



ELSEVIER

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Noble gas signals in corals predict submarine volcanic eruptions

A.M. Álvarez-Valero^{a,*}, R. Burgess^b, C. Recio^a, V. de Matos^c, O. Sánchez-Guillamón^d,
M. Gómez-Ballesteros^d, G. Recio^a, E. Fraile-Nuez^d, H. Sumino^e, J.A. Flores^a, M. Ban^f, A. Geyer^g,
M.A. Bárcena^a, J. Borrajo^h, J.M. Compañáⁱ

^a Department of Geology, University of Salamanca, Spain

^b School of Earth and Environmental Sciences, University of Manchester, UK

^c DOP, University of Azores & MARE, Marine and Environmental Sciences Centre, Portugal

^d Spanish Institute of Oceanography, Spain

^e Department of Basic Science, Graduate School of Arts and Sciences, University of Tokyo, Japan

^f Department of Earth and Environmental Sciences, University of Yamagata, Japan

^g Institute of Earth Sciences Jaume Almera, ICTJA-CSIC, Barcelona, Spain

^h Department of Physics, Engineering and Medical Radiology, University of Salamanca, Spain

ⁱ General Service of X-ray Diffraction, University of Salamanca, Spain

ARTICLE INFO

Keywords:

Noble gases
Submarine volcano
El Hierro Island
Eruption prediction
Black coral
Canary Islands

ABSTRACT

Deep-water corals growing in close proximity to the 2011 submarine eruption at Tagoro (El Hierro Island; Canary Archipelago, Spain) have revealed their ability to record the magmatic helium (³He) signal during a period of months prior to the eruption with magmatic ³He/⁴He ratios of 3.6–5.0 R_A. This is similar to the range of He isotope values (3–10 R_A) obtained from olivine samples from basinites erupted during the 2011 Tagoro eruption. Whip-like black corals (Anthozoa: Antipatharia: Antipathidae: *Stichopathes*) growing on basaltic rocks trapped ³He within their skeletons. We used a theoretical growth rate to estimate the time of trapping of ³He between release from the magmatic source at depth to trapping by the aquatic organisms. Our findings suggest that magmatic ³He emission occurred a few months before the beginning of the seismic activity in the region, the latter occurring four months in advance of the beginning of the eruption. This discovery implies that corals living in submarine volcanic areas may act as archives of noble gases released before the beginning of an eruption, and that the continuous monitoring of ³He may help to constrain the arrival time of a subaqueous eruption with potential applications in volcano eruption forecasting.

1. Introduction

One of the most important outcomes from studying volcanoes is the development of a reliable rapid warning system of a volcanic eruption. This information is essential to help minimize the impact of these natural phenomena on populations and infrastructure.

In general, during explosive volcanism, gas emissions and seismic tremors are often the first geochemical and geophysical indicators of the beginning of a volcanic event. In both cases, these are signals of an eruption that has already started (e.g. Terakawa et al., 2016) which impacts on reaction time of society to respond to such events (e.g. the tragic episode on September 2014, at Mount Ontake, Japan). Volcanism on Earth is predominantly submarine, and despite extensive physical and geochemical research, it is mainly focussed on processes (e.g. seawater-rock interactions) occurring once the eruption is underway.

Within the sub-aqueous environment, corals have been recognized

as exceptionally valuable archives of past environmental conditions recorded by the isotopic and chemical compositions of their skeletons which grew in equilibrium with ocean water. Due to the strong coupling between atmospheric and hydrologic cycles, isotopic data from corals have been used to retrieve a wealth of high-resolution paleoclimate information (e.g. Adkins et al., 1998; Gagan, 2000; Montagna et al., 2006; Gaetani et al., 2011; Robinson et al., 2014). In addition, corals are widespread on continental margins and seamounts at all latitudes, are amenable to precise and accurate dating and can live tens to thousands of years (Eakin and Grottole, 2006; Warner et al., 2012; Prouty et al., 2015).

Noble gases are little affected by chemical or recycling processes in the inner Earth, have distinct isotopic and elemental compositions indicative of their source, and are present dissolved in both magma and water. Noble gases provide fundamental insights into different mantle source components of mid-ocean ridge basalts (e.g., Burnard, 2001,

* Corresponding author.

E-mail address: aav@usal.es (A.M. Álvarez-Valero).

<http://dx.doi.org/10.1016/j.chemgeo.2017.05.013>

Received 25 November 2016; Received in revised form 9 May 2017; Accepted 15 May 2017
0009-2541/ © 2017 Elsevier B.V. All rights reserved.

2004; Burnard et al., 2003, 2004; Parai et al., 2012; Tucker et al., 2012; Graham et al., 2014; Stroncik and Niedermann, 2016) and ocean island basalts (Gonnermann and Mukhopadhyay, 2009; Weston et al., 2015), and are also powerful tools to reconstruct past climatic and environmental conditions in water samples (e.g., Kipfer et al., 2002; Brennwald et al., 2004, 2005; Holzner et al., 2008; Papp et al., 2010; Kluge et al., 2014). However, the application of noble gases in biogenic materials has been limited, apart from the radiogenic ^4He found in calcareous tissues as minute fluid inclusions (e.g. Copeland et al., 2007; Mukhopadhyay and Kreyck, 2008), noble gases have only been analysed previously in a single study in fluid inclusions in scleractinian corals (Papp et al., 2010).

Due to their low solubility, during decompression of magma noble gases escape from the melt phase (Hilton and Porcelli, 2003). In the submarine setting, noble gases are present dissolved in sea water and as gas bubbles (e.g. Kipfer et al., 2002; Holocher et al., 2003; Holland and Ballentine, 2006; Klump et al., 2007), and the dissolved gases are potentially available to be absorbed by marine organisms growing in the water.

Although, living organisms have never been considered as an informative material in volcanologic-petrological research, if noble gases are retained by sessile organisms that live close to a volcanic vent, some could prove to be reliable archives of eruptive gas emissions. Both solid calcareous and organic (antipathin) coral skeletons are promising geochemical archives for noble gases, due the water chemistry dependent incorporation of elements during their incremental growth (Raimundo et al., 2013; Robinson et al., 2014; Tanaka et al., 2015). Although less studied and with no fluid inclusions reported so far, antipatharian corals have been found to retain over 22 different elements in their skeleton (Goldberg et al., 1994; Nowak et al., 2009).

The antipatharian corallum is arranged in concentric growth rings formed by the deposition around a central canal of successive micro-layers of antipathin (a composite of chitin fibres included in a matrix of carbonates, lipids and proteins), tightly bound to the next by an organic cement (Kim et al., 1992). The antipatharian skeleton is formed by 90–50% scleroprotein (34.5% glycine, 14.9% alanine, 13.0% histidine), 1–18% chitin fibrils, 0.2–5% lipids, 1–3.9% carbohydrates and around 20% water (e.g. Goldberg, 1978; Kim et al., 1992). Although inorganic ions (Ca, I, Mg) seem to be of potential anatomical and physiological importance, understanding of the role of inorganic compounds in the construction and function of the coral skeleton are not well-understood (Goldberg et al., 1994; Nowak et al., 2009; Raimundo et al., 2013).

