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Volcanic CO_2 seep geochemistry and use in understanding ocean acidification

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Abstract Ocean acidification is one of the most dramatic effects of the massive atmospheric release of anthropogenic carbon dioxide (CO_2) that has occurred since the Industrial Revolution, although its effects on marine ecosystems are not well understood. Submarine volcanic hydrothermal fields have geochemical conditions that provide opportunities to characterise the effects of elevated levels of seawater CO_2 on marine life in the field. Here, we review the geochemical aspects of shallow marine CO_2-rich seeps worldwide, focusing on both gas composition and water chemistry. We then describe the geochemical effects of volcanic CO_2 seepage on the overlying seawater column. We also present new geochemical data and the first synthesis of marine biological community changes from one of the best-studied marine CO_2 seep sites in the world (off Vulcano Island, Sicily). In areas of intense bubbling, extremely high levels of pCO_2 (> 10,000 µatm) result in low seawater pH (< 6) and undersaturation of aragonite and calcite in an area devoid of calcified organisms such as shelled molluscs and hard corals. Around 100–400 m away from the Vulcano seeps the geochemistry of the seawater becomes analogous to future ocean acidification conditions with dissolved carbon dioxide levels falling from 900 to 420 µatm as seawater pH rises from 7.6 to 8.0. Calcified species such as coralline algae and sea urchins fare increasingly well as sessile communities shift from domination by a few resilient species (such as uncalcified algae and polychaetes) to a diverse and complex community (including abundant calcified algae and sea urchins) as the seawater returns to ambient levels of CO_2. Laboratory advances in our understanding of species sensitivity to high CO_2 and low pH seawater, reveal how marine organisms react to simulated ocean acidification conditions (e.g., using energetic trade-offs for calcification, reproduction, growth and survival). Research at volcanic marine seeps, such as those off Vulcano, highlight consistent ecosystem responses to rising levels of seawater CO_2, with the simplification of food webs, losses in functional

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diversity and reduced provisioning of goods and services for humans.

Keywords Calcifying species · Ecosystem effects · Natural analogues · Submarine hydrothermalism

Introduction

Rising atmospheric carbon dioxide levels, from fossil fuel combustion and other human activities, are increasing seawater CO_2 levels and reducing the carbonate saturation of estuarine, coastal, and surface open-ocean waters (IPCC 2019; Doney et al. 2020). This has globally expanded the volume of seawater that is corrosive to carbonate (Tittensor et al. 2009) and first came to world attention when ocean acidification caused mass oyster spat mortality, threatening a $270 million/year aquaculture industry in Washington State, USA (Ekstrom et al. 2015). Field manipulations of seawater CO_2 have shown that ocean acidification causes carbonate saturation state to fall below levels suitable for globally important coral reefs (Albright et al. 2018) and laboratory studies show that acidification can reduce the nutritional value of seafood as it lowers caloric content and levels of protein, lipid and carbohydrate (Lemasson et al. 2019). Thus acidification puts at risk many of the valuable ecosystem services that the ocean provides to society, such as fisheries, aquaculture, and shoreline protection (Hall-Spencer and Harvey 2019; Doney et al. 2020).

Although the chemistry of ocean acidification (OA) is well understood, there is uncertainty about the ecosystem effects of these changes. Laboratory experiments show that OA may affect all marine life, for example through changes in gene expression, physiology, reproduction and behaviour (IPCC 2019). However, it is difficult to scale-up from these results as most laboratory studies address only the effect of one or two parameters on a single organism, since multiparameter studies using multiple species are logistically challenging (Riebesell and Gattuso 2015). In the past 10 years, work using natural gradients in pCO_2 has shown the long-term effects of OA on ecosystem properties, functions and services. Many studies have been conducted at shallow submarine hydrothermal vents around active volcanoes (here referred to as hydrothermal CO_2 seeps), where large amounts of CO_2 are injected into seawater (Fig. 1; Hall-Spencer et al. 2008). These shallow (< 200 m) hydrothermal CO_2 seeps (Tarasov et al. 2005; Dando 2010; González-Delgado and Hernández 2018) provide natural analogues to study the impact of OA on ecosystems. Volcanic CO_2 seeps also help further our understanding of the subsurface hydrothermal structure of coastal volcanoes, where a significant fraction of the hydrothermal output can occur offshore (Italiano and Nuccio 1991; Pichler et al. 1999a; Di Napoli et al. 2016). From a geochemical viewpoint, these sites allow studies of the dispersion patterns of seep-carried CO_2 and water-soluble chemicals in seawater (Boatta et al. 2013; Price and Giovannelli 2017; Pichler et al. 2019).

Here, we review the geochemistry of hydrothermal CO_2 seeps and use one of the best-known sites (off Vulcano Island, Sicily) as a case study. This expands on (and complements) recent excellent reviews on the topic (Dando 2010; Price and Giovannelli 2017; González-Delgado and Hernández 2018) by (i) combining available gas and aqueous compositional data for 56 seeps to illustrate quantitatively (in a set of key plots) the *processes* that govern and control their chemistry; (ii) providing a combination of new geochemical and biological data from Vulcano, including a demonstration on the potential of novel geochemical techniques to study seeps; (iii) presenting a novel and systematic analysis of biological data on how the abundances of higher taxa change at Vulcano in response to OA. Doing so, we present recent advances in biological research when using volcanic

Fig. 1 Example of vent forming sites/fields in shallow waters from Baia di Levante, Vulcano Island (Italy) Photo credit: Nicolas Floc'h

CO_2 seeps to assess the potential effects of OA and discuss ecosystem responses, describing which organisms survive well in acidified conditions and which do not. We end by presenting future research paths to be explored.

Marine CO_2 seeps

Types of submarine CO_2 seeps

Carbon dioxide-rich fluid venting on the seafloor is a common geological process. The discovery of vigorous fluid venting at Middle-Oceanic Ridges (MOR) in the 1970s boosted a plethora of studies on both the chemical properties of these 'black and white smokers' and on the biological communities leaving therein (Von Damm 1990; Tunnicliffe 1991). Gas venting at MORs is now recognised as a primary pathway of volatile (CO_2, noble gases) exchange from the Earth's mantle to the hydrosphere and atmosphere (Marty et al. 2013). MOR fluids have also been intensively studied because they transport the key chemical ingredients for life (e.g., reduced compounds of the elements C, O, N, S), and are thus potential candidate sites for the origin of life on our planet (Baross and Hoffman 1985). Recent focus has been on these fluids as sources of Fe, Mn, Zn and other micronutrients to the ocean, and on their role in the formation of massive sulphide deposits (Hannington et al. 2005, 2011). However, MOR seeps, alongside with their equivalent in active subduction zones (see de Ronde and Stucker 2015 for a review), typically occur several km deep in the ocean, far from coasts and well below the euphotic zone. They have low biological diversity and a fauna that relies on carbon fixation by chemosynthesis (Tunnicliffe 1991). Consequently, these deep vents are nosuitable proxies for studying the effects of OA on coastal marine biological communities (Dando 2010; González-Delgado and Hernández 2018).

Here, we focus on CO_2 seeps in shallow (< 200 m) waters which have marine communities that are more diverse and are not dominated by chemosynthetic organisms (Tarasov et al. 2005; Dando 2010; González-Delgado and Hernández 2018). Shallow high CO_2 areas can be produced by a variety of processes, including (González-Delgado and Hernández 2018): (i) karstic groundwater inflow (e.g., Yucatan Peninsula, Gulf of Mexico; Crook et al. 2016); (ii) rainwater and meteoric water inflow into small confined seawater basins, combined with high rate of respiration by living organisms (e.g., Rocas Islands of Palau Oceania; Shamberger et al. 2014); (iii) upwelling of seawater rich in inorganic C (e.g., Kiel Bay in the Baltic Sea; Thomsen et al. 2010); and (iv) discharge at the seafloor of CO_2-rich volcanic-hydrothermal fluids. This latter process can lead to both seawater acidification and to (small and confined) temperature increases (Di Napoli et al. 2016). It is on category (iv) above that we focus on below.

Global occurrence of shallow hydrothermal CO_2 seeps, and their geological significance

Submarine CO_2 seeps are likely to exist around any active coastal or island volcano, or on top of shallow seamounts (Price and Giovannelli 2017). The relatively small number of reports reflects technical challenges in locating and exploring them. Of the 70 reported shallow volcano-related seep locations (Price and Giovannelli 2017), we have identified 56 (Fig. 2) for which chemical and biological information exists (see Table S1, Fig. 2 caption for data provenance). The geographical distribution of these sites, illustrated in the map of Fig. 2, shows clusters in specific areas (e.g., the Mediterranean, Japan-southeast Asia and US). In the field, volcano-related seeps occur as single, gas-rich vents bubbling through the overlying seawater column or, more frequently, as cluster of vents forming sites/fields tens to several hundred square meters in size (Fig. 1). In addition to focused vent emissions, so called "diffuse vents" have also commonly been reported.

Throughout this review, we refer to these volcano-related seeps as hydrothermal CO_2 seeps because, geologically speaking, they are due to the interaction between fluids rising from volcanic hydrothermal systems and seawater (Fig. 3). These dynamic environments exhibit large spatial and temporal variations in aqueous fluid and gas chemistry (as well as in their discharge rates), owing to the complex interplay of factors such as local hydrothermal/geological setting, temperature, pressure, pH, fluid-rock interaction extent, and host rock geology. Broadly speaking, submarine hydrothermal systems form as seawater-derived (or meteoric-derived) waters percolate through permeable volcanic rocks, and become heated by dissolving magmatic volatiles rising from deep-

