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Diverging seasonal extremes for ocean acidification during the twenty-first century

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How ocean acidification will affect marine organisms depends on changes in both the long-term mean and the short-term temporal variability of carbonate chemistry^{1,2,3,4,5,6,7,8}.

While the decadal-to-centennial response to atmospheric CO₂ and climate change is constrained by observations and models^{1,9}, little is known about corresponding changes in seasonality^{10,11,12}, particularly for pH. Here we assess the latter by analysing 9 Earth System Models (ESMs) forced with a business-as-usual emissions scenario¹³. During the twenty-first century, the seasonal cycle of surface-ocean pH was attenuated by 16±7 %, on average, while that for hydrogen ion concentration [H⁺] was amplified by 81±16 %. Simultaneously, the seasonal amplitude of aragonite saturation state (Ω_{arag}) was attenuated except in the subtropics where it was amplified. These contrasting changes derive from regionally varying sensitivities of these variables to atmospheric CO₂ and climate change and diverging trends in seasonal extremes in the primary controlling variables (temperature, dissolved inorganic carbon, and alkalinity). Projected seasonality changes will tend to exacerbate impacts of increasing [H⁺] on marine organisms during summer and ameliorate impacts during winter, although the opposite holds in the high latitudes. Similarly over most of the ocean, impacts from declining Ω_{arag} are likely to be intensified during summer and dampened during winter.

45 Ocean CO₂ uptake affects marine chemistry via ocean acidification^{1,9,14}, a process that
46 increases concentrations of CO₂, H⁺ and HCO₃⁻, and reduces levels of pH and CO₃²⁻. Although
47 much effort has been devoted to assessing the direct and indirect effects of increasing
48 atmospheric CO₂ on the mean state of these ocean carbonate chemistry variables, few
49 studies have addressed the corresponding changes in their seasonal cycles^{10,11,12}.

50
51 The seasonal cycles of ocean carbonate chemistry variables are the result of variations in the
52 seasonality of different physical and biological processes^{6,7}. Those for pCO₂ and pH are
53 largely regulated by variations in temperature in the subtropics, while at higher latitudes
54 their oscillations are typically dominated by biological uptake and release of CO₂
55 (photosynthesis and respiration). In contrast, temperature plays a minor role in controlling
56 the seasonal cycles of the carbonate saturation state of seawater ($\Omega = [Ca^{2+}][CO_3^{2-}]/K_{sp}$)
57 even at lower latitudes; rather, it is the variability of total alkalinity and dissolved inorganic
58 carbon that dominates^{6,7}.

59
60 To survive, marine organisms must cope with variations in their local environment, however
61 many may be highly sensitive to changes in ocean carbonate chemistry^{15,16}. Calcifying
62 species such as echinoderms, byozoans and cnidarians exhibit depressed calcification,
63 growth and survival rates at lower $\Omega_{arag/calc}$ (refs. ^{3,4,15}). In teleost fish and marine
64 invertebrates, ion exchange is reduced by extracellular acidosis or high external [H⁺],
65 depressing protein synthesis and metabolic rates¹⁷. Physiological and behavioural
66 functioning is also sensitive to pCO₂, with high external concentrations impairing olfactory
67 discrimination¹⁸ and predator-prey responses¹⁹.

68
69 Accounting for seasonal variability in carbonate chemistry influences the timing of the
70 projected onset of CaCO₃ undersaturation^{10,11,20}, when waters become corrosive to pure
71 aragonite ($\Omega_{arag} < 1$) and calcite ($\Omega_{calc} < 1$) (i.e., metastable and stable forms of CaCO₃). These
72 seasonal variations also affect when surface waters will reach a proposed threshold, beyond
73 which pCO₂ levels may become damaging¹². Here we explore how seasonality of surface-
74 ocean [H⁺], pH and Ω_{arag} will respond to projected increases of atmospheric CO₂ and climate
75 change during the twenty-first century. Unlike studies that have assumed unchanging
76 seasonality, combining observational estimates of present seasonality (repeated in time)
77 with model projections of the change in mean state^{10,11}, we use an ensemble of 9 Earth
78 System Models (ESMs) containing coupled ocean biogeochemistry schemes. Thus we assess
79 how seasonality is affected by increasing concentrations of atmospheric CO₂ and climate-
80 change driven changes in sea surface temperature and biology^{9,21}.

