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Detecting regional anthropogenic trends in ocean acidification against natural variability

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Since the beginning of the Industrial Revolution humans have released ∼500 billion metric tons of carbon to the atmosphere through fossil-fuel burning, cement production and land-use changes[1,2]. About 30% has been taken up by the oceans[3]. The oceanic uptake of carbon dioxide leads to changes in marine carbonate chemistry resulting in a decrease of seawater pH and carbonate ion concentration, commonly referred to as ocean acidification. Ocean acidification is considered a major threat to calcifying organisms[4–6]. Detecting its magnitude and impacts on regional scales requires accurate knowledge of the level of natural variability of surface ocean carbonate ion concentrations on seasonal to annual timescales and beyond. Ocean observations are severely limited with respect to providing reliable estimates of the signal-to-noise ratio of human-induced trends in carbonate chemistry against natural factors. Using three Earth system models we show that the current anthropogenic trend in ocean acidification already exceeds the level of natural variability by up to 30 times on regional scales. Furthermore, it is demonstrated that the current rates of ocean acidification at monitoring sites in the Atlantic and Pacific oceans exceed those experienced during the last glacial termination by two orders of magnitude.

Skeletons and shells of marine calcifiers are made of different crystalline forms of calcium carbonate, such as calcite or aragonite. A decrease in the saturation state of calcium carbonate can result in decreased calcification and increased dissolution of calcium carbonate[5,7,8]. As aragonite is the more soluble form, its saturation state (Ω_{Ar}, see Supplementary Information for details) can be regarded as a measure for ocean acidification.

Here we present results from a model simulation over 1,300 years (800–2099 AD) that was conducted with a state-of-the-art coupled carbon cycle–climate model (MPI-ESM, see Supplementary Information for details) forced by the most recent reconstructions of solar and volcanic radiative perturbations, land-use changes, aerosols and orbital variations. The model is also subject to historical CO_2 emissions and the A1B greenhouse-gas emission scenario (Fig. 1a,b; ref. 9). The knowledge of the pre-industrial, natural variability (defined here by the years 800 AD to 1750 AD) of the surface aragonite saturation state (Ω_{Ar}^{surf}) will permit a robust determination of regional signal-to-noise ratios using recent observed and future projected anthropogenic negative trends in Ω_{Ar}^{surf}. Furthermore, we present simulations of the Last Glacial Maximum (LGM) conducted with the models LOVECLIM and MIROC (see Supplementary Information for details) to quantify the impact of the reconstructed ∼90 ppmv increase in atmospheric CO_2 between the LGM and pre-industrial times on Ω_{Ar}^{surf}. This will allow us to put recent anthropogenic trends in ocean acidification into the context of the most recent natural event of carbon cycle–climate reorganization.

According to the MPI-ESM simulation of the pre-industrial surface waters, local marine ecosystems have been exposed to a diverse range of natural variability in both the amplitude of the annual cycle and the interannual variability of Ω_{Ar}^{surf} (Supplementary Fig. S1). For example, the Galápagos Islands are located in the centre of upwelling-driven variability, whereas reefs in the Caribbean are only exposed to small interannual changes in carbonate ion concentration. This spatial heterogeneity in natural variability, together with the local equilibration timescale of surface waters to increasing atmospheric pCO_2 and the net air–sea flux of CO_2 are likely to affect the regional impacts of ocean acidification on calcifying marine ecosystems.

Figure 1c,d shows the simulated spatially averaged Ω_{Ar}^{surf} for the main coral reef locations in the Pacific, the Southern Indian Ocean and the Caribbean (see Fig. 1e, dashed blue lines for the averaging regions). Our results reveal that current levels of Ω_{Ar}^{surf} are already considerably lower than the long-term pre-industrial mean. In a recent study[8] a linear relationship was proposed between Ω_{Ar}^{surf} and coral calcification rates. Using this estimate, our model results suggest that calcification rates at coral reef locations in the western tropical Pacific and the Caribbean may have already dropped by ∼15% with respect to their pre-industrial values. This result extends the findings of a previous study[10] that used present-day Ω_{Ar}^{surf} as a reference. Using historical CO_2 emissions and the A1B greenhouse-gas emission scenario (Fig. 1a,b), a drop to about 60% in coral reef calcification is projected for the end of the twenty-first century. It is important to note that carbonate chemistry is only one factor controlling coral calcification rates. Other factors include the effects of light, nutrients and temperature. The synergistic or combined effects are as yet poorly understood.