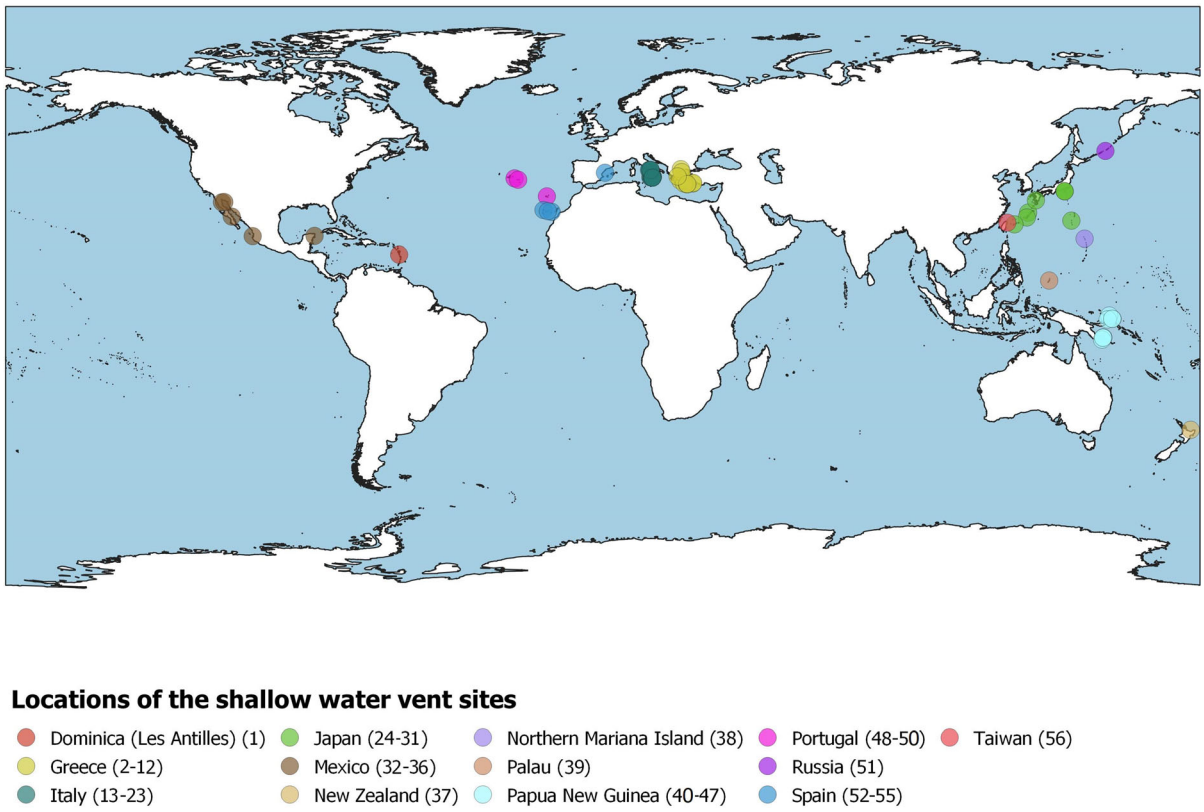

Fig. 2 Locations of shallow water vent sites. The number in brackets refers to the ID code of each location, see Table S1 for further details. (Color figure online)

seated magma storage zones (Price and Giovannelli 2017) (Fig. 3). As such, hydrothermal systems act as chemical filters, scavenging water-soluble magmatic volatiles to hydrothermal solutions (as Cl^{-}, SO_4^{2-}, HS^{-}, etc.) and minerals (sulphides, silicates), and converting magmatic volatiles (CO_2, CO, SO_2) into hydrothermal gases (CH_4, H_2S) via equilibrium gas–water-rock reactions at reservoir P–T-redox conditions (Giggenbach 1980, 1997; Chiodini and Marini 1998; Fischer and Chiodini 2015) (Fig. 3). At reservoir conditions, hydrothermal fluids are typically two-phase (liquid + reservoir gas) but liquid-dominated (Giggenbach 1997). This aqueous phase is typically a Na–K–Cl brine (Price and Giovannelli 2017) enriched in alkalis and Ca due to extensive leaching of the host rocks (see "Aqueous fluid chemistry" section), and boils to steam as it decompresses upon ascent through geological discontinuities (faults or permeability barriers) (Chiodini and Marini 1998). Upon approach to the near-seafloor, steam and brine mix with cool infiltrating seawater, enriching the residual steam phase in CO_2 (that has limited water solubility at hydrothermal conditions) and the residual liquid in seawater components (Mg, Na, K, Cl). Finally, upon discharge, the CO_2-rich gases bubble through, and partially dissolve into, seawater, increasing seawater CO_2 partial pressure (pCO_2) and Dissolved Inorganic Carbon (DIC), and lowering surrounding seawater pH. The C-rich plumes that develop in the water column range considerably in size, as they depend on vent/site/field geometry, fluid (liquid + gas) output rate, temperature (controlling buoyancy) and hydrodynamic parameters (e.g., seawater current) (Fig. 3). The gradients in seawater carbonate chemistry create environments that allow studies into the impact of OA on local ecosystems.

The Baia di Levante hydrothermal CO_2 vents

One CO_2 seep intensively studied by OA research is the Baia di Levante site in Vulcano Island (Aeolian Islands, Sicily) (Boatta et al. 2013). This small bay,

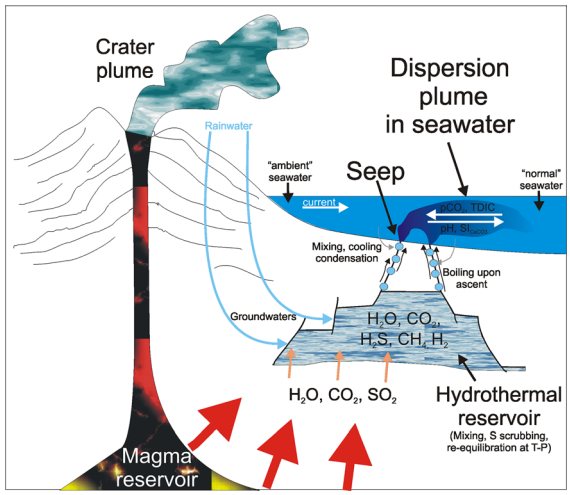

Fig. 3 Geological sketch (not to scale) illustrating the mechanisms governing origin and chemistry of CO_2 hydrothermal seeps at a costal/insular volcano (see discussion). Red and orange arrows refer to magmatic volatile release from magma and injection into the hydrothermal system, respectively. Light blue and grey arrows identify meteoric recharge and entraining seawater, respectively. The white arrows indicate increasing DIC/pCO_2 and Saturation Index (SI)/pH in the seawater column. (Color figure online)

located on the north-eastern margin of the island (Fig. 4), is well known since antiquity for the presence of numerous CO_2-rich submarine fumaroles discharging on the seafloor at less than a few meters depth (Italiano and Nuccio 1991; Italiano et al. 1984, 1994; Chiodini et al. 1993, 1995; Capaccioni et al. 2001; Italiano 2009). These fumaroles have compositions typical of hydrothermal steam samples ($\sim$ 90 mol% H_2O; $\sim$ 90 mol% CO_2 and 2 mol% H_2S on a dry gas basis; see "Chemical impact of hydrothermal CO_2 venting on the seawater column" section), and are thus interpreted as vapours deriving from boiling of hydrothermal brines rising from a shallow geothermal aquifer, identified during exploratory drilling (in 1951–1957) in the Levante Bay beach area (Sommaruga 1984). The geothermal aquifer itself is thought to be fed by magma-derived fluids similar to those feeding the La Fossa Crater further to the south (Chiodini et al. 1993, 1995; Paonita et al. 2013), although some authors (e.g., Tedesco 1995) have argued for a link with the Vulcanello magmatic system instead (Fig. 4). The dissolution of rising H_2S-rich hydrothermal steam leads to reduced (Eh as low as $-$ 150 mV) and H_2S-rich (166–273 µmol/kg) conditions close to shore at the main submarine vents in the bay (Sedwick and Stüben 1996; Boatta et al. 2013). The high CO_2 output ($\sim$ 3.6 ton/day of CO_2 are discharged by submarine fumaroles into the bay; Inguaggiato et al. 2012) results in acidic conditions (pH as low as $\sim$ 6.5; see below) close to the vents. Also, CO_2 seeping at the seafloor leads to strong pH gradients throughout the entire bay, with pH ranging

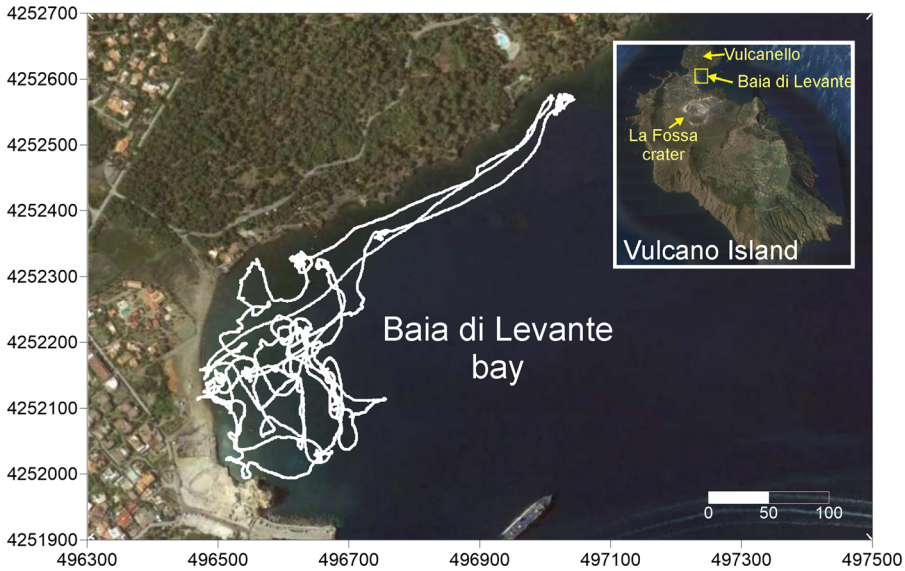

Fig. 4 The Baia di Levante Bay area on Vulcano island (top right inset). The white line identifies the track of the pCO_2 measurement profile along the bay

from vent-related values (< 6) to normal seawater levels (8.1) in a few hundreds meters from the vent (see below). These conditions make the Baia di Levante a natural laboratory to characterise the impact of OA on marine ecosystems (Boatta et al. 2013).

Chemistry of hydrothermal CO_2 seeps

Gas geochemistry

Collecting total (gas + steam) seep samples is technically difficult in the field. The steam fraction of shallow submarine hydrothermal CO_2 seeps is in fact rarely measured (gas analyses are typically expressed on a dry basis, as mol%, ppmv, mmol/mol or µmol/mol of the dry free gas; see Table S2). However, the few data available (e.g., Chiodini et al. 1995) confirm that, similar to their subaerial equivalents (Giggenbach 1980; Chiodini and Marini 1998), submarine hydrothermal seeps are mainly dominated by steam.

On a dry basis, shallow hydrothermal seeps are dominated by CO_2. Table S2 lists some free gas analyses taken at several CO_2 seeps worldwide (see Fig. 2 for their location). Our compilation is not exhaustive of all shallow submarine vents studied, but includes gas compositional data for all (at least, to the best of our knowledge) those seeps studied so far for their ecology and biology. As such, our compilation is based upon (and is an updated version of) previous cataloguing efforts (Tarasov et al. 2005; Dando 2010; Price and Giovannelli 2017; Gonzáles-Delgado and Hernández 2018; Global CCS institute 2018).

