MOLECULAR CHARACTERIZATION OF A TEMPERATE BEACHROCK FORMATION IN THE NERBIOI-IBAIZABAL ESTUARY (ARRIGUNAGA BEACH, BAY OF BISCAY). A. Iturregi<sup>1\*</sup>, N. Arrieta, I. Martínez-Arkarazo, X. Murelaga, J.I. Baceta<sup>2</sup>, A. Sarmiento<sup>3</sup> and J.M. Madariaga. <sup>1</sup> Department of Analytical Chemistry, University of the Basque Country (UPV/EHU), P.O. Box 644, E-48080 Bilbao, Spain. <sup>2</sup> Department of Stratigraphy and Palaeontology, University of the Basque Country (EHU/UPV), P.O. Box 644, E-48080 Bilbao, Spain. <sup>3</sup> Raman-LASPEA laboratory, SGIker, University of the Basque Country (EHU/UPV), P.O. Box 644, E-48080 Bilbao, Spain. \*Tel.: +34 946018298, e-mail address: aiturregui005@ikasle.ehu.es

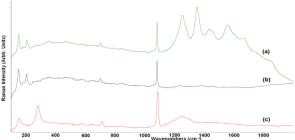
Beachrocks are well-cemented coastal sedimentary formations resulting from the precipitation of carbonate cements in the intertidal zone. The cementing agents of beachrocks are composed predominantly of CaCO<sub>3</sub> polymorphs, high magnesian calcite (HMC) and low magnesian calcite (LMC). Several processes have been described for beachrock cementation, such as, precipitation of carbonates from evaporation of sea water, precipitation from ground water, precipitation in the salt and fresh waters mixing zone and CO<sub>2</sub> degassing from beach ground waters [1-4]. The majority of beachrocks are found predominantly in tropical/subtropical and low latitude coasts (0° - 40° latitude). Nevertheless, there are some evidences of beachrock occurrence at upper latitudes [5]. This work is related to a beachrock formation in Arrigunaga beach (43°21'N-3°1'W) located in the Nerbioi-Ibaizabal Estuary. The purpose of this work was the characterization of the cements of those beachrock outcrops so as to continue a research programme aiming to clarify the processes involved on the cementation of the beaches located in the vicinity of the Estuary.

Different samples were gathered along the beach and classified depending on their relative location in the intertidal zone, distinguishing between high, mid and low intertidal zone. At first instance, the granulometric characterization on the disgregated beachrock samples showed that the majority of the grains belonged to the 250µm and 2mm diameter fractions, although in the hardest (most compacted) samples the amount of the grains corresponding to the diameter less than 75µm was substantially higher. Two raman equipments with different laser wavelengths were used for the molecular characterization: (i) an InnoRaman (B&WTEK<sub>INC</sub>) ultramobile spectrometer, equipped with 20x and 50x focusing lens, an excitation wavelength of 785 nm (nominal laser power 255 mW), a CCD detector (Peltier cooled) and BWSpec 3.26 38 software for data acquisition. (ii) A Renishaw InVia microRaman spectrometer coupled to a DMLM Leica microscope with 5x, 20x, 50x and 100x long-distance lens, a 514 nm as excitation source (nominal laser power 50 mW) and CCD detector (Peltier cooled). Spectra treatment was performed with the Wire 3.2 software (Renishaw, United Kingdom) in both cases.

Researches carried out in an adjacent beach, describe different types of cement generations within the beachrock formations. The first generation was mainly

HMC, followed by aragonite and mixtures of CaCO<sub>3</sub> polymorphs, silicates and iron oxides in high amounts [6]. Nonetheless, the Raman analyses of this work revealed that the vast majority of the cement in the study area is aragonite in the whole intertidal zone. HMC is only occasionally found acting as cement in the low intertidal zone and no evidences of the iron oxide based cements are observed. Concerning to the low intertidal zone, calcite was also found sporadically (Fig. 1). Furthermore, the studied beachrock is less cemented than the outcrops analized in the previous work.

These all differences found regarding the cement generations could be attributed to the location of the beaches; that is, to be situated in the interior or out of the Estuary.



**Figure 1.** Raman spectra of different points in the intertidal zone: (a) HMC appearing occasionally in the low intertidal zone (b) aragonite (mid); (c) aragonite and silicates (mid).

Apparently, the studied beachrock is less cemented than other outcrops analized nearby, so more analyses must be carried through it to understand the processes of beachrock formation in each setting.

References [1] Beier J.A. (1985) J. Sediment. Petrol. 55, 755-761.[2] Russell R.J. (1963) J.Trop.Geogr. 17, 24-27. [3] Hanor J.S. (1978) J. Sediment. Petrol. 48, 489-501.[4] Milliman J.D. (1974) Marine Carbonates, Springer-Verlag, 375 .[5] Kneale D. et al. (2000) Sediment. Geol. 132, 165-170. [6] Arrieta N. et al. (2011) Spectrochim. Acta A. doi:10.1016/j.saa.2011.01.031.

Acknowledgements. This work has been financially supported by the Basque Government through the Environmental Analytical Chemistry Project (ref. IT-245-07). Technical support provided by the Raman-LASPEA laboratory of the SGIker (UPV/EHU, MICINN, GV/EJ, ERDF and ESF) is gratefully acknowledged. N. Arrieta is grateful to the University of the Basque Country (UPV/EHU) for her predoctoral fellowship.