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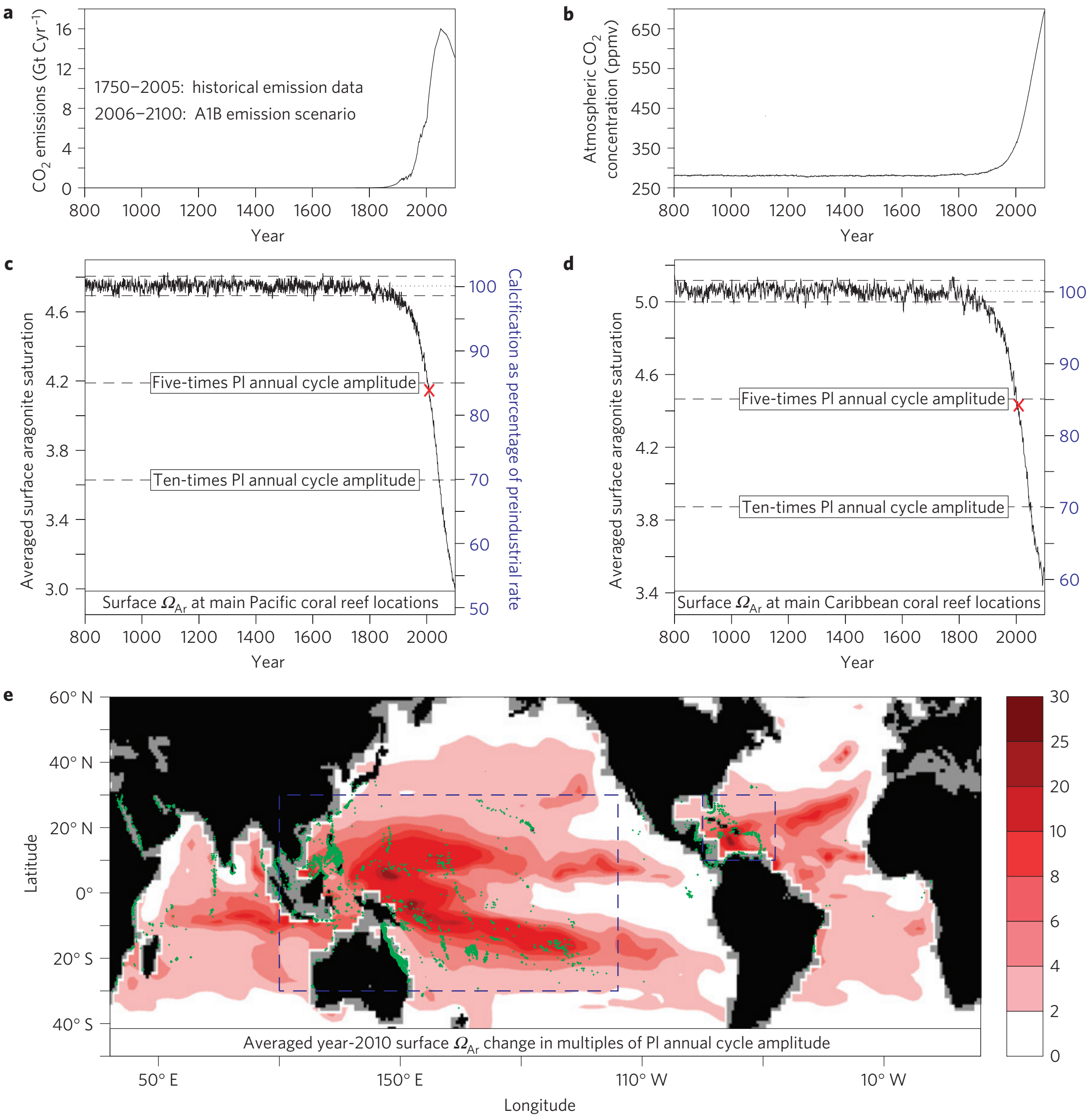

