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A multi-decadal delay in the onset of corrosive ‘acidified’ waters in the Ross Sea of Antarctica due to strong air-sea CO₂ disequilibrium

Ben I. McNeil,¹ Alessandro Tagliabue,² and Colm Sweeney³

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[1] Antarctic coastal waters have an abundance of marine organisms that secrete the mineral aragonite for growth and survival. Increasing oceanic anthropogenic CO₂ uptake will push these waters to a point whereby aragonite will start to geochemically corrode, with direct consequences for the Antarctic ecosystem. Here we combine surface CO₂ data in the Ross Sea, Antarctica with a regional ocean/sea-ice model to better pinpoint the timing of corrosive conditions. Our analysis suggests sea-ice cover and deep-water entrainment during winter results in 65% lower storage of anthropogenic CO₂ in comparison to atmospheric CO₂ equilibrium. This means that instead of corrosive ‘acidified’ waters beginning as early as the winter of 2015, anthropogenic CO₂ disequilibrium delays its onset by up to 30 years, giving this Antarctic marine ecosystem a several decade reprieve to corrosive conditions. Our results demonstrate a broader importance of understanding natural oceanic carbon cycle variability for the onset of corrosive conditions. **Citation:** McNeil, B. I., A. Tagliabue, and C. Sweeney (2010), A multi-decadal delay in the onset of corrosive ‘acidified’ waters in the Ross Sea of Antarctica due to strong air-sea CO₂ disequilibrium, *Geophys. Res. Lett.*, 37, L19607, doi:10.1029/2010GL044597.

1. Introduction

[2] The recent anthropogenic increase in atmospheric CO₂ via fossil fuel emissions and land use change is exposing ecosystems to a higher CO₂ world. The immediate impact of increasing CO₂ on the ocean is a change in the chemical composition that results in a lowering of both seawater pH and carbonate ion (CO₃²⁻) concentrations. These changes, together known as ‘ocean acidification’ have direct consequences for the marine calcium carbonate (CaCO₃) cycle and those species that interact, exploit and secrete the mineral. Marine biological calcification requires adequate availability of seawater carbonate ions, which is often represented using the calcium carbonate (CaCO₃) saturation state of seawater: $\Omega_x = \frac{[Ca^{2+}][CO_3^{2-}]}{\lambda_x}$, where λ is the solubility coefficient and $_x$ represents the different forms of CaCO₃ (e.g. calcite and aragonite). Since variations of [Ca²⁺] are minor in the ocean, Ω is largely controlled by [CO₃²⁻]

variations along with the temperature, pressure and salinity of the seawater. Aragonite is the more soluble form of calcium carbonate and is secreted by many marine organisms and coral reefs. Experiments have shown that calcifying marine organisms are highly susceptible to changes in the aragonite saturation state (Ω_{ARAG}) [Fabry *et al.*, 2008; Langdon *et al.*, 2000]. Lowering Ω_{ARAG} is explicitly linked to rising oceanic partial pressure of CO₂ (pCO₂) and there will be a point in the future where carbonate ion concentrations are lowered to a level where under-saturation of aragonite ($\Omega_{ARAG} < 1$) will occur [Feely *et al.*, 2008; McNeil and Matear, 2008; Orr *et al.*, 2005; Yamamoto-Kawai *et al.*, 2009]. When this occurs, the net geochemical response will be for aragonite shells to dissolve with potential large ramifications to marine calcifiers [Cohen and Holcomb, 2009] and the wider ecosystem.

