Historical reconstruction of Ocean Acidification in the Australian region

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1. Abstract

The ocean has become more acidic over the last 200 years in response increasing atmospheric carbon dioxide (CO_2) levels. Documenting how the ocean has changed is critical for assessing how these changes impact marine ecosystems, and for the management of marine resources. Here we use present day ocean carbon observations, from shelf and offshore waters around Australia, combined with neural network mapping of CO_2, sea surface temperature and salinity to estimate the current seasonal and regional distributions of carbonate chemistry (pH and aragonite saturation state). The observed changes in atmospheric CO_2 and SST and climatological salinity are then used reconstruct pH and aragonite saturation state changes over the last 140 years (1870–2013). The comparison with data collected at Integrated Marine Observing System National Reference Station sites located on the shelf around Australia shows both the mean state, and seasonality in the present day is well represented by our reconstruction, with the exception of sites such as the Great Barrier Reef. Our reconstruction predicts that since 1870 an average decrease in aragonite saturation state of 0.48 and of 0.09 in pH has occurred in response to increasing oceanic uptake of atmospheric CO_2. Large seasonal variability in pH and aragonite saturation state occur in Southwestern Australia driven by ocean dynamics (mixing) and in the Tasman Sea by seasonal warming (in the case of aragonite

saturation state). The seasonal and historical changes in aragonite saturation state and pH have different spatial patterns and suggest that the biological responses to ocean acidification are likely to be non-uniform depending on the relative sensitivity of organisms to shifts in pH and saturation state. This new historical reconstruction provides an important link to biological observations that will help to elucidate the consequences of ocean acidification.

2. Introduction

The ocean plays a key role in reducing the rate of global climate change, absorbing approximately 30% of the anthropogenic CO_2 emitted over the last 200 years (Ciais et al., 2013), and more than 25% of current CO_2 emissions (Le Quéré, 2015). The CO_2 taken up by the ocean reacts in seawater, leading to decreases in pH and dissolved carbonate ion concentrations (CO_3^{2-}), these changes being collectively referred to as ocean acidification. Over the past 200 years, it is estimated that there has been a 0.1 unit reduction in the ocean's surface pH, or 26% increase in the concentration of hydrogen ion concentrations in seawater (Doney et al., 2009).

Current projections suggest that the increase in hydrogen ion concentration is likely to be greater than 100% (than the preindustrial period) by the end of the century under high emissions trajectories e.g. Matear and Lenton (2014). Furthermore these changes will persist for many millennia e.g. Frolicher and Joos (2010). Ocean acidification is likely to impact the entire marine ecosystem - from microbial communities to top predators. Factors that can be impacted include reproductive health, organism growth and physiology, species composition and distributions, food web structure and nutrient availability (Aze et al., 2014; Doney et al., 2012; Dore et al., 2009; Fabry et al., 2008; Iglesias-Rodriguez et al., 2008; Munday et al., 2010; Munday et al., 2009).

Aragonite is a metastable form of calcium carbonate that is produced by major calcifiers in coral reef ecosystems, including reef building corals, and is the predominant biogenic carbonate mineral in warm and shallow waters of the tropics (Stanley and Hardie, 1998). The aragonite saturation state of seawater has been used as a proxy for estimating net calcification rates for corals e.g. Langdon (2005). Projections suggest that by as early as 2050 growth rates of reef building coral may

slow to such levels that coral reefs may start to dissolve (Silverman et al., 2009). The impact of acidification combined with other stressors, such as ocean warming, has implications for the health, longer-term sustainability and biodiversity of reef ecosystems (Doney et al., 2012; Dore et al., 2009).

The impact of these changes on the marine environment is fundamental for the management of future marine resources, for nations like Australia with its extensive coastline and regions of international significance such as the Great Barrier Reef. An historical record of the changes that have occurred since the preindustrial period allows us to (i) correctly attribute observed responses over the historical period; (ii) assess how well climate models represent spatial patterns of ocean acidification for the period that overlaps observations (e.g. IPCC AR5); (iii) quantify the magnitude of seasonal variability, and identify the drivers of this variability; and (iv) provide important boundary conditions for high resolution regional models.

Despite the potential impacts of ocean acidification for the Australian region, the number of carbonate chemistry measurements remains sparse. The few datasets collected only characterise variability and the mean state in specific environments e.g. (Shaw et al., 2012; Albright et al., 2013) or attempt to synthesize these into regional or habitat-based studies e.g. Gagliano et al. (2010). The only seasonally-resolved observational dataset available to characterize the mean state around Australia in the present day is Takahashi et al. (2014), but this data has coarse resolution and only focuses on the open ocean areas. Studies that have reconstructed the longer-term variability of ocean acidification from coral proxies have been of regional scale, and are temporally coarse e.g. Pelejero et al. (2005) and Calvo et al. (2007).

The goals of our study are: (i) reconstruct the observed variability and mean state in pH and aragonite saturation state in the present day around Australia at high spatial resolution and (ii) reconstruct the changes that have occurred in the Australian region over the last 140 years (1870-2013). To this end, we first develop a new salinity-alkalinity relationship for Australian waters based on observations collected around Australia over the last two decades. We then assess our reconstructed pH and aragonite saturation state fields with data collected around Australia at the Integrated

Marine Observing System National Reference Stations (IMOS-NRS; Lynch et al., 2014). Finally, we present the reconstructed aragonite saturation state and pH in the Australian region and discuss the seasonal and long-term changes in these fields. The reconstructed fields as well as the calcite saturation state, dissolved inorganic carbon dioxide (DIC), total alkalinity (TALK), sea surface temperature and salinity are all available online at http://imos.aodn.org.au.

3. Methods

In this study we focus on the Australian region (Figure 1) delineated nominally by the Subtropical Front (45° S) in the south and the equator (0°) in the north, and between 95°E and170° E. This region encompasses part of the eastern Indian Ocean and Indonesian Seas and a large part of the Tasman and Coral Seas. The seasonal cycle of physical, chemical, and biological properties of the surface ocean mixed layer in this region are described in Condie and Dunn (2006), and will not be described further in this paper. The characterization of the carbon system requires two of six potential carbon parameters (i.e. pH, total dissolved inorganic carbon, total alkalinity, partial pressure of carbon dioxide pCO_2, bicarbonate, carbonate), from which all the parameters of the ocean carbon system can be calculated. We first use pCO_2 and total alkalinity to reconstruct the changes in ocean acidification.

Oceanic values of pCO_2 were taken from an updated version of Sasse et al. (2013) that used a self-organizing multiple linear output (SOMLO) approach to predict pCO_2 values around Australia on a 1° x 1° degree grid each month for the nominal year of 2000. The SOMLO approach utilizes a global network of bottle-derived pCO_2 and corresponding standard hydrographic parameters (SHP; temperature, salinity, dissolved oxygen and phosphate; N=17753), collected from more than 263 cruises and the HOTS and BATS time series sites, for more information on the individual cruise data please see Table A1 in Sasse et al (2013). This data was first clustered into 49 neurons (or bins) based on similarities and homogeneity. Principle component regressions were then derived between pCO_2 and the SHP using data within each neuron. This can be thought of as a local-scale optimization, which follows the nonlinear clustering routine. To then predict pCO_2 values for any set of SHP, a

similarity measure is first used to establish which neuron best represents the SHP measurements, once established, pCO_2 values are predicted using the regression parameters of that neuron. Independent testing by Sasse et al. (2013) reveals the SOMLO approach predicts open-ocean pCO_2 values with a global uncertainty of 22.5 µatm (RMSE), which decreases to 16.3 µatm (RMSE; N=859) within the Australia region. Monthly pCO_2 climatologies presented in Sasse et al. (2013) were derived using the World Ocean Atlas (WOA) 2009 product (Antonov et al., 2010; Garcia et al., 2010a; Garcia et al., 2010b; Locarnini et al., 2010), which we update here via the WOA 2013 product (Garcia et al., 2014a, b; Locarnini et al., 2013; Zweng et al., 2013). We note that these pCO_2 values provide significantly higher spatial data coverage than the global climatology of Takahashi et al. (2009).