In our inventory (n = 207 gas analyses), the mean CO_2 content is 87 ± 20.7 vol%. The range is wide, from 0.4 to 99.6 vol%, but only 14 out of the 207 gas analyses have $CO_2 < 50\%$. Where this occurs, the reduced CO_2 contents are systemically associated with increasing N_2 and O_2 contents (Table S2). Thus, the large spread of CO_2 contents in our compilation mostly reflects variable extents of magmatic gas dilution by air components (Fig. 5a), either deep in the hydrothermal reservoir or (more likely) during steam migration toward the surface and/or upon discharge on the seafloor. Shallow dilution by air is likely implicated by samples with N_2/O_2 of ~ 3.7 (the typical air ratio), while deeper (reservoir) air entrainment is perhaps more likely for N_2-rich samples with N_2/O_2 ratios $> > 3.7$. In hydrothermal reservoirs, atmospheric oxygen is consumed by redox reactions between fluids and host rocks (Giggenbach 1987) and, when this happens, the resulting surface gas emissions typically depart from the pure CO_2-air mixing line (green solid line of Fig. 5). In addition to atmospheric O_2 consumption, magmatic N_2 feeding to the source hydrothermal systems (Pichler et al. 1999a) can also justify the N_2-enriched samples. Figure 5a also shows that the Baia di Levante seeps plot at the CO_2-rich range (CO_2: 94.5 ± 5.9 vol%) of the global population, with only two samples having < 80% CO_2 (and > 20% N_2).

In addition to CO_2, N_2 and O_2, hydrothermal CO_2 seeps contain a number of reduced gases at minor (tens of %) to trace (ppmv) levels. H_2, CH_4 and H_2S are the most commonly reported species (Table S2). Deep in the hydrothermal reservoir, these reduced trace components ultimately result from hydrothermal re-equilibration (in either vapour or liquid phase) of the feeding magmatic gas H_2O, CO_2 and SO_2 at reservoir temperature, pressure and redox conditions (expressed by oxygen fugacity, fO_2), according to (Giggenbach 1980, 1987):

$$H_2O \leftrightarrow H_2 + 0.5O_2 \quad (1)$$

$$CO_2 + 2H_2O \leftrightarrow CH_4 + 2O_2 \quad (2)$$

$$SO_2 + H_2O \leftrightarrow H_2S + 3/2O_2 \quad (3)$$

In the reservoir, hydrothermal H_2S (schematically formed by reaction (3)) can also be dissolved into the hydrothermal liquid, or precipitated into newly forming mineral phases, by a variety of reactions, among which:

$$H_2S + FeS \leftrightarrow 2H^+ + H_2 + FeS_2 \quad (4)$$

$$6H_2S + Fe_3O_4 \leftrightarrow 4H_2O + 2H_2 + 3\,FeS_2 \quad (5)$$

where FeS_2, FeS and F_3O_4 are hydrothermal minerals pyrite, pyrrhotite and magnetite (native S, sulphates, and dissolved SO_4^{2-}, can also be formed; Giggenbach 1980). Thus, at least to a first order, the H_2, CH_4 and H_2S contents in the hydrothermal seeps discharged at the seafloor will reflect the T–P–fO_2 conditions of their source reservoirs, e.g., they will record to some extent the gas compositions fixed by the T–P–fO_2 dependencies of relations (1) to (5), and by the extent of S scrubbing to hydrothermal brines/minerals.

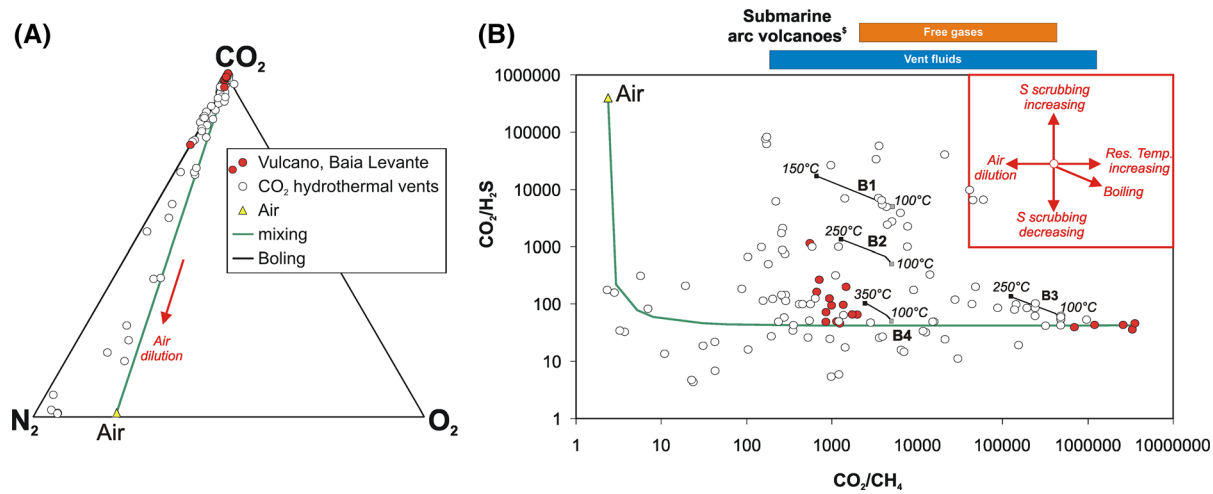

Fig. 5 **a** Triangular plot of CO_2, N_2, and O_2 contents in hydrothermal CO_2 seeps worldwide (data from Table S2). The mixing curve between pure CO_2 and air is shown in green; **b** scatter plot of CO_2/CH_4 vs. CO_2/H_2S ratios in hydrothermal CO_2 seeps. The red arrows in the red box (top right) illustrate schematically the compositional change resulting from the different processes that govern the global variability in CO_2 seep composition. Curves B1–B4 are obtained from iso-enthalpic boiling of four distinct reservoir fluids (black squares) at 150–350 °C down to a separation temperature (grey squares) of 100 °C. Reservoir gas compositions (all in mmol/kg) are: B1: CO_2: 500, H_2S: 0.1, CH_4: 0.1; B2: CO_2: 500, H_2S: 1, CH_4: 0.1; B3: CO_2: 500, H_2S: 10, CH_4: 0.01; B4: CO_2: 500, H_2S: 10, CH_4: 0.1. These compositions are not meant to model any hydrothermal system in particular, but rather to explore the typical compositional range of hydrothermal systems in general

Because hydrothermal reservoirs can span a wide range of T–P–fO_2conditions (Chiodini and Marini 1998), it is not surprising that the measured H_2, CH_4 and H_2S contents in the CO_2 seeps vary so widely in our catalogues, as graphically illustrated by the CO_2/CH_4 vs. CO_2/H_2S scatter plot of Fig. 5b. For CH_4, part of the spread can also be justified by additional contributions from other sources/processes, including biogenic and thermogenic sources (e.g., low- and high-T organic matter decomposition) and/or abiotic methane formed by reaction other than (2) (e.g., via the Fischer Tropsch reaction) (Chen et al. 2016 and references therein). However, we cannot rule out the possibility that, for such minor components, part of the variability is due to sampling artefacts (e.g., O_2 entrainment, and consequent oxidation) and/or analytical/instrumental errors.

An additional complication is related to the contrasting aqueous solubility of CO_2, H_2, CH_4 and H_2S at hydrothermal conditions (Giggenbach 1980), because of which these gases will differentially separate into the hydrothermal steam that forms as reservoir fluids rise (from the reservoir) toward the surface and boil (Chiodini and Marini 1998). To illustrate the effect of boiling, four distinct boiling curves (B1-B4) are shown in Fig. 5b calculated for iso-enthalpic boiling of different hypothetical reservoir fluids (with initial CO_2, H_2S and CH_4 contents of 500, 0.1–10 and 0.001–0.1 mmol/kg). These lines are only shown for the sake of illustration, and do not attempt in any case to quantitatively mimic the trends exhibited by natural samples. Yet, the model boiling curves demonstrate that the CO_2/CH_4 ratio will increase, and the CO_2/H_2S ratio will decrease, as reservoir fluids cool by iso-enthalpic boiling, from 150–350 °C (the characteristic temperature range of hydrothermal reservoirs; Chiodini ad Marini, 1998) down to a separation temperature of 100° (the seafloor discharge temperature of the majority of the CO_2 seeps). The curves also show that, for a given reservoir fluid composition, the 'reservoir' gas CO_2/CH_4 ratio will increase with reservoir temperature (compares curves B1, B2 and B4 in Fig. 5b).

Because of their contrasting aqueous solubilities, CO_2, H_2, CH_4 and H_2S can undergo additional fractionation as the rising hydrothermal steam approaches the seafloor, interacts with seawater, and eventually condenses. For example, Caracausi et al. (2005) demonstrated the chemistry of the temporal/spatial variability in the Panarea CO_2 seeps in 2002–2003 was strongly linked to selective low-temperature gas dissolution in seawater during steam

condensation, perhaps in the vents' shallow feeding (conduit) systems.

The Baia di Levante CO_2 seeps cluster into two distinct areas (Fig. 5b). A first group is characterised by extremely high (> 100,000) CO_2/CH_4 ratios, and have been interpreted as formed by boiling down to 100 °C of fluids ascending from a ~ 150 °C reservoir (Capaccioni et al. 2001). A second cluster of samples is characterised by lower CO_2/CH_4 ratios (~ 1000) and somewhat higher (up to > 1000) CO_2/H_2S ratios, which we ascribe to a combination of (i) some extent of atmospheric dilution (many samples fall on, or nearby of, the air-pure CO_2 mixing line), (ii) lower reservoir temperatures (~ 100 °C; Capaccioni et al. 2001), and (iii) higher extents of S scrubbing to hydrothermal minerals (pyrrhotite, according to Capaccioni et al. 2001).

