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Volcanic carbon dioxide vents show ecosystem effects of ocean acidification

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The atmospheric partial pressure of carbon dioxide (p_{CO_2}) will almost certainly be double that of pre-industrial levels by 2100 and will be considerably higher than at any time during the past few million years[1]. The oceans are a principal sink for anthropogenic CO_2 where it is estimated to have caused a 30% increase in the concentration of H^+ in ocean surface waters since the early 1900s and may lead to a drop in seawater pH of up to 0.5 units by 2100 (refs 2, 3). Our understanding of how increased ocean acidity may affect marine ecosystems is at present very limited as almost all studies have been *in vitro*, short-term, rapid perturbation experiments on isolated elements of the ecosystem[4,5]. Here we show the effects of acidification on benthic ecosystems at shallow coastal sites where volcanic CO_2 vents lower the pH of the water column. Along gradients of normal pH (8.1–8.2) to lowered pH (mean 7.8–7.9, minimum 7.4–7.5), typical rocky shore communities with abundant calcareous organisms shifted to communities lacking scleractinian corals with significant reductions in sea urchin and coralline algal abundance. To our knowledge, this is the first ecosystem-scale validation of predictions that these important groups of organisms are susceptible to elevated amounts of p_{CO_2}. Sea-grass production was highest in an area at mean pH 7.6 (1,827 µatm p_{CO_2}) where coralline algal biomass was significantly reduced and gastropod shells were dissolving due to periods of carbonate sub-saturation. The species populating the vent sites comprise a suite of organisms that are resilient to naturally high concentrations of p_{CO_2} and indicate that ocean acidification may benefit highly invasive non-native algal species. Our results provide the first *in situ* insights into how shallow water marine communities might change when susceptible organisms are removed owing to ocean acidification.

Short-term laboratory experiments show that many calcareous organisms may be unable to build their skeletons as oceans acidify over the next 100 years[6,7]. This may combine with other stresses, such as global warming, to drive tropical coral reefs towards functional collapse[8]. However, attempts to determine whether expectations on the basis of laboratory experiments and modelled predictions translate to field conditions have been hindered by the difficulty of imitating ocean acidification conditions *in situ* for sufficient periods to affect communities of macroorganisms.

Natural CO_2 flux from volcanic vents and high heat flow areas amounts to less than 0.5% of anthropogenic emissions to the global carbon budget, but can alter local ocean chemistry[9,10]. Marine CO_2 vents are abundant in the Mediterranean, especially around Italy and Greece where they typically eject volcanic fluids containing up to 1–2% hydrogen sulphide[10,11]. Some marine CO_2 vents are at ambient seawater temperature and lack toxic sulphur compounds; such vents can prevail for years to millenia[12] and may be used as natural experiments to advance our understanding of ocean acidification at the ecosystem level.

We studied cold vent areas off Ischia in Italy (Fig. 1) where sea water was being acidified by gas comprising 90.1–95.3% CO_2, 3.2–6.6% N_2, 0.6–0.8% O_2, 0.08–0.1% Ar and 0.2–0.8% CH_4 (no sulphur). Salinity (38%) and total alkalinity (2.5 mequiv. kg^{-1}) were homogeneous between survey stations and temperature-matched ambient seasonal fluctuations (13–25 °C). Vents occurred on the north and south sides of Castello d'Aragonese (40° 043.84′ N; 13° 57.08′ E) adjacent to a steeply sloping rocky shore. At the south vent site gas was emitted at 1.4×10^6 litre day^{-1} in an area of about 3,000 m^2 (mainly >5 vents m^{-2}); at the north site gas was emitted at 0.7×10^6 litre day^{-1} in an area of about 2,000 m^2 (mainly <5 vents m^{-2}). No seasonal, tidal or diurnal variation in gas flow rates was detected in 2006–07. The pH and saturation states (Ω) of calcite and aragonite varied with sea state, being lowest on calm days, and showed large decreases as p_{CO_2} amounts increased from approximately 300 to more than 2,000 µatm through the venting gas fields (Fig. 2 and Supplementary Table 2). Here we examine ecological tipping points along gradients of increasing p_{CO_2}, comparing normal pH stations (N_1, S_1 and P_1–P_2) with three stations that had reductions in mean pH of 0.2–0.4 units (N_2, S_2 and P_3; Fig. 1) and three stations (P_4, N_3 and S_3) with reductions in mean pH of 0.6–1.5 units which are more representative of the localized effects to be expected from deliberate CO_2 sequestration[13] rather than from global ocean acidification.

