



Short Visit Grant  or Exchange Visit Grant

### Scientific Report

**Proposal Title:** Ocean carbonate chemistry dynamics in the Gulf of Cádiz

**Application Reference N°:** 6688

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#### 1) Purpose of the visit

Measurement of the inorganic carbon system is a key requirement for ocean acidification studies, as it forms the basis for assessments of biogeochemical responses to changes in ocean carbonate chemistry as a result of rising atmospheric CO<sub>2</sub> concentrations.

One of the emerging and alarming issues concerning ocean acidification, due to oceanic uptake of increasing anthropogenic carbon dioxide (CO<sub>2</sub>) and subsequent changes in the concentration of carbonate and bicarbonate ions, are the consequences for marine organisms and ecosystems, particularly for those reliant on the generation and accumulation of calcium carbonate (CaCO<sub>3</sub>), shells, tests, skeletons, and/or structures. Oceanic uptake of CO<sub>2</sub> drives the carbonate system to lower pH and lower saturation states of the carbonate minerals calcite, aragonite, and high-magnesium calcite, the materials used to form supporting skeletal structures in many major groups of marine organisms. A variety of evidence indicates that calcification rates will decrease, and carbonate dissolution rates increase, as CaCO<sub>3</sub> saturation state decreases. The important role of calcification in the global carbon cycle has been increasingly recognized. Furthermore, the uptake of anthropogenic CO<sub>2</sub> by the ocean generates ocean acidification, which has recently been suggested as one of the perhaps most harmful threats to Cold-Water Corals (CWCs) [1].

The Short Visit Grant 6688 “Ocean carbonate chemistry dynamics in the Gulf of Cádiz” within the ESF framework activity entitled “Col-water Carbonate Mounds in shallow and deep time – The European Research Network – COCARDE-ERN” was executed from September 15 to September 25 this Autumn, at the Universidade de Cádiz (UCA), Centro Andaluz de Ciencia y Tecnología Marinas (CATYCMAR), which is part of the Campus de Excelencia Internacional del Mar (CEIMAR).

The first objective of this visit was to develop methodological protocols for seawater chemistry, mainly on pH, and total alkalinity with automated instruments. Additional objectives were to compare recent measurements of seawater chemistry in the Gulf of Cádiz (GoC) with ancillary data to unravel recent changes in calcite and aragonite saturation states; to combine measurements of seawater chemistry and geochemical proxies, to unveil if carbonate precipitation/dissolution are related to the CWC mound system in the shelf of Gulf of Cádiz (GoC).

## 2) Description of the work carried out during the visit

Coastal ocean seawater samples from the GoC were collected at three stations within the Bay of Cádiz, within the GoC, on September 20, 2014 (Figure 1), under the research project "Flujos a la atmosfera de gases con efecto invernadero en el Parque Natural Bahía de Cádiz: interrelación con factores antropicos" (Ref. CTM2011-27891). The Bay of Cádiz is located in the west of the GoC, between 36° 23' to 36° 37' N and 6° 8' to 6° 15' W (Fig. 1). The main water inputs into the inner bay are the tidal exchange with the ocean and a number of smaller creeks and channels that connect to the surrounding salt marshes.



Fig. 1. Map of the northeastern shelf of the GoC showing the location of sampled stations in the shallow coastal ocean: a) Rio Guadalete (RGT); b) Rio San Pedro (RSP), and c) Canal Sancti Petri (CSP).

At each station seawater samples were collected in pre-washed and combusted 300 mL Duran borosilicate glass bottle with ground glass stopper, and fixed with a saturated solution of 100  $\mu$ l mercury chloride ( $\text{HgCl}_2$ ) following the methods outlined in the DOE handbook [2]. The glass stopper was greased (Apiezon) to seal bottles air-tight. Samples were stored in the dark, and analysed for TA within 24 hours back in the laboratory. Prior to TA measurements, seawater samples were filtered with GF/F 47 mm diameter filters.

Measurement of total alkalinity (TA) was done in duplicate using an automated potentiometric titrator “Metrohm Titrando 905 analyzer” coupled with a pH probe and PT-100 temperature probe. Potentiometric titration was carried out in an open cell (nominal value 100 mL) by adding hydrochloric acid ([HCl] 0.1M in 0.7M NaCl) with an automated burette (Metrohm Dosino 800).