Figure 1 | Regional signal-to-noise ratio of Ω_{Ar}^{surf}. **a**, Carbon dioxide (CO_2) emissions (Gt Cyr^{-1}) used as forcing of the MPI-ESM. **b**, Atmospheric CO_2 concentration (ppmv) simulated by the MPI-ESM. **c**, Simulated annual-mean Ω_{Ar}^{surf} averaged over the main Pacific coral reef locations (green dots in the blue rectangle in **e**). Dotted line: pre-industrial (PI) average of simulated Ω_{Ar}^{surf}. Dashed lines: simulated amplitude of mean pre-industrial annual cycle of Ω_{Ar}^{surf}. Right axis: calcification rate with respect to pre-industrial level using ref. 8. Red cross indicates year 2010. **d**, Same as **c** for the main Caribbean coral reef regions (green dots in the blue rectangle in **e**). **e**, Simulated year-2010 change in Ω_{Ar}^{surf} with respect to the simulated pre-industrial average in multiples of simulated pre-industrial amplitude of the annual cycle.

The uncertainty of the ecological response to these projected changes is considerable at present.

The pre-industrial amplitude of the local annual cycle in Ω_{Ar}^{surf} can be regarded as a metric of natural variability to which aragonite-calcifying organisms have been exposed to over a long time and to which they have successfully adapted. Any reduction of Ω_{Ar}^{surf} below the minima given by the range of the unperturbed annual cycle will be interpreted here as a stress to these organisms and their associated ecosystems. Past anthropogenic CO_2 emissions have already pushed the aragonite saturation state of seawater far outside the range of natural variability (Fig. 1c,d). The difference between current and pre-industrial Ω_{Ar}^{surf} exceeds the natural annual cycle range already by a factor of five for the Pacific and Atlantic warm pool reefs (Fig. 1c,d).

Overall, the simulated ratio between the anthropogenic change (Ω_{Ar}^{surf} (2010)–Ω_{Ar}^{surf} (pre-industrial)) and the natural variability (expressed in terms of the local, pre-industrial annual cycle range) differs substantially on a regional scale (Fig. 1e). As a result of large natural variability induced by annual to interannual changes in upwelling, equatorial Pacific coral reefs from Galápagos to western Kiribati are projected to experience the most moderate relative decline of the aragonite saturation state due to anthropogenic CO_2 emissions. However, a recent study[11] confirmed a decline in some coral species occurring also in the eastern equatorial Pacific. Further to the west, and in off-equatorial regions of Micronesia, Polynesia and Melanesia, a smaller natural variability in Ω_{Ar}^{surf} (Supplementary Fig. S1) leads to a larger anthropogenic signal-to-noise ratio, attaining values of 6–30. It should be noted here that the western equatorial Pacific is the only region in our simulation in which the pre-industrial interannual variability of Ω_{Ar}^{surf} is slightly larger than its annual cycle (Supplementary Fig. S1). However, even when assuming that the pre-industrial interannual variability is a measure for the corals' 'comfort' zone, present-day values of Ω_{Ar}^{surf} are already exceeding this threshold by a factor of between two and ten.

A large amplitude in the annual cycle corresponds to a smaller signal-to-noise ratio, as documented for higher latitudes in Fig. 1e. However, the combination of a large annual cycle range on top of the anthropogenic signal can lead, in fact, to an earlier undersaturation. On the basis of empirical estimates for the seasonal cycle of carbonate chemistry parameters, it was concluded[12] that undersaturation with respect to aragonite will occur at the surface of the Southern Ocean roughly by the year 2030. Our simulation can confirm this prediction, and it further documents that values of $\Omega_{Ar}^{surf} < 1$ will be found in 30–50% of the ocean poleward of 40° S by the year 2100.

