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Chapter 4

The Emissions of the Tagoro Submarine Volcano (Canary Islands, Atlantic Ocean): Effects on the Physical and Chemical Properties of the Seawater

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Additional information is available at the end of the chapter

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Abstract

This chapter presents the changes and evolution of the physical and chemical properties of the seawater south of the El Hierro Island (Canary archipelago, Atlantic Ocean) as a consequence of the emissions of the Tagoro submarine volcano, over a 6 year study from 2011 to 2016. Since the eruption, a series of oceanographic studies have been carried out in the area focusing on the evolution of the redox potential and the pH, two master variables that control the chemical equilibrium in sea water. The changes experienced by the carbon dioxide system, the variations in the concentration of Fe(II) and their correlation with the decrease in the pH during the evolution of the volcano, from the beginning of the eruptive stage to the post-eruptive phase, are discussed. The increased TDFe(II) concentrations and the low associated pH_T values have controlled the occurrence of an important fertilization event in the sea water around the volcano at the Island of El Hierro, providing optimal conditions for the regeneration of the area. The sites like the Tagoro submarine volcano, in its degasification stage, provide an excellent opportunity to study the carbonate system in a high CO_2 world, the volcanic contribution to the global volcanic carbon flux and the potential environmental impact of these emissions on the surrounding ocean and the ecosystem.

Keywords: submarine volcano, CO_2, acidification, fertilization, pH, ferrous iron, redox potential

1. Introduction

The eruption of a volcano in the ocean generates important changes in the physical and chemical properties of the sea water that also affects the marine organisms in the area. When this eruption occurs in distant and deep places, they may go unnoticed if they are not specifically monitored.

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However, when these eruptions occur near shore, in shallow areas, the effects are more evident. Moreover, they directly emit fluids into the photic zone where they influence the primary production. The emitted metals, such as iron are biologically essential micronutrients whereas others, such as the copper, can be toxic at nanomolar concentrations [1].

This chapter focuses on the geochemical changes observed in the seawater around the shallow submarine volcano Tagoro, Canary Islands, Atlantic Ocean, from its eruption period in 2011 until its degasification stage between 2012 and 2016. Since its eruption, a series of oceanographic studies has been carried out in the area and the evolution of some physical and chemical properties has been monitored. The study has been divided into two parts. The first one covers the eruptive phase, which lasted 5 months, from October 2011 until March 2012. At this time, drastic changes in the carbon dioxide system and in the emissions of reduced species were observed south of the El Hierro Island as well as an enrichment of Fe(II) and nutrients, which generated an episode of natural ocean acidification and a fertilization event [2, 3]. The second part focuses on the post-eruptive phase, during which noticeable anomalies in the carbon dioxide parameters and Fe(II) were only found close to the main crater of the volcano. Physicochemical anomalies were still observed in 2016 close to the volcanic area. During the second period, the studies were concentrated in the volcanic edifice, and different sampling strategies, including high-resolution sampling along the volcanic edifice and tow-yo and yo-yo studies, were undertaken in order to detect the anomalies [4].

2. The underwater eruption and changes observed in the surface water

2.1. Geological setting

The island of El Hierro is the westernmost island of the Canary Archipelago located in the north-eastern Atlantic Ocean. The Canary Islands were originated in the Early Miocene as the African plate moved over a mantle hotspot [5, 6]. The islands show a general age progression from the eastern islands (>20 Ma) toward western islands (<2 Ma) [7]. The El Hierro Island is the youngest, with 1.12 million years of age [8]. The oldest subaerial rocks in El Hierro have been dated back at 1.12 ± 0.02 Ma and the only known subaerial prehistoric eruptions have been dated back to 4000 and 2500 year ago [8]. The island is the emergent top of a volcanic shield, which rises from 3800 to 4000 m depths and grows up to 1500 m above sea level. Its subaerial part (280 km^2) shows the characteristic shape of three convergent rifts, separated by at least three important landslides [9–11].

The submarine eruption of the Tagoro volcano, in 2011, was the first submarine eruption reported in about 600 years of historical records in the Canary Islands and the first one to be monitored from the initial caldera unrest [12].

2.2. A new submarine volcano

In October 2011, after 3 months of volcanic unrest with more than 12,000 earthquakes (M < 4.3) and 5 cm of ground deformation [12], a submarine eruption took place in the island of El Hierro, in the north-eastern Atlantic Ocean, in a shallow coastal area, at a depth of 300 m

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(**Figure 1**). The volcano was located 1.8 km south of the island of El Hierro at 27°37′07″N–017°59′28″W. Over 5 months, the volcanic edifice grew up to 88 m below sea level. During that period, six geophysical surveys were carried on board the *R/V Ramón Margalef* in order to monitor the changes in the bathymetry of the area [13, 14]. Moreover, several hydrographic cruises were carried out to study the changes in the physical, chemical and biological properties in the water column from the beginning of the eruptive stage to the post-eruptive phase [2–4].

The evolution of the volcanic edifice between 2011 and 2012 [13, 14] can be briefly described as follows:

- The first survey in the area was carried out on October 23. The base of the active volcano was found at a depth of 300 m. The volcano was located on a rift with lava flowing south-westwards. It was 650 m wide and its peak was situated at a depth of 220 m below the sea level.
- In January 2012, the cone had risen to a depth of 130 m.
- In February 2012, it reached its maximum elevation of 88 m below sea level.

While both the structure and the height of the volcano were changing, the emission of fluids gave rise to a plume in the water column that, due to the currents, also extended to its surroundings. The emission plume was also modified during that time by the dynamics of both the volcano growth and the oceanographic conditions [3]. Additionally, in the surface, the plume was

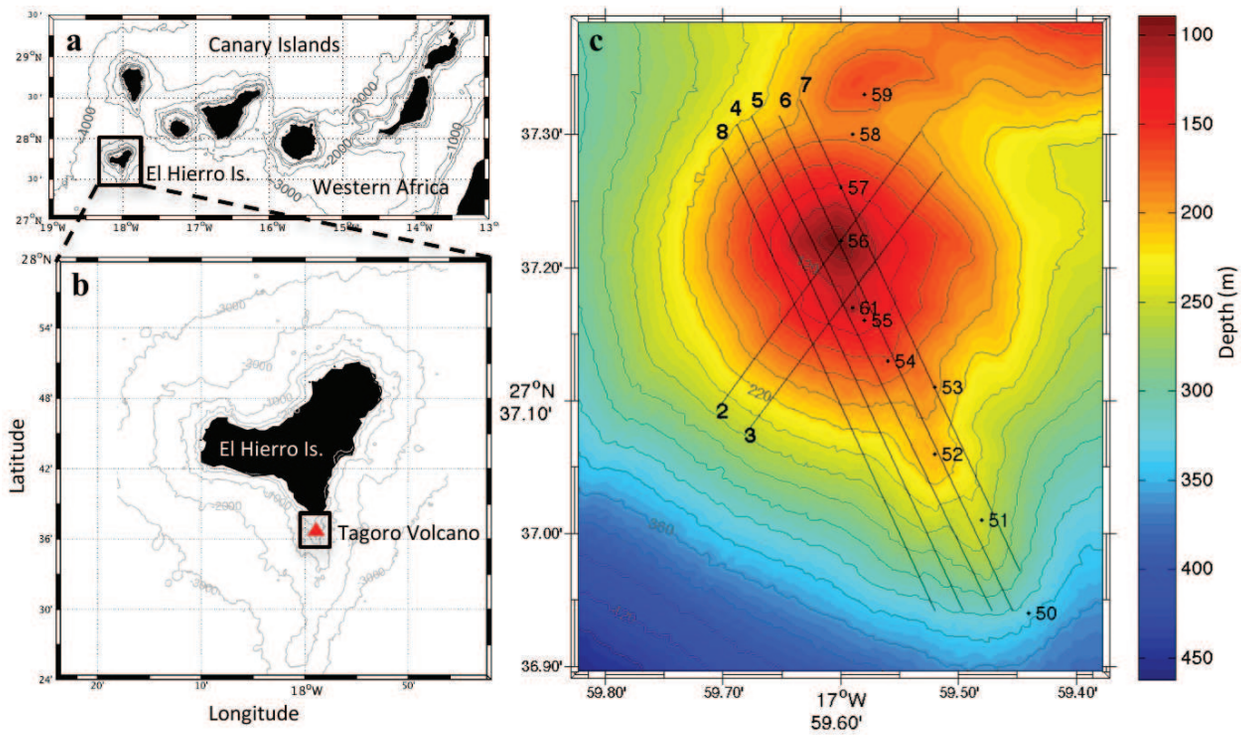


Figure 1. (a) Location of the volcanic edifice within the Canary Archipelago. (b) Island of El Hierro with the location of the submarine volcano Tagoro. (c) Location of the tow-yo lines and CTD stations. The maps were generated using Matlab 7.12 R2011a.

affected by changes in the meteorological and hydrodynamic conditions. In the first months, the plume (**Figure 2**) was observed from the coast and also through satellite images [15, 16].

