



How fast is the Patagonian shelf-break acidifying?



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ABSTRACT

Anthropogenic carbon (C_{ant}) concentration is determined according to the TrOCA method, from carbonate system data and hydrographic parameters collected during two consecutive spring cruises (2007 and 2008) in the Argentinean Patagonian shelf-break zone between 36°S and 50°S. C_{ant} has intruded the water column until intermediate depths, with no C_{ant} below 1000 m, in the deeper waters (i.e., North Atlantic Deep Water and Antarctic Bottom Water) of the Northern sector of the study area (i.e., North of 38°S). The higher C_{ant} concentration is observed in Subantarctic Shelf Water in the Southern region, whereas in the Northern sector both Tropical Water and South Atlantic Central Water are equally affected by C_{ant} intrusion. The Antarctic Intermediate Water represents the depth-limit achieved by C_{ant} penetration, reinforcing the role that this water mass plays as an important vehicle to transport C_{ant} to the oceans interior. The estimated C_{ant} average ($\pm$ method precision) is $46.6 \pm 5.3 \mu\text{mol kg}^{-1}$ considering the full depth of the water column. The ocean acidification state (ΔpH) shows an average ($\pm$ standard deviation) of -0.11 ± 0.05 , thus, indicating an annual pH reduction of -0.0010 yr^{-1} since the Industrial Revolution (c.a. 1750). The degree of aragonite saturation is lowered towards undersaturation levels of calcite. The Patagonian shelf and shelf-break zones—a strong CO₂ sink region in the global ocean—are likely a key area for C_{ant} intrusion in the southwestern South Atlantic Ocean.

1. Introduction

Global ocean carbon dioxide (CO₂) sink was estimated to be $2.0 \pm 1.0 \text{ Pg C yr}^{-1}$ (Takahashi et al., 2009). The uptake of atmospheric CO₂ has likely consequences to the marine ecosystems, as a result of pH decrease and ocean acidification induced by the human component (Ciais et al., 2013). Together with naturally produced carbon, ~28% of the anthropogenic emissions are absorbed by the oceans (Ciais et al., 2013; Le Quéré et al., 2015). The anthropogenic CO₂ ocean uptake, and consequently its chemical reaction with seawater, is the primary cause of ocean acidification (e.g., Doney et al., 2009a, 2009b, 2009c) and this process, leading to a decrease in water masses pH, might be causing consequences at organisms, ecosystems and economic levels (e.g., Kerr et al., 2016). Those effects have a particular impact on marine calcifying organisms (e.g., Mostofa et al., 2016; Wanninkhof et al., 2015). Therefore, a refined regional estimation of the anthropogenic carbon (C_{ant}) distribution and its implied

changes on the marine carbon cycle are extremely important for public policy development and future climate change projections (e.g., Le Quéré et al., 2015, 2013).

The Patagonian continental shelf (Fig. 1) is thought to be one of the most productive shelf regions worldwide (e.g., Longhurst et al., 1995). This area is characterized as a *Class 1 Large Marine Ecosystem* because of its high primary productivity, normally exceeding $300 \text{ g C m}^{-2} \text{ yr}^{-1}$ (Behrenfeld and Falkowski, 1997). This region has also been shown to develop massive and re-curent coccolithophorid blooms, particularly in summer (e.g., Signorini et al., 2006; de Souza et al., 2011; Painter et al., 2010; Garcia et al., 2011; Segura et al., 2013; Gonçalves-Araújo et al., 2016). Together with the physical, biological and economic importance of this region, the Argentinean Patagonia surface waters are recognized as an area of strong atmospheric CO₂ uptake (Bianchi et al., 2005; Bianchi et al., 2009; Kahl et al., 2017), with more intense uptake during the spring season, normally associated with strong phytoplankton blooms (Garcia et al., 2008; Bianchi et al., 2009; Gonçalves-

