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Multiscale mechanical consequences of ocean acidification for cold-water corals

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Ocean acidification is a threat to deep-sea corals and could lead to dramatic and rapid loss of the reef framework habitat they build. Weakening of structurally critical parts of the coral reef framework can lead to physical habitat collapse on an ecosystem scale, reducing the potential for biodiversity support. The mechanism underpinning crumbling and collapse of corals can be described via a combination of laboratory-scale experiments and mathematical and computational models. We synthesise data from electron back-scatter diffraction, micro-computed tomography, and micromechanical experiments, supplemented by molecular dynamics and continuum micromechanics simulations to predict failure of coral structures under increasing porosity and dissolution. Results reveal remarkable mechanical properties of the building material of cold-water coral skeletons of 462 MPa compressive strength and 45–67 GPa stiffness. This is 10 times stronger than concrete, twice as strong as ultrahigh performance fibre reinforced concrete, or nacre. Contrary to what would be expected, CWCs retain the strength of their skeletal building material despite a loss of its stiffness even when synthesised under future oceanic conditions. As this is on the material length-scale, it is independent of increasing porosity from exposure to corrosive water or bioerosion. Our models then illustrate how small increases in porosity lead to significantly increased risk of crumbling coral habitat. This new understanding, combined with projections of how seawater chemistry will change over the coming decades, will help support future conservation and management efforts of these vulnerable marine ecosystems by identifying which ecosystems are at risk and when they will be at risk, allowing assessment of the impact upon associated biodiversity.

Ocean acidification is of concern to both tropical and cold-water coral (CWC) reefs¹. It can cause a reduction in the growth rate of *live* coral², and dissolution of *dead* coral material (skeletons no longer covered in soft tissue)³. In tropical reefs, this can lead to a reduction in net growth rate^{2,4,5}. For CWC reefs, found between 40 to 3000 m deep⁶, the threat is more significant and could result in dramatic and rapid habitat loss because of two factors: (i) CWC reef habitats and the biodiversity provision afforded by them is mostly provided by *dead* coral material. (ii) The aragonite saturation horizon (ASH), which is the depth at which aragonite (the calcium carbonate polymorph used by scleractinian corals to build their skeleton) becomes undersaturated, will rise above the majority (~70%) of CWC reefs over this century due to ocean acidification^{1,7}. Currently, most CWC reefs are above the ASH (aragonite concentration $\Omega_{Arag} > 1$)⁸, and the few reefs found below the ASH ($\Omega_{Arag} < 1$, Fig. 1a) have a marked absence of *dead* coral and low habitat complexity⁹.

The occurrence of *live* coral below the ASH (Fig. 1a) complements experimental research on *Lophelia pertusa* (also known as *Desmophyllum pertusum*) to date, indicating that *live* coral can continue to calcify under projected future temperature and ocean acidification conditions^{11–16}. However, this ignores the larger and more serious ecosystem-scale threat to these habitats and associated biodiversity from a shoaling ASH; the potentially rapid loss of structural integrity and habitat complexity. This is of particular concern as high biodiversity associated with CWC reefs is strongly related to their structural complexity^{17–19}. The majority of a CWC habitat is typically

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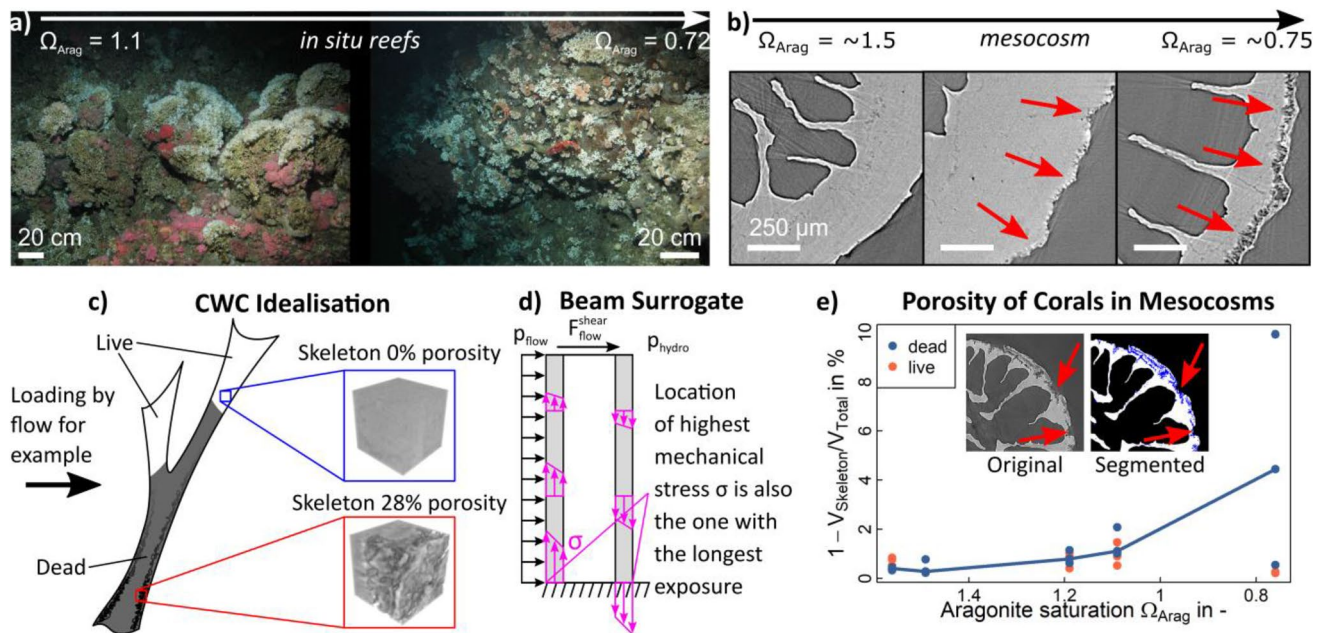


Figure 1. Cold-water corals (CWCs) in an acidifying ocean: **(a)** The transition of a high complexity reef with *live* coral (white tips) and *dead* coral (grey thicket) skeleton at $\Omega_{Arag} > 1$, to one with low complexity and no *dead* skeleton at $\Omega_{Arag} < 1$, is governed by collapse of the foundation framework due to rapidly increasing porosity in *dead* coral skeleton and subsequent dissolution when subjected to corrosive conditions (decreasing Ω_{Arag}). **(b)** CWC skeletons exposed to future oceanic conditions for 12 months in vitro showed significantly increased porosity⁹ (red arrows) for low Ω_{Arag} . This was measured as skeleton pore volume (blue inlays in **(e)**) over total skeletal volume (white + blue inlays in **(e)**), which is a conservative approach. For a pre-defined volume of interest, e.g. the red one in **(c)** with 120 μm edge length, porosity was 28%. If the coral is simplified as a hollow beam loaded by, e.g. loads due to water flow (P_{flow} , F_{flow}^{shear}) and hydrostatic pressure (P_{hydro}), it becomes clear that porosity and dissolution affect the reef at its weakest point **(c,d)**. **(e)** Porosity increased significantly with decreasing Ω_{Arag} in *dead* but not in *live* skeletons⁹. (Images and data from^{9,10}).

dead coral²⁰, with the living coral concentrated at the outermost parts of the reef where the coral is able to access and capture passing prey^{5,21}. This *dead* framework enhances the metabolic activity of CWC reefs and supports resource retention and recycling in the deep sea²². Coral framework also captures mobile sediment, leading to substantial deep-water coral reef and coral carbonate mound development⁶. The ability of *dead* coral framework to support living colonies by sustaining external loads is therefore of paramount importance not only for CWC habitat complexity and its ability to support other species, but for reef and mound formation and function.

To understand how future coral habitats may degrade, we need to consider the structural stability of the coral itself. Figure 1b,e suggest that loss of material, facilitated through an increase in porosity and a decrease in wall thickness, is exponentially related to a decrease in aragonite saturation⁹. This produces a relationship between a geochemical marker caused by ocean acidification (aragonite concentration) and a property affecting structural stability of the coral. To make sense of this, we can consider dissolution in a theoretical coral (Fig. 1c) modelled as a hollow beam fixed at its base with a load applied from the side, e.g. pressure and shear force due to water flow as well as hydrostatic pressure (Fig. 1d). Loss of material as increasing porosity and decreasing wall thickness in critical points of the outer mineralised skeleton increases fragility of the whole structure at its weakest point. This leads to early onset of mechanical failure, crumbling and collapse of CWCs.

The mechanism underpinning this shift can be described using mathematical and computational modelling that captures the complex structure of corals, combined with an appropriate material model that describes the mechanical stress–strain behaviour under load and, most importantly, that captures the impact of changing aragonite concentration. This allows prediction of failure rates of coral structures which, if combined with projections of how aragonite saturation will change over the coming decades, would allow us to estimate the timescales of this failure. Such an estimation would support future conservation and management efforts of these vulnerable marine ecosystems by understanding *which* ecosystems are at risk, *when* they will be at risk, and *how* much of an impact this will have upon associated biodiversity. However, understanding the multiscale material behaviour of CWCs and the mathematical and computational models that explain it are key gaps at present.

We aim to investigate the multiscale mechanical behaviour of CWC skeletons and analyse its deterioration with decreasing aragonite concentration and we develop a predictive model that can be interrogated for in silico experimentation. Specifically, our objectives are to (i) develop a multiscale material model that allows us to analyse multiscale mechanical consequences of ocean acidification for CWC skeletons; (ii) use dissolution data from long term experiments and in situ samples to analyse the impact of ocean acidification on the mechanical behaviour of the CWC skeleton; and (iii) demonstrate climate change induced increase in CWC fragility on a representative *L. pertusa* sample.