2.3. Signal of the eruption in the sea surface

In the surface waters, evident signals were observed as a consequence of the volcanic emissions in the first 5 months of the eruption. The most important were observed around the volcanic edifice (**Figure 3**), but the effect of the volcano emissions reached the whole southern part of the Island of El Hierro. Some influences were also observed in the northern part, as a consequence of the currents in the area [16]. The most important observations in the surface waters were:

- The discolouration of the water ranging from light-green to milky-blue to a dark brown colour.
- Bubbling and degassing.
- Abundant rock fragments floating on the ocean.

The strongest eruptive episode took place between November 5 and 8 with large bubbles rising to 10–15 m above sea level [3].

The eruption produced lava balloons that were collected while floating and degassing at the sea surface above the vent [17]. Studies from petrological and geophysical data indicated that

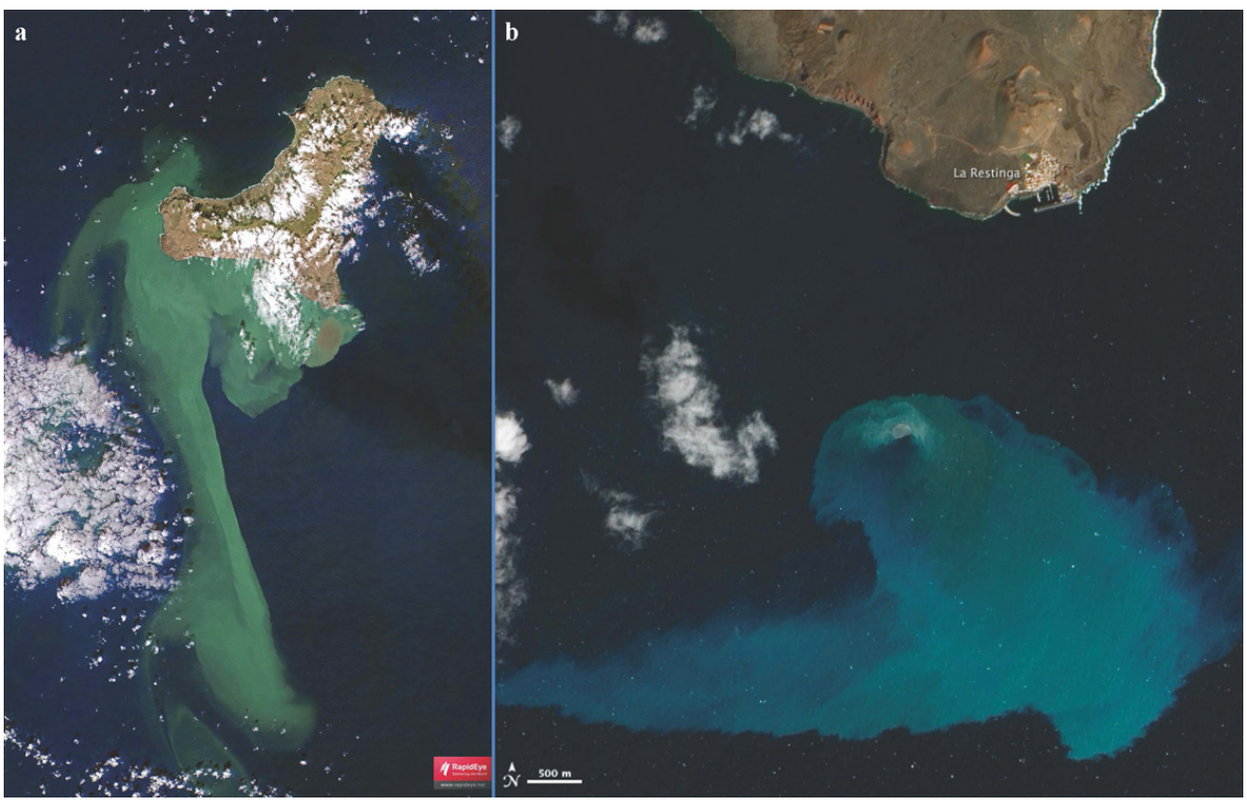


Figure 2. (a) A true colour, high-resolution RapidEye satellite image featuring a gigantic stain visible on the surface of 'El Mar de las Calmas' (November 26, 2001). (b) Image acquired by the Advanced Land Imager (ALI) aboard the Earth Observing-1 satellite (NASA award-winning image 2013).

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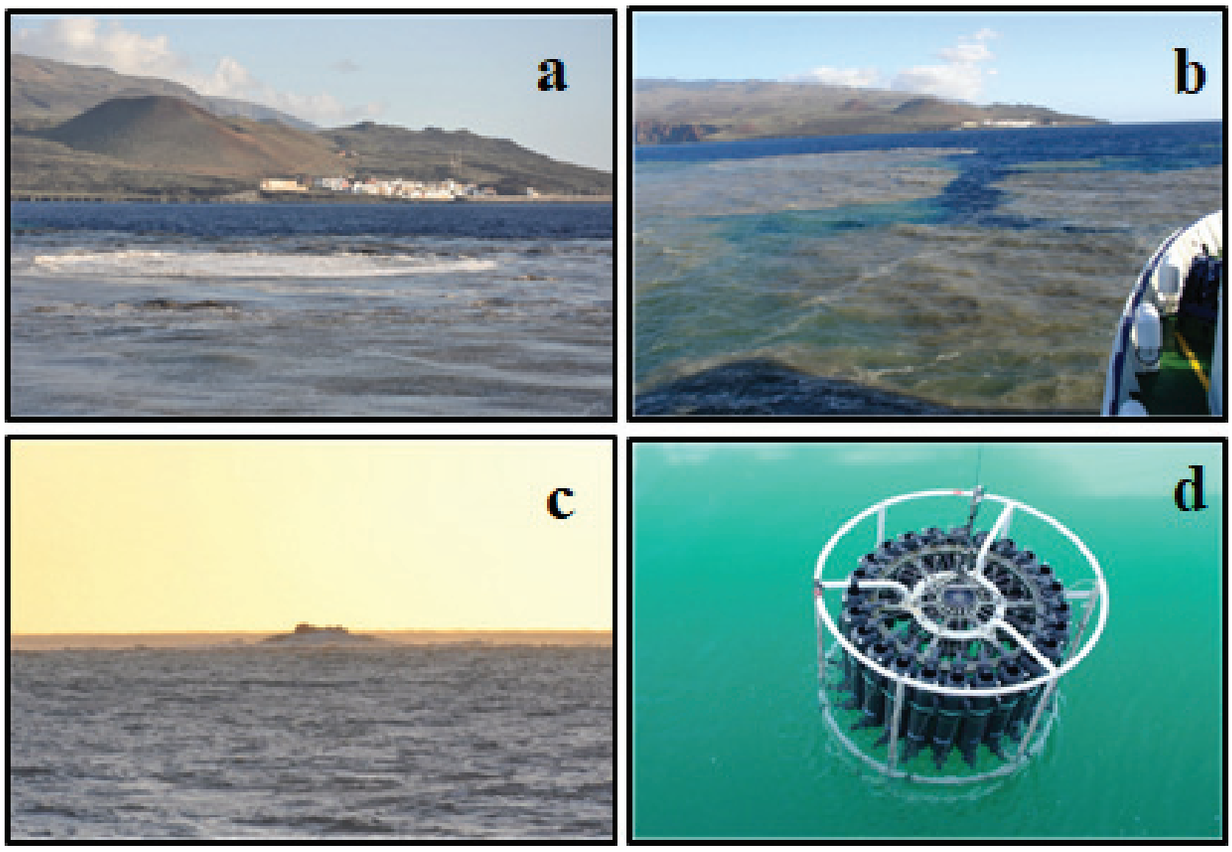