Concern has been raised (see discussion in Gonzáles-Delgado and Hernández 2018) that the presence of reducing compounds (in particular H_2S, being toxic for biota) in hydrothermal CO_2 seeps may render them unsuitable proxies for the real natural conditions of a future CO_2-rich ocean. A look into the Earth's geological past shows, however, that periods characterised by high atmospheric CO_2 (Foster et al. 2017) have not only been associated with global ocean warming, but have also recurrently led to oceanic anoxia, where reducing gas compounds (such as H_2S and CH_4) do become significant (Jenkyns 2003; Meyer and Kump 2008). For example, in the high-CO_2 Mesozoic greenhouse world (Royer et al. 2007), a number of well-documented Oceanic Anoxic Events (OAEs) have been identified (Jenkyns 2010), such as in the early Toarcian (T-OAE; ~ 183 Ma), early Aptian (OAE 1a; ~ 120 Ma), early Albian (OAE 1b; ~ 111 Ma) and Cenomanian-Tutonian (OAE 2; ~ 93 Ma). These OAEs, similarly to that at the Paleozoic–Mesozoic boundary (Wignall and Twitchett 2002), have been caused by rapid perturbation of the atmospheric carbon cycle (Hesselbo et al. 2000; Jenkyns 2010), and have led to biological crises and, in the most extreme cases, to severe mass extinctions (Wignall and Twitchett 1996; Garilli et al. 2015). If, as the geological record suggests, a link exists between swift changes in the C cycle and the establishment of reducing conditions in the ocean, it is possible that the CH_4- and H_2S-rich nature of hydrothermal CO_2 seeps may reinforce their use as proxies for ongoing/future man-made oceanic acidification.

CO_2 output

The impact of shallow submarine hydrothermal CO_2 seeps on the chemistry of the overlying seawater column (see "Chemical impact of hydrothermal CO_2 venting on the seawater column" section) depends on many factors, including the geometry of the fumarolic field, the hydrodynamic properties of the seawater column itself (e.g. seawater current and any vertical stratification in temperature and density), and the CO_2 mass output. This latter parameter (the mass of CO_2 released by a hydrothermal CO_2 vent area/field per unit time) is critical in determining the horizontal and vertical extension of the pCO_2 and dissolved inorganic carbon (DIC) anomaly in seawater.

The Panarea hydrothermal field in northern Sicilian Tyrrhenian coast is the only site to our knowledge for which a systematic temporal record of the CO_2 output exists. Based on using a direct method, Italiano and Nuccio (1991) estimated a typical CO_2 output for this ~ 4 km^2 submarine field of ~ 9×10^6 l/day (corresponding to ~ 26–32 tons/day at the 30–100 °C temperature of the vents). This CO_2 output is estimated to have increased by more than one order of magnitude (up to ~ 4×10^8 l/day) in correspondence to a violent gas burst event that occurred on November 2002 (Caliro et al. 2004). Di Napoli et al. (2016) used the HydroC^{TM}, CONTROS sensor (Fietzek et al. 2014) for real-time measurements of dissolved CO_2 at high temporal and spatial resolution in the seawater column above the Secca delle Fumose CO_2 seep field, Pozzuoli Bay (Italy). From detailed 3D mapping of pCO_2 in seawater, they estimated a CO_2 output from the Secca delle Fumose field (~ 0.14 km^2) of ~ 50 tons/day (or ~ 0.53 kg/s). This is more than a factor 10 higher that the estimated CO_2 output from the Baia di Levante submarine seeps on Vulcano Island (~ 3.6 ton/day; Inguaggiato et al. 2012).

Hydrothermal seeps are very dynamic systems, as the deep geological processes that drive their activity can exhibit large fluctuations in time (Caliro et al. 2004). Obtaining temporal records of CO_2 output variations at submarine hydrothermal CO_2 seeps is thus a key objective of future studies.

Aqueous fluid chemistry

In addition to gas, saline hot water (highest reported temperature, 135 °C; Price et al. 2015) is typically discharged from the seafloor by shallow hydrothermal CO_2 seeps (Price and Giovannelli 2017). These thermal waters can be acidic (Fig. 7) and contain bio-limiting nutrients or toxic elements (Tarasov et al. 2005; Price et al. 2013, 2015; Price and Giovannelli 2017; Pichler et al. 2019; Lu et al. 2020), so geochemical survey work was needed at Vulcano Island to map out areas well suited for ocean acidification studies, away from the influence of factors that would confound the effects of increasing CO_2 levels, such as toxic H_2S (Boatta et al. 2013).

Hydrothermal seep fluids vary widely in composition (Figs. 6, 7) but the relative abundances of anions (Fig. 6a) and cations (Fig. 6b) is usually similar to that of seawater. Most such seeps are fed by infiltrated seawater (although there are examples of meteoric water-fed systems; Pichler et al. 1999a) with mixing with cold seawater during fluid ascent from a reservoir as well as during seafloor discharge (Price et al. 2015; Price and Giovannelli 2017). Relative to seawater, many seeps are enriched in carbon (Fig. 6a) due to CO_2 dissolution sourced by either hydrothermal steam (formed by steam separation from deeper reservoir fluids; Pichler et al. 1999a; cfr 3.1) or magmatic vapours separated by the magmatic source (Caliro et al. 2004). Sulfur is typically depleted relative to seawater due to deposition of hydrothermal sulphates (Alt 1995; German and Von Damm 2003) and sulphides (Hannington et al. 2011) upon hydrothermal infiltration and maturation (Fig. 6a).

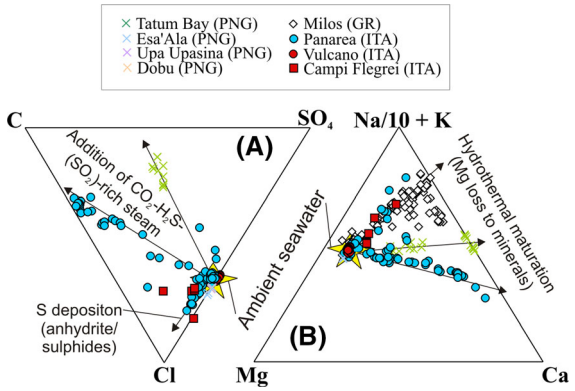

Fig. 6 Triangular plots for anion (**a**) and cation (**b**) contents in some selected, well-studied seeps. Data used to draw the plots are listed in Supplementary Table S3. *Data Sources* Milos: Valsami-Jones et al. (2005), Price et al. (2013), Lu et al. (2020); Tatum bay, PNG: Pichler et al. (1999a), Pichler et al. (2019); Vulcano Island: Sedwick and Stuben (1996), Boatta et al. (2013); Panarea: Italiano and Nuccio (1991), Caracausi et al. (2005), Price et al. (2015); Upa-upasina, Dobu, Esa'Ala, PNG, Fabricius et al. (2011); Campi Flegrei: Di Napoli et al. (2016)

One notable feature of vent fluids (or, at least, of those poorly affected by near-surface mixing with seawater) is their characteristic Mg depletion (Figs. 6b, 7a), which arises from extensive Mg removal from solutions due to formation of hydrothermal phyllosilicates (German and Von Damm 2003; Tivey 2007). Prior to mixing with seawater, hydrothermal vent fluids are, in the majority of the cases, of alkali-chloride composition (Fig. 6b), as typical of 'mature' geothermal waters that have attained full-equilibrium conditions after prolonged fluid-rock interaction with the host rocks at hydrothermal reservoir P–T-conditions (Giggenbach 1988). These fluids exhibit a range of alkalis/Ca ratios (Fig. 6b), reflecting different extents and environments (P–T-conditions) of fluid-mineral interaction from one seep system to another, or even within one single system (Price et al. 2015; Price and Giovannelli 2017).

Vent fluids exhibit a wide range of salt contents, as exemplified for Na in Fig. 7b, implying a multiplicity of sources and processes. A large cluster of seeps plot at Na concentrations slightly lower than seawater, suggesting seawater recharge followed by some extent of Na removal by hydrothermal minerals (e.g., albitization; Tivey 2007) during mineral–fluid interaction. The numerous vents with Na contents plotting well above (e.g., a subset of vents samples form Milos and Panarea) or below (e.g., Tatum bay) seawater (Fig. 7b), point to additional processes, however, and indicate in particular the recurrence of phase separation processes (Butterfield etal. 1990; Von Damm et al. 2003; Foustoukos and Seyfried 2007). Supercritical (above critical point) phase separation (Hedenquist and Lowenstern 1994) deep in the Panarea hydrothermal system has for example being invoked (Price et al. 2015) to explain the formation of saline brines (Na > 600 mM) vented by some seeps (Fig. 7b); while low salinity vent fluids (Na < 400 mM) have recurrently been explained (Pichler et al. 1999a; Price et al. 2013, 2015) by near-surface condensation of hydrothermal steam, formed by sub-critical phase separation (boiling) at depth.

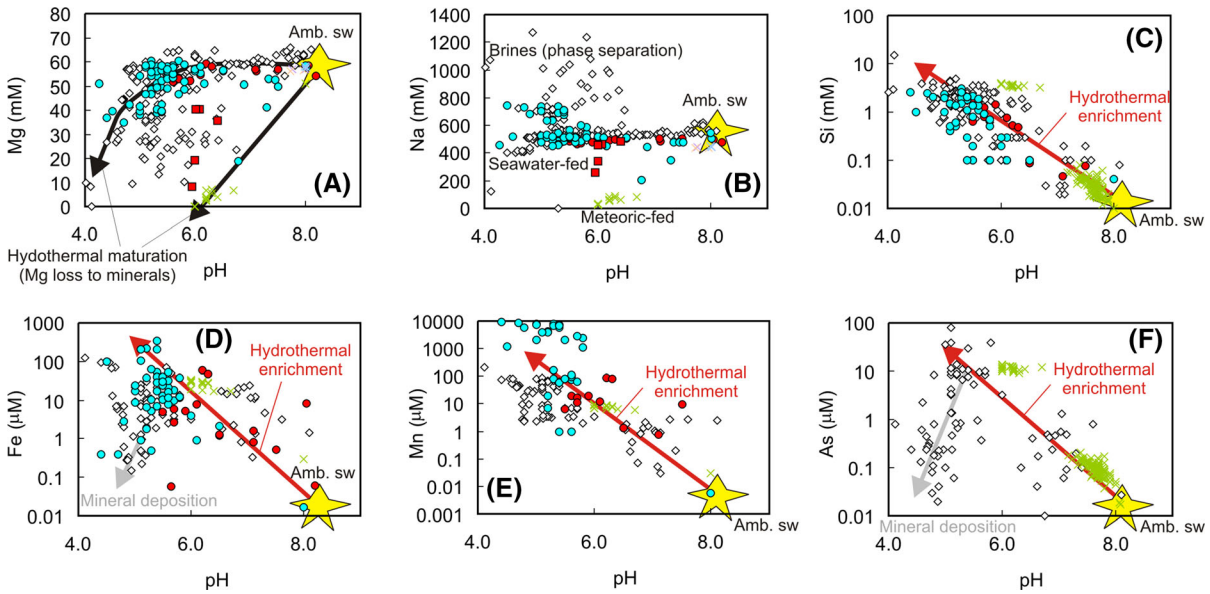

Fig. 7 Scatter plots of pH vs. selected major (Ma, Na), minor (Si) and trace (Fe, Mn, As) contents in some selected seeps (and in the overlying seawater column). Symbols and data-sources are as in Fig. 6

Prolonged high-temperature interactions with reservoir rocks enrich hydrothermal fluids in a suite of minor elements such as Si (Fig. 7c), alkalis (Li, Rb, Cs) and B (Giggenbach 1997). Some of these elements (e.g., Si, B) exhibit conservative behaviour (e.g., they remain in dissolved forms during mixing of seep waters with seawater, and cooling; Fig. 7c), and can thus serve to quantify the extent of seawater entrainment (the mixing proportions of hydrothermal and marine components in the seeps; Italiano and Nuccio 1991; Pichler et al. 1999a, 2019; Caracausi et al. 2005), and to map dispersion and dilution of seep-derived elements into the seawater column (Pichler et al. 1999a, 2019).