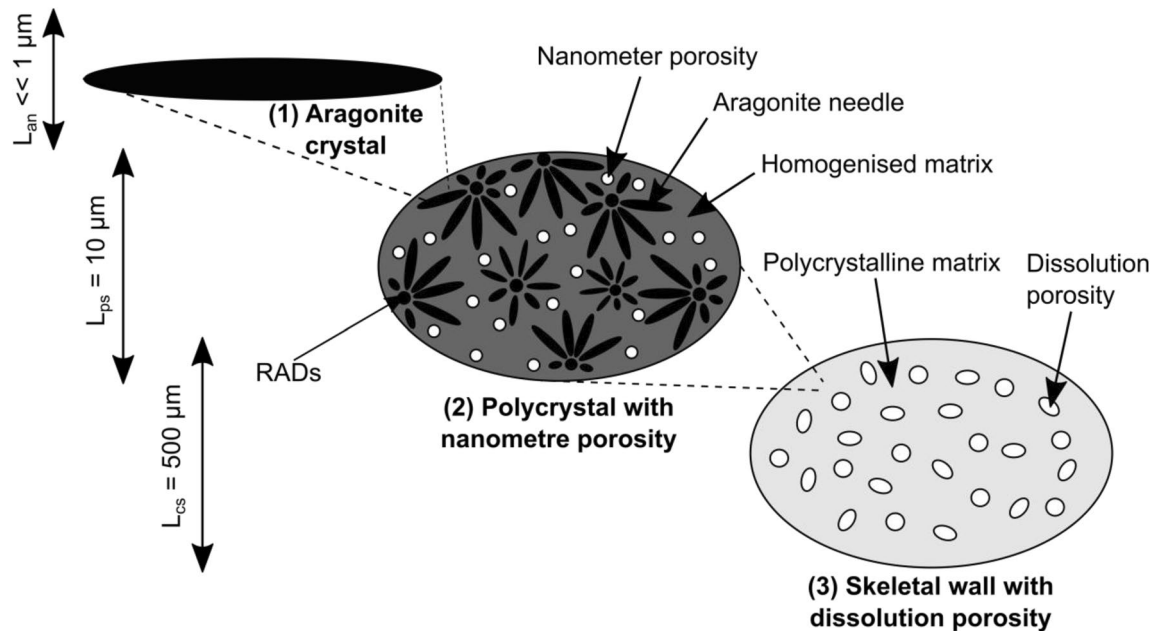


Figure 2. Multiscale model of the skeletal wall: The skeleton of *L. pertusa* consists of needle shaped aragonite crystals with finite aspect ratio. These needles are arranged around rapid accretion deposits and form a polycrystalline matrix which then forms the coral wall. This wall is subject to ocean acidification which generates spheroidal pores.

Materials and methods

Coral samples. Coral samples examined here were previously collected^{9,16} and are from a gradient of environmental conditions ranging from $\Omega_{Arag} < 1$ to $\Omega_{Arag} > 1$ as detailed in Hennige et al.⁹ In situ samples from above and below the ASH, i.e. from acidified waters, were collected in the California Sea Bight ($\Omega_{Arag} = [0.71, 1.04]$). In situ samples from non-acidified waters ($\Omega_{Arag} = [1.67, 2.62]$) were collected from the Mingulay Reef Complex and Porcupine Seabight. All samples were covered with soft tissue prior to in vitro testing and are, therefore, considered to be *live* CWC skeletons.

CWC skeletons as multiscale, polycrystalline materials. CWCs form skeletons ranging across multiple length scales from micron sized crystals to millimetre sized wall structures that are affected by ocean acidification⁹. We propose to model the skeleton exposed to acidified waters as a three-scale, linear elastic material made up of needle shaped, crystalline building blocks that form a polycrystalline matrix (Fig. 2).

CWC skeletons are made up of aragonite needles in the order of $\lesssim 5 \mu\text{m}$ long, 0.1–5wt% organic matrix embedded within the 3D framework^{9,23–26} as a thin film, and a nanometre sized porosity specified by Falini et al.²⁶ to be 3.9%. Aragonite needles protrude from rapid accretion deposits (RADs)²⁷ and, according to some sources, cluster into sclerodermites of diameter $10 \mu\text{m} \times 50 \mu\text{m}$ ²³. The occurrence of sclerodermites is debated^{23,28} and we disregard this potential morphological feature as it is not important for our consideration. Needle accretion leads to CWC skeletons with wall thicknesses $\gg 100 \mu\text{m}$, including translucent and opaque thickening bands^{23,24}. This composition suggests a polycrystalline setup where crystal needles are over an order of magnitude smaller than the structural volume they create (Fig. 2). Previous studies reported a certain degree of ordering that is generated by thickening growth of the skeleton^{28–30}, and ordered crystal arrangements would introduce a certain direction dependence (anisotropy) of the mechanical properties at the skeletal wall level. To assess this, we reanalysed previously published^{9,16} scanning electron microscopy (SEM) and electron backscatter diffraction (EBSD) data of 10 *L. pertusa* samples (Supplementary materials Figure S1) with regards to crystal orientation. A random crystal assembly was observed in SEM surface images (Figure S1). EBSD images also show that 38.5% crystals are oriented in (001), 27.6% in (100), and 33.9% in (010) direction across their cross-sectional areas which are also varying. This is consistent with observations by Pasquini et al.³¹ who reported no preferential organisation of the aragonite needles based on combined data from nanoindentation, electron microscopy, atomic force microscopy, and X-ray diffraction patterns of longitudinal and transverse sections in solitary *Balanophyllia europaea* and colonial *Stylophora pistillata* corals. Crystals protruding from RADs²⁷ in spheroidal fashion can produce such isotropic behaviour and appear as observed in our SEM and EBSD images. Mechanically, this can be considered similar to a random aragonite crystal assembly.

Aragonite needles typically show aspect ratio ranges of 1–100, with the most common aspect ratio to be in the range of 8–12^{32–35}. To corroborate this in our samples, we analysed inverted pole figure images of our EBSD data (Figure S1) to determine crystal aspect ratios. As crystals grow along the (001) axis, we randomly picked 10 crystal needles in 10 samples displaying the (010) or (100) axes and measured the longest vs. shortest axis using ImageJ (V1.52p, National Institutes of Health). The median aspect ratio found in the EBSD cross-sections was 4.86 (2.01–13.85). As these cross-sectional areas represent conic cuts through the crystals (Figure S1), we infer

Source	C ₁₁	C ₂₂	C ₃₃	C ₄₄	C ₅₅	C ₆₆	C ₂₃	C ₃₁	C ₁₂
Experimental values in GPa									
Liu et al. ⁴⁴	171.1	110.1	98.4	39.3	24.2	40.2	41.9	27.8	60.3
Voigt ⁴⁵	159.6	87.0	85.0	41.3	25.6	42.7	15.9	2.0	36.6
Hearmon ⁴⁶	228.8	124.2	85.0	82.6	51.2	94.4	18.9	10.6	102.4
Min	159.6	87.0	85.0	39.3	24.2	40.2	15.9	2.0	36.6
Median	171.1	110.1	85.0	41.3	25.6	42.7	18.9	10.6	60.3
Max	228.8	124.2	98.4	82.6	51.2	94.4	41.9	27.8	102.4
Computational values in GPa									
Fisler et al. ⁴⁷	155.3	104.2	89.9	36.7	12.4	23.3	48.0	54.7	55.9
Xiao et al. ⁴⁸	174.8	112.9	104.7	40.1	26.6	45.6	56.1	41.1	67.9
Pavese et al. ⁴⁹	164.4	112.0	59.2	40.5	33.9	49.0	48.2	39.0	65.3
	157.7	100.9	68.3	36.0	24.1	41.1	50.4	34.1	58.0
	194.2	117.1	71.3	44.1	34.5	43.8	50.2	35.7	65.9
This study	156.1	96.0	66.5	34.1	24.6	38.7	50.8	36.1	59.1
Min	155.3	96.0	59.2	34.1	12.4	23.3	48.0	34.1	55.9
Median	161.1	108.1	69.8	38.4	25.6	42.5	50.3	37.6	62.2
Max	194.2	117.1	104.7	44.1	34.5	49.0	56.1	54.7	67.9

Table 1. Stiffness values for aragonite: Experimental and computational stiffnesses (C_{ij}) for aragonite crystals from the literature as well as stiffnesses computed in this study.

that the lower range of our measurements are distorted but that the upper range represents a good approximation for aragonite needles. These values are comparable to values from the literature^{32–35} and justify approximating aragonite crystals with a prolate spheroidal shape.

These considerations allow us to use continuum micromechanics³⁶ to determine the mechanical properties and study the impact of ocean acidification on the mechanical behaviour on the relevant length scales of the CWC skeleton⁹. In this framework, the exact crystal shape is not critical as we can capture their influence on the mechanical properties through their volume fraction, aspect ratio^{37,38}, and an appropriate representation of the crystal inclusion^{39,40}.

Dissolution, porosity, and affected layer. Hennige et al.⁹ observed acidification induced porosity using synchrotron radiation computed micro-tomography (SR μ CT) in samples from the Southern California Bight, a location where CWCs live in conditions which are analogous to those most CWC reefs may experience by 2099. This has also been observed in Mediterranean coral species subjected to ocean acidification conditions^{41,42}. Although not directly comparable to CWCs due to the zooxanthellate nature of these corals and the higher aragonite concentration at the volcanic test sites, the occurrence of porosity due to acidified waters supports the dissolution theme and illustrates applicability of our modelling beyond CWCs. Hennige et al.⁹ corroborated in situ findings with SR μ CT analyses of samples from 12 months in vitro experiments that mimicked future oceanic conditions (Fig. 1b). When analysing their samples, Hennige et al.⁹ used a conservative measure and related total pore volume to total volume of the coral sample which resulted in low porosity values (Fig. 1e) with porosity measured locally being considerably higher. We reanalysed eight samples treated in in vitro mesocosm experiments⁹ (Fig. 1b) to extract an affected layer thickness and a maximum porosity per volume of interest.

Porosity was quantified similar to Hennige et al.⁹ (Figure S2) and the affected layer thickness was determined using the alpha shape toolbox in Python (Python 3.7). A shape parameter of $\alpha = 0.05$ was selected and used in a slice-by-slice extraction of the affected layer (Figure S2). Radial thickness of this layer was calculated by first determining the medial axis of the shape (Python 3.7, Scikit-image, morphology.medial_axis) and then performing a distance transform. We extracted pores using a connected component analyses (Python 3.7, Scikit-image: measure.label) and measured their degree of anisotropy (Python 3.7 PoreSpy, metrics.regionprops_3D) as the major axis length over the minor axis length of a pore.

Aragonite single crystal elasticity and strength. To develop the envisioned material model, stiffness and strength of the constituent crystal phase are needed. While single crystal stiffness is available from the literature (Table 1), single crystal strength needs to be determined as it may serve as an upper bound of the strength of the polycrystal. CWC skeletons fail in a brittle fashion¹⁶ involving crystal decohesion, which is an interfacial phenomenon, rather than breakage of individual crystals. We, therefore, consider interfacial decohesion as a lower bound of the strength of the polycrystal. For gypsum³⁸ and bone⁴³ it has been proposed that interfacial decohesion of crystal needles are governed by tensile and shear stresses associated with the needle direction.