Figure 3. Signals observed in the surface waters as a consequence of the volcanic emissions. (a) Surface seawater bubbling (November 5, 2011). (b) Colour patches in the surface waters. (c) A 10-m emerged high bubble (November 5, 2011). (d) Light green seawater surface.

mantle-derived basanite magma intruded the lower crust, where it migrated sub-horizontally for ~15 km, and then rapidly transited to the surface, all within a few months [18–20].

3. Eruptive phase and changes in the chemistry of sea water

During the eruptive phase that lasted 5 months (October–March), important changes in the carbon dioxide system and in the emissions of reduced species were observed south of the El Hierro Island. Over this period, intensive water column sampling was carried out. The samples were taken with a conductivity-temperature-depth sensor (CTD)-rosette with 24 Niskin bottles. The pH in total scale (pH_T), the total dissolved inorganic carbon (C_T), the total alkalinity (A_T), Fe(II) and the total sulfur reduced species were measured, together with the temperature, the salinity and the dissolved oxygen. The nutrients and the fugacity of CO_2 (fCO_2) were also analyzed in the most of cruises.

3.1. Changes in the pH and carbonate system

Due to the volcanic emissions of CO_2, SO_2 and H_2S/HS^-, important changes were observed in the pH, with values lower than 6. The largest anomalies, $\Delta pH = 2.9$, were observed in November 5, 2011, during the explosive event, where a 10 m high bubble emerged from the sea surface. The C_T and the A_T also changed, in the surface waters around the volcano, where anomalous values

of C_T and A_T of 7682 and 1338 μmol kg^{-1} were measured, respectively (**Figure 4**). Normal surface values for the area are 2100 μmol kg^{-1} for C_T and 2430.1 μmol kg^{-1} for A_T.

The CO_2 exchanged between the ocean and the atmosphere after being emitted by the volcano was calculated using pH_T and C_T data. $fCO_{2(pH,CT)}$ increased to values as high as 155,000 μatm, reaching 230,316 μatm just after the bubble emerged. The surface seawater in the south-west of the island had $fCO_{2(pH,CT)}$ values in the range of 11,000–19,000 μatm. fCO_2 in the areas unaffected by the volcanic emissions was of 414 ± 2 μatm.

The flux of CO_2, FCO_2, exchanged during the week of the explosive event (November 4–9) was 5×10^{10} gd^{-1}. fCO_2 was computed considering an affected area of 385 km^2 and using a weekly mean wind speed of 7.5 ms^{-1} [3]. The studies carried out by Longpré et al. [17] with samples of

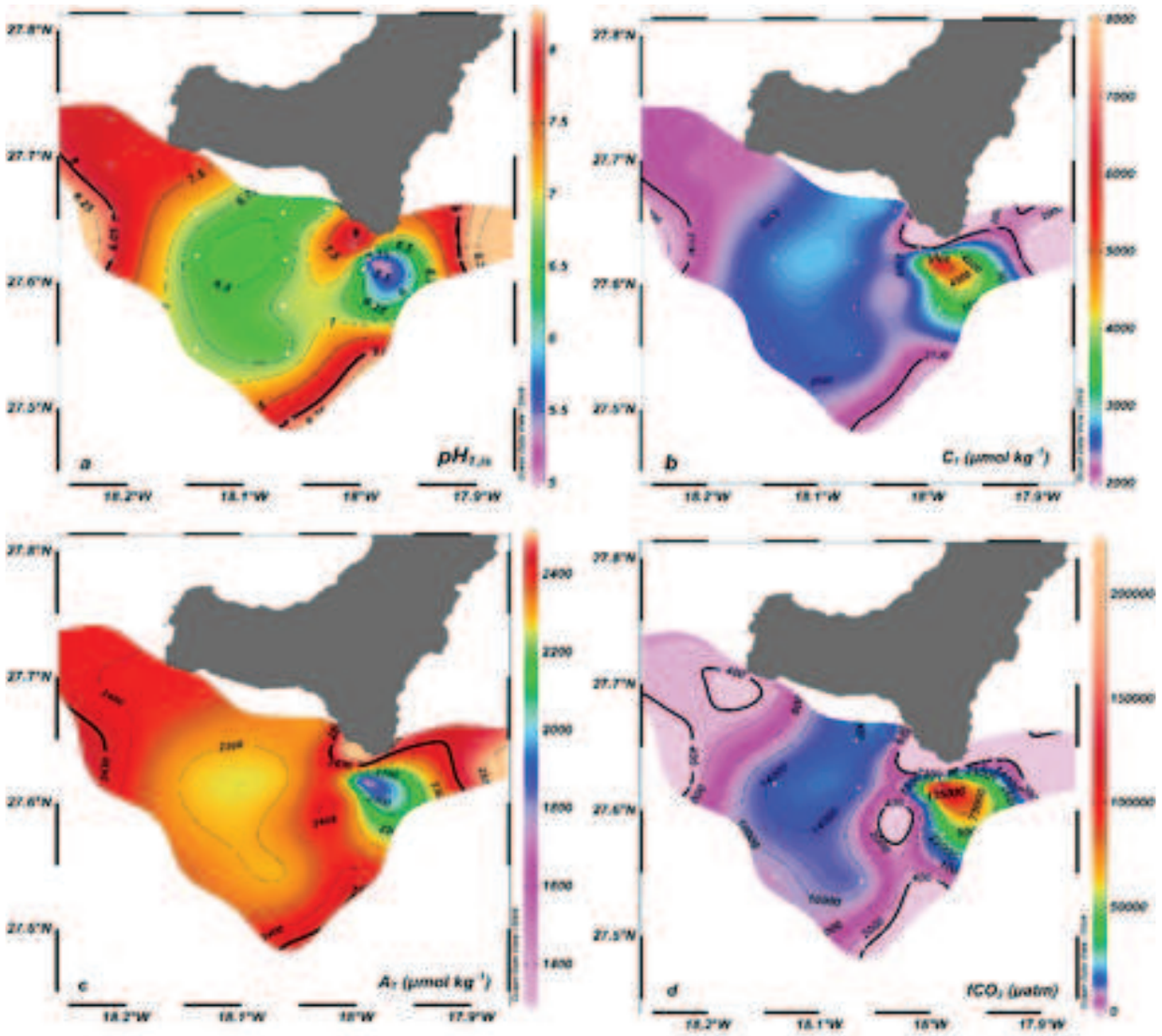


Figure 4. Distributions of the carbonate system variables at 5 m depth around the volcanic area. (a) $pH_{T,is}$ in total scale at in situ conditions. (b) Total dissolved inorganic carbon (C_T, μmol kg^{-1}). (c) Total alkalinity (A_T, μmol kg^{-1}) (d) fCO_2 (μatm).