[3] The coastal waters surrounding the Antarctic continent are particularly vulnerable to ocean acidification since aragonite-secreting pteropods have been shown to represent up to 65% of total zooplankton biomass [Hunt *et al.*, 2008]. Furthermore, biogeochemical processes unique in the Antarctic bring those waters closer to becoming corrosive than elsewhere in the ocean [McNeil and Matear, 2008; Orr *et al.*, 2005]. Natural deep-water CO₂ entrainment during winter months accelerate the onset of ocean acidification in the Southern Ocean, and is a key factor in understanding the timing of future corrosive conditions [McNeil and Matear, 2008]. Although phytoplankton growth during winter is suppressed the dominant Antarctic pteropod species, *Limacina helicina*, is known to have a life-cycle of 1–2 years with important veliger larval development during winter/spring months [Gannefors *et al.*, 2005; Seibel and Dierssen, 2003]. Understanding the seasonal onset of corrosive conditions is therefore important for the future prospects of these important Antarctic calcifying organisms. Despite this, adequate seasonal observations are lacking for Antarctic waters. In this work, we combine oceanic pH and Ω_{ARAG} seasonal measurements in the Ross Sea, Antarctica with a ocean biogeochemical model to understand the dynamics of CO₂ uptake and to more accurately pinpoint the onset of acidified ‘corrosive’ conditions within these waters.

2. In-situ Ω_{ARAG} and pH Variability in the Ross Sea

[4] To investigate the seasonal cycle of pH and Ω_{ARAG} in Antarctic waters, we use Ross Sea CO₂ measurements that were made on a number of oceanographic cruises during 1996 and 1997 as part of the U.S. Southern Ocean Joint Global Ocean Flux Study that have been described else-

¹Climate Change Research Centre, Faculty of Science, University of New South Wales, Sydney, New South Wales, Australia.

²Laboratoire des Sciences du Climat et de l'Environnement, IPSL-CEA-CNRS-UVSQ, Gif sur Yvette, France.

³CIRES, University of Colorado at Boulder, Boulder, Colorado, USA.

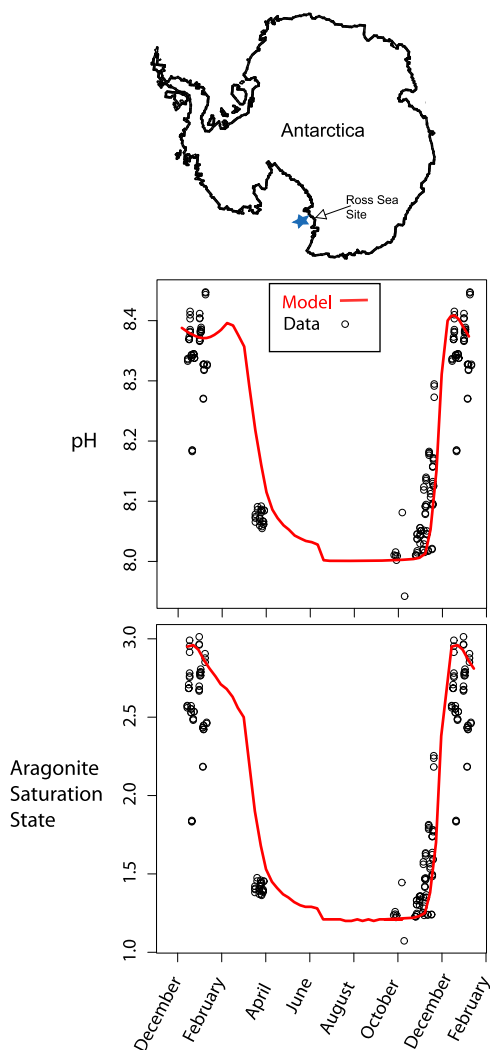


Figure 1. Map of Ross Sea sampling site and sea surface pH and Aragonite Saturation State (Ω_{ARAG}) over an annual cycle at the Ross Sea site (1997–1998). The red line shows the Ross Sea model output averaged between 77–76°S and 175°E–180° in order to encompass the region within which the observations were collected.

where [Sweeney *et al.*, 2000a, 2000b; Sweeney, 2004]. We calculate Ω_{ARAG} and pH via CO_2 dissociation constants [Dickson and Millero, 1987] and present them for the first time in order to understand the natural carbonate cycling and the associated future projections in these waters.