We computed single crystal strength using molecular dynamics simulations assuming that twinned crystal boundaries are of similar strength than the single crystal. The simulations were carried out using open-source software LAMMPS (Large Scale Atomic/Molecular Massively Simulator, <https://lammps.sandia.gov>) developed by Plimpton⁵⁰. The unit cell dimensions of aragonite were $a = 4.961$, $b = 7.967$ and $c = 5.740$ Å with 4 calcium,

Aragonite needle	$e_x \otimes e_x$	$e_y \otimes e_y$	$e_z \otimes e_z$	$e_y \otimes e_z$	$e_z \otimes e_x$	$e_x \otimes e_y$
σ_{Arag} in GPa	4.97	4.00	5.33	4.03	4.06	3.92
Average in GPa		4.77			4.00	
Aragonite interfacial*			σ_{int}^{ut} in MPa		σ_{int}^{us} in MPa	
Nacre interfacial strength			158.33		70.00	
Based on micropillar tests			294.49		130.20	
Polycrystal at $\phi_{np} = 3.9\%$			σ_{poly}^{UT} in MPa		σ_{poly}^{UC} in MPa	
Nacre interfacial			95.45		248.52	
Based on micropillar tests			177.53		462.25	

Table 2. Aragonite and polycrystal yield strength: Yield strengths for the aragonite needle and the polycrystalline coral skeleton not exposed to acidified waters. e_i with $i = (x, y, z)$ denote directions of testing in the molecular dynamics test. σ_{int}^{ut} and σ_{int}^{us} denote interfacial tensile and shear strength of the aragonite crystal while σ_{poly}^{UT} and σ_{poly}^{UC} are the tensile and compressive strengths of the polycrystalline skeleton not exposed to acidified waters, respectively. *Barthelat et al.⁵² argued that dry nacre approximates the brittle, interfacial yield strength of pure aragonite. We assume that a nacre platelet loaded along the in-plane axis resembles a similar loading situation as the aragonite needles in the CWC skeleton. Consequently, we use tensile^{52–54} and shear⁵² strengths for nacre as a lower bound, with a review of tests given by Sun and Bhushan⁵⁵.

4 carbon and 12 oxygen atoms. By following Pavese et al.⁴⁹, the Born-type potential was utilised to account for interactions between Ca–O and C–O and O–O. The dispersive term was included only for O–O interactions. The covalent bond in the CO₃ molecule was modelled by harmonic angular and torsional potentials. The potential parameters were taken from the RIM2 model of Pavese et al.⁴⁹ (see their Table 4 for details). Before performing our tests, we equilibrated atoms by performing Nosé–Hoover thermostat sampled from isothermal-isobaric ensemble (NpT) at 298 K and 1 bar for 48 ps. For uniaxial tensile tests, the flow configuration was a rectangular box with an aspect ratio of 4 containing 24-unit cell along the tensile direction. For shear tests, we used a cubic box with 13,824 unit cells (24 cells in each direction). For all simulations, we employed periodic boundary conditions in all directions and the time-step was set to 0.001 ps. We applied the explicit deformation method, where the dimension of box was changed at a constant engineering strain rate ($\dot{\epsilon} = 0.01$ 1/s unless specified otherwise) to compute elastic constants. The elements of the stiffness tensor were extracted from three tension and three shear deformations following Clavier et al.⁵¹. Strength of the crystal was measured as the maximum stress for each loading mode (Fig. 3, Table 2).

Our molecular dynamics analyses provided results for a perfect, theoretical crystal. To propose a failure criterion, we need to identify tensile and shear stresses of the interface between two crystals, compare them to these single crystal results, and use the lower set of values to model failure at the crystal length scale (“Section [Strength of the CWC skeleton not exposed to acidified waters](#)”). To our knowledge, interfacial tensile and shear stresses for CWC skeletal aragonite needle assemblies have not been measured and we consider nacre as a proxy-material (Table 2). Like CWC skeletons, nacre is made of aragonite but in the form of platelets that are impregnated with a protein layer. It has volume fractions of 95wt% aragonite and 5wt% organic material⁵² that are comparable to CWC skeletons. Nacre platelets loaded along the in-plane axis, as for example during compression bending of the shell, resemble a similar loading situation as the aragonite needles in our case with tensile and shear stresses associated with the platelet axis governing the failure. Barthelat et al.⁵² argued that dry nacre approximates the brittle, interfacial yield strength of pure aragonite which resembles the situation in our material model (Fig. 2).

Elasticity of the CWC skeleton not exposed to acidified waters. We enforced transverse isotropy of the median experimental stiffness tensor of aragonite (Table 1) to reduce the computational costs of determining skeletal stiffness and strength, so that $C_{00} = \frac{1}{2}(C_{11} - C_{22})$, $C_{03} = \frac{1}{2}(C_{31} - C_{23})$, $C_{01} = C_{12}$, and $C_{66} = \frac{1}{2}(C_{11} - C_{12})$. This simplification results in slightly lower values than the experimental median but is within the range of values reported for aragonite (Table 1) as well as calcite⁵⁶, another polymorph of calcium carbonate. We modelled the coral skeleton (CS) as a polycrystal consisting of randomly oriented aragonite needles with stiffness \mathbb{S}_{Arag} and spherical nano-porosity (ϕ_{np}) of 3.9%²⁶ as reference value. This random needle setup warranted a self-consistent scheme⁴⁰ which we modified to include transverse isotropic crystals following proposals for gypsum and bone by Sanahuja et al.³⁸ and Fritsch et al.⁵⁷, respectively. We formulated stiffness of the polycrystalline CWC skeleton based on the median experimental aragonite stiffness (Table 1). In addition to \mathbb{S}_{Arag} , the effective polycrystalline stiffness tensor, \mathbb{S}_{CS} , depends on the volume fraction of the crystals ($1 - \phi_{np}$), their aspect ratio, as well as ϕ_{np} that is filled with organic matter which we assumed does not contribute to the stiffness of the skeletal wall. The homogenised stiffness tensor for the coral skeleton can then be given as:

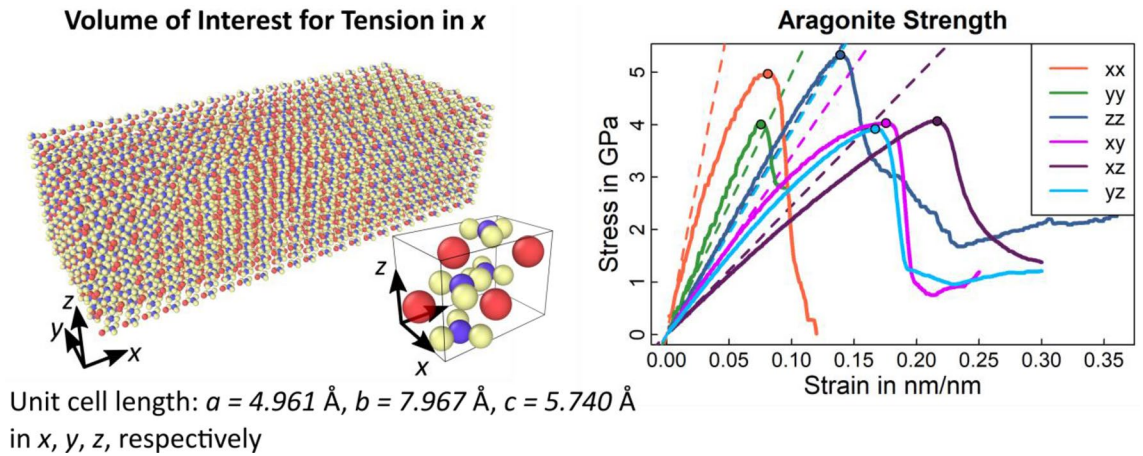


Figure 3. Aragonite stiffness and strength: An aragonite volume of interest with $24 \times 6 \times 6$ unit cells of dimension $a \times b \times c$ was used to determine crystal strength. The left image shows the setup used in the tensile tests along x and an animation of this test is shown in Video S1 and S2 (supplementary material). The model was verified against experimental stiffness values (Table 1) before conducting the strength test whose results are shown on the right. Maximum bearable stress is indicated by solid circles in each stress–strain curve in the image on the right.

$$\begin{aligned} \mathbb{S}_{CS} = (1 - \phi_{np}) \int_{\varphi=0}^{2\pi} \int_{\theta=0}^{\pi} \mathbb{S}_{Arag}(\varphi, \theta) : \left(\mathbb{I} + \mathbb{P}_{ndl}^{CS}(\varphi, \theta) (\mathbb{S}_{Arag}(\varphi, \theta) - \mathbb{S}_{CS}) \right)^{-1} \frac{\sin \theta}{4\pi} d\theta d\varphi : \\ \left((1 - \phi_{np}) \int_{\varphi=0}^{2\pi} \int_{\theta=0}^{\pi} \left(\mathbb{I} + \mathbb{P}_{ndl}^{CS}(\varphi, \theta) (\mathbb{S}_{Arag}(\varphi, \theta) - \mathbb{S}_{CS}) \right)^{-1} \frac{\sin \theta}{4\pi} d\theta d\varphi + \right. \\ \left. \phi_{np} \left(\mathbb{I} + \mathbb{P}_{sph}^{CS}(\mathbb{S}_{np} - \mathbb{S}_{CS}) \right)^{-1} \right)^{-1}. \end{aligned} \tag{1}$$

Therein, \mathbb{I} is the 4th order identity tensor ($\mathbb{I}_{ijkl} = (\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})/2$), \mathbb{P}_{Arag}^{CS} is the 4th order Hill tensor which is defined by $\mathbb{P}_{ndl}^{CS} = \mathbb{R} : \mathbb{S}_{CS}^{-1}$ and \mathbb{R} is the 4th order Eshelby tensor for the chosen inclusion problem. The Eshelby tensor solutions for inclusion shapes³⁹ used in this study are provided in supplementary material Section S3. The ‘:’ symbol denotes the double inner product of two tensors. \mathbb{S}_{CS} is the effective tensor stiffness of the coral skeleton whose determination requires an iterative solution approach (Mathematica 12.1).