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basanite lava balloon indicated that the initially high volatile contents of this material and the intense shallow level of degassing led to submarine Strombolian-type explosivity at El Hierro [17]. The authors stated that their conclusions were consistent with the construction of a 200–300 m tall submarine cone [14], and the strong bubbling at the ocean surface. They estimated that the Tagoro eruption released at least 1.3–2.1 Tg CO_2 and 1.8–2.9 Tg S to the environment. However, they emphasize that these amounts must be considered as minima, particularly for CO_2. Taking into account the fluxes of the CO_2 calculated in the water column during the week from November 4th to 9th, 2011 by Santana-Casiano et al. [4], coincident with the most intense bubbling and degassing at the surface water, and extrapolating over the entire course of the eruption (147 days), they estimated an upper limit of 7.4 Tg CO_2 for the CO_2 emissions [17].

3.2. Emission of reduced species and changes in E_x and O_2

During the period of volcanic activity, the emission of reduced species such as iron and sulfur, contributed to decrease both the redox potential (E_R) and the concentration of dissolved oxygen (O_2) in the system (**Figure 5**). The oxygen decreased due to the oxidation of the reduced species emitted by the volcano. The presence of these reduced species produced low redox potential which reached values of −0.03 V. Background redox potential was 0.2 V.

Fe(II) species were present as Fe^{2+}, $Fe(OH)^+$, $Fe(OH)_2$, $FeCl^+$, $Fe(HCO_3)^+$ and FeHS [21]. The concentration of Fe(II) reached values higher than 50 μmol kg^{-1}. Normal dissolved Fe(II) values in the ocean surface are <0.2 nM. The reduced sulfur species were present as H_2S, HS^-, S^{2-}, S^0, SO_3^{2-}, S_x^{2-}, $S_2O_3^{2-}$ and $S_4O_6^{2-}$ [22] with a total concentration of 476 μmol kg^{-1} in the stations close to the volcano.

The flux and oxidation of Fe(II) and reduced sulfur species were so high that oxygen values were often below detection limit. Patches of anoxia at 100 m depth in the affected area were observed. The low oxygen concentrations in these waters together with the low pH_T values contributed to the high mortality of marine biota that was observed in the area after the first two months of the eruption [2].

3.3. Nutrient enrichment in the area

An important input of nutrients was produced in the area. Concentration of nitrate and silicate higher than 3 and 17 μmol kg^{-1}, respectively, were found in the surface waters, while at 100 m depth, values increased to 8 μmol kg^{-1} for the nitrate and 23 μmol kg^{-1} for silicate. In the oligothrophic areas not affected by the volcano, the concentration of these nutrients in the first 100 m is close to the detection limit. Phosphate values increased by one order of magnitude between 100 and 125 m depths, reaching maximum values of 0.6 μmol kg^{-1}. In surface water, the total value of Fe(II) was 12.7 μmol kg^{-1}, where 3.3 μmol kg^{-1} was dissolved and thus bio-available for the marine organisms. These compounds were directly introduced into the photic zone where they affected the primary production. The presence of nutrients together with the input of Fe(II) produced an enrichment in this oligotrophic area, resulting in a fertilization event caused by the shallow volcano emissions [3].

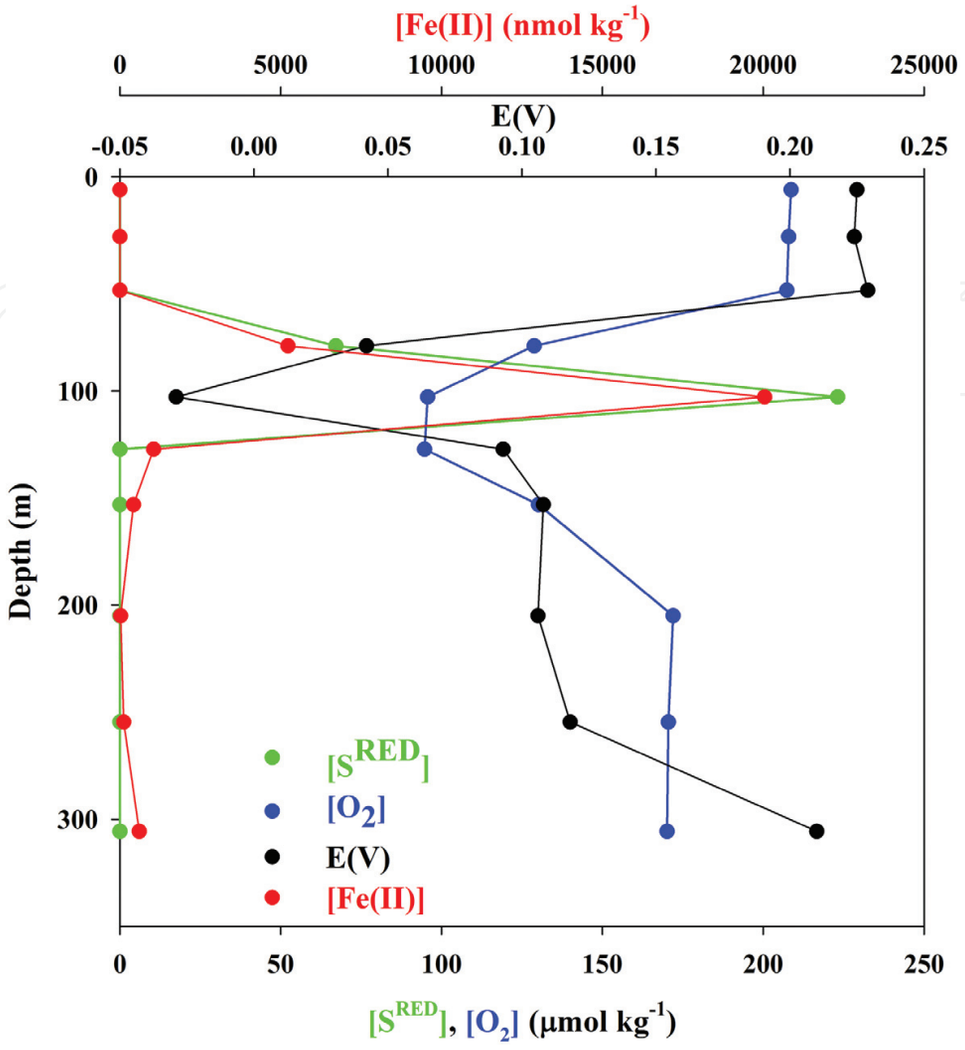


Figure 5. Vertical profiles of reduced sulfur species (green), total Fe(II) (red), dissolved oxygen concentration (blue) and redox potential (black) during November 2011.

3.4. pH and E_x, two variables that control the chemical equilibria

In the context of climatic change, it is known that due to anthropogenic CO_2 emissions the pH in the ocean surface waters is decreasing by about 0.02 pH units/decade and it will decrease by about 0.3–0.4 units at the end of this century [23, 24]. In the El Hierro waters, the pH decreased by 3 units in less than 1 week. As a result of the ongoing magmatic activity, the submarine eruption produced an unprecedented episode of severe acidification that affected the chemical equilibria in the sea water (**Figure 6**). As a consequence of the emission of reduced species, the E_x drastically changed from values higher than 0.2 V, characteristic of oxygenated waters, to values lower than −0.1 V, due to the corrosive environment. In **Figure 6**, the chemical speciation for normal ocean conditions is represented in blue (by dots) and the changes due to the volcanic emissions in orange (by stripes). Changes in the CO_2 (**Figure 6a**) and Fe(II) speciation were produced (**Figure 6b**).