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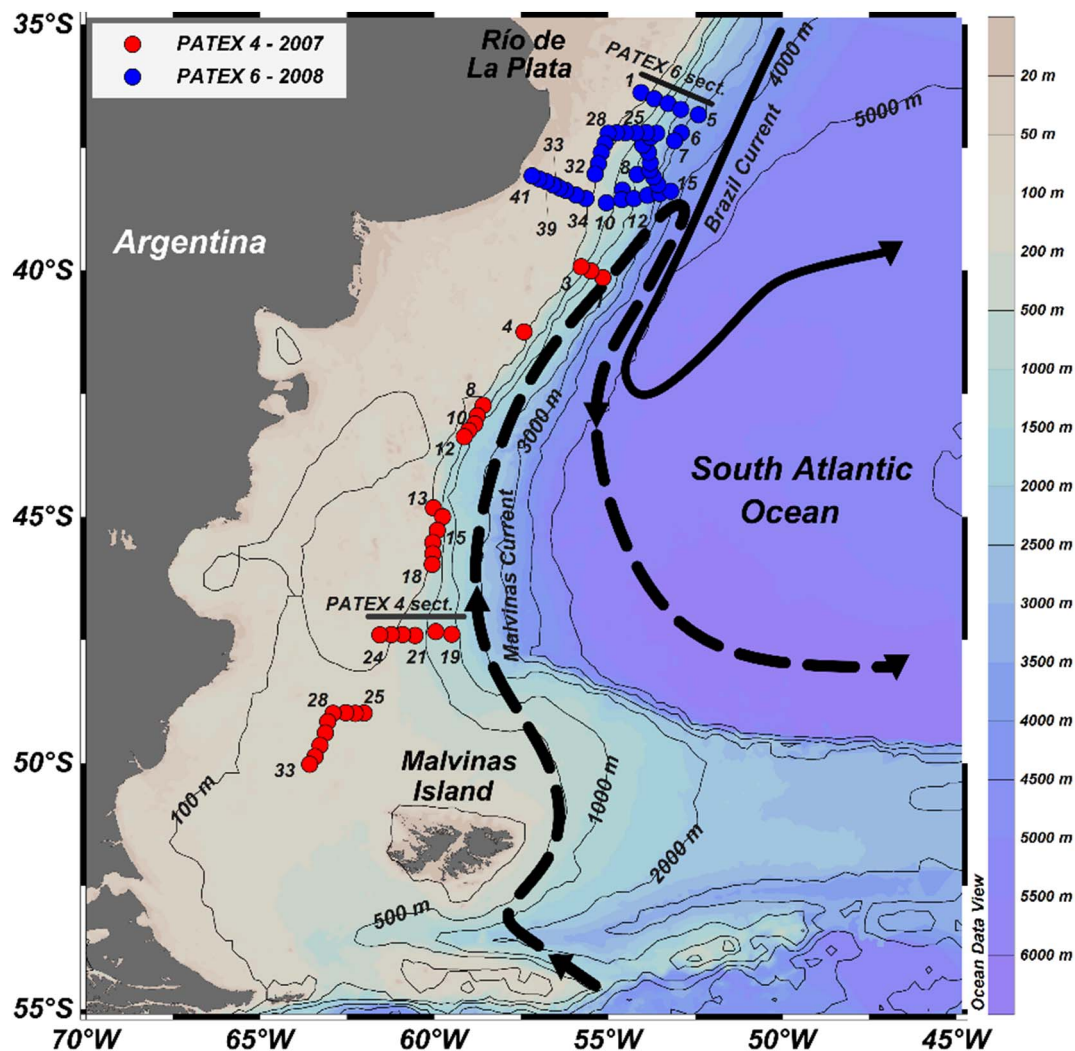


Fig. 1. Map of the study region in the Argentinean Patagonia, Southwestern South Atlantic Ocean. The position of hydrographic stations occupied during PATEX 4 (spring of 2007; red dots) and PATEX 6 (spring of 2008; blue dots) cruises are shown as the coloured dots. The main schematic flows of Brazil (black straight line) and Malvinas (black dashed line) currents are shown by arrows (see Strub et al., 2015 for details about the regional ocean circulation in the area). The bottom bathymetry is represented by both isobath contour and colour shadings. Two marked cross-shelf transects (one for each cruise) have been selected for displaying hydrographic and carbonate system properties. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Araújo et al., 2016).

Bianchi et al. (2005) concluded that during the summer and autumn the coastal region of the Patagonian shelf acted as a source of CO_2 to the atmosphere, whereas the mid-shelf and shelf-break acted as CO_2 sink, with a transition between those patterns in the frontal system area. In another study, Bianchi et al. (2009) characterized the Patagonian mid-shelf and shelf-break as a major area for CO_2 sink from spring to autumn and concluded that this is one of the strongest CO_2 sink areas of the world.

Few and recent studies have reported the C_{ant} storage and ocean acidification levels in the South Atlantic Ocean (e.g., Ríos et al., 2012; Salt et al., 2015; Woosley et al., 2016). In addition, Kerr et al. (2016) recently highlighted the needs for better comprehension of the marine carbonate system changes in the boundary zone between the coastal and open ocean regimes of the western South Atlantic Ocean.

In general, marginal seas are frequently understudied regarding C_{ant} , mainly because they are considered to play a minor role in the global CO_2 sink, due to their comparatively small surface area when compared with large open ocean regions. However, recent studies pointed out that the marginal seas have a strong potential to affect the marine carbon cycle (e.g., Chen and Borges, 2009; Laruelle et al., 2013) and a tendency to uptake, storage and export C_{ant} off the shelf (Lee

et al., 2011).

In this context, and considering that C_{ant} estimations in the Patagonian shelf-break region are not yet available in the literature, this work aims to identify the ocean acidification state (ΔpH) by conducting the first quantification of C_{ant} in the various water masses occurring in the study region. In addition, the saturation states (Ω) of aragonite (Ω_{Ar}) and calcite (Ω_{Ca}) are discussed, since (i) marine organisms have different sensitivities and responses to ocean acidification and (ii) critical undersaturation levels could trigger an ecosystem response, which can affect geochemical processes mediated by organisms. That is particularly true for planktonic calcifying species, such as coccolithophorids and pteropods.

2. Oceanographic features of the Patagonian shelf-break zone

The Patagonian shelf-break zone (Fig. 1) is a dynamically complex region, due to the presence of distinct shelf and open ocean water masses from diverse sources. The main upper ocean circulation between 28°S and 38°S is dominated by the poleward flow of the Brazil Current, a western boundary current carrying warm and salty waters southwards (e.g., Piola et al., 2000; Möller et al., 2008; Strub et al., 2015). South of 38°S , the ocean circulation is dominated by the northward flow of

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