Ocean acidification is anticipated to affect marine ecosystems well beyond the coral reef realm[13–17]. Laboratory and mesocosm experiments show diverse impacts of ocean acidification on different groups of organisms, or even individual species within the same group. Recent studies using open ocean samples indicate that individual coccolithophores mass[18] and foraminfera shell weight[14] decline as CO_2 concentrations increase.

Observations in the North Pacific[19] reported a −0.06 change in surface ocean pH between 1991 and 2006 in the upper 500 m, of which 52% can be attributed to natural variability. Given the irregular sampling of chemical parameters in most parts of the ocean, a detection of ocean acidification and the determination of its local magnitude can be challenging. Our model-based estimates of anthropogenic change in Ω_{Ar}^{surf} reveal that since the mid-twentieth century the anthropogenic signals have exceeded the pre-industrial interannual variability by at least a factor of two in vast areas of the global oceans (Fig. 2). Applying an exceedance factor of two as a detection limit it becomes apparent that the anthropogenic impact on Ω_{Ar}^{surf} is detectable in almost the entire ocean by year 2010, except for the tropical eastern Pacific and the frontal regions near the subpolar gyres. In the Caribbean, a region with very high signal-to-noise ratio, the detection limit was already exceeded at the beginning of the twentieth century. By around 1980, the anthropogenic signal exceeded the natural range in this region by a factor of ten, in accordance with previous observational estimates[20] (Supplementary Fig. S2). According to our modelling results, a robust detection of the anthropogenic signal in Ω_{Ar}^{surf} in the eastern equatorial Pacific against the background variability has been possible for the past 10–20 years. By year 2020–2060, the anthropogenic signal in this region will exceed the natural variability range in aragonite saturation state by at least a factor of five.

In our effort to compare the twentieth century trends of Ω_{Ar}^{surf} with other geochemical trends from the Late Quaternary, we select another benchmark period: the last glacial termination. The concomitant change in atmospheric $p\mathrm{CO}_2$ from ∼190 ppmv to ∼280 ppmv between 17,000 and 11,000 years BP (ref. 21) represents the most recent increase of such magnitude preceding the industrial revolution. Here we study the effect of the deglacial CO_2 rise on the surface aragonite saturation using two different Earth system models: LOVECLIM and MIROC (see Supplementary Information for details). Switching from LGM to pre-industrial equilibrium conditions generates a decrease of the surface aragonite saturation state of 0.88 (0.64) units in LOVECLIM (MIROC), which is in good agreement with reconstructions[18] (Supplementary Fig. S4). These simulated changes (Fig. 3a), although being somewhat larger even than the change from pre-industrial to present-day conditions simulated by the MPI-ESM (Fig. 3f), occurred over a time period that was two orders of magnitude longer than the industrial period.

To compare the simulated Ω_{Ar}^{surf} changes and their rate of change with previous observations, we focus on continuous records of Ω_{Ar}^{surf} from several monitoring sites in the Pacific[22] and the Atlantic[20,23,24] covering the last two to three decades (Fig. 3b–e). The observed decadal changes are dominated by a trend signal, a pronounced