To extend the oceanic pCO_2 values into the past and the future, the value of ΔpCO_2 ($pCO_{2air} - pCO_{2sea}$) was first calculated using the oceanic pCO_2 values of Sasse et al. (2013) for the year 2000. This ΔpCO_2 value was then transformed into a time series of oceanic pCO_2 between 1870 to 2013, by adding this to the observed atmospheric CO_2 value over this period using the atmospheric history constructed by Le Quéré et al (2015).

As only limited measurements of total alkalinity (TALK) exist in the Australian region, we develop and use the relationship between TALK and salinity to estimate TALK in the Australian region. While many studies have quantified this relationship globally e.g. Takahashi et al. (2014) and Lee et al. (2006) and regionally e.g. Kuchinke et al. (2014), to date no specific relationship has been developed for the entire Australian region.

To develop this relationship 2772 concomitant measurements of salinity and alkalinity collected in the Australian region over the last two decades were used. (Table 1; Figure 1). From this data we determined our alkalinity-salinity relationship to be:

$$\text{TALK } (\mu\text{mol/kg}) = (2270.0 \pm 0.1) + (64.0 \pm 0.3) * (\text{SAL} - 35.) \qquad (1)$$

This relationship is based on a type 2 linear regression, accounting for uncertainty in both the salinity and TALK measurements of 0.05 and 3 µmol/kg respectively. This

new relationship was applied to the climatology of salinity (0.5° x 0.5°/daily) taken from the CSIRO Atlas of Regional Seas 2012 (CARS; Ridgway et al., 2002) as no long-term high spatial and temporal resolution observations of ocean surface salinity at present exist around Australia (nor globally). Nevertheless, based on sparse measurements Durack and Wijffels (2010) suggested that there has been an amplification of the global hydrological cycle that has resulted in surface salinity changes over the last 50 years. Their estimated changes around Australia are not uniform and are typically less than ± 0.1, which introduces only a 6.4 μmol/kg change in TALK for the 50-year period. The influence of the changes on the carbonate chemistry (pH and aragonite saturation state changes of about 0.001 and 0.02 respectively), are small compared to the changes predicted from increasing atmospheric CO_2 thereby allowing us to assume that the CARS salinity used has not changed in our calculations.

Sea surface temperature (SST) measurements from 1870 to the present day were obtained from the HadiSST v1.1 dataset (1°x1°; Rayner et al., 2003). Higher resolution datasets do exist, e.g. NOAA OI V2 (0.25° x 0.25°; Reynolds et al., 2007), but none have estimates beyond the last 3 decades, and we chose the 1°x1° product to extend our reconstruction back to the pre-industrial period.

We first calculated DIC from TALK, SST and pCO_2 in the period 1870-2013, using the method following Lenton et al. (2012) that used the dissociation constants of Mehrbach et al. (1973) refitted by Dickson and Millero (1987). Our implementation of carbonate chemistry is derived from the OCMIP3 framework (O. Aumont, C. Le Quéré, and J. C. Orr, NOCES Project Interannual HOWTO, 2004, available at http://www. ipsl.jussieu.fr/OCMIP/).

This approach calculates the magnitude of the seasonal cycle of DIC, rather than pCO_2. The pCO_2 seasonality changes over time in response to changes in the Revelle factor and will influence the air-sea gradient in pCO_2, which drives net flux across the air-sea boundary e.g. Hauck and Völker (2015). To correct for this, we first calculated the (detrended) seasonal anomaly of DIC in the period 1995-2006. We then added this seasonal cycle of DIC to the (deseasonalised) long-term DIC record (1870-2013). This allows us to reconstruct the historical DIC fields, and the changes in the

198 magnitude of the oceanic pCO_2 in response to the Revelle Factor to be accounted for.

199 We then added this seasonal cycle to the deseasonalised long-term DIC record (1870-
200 2013) to reconstruct the DIC fields, thereby allowing pCO_2 to change. The
201 reconstructed DIC fields were then used in conjunction with our derived TALK fields
202 to calculate changes in ocean acidification in the period 1870-2013. As the resolution
203 of SST and pCO_2 fields are nominally 1°x1° monthly fields, all values were calculated
204 on a 1°x1° grid at in-situ temperatures. The values of pH were calculated using the
205 total scale following recommendations of Riebesell et al. (2010) while aragonite and
206 calcite saturation states were calculated following Mucci (1983). To assess the
207 uncertainty in the reconstructed ocean acidification values, we compared these with
208 the values calculated from individual cruises, this allowed us to estimate the
209 uncertainty (RSME) to be 0.02 and 0.1 in pH and aragonite saturation state
210 respectively.

211 **4. Results and Discussion**

212 **4.1 Assessment of the mean state and seasonal variability at coastal NRS sites**

213 The ability of our reconstruction to predict the mean state and seasonality of ocean
214 acidification around Australia was evaluated by comparing our calculated aragonite
215 saturation state and SST data with carbonate chemistry and SST measurements made
216 over the last few years from seven of the eight Australian IMOS-NRS sites (Figure 2;
217 https://imos.aodn.org.au). The Darwin NRS site was not used in the comparison due
218 to the small number of measurements at this site. To assess how well the observed
219 response at the NRS sites were captured, we calculated both the correlation
220 coefficient (*R*) and the bias (or bias function) shown in Table 2.

221 The observed responses from the NRS sites compared with HadiSST are shown in
222 Figure 3. There is a good correlation in SST at all sites ($r > 0.84$, Table 2) providing
223 confidence that HadiSST represents the character of the seasonal variability. However
224 while HadiSST captures the SST variability, there were some biases in the mean SST
225 value (Table 2). These biases, e.g. Rottnest Island, likely reflect local process in the
226 coastal environment at the NRS e.g. Lima and Wethey (2012) that are poorly captured
227 by the much larger spatial scale of the HadiSST product.

The reconstructed aragonite saturation state (Ω_{AR}) shows good agreement with values calculated from observations (Figure 4). The implication is that the salinity - total alkalinity relationship and calculated pCO_2 fields, which are derived mostly from offshore data, are valid for most of the IMOS-NRS sites, which tend to be located on the outer shelf. Exceptions are the Ningaloo and Yongala sites, where our reconstruction overestimates the observed values of aragonite saturation state while SST agrees well with HadiSST (Table 2). The total alkalinity - salinity relationship may not hold at these two sites due to the influence of net calcification on nearby coral reef systems and possibly sediment-water exchange that could alter the total alkalinity e.g. Shaw et al. (2012).

Apart from the offsets at the Yongala and Ningaloo sites, the reconstructed aragonite saturation state does recreate the range determined at most locations (e.g. Maria Island, Port Hacking, Rottnest, and North Stradbroke Island). Limited sampling at Kangaroo Island, Esperance and Ningaloo sites prevented direct comparisons of the seasonal variability, although the reconstructed variability appears plausible based on available measurements.

Overall the ability of our reconstruction to capture the mean state and variability of ocean acidification at the IMOS-NRS sites, gives us confidence in the reconstruction of ocean acidification in the shelf and offshore waters around Australia, and to extend our reconstruction back in time.