Strength of the CWC skeleton not exposed to acidified waters. The failure mechanism for CWC skeletons is brittle with decohesion and breakage of crystal arrangements¹⁶. We modelled failure of the most adversely loaded aragonite crystal using a Mohr–Coulomb criterion^{38,58}

$$\sigma_{nm} + \beta \sigma_{nt} = \sigma_{int}^{ut} \tag{2}$$

with σ_{nm} the stress in normal direction, σ_{nt} the stress in tangential direction and $\beta = \sigma_{int}^{ut} / \sigma_{int}^{sh}$ the ratio between tensile and shear yield stress of the aragonite crystal (Table 2, Fig. 4). We switched length scales between the polycrystal arrangement and the aragonite needle using concentration tensor $\mathbb{B}(\varphi, \theta)$ ^{38,57,59,60}

$$\begin{aligned} \mathbb{B}(\varphi, \theta) = \mathbb{S}_{Arag}(\varphi, \theta) : \left[\left(\mathbb{I} + \mathbb{P}_{ndl}^{CS}(\varphi, \theta) : (\mathbb{S}_{Arag}(\varphi, \theta) - \mathbb{S}_{CS}) \right)^{-1} : \right. \\ \left. \left((1 - \phi) \int_{\varphi=0}^{2\pi} \int_{\theta=0}^{\pi} \left(\mathbb{I} + \mathbb{P}_{ndl}^{CS}(\varphi, \theta) (\mathbb{S}_{Arag}(\varphi, \theta) - \mathbb{S}_{CS}) \right)^{-1} \frac{\sin \theta}{4\pi} d\theta d\varphi + \right. \right. \\ \left. \left. \phi \left(\mathbb{I} + \mathbb{P}_{sph}^{CS}(\mathbb{S}_{np} - \mathbb{S}_{CS}) \right)^{-1} \right)^{-1} \right] : \mathbb{S}_{CS}^{-1} \end{aligned} \tag{3}$$

so that, the average stress in an aragonite needle with direction $\mathbf{n} = \mathbf{n}(\varphi, \theta)$ (Figure S3) in the polycrystal due to a macroscopic stress on the polycrystal becomes:

$$\sigma_{Arag}(\varphi, \theta) = B(\varphi, \theta) : \mathbf{S} = B(\varphi, \theta) : \mathbf{S}\hat{\mathbf{S}}. \tag{4}$$

In this equation $S = \|\mathbf{S}\|$ is the magnitude of the stress tensor and $\hat{\mathbf{S}} = \mathbf{S} / \|\mathbf{S}\|$ its direction. We computed the stress components along the needle long axis $\mathbf{n} = \mathbf{n}(\varphi, \theta)$ and the one tangential to the needle long axis $\mathbf{t} = \mathbf{t}(\varphi, \theta, \psi)$ (Section S4) as

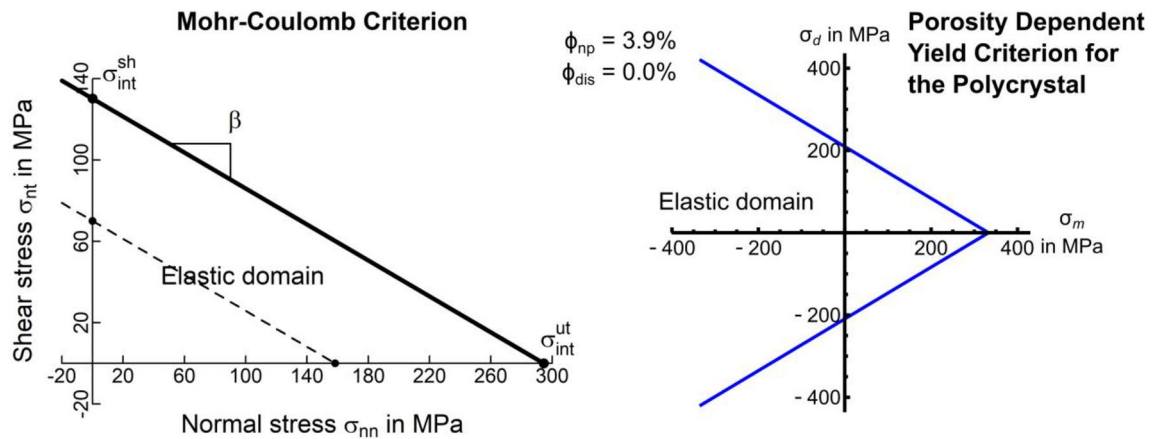


Figure 4. Yield criteria for the cold-water coral skeleton: Left image shows an interfacial Mohr–Coulomb criterion (Eq. 3) of the aragonite crystals using interfacial tensile σ_{int}^{ut} and shear σ_{int}^{sh} strengths based on micropillar tests (solid line) as well as for nacre aragonite interfacial strengths (dashed line). Right image shows a porosity dependent quadric yield criterion⁶¹ plotted along its trisectrix with mean stress σ_m and deviatoric stress σ_d . The criterion can incorporate increasing porosities (Fig. 7) due to acidification and erosion processes and is plotted here with no dissolution porosity ϕ_{dis} . Since its material parameters are derived from the underlying polycrystal elasticity and crystalline yield behaviour, its parameters contain a $\phi_{np} = 3.9\%$.

$$\begin{aligned}\sigma_{nn} &= \mathbf{n} \cdot \boldsymbol{\sigma}_{Arag}(\varphi, \theta) \cdot \mathbf{n} \quad \text{and} \quad \sigma_{nt} = \mathbf{n} \cdot \boldsymbol{\sigma}_{Arag}(\varphi, \theta) \cdot \mathbf{t} \\ \sigma_{nn} &= \mathbf{n} \cdot (\mathbb{B}(\varphi, \theta) : \mathbf{S}) \cdot \mathbf{n} \quad \text{and} \quad \sigma_{nt} = \mathbf{n} \cdot (\mathbb{B}(\varphi, \theta) : \mathbf{S}) \cdot \mathbf{t}.\end{aligned}\quad (5)$$

We used Eq. (2) and the interfacial strengths of aragonite (Table 2) to calculate strength for the polycrystalline skeletal wall for different stress directions \mathbf{S}

$$\begin{aligned}\text{Max} \quad & \mathbf{n} \cdot (\mathbb{B}(\varphi, \theta) : \hat{\mathbf{S}}) \cdot \mathbf{n} + \beta \left| \mathbf{n} \cdot (\mathbb{B}(\varphi, \theta) : \hat{\mathbf{S}}) \cdot \mathbf{t} \right| \\ \text{with} \quad & 0 = \varphi, 0 \leq \theta < \pi, 0 \leq \psi < 2\pi\end{aligned}\quad (6)$$

This yielded the direction of maximum stress. We discretised the angular range with increments of $\Delta\theta = \pi/128$ and $\Delta\psi = \pi/32$ with the aim to find the maximum of Eq. (6) (NMaximize, Mathematica 12.1) and, thus, failure associated with the most adversely loaded crystal⁶². Evaluating Eq. (2) for these maximal stress directions allowed us to calculate corresponding, micromechanically informed, elastic limits in tension σ_{poly}^{ut} and compression σ_{poly}^{uc} for the polycrystalline skeleton that is not affected by ocean acidification, but which incorporates $\phi_{np} = 3.9\%$:

$$S = \frac{\sigma_{int}^{ut}}{\mathbf{n} \cdot (\mathbb{B}(\varphi, \theta) : \hat{\mathbf{S}}_{33}) \cdot \mathbf{n} + \beta \left| \mathbf{n} \cdot (\mathbb{B}(\varphi, \theta) : \hat{\mathbf{S}}_{33}) \cdot \mathbf{t} \right|}.\quad (7)$$

We considered compression and tension along $\mathbf{e}_3 = (0, 0, 1)$ to calculate the yield strengths of the polycrystal in tension σ_{poly}^{ut} and compression σ_{poly}^{uc} following an approach used for quantifying yield envelopes for other mineralised tissues⁶³. Compression and tension are sufficient to identify a polycrystalline yield envelope as we assumed isotropy (“Section CWC skeletons as multiscale, polycrystalline materials”). The resulting polycrystalline yield criterion (Fig. 4) features a conical shape (Drucker-Prager failure criterion) with tensile and compressive strengths σ_{poly}^{ut} and σ_{poly}^{uc} based on σ_{int}^{ut} and σ_{int}^{sh} (Table 2). The conical shape has the additional benefit that it reflects adaption to the large hydrostatic pressures encountered by CWCs that suggest that incompressibility under triaxial loading is important.

Micropillar compression tests of the skeleton not exposed to acidified waters. To complement our predictive modelling with experimental strength tests, we performed micropillar compression tests adopting previous protocols^{64,65} on $n = 12$ CWC samples (“Section Coral samples”, Section S8). We selected samples that were covered with soft tissue upon retrieval. These can, thus, be considered *live* coral skeletons, not affected by ocean acidification⁹. We selected three samples from the Mingulay Reef Complex and three from the Porcupine Seabight in the NE Atlantic that represent non-corrosive oceanic conditions as well as six samples from the California Sea Bight which were collected at or below the ASH which represents a corrosive oceanic environment⁹.

We repolished the samples using previous preparation protocols⁹ and fabricated micropillars using ultrashort pulsed laser ablation (Section S5). On each of the 12 CWC samples two arrays of six micropillars were manufactured (Figure S4). For each sample, we selected six of the micropillars and conducted destructive micropillar compression tests using a custom-made portable microindenter (Aleminis AG, Switzerland) equipped with an 88 μm diameter conical diamond punch^{64,65}. We calibrated frame compliance prior to testing using a Berkovich probe and a standard fused quartz sample⁶⁶. Each pillar was compressed uniaxially at a rate of 0.05 $\mu\text{m/s}$ to a total

displacement of 10.25 μm . Partial unloading was conducted by retracting the probe 0.25 μm for every 0.75 μm the probe travelled. Load and displacement were recorded simultaneously throughout each test at 30 Hz.

The large taper angle that results from using laser ablation (Figure S4) without subsequent focussed ion beam milling^{64,65} did not allow direct conversion of experimentally observed forces into stresses. To interpret the micropillar compression tests we implemented our material model into an elasto-viscoplastic framework (Sections S7, S7.1) as a user defined material for Abaqus (v6.16, Dassault Systèmes). We generated a finite element model of the micropillar (Section S7, Figure S6) and conducted in silico micropillar compression tests similar to our experimental ones.