This fast potentiometric titration method for TA measurement takes about 8 minutes per sample, thus meeting the time constraints and large sample numbers collected for TA analysis during oceanographic cruises. A Metrohm TiAmo software system connected with the automated titrator was used to follow the titration curve and determine the end point for TA (Figure 2). The method consists in a series of steps including initial measurement of T (°C), pH and Eh (mV), and finally measurement of pH at the end of the titration curve.

The pH was measured with a pH probe (Metrohm) calibrated using the buffer Tris/Tris-HCl (ionic strength 0.7M) on the Total pH Scale with an accuracy of  $\pm 0.003$ . The temperature of the sample was determined using a temperature sensor PT-100, and pH values were subsequently corrected to the in-situ temperature of the seawater samples. The TRIS buffer used to standardize the pH electrode was prepared according to the DOE handbook [2].

In order to check the accuracy of the pH and TA measurements, seawater samples of CO<sub>2</sub> reference material (CRM, batch 128, distributed by A.G. Dickson from Scripps Institution of Oceanography; [http://cdiac.ornl.gov/oceans/Dickson\\_CRM/batches.html](http://cdiac.ornl.gov/oceans/Dickson_CRM/batches.html)) were analysed before, during, and at the end of the analytical sessions.

Based on the measured values of pH (total scale), total alkalinity, temperature, and salinity, we used CO2SYS Software [3] to calculate pCO<sub>2</sub>,  $\Omega$ aragonite, and total DIC using the first and second dissociation constants (K1 and K2) of carbonic acid in seawater from Mehrbach et al. [4], refit by Dickson and Millero [5].

The salinity was measured using a salinometer (Beckman, Mod. RS-10) with an accuracy of  $\pm 0.001$ .

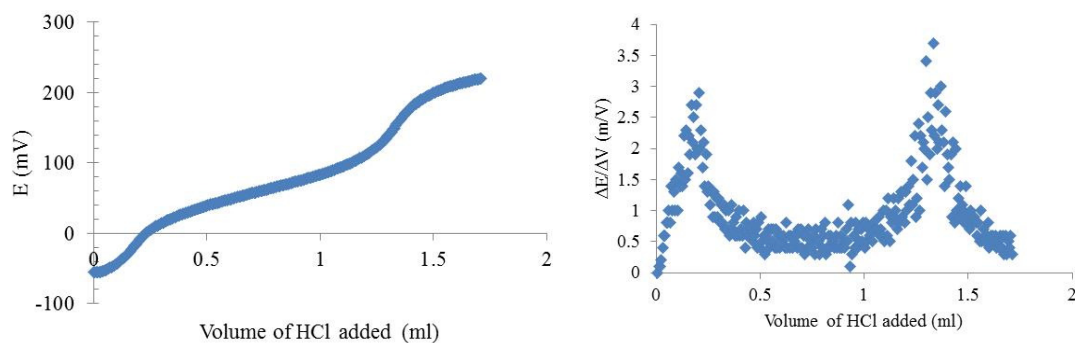


Fig. 2. Typical titration curve when seawater reference material is titrated with HCl 0.1 (CRM Batch 128 distributed by A.G. Dickson from Scripps Institution of Oceanography). EMF of the electrode used for evaluation of the equivalence volumes  $v_1$  and  $v_2$ . TA is proportional to  $v_2$ , and can thus be calculated directly from  $v_2$ .

### 3) Description of the main results obtained

The comparison of data derived from seawater samples at shallow sampling sites, surveyed within this project with respect to pH, total alkalinity (TA), calcite ( $\Omega_c$ ) and aragonite saturation ( $\Omega_a$ ),  $p\text{CO}_2$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$  reveals characteristic patterns (Table 1), which were primarily due to the coastal influence, and addition of freshwater run-off.

Table 1. Salinity, temperature, pH, total alkalinity (AT) measured during the survey of 20<sup>th</sup> September 2014 at 3 sampling areas in the coastal ocean in the GoC. (see Figure 1).