In the oceanic regions where submarine volcanoes experience magmatic or hydrothermal activity, the physicochemical properties of sea water change, modifying the system. The changes

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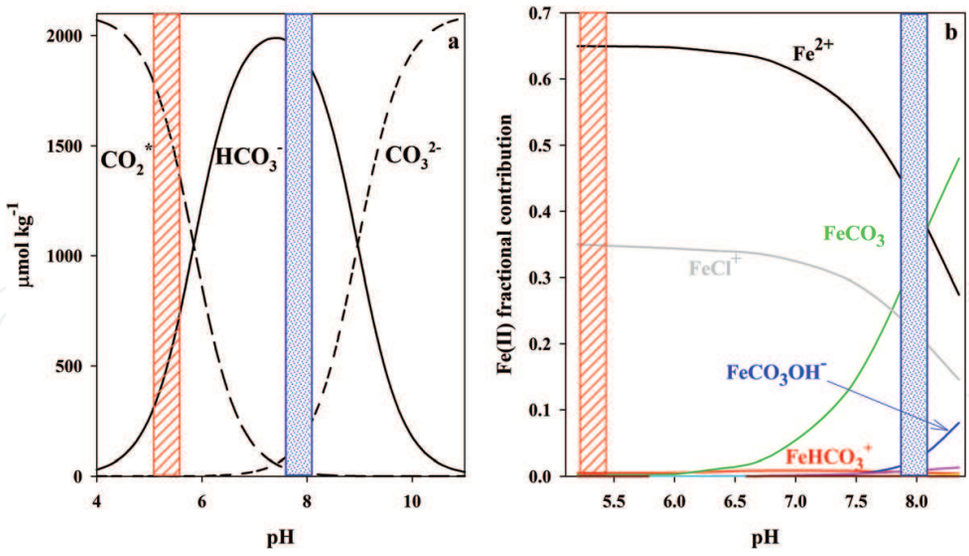


Figure 6. Chemical speciation of the (a) carbonate system and (b) Fe(II) in seawater as a function of the pH.

observed in pH_T were a consequence of the emissions of CO_2, SO_2 and H_2S/HS^- the submarine volcano (Eqs. (1)–(5)). As soon as the volcanic fluid mixes with seawater, the dissolved reduced species, Fe(II), Mn(II) and H_2S/HS^-, produce changes in the E_x. These species in contact with the oxygenated seawater are oxidized, consuming oxygen and acidifying the system (Eqs. (6)–(9)). The emission of Fe(II) also contributed to acidifying the system due to the reaction of Fe(II) with H_2S (Eq. (10)). Part of the pH decrease is compensated by reactions that also contribute to increase the alkalinity (Eqs. (11)–(13)).

After its emission, Fe(II) is oxidized (Eq. (8)) and precipitates into various mineral forms, mainly oxy-hydroxide [25, 26] forming massive deposits of iron. A fraction of the total emitted iron (4%) is stabilized against loss from solution due to complexation by dissolved organic ligands (Eq. (14)), or by incorporation into inorganic or organic colloids which reside within the dissolved size fraction [27, 28]. Moreover, reduced species of Fe and S form FeS colloidal complexes (Eq. (12)), which remain suspended in the water and are modified as the pH changes [29]. These nanoparticles can remain suspended in the deep sea for years with slower settling rates [30], solubilizing and releasing the Fe(II).

$$CO_2 + H_2O = H_2CO_3 \quad (1)$$

$$H_2CO_3 = H^+ + HCO_3^- \quad (2)$$

$$3SO_2 + 2H_2O = S(0) + 2H_2SO_4 \quad (3)$$

$$4SO_2 + 4H_2O = H_2S + 3H_2SO_4 \quad (4)$$

$$HS^- + 4H_2O = SO_4^{2-} + 10\,H^+ + 8e^- \quad (5)$$

$$H_2S + O_2 = 2H^+ + SO_4^{2-} \quad (6)$$

$$Mn(II) + ½\,O_2 + H_2O = MnO_2 + 2\,H^+ \quad (7)$$

$$Fe(II) + ¼\ O_2 + H_2O = ½\ Fe_2O_3 + 2\ H^+ \quad (8)$$

$$FeS + 9/8\ O_2 + H_2O = ½\ Fe_2O_3 + H_2SO_4 \quad (9)$$

$$Fe(II) + H_2S = FeS + 2\ H^+ \quad (10)$$

$$FeS + 4\ MnO_2 + 8\ H^+ = 4\ Mn(II) + SO_4^{2-} + Fe(II) + 4\ H_2O \quad (11)$$

$$FeS + 2\ Fe(OH)_3 + 6\ H^+ = 3\ Fe(II) + S(0) \quad (12)$$

$$2NaAlSi_3O_8 + 2\ CO_2 + 3\ H_2O = Al_2Si_2O_5(OH)_4 + 2\ Na^+ + 2\ HCO_3^- + 4\ SiO_2 \quad (13)$$

$$Fe(II) + L = Fe(II) - L \quad (14)$$

The conclusions obtained by Longpré et al. [17] through study of volatiles and trace element concentrations from the Tagoro lava balloons agreed with the changes in the carbonate variables and redox species observed in the water column. They also indicated a strong degassing and associated redox change of the initially volatile-rich and oxidized magma as it ascended from the mantle to produce the submarine eruption.

3.5. Effect of the chemical emissions on the biota

The volcanic emissions had important consequences on the biota. Organisms were observed to modify their distribution and survival and there was an alteration of the diurnal vertical migration of the pelagic communities [2]. Small picophytoplankton, such as *Prochlorococcus* and *Synechococcus*, showed a significant decline in abundance in the volcanic area at depths greater than 75 m if compared to that one in unaffected stations. However, heterotrophic prokaryotes increased with depth [2]. With respect to the bacterioplankton, there was an important change and groups often associated with deep-sea hydrothermal vents or sulfur-rich springs were observed [31]. The increase in temperature and acidification, the decrease in oxygen and the precipitation of chemical compounds resulted in a reduction of the epipelagic stocks and a disruption of the nocturnal ascent of mesopelagic organisms [32]. Once the eruption ceased, the distribution and abundances of the pelagic biota returned to baseline levels.

The increased amount of nutrients in the euphotic zone, together with the high dissolved iron concentrations, may contribute to the regeneration of the productivity in the area. The findings highlight that the same volcano that was responsible for the creation of a highly corrosive environment, affecting marine biota, has also provided the nutrients required for the rapid recuperation of the marine ecosystem.

4. The post eruptive phase and effects on the water chemistry

In March 2012, the magmatic activity stopped and the system evolved into a degasification phase. In April, the composition of the gases close to the summit was primarily CO_2 with dissolved reduced S species below 1 μmol kg^{-1} in the water column. The affected area was

reduced to 0.5 km around the main crater of the volcano. In this area, a decrease of pH_T values to 6.1 (1.9 units below the normal values) was observed and the C_T was 4191 μmol kg^{-1} [3]. The evolution of the chemical properties during the post-eruptive phase was studied from 2013 to 2016. The physical and chemical anomalies were still being observed close to the volcanic area. During this period, the study was concentrated in the volcanic edifice and a transect following the main cone was repeated twice a year. In order to detect anomalies, different strategies over the volcanic edifice, high-resolution study, yo-yo (**Figure 7a**) and tow-yo (**Figure 7b**) studies, were also followed.

4.1. High-resolution study over the volcanic edifice

During the degasification phase, the oceanographic study of the area was mainly concentrated in the volcanic edifice. High-resolution sampling along the volcano was repeated twice every year from 2013 to 2016. In these studies, 10 stations following the alignment of the main and secondary cones of the submarine volcano were repeated (**Figure 1c**). In these stations, water samples were taken at different depths and the signal of CTD, pH and oxidation-reduction potential (ORP) sensors were also recorded.

The vertical distributions of pH and C_T, A_T and Fe(II) along the high-resolution section across the volcano were measured. Negative anomalies in pH values and positive anomalies in C_T, A_T and TDFe(II) were observed close to the main crater [4, 33]. In **Figure 8**, the anomalies in pH and C_T are shown between stations 53 and 56 for the cruises on March and November 2013 (**Figure 8**). The results from these cruises also confirmed important positive anomalies in TDFe (II), coincident with negative anomalies in pH located in the proximity of the main cone [33].