[5] Figure 1 shows the geographic location of the Ross Sea sampling site along with the in-situ observations and model estimate over the annual cycle (see below for model description). Ross Sea surface ocean CO_2 concentrations

over an annual cycle undergo extreme changes with pCO_2 rapidly increasing from $\sim 100 \mu\text{atm}$ up to $\sim 450 \mu\text{atm}$ between summer and autumn among the sites [see Sweeney, 2004]. This more than fourfold increase in CO_2 drives a rapid decline in aragonite saturation state (Ω_{ARAG}) from nearly 3–4 during the summer months to 1.1–1.2 during autumn/winter (Figure 1) along with a coinciding pH drop of up to ~ 0.6 units. These observed annual seasonal changes in carbonate conditions are significant when compared with the likely magnitude of changes associated with 21st century anthropogenic ocean acidification. For example, the average pre-industrial surface ocean aragonite saturation state (~ 3.5) is projected to decline ~ 1.2 under a business-as-usual CO_2 scenario by the end of the century [McNeil and Matear, 2007]. This magnitude of change is only about one-third of the observed changes shown here over an annual cycle in the Ross Sea.

[6] Recent evidence along the continental shelf of North America shows how upwelling of carbonate-depleted deep waters can drive surface conditions to become seasonally corrosive [Feely *et al.*, 2008]. Our in-situ results indicate near-corrosive levels of Ω_{ARAG} in the Ross Sea (~ 1.1 – 1.2) during late spring (November, Figure 1). The low Ω_{ARAG} is due to the entrainment of carbonate depleted circumpolar deep water (CDW) on the Ross Sea Shelf which is known to occur in the region [Sweeney, 2004]. Unfortunately however, winter-time Ω_{ARAG} aren't available, the period most susceptible to entrainment of corrosive CDW. We estimate the surface winter-time Ω_{ARAG} by employing a water mass analysis. Deep waters moving onto the Ross Shelf have been estimated to be a combination of 50% CDW, 25% Antarctic Surface water (ASW) and 25% winter water (WW) [Sweeney, 2004]. Taking observed carbonate values for these water masses (see Table 1) and assuming deep wintertime entrainment, surface waters in winter do not become corrosive, just managing to maintain saturation levels ($\Omega_{\text{ARAG}} \sim 1.08$), close to those observed during spring (See Table 1). Even if Circumpolar deep water (CDW) was to be 100% entrained into the surface Ross Sea during the winter, it is unlikely that Ω_{ARAG} would become corrosive. As noted by Sweeney [2004] using hydrographic observations, mid-spring (October) surface conditions in the Ross Sea are subject to similar processes (deep convection and sea-ice) to winter and therefore a significant deviation from carbonate conditions found during October is unlikely. This conclusion is verified using the results from our Ross Sea biogeochemical model (see below for explanation) which also suggests no change in pH or Ω_{ARAG} between August (winter) and the November (Spring) period. The extreme variations in Ω_{ARAG} shown here imply that Ross Sea aragonite-secreting organisms (such as pteropods) have either adapted to or undergo intense seasonal biophysical variations associated with the extreme seasonal changes. This

Table 1. Average Values of Physical and Chemical Properties for Water Masses Found in the Ross Sea^a

Water Mass	Temperature (C)	Salinity	DIC ($\mu\text{mol kg}^{-1}$)	ALK ($\mu\text{mol kg}^{-1}$)	PO_4 ($\mu\text{mol kg}^{-1}$)	SiO_4 ($\mu\text{mol kg}^{-1}$)	Contribution	Ω_{ARAG}
CDW	1.17 ± 0.25	34.70 ± 0.02	2255 ± 1	2330	2.22 ± 0.01	93.5 ± 1.2	50%	1.01
AASW	-0.96 ± 0.57	34.11 ± 0.18	2193 ± 2	2310	1.96 ± 0.05	55.5 ± 5.2	25%	1.37
WW	-1.64 ± 0.18	34.30 ± 0.05	2218 ± 2	2320	2.09 ± 0.05	73.0 ± 5.3	25%	1.23

^aTemperature, salinity and DIC are taken from Sweeney [2004]. Circumpolar Deep Water (CDW, Maximum temperatures below 150 m), Winter Water (Tmin, Minimum T in upper 100 m) Antarctic Surface Water (AASW, values based on salinity versus concentrations trend).