In this study we aim to investigate whether magmatic noble gases released during a submarine volcanic event and dissolved in seawater are retained within in the skeletal material of corals growing in close proximity to the vent.

2. Material and methods

2.1. Studied area and material from El Hierro submarine volcano (Tagoro)

After three months of volcanic unrest, characterized by > 10,000 earthquakes (magnitude up to 4.3) and 5 cm of ground deformation, on October 2011 the Spanish National Geographic Institute (IGN) recorded a substantial decrease of seismicity together with continuous volcanic tremor (available at www.ign.es; López et al., 2012). This indicated the beginning of an underwater eruption that gave rise to a new shallow submarine volcano (Tagoro) south of the El Hierro Island (Spain; Fig. 1A and B). The eruptive process released large quantities of mantle-derived gases, solutes and heat into the surrounding waters. Periodic bathymetric mapping carried-out by the Spanish Institute of Oceanography (IEO) located the main vent 1.8 km offshore of the southern coast of El Hierro and indicated a major growth of the volcano from an initial 300 m depth to 88 m below the sea surface (Fig. 1C; e.g. Fraile-Nuez et al., 2012, 2016). Tagoro, a submarine monogenetic volcano located on the continental slope under El Hierro Island is

characterized by the eruption of mafic magmas mainly basanites (Stroncik et al., 2009; Martí et al., 2013). Basanites (hosting corals) were collected during trawl-dredgers (DA01 and DA08 shown in Fig. 1C) after March 2013 by the periodic (two per year) oceanographic cruises of the IEO (the rocks and corals studied here were collected in October 2013). Sampling targeted an area extending from the Tagoro's crater vent to a radius of c. 2 km of the surrounding area (Fig. 1C; Fraile-Nuez et al., 2016).

The bubble-rich basanites contain (micro)phenocrysts of mainly olivine, clinopyroxene (augite), ulvospinel (titanomagnetite), and locally plagioclase (mostly as microlites within the mesostasis). The olivine grains exhibit variable shapes from hipidiomorphic to anhedral.

The coral organisms selected for analysis were growing on the basanites (Fig. 1D) erupted during an event prior to the one in 2011 (Fraile-Nuez et al., 2012) and at a short distance (1.5 km) north-westward from the vent. The substrate basanites shows signs of alteration compared to the fresh basaltic rocks of the 2011 eruption based on: (1) their more evolved morphology such as blocks rounded as pillows (see also: Stroncik et al., 2009); and (2) a seawater altered surface with local richly-colonized areas of abundant marine organisms, including whip-like black corals (Fig. 1D), up to 50 cm in length and 1.5 mm in diameter. The black corals were classified at the lowest possible taxa (genus) as being *Stichopathes* sp. based morphology (see Section 3.1; Kim et al., 1992; Bo et al., 2009). Yellowish colonial corals were also present in dredged samples and identified as *Lophelia pertusa* sp. (Fig. 1E; Brito and Ocaña, 2004).

We have determined the He, Ne and Ar concentrations and isotopic ratios from eight olivine samples of basanites from the 2011 eruption of Tagoro and four black coral skeletons living on older basanites. In addition, two colonial corals (yellowish Scleractinia: *Lophelia pertusa* sp. collected at dredge DA01) were analysed for noble gases to determine if the capability to trap magmatic gases is a more geographically widespread feature of these organisms.

2.2. Coral skeleton characterisation

Goldberg (1978) suggested that the organic skeletons of black corals might contain inorganic carbon compounds within their inner growing channels. In order to characterize the nature of the coral skeletal materials the samples were characterized using complementary analytical techniques at the laboratories of the University of Salamanca (Plataforma NUCLEUS) using: (1) X-ray powder diffractometry (XRPD) to characterize any crystalline phases that may be present in the skeletons. A coral sample was crushed and homogenised in an agate mortar. An XRD pattern was obtained using a Bruker D8 Advance (theta-2theta configuration) and $\text{CuK}\alpha$ radiation (40 kV and 30 mA). The diffractogram was obtained between 2 and 65° (2-Theta) with a step size of 0.02° and a total acquisition time of 6 h. Initial tests showed only amorphous phases, so a silicon zero background sample holder was utilized; (2) micro-computed tomography (micro-CT) analysis to visually explore the internal structures of the skeletons. An Argus (SUINSA Medical Systems) microtomograph was used with scans performed at 40 kV and 500 μA (effective transverse and axial fields of view of 6.7 and 4.8 cm, respectively). Samples were set on a rotation stage, and transmission images were obtained for each 0.33° of rotation with a total of 1200 images. The isotropic pixel edge size is 30 μm . Three-dimensional (3D) analyses were reconstructed from the transmission images using ImageJ software (Abràmoff et al., 2004); (3) stable isotope ($^{13}\text{C}/^{12}\text{C}$ and $^{15}\text{N}/^{14}\text{N}$) analysis to test for any potential isotopic variations between the base and top of the corals skeletons, and also to reveal the presence of organic and inorganic carbon isotopic ratios. Dried black coral samples from trawl DA06 (Fig. 1C) were ground by hand using an agate mill and measured using a ISOPRIME elemental analyser-continuous flow-isotope ratio mass spectrometer (EA-CF-IRMS); and (4) Scanning Electron Microscope (SEM) analysis (secondary electron detector) at the Centro de Láseres Pulsados, to explore for

