

## Short Note

## Natural seasonal variability of aragonite saturation state within two Antarctic coastal ocean sites

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## Introduction

Production of aragonite shells by many marine organisms via calcification requires adequate availability of seawater carbonate ions ( $\text{CO}_3^{2-}$ ), which is often represented by the aragonite saturation state of seawater:  $\Omega = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{\lambda}$ , where  $\lambda$  is the solubility coefficient of calcium carbonate in the form of aragonite. Changes in  $\Omega_{\text{ARAG}}$  are explicitly linked to rises and falls in oceanic partial pressure of  $\text{CO}_2$  ( $p\text{CO}_2$ ) through alterations in equilibrium  $\text{CO}_2$  chemistry in seawater. The coastal Southern Ocean ecosystem in particular, is most vulnerable to future declining  $\Omega_{\text{ARAG}}$  via anthropogenic  $\text{CO}_2$  uptake (Orr *et al.* 2005, McNeil & Matear 2008) since pteropods (aragonite secreting zooplankton) make up a large proportion of its biomass (Accornero *et al.* 2003, Hunt *et al.* 2008). Spatio-temporal variability in surface ocean  $\Omega_{\text{ARAG}}$  is scarce for coastal Antarctic waters. Here, we report data on seasonal variability of  $\Omega_{\text{ARAG}}$  from two independent Antarctic sites (Ross Sea and Prydz Bay, see Fig. 1).

## Methods

We calculated  $\Omega_{\text{ARAG}}$  using  $\text{CO}_2$  dissociation constants (Dickson & Millero 1987) from two reported  $p\text{CO}_2$  datasets in the Ross Sea and Prydz Bay, East Antarctica. The Ross Sea  $\text{CO}_2$  measurements were made during intermittent/sea ice-free periods in 1996–97 as described elsewhere (Sweeney 2003). The Prydz Bay  $\text{CO}_2$  measurements were collected one kilometre offshore from Australia's Davis Station in Prydz Bay, East Antarctica from 1993–95 as described elsewhere (Gibson & Trull 1999). During ice-free periods (December–March), samples were collected at the surface while during ice cover (March–November), samples were collected at 2–20 m via drill hole.

## Results

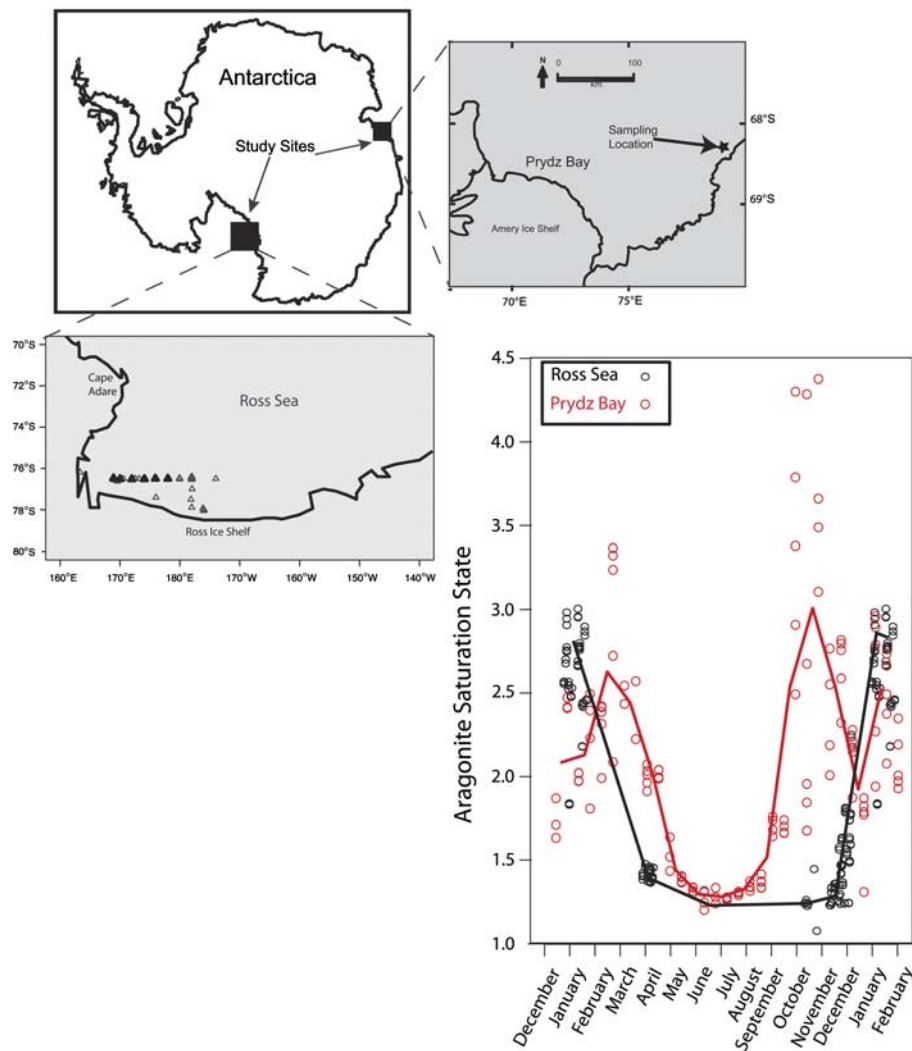
Surface ocean  $\text{CO}_2$  concentrations over an annual cycle undergo extreme changes at both the Ross Sea and Prydz Bay sites, with  $p\text{CO}_2$  rapidly increasing from *c.* 100  $\mu\text{atm}$

