s) quadrupole splitting.  $\varepsilon = (e^2 V_{zz}Q/4) (3\cos^2\theta - 1) (mm/s)$  quadrupole shift estimated for the sextets. B<sub>hf</sub> (tesla) magnetic hyperfine field;  $\Gamma$  (mm/s) line-width; I relative area. Estimated errors  $\leq 0.02$  mm/s for IS, QS,  $\varepsilon$ ,  $\Gamma$ , <0.2 T for B<sub>hf</sub> and <2% for I.

proportions (see the downward decrease of quartz proportion given in Table 1). Gallium is also enriched in the surface and sub-surface levels (S and D), as well as in the terrigenous matrix of the nodular horizon, due to the incorporation of  $Ga^{3+}$  in the clay minerals structure substituting  $Al^{3+}$ as already suggested by Prudêncio et al. (2010a). Enrichments of Ga in the clay sized fraction of sediments were already found by Marques (2007). The significant decrease of Ta with depth also suggests that a significant fraction of this element may be incorporated in phyllosilicates, particularly micas. Different generations of micas, both primary and secondary, associated with Ta oxides have been studied by Van Lichtervelde et al. (2008).

Zirconium and hafnium decrease with depth suggesting that these elements are present mainly in zircon and an associated decrease of quartz and carbonate dissolution at the surface and sub-surface levels. Thorium is also depleted with depth, which can be due to its preferential presence in heavy resistant minerals in upper levels.

By comparison of the REE contents of the whole samples in the weathering profile with the parent rock (Fig. 3), they are found to be more common in surface levels (S, D and C). However they do not appear to be retained in the same way. After normalizing with Sc, REE variations with depth can be evaluated (Figs. 6 and 12): (a) there is an enrichment of LREE (La and Ce) especially in the upper levels which can be explained by their sorption into clay minerals and iron oxides;

(b) a strong loss of MREE in the upper levels certainly related to carbonate dissolution and breakdown of other original materials. A stronger Eu loss occurs corresponding to its release after the breakdown of feldspars; the HREE are more retained than the MREE in the upper levels due to their partial presence in heavy minerals like zircon; (c) all REE are enriched in the nodular and laminar-structured calcrete particularly the MREE and HREE; (d) there is a tendency for relative Ce depletion with depth, except the laminar calcrete level where a lower negative Ce anomaly occurs (Fig. 4); (e) a less distinct negative Eu anomaly from the top to the bottom of the profile, indicating a preferential retention of Eu (as Eu<sup>2+</sup>) by secondary carbonates in the calcrete after the breakdown of primary minerals like feldspars. This hypothesis is in agreement with (i) the existence of a small positive Eu anomaly in the  $<2 \mu m$  fraction/whole sample of the surface and sub-surface levels (S and D) where calcite was identified by XRD; and (ii) the  $<2 \mu m$  fraction of the terrigenous matrix of the nodular horizon, with an absence of calcite and no significant Eu anomaly (Fig. 8 and Table 1).

Thus the variation of REE with depth may be explained as following: during the dissolution/breakdown of primary minerals like carbonates and feldspars in the upper levels REE are partially released; sorption into clay minerals and iron oxides of LREE (La and Ce) may occur; the fraction of HREE present in heavy minerals like



Fig. 11. Changes of the Co/Sc, U/Sc and Br/Sc ratios with depth in the Slimene pedogenic calcrete profile (refer to Fig. 2 for abbreviations).



Fig. 12. Variation of the Sc-normalized REE profiles with depth in the Slimene pedogenic calcrete profile (refer to Fig. 2 for abbreviations).

zircon remains in the upper levels; MREE and part of the HREE migrate downwards and are incorporated in pedogenic calcite in calcrete.

Concerning the other chemical elements studied, the differences found between the geochemical pattern of the <2 µm fraction of the parent rock and the upper levels appears to be related to the clay minerals present, since higher K, Fe, Sc and Cr contents are found in upper levels where illite and chlorite also occur (Table 1). Clay minerals and iron oxides are the main carriers of these elements in the <2 µm fraction. As shown for surface and sub-surface levels (S, D) and the terrigenous matrix (C) of the nodular level, Fe is more reduced in the upper level indicating that it is leached as Fe<sup>2+</sup>. Fe<sup>3+</sup> occurs in iron oxides (goethite and hematite) and clay minerals. The occurrence of iron in hematite and goethite in pedogenic calcrete in southern

Australia was also found by Grevenitz (2006). The goethite/hematite ratio appears to increase with depth; and  $Fe^{2+}$  is mainly present in clay minerals. Manganese has a different behavior, probably present mainly as Mn oxides.

Thus, microfauna, mineralogical and chemical variations in the Slimene weathering profile point to a long term aerial exposure of the old dune in a semi-arid carbonated environment leading to the development of a pedogenic calcrete profile. Dissolution of both inorganic and organic carbonates occurs in the surface and subsurface levels, and precipitation of secondary calcite occurs down the profile as nodular and laminar-structured in the vadose zone. The most significant chemical variations associated with this process are enrichments of Co, U, Br, and REE, especially MREE and HREE in calcrete.

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