81
82 Ocean biogeochemistry models (OBM) generally reproduce the amplitude and phase of
83 observational estimates for seasonal air-sea CO₂ fluxes in the Pacific²², Atlantic²³ and Indian
84 Oceans²⁴ while their skill in high latitude regions is more limited^{23,25,26}. We found consistent
85 results for the CMIP5 ESMs that include an OBM. The models broadly capture the zonal-
86 mean patterns of seasonal changes in [H⁺] ($r \sim 0.8$) and Ω_{arag} ($r \sim 0.95$) of observational
87 climatologies (Supplementary Figs. 1-6). Hence they appear to offer the best option to assess
88 projected changes in seasonality during the coming century. Nonetheless, model
89 performance in the Southern Ocean is particularly limited, with certain models negatively
90 correlated with the [H⁺] climatology, possibly due to excessive simulated warming in

91 summer²⁵ or underestimated winter convective CO₂ entrainment and the impact of
92 biological CO₂ uptake²⁶.

93
94 Projected trends in seasonality were evaluated for the business-as-usual (2006-2100)
95 Representative Concentration Pathway 8.5 (RCP8.5)¹³ relative to results from the historical
96 simulation²⁷ (1990-1999). Changes in seasonality were determined by subtracting a cubic
97 spline fit from the monthly time series in each grid cell and calculating the annual peak-to-
98 peak amplitude for each year of the detrended dataset. Both the mean state and seasonality
99 of projected [H⁺], pH and Ω_{arag} change over the twenty-first century, as illustrated in Figure 1
100 for one model.

101
102 During this century, the amplitude of seasonal cycle in [H⁺] is projected to increase by 81±16
103 % (multi-model mean ± 1SD) (Fig. 2a). Increases in seasonal amplitudes of [H⁺] are generally
104 higher in the high latitudes, particularly in the Arctic where the average amplification is
105 147±57 % (Fig. 3a, S8). Yet unlike the seasonal amplitude for [H⁺], that for pH is projected to
106 decline globally, on average by 16±7 % during the twenty-first century (Fig.2b). Attenuation
107 is generally more intense in the low and mid-latitudes but also occurs over most of the high-
108 latitude ocean (Fig. 3b, S8). Given that pH is directly related to [H⁺], it is counterintuitive that
109 while the seasonal amplitude in [H⁺] increases, the seasonal amplitude in pH declines.
110 However, the log transformation implies that

$$111 \quad d \text{pH} = \frac{-1}{2.303} \frac{d[\text{H}^+]}{[\text{H}^+]} \quad (1)$$

112 That is, the seasonal amplitude of pH depends not only on the seasonal amplitude of [H⁺] but
113 also on the annual mean [H⁺]. For the seasonal amplitude in pH to remain constant in time,
114 the relative change in the seasonal amplitude of [H⁺] would have to equal the relative
115 change in annual mean [H⁺]. Although the CMIP5 models project that the global mean,
116 seasonal amplitude of [H⁺] increases by 81±16 % over the twenty-first century, the annual
117 global mean [H⁺] simultaneously increases by 117±3 %. Hence their combination results in
118 reduced seasonal amplitude of pH. In contrast, in the parts of the Arctic and Southern Ocean
119 that exhibit increases in the seasonal amplitude of pH, the relative change in the seasonal
120 amplitude of [H⁺] is larger than the relative change in the [H⁺] mean state. Yet in those
121 regions, there is less agreement among models about the sign of these changes (Figs. 3b,
122 S8).

123
124 Regarding Ω_{arag} , its global average seasonal amplitude is attenuated by 9±8 % during the
125 twenty-first century (Fig. 3c). Attenuation can exceed 40 % in the temperate-to-polar zones,
126 while in the subtropics, where the amplitude of the seasonal cycle of Ω_{arag} is much smaller
127 (Supplementary Fig. 7), there is amplification of up to 30 % (Fig. 3c), as discussed below.
128 These projected changes in the seasonal amplitude of [H⁺], pH and Ω_{arag} result from
129 nonidentical changes in both the seasonal maxima and minima (Fig. 1, S12).