4.2. Yo-yo studies

The yo-yo studies consist of raising and lowering the rosette with the CTD sensors at one location and taking samples at different depths. In the Tagoro volcano, the stations were selected from the results obtained in the high-resolution study (**Figure 8**).

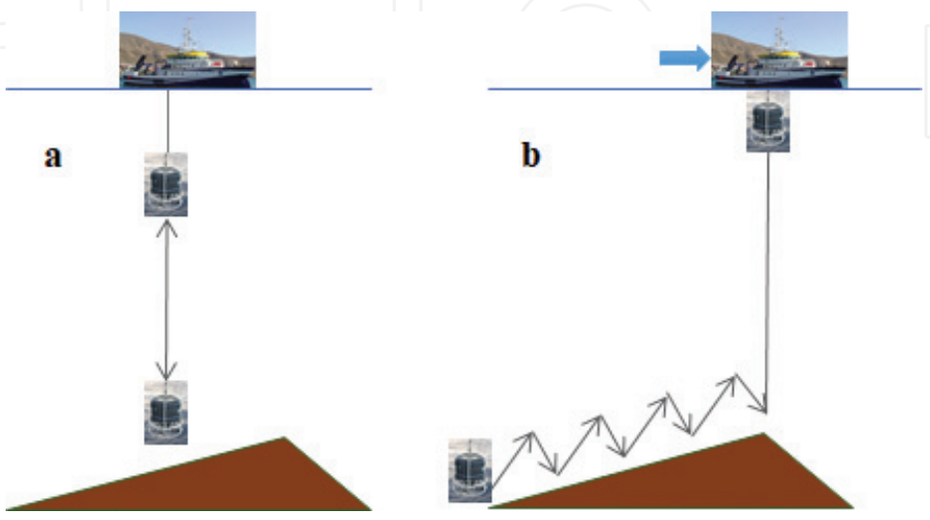


Figure 7. Diagram showing (a) a yo-yo and (b) a tow-yo procedure with CTD-pH-ORP sensors coupled to a rosette.

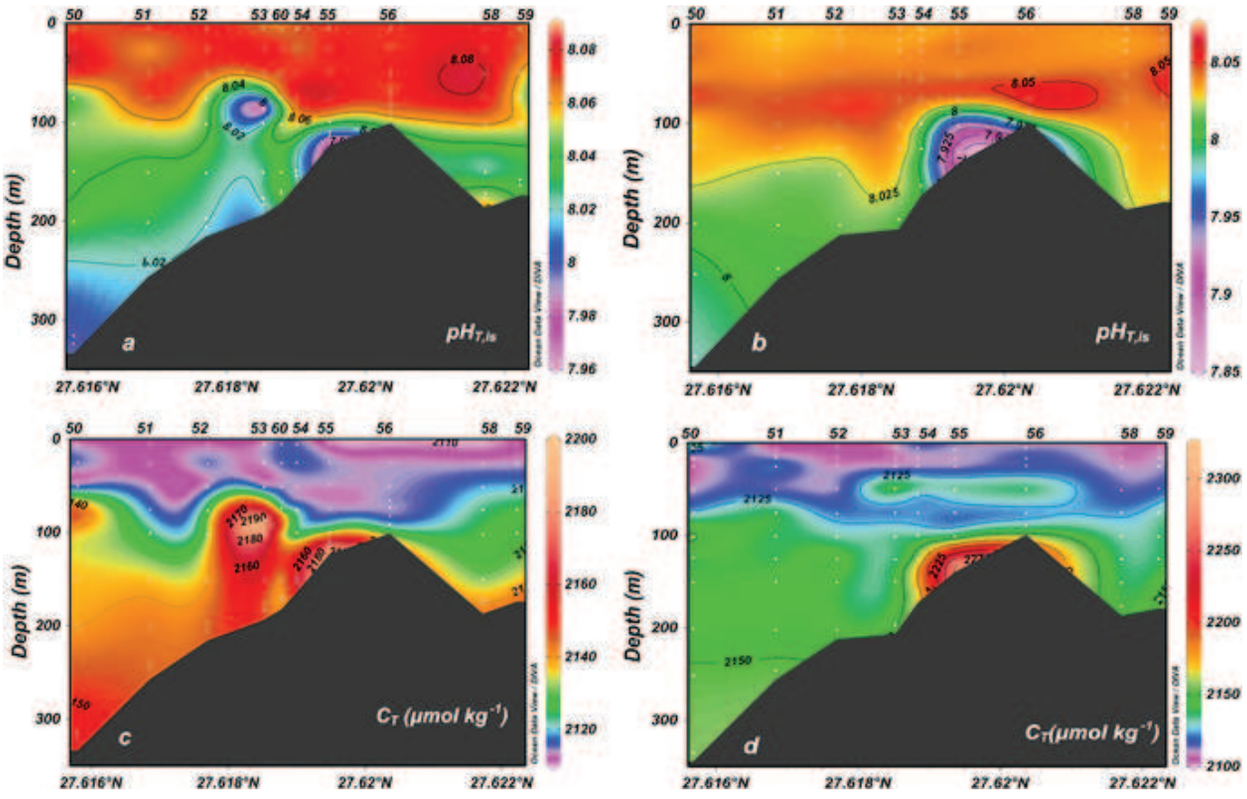


Figure 8. High-resolution studies. $pH_{T,is}$ distribution during VULCANO cruises (a) March 2013 and (b) October 2013. C_T distribution during (c) March 2013 and (d) October 2013.

In order to obtain continuous records of pH and ORP during the yo-yo, together with temperature and salinity measurements, a pH sensor was added to the normal rosette-CTD package in November 2013, and an ORP sensor in March 2014. In this way, CTD-pH-ORP yo-yo studies were carried out at the selected stations, from the surface to 2–3 m above the seabed. Water column sampling for discrete pH, A_T, C_T and TDFe(II) was carried out in the cast where maximum anomalies were detected with the sensors. The time between each cast was 10 min and the total duration of the yo-yo study was between 6 and 10 h. Anomalous values of pH, C_T, A_T and TDFe(II) were observed close to the bottom around the main crater area during the yo-yo study. The pH values were lower than those expected at that depth, and C_T and A_T values higher than usual. There was a high correlation between the anomalies observed for the different variables measured in all the cruises from 2013 to 2016 (**Figure 9**). The yo-yos carried out at station 56 (with 38 casts) and station 61 (with 61 casts) in March 2014 also showed an important fluctuation in pH and δ(ORP)/δt signals related mostly with direction and velocity changes in the local currents, associated with an M2 tidal mode with a period of 12 h. The anomalous values found again in the variables sampled (pH, C_T and A_T) were internally consistent. Therefore, those anomalies were related to CO_2 additions from the hydrothermal vents without other acid gasses acting in a significant way [4]. The fluid emissions producing these changes were ~57% CO_2 and 43% carbonate alkalinity (HCO_3^-, CO_3^{2-}). Positive anomalies for TDFe(II) were also observed and were well correlated with the decrease in pH [33]. A decrease in pH contributed to decrease the oxidation rate of Fe(II) [34] and favoured the persistence of this metal in the medium.