The hot, reducing conditions of hydrothermal systems mobilise trace elements (e.g., Fe, Mn, Cu, Pb, Zn, Cd, As, and many others) by leaching from rocks, leading to orders of magnitude enrichment in seeps relative to seawater (see Tarasov et al. 2005) (Fig. 7d–f). Trace elements play a wide range of possible roles in (and effects on) living organisms, from essential/bio-limiting to harmful/toxic (Stumm and Morgan 1995; Rainbow 2002). As such, care is needed when using these systems as natural proxies or studying OA effects on marine organisms. Trace element contents in seawater surrounding hydrothermal seeps have been measured in several cases, including at Vulcano Island, the main focus of this paper (Boatta et al. 2013; Brinkman 2014; Donnarumma et al. 2019; Pichler et al. 2019; Zitoun et al. 2020). Bio-availability of trace-elements depends on metal speciation (Rainbow 2002; Vizzini et al. 2013; Mishra et al. 2020) and so seeps provide areas in which to assess the effects of ocean acidification on trace element toxicity. One key aspect to address is to assess which metals precipitate to minerals upon contact with cold seawater (e.g., Pichler et al. 1999b; Becke et al. 2009; Price and Pichler 2005; Price et al. 2013) and which dissolve and disperse to potentially have wider-scale consequences on ecosystems.

The trace-element vs. pH trends illustrated in Fig. 7d–f offer some useful (though preliminary) clues. The Mn vs. pH plot of Fig. 7e, for example, shows a relatively uniform trend of increasing Mn concentrations (of up to 7 orders of magnitude above seawater) at increasingly acidic (pHs of 4–7) seep conditions. This points to relatively wide Mn mobility over a range of aqueous environments (Lupton et al. 2011). In contrast, Fe (Fig. 7d) and As (Fig. 7f) show more complex behaviours when plotted vs. pH. Although we cannot rule out these trends partially reflect unsuccessful sampling of pure hydrothermal end-members, we consider more likely that the observed contrast between Mn and Fe/As behaviours

imply non-conservative behaviour and scavenging of the latter elements to mineral phases (e.g., oxy-hydroxides and sulphides; e.g., Pichler and Veizer 1999; Pichler et al. 1999a, b; Becke et al. 2009; Price and Pichler 2005; Price et al. 2013) upon mixing/cooling in the upflow zone (especially at pH < 5.5 and 7; Fig. 7). Extensive work on As, in particular, has shown that while this element can be extremely enriched in seeps (Pichler et al. 1999a, b; Price et al. 2013), only moderate enrichments in the overlying seawater column (relative to reference seawater) are produced owing to extensive precipitation of As-rich oxy-hydroxides upon seep discharge (Pichler and Veizer 1999). This fact, combined with lack of visible impacts on coral communities, led Pichler et al. (2019) to conclude that the high As load transported by those seeps did not result in major biological consequences. This topic has been examined in most detail with regard to seagrasses, since the question arose as to why they thrive at some CO_2 seeps but not others. At some seeps seagrasses are abundant where CO_2 bubbles up through the seabed, and the plants are thought to benefit from the increased availability of Dissolved Inorganic Carbon for photosynthesis and a decreased cover of epiphytic coralline algae on their leaves (Martin et al. 2008; Russell et al. 2013). However seagrasses do badly close to some CO_2 seeps due to H_2S and/or metal toxicity (Vizzini et al. 2013). At Vulcano and other Mediterranean seeps areas with bioavailable toxins can be avoided by moving away from the seeps to where levels of seawater CO_2 are below 1000 µatm (Mishra et al. 2020), although bioavailable species can occasionally reach toxic thresholds in these more distal environments, too. The conclusion is that, although geochemical surveys of seep sites are warranted, trace element enrichment in shallow hydrothermal CO_2 vents should not prejudice their use as natural proxies for OA studies. However, as seeps are very dynamic multiple stressor environments, areas suitable for OA studies must be carefully selected using comprehensive (gaseous, major, minor and trace aqueous species) chemical characterization.

Chemical impact of hydrothermal CO_2 venting on the seawater column

pCO_2 distribution in seawater

Upon exiting the seafloor, CO_2 bubbles vented from the seeps dissolve into seawater (Fig. 1), via reactions:

$$CO_{2(g)} \leftrightarrow CO_{2(aq)} \quad (6)$$

$$CO_{2(aq)} + H_2O \leftrightarrow H_2CO_{3(aq)} \quad (7)$$

CO_2 can dissolve either partially or totally in the seawater column, depending on seep discharge rate (CO_2 output; cfr. 3.2) and vent emission depth. If the CO_2 output is high enough, and the seawater column only shallow, part of the gas can freely escape at the seawater–air interface, leading to gas bubbling at surface (Fig. 1). In both cases, the ultimate effect is to raise seawater Total Dissolved Inorganic Carbon (TDIC) and CO_2 partial pressure (pCO_2).

Traditionally, seawater pCO_2 values in the surroundings of hydrothermal CO_2 seeps have been determined by numerically solving dissolved C speciation from co-measured TDIC and pH. Results obtained at the different CO_2 seeps worldwide, illustrated in Fig. 8a, demonstrate a transition from 'normal seawater' pCO_2 ($\sim$ 400 µatm) in background (control) sites far from the vents, to circa $\sim$ 1000 µatm at "intermediate" (meters to tens on meters) distance from the vents, to exceptionally high pCO_2s ($\geq$ 10,000 µatm) in near-vent conditions. The most extreme pCO_2 conditions (up to 52,000 µatm) have been observed offshore Ischia volcano, in Italy (Hall-Spencer et al. 2008). It is along pCO_2 gradients of 300–1000 µatm that biological research focuses in the attempt to characterise the response of biological communities to enhanced seawater CO_2 levels (Agostini et al. 2018; see "Biological experiments at volcanic CO_2 seeps as analogues of ocean acidification" section).

The advent of novel, portable instruments for real-time measurement of dissolved CO_2 in seawater is now paving the way to mapping seawater pCO_2 distribution around hydrothermal seeps at much finer spatial resolution (e.g., Di Napoli et al. 2016). In our Baia di Levante example, we used a HydroC^{TM} pCO_2 sensor (from CONTROS Systems and Solutions, Fietzek et al. 2014) and a multi-parameter probe (Ocean Seven 303 CTD, IDRONAUT) to map the

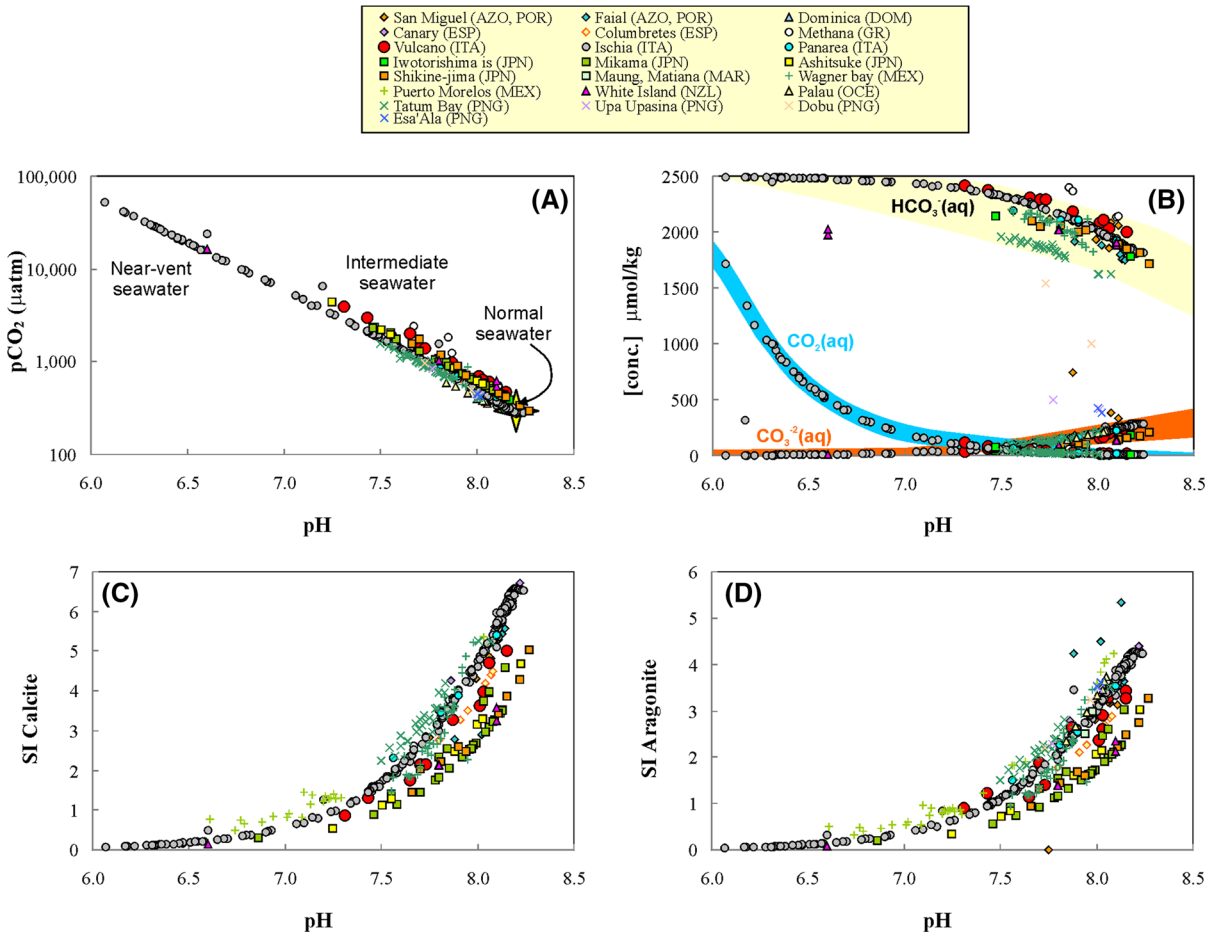

Fig. 8 Scatter plots illustrating seawater carbon chemistry at hydrothermal CO_2 seeps worldwide (data from Table S4). **a** pH vs. pCO_2; **b** pH vs. dissolved C species; **c** pH vs. calcite Saturation Index (SI); **d** pH vs. aragonite Saturation Index (SI). pCO_2, dissolved C speciation and SIs are equilibrium values calculated from measured pH and Total Dissolved Inorganic Carbon (TDIC)

pCO_2 in the bay (Fig. 9a, b). The pCO_2s obtained from both sensors (HydroC^{TM} and Ocean Seven 303) matched well those derived from traditional techniques (Capasso and Inguaggiato 1998) that use directly sampled seawater samples (see Fig. 9c), providing further validation for these new generations of instruments (Fietzek et al. 2014).

