



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 <math><2\ \mu\text{m}</math> 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^{3+} 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.

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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; Ramakrishnan 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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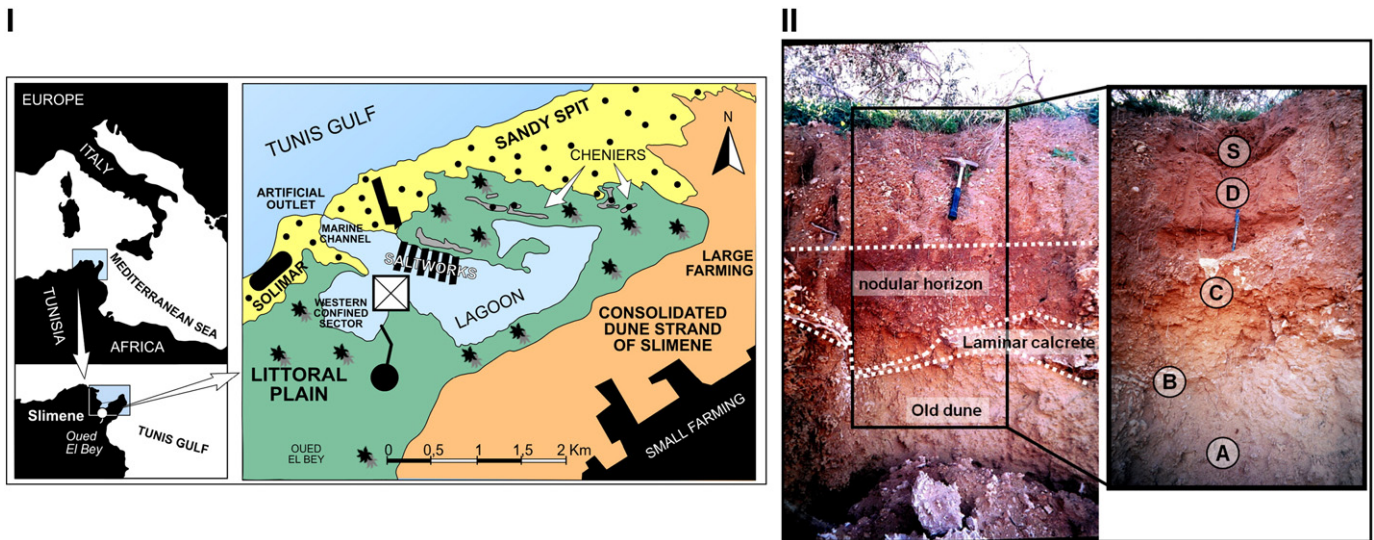


Fig. 1. I) El Melah lagoon area: location of the calcrete profile (square); II) The pedogenic calcrete profile before (left) and after (right) cleaning and sampling with the identification of the sampled levels. A—old dune; B—laminar-structured level; C—nodular horizon; D—sub-surface horizon (25–50 cm 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 Korbus (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, tidal-flood 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 $<2\ \mu\text{m}$ 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 Ramakrishnan 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^{4+} after the oxidation of Ce^{3+} 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 calcite 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 $<2\ \text{mm}$ and ground. Nodules and laminar calcrete were finely ground. The $<2\ \mu\text{m}$ 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

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