The speciation of inorganic carbon in estuarine and interstitial waters

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ABSTRACT

A calculation procedure to obtain pH, total alkalinity and concentration of inorganic carbon, based on the application of Gran functions, is described. An iterative program was used to optimise the electrode standard potential (E_0) and inorganic carbon concentration. Alkalinities higher than 15 mM were detected in interstitial waters from sediments collected in Cadiz Bay. A contribution of 20 % was associated with those acid-based species other than inorganic carbon. Speciation of inorganic carbon in estuarine waters was characterised using laboratory simulation techniques. Total carbonate and alkalinity, as well as inorganic carbon concentration, present conservative behaviour in the mixing process of waters having different salinities.

Key words: CO_2, interstitial waters, estuarine waters, total alkalinity, inorganic carbon.

RESUMEN

Especiación del carbono inorgánico en sistemas estuáricos y agua intersticial

En este trabajo se presenta un procedimiento de cálculo para la obtención del pH, alcalinidad total y concentración de carbono inorgánico, basado en la aplicación de funciones de Gran. Para ello, se ha utilizado un programa iterativo que optimiza el potencial estándar del electrodo y la concentración de carbono inorgánico. Mediante la aplicación de este método se muestran algunas características del sistema del carbónico en el agua intersticial y en sistemas estuáricos. En el agua intersticial de los sedimentos de la bahía de Cádiz se han detectado alcalinidades superiores a 15 mM a profundidades mayores de 10 cm, existiendo una contribución de hasta un 20 % de especies con carácter ácido-base diferentes al carbono inorgánico. La especiación del carbono inorgánico en aguas estuáricas se ha caracterizado utilizando técnicas de simulación en el laboratorio. Se ha observado que tanto la alcalinidad total, como la alcalinidad de carbonato y la concentración de carbono inorgánico presentan un comportamiento conservativo en procesos de mezcla de aguas de diferentes salinidades.

Palabras clave: CO_2, aguas intersticiales, aguas estuáricas, alcalinidad total, carbón inorgánico.

INTRODUCTION

The biogeochemical cycles characterise all possible processes occurring in oceanographic systems. Along with the water cycle, the carbon cycle constitutes, in terms of mass transfer between the continents, the oceans and the atmosphere, one of the most active sets of processes which control the behaviour of many other elements on the Earth's surface. An important aspect of the carbon cycle is the CO_2 exchange between the water surface and the atmosphere, a process associated with an increase in the atmosphere's CO_2 and inorganic carbon concentrations, and in the ocean's inorganic carbon, leading to a progressive rise in the World Ocean's alkalinities.

In the global balance, it is important to include the effect produced by these aquatic systems, especially the coastal areas and the continental systems. The CO_2 fluxes registered in these areas indicates that they are a source of atmospheric CO_2. This is due to the high levels of organic matter proceeding from different sources, such as high primary production or contamination from anthropogenic sources.

In the coastal areas, organic matter is rapidly sediment-bound. Mineralisation produces high inorganic carbon fluxes measured through the water-sediment interface. The benthic fluxes are highly variable in littoral systems, and reported values range from 50-200 mmol m² day⁻¹ (Andersen and Hargrave, 1984; Forja, Blasco and Gómez-Parra, 1994; López *et al.*, 1995). Due to this phenomenon, some authors consider these 'littorals oceans' to constitute a different compartment in the inorganic carbon biogeochemical cycle; CO_2 emissions to the atmosphere in these areas have been estimated at 0.4×10^9 t year⁻¹ (Holligan and Reiners, 1992).

In the continental systems, the current level of knowledge is relatively low. Nevertheless, some recent and dangerous episodes, such as the 1983 event at Lake Nyos, Cameroon (Nojiri *et al.*, 1993), which resulted in 1 700 fatalities due to direct CO_2 emissions, illustrate the need to study these systems.

