SPECTROSCOPIC CHARACTERIZATION OF FERRUGINOUS CEMENTS IN A TEMPERATE BEACHROCK FORMATION CLOSE TO NERBIOI-IBAIZABAL ESTUARY (TUNELBOKA COVE, BAY OF BISCAY).

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Beachrocks are coastal sedimentary formations mainly occurring along equatorial-tropical coasts that result from a relative rapid cementation of beach sediments by the precipitation of carbonate cements. A series of physico-chemical and biologically-induced processes have been invoked to explain such rapid cementation [1-4]. Beachrock cements are usually dominated by $CaCO_3$ polymorphs which rarely are overlied by non continuous iron-rich dark layers [5].

The present work is focused on the occurrence of an unusual temperate setting (43ºN latitude) beachrock located in Tunelboka cove, close to the Nerbioi-Ibaizabal estuary (Bay of Biscay, North of Spain).

A previous research work carried out on the area and in some adjacent beaches which present these lithified structures, revealed the existence of different cement generations (CG) by means of Raman microspectroscopy, SEM-EDX analyses and petrographic descriptions: CG 1 (aragonite, high-magnesium calcite and silicates), CG 2 (aragonite) and CG 3 ($CaCO_3$ polymorphs and iron oxides) [6].

Besides the $CaCO_3$ cements, some iron containing cements enclosing the beach grains were also observed in several lithified outcrops of the Tunelboka cove. The ferruginous cements appeared in two forms: (i) accompaining carbonate cements as discontinuous an non-homogeneous layers and as (ii) uniform an continuous cements between the beach grains. To our knowledge, the second cementing form has not been described previously in beachrock formations in contrast to the (i) cements.

The characterization of the ferruginous cements have been carried out by means of Raman spectroscopy. For that purpose, an InnoRaman® (B&WTEK$_{INC}$) ultramobile spectrometer, equipped with 20x and 50x focusing lens, an excitation wavelength of 785 nm, a CCD detector (Peltier cooled) and BWSpec 3.26_38 software for the data acquisition was used.

First of all, the effect of laser power was studied in order to avoid decomposition/transformation processes of oxides and hydroxyoxides during measurements [7].

The Raman spectra taken in the (i) cements, showed limonite ($FeO(OH)\cdot nH_2O$, with Raman bands at 241w, 298s, 393vs, 478w, 548m), aragonite ($CaCO_3$, 146w, 205m, 705m, 1085vs) and silicates mixtures (1159br, 1258vs, 1365br, 1837br, 1939br). Exporadically mixtures of limonite and quartz (SiO_2, 205m and 465vs) or hematite (α-Fe_2O_3, 225vs, 292vs, 410s, 496m, 611m) and aragonite mixtures were observed as well.

The Raman spectra got in the continuous ferruginous cements (ii), revealed limonite as the main cementing mineral phase. Frecuently, hematite remains were also identified into the limonite cement (Fig. 1). Moreover, traces of other mineral phases such as wüstite (FeO, 459br, 653br), anatase (TiO_2, 147vs, 199w, 398s, 510m, 638s), magnetite (308m and 668vs) and lepidocrocite (γ-FeO(OH), 213m, 246vs, 304m, 344m, 373vs, 523m, 645m) were also identified. It is remarkable that lepidocrocite appeared as a thin layer covering hematite grains, which suggest the superficial transformation of hematite. Indead, hematite is thought to be the main original iron containing mineral coming from a submarine disposal area located 4 miles north of the mouth of the estuary where old steel factories dumped rubble derived from blast furnace during the first half of the XX century.

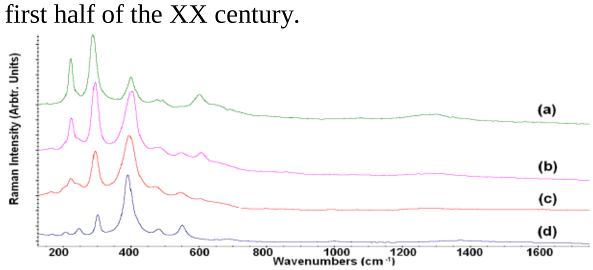

Fig. 1. Raman spectra obtained from the continuous ferruginous cement, (ii). (a) hematite, (b) and (c) different hematite proportions in limonite based cement; (d) limonite.

Taken into account the mineral phases identified by Raman, our hypothesis is that the iron mineral wastes arrived to the beach, cemented and part of them disolved by different mechanisms (including acid aerosols attack) to reprecipitate as limonite.

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