130
131 To further investigate the causes of changes in seasonal amplitudes of derived variables [H⁺]
132 and Ω_{arag} , we used 2 complementary approaches: (1) idealised simulations and (2) first-order
133 Taylor-series deconvolution. The idealised simulations partition the geochemical versus
134 radiative effects of increasing atmospheric CO₂, where the geochemical effect is due to

135 ocean carbon uptake and the radiative effect influences carbonate chemistry through rising
 136 temperatures and simultaneous changes in marine biological activity. The deconvolution
 137 quantifies how the seasonal amplitude of each derived variable (Δy), is affected by changes
 138 in temperature (T), salinity (S), dissolved inorganic carbon (C_T) and total alkalinity (A_T), i.e.,
 139 four model variables used to calculate carbonate chemistry. That is for $y = f(C_T, A_T, T, S)$,

$$\Delta y = \left(\frac{\partial y}{\partial C_T}\right) \Delta C_T + \left(\frac{\partial y}{\partial A_T}\right) \Delta A_T + \left(\frac{\partial y}{\partial T}\right) \Delta T + \left(\frac{\partial y}{\partial S}\right) \Delta S \quad (2)$$

141
 142 where the partial differentials are estimated numerically and ΔT , ΔC_T , ΔA_T and ΔS are the
 143 changes in input variables, synchronous with Δy , assuming other contributions are negligible.
 144 For the change in amplitude, Equation (2) is evaluated separately with decadal mean
 145 seasonal cycles for the first and last simulated decades of the RCP8.5 scenario, and then the
 146 latter is subtracted from the former.

147
 148 This deconvolution illustrates how the proximate drivers of seasonal amplification of $[H^+]$
 149 vary spatially. In the mid-to-high latitudes it is the residual effect of opposing increases in the
 150 terms for dissolved inorganic carbon ($(\partial H^+/\partial C_T)\Delta C_T$) and total alkalinity ($(\partial H^+/\partial A_T)\Delta A_T$) that
 151 dominates. However, in the low latitudes, changes in these two terms largely compensate,
 152 so it is the increase in the temperature term ($(\partial H^+/\partial T)\Delta T$) that dominates (Supplementary
 153 Fig. 9). Because the sensitivities of H^+ to C_T and A_T (partial differentials) are roughly equal and
 154 opposite, it is the balance between ΔC_T and ΔA_T that control the change in seasonal
 155 amplitude of $[H^+]$ in the mid-to high latitudes (Supplementary Fig. 10). One cannot assume
 156 that ΔA_T remains constant while only ΔC_T will change. For instance, changes in ΔA_T will be
 157 decoupled from those of ΔC_T due to an altered hydrological cycle. Increased freshwater
 158 input dilutes C_T and A_T , but C_T then tends to equilibrate with atmospheric CO_2 , unlike A_T .
 159 Hence addition of low alkalinity freshwater reduces pH, despite the opposite tendency from
 160 dilution alone. The high latitudes will experience this effect most, from enhanced
 161 precipitation, ice melt, and river runoff. Decoupling will also result from anthropogenic CO_2
 162 invasion and changes in primary production. In the low latitudes, while the C_T and A_T terms
 163 are small and compensating, the temperature term dominates, enhanced by a doubling of
 164 $\partial H^+/\partial T$ (Supplementary Fig. 11). The ultimate drivers of this seasonal amplification in $[H^+]$ are
 165 demonstrated by the idealised simulations, which show that it is the geochemical effect of
 166 increasing atmospheric CO_2 and consequently reduced buffer capacity^{29,30} that is responsible
 167 for 92 % of global amplification, while the radiative effect provides minor reinforcement (Fig.
 168 4, S13).

169
 170 For Ω_{arag} , the proximate drivers of the general attenuation of its seasonal amplitude are a
 171 decline in the C_T term ($(\partial \Omega_{arag}/\partial C_T)\Delta C_T$) which typically outweighs an opposing increase in the
 172 A_T term ($(\partial \Omega_{arag}/\partial A_T)\Delta A_T$) (Supplementary Figs. 9-10). In the subtropics though, there is little
 173 change in the A_T term, while the C_T term increases due to a larger change in ΔC_T , driving
 174 amplification of the Ω_{arag} seasonal cycle in these regions. The ultimate driver of the seasonal
 175 attenuation in Ω_{arag} is the geochemical effect of increasing atmospheric CO_2 which is
 176 responsible for >100 % of global attenuation, being partly offset by the radiative effect (Fig.
 177 4, S13). In contrast, the subtropical amplification of the seasonal cycle of Ω_{arag} results from
 178 the radiative effect driving enhanced amplification over the low latitudes in combination
 179 with the weaker attenuation from the geochemical effect in the subtropics.