Incorporating the impact of ocean acidification on skeletal stiffness and strength. After creating a model for the skeleton not affected by ocean acidification, we incorporate the mechanical impact of ocean acidification on stiffness and strength. We determined a significant increase of porosity after subjecting CWC samples to acidified water resembling a future ocean (Fig. 1c,e, Figure S2). Assuming the shape of these pores to be spheroidal with random orientations allowed us to model dissolution as spherical inclusion. As we obtained an isotropic stiffness tensor for the mineralised coral skeleton (“Section Elasticity of the CWC skeleton not exposed to acidified waters”), we used a Mori–Tanaka scheme^{59,67} to incorporate acidification induced porosity (Figs. 1, 2, Figure S2). Both the coral skeleton (matrix) and the pores (inclusion) can be represented by their respective stiffness tensors (\mathbb{S}_{CS} and \mathbb{S}_{PO} , respectively) and volume fractions ϕ , such that $\phi_{CS} + \phi_{OA} = 1$. The inclusions are assumed to be subject to the same homogeneous load so that the skeleton exposed to acidified waters represents a matrix-inclusion type composite³⁶ and its stiffness can be written as:

$$\mathbb{S}_{OA} = \left(\phi_{CS} \mathbb{S}_{CS} + \phi_{PO} \mathbb{S}_{PO} : \left(\mathbb{I} + \mathbb{P}_{PO}^{MT} (\mathbb{S}_{PO} - \mathbb{S}_{CS}) \right)^{-1} \right) : \left(\phi_{CS} \mathbb{I} + \phi_{PO} \left(\mathbb{I} + \mathbb{P}_{PO}^{MT} (\mathbb{S}_{PO} - \mathbb{S}_{CS}) \right)^{-1} \right)^{-1} \quad (8)$$

This stiffness tensor incorporates acidification induced porosity into the reversible mechanical behaviour of the CWC skeleton. We then used tensile and compressive strengths σ_{poly}^{ut} and σ_{poly}^{uc} of the polycrystalline CWC skeleton not exposed to acidified waters (Eq. 6, “Section Strength of the CWC skeleton not exposed to acidified waters”), to incorporate acidification induced porosity into a failure criterion of the CWC skeleton. Based on our considerations in “Section Strength of the CWC skeleton not exposed to acidified waters”, we used a conic criterion that was first proposed by Maghous et al.⁶⁸ and generalised by Schwiedrzik et al.⁶¹:

$$Y_{OA}(\mathbf{S}) := \sqrt{\mathbf{S} : \mathbb{F} \mathbf{S}} + \mathbf{F} : \mathbf{S} - 1 = 0 \quad (9)$$

with $\mathbb{F} = \frac{1 + \frac{2}{3}\phi_{OA}}{(1 - \phi_{OA})^2 h^2 T^2} (\mathbb{I} \otimes \mathbb{I}) - \frac{\frac{1}{3} + \frac{1}{18}\phi_{OA}}{(1 - \phi_{OA})^2 h^2 T^2} (\mathbb{I} \otimes \mathbf{I})$, and $\mathbf{F} = \frac{1}{3(1 - \phi_{OA})h} \mathbf{I}$ in which cohesion $h = \frac{2}{3} \frac{\sigma_{poly}^{ut} \sigma_{poly}^{uc}}{\sigma_{poly}^{uc} - \sigma_{poly}^{ut}}$ and

friction coefficient $T = \sqrt{6} \frac{\sigma_{poly}^{uc} - \sigma_{poly}^{ut}}{\sigma_{poly}^{uc} + \sigma_{poly}^{ut}}$. \mathbf{I} denotes the identity tensor, $\mathbf{A} \otimes \mathbf{B} = (A_{ik} B_{jl} + A_{il} B_{jk})/2$ the symmetric

product, and \otimes the tensor product or dyad. Section S6 illustrates how cohesion h and friction coefficient T are derived and Section S7 details how this was implemented into an elasto-viscoplastic framework within the finite element package.

The impact of ocean acidification on an exemplary coral colony. To show the impact of ocean acidification on a real coral structure, we used the developed material model in an image based finite element model of a coral specimen of *L. pertusa* (Fig. 5, Figure S6). The coral specimen was scanned in a clinical CT (Toshiba Aquilon 64) with an X-ray source voltage of 120 kV and a current of 600 mA⁶⁹. The resulting CT image was reconstructed with a voxel size of 0.35 mm in plane, 0.3 mm slice distance, and exported to DICOM-format.

We subjected the model to an increased porosity and acidification induced thinning. The impact of porosity was captured through our micromechanical material model. Thinning due to acidification, i.e. loss of wall thickness, was induced on the outer surface of the coral and was implemented in Python using *SimpleITK* and *Scikit-Image* libraries (Fig. 5, Video S3). Images were first smoothed using a recursive Gaussian filter ($\sigma = 0.3$) and binarized using the Maximum Entropy algorithm. Unconnected regions were removed, and a 3D morphological geodesic active contour algorithm⁷⁰ was employed to detect the outer surface of the coral specimen and mask-out both the coral skeleton and internal pores and cavities. The resulting contour image was up-sampled by a factor of 3 in x- and y-direction and a morphological erosion of approximately 0.12 mm, 0.23 mm, or 0.35 mm (1/3, 2/3 and 3/3 of the original voxel size) was performed to simulate progressive thinning of the outer layer (Figure S2) and which was motivated by the thickness of the affected layer identified in “Sections Dissolution, porosity, and affected layer and Dissolution, porosity, and affected layer”. Finally, the binarized image of the coral specimen was multiplied by the eroded contour images to obtain a final 3D binary dataset of the eroded coral specimen. The four resultant 3D images (i.e. no thinning and three erosion steps) were converted to tetrahedral meshes with four-noded tetrahedral elements with maximum size of approximately 0.5 mm using *pygalmesh*. We then imported these meshes into Matlab (R2020a), assigned boundary conditions, and generated input files for Abaqus (Section S7.2, Figure S6). Boundary conditions mimicked a contact pressure load on the coral skeleton surface simulating an artificially chosen sea current with a velocity of 3 m/s in a direction perpendicular to the longitudinal axis of the skeleton (Section S7.2, Figure S6). This velocity was chosen to firmly overload the sample and represents three times the maximum water current reported by Haugan et al.⁷¹ (0.3–1 m/s). Note that this is an academic example to illustrate the effect of increasing velocity and loss of skeletal wall thickness.

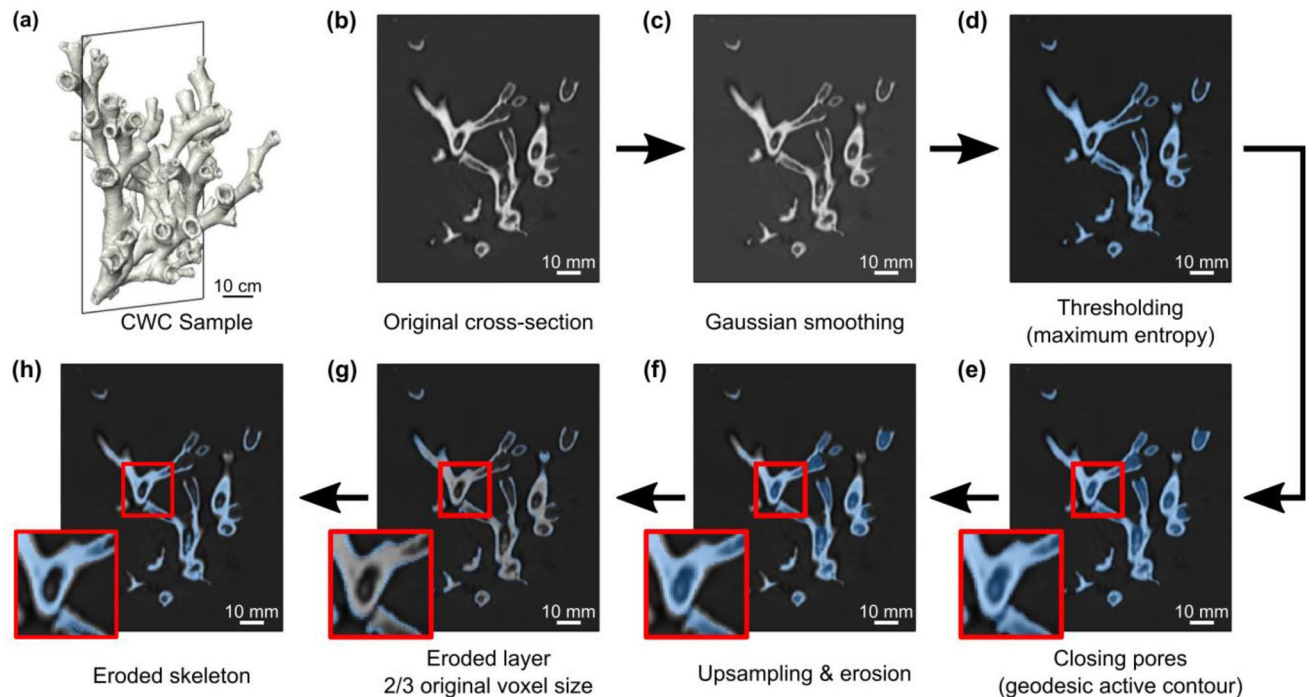


Figure 5. Incorporating dissolution on a representative coral specimen: (a) 3D render of the exemplary cold-water coral (CWC) specimen. (b) Original cross-section through the XZ plane; (c) Gaussian filter was applied ($\sigma = 0.3$); (d) Coral skeleton was segmented using Maximum Entropy algorithm threshold; (e) A 3D morphological geodesic active contour algorithm was implemented to detect the outer surface and fill the pores and cavities in the skeleton. (f) The contour image was up-sampled and eroded in steps of 1/3 of the original voxel size. (g) 0.23 mm eroded layer (blue) superimposed to the original CT cross-section (grey) and 0.23 mm eroded layer (blue). (h) Final image composite of the eroded coral skeleton (blue) and the original CT cross-section (grey). See Video S3 for a visualisation of the image processing steps as well as Figure S6 for the finite element models.

Statistical analyses. Statistical analyses were performed using Gnu R⁷² (Rstudio 1.4.1103). To test normal distribution of data, quantile–quantile plots and Shapiro–Wilk post-hoc tests were used. If normality was given, groups were compared using Student’s t-tests otherwise Wilcoxon rank sum tests were used. We assumed a significance level of $p = 0.05$. Sample data is presented by means of distribution independent median and ranges.

Results

Dissolution, porosity, and affected layer. Affected layer thickness was found to be up to 109.17–253.13 μm and the affected layer contained porosities of 10.6–33.3% (Figure S2). Using the connected component analyses we extracted $3,135,825 \pm 2,098,230$ pores/sample. The average degree of anisotropy was found to be 1.9 which suggests a spheroidal shape of dissolution pores. These pores were however not aligned but randomly oriented, which justifies approximation of the pore shape by a sphere with aspect ratio 1. Given this, the assumptions made in “Section [Incorporating the impact of ocean acidification on skeletal stiffness and strength](#)” for the pore shape are justified and usable to investigate the mechanical impact of ocean acidification on these CWC skeletons.