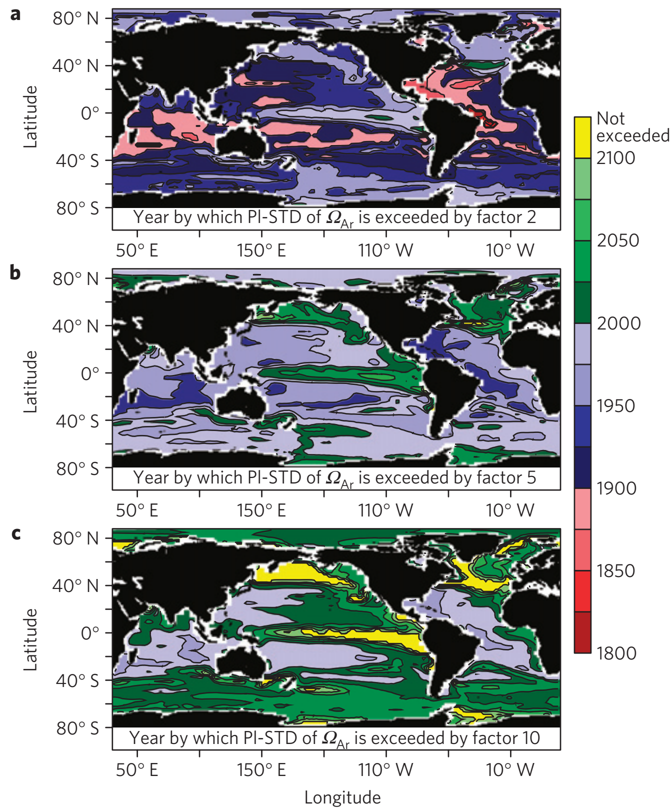

Figure 2 | First year of detectability of anthropogenic Ω_{Ar}^{surf} trend. a, Year by which simulated changes in Ω_{Ar}^{surf} (with respect to the pre-industrial mean) exceed simulated pre-industrial (800–1750 AD) standard deviation (PI-STD, based on annual-mean values, see also Supplementary Fig. S1) by a factor of two. **b**,**c** same as **a** for factors of five and ten respectively. Areas with yellow shading indicate regions where the pre-industrial standard deviation is not exceeded by the respective factor during the course of the model simulation.

annual cycle and interannual variability (Supplementary Fig. S2). The observed trends off the Canary Islands, Bermuda, Hawaii, and in the Caribbean amount to about −0.09, −0.04, −0.08, −0.09 units per decade respectively (Fig. 3i–l). These values are higher than the simulated globally averaged trends over the entire twentieth century, but close to the simulated global values for the twenty-first century (Fig. 3m,n).

The observed present-day, anthropogenic rate of change in Ω_{Ar}^{surf} is one to two orders of magnitude larger than estimated for the last glacial termination (Fig. 3h–l) . Already, the weakest observed rate of change in Bermuda exceeds the glacial–interglacial trend by a factor of 32(56) over the LOVECLIM (MIROC) estimates for the last glacial termination. In the Caribbean, where the largest regional trends are reported, the Ω_{Ar}^{surf} decrease over the past ∼20 years reaches 78(136) times the glacial–interglacial rate of change documented by LOVECLIM (MIROC).

Summarizing, we conclude that it is virtually certain that anthropogenic trends already exceed the natural variability on regional scales and are hence detectable in many areas of the world's ocean. However, the eastern tropical Pacific is an exception and exhibits the weakest signal-to-noise ratio owing to high ENSO-related natural variability in carbonate chemistry.

An unresolved question to address in future studies is how the detectability of anthropogenic Ω_{Ar}^{surf} trends translates into the detectability of the anthropogenic influence on the functionality of marine ecosystems. Marine organisms are exposed to a multitude of other anthropogenic stress factors. Corals, for instance, experience