180

181 We have shown that under a business-as-usual emissions scenario, the seasonal variability of
182 ocean carbonate chemistry is projected to change substantially during this century. Despite
183 the diversity of OBMs in the multi-model ensemble^{9,21}, spatial patterns of the change in
184 seasonal amplitude of $[H^+]$, pH, and Ω_{arag} are generally consistent (Fig. 3, S8). Previously it
185 was shown that increasing atmospheric CO_2 will amplify the seasonal cycle of surface-ocean
186 pCO_2 (ref. ¹²), potentially resulting in earlier exposure to detrimental pCO_2 conditions for
187 marine organisms. Here we show that increasing atmospheric CO_2 must also amplify the
188 seasonal cycle of $[H^+]$ in a similar manner. This is consistent with the near-linear relationship
189 between $[H^+]$ and pCO_2 for annual-mean trends during the twenty-first century³¹.

190

191 Amplified $[H^+]$ seasonality may worsen impacts from the long-term mean increase in $[H^+]$,
192 potentially resulting in earlier seasonal exposure to conditions that cause physiological
193 acidosis and depress protein synthesis and metabolic rates in marine organisms. In the low
194 latitudes, this enhanced exposure is most likely to occur during summer when warming
195 drives the $[H^+]$ seasonal high. In the high latitudes, enhanced exposure is most likely to occur
196 when the effect of photosynthesis on $[H^+]$ drawdown is limited^{6,7}. But amplified $[H^+]$
197 seasonality will also diminish exposure to conditions that cause acidosis during seasonal
198 lows, e.g., in winter months in the low-latitudes and during phytoplankton blooms in the
199 high-latitudes.

200

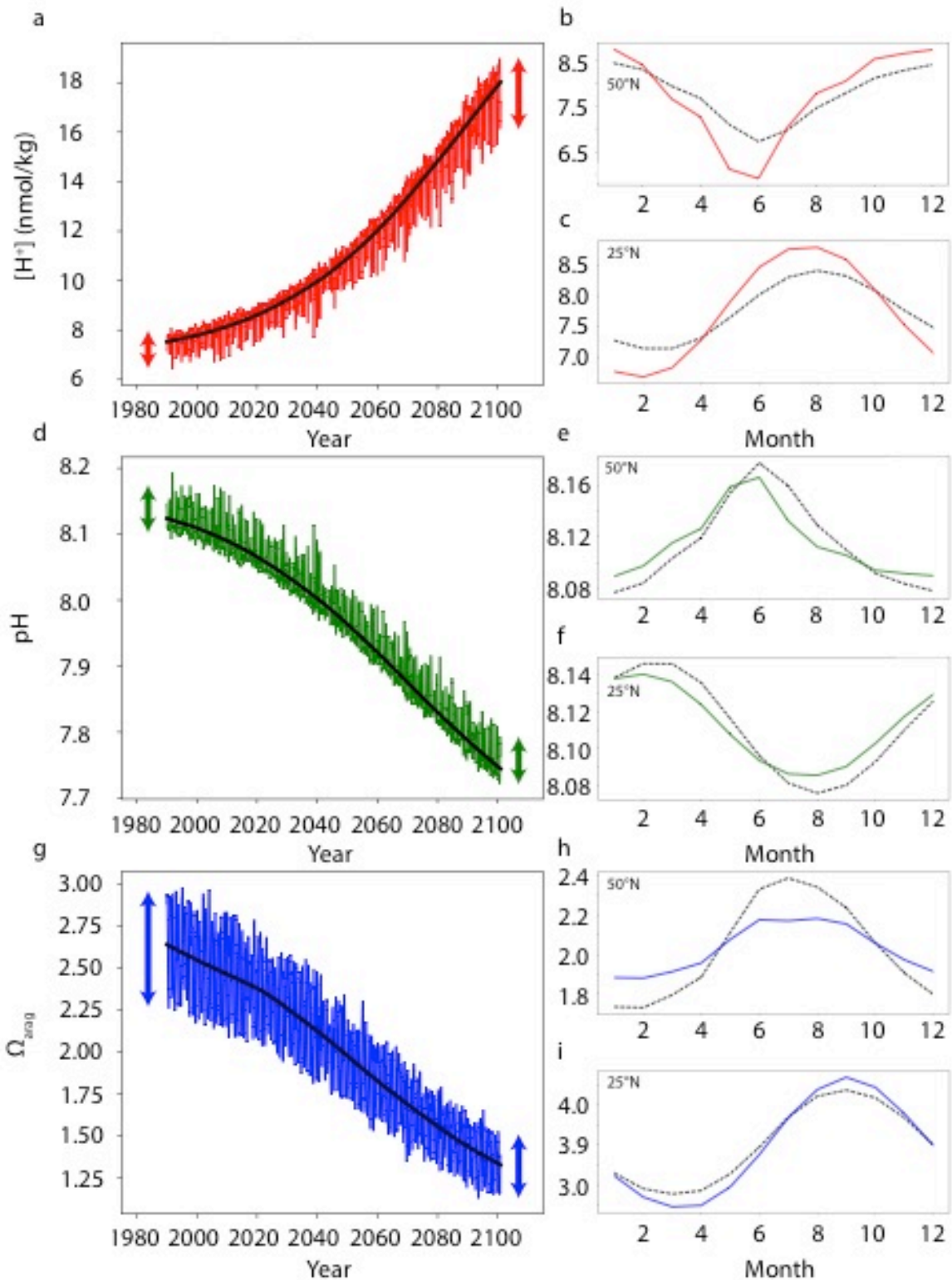
201 The seasonal amplitude of Ω_{arag} is projected to amplify in some regions and attenuate in
202 others. Attenuation dominates throughout most of the ocean owing to increases in aqueous
203 carbon dioxide $[CO_2^*]$, which reduces carbonate ion $[CO_3^{2-}]$ and hence the buffer capacity. In
204 the subtropics though, the seasonal amplitude of Ω_{arag} increases because amplification
205 driven by the radiative effect of CO_2 dominates the locally weak geochemical effect. The
206 general attenuation of the seasonal amplitude of Ω_{arag} is likely to exacerbate the impact of
207 declining Ω_{arag} during the summer high while dampening the impact of declining Ω_{arag} during
208 the winter low.