Aragonite single crystal elasticity and strength. Aragonite single crystal elasticity determined using molecular dynamics was in good agreement with experimental and computational values from the literature (Table 1). Therefore, we consider our models suitable to determine single crystal strength. Strength was slightly anisotropic (Fig. 3) and we averaged tensile and shear strengths to 4.77 GPa and 4.00 GPa (Table 2), respectively. Interfacial failure strengths from nacre as a proxy-material (Table 2) were significantly lower than these single crystal strengths which indicates that interfacial rather than crystal failure dominates. Consequently, we used strengths reported for nacre under tension and shear (Table 2) as surrogates for the interfacial failure strengths at the aragonite needle level as initial values in our computations (“Section [Micropillar compression tests of the skeleton not exposed to acidified waters](#)”).

Elasticity of the CWC skeleton not exposed to acidified waters. When increasing ϕ_{np} , skeletal stiffness \mathcal{S}_{CS} is significantly reduced (Fig. 6a). Small changes in ϕ_{np} resulted in a linear decline of skeletal stiffness that became non-linear for porosities above 20% result which is illustrated in Fig. 6 for Young’s modulus and Poisson’s ratio. Varying the aspect ratio while keeping ϕ_{np} fixed results in very subtle changes in \mathcal{S}_{CS} for small porosities but more significant changes for higher porosities (Fig. 6b). This compares well to results by Sana-

Polycrystal Elasticity and micropillar example

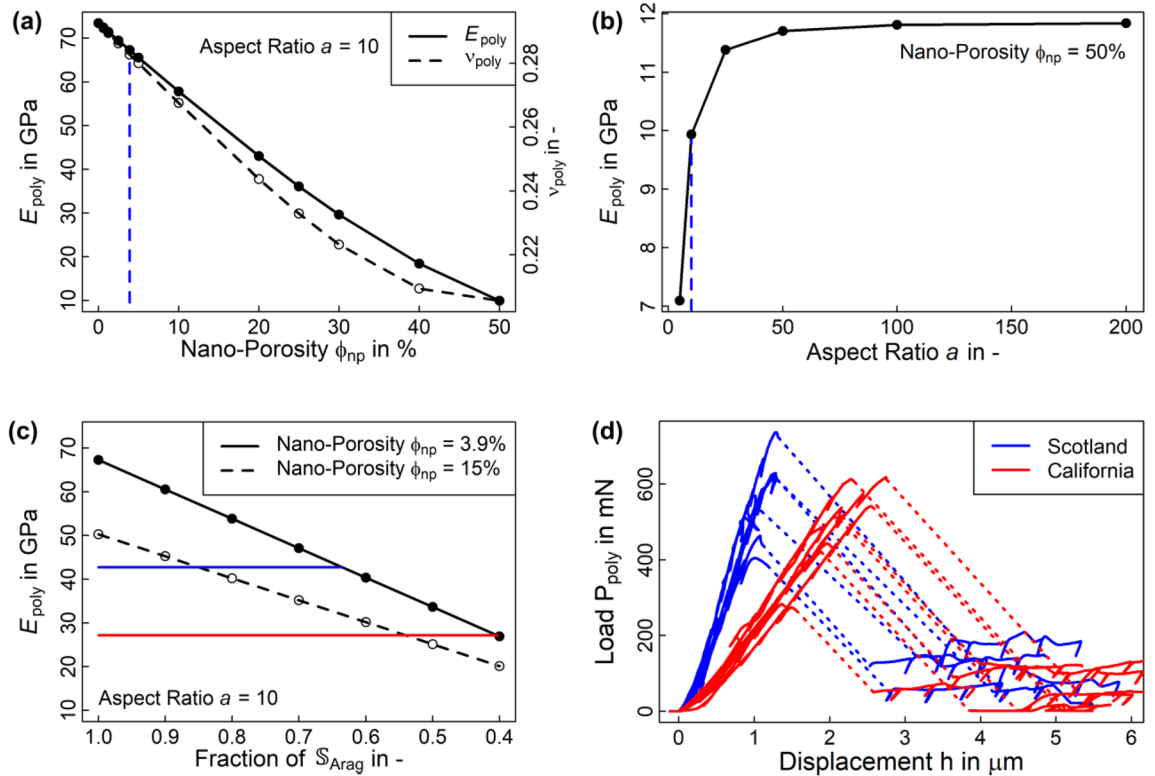


Figure 6. Elasticity of the unaffected cold-water coral skeleton: (a) Young's modulus E_{poly} and Poisson's ratio ν_{poly} of the polycrystal depending on ϕ_{np} and shown for a crystal with an aspect of 10. The dashed blue line represents the chosen $\phi_{np} = 3.9\%$ for analysing strength. (b) illustrates the dependence of Young's modulus E_{poly} on the crystal aspect ratio a at $\phi_{np} = 50\%$. The dashed blue line illustrates the aspect ratio of 10 chosen for analysing strength. We illustrate dependence on the aspect ratio for $\phi_{np} = 50\%$ because for $\phi_{np} = 3.9\%$ Young's modulus varies ± 0.12 GPa only. At $\phi_{np} = 50\%$, a higher aspect ratio than 10 could increase stiffness about 1.5 GPa. (c) Dependence of E_{poly} on the stiffness of the aragonite crystals where we degraded S_{Arag} without changing its symmetry. Blue lines indicate medians of the Scottish (dashed) and California Sea Bight (dotted) samples. (d) compliance corrected results of six micropillar compression tests from two representative sample. Tests feature linear elasticity and a brittle behaviour after passing the ultimate point. The dashed line covers the zone of brittle failure that is expanded by compliance correction. See also Figure S4 for a SEM image of the micropillars.

huja et al.³⁸ and Fritsch et al.⁵⁷ and suggests that an aspect ratio of the aragonite crystals of 10 was a reasonable choice^{32–35} for our purposes.

Micropillar compression tests of the skeleton not exposed to acidified waters. We obtained 144 usable micropillars on the 12 CWC samples ("Section [Micropillar compression tests of the skeleton not exposed to acidified waters](#)", Figure S4) with surface and base diameters of 28.96 μm (27.76–30.51 μm) and 86.5 μm (81.52–90.21 μm), a taper angle of 15.02° (12.16–18.19°), and a height of 110.77 μm (90.20–129.44 μm). We randomly selected six of the micropillars per sample for compression testing. Testing to failure resulted in a brittle response without damage accumulation (Fig. 6d) with a median ultimate force of 517.86 mN (154.30–736.78 mN) and a median pillar stiffness of 487.9 mN/ μm (225.02–1078.14 mN/ μm). When separating these results into high and low aragonite concentration groups ("Section [Coral samples](#)"), we obtain median ultimate forces of 516.40 mN (154.30–736.78 mN) and 517.86 mN (163.79–718.93 mN) that are not significantly different ($p \rightarrow 1$). However, we obtained median pillar stiffnesses of 633.41 mN/ μm (225.02–1078.14 mN/ μm) and 401.98 mN/ μm (243.24–594.16 mN/ μm) which are significantly lower for the low aragonite concentration group ($p < 10^{-12}$).

When interpreting the micropillar compression tests with our finite element model (Section S7) using the model predicted stiffness of a CWC skeleton with $\phi_{np} = 3.9\%$ (Fig. 6) without further changes due to ocean acidification, we obtained a structural stiffness of the micropillar of 956.16 mN/ μm . This is higher than the experimental median but within the range identified in the micropillar tests for healthy aragonite concentrations of 1.67–2.62. It is, however, higher than the results for samples from below the ASH (Fig. 6d).

When using the polycrystalline yield criterion (Fig. 4) with tensile and compressive strengths σ_{poly}^{ut} and σ_{poly}^{uc} based on σ_{int}^{ut} and σ_{int}^{sh} derived from nacre (Table 2) in our micropillar finite element model, we obtained an ultimate force of 289 mN. This is significantly lower than the experimentally achieved ultimate forces of 517.86

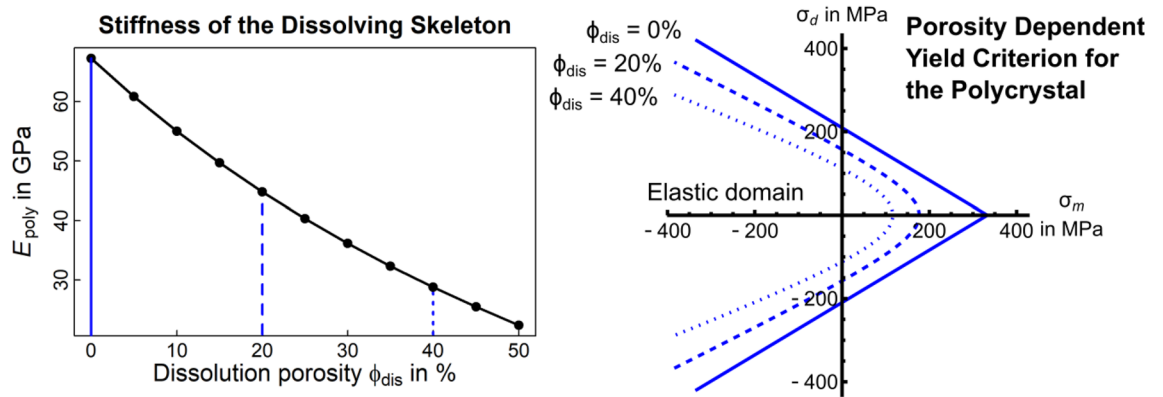


Figure 7. Impact of ocean acidification on cold-water coral skeletal stiffness and strength: Left, the effect of increasing porosity due to ocean acidification on the stiffness of the polycrystalline CWC skeleton. Small increases in porosity significantly lower the ability of the skeleton to resist external loading. Right, increasing porosity due to ocean acidification significantly lowers the limit bearable load the *dead* skeleton can withstand so that much lower loads are needed to break the CWC skeleton.

mN. Using the interfacial tensile and shear strengths for the aragonite single crystal would result in values over an order of magnitude larger. When increasing the interfacial yield strengths by a factor of 1.86 and keeping the ratio $\sigma_{int}^{ut}/\sigma_{int}^{us}$ similar to that of nacre, we obtained tensile and compressive polycrystal yield strengths (Table 2) that yield an ultimate force in our micropillar finite element model of 517.17 mN which is in good agreement with our experimental results. We therefore reject nacre as a surrogate material and consider the strengths derived by combining micropillar test results and the FE analyses as the active interfacial and polycrystalline strengths of the CWC skeleton (Table 2).