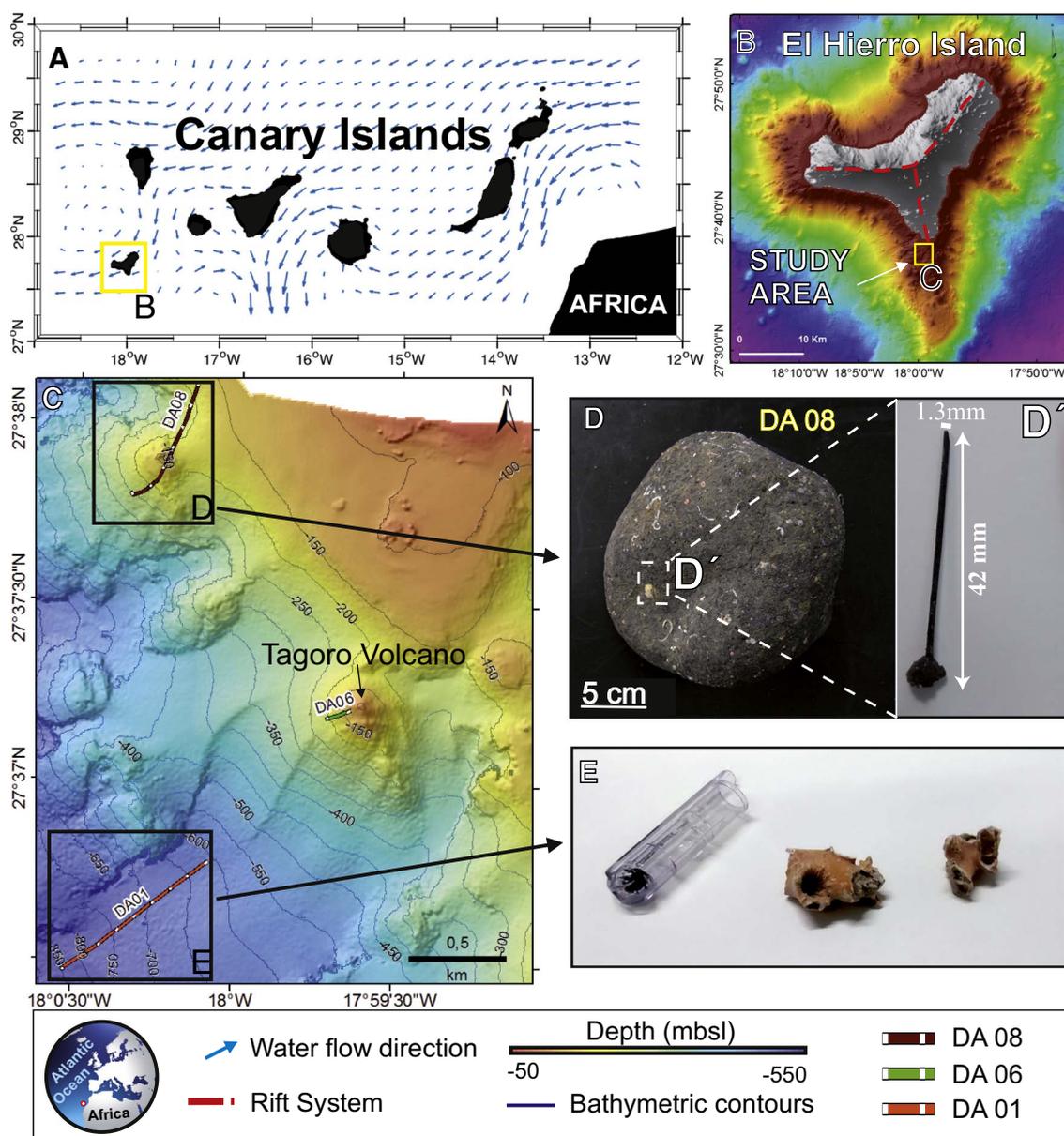


Fig. 1. (A, B, C) Location and bathymetric details of El Hierro, Canary Islands, and the submarine volcano, Tagoro, located c. 2 km southward from the island (Fraile-Nuez et al., 2016). Geographical coordinates of the collection sites of the studied corals and olivine-hosted basalts are along the three indicated track-lines of the dredges (DA); (D) Basaltic rock (from a previous eruption from the one in 2011) colonized by organisms including the black corals highlighted on the right and in Fig. 2. (E) Yellowish coral skeleton (*Lophelia pertusa* sp.) used as reference sample (see text and Table 1 for details).

the presence of vesicles below the detection limit of micro-CT. The SEM used an EHT of 14.27 kV, a working distance of 6–10 mm, and irrigating probe at 102 pA.

2.3. Noble gas analysis

Basanites were crushed and sieved to hand-pick olivine phenocrysts of 1–3 mm diameter, which were also inspected under a binocular microscope to ensure that they were free from any adhered matrix of basaltic glass. Coral samples were removed from their basalt substrate, and the black corals was subdivided into upper and lower sections of approximately 1–2 cm length (Fig. 2, A – lower, and B – upper sections respectively). Noble gas analyses were performed on two different Thermo-Helix mass spectrometers: a Helix SFT Split Flight Tube (SFT) at the University of Salamanca, and a Helix MC (MC) Multi-Collector at the University of Manchester. The advantage of using two spectrometers is in cross-checking reproducibility of representative analysis.

Noble gases were extracted from coral and olivine samples using the following techniques: in vacuo crushing of olivine and corals (MC and SFT); laser heating of olivines (SFT); and furnace heating of corals (SFT).

An on-line crusher tube containing a magnetically operated plunger was used for crushing samples on the SFT using 500 strokes, whereas for the MC, modified Nupro® valve crushers were used (Stuart et al., 1994). For laser analysis of olivine, a Fusions 10.6, 50 W CO₂ laser was operated at up to 40% power for 100 s duration with a beam diameter of 1–2 mm to irradiate ≤ 10 mg of olivine grains. Coral samples were heated (decomposed) using a resistance furnace (SFT) at a temperature of 850 °C for 30 min.

For both mass spectrometers, the extracted gases were exposed to a sequence of getters to purify the noble gases. Helium was separated from heavy noble gases by utilizing a charcoal cold finger cooled with liquid nitrogen. Following the analysis of He isotopes, the Ar was liberated from the cold finger by heating to 60 °C. For the furnace