Here, we used a small boat to profile the bay along the track shown in Fig. 4, while our sensor kit was continuously acquiring data (at 1 Hz rate). From this, the lateral variability of seawater pCO_2 at a constant depth ($\sim$ 0.5 m) was obtained, which is ultimately illustrated by the map of Fig. 9. The map demonstrates the ability of these novel sensor kits to finely resolve (in real-time) dissolved CO_2 in seawater around seeps with much improved spatial resolution than possible with traditional methods (direct sampling). We recommend increased use of these sensors in future OA and seabed carbon capture and storage studies.

pH and ocean acidification

The dissolution of CO_2 in seawater around seeps has several environmental consequences. The dissociation of the carbonic acid ($H_2CO_{3(aq)}$; see relation (7)) lowers the pH (Fig. 8a), alters the normal seawater dissolved carbon speciation (Fig. 8b), and lowers the seawater saturation state of calcite and aragonite (Fig. 8c, d). At intermediate conditions, meters to tens of meters from the seeps, seawater acidity is typically

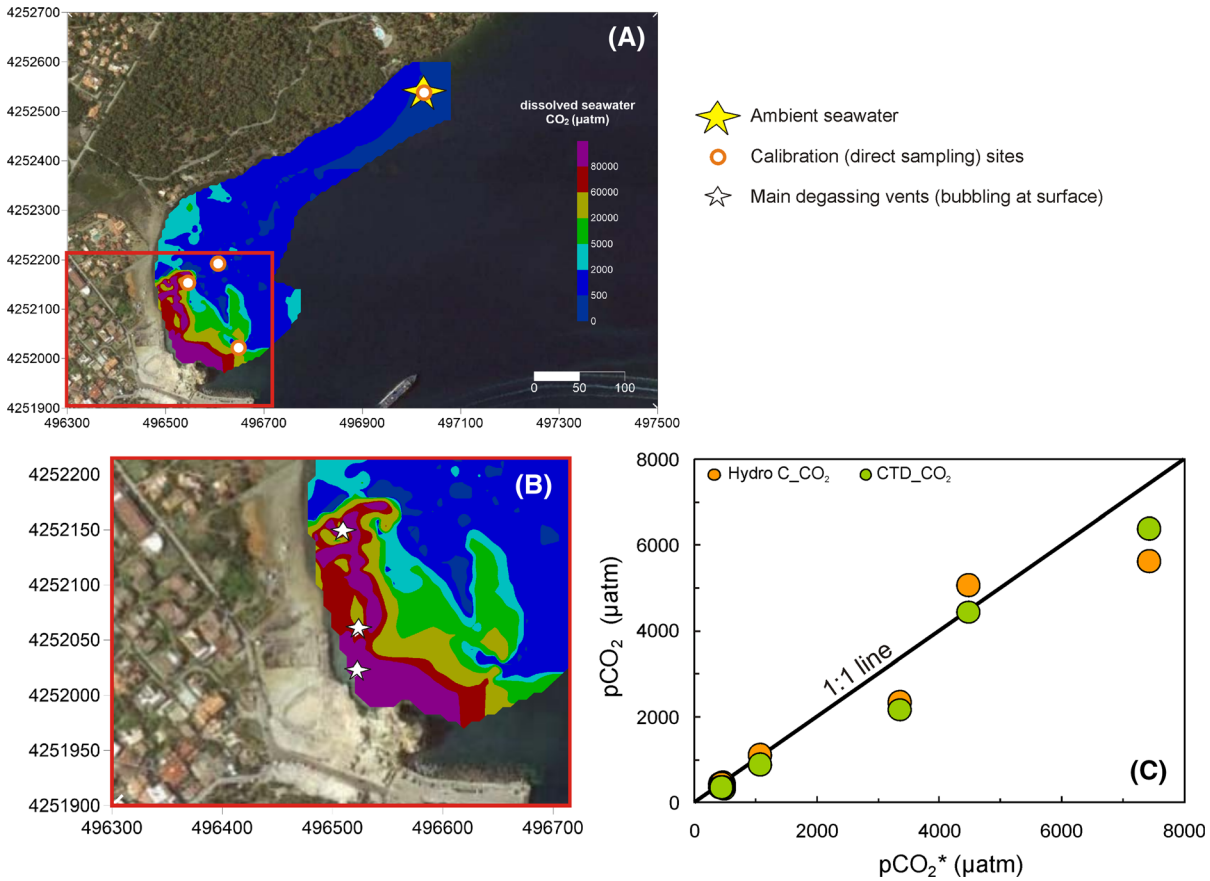

Fig. 9 **a** A map of seawater pCO_2 distribution in the Baia di Levante bay. The map was generated from in-situ real-time measurements of dissolved CO_2, obtained using a HydroC^{TM} sensor (for $CO_2 < 6000$ µatm) and an Ocean Seven 303 IDRONAUT CTD (for $CO_2 > 6000$ µatm). Measurements were obtained using a small boat and proofing along the track shown in Fig. 4 (bottom, right). The use of the HydroC^{TM} and IDRONAUT CTD sensors to measurement of dissolved CO_2 in seawater was initially validated against results from conventional direct sampling, as shown in (**c**). Water samples for sensor comparison were collected in sites indicated by white circles; **b** a detail of (**a**). Stars identify the position of the main degassing vents (where gas bubbling at the free seawater surface was also concentrated); **c** comparison between pCO_2 values measured by the HydroC^{TM} sensor (orange diamonds) and the Ocean Seven 303 IDRONAUT CTD (green diamonds) (both on the y-axis) and those measured with the direct sampling technique of Capasso and Inguaggiato (1998) method (x-axis). The dashed line represents the 1.1 line (e.g., it identifies perfect match between instrumental and direct sampling derived pCO_2s). The best-fit regression lines are respectively: y = 0.99x-65, $R^2 = 0.93$ (for direct vs. HydroC^{TM} datasets) and y = 0.87x-27, $R^2 = 0.99$ (for direct vs. IDRONAUT CTD datasets). Overall, our test shows that the HydroC sensor pCO_2 results are well consistent with those derived in laboratory on the directly sampled seawater samples (method of Capasso and Inguaggiato 1998). This agreement provides mutual validation for the 3 techniques. (Color figure online)

up to 0.2–1 log units lower (pH of 8 to 7) than ambient seawater (Fig. 8a), dissolved $CO_{2(aq)}$ concentrations increases at the expense of the carbonate ion ($CO_3^{2-}{}_{(aq)}$) (the two species attain similar abundances at pH ∼ 7.5, while $CO_{2(aq)}$ prevails over $CO_3^{2-}{}_{(aq)}$ at pH < 7.5; Fig. 8b), and the calcite/aragonites Saturation Indexes (SIs) drop, from ∼ 4–6 to ∼ 1–2 (Fig. 8b, c). In the most extreme conditions (in the near-vent environment), where pCO_2 exceeds 10,000 µatm, the pH becomes acidic (6.5 to 6; Fig. 8a) and $CO_3^{2-}{}_{(aq)}$ concentrations are largely suppressed (Fig. 8b), ultimately unstabilising carbonate minerals (Fig. 8c, d). The same transition, from 'normal seawater' to 'acidified seawater' conditions can be captured by independent pCO_2 and pH measurements while approaching the active seeps, as in our Baia di Levante example (Fig. 10).

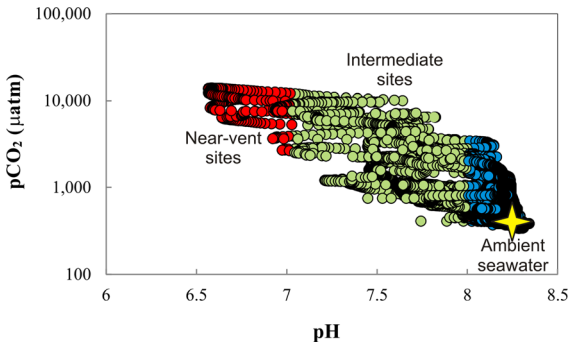

Fig. 10 Seawater pH vs. pCO_2 scatter plotat Baia di Levante (Vulcano Island). pH was measured with the Ocean Seven 303 IDRONAUT CTD, while pCO_2 was real-time in-situ determined via either the HydroC^{TM} sensor (for $pCO_2 < 6000$ µatm) or the Ocean Seven 303 IDRONAUT CTD (for $pCO_2 > 6000$ µatm). Measurements were taken at constant seawater depth at a constant depth of $\sim$ 0.5 m along the measurement grid shown in Fig. 4. We categorize samples in near-vent sites (pH < 7), intermediate sites (7 < pH < 8) and near-ambient sites (pH > 8). These three categories correspond to distances from the vent areas of < 10 m, 10–100 m and > 100 m, respectively

Biological experiments at volcanic CO_2 seeps as analogues of ocean acidification

In addition to their global significance in geological CO_2 flux, many submarine seeps provide opportunities to improve predictions about the effects of OA on the marine biota and ecosystem structure and function. Such seeps allow assessments of the effects of high CO_2 levels and lowered seawater pH on spatial and temporal scales sufficiently large to set up experiments to address responses from individual organisms to ecosystems (Gaylord et al. 2015; Hall-Spencer and Harvey 2019). Most research using seep sites to assesses the biological effects of OA have avoided localised areas with raised temperature, anoxia and/or toxic metals (Boatta et al. 2013) (Fig. 9), although such sites provide ample opportunities to assess the combined effects of multiple stressors. In this regard, a recent attempt was made along the pCO_2/pH gradient off Vulcano Island (Southern Italy), combining the naturally occurring carbonate chemistry gradient with an in-situ manipulation of temperature conditions and assessing how these environmental stressors affect the fitness of a reef building species. Under an end of the century scenario of both stress factors ($\sim$ 1000 µatm and + 2 °C) translaplanted vermetid reefs exhibited compromised oxygen consumption and bio-mineralization processes leading to impaired development and recruitment (Alessi et al. 2019).