4.2 Annual mean state

The mean state of aragonite saturation state around Australia for the period 2000-2009 is shown in Figure 5. The mean state shows a strong latitudinal gradient in aragonite saturation increasing from values of 1.8 in the southern part of the domain to values greater than 3.9 across Northern Australia and into the Coral Sea. The Coral Sea and Western Pacific form part of the coral triangle, a globally significant region in terms of coral and marine diversity (Bell et al., 2011). We see that our reconstructed values in the Coral Sea and into the Western Pacific are also consistent with the observational values of 3.9 calculated by Kuchinke et al. (2014) in this region. This value is well above 3.5, considered to be a key threshold at which corals move from

healthy to marginal conditions (Guinotte et al., 2003).

Ricke et al. (2013), using results from an ensemble of CMIP5 simulations and GLODAP data reported that in the Coral Sea, the present-day values of aragonite saturation state are much less than the 3.5 threshold (Guinotte et al., 2003). These differences are explained by their correction of the CMIP5 simulations to GLODAP DIC and TALK values (Key et al., 2004) that have very few measurements in this region.

The annual mean state of pH for the period 2000-2009 is shown in Figure 5. In contrast with aragonite saturation state there is an increasing latitudinal gradient from ~8.1 in Northern Australia to ~8.14 in Southern Australia. The reconstructed values show good agreement with observations collected on the southern Papua New Guinea coast by Fabricius et al. (2011). However, south of Australia, the pH decreases again to values comparable with those seen in Northern Australia.

The spatial gradients of pH and aragonite saturation state as function of latitude are consistent with the large-scale gradients calculated from observations of carbonate chemistry from GLODAP (Key et al., 2004). The distribution of aragonite saturation state is set by both the large-scale distribution of SST, which shows a strong latitudinal gradient, and TALK. Consequently the spatial differences between aragonite saturation state and pH are driven by temperature e.g. Zeebe and Wolf-Galdrow (2001).

4.3 The Seasonal Cycle

The seasonal standard deviation (2-sigma) of aragonite saturation state and pH reveal large spatial differences in the magnitude of the seasonal variability (Figure 5, lower panels). Large seasonality in aragonite saturation state is evident at > 0.4 units. This spatial pattern of this seasonality is quite heterogeneous, with the largest variability occurring along the East Coast of Australia, in the Tasman Sea, and off Southern Australia. The low seasonal variability predicted in the Coral Sea means that aragonite saturation state is above 3.5 even in the winter months. Strong and heterogeneous seasonality in pH is also present at > 0.06 units, around Australia, with

289 the largest range in Southern Australia.

290 The locations of large seasonality in aragonite saturation state and pH off Southern
291 Australia are associated with regions of deep winter mixing > 200m (Condie and
292 Dunn, 2006). Here, the seasonal deepening of the mixed layer in winter supplies
293 carbon, alkalinity and nutrients to the surface ocean, which in turn alter the chemistry
294 of the surface waters inducing large seasonal variability in ocean acidification values
295 in the surface ocean. That the large seasonal variability in aragonite saturation state is
296 not associated with large seasonal variability in pH along the East Coast of Australia
297 and in the Tasman Sea, suggests that here the dominant driver of seasonality
298 variability is SST rather than ocean dynamics.

299 An important consequence of the decoupling of the spatial patterns of pH and
300 aragonite saturation state is that the biological responses to ocean acidification at the
301 seasonal scale may also be decoupled as the susceptibility to pH and aragonite
302 saturation varies between organisms. This has implications for understanding
303 ecosystem responses to ocean acidification.

304 Areas of large seasonal variability are also present along parts off northern Australia
305 and off Papua New Guinea. These are primarily driven by large seasonal changes in
306 sea surface salinity driving changes in TALK and DIC which influences the pH and
307 aragonite saturation state.

308

309 **4.4 Comparison with Takahashi et al (2014)**

310 In this section the reconstructed annual mean and seasonality of pH and aragonite
311 saturation state are compared with those that calculated nominally for 2005
312 (Takahashi et al., 2014); hereafter-denoted T14 (Figure 6). The data of T14 are based
313 on oceanic pCO_2 measurements and regional potential alkalinity versus salinity
314 relationships, at a resolution of 4°x5°. Since T14 excludes Equatorial Pacific (north of
315 8°S) data and coastal data, we can only compare our results T14 away from these
316 regions.

317 The T14 spatial pattern of annual mean aragonite saturation state appears to be in

reasonable agreement with our reconstruction for most waters around Australia. An exception is off Northwestern Australia where the mean aragonite saturation state of T14 appears to be an under-estimate. Large differences in the seasonal changes also occur off the east coast of Australia and to the South of Australia. The magnitude of the seasonal variability (in T14) is lower than our reconstruction.

The pH values of T14 and our reconstruction both show the highest values in the subtropical waters, although T14 mean values are higher off eastern Australia and lower to the South of Australia. Overall there is quite poor agreement in both the magnitude and spatial pattern of pH variability for most regions.

That the spatial pattern of the seasonal cycle of aragonite saturation state is not reproduced along the East Coast of Australia and in the Tasman Sea, and the variability in Southern Australia is not seen in either pH nor aragonite saturation state, suggests that while the seasonal response of SST is captured in T14, the seasonal ocean dynamics are not well represented. Furthermore the magnitude of the seasonal cycle appeared to be underestimated in T14, this likely reflects the coarser resolution of T14 product than our reconstruction (4°x5° vs. 1°x1°) and the spatial interpolation required to generate T14.

As a result of this analysis we believe that in the Australian region our reconstruction offers an improved and higher resolution representation of the mean state and seasonality than T14. This comparison also underscores the need for such ongoing regional analyses, and the limitations of using large-scale global products such as T14 to understand regional variability and change.

4.5 Historical Changes

The historical change in ocean acidification since 1870 is represented in Figure 7 by the changes in the mean annual values of pH and aragonite saturation state between the period 1870-1889 and 1990-2009. The corresponding changes in sea surface temperature (HadiSST; Rayner et al., 2003) are shown over the same period in Figure 8, indicate a small net warming of the waters around Australia. This warming has been relatively uniform with the exception of the northern edge of the Southern

Ocean, and Southeastern Australia which has been identified as a marine hotspot Hobday and Pecl (2013). Consequently the SST changes alone cannot explain the large ocean acidification changes, suggesting these are due to changes in ocean carbon uptake, rather than changes in SST. The changes with time in pH and saturation state at the IMOS-NRS sites are plotted in Figure 9.

We estimate that over the last 120 years there has been a (spatial) mean decrease in aragonite saturation state of 0.49. However as illustrated in Figure 9, these decreases are not constant with time and the change in aragonite saturation state is accelerating. There is also a strong latitudinal gradient in magnitude of the decrease, with larger changes occurring in Northern Australian waters (Ningaloo and North Stradbroke Island) and smaller changes to the south (Maria Island). This pattern of change around Australia is consistent with large-scale chemical buffering capacity of the ocean (Revelle factor) which increases from ~ 9 at the equator to >11 at bottom of the study region e.g. Sabine et al. (2004).

Consistent with aragonite saturation state over the last 120 years there has been a net decease in pH of 0.09 units, very close to the estimated global decrease of 0.1 pH by Caldeira and Wickett (2003) over a similar period. Consistent with aragonite saturation a strong latitudinal gradient in pH is evident, but it is the inverse. The largest changes in pH have occurred in Southern Australia e.g. Maria Island (Figure 9), with the smallest changes in Northern Australian waters (e.g. Yongala (Figure 9) is about 75% of the change experienced in the south). This spatial response of pH is primarily set by the gradient of ocean mean temperature that acts to increase pH in colder waters (Figure 8).