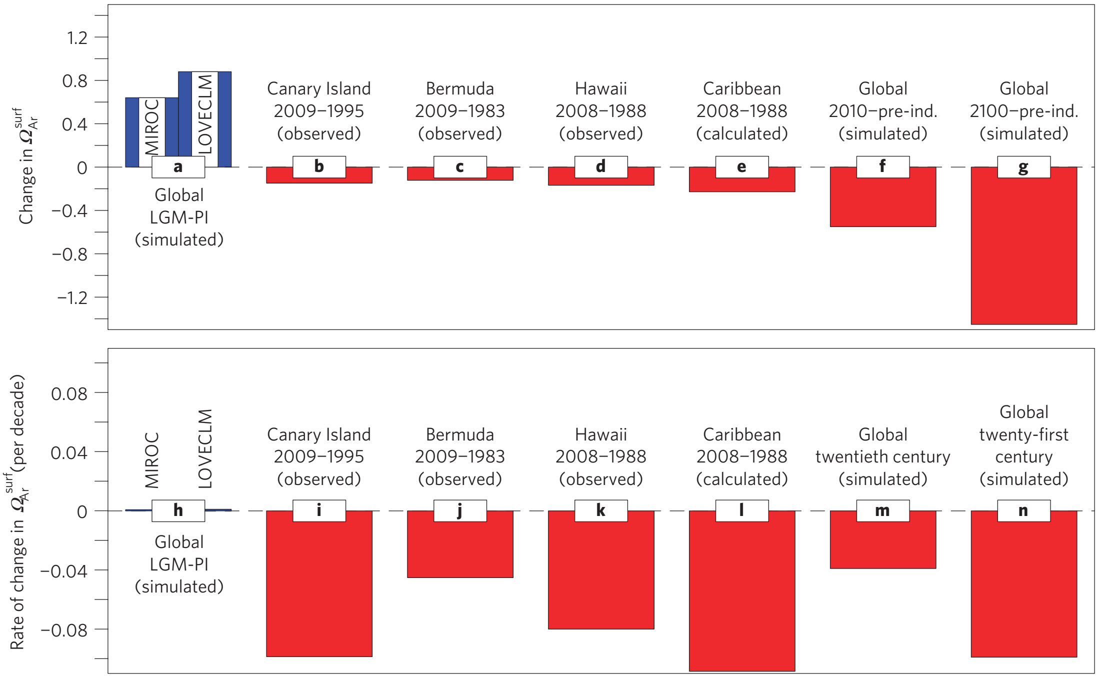

Figure 3 | Current Ω_{Ar}^{surf} trends in the context of the Last Glacial Termination. a, Globally averaged change in Ω_{Ar}^{surf} between pre-industrial (PI) times and the Last Glacial Maximum as simulated by the LOVECLIM and the MIROC model respectively. **b–e**, Trends in Ω_{Ar}^{surf} for the European Station for Time series in the Ocean (1995–2009) (**b**), the Bermuda Atlantic Time-series Study (1983–2009) (**c**), Station ALOHA (1988–2008) (**d**) and the Caribbean region (1988–2008; ref. 20) (**e**). **f**,**g**, Globally averaged change in Ω_{Ar}^{surf} as simulated by the MPI-ESM for the years 2010 (**f**) and 2100 (**g**) respectively (with respect to the pre-industrial average). **h–n**, Rates of change in Ω_{Ar}^{surf} (per decade) for glacial–interglacial as in **a** (**h**), observations as in **b–e** (**i–l**) and the twentieth (**m**) and twenty-first century (**n**), respectively.

increasing stress from ocean acidification, surface warming[25] and coastal pollution[26]. These stress factors probably do not simply add up, but combine in a species-dependent manner[27]. Tropical surface temperatures are projected to increase at a rate that would lead to massive coral bleaching and mortality in the next three to five decades[28]. Combined with a detectable change due to reduced ocean aragonite saturation and the corresponding estimated drop in carbonate accretion of ∼15% since the industrial revolution (Fig. 1c,d), severe reductions are likely to occur in coral reef diversity, structural complexity and resilience by the middle of this century.

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Author contributions

The paper was written by T.F. and A.T. Data analysis and interpretation were carried out by T.F., A.T., M.H., D.K.G., N.R.B., M.J.C., J.E.D., M.G-D., J.M.S-C., T.I., J.H.J., M.O.C., E.M. and A.M. Observational data were provided by N.R.B., M.J.C., J.E.D., M.G-D. and J.M.S-C. Data for the Caribbean region were calculated by D.K.G. Last Glacial Maximum modelling data were provided by T.F., M.O.C., A.A-O. and A.M.

Additional information

The authors declare no competing financial interests. Supplementary information accompanies this paper on www.nature.com/natureclimatechange. Reprints and permissions information is available online at http://www.nature.com/reprints. Correspondence and requests for materials should be addressed to T.F. or A.T.