Rocky-shore stations with a mean pH of 7.8–7.9 (mean p_{CO_2} 804–957 µatm) showed a 30% reduction in species numbers (notably calcifiers) compared with the normal pH stations (Supplementary Tables 3 and 4). Temporal variability in p_{CO_2} will have contributed to the pronounced biodiversity shifts observed, as these stations experienced short periods of pH as low as 7.4–7.5. Organisms with aragonite skeletons were common outside the vents (for example, *Halimeda* algae and the corals *Caryophyllia*, *Cladocora* and *Balanophyllia*) but were absent at mean $\Omega_{arag} \leq 2.5$ (minimum Ω_{arag} 0.8–1.2), providing *in situ* support for predictions of global coral reef dissolution at these concentrations[8]. Although scleractinians can survive skeletal dissolution as polyps in the laboratory[14], reduced calcification due to low Ω_{arag} may result in increased risk to predation or competition in open ecosystems. The only Cnidaria in waters undersaturated with aragonite were anemones such as *Anemonia viridis*, which may benefit from increased p_{CO_2} for photosynthesis of its endosymbiotic dinoflagellates. Although atmospheric diffusion of CO_2 is not predicted to result in aragonite undersaturation in shallow waters of the Mediterranean,

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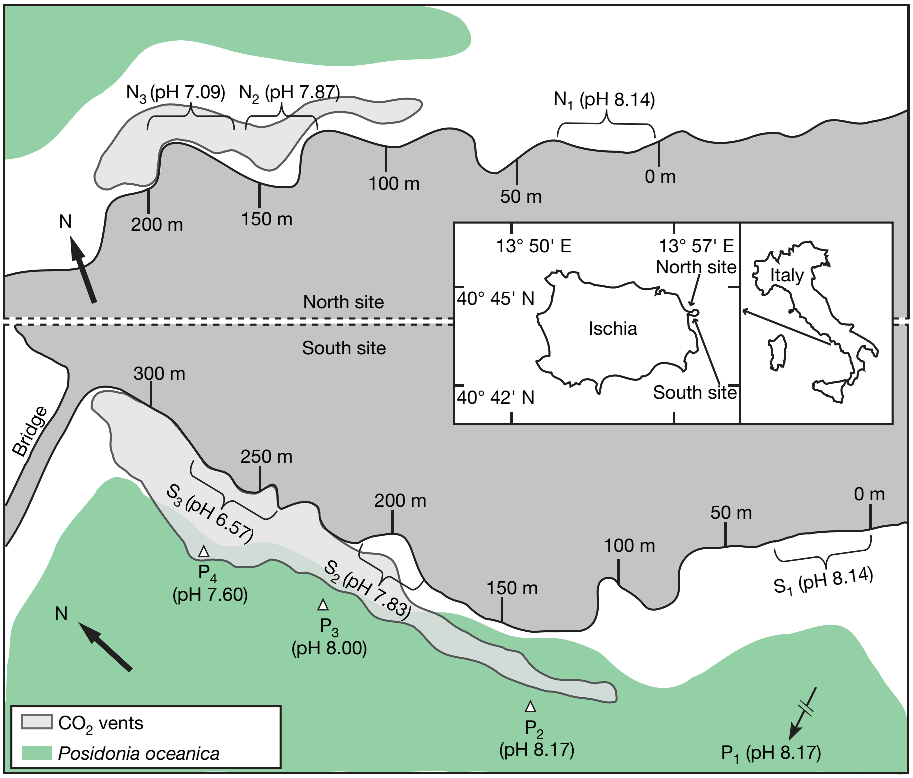

Figure 1 | Map of CO_2 vent sites north and south of Castello d'Aragonese, off Ischia Island, Italy. Mean surface pH is shown at 35-m-wide rocky-shore stations N_1–N_3 and S_1–S_3. Mean subtidal pH is shown at stations P_1–P_4, together with the distributions of CO_2 vents and *P. oceanica* sea-grass meadows. Reference station P_1 was at a 3-m depth, 400 m from the arrow shown.

observations of such areas are relevant to the localized effects caused by deliberate CO_2 sequestration and to the widespread effects predicted for areas that at present have low Ω_{arag}, given that high-latitude pteropods and coral reefs may be unable to make their skeletons by the year 2100 (refs 7, 13).