4.7 Robustness of the reconstruction

The reconstructed time series of aragonite saturation state and pH are driven wholly by SST and atmospheric CO_2, thereby neglecting any changes in salinity and/or biological production. Observationally, studies have suggested that in some regions around Australia changes in salinity over the last 50 years have occurred e.g. Durack and Wijffels (2010), while other regions have remained constant over the last 200 years e.g. Calvo et al. (2007). If we assume, consistent with Durack et al. (2012), that

379 the changes are related to evaporation – precipitation (E-P) rather than local riverine
380 input which can have large local inputs of DIC, TALK and potentially nutrients
381 (Hieronymus and Walin, 2013), then any increase in salinity can be treated as
382 freshwater input only. Consequently given the small trends, relative to the mean, and
383 the very low sensitivity of oceanic pCO_2 to freshwater input (< 1%), it is highly
384 unlikely that such changes would make such a significant difference on pH or
385 aragonite over the last 50 years. This is perhaps not surprising given that freshwater
386 water changes act as a dilution flux i.e. acting equally on DIC and total alkalinity
387 (Lenton et al., 2012).
388
389 The roles of nutrients driving variability and change in ocean acidification are also not
390 considered in this study, as we assume that nutrients are zero around Australia. While
391 this is not strictly true, most waters around Australia are oligotrophic in nature
392 (Condie and Dunn, 2006). If the climatological values of silicate and nitrate from
393 CARS (Ridgway et al., 2002) are used to calculate carbonate chemistry, we find only
394 a small bias (0.0007 in aragonite saturation state and 0.005 in pH) in our
395 reconstruction (well within the uncertainty). While we would like to have used a time-
396 evolving field, analogous to salinity, at present no long-term time series are available
397 to use in this reconstruction.

398 In this study we assumed that the seasonal air-sea disequilibrium (ΔpCO_2) is
399 seasonally time invariant i.e. no interannual variability. While some studies have
400 argued this variability maybe important at shorter-term timescales e.g. Sitch et al
401 (2015), it is less clear how important these are on longer time series e.g. McKinley et
402 al (2011). This is further complicated as the existing products of oceanic pCO_2 fields
403 e.g. Landschützer et al. (2014) only extend back in time several decades reflecting the
404 limit of historical observations. Nevertheless to assess how important this term could
405 be, we assumed an upper bound from the published study of McNeil and Matear
406 (2008) who, in the more dynamically and biologically active Southern Ocean,
407 calculated the error introduced by assuming a fixed (air-sea) disequilibrium term.
408 From this study we can see that for an equivalent increase in (future) atmospheric CO_2
409 levels, that the error introduced into our calculation of pH and aragonite saturation
410 state falls well within the reported uncertainty of our reconstruction.

411 **5. Conclusion**

412 To explore how Australia's marine environment has changed, we have synthesized
413 newly acquired in-situ observations of carbon chemistry around Australia to: (i)
414 provide an new estimate of the mean state and seasonality of pH and aragonite
415 saturation state; and (ii) reconstruct the changes in ocean acidification around
416 Australia since 1870.

417 In this work we developed a new total alkalinity-salinity relationship for the
418 Australian region. This relationship was used in conjunction with observed salinity
419 and oceanic and atmospheric CO_2 and SST data, to reconstruct the present and past
420 changes in pH and aragonite saturation state. Our reconstructed fields were compared
421 against the Takahashi et al (2014) climatology, and high-resolution data collected at
422 the IMOS-NRS sites. We found good agreement between our reconstructed fields for
423 the observed annual mean and seasonal cycles at the shelf IMOS-NRS sites except
424 regions such as the Great Barrier Reef where near shore processes and coral reef
425 metabolism could alter the pH and saturation state.

426 Our regional reconstruction provides much higher spatial and temporal resolution than
427 previous global estimates. This highlights the importance of regional analyses and
428 reconstructions in estimating and understanding region changes. An important result
429 of this study is that at present the Coral Sea is not experiencing marginal conditions
430 (values of aragonite saturation state < 3.5) with respect to ocean acidification as has
431 been suggested.

432 Large changes in aragonite saturation state and pH have occurred over the last 140
433 years in response to increasing oceanic uptake of atmospheric CO_2. A net (spatial)
434 mean decrease in pH of 0.09 is seen in the period (1990-2009) – (1889-1870),
435 together with a net decrease in aragonite saturation state of 0.49, both of which are
436 consistent with previous estimates of the historical changes. Importantly, due to ocean
437 chemistry, the spatial pattern of the change in aragonite saturation state and pH are
438 different. In this study we found the largest changes in aragonite saturation state
439 occurred at mid and low latitudes, and the largest changes in pH occurred at higher
440 latitudes.

441 The large seasonal variability around Australia is heterogeneous, with distinctly

442 different spatial patterns in aragonite saturation state and pH, with the exception of
443 from South of Australia where variability is driven by deep winter mixing. For
444 aragonite saturation state, large seasonal variability occurs off the East Coast of
445 Australia and in Tasman Sea driven by seasonal variability in ocean temperatures

446 That the variability in aragonite saturation state and pH are spatially different over
447 temporal and regional scales, implies that biological responses and impacts are likely
448 vary. Further, this suggests that both pH and aragonite (or calcite) saturation state
449 need to be considered independently in assessing ecosystem responses and changes.

450 This historical reconstruction also provides useful information to link with biological
451 observations to help understand observed changes and aid in the design of future
452 work, thereby elucidating the consequences of Ocean Acidification. To facilitate this
453 all of the reconstructed data is available at http://imos.aodn.org.au

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7. Figures and Tables

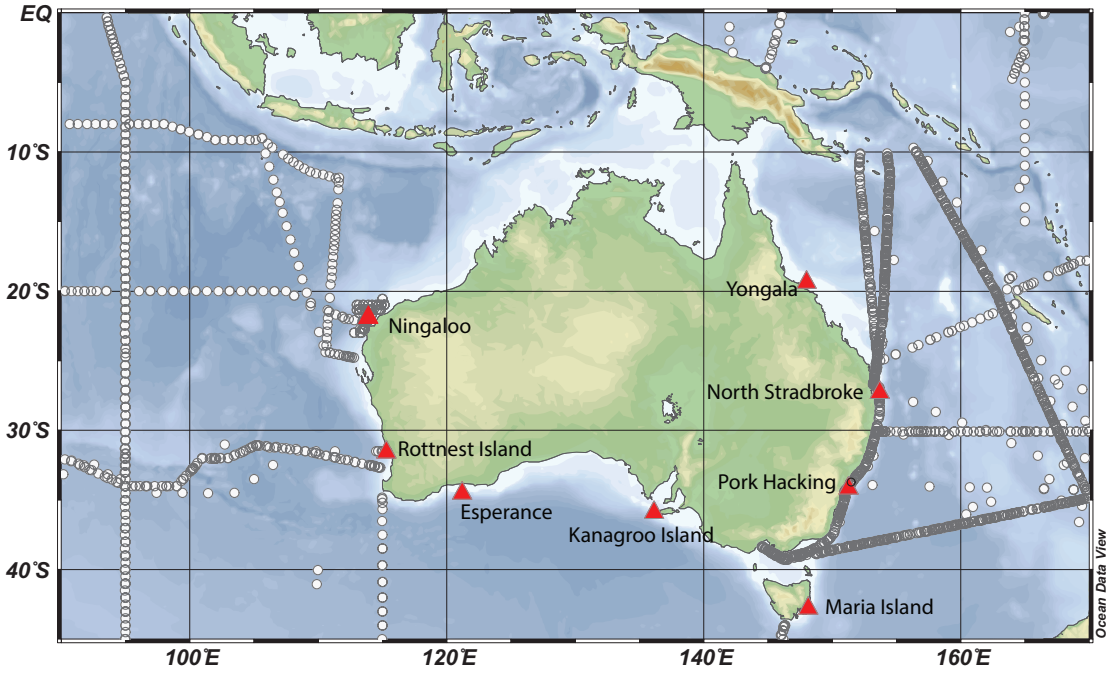
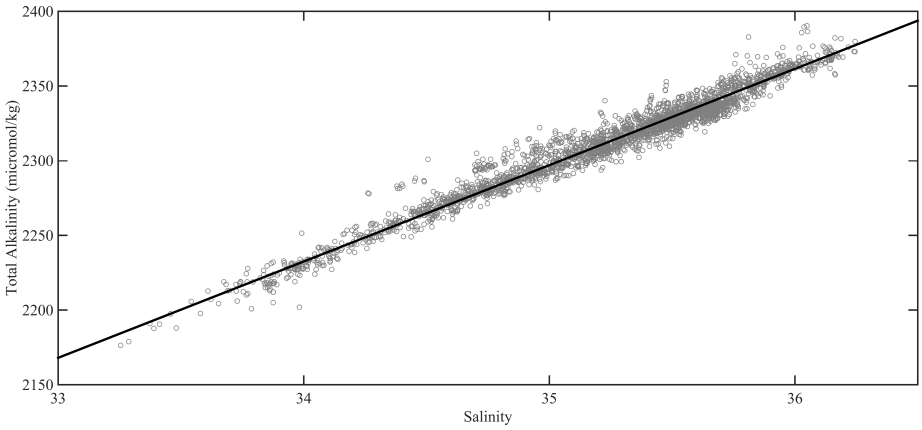