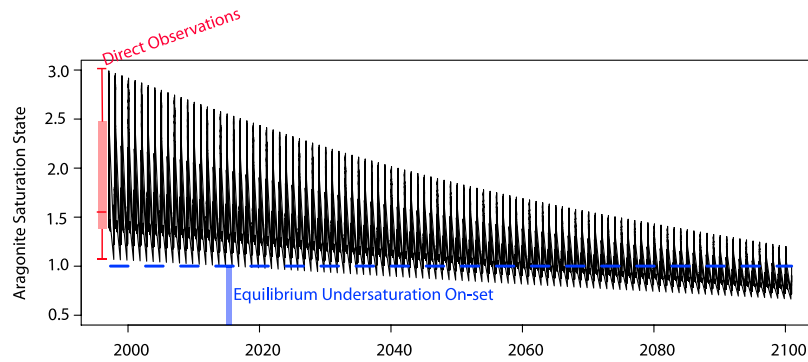


Figure 2. Equilibrium projection of Aragonite Saturation State (Ω_{ARAG}) from 1995 to the year 2100 under the IPCC IS92a atmospheric CO_2 scenario assuming equilibrium oceanic anthropogenic CO_2 uptake for the Ross Sea, Antarctica. The observed seasonal cycle is represented with a box and whiskers plot, where the median, 1st and 3rd quantiles and minimum and maximum levels are represented. The corrosive point for aragonite are shown by the horizontal dotted lines.

will be important to explore with coinciding biological studies in order to better understand the resilience of Antarctic calcifiers to future ocean acidification.

3. When Do Ross Sea Waters Become Corrosive for Aragonite?

3.1. Equilibrium Onset of Aragonite Undersaturation

[7] The extreme natural variations in seasonal oceanic pH and Ω_{ARAG} found in the Ross Sea can both amplify and suppress the onset of future anthropogenically-induced ‘corrosive’ waters depending on the time of year. Knowledge of the natural carbonate cycle gives us an opportunity, for the first time, to pinpoint the future onset of aragonite under-saturation over the annual cycle these waters. Assuming the observed annual carbonate cycle does not change, we use the IPCC IS92a scenario to determine the onset of aragonite undersaturation from the observations (Figure 2) based on standard CO_2 dissociation constants [Dickson and Millero, 1987]. Under the assumption of equilibrium conditions, we find that during the winter/spring period, undersaturation of aragonite would occur by 2015 in the Ross Sea (Figure 2). However, we know that in the Ross Sea and the greater Antarctic region it is not sufficient to assume equilibrium with the atmosphere since entrainment of deep waters and sea-ice formation limits residence times and CO_2 gas exchange, thereby creating a significant CO_2 disequilibrium with increasing atmospheric CO_2 levels.

3.2. Quantifying CO_2 Disequilibrium Dynamics Using a Regional Model of the Ross Sea

[8] Air-sea CO_2 disequilibrium would be particularly evident in the Ross Sea where both Antarctic bottom waters are formed and entrainment of deep waters have been shown to alter CO_2 uptake dynamics considerably [Arrigo *et al.*, 2008; Sweeney, 2004]. To investigate the importance of air-sea CO_2 disequilibrium in the Antarctic, we use a coupled ice-atmosphere-ocean biogeochemistry model of the Ross Sea to simulate the natural carbon dynamics and the dominant processes driving its variability such as sea-ice dynamics, biological production, polynya dynamics and deep-water ventilation. The three-dimensional Coupled Ice, Atmosphere, and Ocean (CIAO) model used here [Arrigo *et al.*, 2003; Tagliabue and Arrigo, 2005] simulates bio-