For oceanic waters, precise methods have been developed to measure alkalinity (AT) and the inorganic carbon speciation system (Dickson, 1981; Anon., 1994; Gómez-Parra and Forja, 1994). This enables us to establish the fluxes by measuring pCO_2 in both phases (gas-water). One of the problems of studies involving littoral marine zones is related to methodology. Therefore, this paper pre-sents methods for determining alkalinity and speciation of inorganic carbon in systems, and describes CO_2 distribution in samples from estuaries and interstitial waters.

MATERIALS AND METHODS

The procedure employed is based on the determination of alkalinities by potentiometric titrations, considering the influence of those acid-based systems different to CO_2 that potentially can affect CO_2 measurement.

We used thermostated cells, an automatic titroprocesador (670, Methrom) with combined glass electrode of Ag/AgCl (6.0210.100, Methrom), and a thermometer.

The study was carried out using interstitial waters from sediments collected in Cadiz Bay and samples from an estuarine simulator (Gómez-Parra *et al.*, 1994). In both cases, titration was performed dynamically, using HCl (0.1M).

Sediments were sampled with a 45-mm i.d. gravity core. They were sliced at 1-cm intervals and the sections thus obtained were centrifuged at 24 000 g for 30 min. This process makes it possible to obtain 70-80 % (3-5 cm³) of the total water contained in the samples. Handling of sediment cores and subsequent analysis of interstitial waters were performed in an inert atmosphere.

RESULTS AND DISCUSSION

Typical titration curves are shown in figures 1 and 2. The first inflexion point is associated with HCO_3^- formations from CO_3^{2-}, whereas the second was with CO_2 formation from HCO_3^-. The inorganic carbon quantification was based on the linear approaches from the titration curves (Gran functions). Figure 1 shows the estuarine water titration of a low salinity sample, with alkalinity values lower than those measured in oceanic waters.

In figure 2, an interstitial water titration is shown. The initial pH and inorganic carbon were both high. For the Gran function calculations, we included sulphate, fluoride, phosphate, borate, silicate, ammonia and sulphur species. Their contribution to the Gran functions were established using pH values of 7.25 for the first inflexion point and 4.5 for the second, and using these formulae:
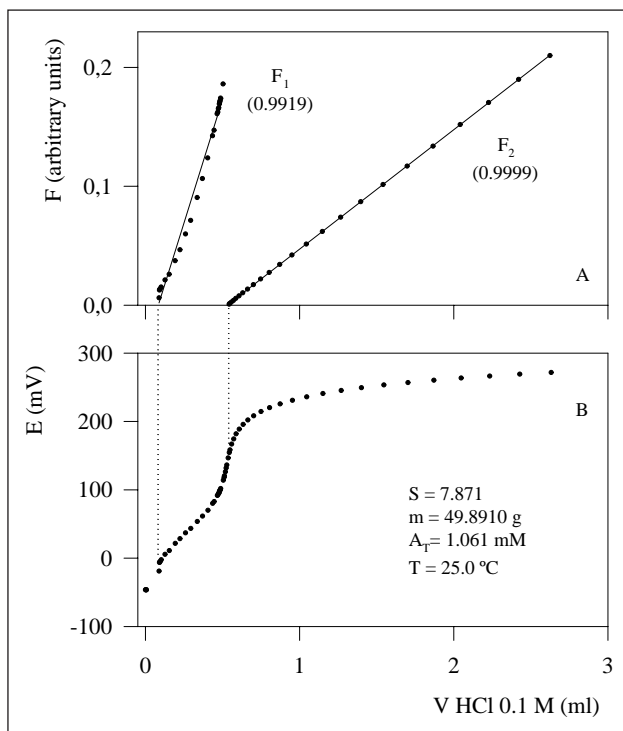
Figure 1. (A): Tritration curve with HCl 0.1 M of estuarine water sample. (B): Linearisation of the same titration curves using Gran functions