Mesocosm experiments have led to predictions that Corallinaceae, which help to protect against coral reef erosion in the tropics, are vulnerable to ocean acidification due to the solubility of their high magnesium calcite skeletons[15,16]. We found that Corallinaceae cover was significantly reduced at lowered pH (Table 1 and Supplementary Tables 2–4). As coralline algal cover fell from >60% outside the vent area to zero within it, non-calcareous algal cover increased significantly from near zero to >60% (Fig. 2 and Table 1). A suite of algal genera proved to be resilient to naturally high amounts of p_{CO_2} (for example, *Caulerpa*, *Cladophora*, *Asparagopsis*, *Dictyota* and *Sargassum*), some of which include invasive alien species that have begun to alter shallow marine ecosystems worldwide[17]. This adds to previously scant experimental information about the sorts of marine phototrophs that have enhanced growth and undiminished rates of photosynthesis at elevated concentrations of CO_2 (refs 4, 5, 18, 19).

The analysed *Posidonia oceanica* shoots were >10 yr old at the subtidal study sites and will have integrated the effects of lowered pH over this time. Sea-grass leaves at P_1 (pH 8.2) had 75% cover of calcified epiphytes but only 2% cover at P_4 (mean pH 7.6) with a significant reduction in epiphytic calcium carbonate per leaf (Table 1 and Figs 3 and 4). When heavily epiphytised leaves were transplanted from station P_1 to P_4 they showed complete dissolution of Corallinaceae in 2 weeks, whereas transplants moved within P_1 were unaffected. Mesocosm experiments have shown that sea-grass production can be enhanced at high p_{CO_2}(ref. 19). We found no difference (Table 1) in the photosynthetic performances of individual *P. oceanica* leaves between the four stations (mean ± s.e.m., photosynthetic efficiency (F_v/F_m) 0.74 ± 0.01 and electron transport rates $(ETR)_{max}$ 8.4 ± 1.9, $n = 40$) but sea-grass production was high-

Table 1 | Analysis of ecological tipping-points along marine acidity gradients

Category, site	*F* (d.f.)	*P* value	Tukey's test, site comparison
Corallinaceae cover, north	$F_{2,21} = 43.8$	0.000	$N_1 > N_2 > N_3$
Corallinaceae cover, south	$F_{2,21} = 48.0$	0.000	$S_1 > S_2 = S_3$
Non-calcareous crustose algal cover, north	$F_{2,21} = 0.31$	0.74	NS
Non-calcareous crustose algal cover, south	$F_{2,21} = 62.5$	0.000	$S_1 = S_2 < S_3$
Sea-grass epiphyte weight, south	$F_{3,315} = 176.2$	0.000	$P_1 > P_2 > P_3 > P_4$
Sea-grass F_v/F_m, south	$F_{3,36} = 0.13$	0.93	NS
Sea-grass ETR_{max}, south	$F_{3,36} = 0.06$	0.98	NS
Sea-grass shoot density, south	$F_{3,16} = 67.6$	0.000	$P_1 = P_2 = P_3 < P_4$
Sea urchin abundance, north	$F_{2,9} = 14.7$	0.001	$N_1 > N_2 = N_3$
Sea urchin abundance, south	$F_{2,9} = 65.3$	0.000	$S_1 > S_2 = S_3$
C. stellatus abundance, north	$F_{2,21} = 0.72$	0.50	NS
C. stellatus abundance, south	$F_{2,21} = 29.4$	0.000	$S_1 = S_2 > S_3$
O. turbinata abundance, north	$F_{2,21} = 3.50$	0.049	$N_1 = N_2 > N_3$
O. turbinata abundance, south	$F_{2,21} = 6.39$	0.007	$S_1 = S_3 < S_2$
P. caerulea abundance, north	$F_{2,21} = 22.8$	0.000	$N_1 > N_2 > N_3$
P. caerulea abundance, south	$F_{2,21} = 9.24$	0.001	$S_1 = S_2 > S_3$