209

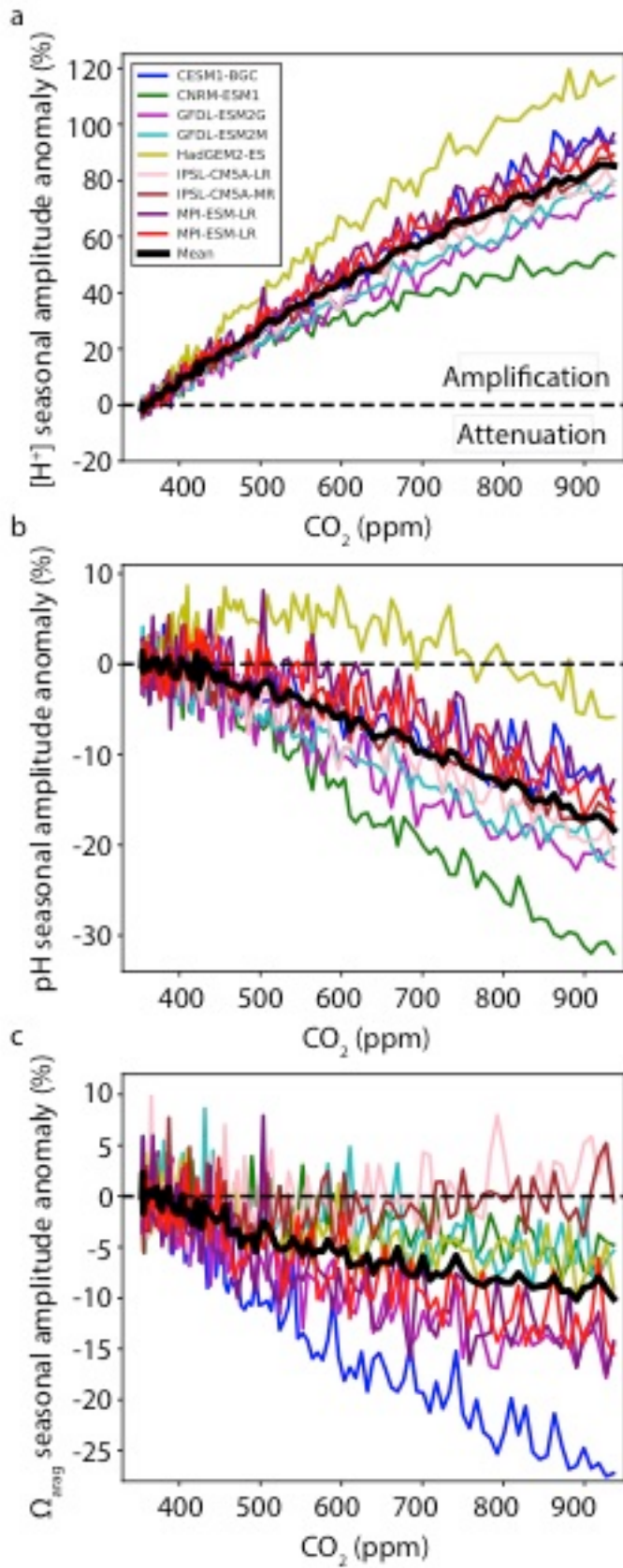
210 The same processes that will affect future seasonal variability, particularly the direct
211 geochemical effect from the atmospheric CO_2 increase and the corresponding indirect effect
212 from radiative warming, are likely to affect future diurnal variability. Indeed we estimate an
213 amplification of the diurnal cycle of $[H^+]$ (122%) and an attenuation of the diurnal cycle of
214 Ω_{arag} (20%) that are similar to our estimates for the seasonal cycle, based on differences in
215 observations of diel pH variability reported for two adjacent sites in the Bay of Naples, a
216 control station and a station where natural venting of pure CO_2 has perturbed oceanic pCO_2
217 to reach levels expected for the late twenty-first century (Table S2; ref. ³²). Future research
218 should assess how altered carbonate chemistry variability on both diurnal^{33,34} and seasonal
219 timescales will affect marine organisms, especially those suspected to be vulnerable to
220 ocean acidification.