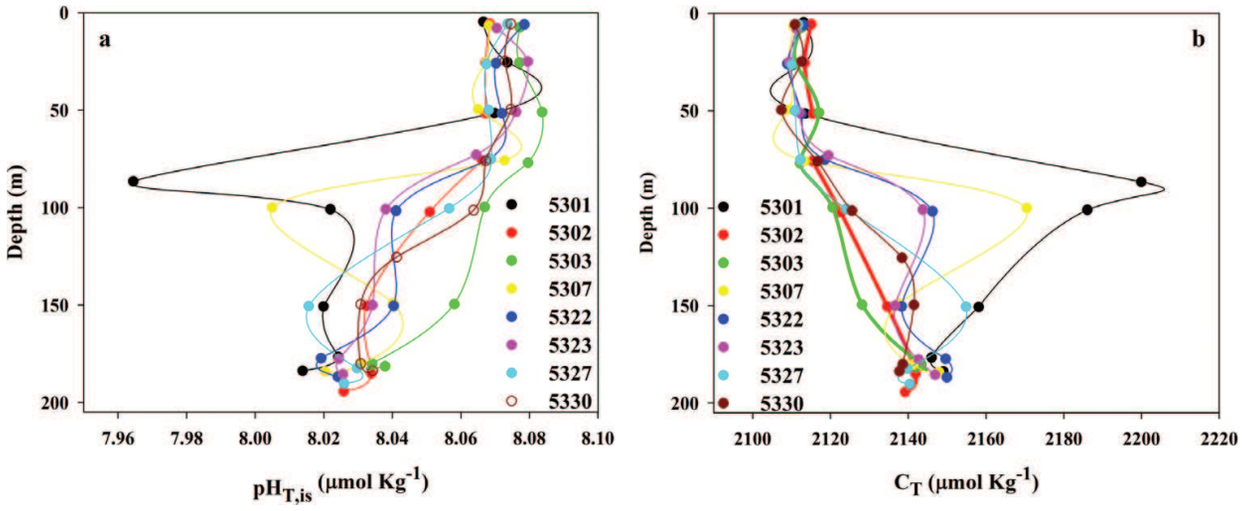


Figure 9. Yo-yo study for the carbonate variables (a) $pH_{T,is}$ and (b) C_T (µmol kg^{-1}) at the station 53, during VULCANO cruise March 2013.

4.3. Tow-yo studies

In the tow-yo studies, the SeaBird 911+ CTD-pH-ORP sensors were towed by the ship, moving at a velocity of 0.4 knots, following a saw tooth pattern by a continuous lowering and raising of the instruments between 2–3 and 40 m above the seafloor, from the base to the top of the submarine volcano. At least seven tow-yos were carried out in the area (**Figure 1c**). Four parallel tow-yos followed the topography of the principal and secondary cones and another two tow-yos were perpendicular to these.

The characteristic reduced and acid emissions of the fluids from the submarine volcano Tagoro allowed us to detect anomalies related with changes in the chemical potential and the proton concentration using ORP and pH sensors, respectively [4]. The combination of ORP and pH sensors with the CTD was used since 2014. The ORP sensor responded very quickly to the presence of reduced chemicals in the water column and the magnitude of this change was examined by the time derivative of ORP, δ(ORP)/δt. For pH changes, ΔpH was defined as the mean pH for each depth at a reference station, in an area not affected by the vent emission, subtracted from each point measured near the volcanic edifice. When δ(ORP)/δt and ΔpH versus latitude were plotted, the anomalies in pH and ORP were observed to follow the same pattern in latitude and longitude (**Figure 10**). This indicated that the emissions of both acid and reduced components must be produced in the same area.

ΔpH values of −0.25 at 100 m depths, as obtained in 2014, cannot be explained by the arrival of water from the surrounding depths [4]. This ΔpH corresponds with a pH value of 7.89, and is only found at a depth of 900 m in the unaffected surrounding water. The same behaviour was observed in November 2015 and 2016 cruises for pH, with ΔpH lower than −0.25 (**Figure 10**), clearly indicating that the degasification process was still taking place. Anomalous ORP values were also observed (**Figure 10**) at the same latitude as the pH anomalies.

Contour maps of the affected surface over the volcano can be obtained from the anomalies of ORP and pH observed in the tow-yo studies. The area of emission during VULCANO0314 was

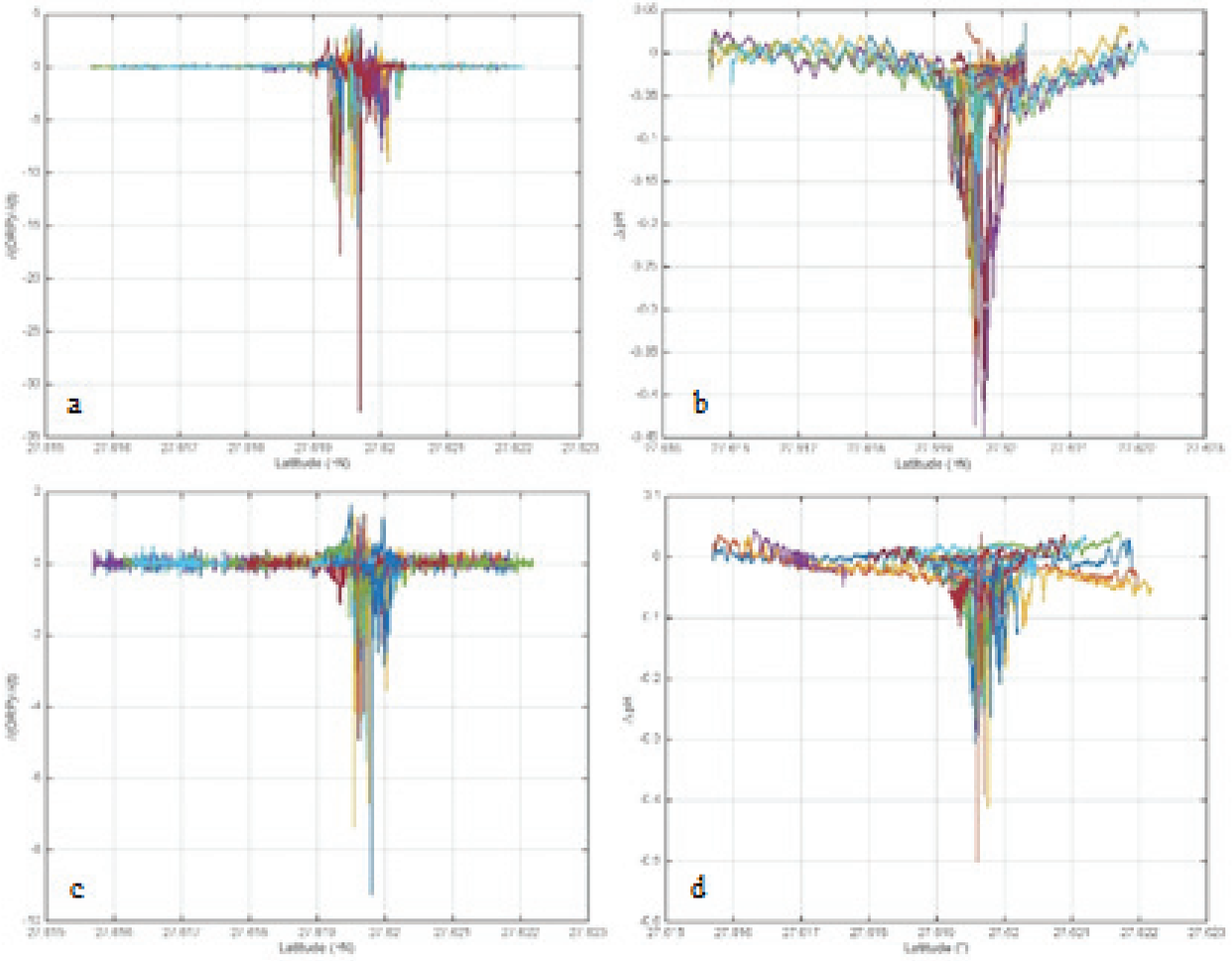


Figure 10. Plots of (a) δ(ORP)/δt and (b) ΔpH versus latitude obtained from tow-yos during VULCANO cruise October 2015 and 2016 (c) δ(ORP)/δt and (d) ΔpH versus latitude during VULCANO 2016.

13,000 ± 800 m^2 and the volume affected 206,000 ± 50,000 m^3. **Figure 11** shows the locations of the anomalous ORP values and the position of the emitting vents for the 2014 and 2016 cruises.