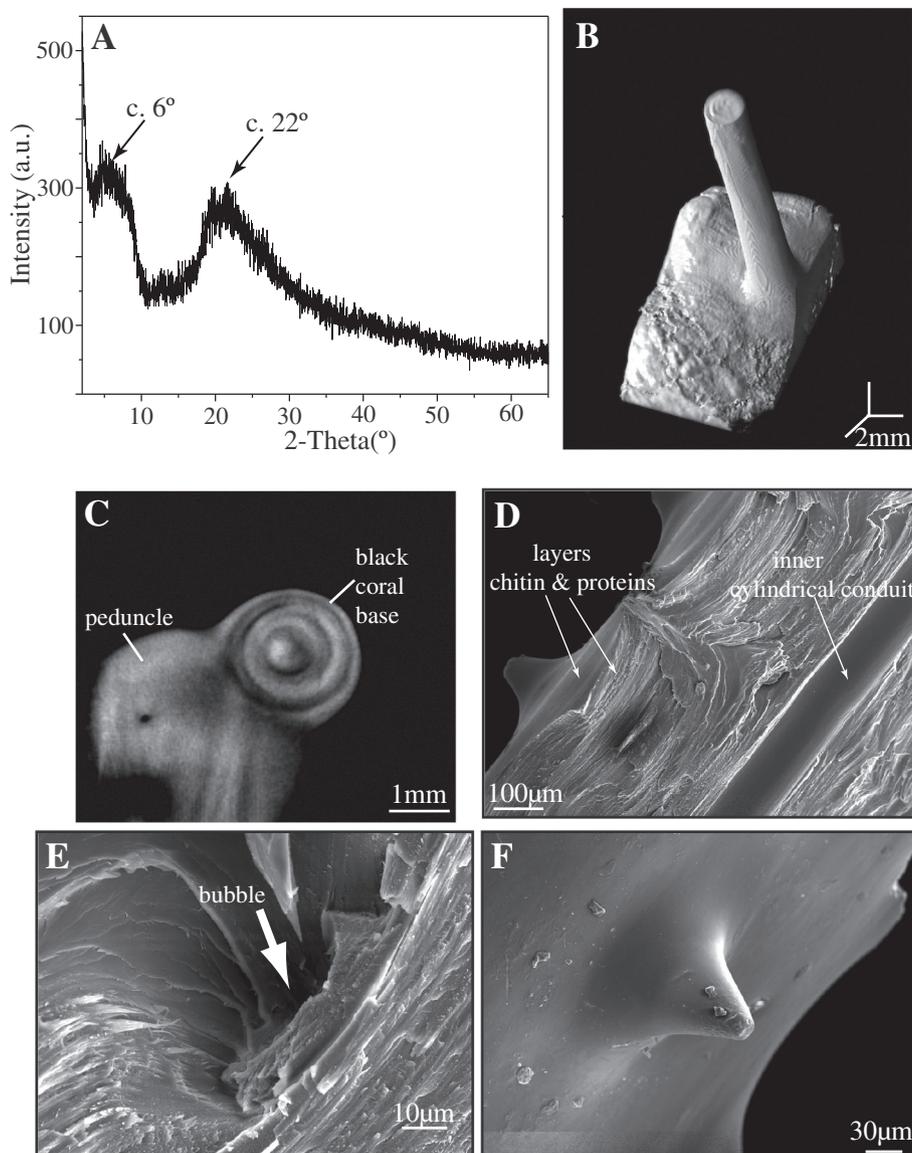


Fig. 2. (A) X-ray diffractogram showing a pattern of two broad bands at c. 6 and 22° (2-Theta) that indicates the absence of long-range order in the skeletons, i.e. composed of amorphous material; (B) (C) Three and two (single microtomographic slice) dimensional views of a black coral sample (plus peduncle and part of the colonized rock), respectively, showing the different growth “rings” and its inner conduit. SEM-SEI images of a longitudinal section of a black coral skeleton showing the growing patterns of the chitin and proteins layers and the spines distribution (D); revealing the existence of tiny bubbles that are below the detection limit of the micro-CT (E); and detail of one external spine (F).

experiments, an additional Ti-sponge furnace at 900 °C was used to remove any organic compounds released from the coral during heating. During the heating step large amounts of CO₂ were released during decomposition of the coral skeleton. To remove CO₂, an empty steel cold finger cooled with liquid nitrogen was in contact with the gas for 90 min before noble gases were admitted to the mass spectrometer. During the trapping period the CO₂ concentration (and any other condensable gases) was monitored every 5 min using a quadrupole mass spectrometer installed in the line, and noble gases were not admitted to the SFT until the background pressure was < 10⁻⁷ atm.

Blanks were analysed after each reloading of the crushers and the furnace, as well as after each laser ablated sample. The average 850 °C furnace blank (corals) was $5.3 \pm 0.1 \times 10^{-12} \text{ cm}^3 \text{ } ^4\text{He}$, and $2.3 \pm 0.02 \times 10^{-10} \text{ cm}^3 \text{ } ^{40}\text{Ar}$. Blanks for the crusher and laser (corals and olivines) were between 1.1 and $2.2 \pm 0.1 \times 10^{-12} \text{ cm}^3 \text{ } ^4\text{He}$, and $1.0\text{--}4.9 \times 10^{-10} \text{ cm}^3 \text{ } ^{40}\text{Ar}$. Standard calibrations were analysed daily (commercial high purity He pipette and atmospheric noble gases) to determine the sensitivity of the mass spectrometers. Accuracy of the

volumes of He delivered from the pipettes is better than $\pm 1\%$, with a reproducibility in the measured amount of gas inlet to the MC and SFT mass spectrometers of $\pm 0.2\%$ for five to ten successive standard analyses.

3. Results

3.1. Coral morphology, stable isotope and chemical composition

Diffractograms revealed that the X-ray pattern (Fig. 2A) of the black corals only exhibits two broad bands at around 6 and 22° (2-Theta) indicating the absence of long-range order in the skeletons. Thus they are only composed of amorphous material (Nowak et al., 2009; Juárez de la Rosa et al., 2012). Three dimensional (3D) micro-CT images (Fig. 2B) revealed different skeletons densities within the same black coral sample, but apparently, no evidence of vesicles or inclusions as potential trapping sites for noble gases.

$\delta^{13}\text{C}_{\text{PDB}}$ of the black corals are between -19.59 ± 0.18 to

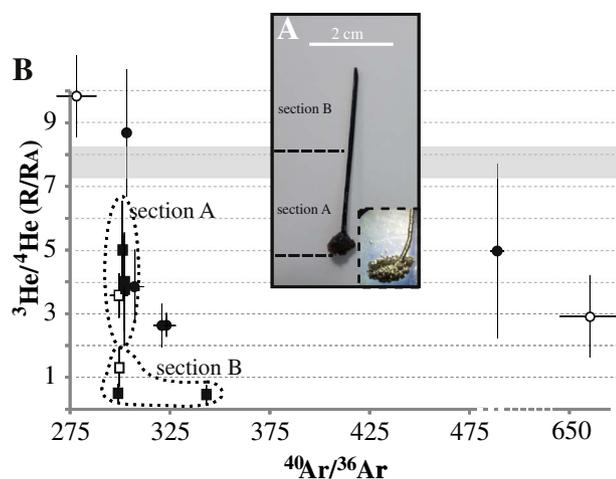


Fig. 3. Helium isotopic ratios from both the basaltic olivines and black corals (image of a representative skeleton –A–, and detail after thermally decomposition into oxide phases); the later revealing a clear contribution of mantle component (B). Symbols: squares – coral; circles – olivine; solids – crushing; open – heating (laser or furnace). For reference, the range of helium isotope data for El Hierro Island are shown by the grey box (7.23–8.19 R_A) determined for subaerial olivine-bearing lavas. (Data from Day and Hilton, 2011)

– $20.07 \pm 0.37\%$ (1σ) and not consistent with the presence of inorganic carbon. In addition, C and N ($\delta^{15}\text{N}_{\text{AIR}} = 5.21 \pm 0.47$ – $6.99 \pm 0.88\%$; 1σ) isotopic ratios are similar between the base and top of the black skeletons (sections A and B, e.g. of Fig. 3A, respectively), and do not relate to the growing distance from the vent (i.e. DA08 is at a distance of c.2 km from Tagoro's vent whereas: DA06 is growing on the vent).

SEM images assisted in classification of the black coral as (Fig. 2D, E, F) *Stichopathes* sp. based on their unbranched corallum and presence of a single line of polyps on one side of the stem.

3.2. He and Ar isotopes

Noble gas data from olivine samples are given in Table 1 and the He and Ar isotopic data are shown in Fig. 3. The lower sections of the *Stichopathes* sp. skeletons (section A of the representative example in Fig. 3A) revealed magmatic $^3\text{He}/^4\text{He}$ ratios of 3.6–5.0 R_A ($R_A = ^3\text{He}/^4\text{He}$ ratio in air = 1.38×10^{-6}). In contrast, the upper

Table 1

Noble gas isotope data for corals and olivine samples determined in this study. Uncertainties are 1σ .