up to *c.* 450  $\mu\text{atm}$  from summer to autumn. This more than fourfold increase in  $\text{CO}_2$  drives a rapid decline in  $\Omega_{\text{ARAG}}$  from up to 4.5 in summer to *c.* 1.1 in autumn (Fig. 1). Geochemical aragonite dissolution occurs when  $\Omega_{\text{ARAG}} < 1$ , which is nearly reached during October in the Ross Sea (Fig. 1). Winter data is not available, but it is probably similar to autumn conditions (Sweeney 2003).

## Discussion

We put the natural seasonal variations observed for  $\Omega_{\text{ARAG}}$  at these two sites (Fig. 1) into context against the decadal changes likely due to anthropogenic  $\text{CO}_2$  absorption. The average  $\Omega_{\text{ARAG}}$  for both sites is *c.* 1.9 (Fig. 1) with a mean  $p\text{CO}_2$  of 246  $\mu\text{atm}$  and total alkalinity of 2300  $\mu\text{mol kg}^{-1}$ . Using a mean temperature (*c.*  $-1.1^\circ\text{C}$ ) and salinity (33.4), we can calculate the upper-bound equilibrium changes in  $\Omega_{\text{ARAG}}$  since pre-industrial times. Under mean conditions for the year 1995,  $\Omega_{\text{ARAG}}$  is estimated to be 0.55 lower since pre-industrial times (the year 1780), which is an upper bound. In reality however these Antarctic surface waters are not in equilibrium with the atmosphere due to sea ice hindrance of air-sea gas exchange and dilution from older deep waters (McNeil & Matear 2008). Natural seasonal variations (*c.* 3.2) are nearly six times the magnitude of anthropogenic acidification (*c.* 0.55) since pre-industrial times (Fig. 1).

The large natural variations in coastal Antarctic  $\Omega_{\text{ARAG}}$  suggest that aragonite secreting species such as pteropods must be able to endure extreme changes in  $\Omega_{\text{ARAG}}$ . Alternatively pteropods may undergo large variations in biomass dynamics that are partially driven by the changes in  $\Omega_{\text{ARAG}}$  shown here. Studies based on a range of different methodologies suggest the lifecycle of Antarctic relevant pteropods (*Limacina helicina* Phipps) are longer than one year, with some juvenile species undergoing development during the winter months (Hunt *et al.* 2008). If this longer life cycle is true for the most abundant Antarctic pteropod (*Limacina helicina*), our results may suggest a high resilience to  $\Omega_{\text{ARAG}}$  variations given the dominance of this pteropod in sediment traps in the Ross Sea (Accornero *et al.* 2003).



**Fig. 1.** Geographic location of two Antarctic coastal sites (Ross Sea and Prydz Bay), along with the surface observations over the annual cycle for aragonite saturation state ( $\Omega_{\text{ARAG}}$ ).

Understanding calcification changes for a particular species in a high  $\text{CO}_2$  ocean has required laboratory experiments where  $\Omega_{\text{ARAG}}$  levels are artificially decreased from 5 to 2 (Riebesell *et al.* 2000). The observed threefold changes in  $\Omega_{\text{ARAG}}$  shown here over a few months are of the same order of magnitude as those conditions used in artificial laboratory  $\text{CO}_2$  experiments. This makes the Antarctic coastal oceans a perfect natural mesocosm to investigate resilience of Southern Ocean marine ecosystems to ocean acidification.

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