Figure 2. (A): Titration curve with HCl 0.1 M of interstitial water sample. (B): Linearisation of the same titration curves using Gran functions

$$F_1 = (v_0 + v) \, ([H^+] + [CO_2] + [HSO_4^-] + [HF] + 2[H_3PO_4] + [H_2PO_4^-] + [H_2S] - [CO_3^{2-}] - [B(OH)_4^-] - [SiO(OH)_3^-] - [NH_3] - [PO_4^{3-}] - [S^{2-}] - [OH^-])$$

$$F_2 = (v_0 - v) \, ([H^+] + [HSO_4^-] + [HF] + [H_3PO_4] - [HCO_3^-] - 2[CO_3^{2-}] - [B(OH)_4^-] - [SiO(OH)_3^-] - [NH_3] - [HPO_4^{2-}] - 2[PO_4^{3-}] - [HS^-] - 2[S^{2-}] - [OH^-])$$

($[H^+]$ is expressed in the free concentration scale).

Both functions (F_1 and F_2) change linearly with the volume of added acid. However, the direct utilisation of this Gran function presents some problems; one of them is because the standard potential is not well known. Therefore, hydrogen ion concentration during the titration and the initial concentration of inorganic carbon in the sample are unknown. This is the objective studied here.

Adequate processing of experimental data resolves these questions. Firstly, we approached these two equivalency volumes by considering the initial inorganic carbon concentrations as zero, and using a typical established value for the electrode standard potential. Thus, we could determine (as a first quantification) the inorganic carbon concentration:
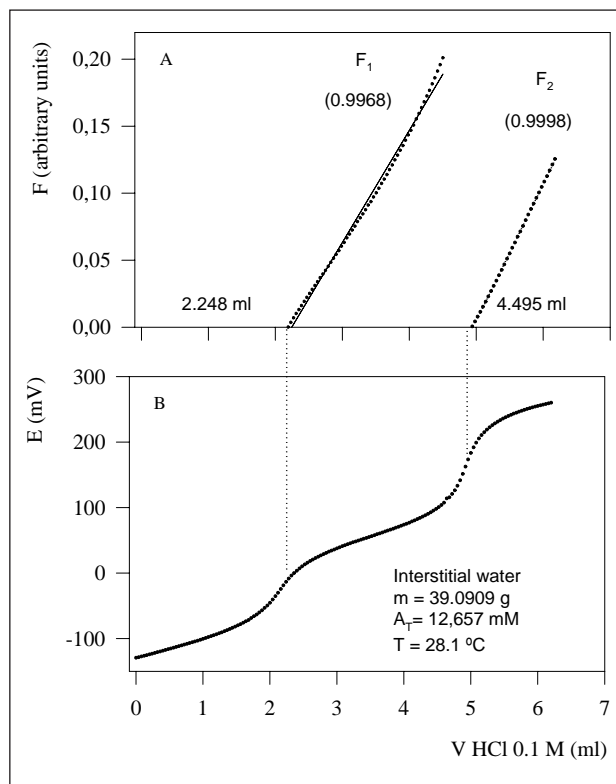
$$I.C. = \frac{(V_{e,2} - V_{e,1}) \, M_t}{v_0}$$

Then, we could optimise this initial I.C. concentration by iteration, using this expression for total alkalinity:

$$A_T = \frac{V_{e,2} \, M_t}{v_0}$$

as well as:

$$I.C. = (A_T - [B(OH)_4^-]_0 - [SiO(OH)_3^-]_0 - [NH_3]_0 - [HPO_4^{2-}]_0 - [PO_4^{3-}]_0 - [HS^-]_0 - 2[S^{2-}]_0 - [OH^-]_0 + [H^+]_0 + [HSO_4^-]_0 + [HF]_0 + [H_3PO_4]_0) \cdot [(K_{1,c}[H^+]_0 + 2K_{1,c}K_{2,c})/([H^+]_0^2 + K_{1,c}[H^+]_0 + K_{1,c}K_{2,c})]^{-1}$$

where the subscripts 0 are associated with the initial concentrations. We repeated this process (in calculations F_1 and F_2) until we reached a steep error (Gran functions) equal to or lower than 1 μM. Later, during the external cycle calculation, we optimised the E_0 value, using the acid shape in the titration curves, in which E_0 is highly stable. In this

zone, the hydrogen concentrations could be related to the excess volume in the second inflexion point, taking into account the formation of those highly acid species such as bisulphate, fluorhidric and phosphoric acids.