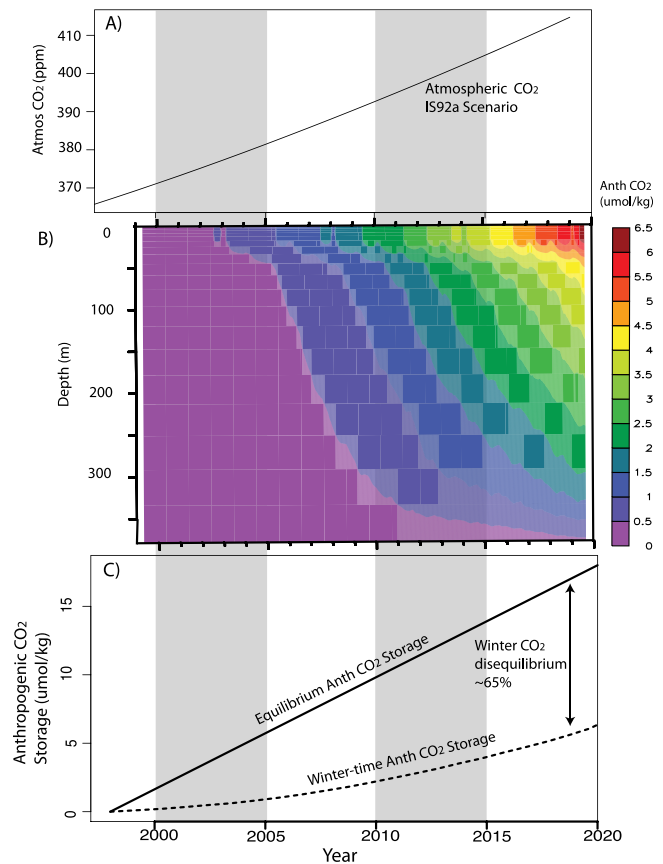


Figure 3. (a) Atmospheric CO_2 scenario (IPCC is92a) used in the model analysis. (b) Winter-time anthropogenic CO_2 storage ($\mu\text{mol}/\text{kg}$) between 1997 and 2020 at a specific location in the central Ross Sea (76.5°S , 177°E) simulated using a three-dimensional regional ocean biogeochemistry model. (c) Ross sea winter-time surface ocean anthropogenic CO_2 ‘disequilibrium’. Solid line represents anthropogenic CO_2 storage under equilibrium conditions from the atmospheric CO_2 increase in Figure 3a, while the dotted line represents the actual simulated winter-time anthropogenic CO_2 storage. Winter-time anthropogenic CO_2 disequilibrium is simulated to be $\sim 65\%$ in the Ross Sea.

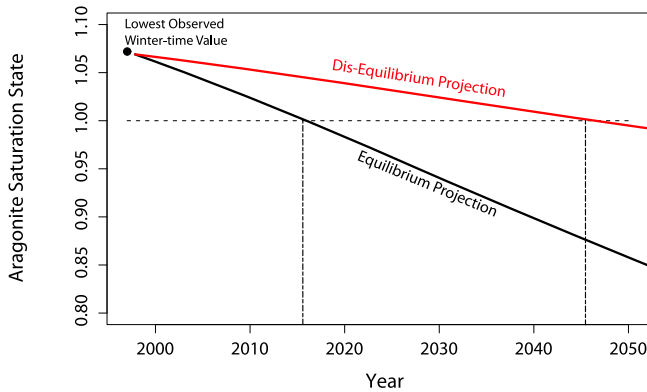


Figure 4. Equilibrium and dis-equilibrium projections of winter-time Aragonite Saturation State (Ω_{ARAG}) from 1997 to the year 2050 under the IPCC IS92a atmospheric CO_2 scenario for the Ross Sea. The significant winter-time CO_2 disequilibrium delays the onset of corrosive conditions by about 30 years.

logical dynamics coupled with the full carbon system as well as seasonal mixing processes, carbon export, and air-sea CO_2 exchange. Sea-ice data is used from satellite SSM/I data obtained from the EOS Distributed Active Archive Center (DAAC) at the National Snow and Ice Data Center, University of Colorado, Boulder, Colorado. The open boundary conditions were fixed over the time-frame of the simulation. The model was spun up to equilibrium and then run over an annual cycle for 1997 atmospheric conditions and directly compared to the observations. The model captures the timing and magnitude of the large pCO_2 drawdown very well [see also Arrigo *et al.*, 2008] and importantly for this study, also captures the extreme variations of Ω_{ARAG} in comparison to the in-situ observations to within 10% (see Figure 1).