Figure 1 Locations (circles) of the concomitant measurements of alkalinity and salinity used to develop a new salinity-alkalinity relationship for the Australian Region, the cruises are listed in Table 1. Overlain on this plot (red triangles) are the locations of IMOS National Reference Stations (NRS) used in this study.



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690 Figure 2 The new salinity-alkalinity relationship developed for the Australian Region
691 based on observations (Figure 1) collected in the period 1992-2011. The individual
692 cruises are listed in Table 1.
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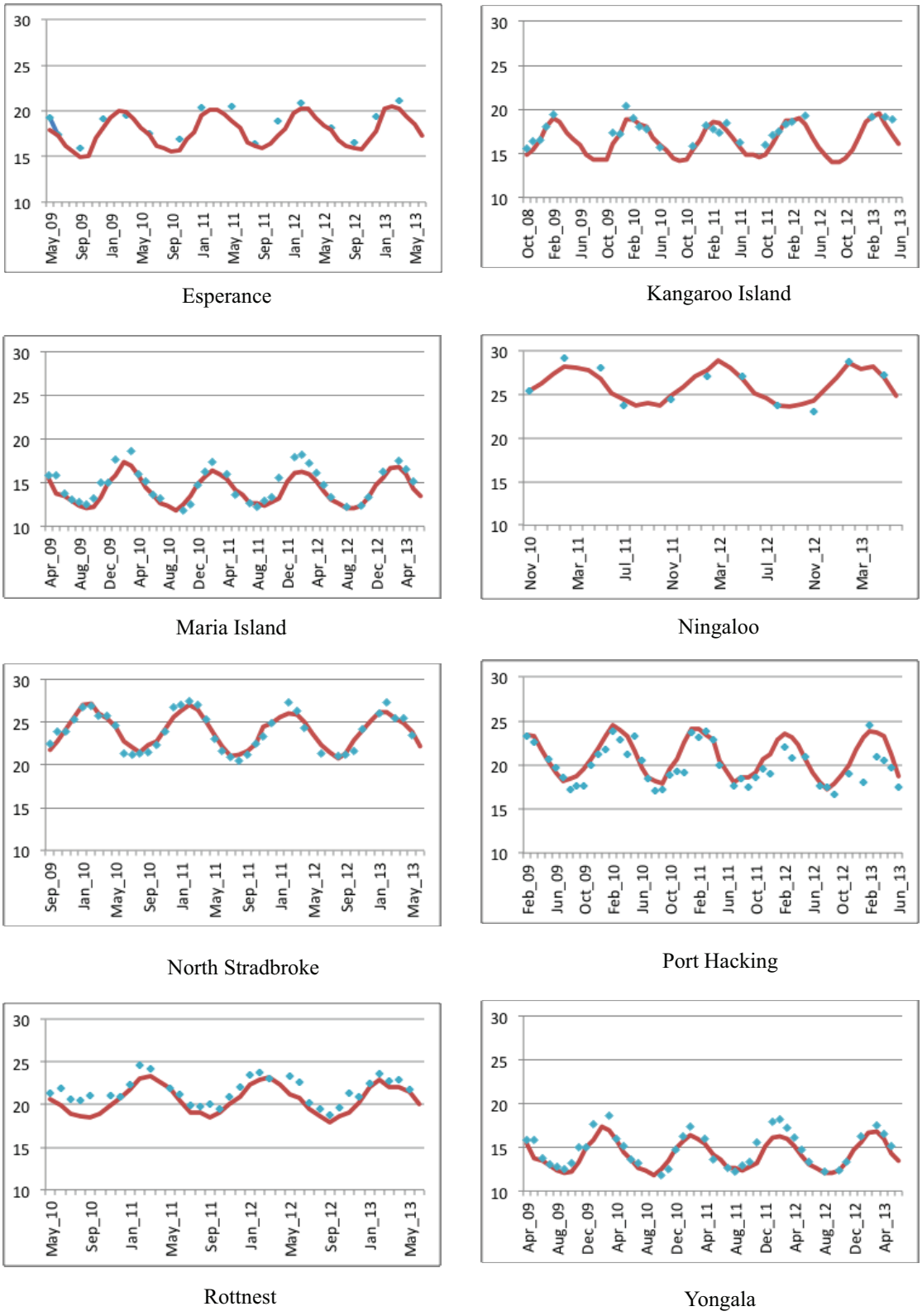
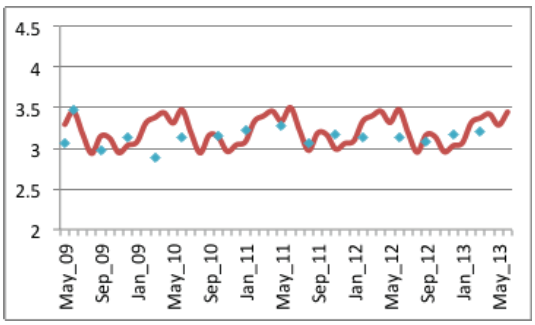


Figure 3 Comparison of sea surface temperature from the observations at the IMOS National Research Stations with HadiSST (Rayner et al, 2003)



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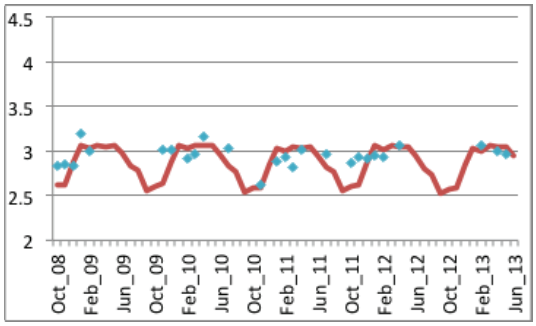

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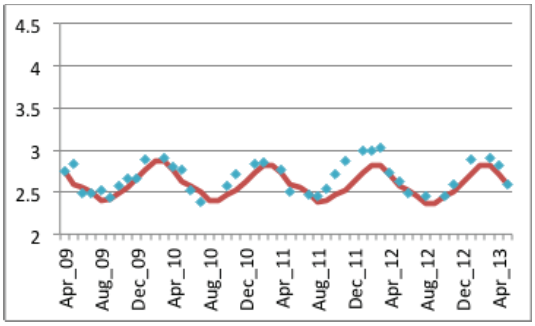