Sample	Gas extraction method	^4He ($\times 10^{-7}$ cm 3 /g)	^{36}Ar ($\times 10^{-9}$ cm 3 /g)	$^3\text{He}/^4\text{He}$ (R/R_A)	$^{40}\text{Ar}/^{36}\text{Ar}$	$^4\text{He}/^{40}\text{Ar}^*$
Olivine crystals						
1 (DA08)	Crush	3.1 ± 0.01	0.8 ± 0.05	5.0 ± 2.7	482 ± 4	2.1 ± 0.3
2 (DA08)	Crush	3.4 ± 0.04	72 ± 3	8.7 ± 3.6	420 ± 10	0.6 ± 0.1
3 (DA01)	Crush	1.0 ± 0.02	0.4 ± 0.03	2.6 ± 0.6	324 ± 3	7.8 ± 0.7
4 (DA01)	Crush	1.2 ± 0.04	0.4 ± 0.03	2.6 ± 0.3	325 ± 3	7.8 ± 0.8
5 (DA08)	Crush	3.2 ± 0.01	1.7 ± 0.09	3.6 ± 1.1	307 ± 3	1.6 ± 0.4
6 (DA08)	CO $_2$ -laser	3.0 ± 0.11	0.5 ± 0.09	9.7 ± 1.3	285 ± 1	3.9 ± 0.5
7 (DA08)	CO $_2$ -laser	4.0 ± 0.14	0.5 ± 0.08	2.9 ± 1.4	654 ± 13	0.2 ± 0.04
Black coral						
1 (base, DA08)	Furnace	1.1 ± 0.04	1.9 ± 0.08	3.6 ± 0.7	305 ± 3	–
1 (top)	Furnace	1.5 ± 0.05	n.d.	1.3 ± 0.4	–	–
2 (base, DA08)	Crush	0.69 ± 0.03	31 ± 1.1	5.0 ± 1.6	305 ± 2	–
2 (top)	Crush	4.0 ± 0.01	33 ± 1.2	0.5 ± 0.2	304 ± 2	–
3 (base, DA08)	Crush	0.81 ± 0.03	1.9 ± 0.06	3.8 ± 1.8	305 ± 4	–
3 (top)	Crush	2.1 ± 0.02	1.5 ± 0.09	0.5 ± 0.2	305 ± 9	–
4 (base, DA08)	Crush	0.75 ± 0.08	1.3 ± 0.08	4.0 ± 1.1	302 ± 3	–
Yellowish coral						
1 (DA01)	Crush	0.08 ± 0.02	10.7 ± 0.06	–	304 ± 1	0.06 ± 0.004

half of the coral skeletons (section B, Fig. 3A) showed lower, air-like He isotope values of between 0.5 and 1.3 R_A (Table 1). Olivine phenocrysts from the lavas erupted in October 2011 gave a slightly greater range of $^3\text{He}/^4\text{He}$ ratios of between 2.6 and 9.7 R_A (Table 1, Fig. 3B). $^{40}\text{Ar}/^{36}\text{Ar}$ values of corals are all indistinguishable within errors with an average of 304, which is slightly above the atmospheric value of 298.6 (Lee et al., 2006). Olivine samples yield a wider range of $^{40}\text{Ar}/^{36}\text{Ar}$ values between 309 and 654, (excluding the anomalously low value from sample 6, Table 1). The $^4\text{He}/^{40}\text{Ar}^*$ ($\text{Ar}^* = ^{40}\text{Ar} - 298.6 \times ^{36}\text{Ar}$) of olivines are mostly between 0.6 and 2.1 (Table 1) similar to the mantle production ratio of ~ 2 . The low levels of Ar released from corals and their low $^{40}\text{Ar}/^{36}\text{Ar}$ values meant $^4\text{He}/^{40}\text{Ar}^*$ values were too imprecise to establish if they record a magmatic signature.

3.3. He and Ar concentrations

The concentration of ^4He in the olivines ranges between 0.97 and 3.4×10^{-7} and is higher than the coral of between 2.0 and 7.5×10^{-8} cm 3 /g and 7.6 – 7.8×10^{-9} cm 3 /g in the basal and top sections, respectively (Table 1). ^4He concentration in the *Lophelia* sp. corals is significantly lower at 1.82×10^{-9} cm 3 /g, with a ^3He concentration below detection (Table 1).

4. Discussion

4.1. Magmatic source of noble gases within the black corals

Recent continuous monitoring studies by Padrón et al. (2013) and Sano et al. (2015) recorded anomalously high emissions of ^3He for several months before the eruptions of Tagoro (in 2011) and Mount Ontake (in 2014). The presence of a higher concentration of this isotope in the coral's lower section shows the ability of black corals to trap ^3He when growing around a submarine volcanic vent that is emitting high levels of ^3He and supports the reliability of their skeletons as a proxy for eruptive events.

Black coral skeletons are predominantly composed of organic matter, however > 22 elements are known to be incorporated during their formation (Goldberg et al., 1994; Nowak et al., 2009). This study increases this list of elements to include noble gases, which are present in all the samples indicating that black coral skeletons are able to incorporate noble gases from the surrounding seawater. The concentration of ^{36}Ar is higher in the corals than in the olivines (c. 3×10^{-8} and 3×10^{-10} cm 3 /g, respectively), and higher relative to average oceanic

basalts ($< 10^{-9} \text{ cm}^3/\text{g}$). It is noted that the submarine gas vents around Tagoro, tapping magmatic He, are not related to any hydrothermal activity (Fraile-Nuez et al., 2012; Santana-Casiano et al., 2016) and are considered to be directly related to degassing of magmatic volatiles. The high $^4\text{He}/^{36}\text{Ar}$ values in the corals of between 0.27 and 0.49, is c. 16 times the Pacific deep water value of 0.0303 (Bieri and Koibe, 1972) and consistent with a He excess from a magmatic source. However the 4He excess is well below values 6500 times higher than seawater described by Stuart and Turner (1998) in fluid inclusion-bearing sulphides at mid-ocean ridge settings enriched in mantle-derived He. It is noted that both the olivine samples and corals show similarly variable $^3\text{He}/^4\text{He}$ ratios between different samples and we suggest that the reason for this may be that the ^3He flux of the magmatic gas is varying with time possibly reflecting mixing of mantle He with crustal/air He in the magma chamber, prior to gas release from the vent.

In summary, our results reveal that corals trap ambient noble gases in seawater, this includes air saturated water and, where present, magmatic noble gases (Fig. 3). The lower section of the coral (Fig. 3A) grew during a period when ^3He was outgassing magmatic volatiles that preceded the 2011 Tagoro eruption. In contrast, during growth of upper sections of the coral (Fig. 3A) the flux of magmatic ^3He had decreased and only seawater noble gases were trapped in the coral skeleton. It is noted that the magmatic system is actively emitting gases at the present day (Santana-Casiano et al., 2013, 2016; Fraile-Nuez et al., 2016).