Two types of experiments are generally employed to investigate the effects of OA at CO_2 seeps: observational and transplantation experiments. In-situ observational experiments assess the species responses along natural pH gradients, generally moving progressively away from the most intense CO_2 bubbling site to ambient CO_2 sites both in intertidal and subtidal zones (e.g. Agostini et al. 2018). Such experiments usually focus on sessile benthic species which are chronically exposed to the pCO_2 and pH gradient moving away from the seep site (Agostini et al. 2018). This approach has also highlighted mechanisms underpinning evolutionary responses of calcifying species in past OA events (Garilli et al. 2015).

In-situ observational studies often precede experiments involving field transplantations where researchers, in the attempt to highlight cause-effect mechanisms, compare responses of single species or entire assemblages and communities to both short- and long-term acidified and natural control conditions (Camp et al. 2018). For practical reasons, most experiments at CO_2 seeps have focused on low motility benthic stages of organisms, such as microbes, macroalgae, anemones, corals, sessile polychaetes, bryozoans, or bivalve and gastropod molluscs (e.g. Goffredo et al. 2014) rather than planktonic, neustonic or highly mobile organisms such as phytoplankton, cephalopods or fish.

Biological studies at CO_2 seeps include the experimental investigation of processes such as calcification/dissolution, growth, survival, settlement, recruitment, reproduction, metabolic performance, behaviour, species interactions and community shifts in relation to spatio-temporal changes in pH, pCO_2 and saturation levels of aragonite and calcite (Camp et al. 2018). In some instances, CO_2 seep research has provided evidence of direct physiological impacts on individuals living along CO_2 gradients, causing impaired growth and reproduction, and hence affecting the population level under elevated pCO_2 conditions (Harvey et al. 2016). Other experiments document shifts in habitat-forming species and consequent reshuffling of species at community-level or imbalanced function at ecosystem-level (e.g., Vizzini et al. 2017; Milazzo et al. 2019). Despite the obvious caution needed to avoid confounding factors,

biological experiments carried out at CO_2 seeps currently provide a powerful tool to assess future ocean conditions, especially for documenting which organisms and processes are most resilient to OA and to assess potential risks for marine populations, communities and ecosystems.

Winners and losers at natural analogues of OA: the Baia di Levante case study

How organisms will respond to OA might depend on energetic trade-offs between the physiological costs of maintaining ion regulation and acid base status and other energetically demanding processes, such as growth, calcification, reproduction, and activity. These determine the life-history traits and therefore the performance and fitness of the organisms. Such responses may be limited not only by a species' physiological plasticity but also by energy availability in the environment. Despite recent advances in understanding the energetic trade-offs that determine species sensitivity to OA in the laboratory, CO_2 seep studies are only starting to reveal how these trade-offs can be affected under natural conditions where species are subjected to additional biotic and abiotic processes that can modify interactions and energy availability (Garilli et al. 2015; Turner et al. 2015).

Meta-analyses of laboratory responses to OA shows that sensitivity varies among life stages, species and broader taxonomic groups (Hendriks et al. 2010; Kroeker et al. 2010, 2013; Harvey et al. 2013; Wittmann and Pörtner 2013; Cattano et al., 2018), although it is difficult to know how this range of responses plays out in the real world without empirical data from natural gradients in OA conditions (Rastrick et al. 2018). Here, we consider the culmination of complex responses of organisms to OA by assessing changes in the abundances of organisms in-situ using effect size analysis (Hedges et al. 1999) along gradients of OA off Vulcano Island (Aeolian Islands, Sicily) (Fig. 11), one of the most intensively used natural laboratories for OA research.

To make comparisons at different pCO_2 levels along the gradient we considered a CO_2 range (ΔCO_2) as the difference between the CO_2 concentration in elevated, intermediate, near-ambient and the control CO_2 condition, that resulted as extreme ($\Delta CO_2 \geq 750$ µatm), intermediate ($750 > \Delta CO_2 > 350$ µatm) and moderate ($\Delta CO_2 \leq 350$ µatm) OA scenarios (Fig. 11).

Our analyses suggest that primary producers like benthic biofilm (cyanobacteria and diatoms), filamentous turf and fleshy algae showed similar magnitude of mean increases in abundance in OA conditions (Fig. 11), as found by Harvey et al. (2019) at Japanese CO_2 seeps. The abundance of crustose coralline algae was not affected under OA, and bivalve abundances increased in extreme low pH/high CO_2 conditions, which are surprising results given that coralline algae and bivalves have been shown to be adversely affected by OA at volcanic seeps in Papua New Guinea and Japan (Fabricius et al. 2015; Agostini et al. 2018) and the Azores (Martins et al. 2020). However, the proliferation of a few hardy taxa and the demise of many others is a common feature in OA research and a reduction in diversity (rather than abundance) can impair ecosystem services (Hall-Spencer and Harvey 2019). Other calcified taxa showed consistent reductions in abundance in the extreme OA scenario, which were similar among coccolithophores, gastropods, bryozoans and serpulid worms. Our evidence that marine taxa potentially vulnerable to low pH conditions may in some instances thrive under OA is not new, as local environmental conditions like nutrient availability (Connell et al. 2017) or exposure over multiple generations (Cornwall et al. 2020), may help some organisms to thrive (Zitoun et al. 2020).

Consistent increases in abundance in OA conditions were detected for anemones, isopods, amphipods, and other polychaetes at all lower pH/elevated pCO_2 levels considered. No effects of acidification were detected on fish abundances (Fig. 11). Our analyses reveal that the magnitude of responses to OA in the field varies among examined groups, suggesting variation in sensitivity when multi-species assemblages are considered with this having important implications for ecosystem responses under OA conditions.

If we look at species diversity, most algal species are resilient to OA, with only around a 5% loss in species diversity at levels projected under the IPCC RCP 8.5 (Brodie et al. 2014). Increased carbon availability stimulates primary production. This can increase the standing stock of kelps and seagrasses (Russell et al. 2013; Linares et al. 2015; Cornwall et al. 2017) although microalgal biofilm and weedy small turf algae dominate at high CO_2 levels in exposed

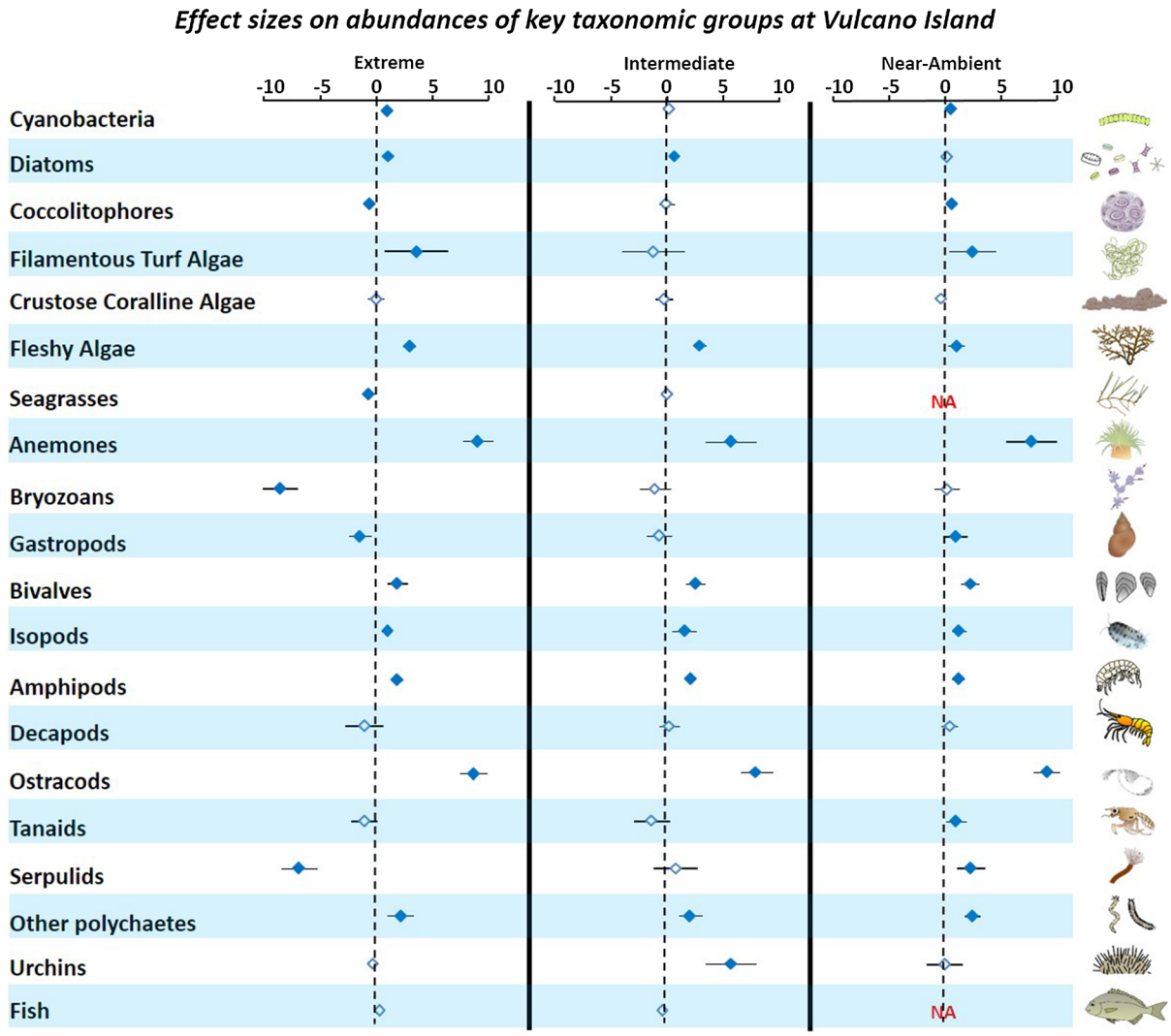

Fig. 11 Effect sizes (± 95% CI) on abundances of different key taxa at Baia di Levante (Vulcano Island, Italy). For each response variable, the response ratio (RR) was calculated with Extreme, Intermediate and near Ambient CO_2 conditions as numerators (i.e., the experimental condition) and the Control condition as the denominator. Empty diamonds represent null effects, while filled ones represent positive or negative significant effects. The response of each group to different pH conditions was analysed using %cover for Cyanobacteria, Diatoms, Coccolitophores, Filamentous turf algae, Crustose coralline algae, Fleshy algae, shoot density for Seagrasses, and density for Anemones, Bryozoans, Gastropods, Bivalves, Isopods, Amphipods, Decapods, Ostracods, Tanaids, Serpulids, other Polychaetes, Sea Urchins and Fish (as MaxN relative abundance). Data from: Suggett et al. (2012), Calosi et al. (2013), Johnson et al. (2013), Ziveri et al. (2014), Apostolaki et al., (2014), Nagelkerken et al. (2015), Harvey et al. (2016); Vizzini et al. (2017), Milazzo et al. (2019), Mishra et al. (2020); Turco G. unpublished data. Images from https://notendur.hi.is/~salvor/myndvinnsla/inkscape/IAN%20Symbol%20Libraries%205.1%20SVG/