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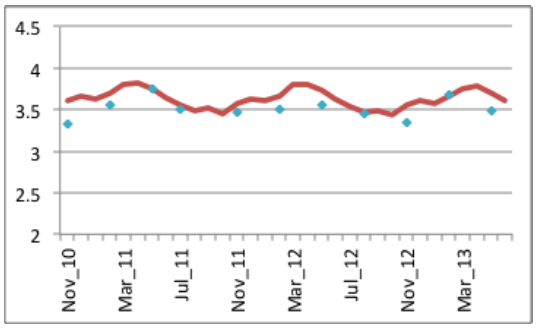

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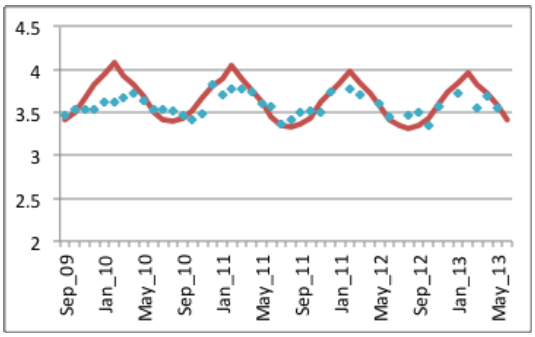

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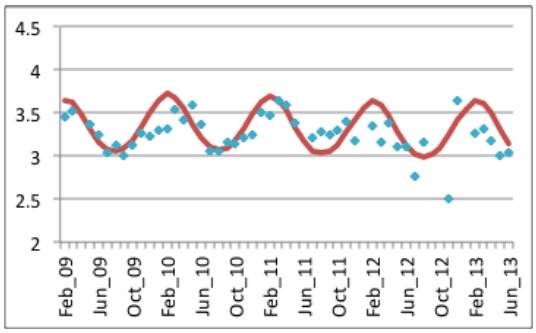

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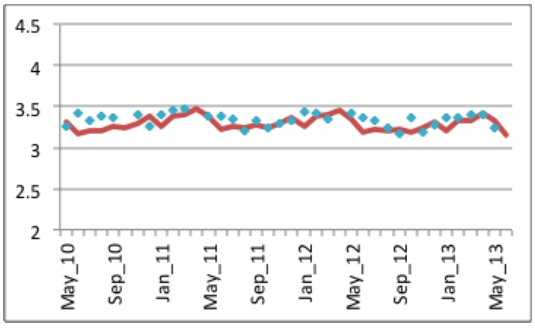
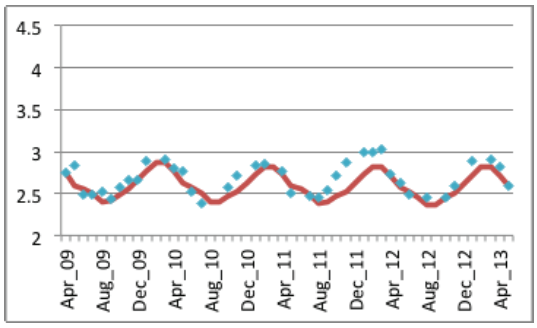
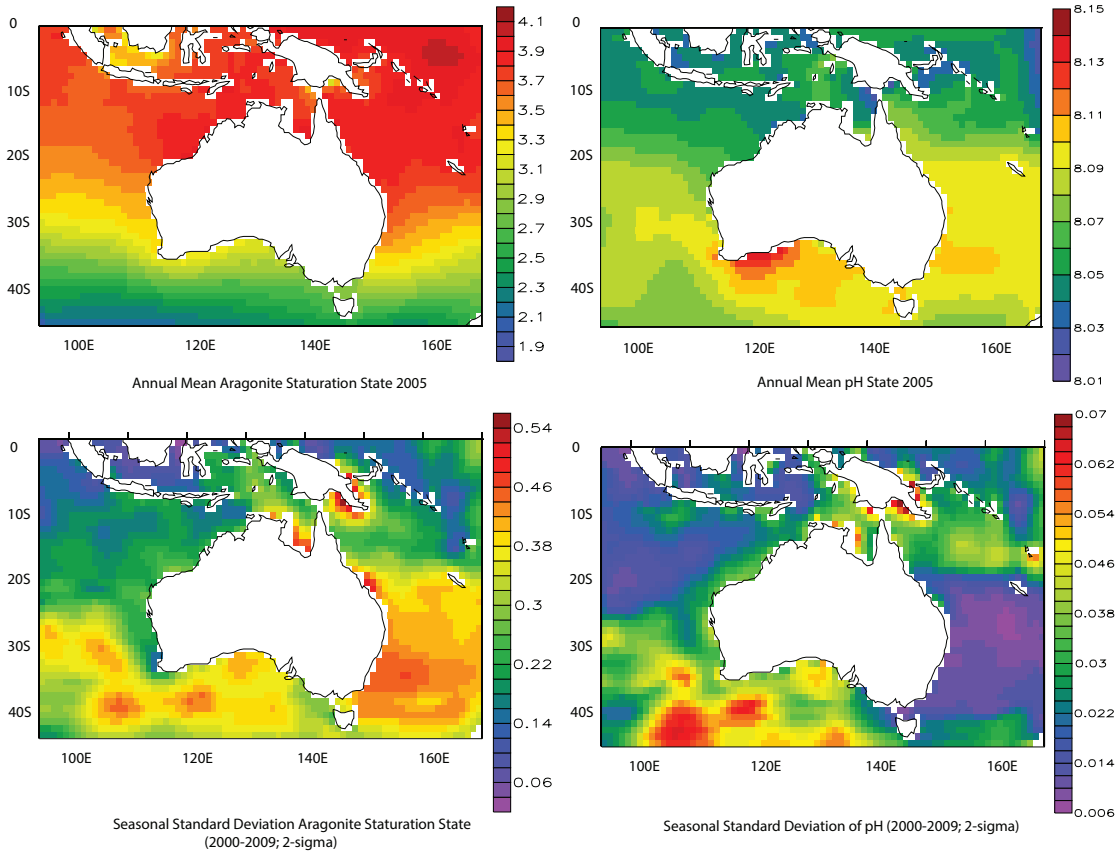


Rottnest



Yongala

Figure 4 Comparison of aragonite saturation state (Ω_{AR}) from the observations at the IMOS National Research Stations with the reconstructed values.



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709 Figure 5 Upper: the reconstructed annual mean aragonite saturation state and pH for
710 the period 2000-2009; Lower: the seasonal variability given by 2 times the standard
711 deviation (2-σ) of the seasonal variability in aragonite saturation state and pH from
712 the period 2000-2009.