4.2. Noble gas trapping by the black coral skeleton

It is well known that carbonaceous materials are able to host noble gases (e.g. Clever, 1979 and references therein; Khriachtchev et al., 2000; McSween and Huss, 2010). However, the mechanisms of trapping, particularly in extant organisms require further biologic, metabolic and physiologic studies. Our results indicate that since noble gases are able to be contained in corals (which has an open circulatory system, Fig. 2D; see Kim et al., 1992) growing at relatively slow rates in close proximity to a volcanic vent with a flux of mantle ^3He , the following trapping sites are considered relevant: (1) scarce fluid inclusions that have been observed using SEM (Fig. 2E); (2) black coral skeletons are composed of laminated composites (Fig. 2D), primarily chitin-impermeable fibrils (c. 15%) and non-fibrillar protein (c. 50%; Kim et al., 1992). Noble gases can be trapped in between the layers which may be secreted as rapidly as one per day or as slow as one per month, or even more slowly. Hence, noble gases may also be incorporated within the chitin during growth; and (3) water is the third most abundant component of the skeletons (c. 20%; Kim et al., 1992) and therefore may contain dissolved seawater noble gases.

4.3. Predicting the time of a submarine eruption

Although black corals were considered to be “the slowest growing organisms of any known fishery past or present” (Grigg, 1993), their growth rates are highly variable between species and locations with a general tendency to decrease with depth (Warner et al., 2012). While vertical growth rates of 3–85 cm/year have been described for *Stichopathes* species, it should be noted that these studies refer to animals living in tropical conditions below 40 m depth with *Stauropathes* sp. colonies collected in Newfoundland at ca. 800–900 m depths, growing only 1.2–1.4 cm per year (see Warner et al., 2012).

Although precise dating of the *Stichopathes* sp. colonies collected in the Canaries archipelago at c. 165–270 m was not possible during this study, an estimation of an age at around 29–30 months (estimated as twice the time elapsed between the last anomalously high emission of ^3He and collection of coral) is in line with the existing literature for coral growth rates (Warner et al., 2012).

5. Conclusions

We have determined the He and Ar concentrations and isotopic ratios from eight olivine samples of basanites from the 2011 eruption of Tagoro and four black coral skeletons (divided into upper and lower sections) living on older basanites.

Results revealed that the bottom sections of the black coral skeletons that have grown during the 2011 eruption of Tagoro, give $^3\text{He}/^4\text{He}$ ratios similar to the olivines in the basanites. The upper parts lack the ^3He enrichment and are assumed to have grown after the eruption ceased. Hence, black corals trap noble gases from in seawater in which they grow.

This research reveals for first time that corals are able to host noble gases. Hence, these organisms may potentially be a novel and useful paleo-volcanic “tool” to constrain and better understand past submarine eruptions in terms of, for instance, their timing, duration, and intensity. Further studies (biology and geochemistry) are required on this subject, particularly focussed on the high-resolution geochemical-morphological records within coral skeletons.

As a function of the growth rate of the studied corals, the mantle-derived ^3He trapped by their skeletons is estimated to occur few weeks earlier than the seismic activity under El Hierro Island, which in turn preceded by a few months, the eruptive event of Tagoro.

Acknowledgements

This research was possible thanks to: (i) the funds provided by the MINECO and FEDER through the project VULCANO I (CTM2012-36317) and the project VULCANA (Vulcana-IEO-2015-2017) funded by the Spanish Institute of Oceanography, both granted to E.F.-N., that provided the oceanographic instruments, cruise and samples; (ii) the funds provided by the MINECO and MEC grants (Spanish Government) to A.M.A.-V. through the programs EXPLORA-CIENCIA (CGL2014-61775-EXP) and José Castillejo (CAS14-00189), respectively. We also thank the invaluable help in the noble gas lab in Manchester by J. Cowpe, N. Curran, K. Street, K. Joy, and L. Ruzie, as well as the assistance of the Ramón y Cajal Research Program (RYC-2011-07584). A.G. also thanks the support provided by the Ramón y Cajal Research Program (RYC-2012-11024). This work integrates the PhD of V. de Matos, whom is funded by a FCT doctoral grant (ref. SFRH/BD/86390/2012, funded through QREN and COMPETE). We very much appreciate the constructive and in-depth comments by N. Stroncik and two anonymous reviewers that helped to improve this contribution. Fruitful discussions with V. Costa and H. Rodrigues about the biochemistry of black coral are also acknowledged.

References

- Abramoff, M.D., Magalhães, P.J., Ram, S.J., 2004. Image processing with ImageJ. *Biophoton. Int.* 11, 36–42.
- Adkins, J.F., Cheng, H., Boyle, E., Druffel, E., Edwards, R., 1998. Deep-sea coral evidence for rapid change in ventilation of the deep north Atlantic 15,400 years ago. *Science* 280, 725–728.
- Bieri, R., Koibe, M., 1972. Dissolved noble gases in the east equatorial and Southeast Pacific. *J. Geophys. Res.* 77, 1667–1676.
- Bo, M., Barucca, M., Biscotti, M.A., Canapa, A., Lopian, H.F.N., Olmo, E., Bavestrello, G., 2009. Description of *Pseudocirrhopathes* (Cnidaria: Anthozoa: Hexacorallia: Antipathidae), a new genus of whip black coral from the Indo-Pacific. *Ital. J. Zool.* 76, 392–402.
- Brennwald, M.S., Peeters, F., Imboden, D.M., Giralt, S., Hofer, M., Livingstone, D.M., Klump, S., Strassmann, K., Kipfer, R., 2004. Atmospheric noble gases in lake sediment pore water as proxies for environmental change. *Geophys. Res. Lett.* 31, L04202.
- Brennwald, M.S., Imboden, D.M., Kipfer, R., 2005. Release of gas bubbles from lake sediment traced by noble gas isotopes in the sediment pore water. *Earth Planet. Sci. Lett.* 235, 31–44.
- Brito, A., Ocaña, O., 2004. Corales de las Islas Canarias. Francisco Lemus Editor, Arafo, Tenerife, pp. 477.
- Burnard, P., 2001. Correction for volatile fractionation in ascending magmas; noble gas abundances in primary mantle melts. *Geochim. Cosmochim. Acta* 65, 2605–2614.
- Burnard, P., 2004. Diffusive fractionation of noble gases and helium isotopes during mantle melting. *Earth Planet. Sci. Lett.* 220, 287–295.