Area	S	T (°C)	pH	TA ( $\mu\text{mol kg}^{-1}$ )	$\Omega_c$	$\Omega_a$	$p\text{CO}_2$	$\text{HCO}_3^-$	$\text{CO}_3^{2-}$
RGT	35.1	24.3	8.15	2399	6.20	4.07	311	1768	258
CSP	36.2	25.3	7.99	2510	5.11	3.38	516	1990	214
RSP	36.4	24.5	8.09	2366	5.62	3.71	364	1786	236

Overall, the analysed samples and additional data from the coastal areas of the GoC [7, 8] plot between AT values of 2,353 and 2,510  $\mu\text{mol kg}^{-1}$ . The lowest value has been recorded at the RSP station (Rio San Pedro), while the highest value has been measured from the CSP station (Canal Sancti Petri). The pH data span between 7.99 and 8.15. The  $p\text{CO}_2$  values of the ambient water masses display large variability in the presented data. The lowest values have been calculated for the Rio Guadalete (RGT station) with 311 ppm while the highest values have been found in the Canal Sancti Petri (CSP station) (516 ppm). The mean value for all sites is 397 ppm. The mean for  $\text{HCO}_3^-$  of all areas is 1,848  $\mu\text{mol kg}^{-1}$ , with the highest values in the Canal Sancti Petri (CSP station) 1,990  $\mu\text{mol kg}^{-1}$  and the lowest value in the Rio Guadalete (RGT station), 1768  $\mu\text{mol kg}^{-1}$ . Finally, the  $\text{CO}_3^{2-}$  content of all samples was calculated. It ranges from 214  $\mu\text{mol kg}^{-1}$  at CSP station (Canal Sancti Petri) and 258  $\mu\text{mol kg}^{-1}$  in the RGT station (Rio Guadalete).

The distribution of inorganic carbon system parameters in the NE shelf of the GoC showed temporal and spatial variability. River input, mixing, primary production, respiration,  $\text{CO}_2$  air–sea exchange, and remineralisation were factors that controlled such distributions [7]. The Bay of Cádiz exhibited a different behaviour, acting as an import of DIC in the early summer and as an export during autumn and winter [8]. Very high concentration gradients have been found between the Rio San Pedro (RSP) and the Bay of Cádiz, which emphasise the role of this tidal creek as intense sources of inorganic carbon to the system [8]. Estuaries are a major boundary in the land-ocean interaction zone where organic carbon (OC) and nutrients are being processed, resulting in a high water-to-air carbon dioxide ( $\text{CO}_2$ ) flux, whereas continental shelves take up  $\text{CO}_2$  from the atmosphere. Several recent articles that reported global estuarine and coastal ocean  $\text{CO}_2$  fluxes concluded that although the global estuarine area is very small, its  $\text{CO}_2$  degassing flux is as large as the  $\text{CO}_2$  uptake by the continental shelf, and that both flux terms are significant in the global  $\text{CO}_2$  flux [9, 10].

Aït-Ameur and Goyet reported that the GoC plays an important role in the anthropogenic carbon sequestration and its storage at depth, thus influencing the biochemical properties of the North Atlantic Ocean waters [11]. The influx of anthropogenic  $\text{CO}_2$  to deep-sea waters is reducing the saturation states for aragonite ( $\Omega_a$ ) and calcite ( $\Omega_c$ ), and this has profound implications for the global distribution of deep-sea corals and other calcifiers.

For aragonite-forming corals the largest changes may occur in the North Atlantic, where the saturation boundary is expected to rise 1–2 km by the year 2100 [12]. Reduced growth rates pattern observed for the single deep-sea coral [13], support the notion that  $\Omega_a$  regulates coral distributions. Values of  $\Omega > 1$  signify supersaturation, and  $\Omega < 1$  signifies undersaturation. Because  $k_{sp}^*$  increases with pressure (the temperature effect is small), there is a transition of the saturation state from  $\Omega > 1$  (calcite-rich) to  $\Omega < 1$  (calcite-depleted) in sediments and seawater with depth.

Calculation of the  $\text{CaCO}_3$  and aragonite saturation state ( $\Omega_c$  and  $\Omega_a$ ) of seawater in the coastal ocean here surveyed (see Figure 1) within the GoC, were made with the program CO2SYS as described above [3] using measurements of AT, pH, temperature and salinity. The  $\Omega_a$  values range from 3.38  $\text{mmol kg}^{-1}$  (Canal Sancti Petri, CSP station) to 4.07  $\text{mmol kg}^{-1}$  at Rio Guadalete (RGT station). The mean of all surveyed sites is 3.72  $\text{mmol kg}^{-1}$ . pH and  $\Omega_a$  varied by approximately 0.16 and 0.69 respectively, over the spatial region investigated here (Table 1).

Flögel et al. [14] recently published a comparison of available carbonate system data for CWC in the North Atlantic, including the Mediterranean, and suggest low quality CWCs are exposed to Dissolved Inorganic Carbon (DIC) concentrations  $< 2,170 \mu\text{mol kg}^{-1}$ . Surface waters ( $< 20$  m depth) in the GoC reported DIC values  $< 2,100 \mu\text{mol kg}^{-1}$ , while bottom waters ( $> 20$  m depth) exceeded 2,300  $\mu\text{mol kg}^{-1}$  [7].