Incorporating the impact of ocean acidification. Figure 7 illustrates the impact of ocean acidification induced porosity on the stiffness of the exposed CWC skeleton. At a maximum porosity of 33.3% as identified in our samples (“Section Dissolution, porosity, and affected layer”), an affected volume of interest would suffer almost 50% loss of stiffness due to acidification. In contrast to in situ samples that show no porosity^{9,41,42}, this is a significant decrease in the ability of the skeleton to resist external loading. Likewise, an increase in porosity dramatically reduces strength of the CWC skeleton affected ocean acidification (Fig. 7).

Using the developed material model in our image based finite element model of a representative CWC colony indicates that the degrading mechanism identified by Hennige et al.⁹ can indeed be captured. Compliance of the structure is significantly increased either through an increase in porosity or through dissolution from the periphery of the skeletal wall (Fig. 8). However, ocean acidification affects the *dead* coral skeleton through a combination of increased porosity and dissolution which leads to a decreased skeletal wall thickness. It is this combination that leads to the most detrimental increase in fragility (Fig. 8).

Discussion

We here report the consequences of ocean acidification on the mechanical properties of CWCs using a multiscale material model complemented by experimental data (in silico and on physical samples). The developed model allows us to analyse failure of CWC colonies affected by ocean acidification over all relevant length scales. Strikingly, the synthesised skeletal building material is 10 times stronger than concrete⁷³ and twice as strong as ultrahigh performance fibre reinforced concrete⁷⁴ or nacre (Table 2). Our results indicate that the strength of the skeletal building material is retained even when skeletons are synthesised under future oceanic conditions (Fig. 6, “Section Micropillar compression tests of the skeleton not exposed to acidified waters”), as we demonstrate in samples from the California Sea Bight, a region that is considered to be representative of end-of-century oceanic conditions⁹. It is important to note the difference in length-scale here. The entire coral branch, apart from the live part⁹, can be acidified and show porosity. However, the skeletal material of these coral branches is not porous but which was synthesised under different oceanic conditions and shows remarkable difference in crystal size. The novel multiscale mechanical properties identified here for the first time contradict the current state-of-knowledge that mineralised skeletons will generally weaken due to climate change. In fact, CWCs retain the strength of their building material despite a loss of its stiffness, and the threat comes rather from a loss of material as acidification induced increase in internal porosity and dissolution. Our multiscale mechanical model delivers a model-based explanation for this stunning feat.

Model verification and validation. To verify our model, we compare predicted stiffness with that derived from our micropillar tests via the associated micropillar finite element model and a set of independent nanoindentation results (“Sections Micropillar compression tests of the skeleton not exposed to acidified waters” and S8, Figure S6c). The ranges in polycrystalline stiffness measured by nanoindentation on *L. pertusa* samples from UK waters (Figure S6c), California Sea Bight⁹, as well as non-zooxanthellate and zooxanthellate corals from the Mediterranean Sea^{31,41,42} are in reasonably good agreement with our predicted polycrystalline stiffness with

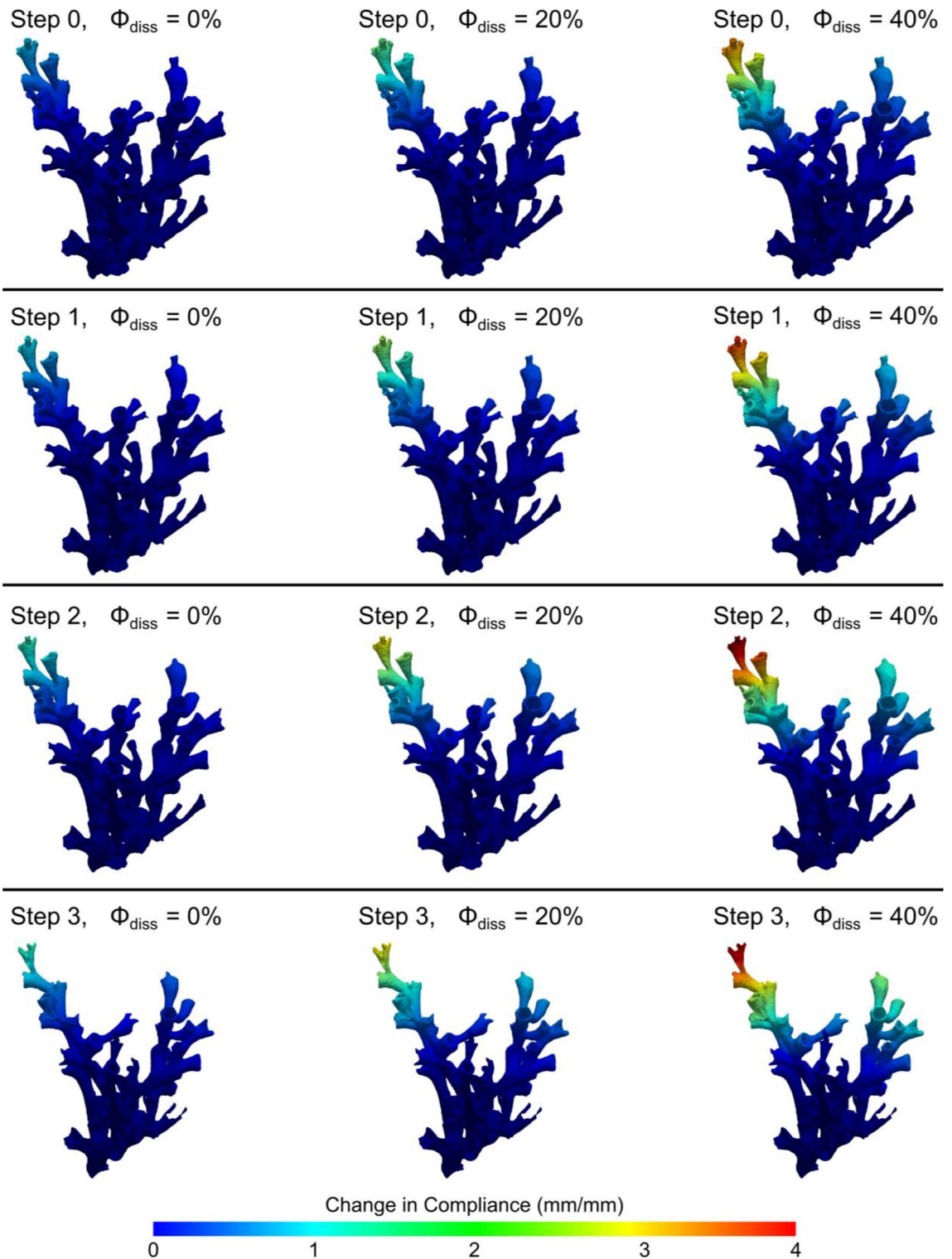


Figure 8. Strength loss of an exemplary *L. pertusa* colony: An increase in skeletal porosity (left to right) and an additional reduction in wall thickness (top to bottom) leads to decreasing load bearing capacity with the combination of both effects (bottom right) yielding a fourfold increase in flexibility resulting in a significantly increased fragility. For illustration purposes, we use deflection normalised on the top left case. The weaker the skeleton becomes the further peripheral elements can be deflected. Consequently, the highest internal loading is found towards the encased base of the coral.

corals from the Mediterranean (red and green areas in comparison to the blue dashed line in Figure S6c). Interestingly, Pasquini et al.³¹ reported homogeneous and isotropic nanoindentation results when testing in different directions which they relate to the microstructure. This supports the isotropy occurring for \mathbb{S}_{CS} through choosing a self-consistent scheme, and implicitly verifies our modelling approach. When using the median transverse isotropic aragonite stiffness tensor, \mathbb{S}_{Arag} , our predicted stiffness agrees very well with the results by Pasquini et al.³¹ (Fig. 6 and S6c), although \mathbb{S}_{CS} gives a higher stiffness than that derived by our nanoindentation results for *L. pertusa* from UK waters (Section S8, Figure S6c) and the California Sea Bight (grey area in Figure S6c). If the minimum aragonite stiffness tensor (Table 1) is used in \mathbb{S}_{CS} , polycrystalline stiffness derived here moves closer to the median nanoindentation stiffness which illustrates the influence of this variable on the overall outcome and needs further consideration.

In comparison to other studies^{31,41,42}, our nanoindentation results show (a) a high variation and (b) a lower median (Figure S6c). The large variation may be attributed to testing different crystal arrangements (sclerodermites²³). This particularly affects the nanoindentation results, as probed volume is considerably smaller than that of our micropillar compression tests. When Hennige et al.⁹ analysed the samples from California Sea Bight, no difference in compositional properties of the skeleton was found. This suggests that the variation (point (a)) is indeed caused by differences between individual crystal assemblies. When comparing nanoindentation results for *L. pertusa* samples from UK waters with those reported for samples from the California Sea Bight⁹ there is no significant difference ($p = 0.08$), although median stiffness in Scottish samples is 8 GPa higher. Note, that we used a one-sided Wilcoxon signed rank test since a Shapiro–Wilk test and quantile–quantile plots rejected normality (“Section Statistical analyses”). Accepting that the idea of significance is gradation rather than a binary condition, the higher 8 GPa median in Scottish samples reflects our findings in the micropillar compression tests. With regards to the low median (point (b)), our nanoindentation testing protocol may have damaged the material underneath the tip and thereby lowered the median stiffness with a potentially greater effect on samples from the California Sea Bight that lived at much lower aragonite concentrations. Such damage may have also contributed to insignificant results when comparing nanoindentation results between samples from the California Sea Bight and UK waters.

This was confirmed by the micropillar tests whose median is closer to the higher values from the literature^{31,41,42} and which show a lower variation (“Section Micropillar compression tests of the skeleton not exposed to acidified waters”, Figure S6c). When evaluating these tests with the micropillar finite element model using our predicted stiffness tensor for the skeleton not affected by ocean acidification and without further modification, we overestimate the median structural stiffness of the micropillars, but are well within the identified range. The striking difference in comparison to our nanoindentation tests is that micropillar stiffness for the samples close to the ASH is significantly lower ($p < 10^{-12}$) while the maximum bearable load is not different ($p \rightarrow 1$). It is important to note that our samples were covered with soft-tissue so that they were not exposed to acidified waters⁹ (Fig. 1). To reach the stiffness of the unaffected skeleton for the low aragonite saturation samples, \mathbb{S}_{CS} would need to include a ϕ_{np} between the crystals of ~20% (Fig. 6). Hennige et al.⁹ did not detect such a difference in ϕ_{np} and concluded that the skeleton above and below the ASH is similar and made of aragonite. A higher ϕ_{np} would also lower the strength of the polycrystalline material and, consequently, maximum bearable force which was not detected in our micropillar tests. ϕ_{np} on its own, therefore, does not provide a satisfying explanation for the detected difference in stiffness.