- Burnard, P.G., Harrison, D.W., Turner, G., Nesbitt, R., 2003. Degassing and contamination of noble gases in mid-Atlantic Ridge basalts. *Geochem. Geophys.* 4, 1002.
- Burnard, P., Graham, D.W., Farley, K.A., 2004. Fractionation of noble gases (He, Ar) during MORB mantle melting: a case study on the southeast Indian ridge. *Earth Planet. Sci. Lett.* 227, 457–472.
- Clever, H.L., 1979. Helium and Neon - Gas Solubilities. IUPAC Solubility Data Series. vol. 1. Pergamon Press Inc., Maxwell House, Fairview Park, Elmsford, New York, pp. 416.
- Copeland, P., Watson, E.B., Urizar, S.C., Patterson, D., Lapen, T.J., 2007. Alpha thermochronology of carbonates. *Geochim. Cosmochim. Acta* 71, 4488–4511.
- Day, J.M.D., Hilton, D.R., 2011. Origin of $^3\text{He}/^4\text{He}$ ratios in HIMU-type basalts constrained from Canary Island lavas. *Earth Planet. Sci. Lett.* 305, 226–234.
- Eakin, C.M., Grotto, A.G., 2006. Coral reef records of past climatic change. In: Phinney, J.T., Hoegh-Guldberg, O., Kleypas, J., Skirving, W., Strong, A. (Eds.), *Coral Reefs and Climate Change: Science and Management. Coastal and Estuarine Studies*, vol. 61. American Geophysical Union, Washington D.C., pp. 33–54.
- Fraile-Nuez, E., González-Dávila, M., Santana-Casiano, J.M., Aristegui, J., Alonso-González, I.J., Hernández-León, S., Blanco, M.J., Rodríguez-Santana, A., Hernández-Guerra, A., Gelado-Caballero, M.D., Eugenio, F., Marcello, J., de Armas, D., Domínguez-Yanes, J.F., Montero, M.F., Laetsch, D.R., Vélez-Belchí, P., Ramos, A., Ariza, A.V., Comas-Rodríguez, I., Benítez-Barrios, V.M., 2012. The submarine volcano eruption at the island of El Hierro: physical-chemical perturbation and biological response. *Sci. Rep.* 2, 486.
- Fraile-Nuez, E., Santana-Casiano, J.M., Vázquez, J.T., Gómez-Ballesteros, M., Sánchez-Guillamón, O., Álvarez-Valero, A.M., Presas-Navarro, C., González-Carballo, M., Castro-Álamo, A., Oosterbaan, M., Domínguez-Yanes, J.F., Herrera, I., 2016. VULCANA 0316 Project Report. <http://www.repositorio.ieo.es/e-ieo/handle/10508/10035>.
- Gaetani, G.A., Cohen, A.L., Wang, Z., Crusius, J., 2011. Rayleigh-based, multi-element coral thermometry: a biomineralization approach to developing climate proxies. *Geochim. Cosmochim. Acta* 75, 1920–1932.
- Gagan, M., 2000. New views of tropical paleoclimates from corals. *Quat. Sci. Rev.* 19, 45–64.
- Goldberg, W.M., 1978. Chemical changes accompanying maturation of the connective tissue skeletons of Gorgonian and Antipatharian corals. *Mar. Biol.* 49, 203–210.
- Goldberg, W.M., Hopkins, T.L., Holl, S.M., Schaefer, J., Kramer, K.J., Morgan, T.D., Kim, K., 1994. Chemical composition of the sclerotized black coral skeleton (Coelenterata: Antipatharia): a comparison of two species. *Comp. Biochem. Physiol. B Comp. Biochem.* 107, 633–643.
- Gonnermann, H.M., Mukhopadhyay, S., 2009. Preserving noble gases in a convecting mantle. *Nature* 459 (7246), 560–563.
- Graham, D.W., Hanan, B.B., Hémond, C., Blichert-Toft, J., Albarède, F., 2014. Helium isotopic textures in Earth's upper mantle. *Geochem. Geophys. Geosyst.* 15, 2048–2074.
- Grigg, R.W., 1993. Precious coral fisheries of Hawaii and the U.S. Pacific Islands. *Mar. Fish. Rev.* 55, 50–60.
- Hilton, D.R., Porcelli, D., 2003. Noble gases as mantle tracers. In: Carlson, R.W. (Ed.), *Treatise on Geochemistry*. vol. 2. Elsevier-Pergamon, Oxford, pp. 277–318.
- Holland, G., Ballentine, C.J., 2006. Seawater subduction controls the heavy noble gas composition of the mantle. *Nature* 441 (7090), 186–191.
- Holoher, J., Peeters, F., Aeschbach-Hertig, W., Kinzelbach, W., Kipfer, R., 2003. Kinetic model of gas bubble dissolution in groundwater and its implications for the dissolved gas composition. *Environ. Sci. Tech.* 37, 1337–1343.
- Holzner, C.P., McGinnis, D.F., Schubert, C.J., Kipfer, R., Imboden, D.M., 2008. Noble gas anomalies related to high intensity methane gas seeps in the Black Sea. *Earth Planet. Sci. Lett.* 265, 396–409.
- Juárez de la Rosa, B.A., Quintana, P., Ardisson, P.L., Yáñez-Limón, J.M., Alvarado-Gil, J.J., 2012. Effects of thermal treatments on the structure of two black coral species chitinous exoskeleton. *J. Mater. Sci.* 47, 990–998.
- Khriachtchev, L., Pettersson, M., Runeberg, N., Lundell, J., Räsänen, M., 2000. A stable argon compound. *Nature* 406, 874–876.
- Kim, K., Goldberg, W.M., Taylor, G.T., 1992. Architectural and mechanical properties of the black coral skeleton (Coelenterata: Antipatharia): a comparison of two species. *Biol. Bull.* 182, 195–209.
- Kipfer, R., Aeschbach-Hertig, W., Peeters, F., Stute, M., 2002. Noble gases in lakes and groundwaters. In: Porcelli, D., Ballentine, C.J., Wieler, R. (Eds.), *Noble Gases in Geochemistry and Cosmochemistry. Reviews in Mineralogy & Geochemistry*, vol. 47. Mineralogical Society of America, Geochemical Society, Washington, pp. 615–700.
- Kluge, T., Marx, T., Aeschbach-Hertig, W., Spötl, C., Richter, D.K., 2014. Noble gas concentrations in fluid inclusions as tracer for the origin of coarse-crystalline cryogenic cave carbonates. *Chem. Geol.* 368, 54–62.
- Klump, S., Tomonaga, Y., Kienzler, P., Kinzelbach, W., Baumann, T., Imboden, D.M., Kipfer, R., 2007. Field experiments yield new insights into gas exchange and excess air formation in natural porous media. *Geochim. Cosmochim. Acta* 71, 1385–1397.
- Lee, J.Y., Marti, K., Severinghaus, J.P., Kawamura, K., Yoo, H.S., Lee, J.B., Kim, J.S., 2006. A redetermination of the isotopic abundances of atmospheric Ar. *Geochim. Cosmochim. Acta* 70, 4507–4512.
- López, C., Martí, J., Abella, R., Tarraga, M., 2012. Applying fractal dimensions and energy-budget analysis to characterize fracturing processes during magma migration and eruption: 2011–2012 El Hierro (Canary Islands) submarine eruption. *Surv. Geophys.* 35 (4), 1023–1044.
