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The seasonal cycle of carbonate system processes in Ryder Bay, West Antarctic Peninsula

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ABSTRACT

The carbon cycle in seasonally sea-ice covered waters remains poorly understood due to both a lack of observational data and the complexity of the system. Here we present three consecutive seasonal cycles of upper ocean dissolved inorganic carbon (DIC) and total alkalinity measurements from Ryder Bay on the West Antarctic Peninsula. We attribute the observed changes in DIC to four processes: mixing of water masses, air–sea CO_2 flux, calcium carbonate precipitation/dissolution and photosynthesis/respiration. This approach enables us to resolve the main drivers of the seasonal DIC cycle and also investigate the mechanisms behind interannual variability in the carbonate system. We observe a strong, asymmetric seasonal cycle in the carbonate system, driven by physical processes and primary production. In summer, melting glacial ice and sea ice and a reduction in mixing with deeper water reduce the concentration of DIC in surface waters. The dominant process affecting the carbonate system is net photosynthesis which reduces DIC and the fugacity of CO_2, making the ocean a net sink of atmospheric CO_2. In winter, mixing with deeper, carbon-rich water and net heterotrophy increase surface DIC concentrations, resulting in pH as low as 7.95 and aragonite saturation states close to 1. We observe no clear seasonal cycle of calcium carbonate precipitation/dissolution but some short-lived features of the carbonate time series strongly suggest that significant precipitation of calcium carbonate does occur in the Bay. The variability observed in this study demonstrates that changes in mixing and sea-ice cover significantly affect carbon cycling in this dynamic environment. Maintaining this unique time series will allow the carbonate system in seasonally sea-ice covered waters to be better understood.

1. Introduction

The Southern Ocean plays an important role in the global carbon cycle through the uptake and storage of atmospheric CO_2 (Sabine et al., 2004) and the formation of deep water masses (Sallée et al., 2012). However, the role of the seasonally sea-ice covered coastal Southern Ocean in the global carbon cycle remains poorly constrained (Lenton et al., 2013) due to a scarcity of observations and the complexity and variability of this environment. If we are to predict future interactions between the changing climate and the carbon cycle in this environment, a better process-based understanding must be developed. The waters of the West Antarctic Peninsula (WAP) exhibit strong seasonal and interannual variability and are experiencing significant climate change. This variability makes the region an ideal location to study carbon system processes and their interactions on various timescales. In the last fifty years the peninsula has seen a rapid increase in air temperature (Vaughan et al., 2003; Turner et al., 2005) and coincident changes in ocean temperature and stratification (Meredith and King, 2005). Most glaciers on the peninsula are retreating (Cook et al., 2005) and, unlike other parts of the Southern Ocean, the Antarctic Peninsula and southern Bellingshausen Sea have experienced a decrease in sea-ice cover (Stammerjohn et al., 2008; Comiso and Nishio, 2008; Parkinson and Cavalieri, 2012). Interannual to decadal variability in the atmospheric circulation of the region has also been observed. There has been a trend towards the positive phase of the Southern Annular Mode (SAM) over recent decades with a concordant intensification of

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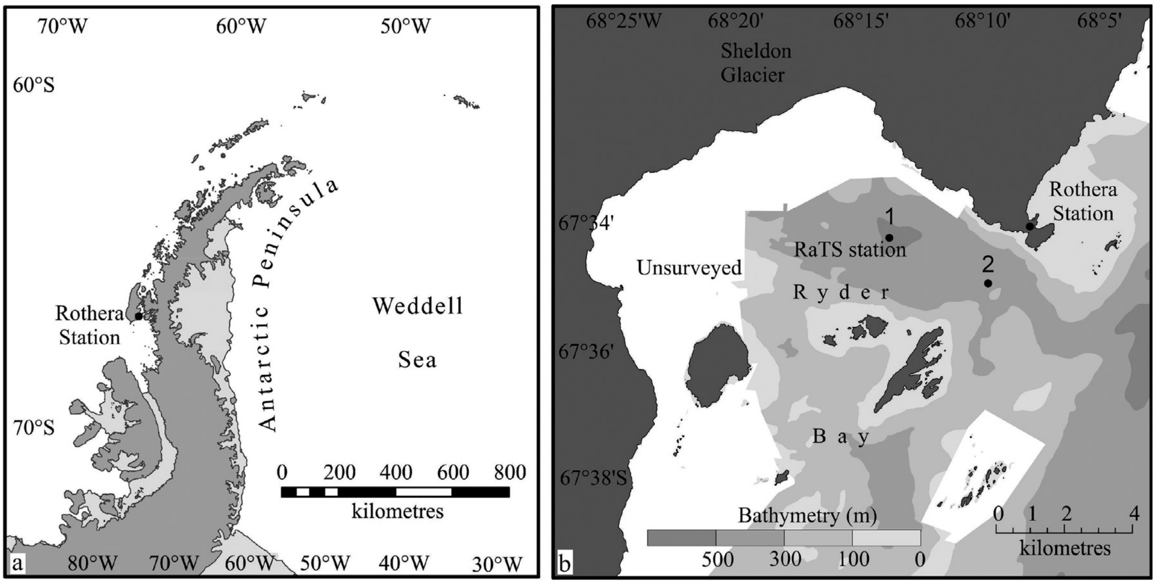