Hence:

$$[H^+] = \frac{v\,M_t - v_0\,A_T}{v_0 + v} - \big[\,([HSO_4^-] - [HSO_4^-]_e) + ([HF] - [HF]_e) + ([H_3PO_4] - [H_3PO_4]_e)\,\big]$$

The vertical profiles of different chemical species measured in interstitial waters obtained from sediments collected in Cadiz Bay are shown in figure 3. Alkalinity increased versus depth to values higher than 15 mM, when the depth was higher than 10 cm. The chemical species, like the nutrients nitrate, phosphate and silicate, as well as those associated with the sulphide system, are very important in interstitial water from marine sediments. The contribution of these species to the total alka-
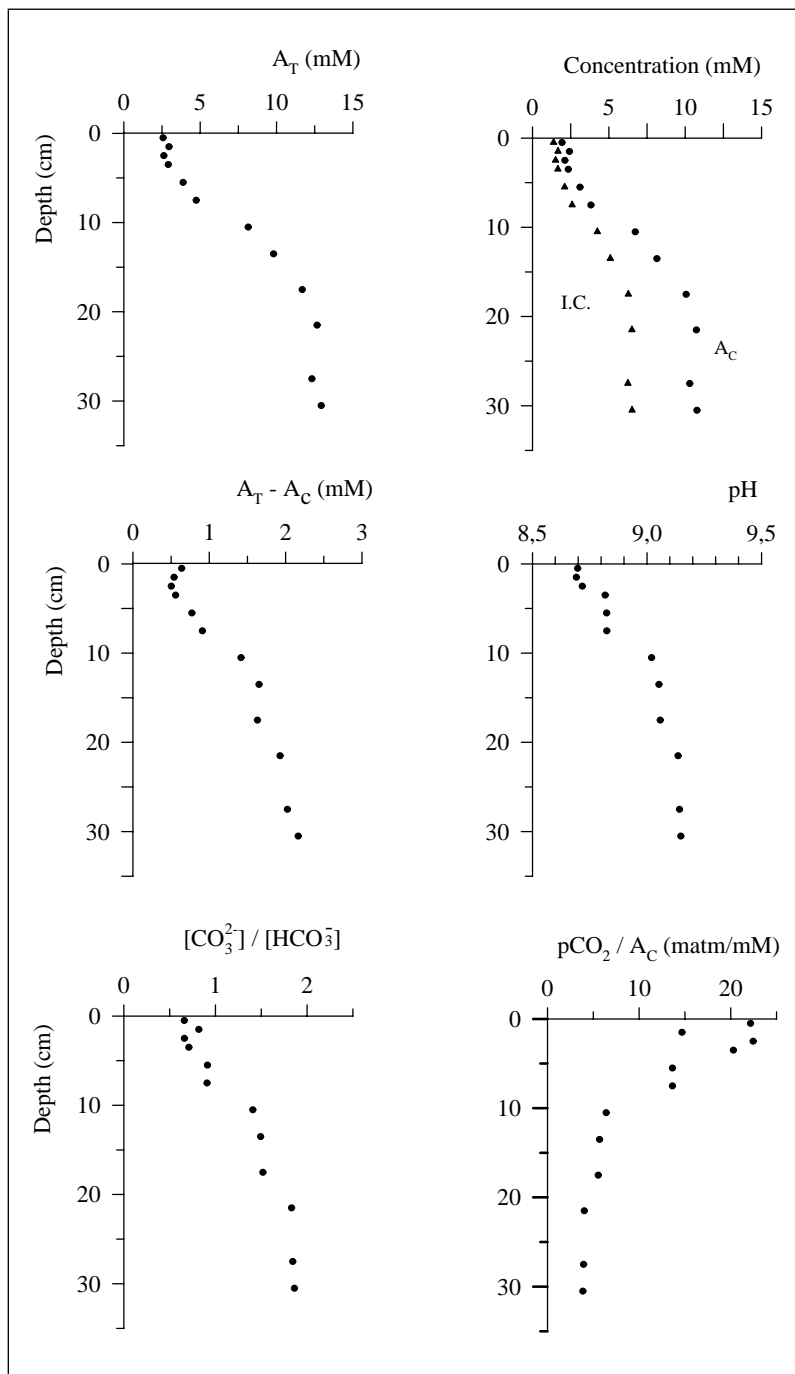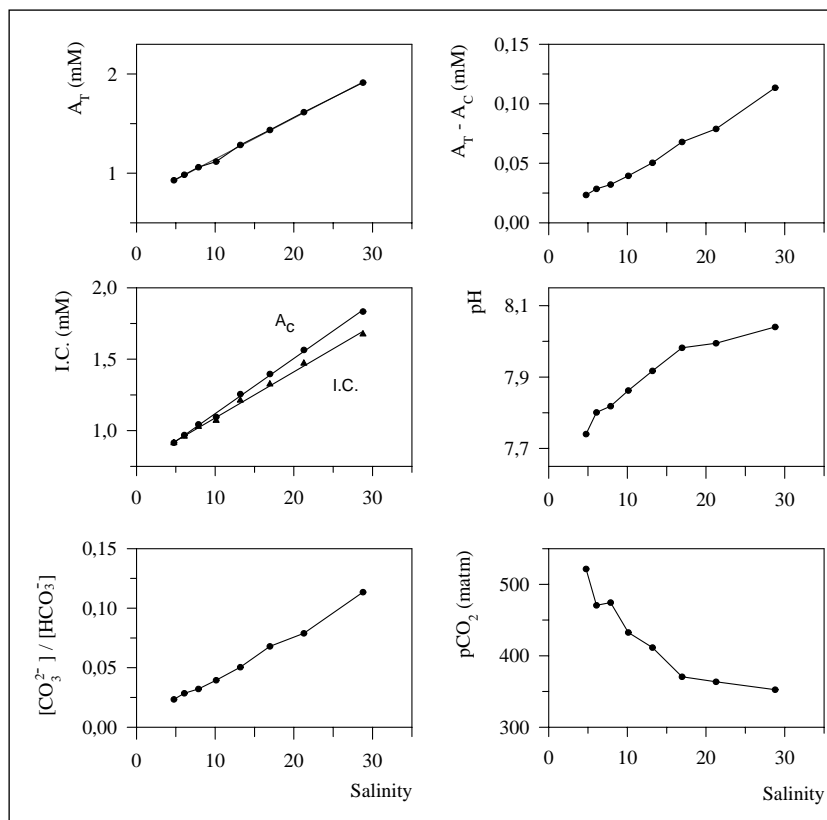