Significant differences were assessed using one-way analysis of variance (ANOVA, *F*) and Tukey's HSD (honestly significant difference) post-hoc tests. Data are from stations north and south of Castello d'Aragonese, Ischia, Italy in spring 2007. d.f., degrees of freedom, NS, not significant.

est at mean pH 7.6 (biomass increased by 2.8 g m^{-2} day^{-1} at mean p_{CO_2} 1,827 μatm) where shoot density was significantly higher (Table 1 and Fig. 3) and approximately 30% higher than that known anywhere else around Ischia[12].

Sea urchins (*Paracentrotus lividus*, *Arbacia lixula*), which have high magnesium calcite skeletons, were the most common large invertebrates on sublittoral rock outside the vents but their abundance was significantly reduced where pH reached minima of 7.4–7.5 (Table 1 and Fig. 2). This supports physiological studies showing that sea urchins are vulnerable to a rise in CO_2, and is a concern as sea urchin loss can drive deteriorations in ecosystem complexity and stability[20,21]. Although sea urchins cannot close off their supply of ambient sea water, some organisms can do this to avoid pH minima. Other calcitic organisms, such as the barnacle *Chthamalus stellatus*, for example, may survive pH minima by closing their rostral plates as

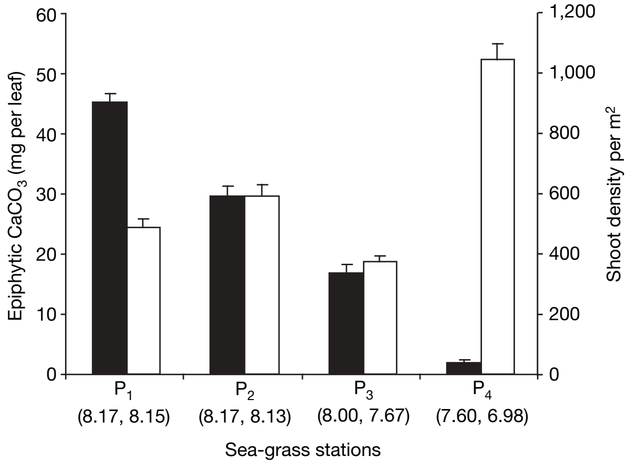

Figure 3 | Sea-grass shoot density and amount of epiphytic $CaCO_3$ on leaves growing at differing pH levels south of Castello d'Aragonese. Shoot density (open column, $n = 4$, mean and s.d.) and epiphytic $CaCO_3$ (filled column, $n = 80$, mean and s.d.) for data from 18 April to 9 May 2007 at various pH levels (mean and minimum values are shown; P_1 $n = 30$, P_2 $n = 16$, P_3 $n = 23$ and P_4 $n = 37$).

their abundance was not significantly reduced until extremely low mean pH 6.6 (Table 1 and Fig. 2). Juveniles of *Osilinus turbinata* and *Patella caerulea* gastropods were absent in areas with pH minima ≤7.4, where all adult gastropod shells (including *Hexaplex trunculus* and *Cerithium vulgatum*) were weakened by the acidified sea water (Figs 2 and 4, Table 1 and Supplementary Video), an effect which probably increases their risk of predation[22].