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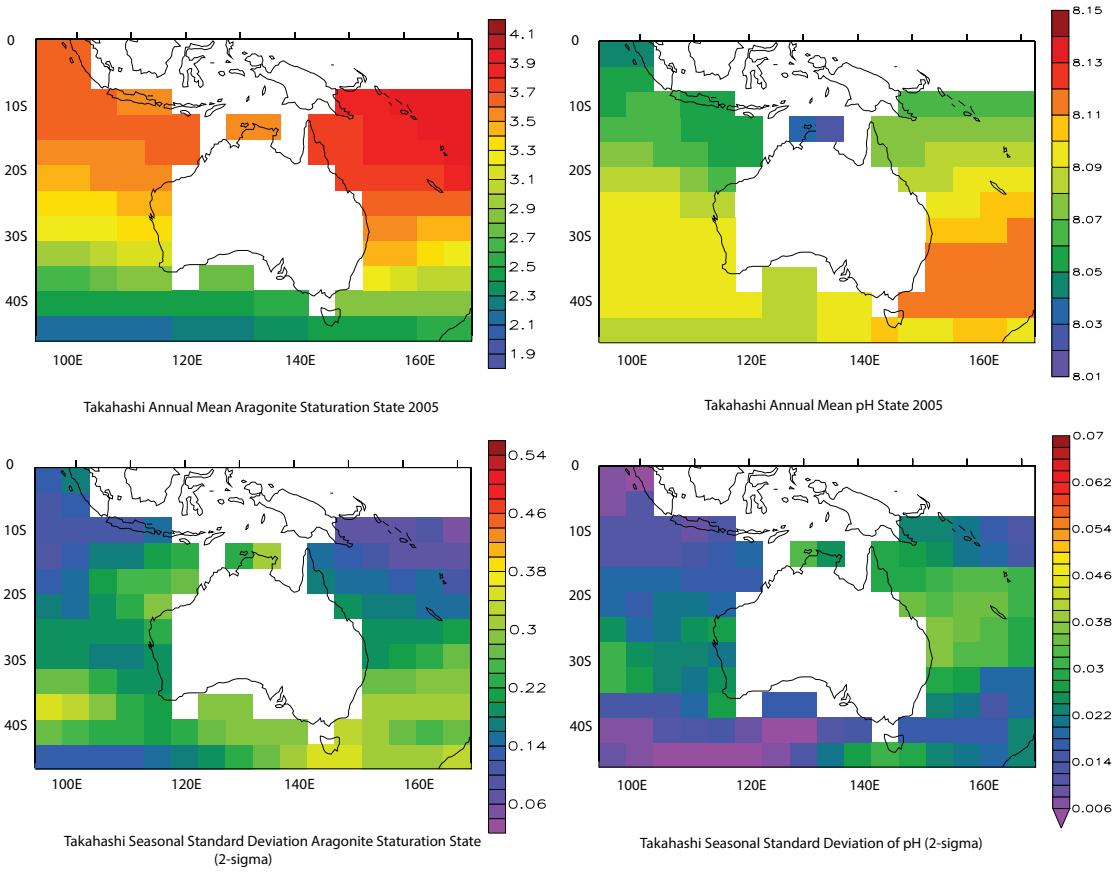

Figure 6 Upper: the annual mean aragonite saturation state and pH for 2005 from Takahashi et al (2014); Lower: standard deviation (2σ) of the seasonal variability in aragonite saturation state and pH for 2005 from Takahashi et al (2014).

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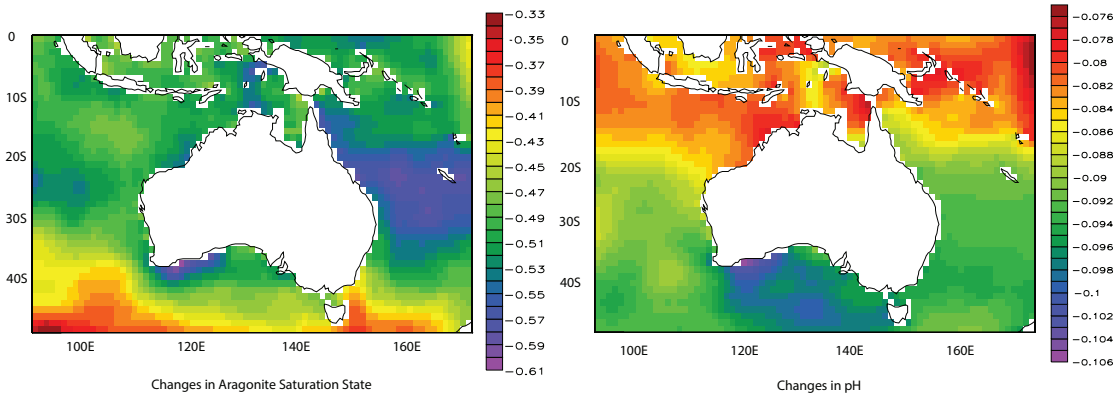

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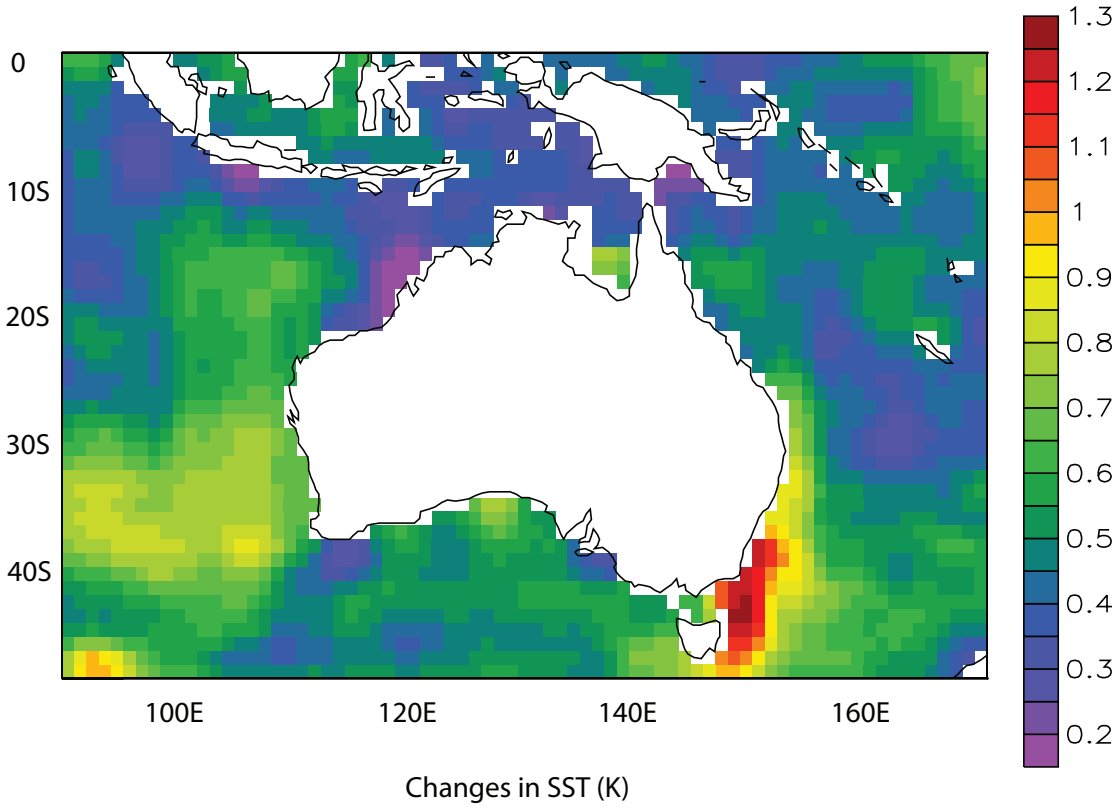
728 Figure 7 Annual mean 120-year differences (2000-2009 and 1880-1889) in aragonite

729 saturation state and pH.