221

222 The diversity in projected changes in seasonal extremes of $[H^+]$, pH, Ω_{arag} and pCO_2
223 emphasizes the need to improve our understanding of the mechanisms that control how
224 specific marine organisms are affected by ocean acidification. In particular, we will need to
225 study the sensitivity of marine organisms to these simultaneous yet contrasting changes in
226 seasonality to be able to assess aggregate effects on marine communities.



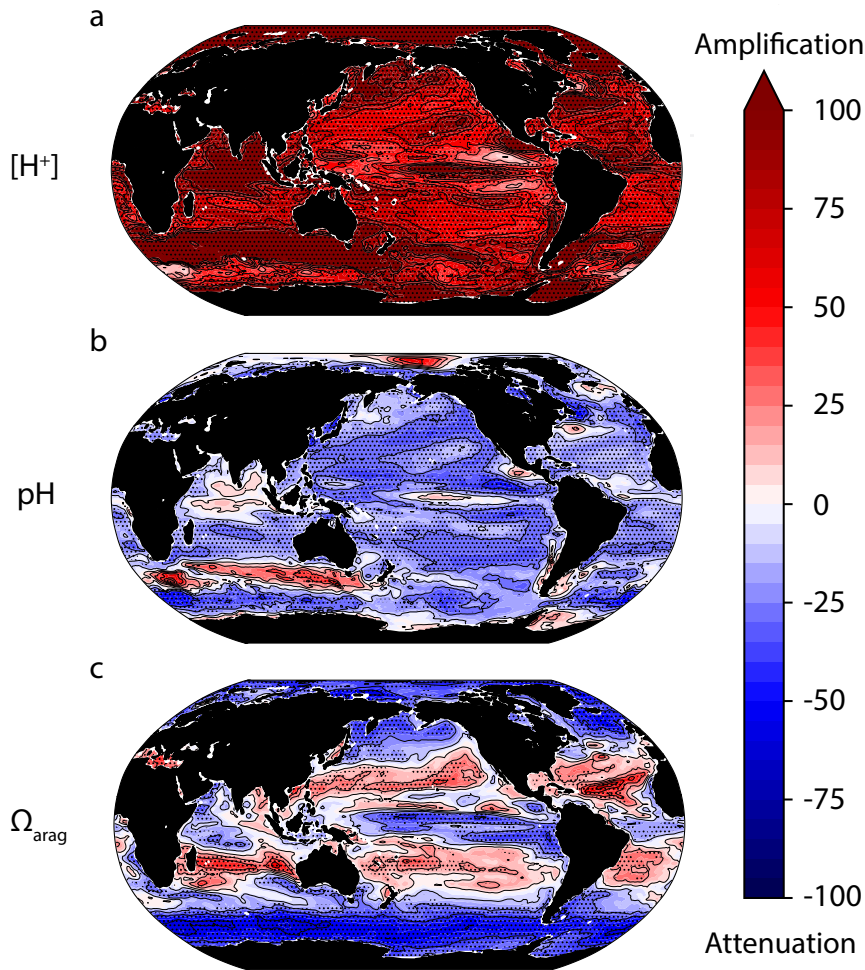
229
 230 **Figure 1. Changing seasonal cycles of carbonate chemistry variables.** The projected **a-c**, [H⁺]
 231 **d-f**, pH and **g-i**, Ω_{arag} under the historical and RCP8.5 scenario of one CMIP5 model (MPI-
 232 ESM-LR). First column, monthly values and the long-term mean trend from an illustrative
 233 grid cell in the South Pacific (110°W, 40°S). Second column, the detrended zonal-mean
 234 seasonal cycles in the periods 1990-1999 (dashed) and 2090-2099 (line) at 25°N and 50°N.