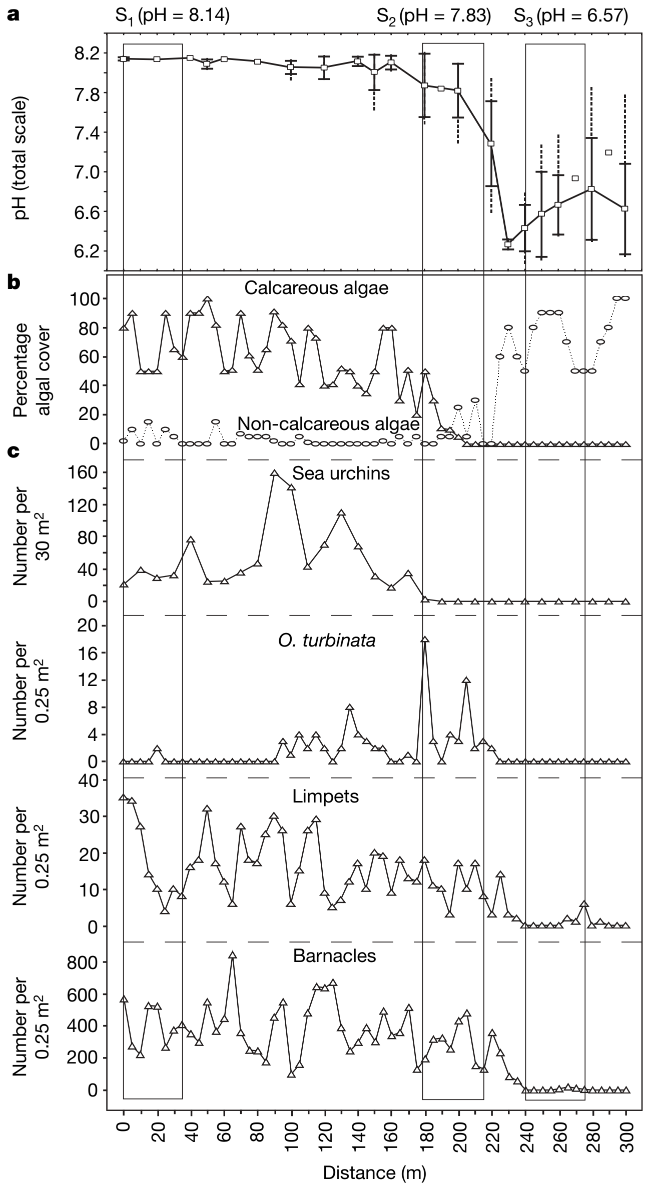

Figure 2 | Variation in pH, cover of algae and abundance of species at CO_2 vents south of Castello d'Aragonese. Data are from stations S_1–S_3 (see Fig. 1) from 18 April to 9 May 2007. **a**, The mean pH ± s.d. (cross bars) is shown. Ranges are denoted by the dotted line; $n = 6$ at 0 m, $n = 11$ at 50 m, 100 m, 250 m and 300 m, $n = 9$ at 220 m, 260 m, 280 m and $n = 12$ at 150 m and 200 m. **b**, The percentage cover of calcareous (triangles) and non-calcareous algae (circles) is shown. **c**, The abundances of sea urchins, *O. turbinata*, limpets and barnacles.