The geodynamic history of the Gulf of Cádiz is reflected in numerous fluid escape structures on the seabed including pockmarks, mud volcanoes, diapiric ridges and carbonate mud mounds. Hydrocarbon-rich fluids expelled at mud volcanoes (MVs) may contribute significantly to the carbon budget of the oceans, but little is known about the long-term variation in fluid fluxes at MVs. While extensive research has been accomplished on the geochemical features of MVs and authigenic carbonates in the GoC [15], future research should increase knowledge on their contribution to the carbon budget and their influence on the CWC in the GoC. In this sense, the project proposal outlined below (see Section 4) will provide measurements of green-house gases such as  $\text{CH}_4$  in the deep areas of GoC, as well as measurements of  $\text{CO}_2$  fluxes by means of continuous measurements and/or benthic chambers.

#### 4) Future collaboration with host institution (if applicable)

On day September 15, Prof. Enrique García-Luque organised a half-day discussion with the following participants: the leader of the Laboratorio de Investigacion Litoral I, Prof. Jesús Forja Pajares, and Prof. Teodora Ortega Díaz. The goal was to establish a network to study ocean carbonate chemistry in the GoC and link it with COCARDE-ERN research activities in Europe, and to search for other funding opportunities.

Prof. Enrique García-Luque (UCA) and myself agreed upon exchange of students and researchers between our research institutions and on the exchange of samples of interest. In this context, we agreed to get prepared for the next call of the programme "THE TALENTIA POSTDOC FELLOWSHIPS". This programme is co-financed by the Marie Curie Program of the European Union (grant agreement no 267226), and offers experienced researchers the opportunity to work during two years at prestigious research centres and/or institutions worldwide, to do their research, and integrate in the Andalusian Knowledge System. The next call is expected in January 2015.

On day September 18, I was invited to join the project proposal "Oceanografía del Golfo de Cádiz en un contexto de cambio global: Interacciones entre circulación oceánica,

flujos biogeoquímicos y redes tróficas", under the "Programa Estatal de Fomento de la Investigación Científica y Técnica de Excelencia" (Proyectos I+D 2014).

The suggested topic to estimate Sediment Accumulation Rates (SARs) and Mass Accumulation Rates (MARs) based on activity–depth profiles of excess  $^{210}\text{Pb}$  ( $^{210}\text{Pb}_{\text{ex}}$ ) on sediment cores from the Gulf of Cadiz was seen very positive by Prof. Jesús Forja Pajares, Prof. Abelardo Gómez Parra, and Prof. Teodora Ortega Díaz (UCA). We agreed to prepare a proposal to explore the shallow and deep biosedimentary environments of the Gulf of Cádiz. Deadline for this proposal is September 29th 2014. The project proposal has been submitted according to the deadline.

6) **Projected publications / articles resulting or to result from the grant (ESF must be acknowledged in publications resulting from the grantee's work in relation with the grant)**

Guerra, R., Righi, S., García-Luque, E. Modern accumulation rates and sources of organic carbon in the NE Gulf of Cádiz (SW Iberian Peninsula). *Journal of Radioanalytical and Nuclear Chemistry* (submitted).

7) **Other comments (if any)**

I thank very much the European Science Foundation (ESF) for funding this work. A big thank to Prof. Jesús Forja Pajares (Universidad de Cádiz) for the warm welcome to his group at the CACTYMAR, the hospitality, and for the training I received over seawater carbonate chemistry and analysis; Prof Teodora Ortega Diaz (University of Cádiz) for her support, and for this opportunity to improve my knowledge on seawater instrumental analysis; along with Prof. Abelardo Gómez Parra (University of Cádiz), for their efforts to involve me in the project proposal "Oceanografía del Golfo de Cádiz en un contexto de cambio global: Interacciones entre circulación oceánica, flujos biogeoquímicos y redes tróficas" and the ongoing project "Flujos a la atmosfera de gases con efecto invernadero en el Parque Natural Bahía de Cádiz: interrelación con factores antrópicos", and all field and laboratory facilities they provided me to participate to the analysis and sampling; Prof Enrique García Luque for the time he dedicated to me and all learning experiences and invaluable guidance over this short visit; and Prof. Laura Martín Díaz for her kindness.

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