The identified interfacial strength (using \mathbb{S}_{CS} with a $\phi_{np} = 3.9\%$, Fig. 6a) at the crystal length scale is 1.86 times higher than was suggested when using nacre as a surrogate material (Fig. 6c). It is, however, much closer to the interfacial strength of nacre than to the strength of the aragonite single crystal (Table 2). The interface, thus, dominates failure as in other polycrystals^{37,38}. While the polycrystal seems to be assembled similarly for low and high aragonite concentrations as long as crystals are there (Figure S1), the fact that the resulting polycrystalline strength is the same suggests that the crystal interface is crucial. Our results suggest that if polycrystalline stiffness decreases, interfacial strength is unaffected and polycrystalline strength is maintained. The lower stiffness but similar strength in the samples at low aragonite concentration is an exciting conundrum.

Retaining strength in a future ocean. Hennige et al.⁹ detected significantly smaller crystals in samples from below the ASH without significant changes in ϕ_{np} or bulk density. This conundrum therefore requires other strategies to modify stiffness and strength of the multiscale material making up the skeleton. Interestingly, Kim et al.⁷⁵ found that including amino-acids in calcite (a polymorph of aragonite) can increase the hardness, which can be considered a proxy for strength, without affecting crystal stiffness. A similar effect was observed in supersaturated calcium-barium carbonate⁷⁶. The mechanism behind this may be the creation of residual stresses by integration of intracrystalline organic or inorganic inclusions in a calcium carbonate that is crystallised from an amorphous precursor material⁷⁷. In addition, smaller crystals have a higher surface to volume ratio so that contact area between them is increased. Such reinforcement may then stabilise the crystal interface so that interfacial cohesive forces increase, and polycrystalline strength remains the same. The reinforcement could be a compensation due to a lack of aragonite as a building material, which was revealed in smaller crystals overall⁹. The lowered stiffness may then either be caused by a breakdown in aspect ratio that can cause lower polycrystalline stiffnesses³⁸ or by lowering aragonite crystal stiffness (Fig. 6c) while increasing load bearing capability to maintain interfacial and polycrystalline strength. In fact, when reducing aragonite stiffness by 30% and 50%, which is close to the median stiffness found in our micropillar tests (blue and red lines in Fig. 6c), our models suggest that maintaining interfacial strength leads to insignificant changes in polycrystalline strengths (1.2% difference). This enables CWCs to cope with more compliant building materials while maintaining load bearing capacity potentially through utilisation of these hardening mechanisms^{75–77}. This is corroborated by findings that skeletons formed under low aragonite concentrations show systematic crystallographic changes

such as adapted crystal orientation and anisotropic distortion of the aragonite lattice⁷⁸ as well as suggestions that aragonite crystallography influences material properties such as strength⁷⁹. Another mechanism to generate more compliant aragonite crystals could also result from crystallisation by attachment of amorphous particles, which Mass et al.⁸⁰ identified as the dominant crystallisation pathway, where flaws may be incorporated during accumulation of amorphous patches prior to proper crystallisation⁸¹. It seems however unlikely that the crystal stiffness is weakened by up to 60%. Re-interpreting the dashed black line in Fig. 6c, we suggest that polycrystal stiffness is reduced by a combination of a slightly higher ϕ_{np} , which may well have been below the detection limit of the techniques used by Hennige et al.⁹, and a moderate reduction of aragonite stiffness.

Our results, therefore, suggest that CWCs have a way to deal with compromised availability of building material, and compensate resulting loss of stiffness through strengthening strategies that result in a significant increase of interfacial strength. This would then point to a conserved synthesis process of the polycrystal even in acidified waters. This also points to the robustness of our modelling as these effects can be explained by our stiffness and strength predictions through the properties at the crystal length scale. The proposed model can therefore capture the impact of crystallo-chemical changes on the multiscale mechanical behaviour of the reef structure⁷⁸. We consider the proposed model usable to quantify elasticity and strength of the coral skeleton not exposed to corrosive waters and, more importantly, to investigate impact of exposure to acidified waters (Fig. 1) and the mechanism suggested by Hennige et al.⁹. Finally, the smaller crystal size at low aragonite concentration may lead to a more crack tolerant material that is less damaged by nanoindentation than samples with larger crystals. This would provide an explanation why the difference in stiffness was not detected by nanoindentation since the potentially induced damage under tip was greater in samples from above the ASH and thereby lowering the stiffness more in these tests.

Ocean acidification. We used the model to test assertions by Hennige et al.⁹ based on in situ and in vitro data that an increase in porosity and loss of material leads to a weakening of the *dead* coral foundation framework which consists primarily of exposed skeleton. For simplicity, we model acidification induced porosity in the whole skeleton and not only towards the outer periphery as identified by Hennige et al.⁹. This is achievable because these hollow, thin-walled structures are loaded primarily under bending, so that the critical stresses are located at the outer periphery (Fig. 1d) with little effect of the internal periphery on the overall load bearing capacity. Increased fragility of such a weakened framework would lead to rapid crumbling of the overall reef structure and a reduction of the biodiversity supporting 3-dimensional complexity. Using a representative coral colony, Fig. 8 illustrates that increasing porosity decreases loadbearing capacity of the skeleton and that this effect is worsened by an additional loss of material following dissolution^{9,16}. The loss of stiffness and strength already at small porosities (Fig. 7) suggests that crumbling due to loss of load bearing capacity is a potentially rapid way in which these habitats will change. The relationship between porosity and aragonite concentration (Fig. 1e, Hennige et al.⁹) provides an interesting opportunity, as porosity could be replaced by aragonite concentration as an independent variable. This would facilitate the use of a geochemical marker to quantify strength of the exposed skeleton in situ along with other variables such as temperature and oxygen concentration that would allow assessing health of the living part of CWCs reefs and, thus, provide means to monitor these sites locally.

It is of course conceivable that ocean acidification induced dissolution on ecosystem scales may be partially slowed by reaching equilibrium through dissolved aragonite even though the ASH is shoaling. In addition to acidification induced porosity, there is evidence³ that future oceanic conditions with higher temperatures and lower oxygen may also lead to a significant increase in the efficacy of bioeroders. Breaking of coral under their own weight due to bioerosion are established but sporadic mechanisms to deteriorate CWC skeletons⁸². These bioeroders such as sponges, fungi, and borers create porosities that are either very similar⁸³ to those observed for low aragonite concentrations⁹ or much larger, but with the same eventual mechanical impact. Tunnicliffe⁸⁴ was able to show the detrimental effect of increasing porosity on the mechanical competence of the coral skeleton by three-point bending testing. The mechanism was then used to explain breakage of colonies of *Acropora cervicornis* whose base was weakened by boring sponges⁸⁵; very similar to the mechanism we described⁹ (Fig. 1) and which is captured by our model. This was corroborated by observations that borers decrease strength and increase fragility in massive corals with a dramatic loss of ability to withstand excessive loading caused by storms⁸⁶. In addition, skeletal wall thinning and a limited uptake in porosity can be induced by Fe–Mn precipitated biofilms⁸⁷. These films generate an edged appearance that is similar to the surface erosion Hennige et al.⁹ report for their in vitro samples and promote attachment of other bioeroders that together result in similar weakening mechanisms – skeletal thinning and increased porosity. Therefore, irrespective of what generates porosity in a future ocean, the threat remains the same for CWC skeletons and the habitat they support.

Our modelling points to some crucial gaps of knowledge. Although we provide a robust estimate for the interfacial strength and an explanation of the variation in the results, our considerations with regards to the lower stiffness and similar maximum force needs experimental verification. The interfacial strength as suggested by nacre as a surrogate material proved too low and rules out a purely protein mediated assembly of the polycrystal. Our findings reject the assumption that dry nacre approximates the brittle, interfacial yield strength of aragonite⁵² and it is an interesting question as to what generates crystal cohesion. Probably the most important gap is the absence of robust exposure times for CWCs under investigation. Hennige et al.⁹ report the results shown in Fig. 1e after 12 months experimental exposure in mesocosm experiments. However, in situ exposure time spans and robust markers to estimate exposure are currently missing. It is therefore not yet possible to use such a material model as a predictive tool to estimate risk of CWC loss. This would require further investigation on increasing porosities under different acidification scenarios to complement and solidify results of Hennige et al.⁹ and in situ measurements of ocean chemistry. As most of the CWC reefs live currently above the ASH^{1,7}, such data would

allow us to establish a baseline of aragonite concentrations with regular measurements allowing establishment of an exposure trajectory and thresholds that indicate time of exposure of CWCs to acidified waters.

Conclusion

We present a multiscale modelling framework that allows the investigation of the load bearing capacity of CWC structures. While our model underpins the dramatic and potentially rapid detrimental effects of ocean acidification to CWC skeletons it is an important step towards developing powerful monitoring tools. The impact of ocean acidification is dependent on the time CWCs are exposed to acidified waters. The model, therefore, allows us to investigate timescales of change as well as the impact of these changes on real reef structures if such an exposure time is known. It would therefore be possible to use the provided data to estimate time to reef crumbling, so that our results ultimately support future conservation and management efforts of these vulnerable marine ecosystems. It represents a crucial step towards understanding *which* ecosystems are at risk, *when* they will be at risk, and *how* much of an impact this will have upon associated biodiversity.

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Author contributions

U.W. and S.H. conceptualised the study and solicited funding. A.O. contributed the molecular dynamics analyses. R.B., S.Mc.P., and J.S. performed laser ablation and associated SEM imaging. M.P.F., S.Mc.P., and UW performed the micropillar compression tests and associated data analyses. S.H. contributed EBSD and synchrotron analyses. E.S. and M.P.F. performed the image-based finite element analyses. CSE and UW conducted the porosity analyses. U.W. performed the nanoindentation analyses. J.B. and J.T. provided the computed tomography dataset of the exemplar sample. The manuscript was written by U.W. with contributions from M.P.F., A.O., S.Mc.P., E.S., R.B., M.R., and S.H. All co-authors assisted in reviewing and editing of the final manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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