- Martí, J., Castro, A., Rodríguez, C., Costa, F., Carrasquilla, S., Pedreira, R., Bolos, X., 2013. Correlation of magma evolution and geophysical monitoring during the 2011–2012 El Hierro (Canary Islands) submarine eruption. *J. Petrol.* 54, 1349–1373.
- McSween Jr., H.Y., Huss, R., 2010. *Cosmochemistry*. Cambridge University Press, New York, pp. 565.
- Montagna, P., McCulloch, M., Taviani, M., Mazzoli, C., Vendrell, B., 2006. Phosphorus in cold-water corals as a proxy for seawater nutrient chemistry. *Science* 312, 1788–1791.
- Mukhopadhyay, S., Kreyck, P., 2008. Dust generation and drought patterns in Africa from helium-4 in a modern Cape Verde coral. *Geophys. Res. Lett.* 35, L20820.
- Nowak, D., Florek, M., Nowak, J., Kwiatek, W., Lekki, J., Chevallier, P., Hacura, A., Wrzalik, R., Ben-Nissan, B., Van Grieken, R., Kuczumow, A., 2009. Morphology and the chemical make-up of the inorganic components of black corals. *Mater. Sci. Eng. C Mater. Biol. Appl.* 29, 1029–1038.
- Padrón, E.M., Pérez, N., Hernández, P., Sumino, H., Melián, G., Barrancos, K., Nolasco, D., Padilla, G., Dionis, S., Rodríguez, F., Hernández, I., Calvo, D., Peraza, M., Nagao, K., 2013. Diffusive helium emissions as a precursory sign of volcanic unrest. *Geology* 41, 539–542.
- Papp, L., Palscu, L., Major, Z., 2010. Noble gas measurements from tiny water amounts: fluid inclusions in carbonates of speleothemes and coral skeletons. In: *Geophysical Research Abstracts*. 7th EGU General Assembly, vol. 12. European Geosciences Union, Vienna, Austria, pp. 432.
- Parai, R., Mukhopadhyay, S., Standish, J.J., 2012. Heterogeneous upper mantle Ne, Ar and Xe isotopic compositions and a possible Dupal noble gas signature recorded in basalts from the Southwest Indian Ridge. *Earth Planet. Sci. Lett.* 359–360, 227–239.
- Prouty, N.G., Roark, E.B., Andrews, A., Robinson, L., Hill, T., Sherwood, O., Williams, B., Guilderson, T., Fallon, S., 2015. Age, growth rates, and paleoclimate studies of deep sea corals. In: Hourigan, T.F., Etnoyer, P.J., Cairns, S.D., Tsao, C.F. (Eds.), *The State of Deep-sea Coral and Sponge Ecosystems of the United States: 2015*. NOAA Technical Memorandum X. NOAA, Silver Spring, pp. 10–10-21.
- Raimundo, J., Vale, C., Caetano, M., Anes, B., Carreiro-Silva, M., Martins, I., de Matos, V., Porteiro, F.M., 2013. Element concentrations in cold-water gorgonians and black coral from Azores region. *Deep Sea Res. Part II Top. Stud. Oceanogr.* 98, 129–136.
- Robinson, L.F., Adkins, J.F., Frank, N., Gagnon, A.C., Prouty, N.G., Roark, E.B., 2014. The geochemistry of deep-sea coral skeletons: a review of vital effects and applications for palaeoceanography. *Deep-Sea Res. II Top. Stud. Oceanogr.* 99, 184–198.
- Sano, Y., Kagoshima, T., Takahata, N., Nishio, Y., Rouleau, E., Pinti, D.L., Fischer, T.P., 2015. Ten-year helium anomaly prior to the 2014 Mt Ontake eruption. *Sci. Rep.* 5, 13069.
- Santana-Casiano, J.M., González-Dávila, M., Fraile-Nuez, E., de Armas, D., González, A.G., Domínguez-Yanes, J.F., Escánez, J., 2013. The natural ocean acidification and fertilization event caused by the submarine eruption of El Hierro. *Sci. Rep.* 3, 1140.
- Santana-Casiano, J.M., Fraile-Nuez, E., González-Dávila, M., Baker, E.T., Resing, J.A., Walker, S.L., 2016. Significant discharge of CO₂ from hydrothermalism associated with the submarine volcano of El Hierro Island. *Sci. Rep.* 6, 25686.
- Stronck, N.A., Niedermann, S., 2016. He, Ne and Ar isotope signatures of mid-ocean ridge basalts and their implications for upper mantle structure: a case study from the mid-Atlantic Ridge at 4–12°S. *Geochim. Cosmochim. Acta* 183, 94–105.
- Stronck, N.A., Klügel, A., Hansteen, T.H., 2009. The magmatic plumbing system beneath El Hierro (Canary Islands): constraints from phenocrysts and naturally quenched basaltic glasses in submarine rocks. *Contrib. Mineral. Petrol.* 157, 593–607.
- Stuart, F.M., Turner, G., 1998. Mantle-derived ^{40}Ar in mid-ocean ridge hydrothermal fluids: implications for the source of volatiles and mantle degassing rates. *Chem. Geol.* 147, 77–88.
- Stuart, F.M., Turner, G., Taylor, R., 1994. He–Ar isotope systematics of fluid inclusions: resolving mantle and crustal contributions to hydrothermal fluids. In: Matsuda, J. (Ed.), *Noble Gas Geochemistry and Cosmochemistry* Terra Scientific Publishing Company, Tokyo, pp. 261–277.
- Tanaka, K., Holcomb, M., Takahashi, A., Kurihara, H., Asami, R., Shinjo, R., Sowa, K., Rankenburg, K., Watanabe, T., McCulloch, M., 2015. Response of *Acropora digitifera* to ocean acidification: constraints from $\delta^{11}\text{B}$, Sr, Mg, and Ba compositions of aragonitic skeletons cultured under variable seawater pH. *Coral Reefs* 34 (4), 1139–1149.
- Terakawa, T., Kato, A., Yamanaka, Y., Maeda, Y., Horikawa, S., Matsuhiro, K., Okuda, T., 2016. Monitoring eruption activity using temporal stress changes at Mount Ontake volcano. *Nat. Commun.* 7, 10797.
- Tucker, J.M., Mukhopadhyay, S., Schilling, J.G., 2012. The heavy noble gas composition of the depleted MORB mantle (DMM) and its implications for the preservation of heterogeneities in the mantle. *Earth Planet. Sci. Lett.* 355–356, 244–254.
- Warner, D., Luck, D.G., Toonen, R.J., 2012. The biology and ecology of black corals (Cnidaria: Anthozoa: Hexacorallia: Antipatharia). *Adv. Mar. Biol.* 63, 67–132.
- Weston, B., Burgess, R., Ballentine, C.J., 2015. Disequilibrium degassing model determination of the ^3He concentration and $^3\text{He}/^{22}\text{Ne}$ of the MORB and OIB mantle sources. *Earth Planet. Sci. Lett.* 410, 128–139.