Fig. 1. (a) Location of Rothera on Adelaide Island at the West Antarctic Peninsula. (b) Location of RaTS sites 1 and 2 in Ryder Bay. From Legge et al. (2015), modified from Venables et al. (2013).

westerly winds (Thompson and Solomon, 2002; Marshall, 2003). The changes in wind are thought to be responsible for part of the observed warming on the peninsula (Marshall et al., 2006) and changes in ice dynamics in the region (Holland and Kwok, 2012). An increase in westerly wind stress may also lead to an increase in upwelling around the Antarctic continent (Hall and Visbeck, 2002), supplying more inorganic carbon to the surface ocean and thereby potentially weakening the strength of the Southern Ocean CO_2 sink (Lenton and Matear, 2007; Lovenduski et al., 2008; Le Quéré et al., 2007).

The global increase in atmospheric CO_2 leads to higher concentrations of CO_2 in the surface oceans with a concomitant decrease in pH and the concentration of carbonate ions, a process referred to as ocean acidification (Feely et al., 2004; Orr et al., 2005). The saturation state of calcium carbonate (Ω) describes the thermodynamic potential for this mineral to precipitate or dissolve and is calculated as the product of the concentrations of dissolved calcium and carbonate ions divided by their product at equilibrium. Wintertime undersaturation of the calcium carbonate mineral aragonite is predicted in the surface waters of the Southern Ocean by 2030 (McNeil and Matear, 2008) and the annual mean saturation state in the Southern Ocean is predicted to be less than 1 by the end of this century (Orr et al., 2005). The polar oceans are especially sensitive to ocean acidification as their low total alkalinity (TA) to dissolved inorganic carbon (DIC) ratio reduces their carbonate buffering capacity (Egleston et al., 2010; Shadwick et al., 2013).

Many marine organisms build calcium carbonate structures and there is growing concern over how ocean acidification may affect these organisms. Pteropods (Comeau et al., 2010; Bednaršek et al., 2012; Manno et al., 2012), foraminifera (Moy et al., 2009) and Antarctic krill (Kawaguchi et al., 2013) may be vulnerable to ocean acidification and resulting changes to their biomass, number and distribution could have significant ecological impacts. However, McNeil et al. (2011) observe that the natural seasonal variation in the saturation state of aragonite is large compared to the changes due to the uptake of anthropogenic CO_2 and suggest that Antarctic pteropods may be resilient to variations in Ω.

Due to the challenges of sampling in the polar environment, there are few measurements of the carbonate system from the coastal Southern Ocean and the vast majority of observations have been in the austral summer. Summer data from the Palmer Long-Term Ecological Research (Pal-LTER) grid show that carbonate chemistry on the WAP shelf is primarily influenced by primary production (Hauri et al., 2015) which is known to be strongly influenced by wind and sea-ice conditions (Vernet et al., 2008; Montes-Hugo et al., 2009, 2010; Venables et al., 2013). In near-shore areas of the West Antarctic, freshwater inputs also affect carbonate chemistry through the dilution of carbonate ions. However, the influence of primary production dominates; biological CO_2 uptake increases the pH and the carbonate ion concentration, increasing Ω (Mattsdotter Björk et al., 2014; Hauri et al., 2015). Very few studies have observed a full seasonal cycle of inorganic carbon in the seasonally ice-covered Southern Ocean. Two full annual cycles of inorganic carbon have been characterised in Prydz Bay, East Antarctica (Gibson and Trull, 1999; Roden et al., 2013). These studies were separated by 15 years and showed the same general pattern of a build up of DIC under ice in winter followed by rapid biological drawdown of inorganic carbon in summer. However, significant differences between the two study periods were apparent, with higher DIC and lower pH in the more recent dataset which the authors attribute to a combination of ocean acidification and variations in primary production (Roden et al., 2013). This comparison highlights the challenges inherent in determining reliable decadal trends in a dynamic, sparsely sampled environment. Multi-year datasets from different locations are required to understand the drivers of the carbonate system and their changes in both time and space. Here, we present three consecutive seasonal cycles of DIC and TA measurements from a coastal time series on the WAP. We quantify carbonate system processes and investigate their seasonal and interannual variability.

2. Methods

2.1. Sampling and analysis

Samples for DIC and TA were collected between December 2010 and February 2014 at the Rothera Time Series (RaTS), about 4 km offshore, in Ryder Bay, on the West Antarctic Peninsula (Fig. 1). Sampling was undertaken from a rigid inflatable boat or through a hole in the ice approximately weekly in summer and every two weeks in winter, weather and ice permitting. If partial ice cover prevented access to the main RaTS site (site 1, Fig. 1) then a secondary site was used (site 2, Fig. 1). Most samples were taken at 15 m depth and some were taken at 40 m. Samples were collected in 250 mL or 500 mL borosilicate glass bottles, poisoned with mercuric chloride and sealed with