[9] To predict future absorption of anthropogenic CO_2 over the annual cycle we performed transient simulations using the IPCC IS92a CO_2 scenario until 2020 (Figure 3). During winter between 1997 and 2020, the model suggests that the Ross Sea surface waters absorb only $6 \mu\text{mol/kg}$ of the anthropogenic CO_2 signal in comparison to a potential storage of $16 \mu\text{mol/kg}$ if equilibrium conditions prevail (Figure 3). Our model analysis suggests the Ross Sea accumulates just 35% of the equilibrated anthropogenic CO_2 signal (Figure 3c), which has significant implications for the future timing of aragonite undersaturation and ocean acidification. This significant anthropogenic CO_2 disequilibrium is driven by a reduction in air-sea gas exchange due to sea-ice cover from April to November along with the surface entrainment of older deep waters that drives insufficient residence times for annual equilibrium accumulation. If we combine this anthropogenic CO_2 disequilibrium with our in-situ Ω_{ARAG} observations, the onset of acidified corrosive conditions is delayed from the year 2015 until 2045 in the Ross Sea (Figure 4).

3.3. Model Caveats

[10] There are two important caveats to our model analysis that may serve to overestimate the simulated anthropogenic CO_2 disequilibrium in the Ross Sea. Firstly, as discussed earlier, half of the waters entrained into the Ross

Sea winter surface are ASW and WW. As these waters originate from the open Southern Ocean ($\sim 55\text{--}60^\circ\text{S}$) near the surface with longer residence times, they would almost certainly have accumulated anthropogenic CO_2 in their transit to the Ross Sea. Our model doesn't include horizontal advection of waters north of 58°S , which would most likely bring the Ross Sea closer to atmospheric equilibrium, although the importance of this is unclear. Secondly, climate change itself will alter the ability of Antarctic waters to accumulate anthropogenic CO_2 . In the Arctic ocean, sea-ice melt and stratification reduces deep mixing and speeds up the rate of anthropogenic CO_2 storage and the onset of ocean acidification [McNeil and Matear, 2007; Yamamoto-Kawai *et al.*, 2009]. A similar stratification in the Antarctic may also occur and thereby accelerate the rate of change of ocean acidification beyond that simulated here.

4. Conclusion

[11] Our analysis shows extreme seasonal variability in aragonite saturation state ($\sim 1.1\text{--}4$) in the Ross Sea surface water. These results imply that important Antarctic aragonite-secreting organisms (such as pteropods) have either adapted over generations to withstand these variations or undergo intense seasonal biomass changes in concert with the extreme seasonal Ω_{ARAG} variations. Using a Ross Sea couple ocean-atmosphere-ice model, we find significant winter-time air-sea CO_2 disequilibrium that delays the onset of corrosive 'acidified' waters by up to 30 years. Our results demonstrate the importance of understanding CO_2 disequilibrium in regions like the Antarctic that maintain strong upwelling and/or sea-ice dynamics before accurate timing of ocean acidification can be estimated.

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- B. I. McNeil, Climate Change Research Centre, Faculty of Science, University of New South Wales, Sydney, NSW 2052, Australia. (b.mcneil@unsw.edu.au)
- C. Sweeney, CIRES, University of Colorado at Boulder, Boulder, CO 80309, USA.
- A. Tagliabue, Laboratoire des Sciences du Climat et de Environnement, IPSL-CEA-CNRS-UVSQ, Orme des Merisiers, F-91198, Gif sur Yvette, France.