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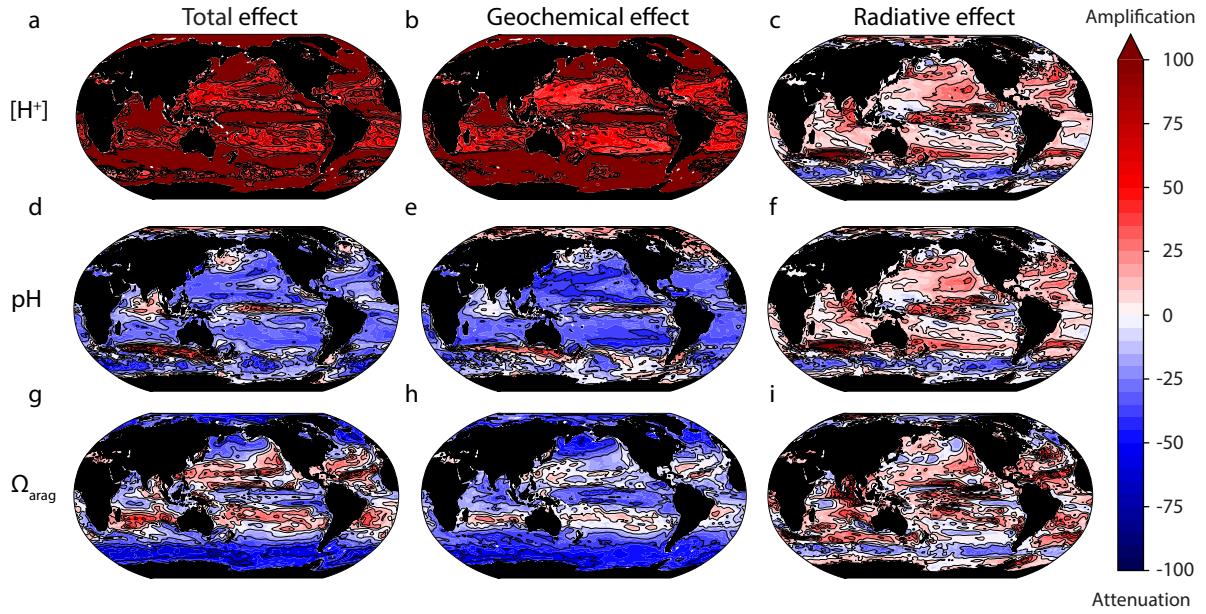
Figure 2. Relative change in the seasonal amplitude of carbonate chemistry variables with rising atmospheric CO₂. Global anomaly in the seasonal amplitudes of a, [H⁺] b, pH and c, Ω_{arag} relative to mean 1990s values as a function of atmospheric CO₂.

21st century change in seasonal amplitude (%)



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Figure 3. The twenty-first century changes in seasonal amplitudes. The model mean anomaly in the seasonal amplitude of **a**, $[H^+]$ **b**, pH and **c**, Ω_{arag} in the 2090s relative to the 1990s. Stippling shows areas of high confidence as determined by model sign agreement with a standard of 8 out of 9 models representing significance.



259
 260 **Figure 4. Partitioning of geochemical and radiative effects of atmospheric CO₂ on**
 261 **seasonality change.** The model mean anomaly (%) in the seasonal amplitudes of **a-c**, [H⁺], **d-**
 262 **f**, pH and **g-i**, Ω_{arag} due to the geochemical, radiative and combined effect of atmospheric
 263 CO₂. Anomalies are calculated for the last decade of 4xCO₂ simulations relative to the first
 264 decade.

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386

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396

397 **Author contributions**

398

399 Both authors conceived this study, J.O. produced the derived variables, and both authors
400 performed the analysis and wrote the manuscript, with L.K. leading the process.

401

402 **Additional information**

403

404 Correspondence and requests for materials should be addressed to L.K.

405

406 **Competing financial interests**

407

408 The authors declare no competing financial interests

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432 **Methods**

433

434 ***Earth System Models***

435

436 Monthly surface-ocean carbonate chemistry fields were computed from monthly output of 9
437 CMIP5 models (Table S1) from prognostic fields for total alkalinity, dissolved inorganic
438 carbon, temperature, salinity, and total dissolved inorganic phosphorus and silicon.
439 Calculations were made offline using the *mocsy* package and the equilibrium constants
440 recommended for best practices³⁵. Output fields were regridded to a regular 1° x 1° regular
441 grid to facilitate multi-model intercomparison. All quoted error bars represent one standard
442 deviation of the multi-model mean.