Figure 3. Vertical profiles of inorganic carbon parameters in interstitial waters from the sediments collected in Cadiz Bay

Figure 4. Evolution of inorganic carbon parameters with salinity in estuarine waters

linity value could be higher than 20 %, whereas in oceanic waters it is almost unappreciable. Another striking feature in these systems are the increasing pH values vs depth, which produces atypical (CO_3^{2-}/HCO_3^-) rates higher than 1. The relative pCO_2 values are higher at the sediment surface.

The estuarine water system has a different pattern compared with the interstitial water system. Total alkalinity (A_T) and carbonate alkalinity (A_C), as well as the inorganic carbon concentration, behave conservatively (figure 4).

This pattern is similar to that measured in oceanic waters. In these oceanic areas, such a parameter (together with the pH) has been used as a tracer, for instance, in a mixture of water body and upwelling systems. As shown in figure 4, in the estuarine systems pH does not show a linear relationship with salinity, which produces a relative increase in the CO_3^{2-} concentration close to the seawater system. Finally, we measured high pCO_2 values at low salinities. This does not indicate an increase in transferring CO_2 through the atmosphere-water interface, because CO_2 solubility increases when salinity decreases. In this case, the solubility of CO_2 is the master variable controlling CO_2 fluxes across the surfaces described.

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