conditions (Agostini et al. 2018; Connell et al. 2018). Shifts in algal community composition greatly alter habitat characteristics (Brodie et al. 2014; Enochs et al. 2015) with this having major implications on associated invertebrate and vertebrate fauna (Fabricius et al. 2014; Cattano et al. 2020).

At tropical, sub-tropical and temperate seeps there is a shift to less diverse coastal ecosystems as pCO_2 levels increase. There is around a 30% fall in animal biodiversity as average pH declines from 8.1 to 7.8 (Fabricius et al. 2011; Agostini et al. 2018; Foo et al. 2018). This is due to direct and indirect effects, such

increased metabolic costs of coping with hypercapnia or increased susceptibility to predation (Sunday et al. 2017). A diverse range of invertebrates build reefs; such as sponges, corals, serpulids, vermetids, oysters, mussels and bryozoans. Reefs are degraded along gradients of decreasing carbonate saturation, due to increased metabolic costs of calcification, chemical dissolution and enhanced bioerosion.

Opportunistic organisms can more easily adapt to acidification (Kroeker et al. 2011; Brown et al. 2018). In the tropics, some corals are able to grow well in acidified conditions, but the habitats they form lack complexity and the reef itself is eroded (Fabricius et al. 2011). These degraded reefs have more fleshy macroalgae, less calcified algae and tend to have fewer invertebrates. The dual effects of increased CO_2 and decreased carbonate alter trophic interactions in both sub-tropical and temperate coastal systems. Reductions in the abundance and size of calcareous herbivores contribute to the overgrowth of weedy turf algae and a simplification of food webs, with losses in functional diversity (Vizzini et al. 2017; Teixidó et al. 2018). In this regard, marine ecosystem services depend on what basic biotic functions are maintained (Connell et al. 2018), which ecosystem engineers and keystone species are retained (Sunday et al. 2017), and whether the spread of nuisance species is avoided (Hall-Spencer and Allen 2015).

Ecosystem effects of OA at CO_2 seeps

In the past 10 years, experimental work using natural gradients in pCO_2/pH has increased worldwide. The ecosystem effects of acidification were first described on a range of coastal Mediterranean habitats off the Castello Aragonese in Ischia Island (Italy). In this shallow seep site, CO_2 bubbling up through the seabed gradually lowers the pH of the water column from present day ambient pH 8.2, through near future pH 7.9, down to worse case predictions of pH 7.4 in the immediate vicinity of seeps (Hall-Spencer et al. 2008). Along these pCO_2 and pH gradients, rocky shore communities with abundant calcareous organisms shift to communities lacking sea urchins, scleractinian corals and vermetid molluscs and with significant reductions in coralline algae. This approach has provided an ecosystem-scale validation of laboratory-based predictions that important groups of organisms are susceptible to elevated levels of pCO_2 in the ocean.

Since then, evidence from CO_2 seeps including coral (Fabricius et al. 2011, 2014; Inoue et al. 2013; Enochs et al. 2015; Agostini et al. 2018) and other calcifying reefs (Milazzo et al. 2014; Linares et al. 2015; Alessi et al. 2019), seagrasses (Garrard et al. 2014; Nagelkerken et al. 2015), and algal dominated habitats in temperate zones (Porzio et al. 2011) has notably increased, showing community structure alterations in response to OA (Fig. 12).

A reduction in community complexity is expected following prolonged exposure to OA (e.g. Kroeker et al. 2011; Sunday et al. 2017), primarily due to the loss of CO_2-sensitive species (e.g. calcifying habitat-forming species) and an increase in primary producers (e.g. fleshy algae and turf-forming algae) boosted by elevated CO_2 conditions (Connell et al. 2018). This shows the dual role of CO_2 as a stressor and a resource for marine ecosystems. Biotic homogenization occurs under OA, with systems at low disturbance (i.e. ambient CO_2 and pH) hosting specialist species with high complementarity and high ecosystem function, while highly disturbed ecosystems (elevated CO_2 and low pH) favoring generalist species and homogenized communities with low function.

Vermetid reef communities transplanted for one year along CO_2 gradients off Vulcano Island, revealed dominance shifts from reef- to non reef-forming habitats (Milazzo et al. 2019). These shifts led to changes in composition, structure and functional diversity of the associated benthic assemblages. Interestingly, community properties (i.e. species richness and abundance) nonlinearly responded to OA conditions, high-order consumers (e.g. carnivores) failed to compensate, and competitive release of minor herbivores occurred under elevated CO_2 levels (Milazzo et al. 2019). Coastal community assemblages often have low functional redundancy (Micheli and Halpern 2005), meaning that CO_2-tolerant species performing a similar functional role may not exist. This suggests the likelihood for the loss of functional traits and groups (e.g. reef-forming species and carnivores) (Sunday et al. 2017; Vizzini et al. 2017; Teixidó et al. 2018), while highlighting the potential for opportunistic species to become more generalist and widen their ecological niche.

Shallow biogenic reefs are particularly sensitive to OA, the degradation of these habitats results in less

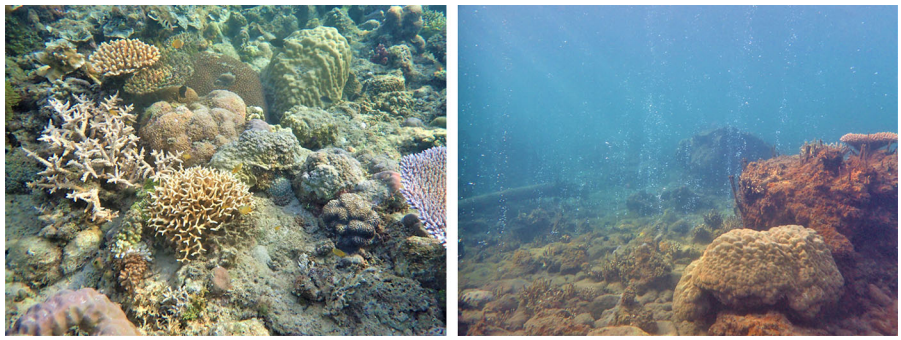

Fig. 12 Evidence of community shifts from ambient to elevated CO_2 levels off a seep site in Papua New Guinea. In ambient locations highly complex and diversified coral reef species which shift into low profile corals and fleshy algae in elevated CO_2 conditions close to the bubbling site. Photo credit: Marco Milazzo

coastal protection and less habitat provisioning for biodiversity and fisheries. Live coral cover on tropical reefs has nearly halved in the past 150 years, and the decline dramatically has accelerated over the past 2–3 decades due to increased water temperature and OA interacting with and further exacerbating other drivers of loss. Natural gradients in seawater CO_2 show that risks to marine goods and services amplify with increasing carbon emissions. When combined with rising temperatures, sea level rise and increasing extreme events, OA further threatens the goods and services provided by coastal ecosystems. This is particularly important for those people and countries that are heavily reliant on marine resources for protection, nutrition, employment and tourism (Lam et al. 2019).

Summary

We have reviewed existing knowledge on the geochemistry and ecology of submarine volcanic CO_2 seeps, especially focusing on the lessons these studies bring for predicting the potential impact of OA under a growing atmospheric CO_2 planet. We have shown that volcanic seeps are CO_2-dominated, but also exhibit a compositional diversity that reflects the complex processes (boiling, mixing and condensation) happening in the subsurface. In addition to CO_2, volcanic seeps are rich in reducing species (H_2S, CH_4, and H_2) whose ecological impacts and significance for future oceanic trends is currently poorly understood. In addition to the gas phase, volcanic seeps typically release a saline aqueous phase (brine) rich in a plethora of trace elements of potentially significant biological importance. In the last decade, there has been a clear call for addressing the important effects of OA on high-level systems of life organization (i.e. biological communities and ecosystems), specifically when making predictions about the impacts of ongoing environmental change. We have shown recent advances in ecological research when using volcanic CO_2 seeps as natural analogues for addressing ecosystem effects and winner and loser species under OA. Indeed, much progress has been made in designing ecological experiments along natural CO_2/pH gradients systems, however great caution is required to assess ecological responses in submarine seeps, especially when their geochemistry is unknown.

Future directions

The study of the chemistry and ecology of volcanic CO_2 seeps is an active field of research. Few shallow water submarine fields have been studied so far, and there is increasing need for a robust synthesis of this information, so future work should prioritize characterizing known (but unstudied) seeps, search for new ones, and assess how marine life acclimates or adapt to the high CO_2 levels found at these sites. From a geochemical viewpoint, CO_2 output estimates are available for only a few systems, and there is an opportunity to use newly developed technologies for in-situ, real-time mapping of pCO_2 in seawater at high spatial and temporal resolution. From a biological point of view, progress is being made in our understanding of how coastal marine communities respond

to rising CO_2 levels. Over the next-decade CO_2 seep research efforts should characterize trace metal interactions with biological processes and make use oflonger-term ecological experiments. Increased interaction and harmonization between geological, chemical and biological expertise looks set to provide improved insights into the responses of marine organisms to global OA.

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Data availability All data used in the manuscript are contained in the associated Supplementary Materials.

Compliance with ethical standards

Conflict of interest The authors declare no conflict of interest.

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