443

444 ***Model evaluation***

445

446 CMIP5 seasonal climatologies constructed from 1995-2004 model output years were
447 compared against the Takahashi et al., 2014 (ref. ⁶) observational climatologies of [H⁺], pH,
448 $p\text{CO}_2$ and Ω_{arag} (Supplementary Figs. 1-6). Model output was regridded to the Takahashi 4° x
449 5° grid with the same ocean mask applied. The models generally capture the zonal-mean
450 patterns of seasonality for observed climatologies of [H⁺], pH, $p\text{CO}_2$ and Ω_{arag} .
451 The multi-model ensemble encompasses the observed seasonal variance for Ω_{arag} yet
452 overestimates the seasonal variance of [H⁺] and $p\text{CO}_2$ (Supplementary Figs. 1-2). This
453 overestimation is driven by the zonal-mean component of seasonal variance (Supplementary
454 Figs. 1-2). Across all carbonate chemistry variables, models have high correlation coefficients
455 for the zonal-mean component of seasonal variability and relatively low correlation
456 coefficients for the zonal-anomaly component of seasonal variability. Model performance is
457 generally best in the subtropics and worst in the Southern Ocean with respect to both [H⁺]
458 and Ω_{arag} (Supplementary Figs. 3-6). Yet in the Southern Ocean, the data used to construct
459 the climatologies are typically summer biased.

460

461 ***Idealised simulations***

462

463 Three out of the 9 models also ran idealised simulations that allowed us to separate the
464 geochemical effect from the CO₂ increase from the radiative forcing effect of the same CO₂
465 increase. More precisely, we used results from three CMIP5 experiments: 1pctCO₂,
466 esmFixClim1 and esmFdbk1. Although these simulations are not directly comparable to
467 those with the RCP8.5 scenario due to different simulation lengths and atmospheric CO₂
468 concentrations, they provide the only means of separating the ultimate geochemical and
469 radiative drivers of seasonality change. In the 1pctCO₂ simulations, the atmospheric CO₂
470 concentration increases from 280 ppm by 1 % per year reaching a doubling (2xCO₂) after 70
471 years (560 ppm) and quadrupling (4xCO₂) after 140 years. In the esmFixClim1 simulations,
472 the atmospheric CO₂ concentration follows that of the 1pctCO₂ simulations while the
473 radiative module of each model experiences a constant atmospheric CO₂ concentration of
474 280 ppm. Conversely, in the esmFdbk1 simulations, the atmospheric CO₂ concentration is
475 held constant at 280 ppm but the radiative module of each model experiences the same CO₂
476 concentration as the 1pctCO₂ simulations. The mean response of the models in the 1pctCO₂
477 simulations is similar spatially to that of the multi-model ensemble in RCP8.5 simulations
478 (Figs. 3, 4). This confirms that atmospheric CO₂ emissions are the driver of patterns of

479 carbonate chemistry seasonality change and validates the use of the esmFixClim1 and
480 esmFdbk1 simulations to partition the radiative and geochemical influences of CO₂. It should
481 be noted that there are limited increases in ocean temperatures in the esmFixClim1
482 simulations that result from changes associated with the terrestrial biosphere, for which
483 elevated CO₂ reduces stomatal conductance, which in turn drives greater surface sensible
484 heat fluxes and thus slight increases in temperatures³⁶.
485

486 ***Taylor-series deconvolution***

487
488 The first-order Taylor-series deconvolution was performed for [H⁺] and Ω_{arag} independently
489 with output from the RCP8.5 simulations (eqn. 2). The partial differential terms were
490 estimated numerically using the *mocsy* package and ΔT, ΔC_T, ΔA_T and ΔS represent the
491 change in input variables synchronous with Δy. This approach reproduces the changes in the
492 seasonal amplitude of each of the derived variables [H⁺] and Ω_{arag} to within much less than 1
493 % as shown in Figure S9. With the exception of the very high latitudes, the deconvolution
494 was broadly consistent across the multi-model ensemble. The zonal-mean influence of the
495 different terms is given in the supplementary material for the representative GFDL-ESM2M
496 model (Supplementary Figs. 9-11).
497

498 ***Data availability***

499
500 All the CMIP5 ESM model data are available via the Earth System Grid Federation (ESGF). The
501 derived data that support the findings of this study are available from the corresponding
502 author upon request.
503

504 ***References***

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