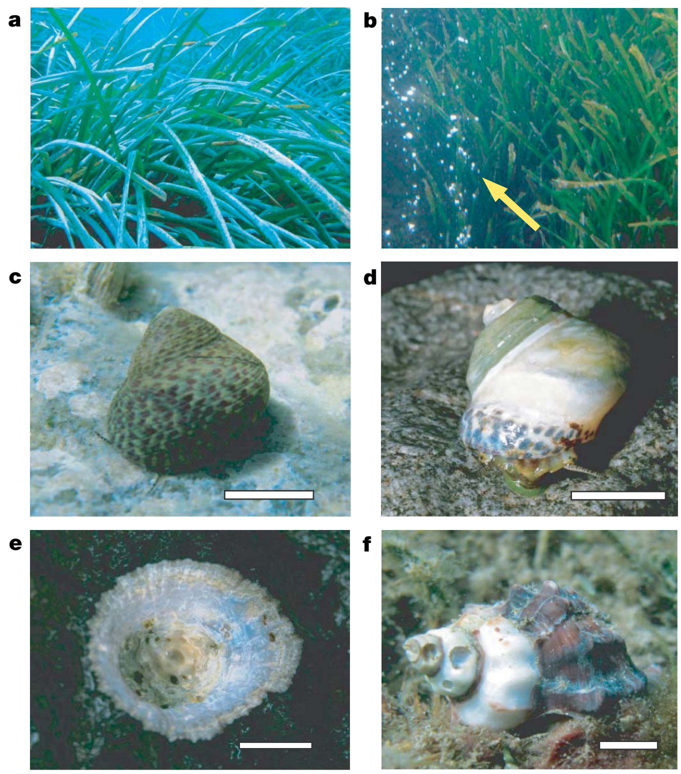

Figure 4 | Dissolution of calcified organisms due to naturally acidified sea water. **a**, **b**, *Posidonia oceanica* with heavy overgrowth of Corallinaceae at pH 8.2 (**a**) and lacking Corallinaceae at mean pH 7.6 (**b**); arrow indicates bubbles from the CO_2 vent field. **c**, **d**, Typical examples of *O. turbinata* with the periostracum intact at pH 8.2 (**c**) and with old parts of the periostracum removed at mean pH 7.3 (**d**). **e**, **f**, Live *P. caerulea* (**e**) and *H. trunculus* (**f**) showing severely eroded, pitted shells in areas of minimum pH 7.4. Scale bars represent 1 cm.

Vent systems are not perfect predictors of future ocean ecology owing to temporal variability in pH, spatial proximity of populations unaffected by acidification and the unknown effects of other global changes in parameters such as temperature, currents and sea level. However, such vents acidify sea water on sufficiently large spatial and temporal scales to integrate ecosystem processes such as production, competition and predation. Lush stands of sea-grass and brown algae can thrive along natural pH gradients where aragonitic and then calcitic calcareous organisms are lost owing to skeletal dissolution. This confirms experimental and modelling predictions that differential responses of benthic species to decreased pH can lead to substantial changes in community structure[4–8,13–16]. Many of the organisms that were adversely affected by reductions in pH at our study sites belong to groups that existed before and after periods of similar reductions in the past (for example, calcified algae, corals and sea urchins)[14]. It is unknown whether there will be sufficient refugia or enough time for these groups to adapt to survive the rapid rate of ocean acidification predicted due to anthropogenic CO_2. This opportunity to observe the tipping points at which principal groups of marine organisms are affected by lowered pH proves that, even without global warming, the projected rise in atmospheric CO_2 concentration is hazardous, as ocean acidification will probably bring about reductions in biodiversity and radically alter ecosystems.

METHODS SUMMARY

Vent gases were collected in pre-evacuated glass flasks partly filled with 0.1 M $Cd(OH)_2$ and 4 N NaOH solution (see Supplementary Video). Uncondensable gases were collected in the headspace, inorganic residual gas compounds were analysed using thermal conductivity chromatographs, methane was analysed with a flame ionization detector and ion chromatography was used to analyse condensable gases such as CO_2 dissolved during collection. Between 18 April and 9 May 2007, surface and bottom water samples were regularly taken for measurements of the spatial and temporal variability in pH (in total scale), total alkalinity and salinity in various weather conditions. In winter 2006, and spring and autumn 2007, intertidal and subtidal SCUBA surveys were made of the main macroorganisms present within and adjacent to the vents to 3 m depth. Epibiont calcium carbonate on *P. oceanica* leaves was quantified along a gradient of pH; leaves that were heavily encrusted with Corallinaceae were transplanted from a reference site into an area with mean pH 7.6 then reassessed after 2 weeks. *Posidonia oceanica* production, growth dynamics and shoot density was estimated at stations P_1–P_4 where their photosynthetic efficiency (F_v/F_m) and electron transport rates (ETR) were measured *in situ* using a diving pulse amplitude modulation (PAM), and in the laboratory using an imaging PAM.

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Supplementary Information is linked to the online version of the paper at www.nature.com/nature.

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Author Contributions All authors were involved with fieldwork and sample analyses. J.M.H.-S. designed the study and wrote the paper along with R.R.-M., M.F. and S.M.T. D.T. analysed gases, S.M. analysed sea-grass epiphytes and seawater chemistry, E.R. and S.J.R. collected intertidal and subtidal data respectively, and M.-C.B. provided sea-grass expertise. All authors discussed results and commented on the manuscript.

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