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731

732 Figure 8 Annual mean 120-year differences (2000-2009 and 1880-1889) in SST.

733

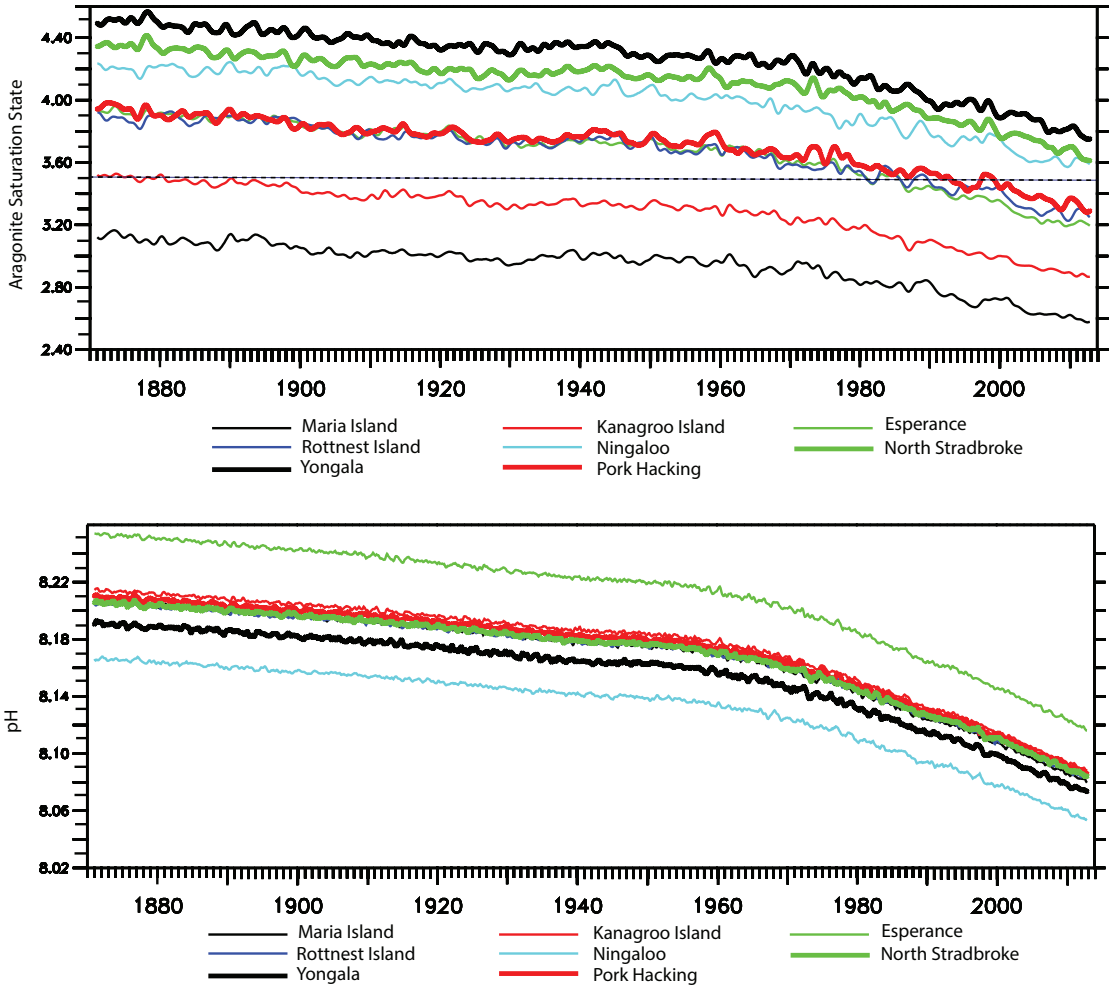

Figure 9 Reconstructed time series of annual mean aragonite saturation state (upper) and pH (lower) at the IMOS-NRSs. Overlain on the upper plot is the threshold for the transition to marginal conditions for coral reefs (3.5) from Guinotte et al. (2003)

Voyage[1]	Region/Expocode	Latitude	Longitude	Period	Number
Section P13	West Pacific 31VIC92_0_1_2	0°S - 5°S	164°E - 165°E	Oct 1992	13
Section P10	West Pacific 3250TN026/1	0°S - 5°S	145°E - 146°E	Oct 1993	11
Section P21	Coral Sea 318M19940327	17°S - 25°S	155°E - 170°E	Jun 1994	49
Section P9	West Pacific 49RY9407_1	0°S - 3°S	142°E - 143°E	Aug 1994	7
FLUPAC	West Pacific 35A319940923	0°S - 15°S	165°E - 167°E	Sep 1994 - Oct 1994	66
Section I8S/I9S	Indian Ocean 316N145_5	32°S - 45°S	95°E - 115°E	Dec 1994 - Jan 1995	29
Section I9N	Indian Ocean 316N145_6	0°S - 32°S	93°E - 106°E	Jan 1995 - Feb 1995	100
Section SR3	Southern Ocean AR9404_1	44°S - 45°S	146°E - 147°E	Jan 1995 - Feb 1995	5
Section I8N/I5E	Indian Ocean 316N145_7	31°S - 34°S	91°E - 115°E	Apr 1995	57
Section I3	Indian Ocean 316N145_8	20°S - 22°S	90°E - 114°E	Apr 1995 - May 1995	31
Section	West Pacific 49HG19950414	1°S - 35°S	153°E - 163°E	Apr 1995 - May 1995	25
Section I4	Indian Ocean 3175MB95_07	31°S - 43°S	90°E - 110°E	Sep 1995 - Oct 1995	28
Section I10	Indian Ocean 316N145_13	9°S - 25°S	106°E - 112°E	Nov 1995	76
Section I2	Indian Ocean 316N145_14_15	8°S - 9°S	90°E - 106°E	Dec 1995	37
Section SR3	Southern Ocean 09AR19960822	44°S - 45°S	146°E - 147°E	Sep 1996 - Oct 1996	5
Section I2	Indian Ocean 09AR20000927	28°S - 34°S	94°E - 115°E	Sep 2000 - Nov 2000	66
Section SR3	Southern Ocean 09AR20011029	44°S - 45°S	146°E - 147°E	Oct 2001	7
Section I5	Indian Ocean 74AB20020301	31°S - 35°S	91°E - 115°E	Apr 2002	34
OISO-10	Southern Ocean 35MF20030123	45°S	146°E	Jan 2003	5
Section P6W	West Pacific 49NZ20030803	30°S	154°E - 170°E	Aug 2003	40
Section I3	Indian Ocean 49NZ20031209	20°S - 22°S	90°E - 113°E	Jan 2004	33
Section I9S	Southern Ocean I09S_09AR20041	35°S - 44°S	115°E	Dec 2004	18
Section P10	West Pacific 49NZ20050525	0°S - 4°S	145°E - 146°E	Jun 2005	18
TransFuture 5	Tasman Sea/ Coral Sea	10°S - 40°S	144°E - 172°E	Feb 2007 - Sep 2011	1460
Section I8S	Indian Ocean I08S_33RR20070	28°S - 45°S	94°E - 95°E	Mar 2007	79
Section I9N	Indian Ocean I09N_33RR20070	0°S - 28°S	93°E - 95°E	Mar 2007 - Apr 2007	103
Section I5	Indian Ocean I05_33RR200903	31°S - 35°S	90°E - 115°E	Apr 2009 - May 2009	128
Section P21	West Pacific 49NZ20090521	18°S - 25°S	154°E - 170°E	Jun 2009	52

Section P6W	West Pacific 318M20091121	30°S	154°E - 170°E	Nov 2009 - Dec 2009	93
SS201004	Indian Ocean	21°S - 23°S	112°E - 115°E	May 2010	92
Total					2772

[1] http://cdiac.ornl.gov/ftp/oceans/

Table 1. Cruise data used to derive the salinity versus total alkalinity relationship for surface waters in Australian regional seas.

	Lat	Lon	SST - *BIAS*	SST - *R*	OmA - *BIAS*	OmA -*R*	n
Esperance	33° 56S	121°51E	0.8	0.93	0.09	-0.06	16
Kangaroo Island	35° 49S	136° 27E	0.38	0.84	0.01	0.03	27
Maria Is	42° 36	148° 14E	0.6	0.93	0.07	0.83	40
Rottnest Is	32° 25S	115° 25S	1.01	0.92	0.06	0.26	33
Ningaloo	21° 52S	113° 57S	0.08	0.95	0.17	0.62	11
Yongala	19° 19S	147° 27S	0.13	0.94	0.27	0.45	37
Port Hacking	34° 5S	151° 6S	0.82	0.89	0.09	0.58	46
North Stradbroke	27° 18S	153° 6S	0.08	0.96	0.06	0.78	40

Table 2: The locations of the NRS sites used in this study, along with the biases, correlation coefficient (*R*) between the SST and aragonite saturation state observed at the site with values from our reconstruction, HadSST and calculated omega, respectively. Also listed are the number of observations used in calculating the Biases and Correlations