CO_2 fluxes from the volcanic edifice can also be estimated from the calculated anomaly area for every contour, the current speed and the average anomalies of C_T. In the Tagoro volcano, the

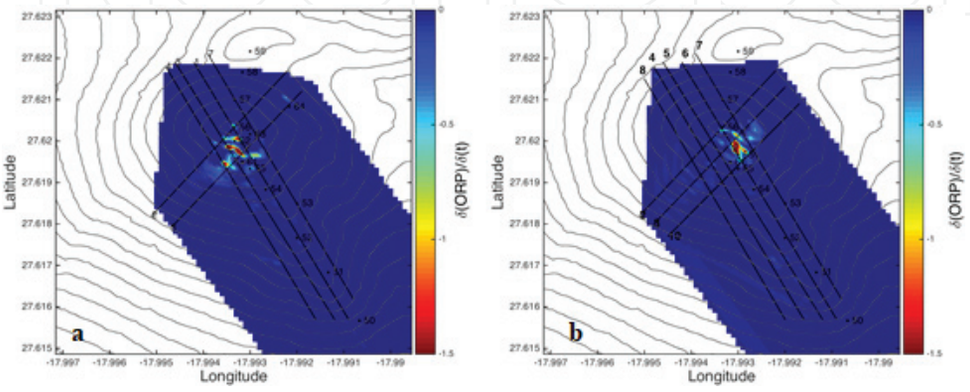


Figure 11. (a) Distribution map of δ(ORP)/δt showing areas affected by diffuse venting during March 2014 (b) March 2016.

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input of CO_2 along multiple sections combined with measurements of oceanic currents produced an estimated volcanic CO_2 flux of $6.0\ 10^5 \pm 1.1\ 10^5$ kg d^{-1} principally transported to the south-west. This emission of CO_2 reduced pH by ~ 0.25–0.30, altering the balance of protons in the surrounding ocean and increasing the seawater acidity by ~20 %.

5. Diving by the volcano

In February 2016, the Tagoro volcano was visited during the POS494-2 with the submersible JAGO (GEOMAR) for direct observation of the eruption site. The JAGO can take two people, a pilot and a scientific observer, to water depths of maximum 400 m. The objectives of POS494-2 were to take a high-resolution video documentation, mapping the eruption site, to sample the fluids and other volcanic and hydrothermal products that formed at the seafloor and to collect chemical and physical sensor data around the active sites (CTD, ORP and pH) 4 years after the eruption [35]. Two dives were done around the volcano, starting not far from the area where strong chemical anomalies had been measured 4 months before. The first visual inspection carried out in the JAGO showed that the anomalous area was an oval-shaped depression of at least several meters in depth and about 10–15 m in diameter. It was situated at the south-eastern flank of the volcano at a depth of 126 m, about 38 m lower than the summit of the volcano. The volcanic rocks at the edges and inside the depression were coated in orange-coloured Fe-oxides. Several pieces of volcanic rock and crusts were collected. Warm water was also seeping diffusely through sediment pores at the bottom of the crater, and occasionally more focused through small vent holes and chimneys that were up to 5 cm high. These chimneys and the orange-coloured Fe-oxides (**Figure 12**) were also observed in the HD images from the ROV Liropus 2000 during VULCANA-0417-ROV cruise. Temperature measurements 20 cm inside the sediment close to a vent site revealed 38°C while the temperature of the ambient seawater was 20°C [35]. Fluid samples were taken with a Teflon bottle directly from the emission vents and compared with the samples obtained at 1 m depth with a Niskin bottle for pH and Fe(II). pH values as low as 7.05 were found, and Fe(II) concentrations higher than

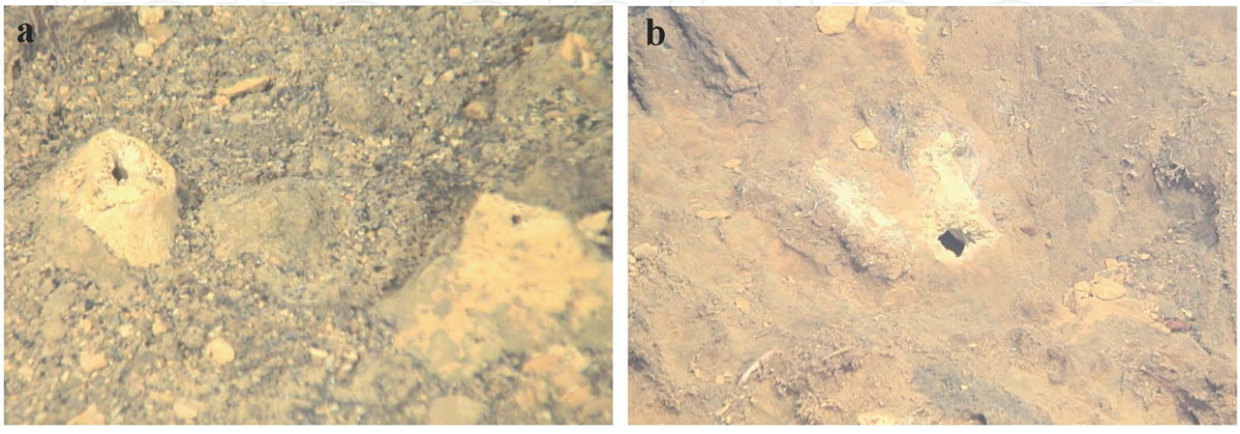


Figure 12. HD images obtained with a Liropus 2000 ROV on board R/V Ángeles Alvariño (Spanish Institute of Oceanography) during April 2017 VULCANA cruise, showing (a) two chimneys and (b) one vent, located in the north flank of the main crater of the submarine volcano Tagoro.

5□M measured compared with the reference values of pH = 7.99 and Fe(II) concentration below 0.5 nM. It was observed that the emission was diffuse and it was close to the floor.

With regard to the ecology in the area, it was observed that the volcanic black rocks were already partly colonized by bivalves (small oysters), brachiopods, sponges and whip corals and a thin coat of whitish bacteria covers most of the surfaces around the vents [35]. A detailed microscopic and molecular study carried out near the summit of the volcanic cone, at about 130 m depth, revealed that the bacteria covers were composed of filaments made of bacterial trichomes enveloped within a sheath and colonized by epibiotic bacteria [36]. This system showed an unprecedented array of metabolic pathways, spanning from the exploitation of organic and inorganic carbon released by volcanic degassing to the uptake of sulfur and nitrogen compounds, providing key competitive advantages for the colonization of the new habitat created by the submarine eruption [36].

6. Conclusions

Sites like the submarine volcano Tagoro, in its degasification stage, provide an excellent opportunity to study the carbonate system, the volcanic contribution to the global volcanic carbon flux, the emissions of trace metals such as TDFe(II) and the potential environmental impact of these emissions on the marine ecosystem.

The inputs of CO_2 along multiple tow-yo sections, combined with measurements of oceanic currents, produced an estimated volcanic CO_2 flux of $6.0\ 10^5 \pm 1.1\ 10^5$ kg d^{-1}, mainly transported to the south-west. These emissions also alter the balance of protons in the surrounding ocean, increasing the seawater acidity by ~20 %. The flux of CO_2 from the Tagoro volcano is comparable to that at other submarine volcanoes like NW Rota-1 ($\sim 1 \pm 0.25\ 10^6$ kg d^{-1}, an erupting submarine volcano in the Mariana arc) but relatively small compared to both the global volcanic flux of CO_2 (~0.1%) and the anthropogenic flux (~0.002%). The global volcanic flux of CO_2 is estimated to be ~ $7.2\ 10^8$ kg d^{-1} considering mid-ocean ridges, arcs and plumes.

The emission of CO_2 from submarine volcanoes generates local ocean acidification that affects the chemical equilibrium and speciation and could impact biological communities, with especially important consequences for organisms that use calcium carbonate in their structures. These emissions also alter the balance of protons in the surrounding ocean, increasing the sea water acidity by ~20 %.

From the yo-yo studies, important anomalies in both pH_T and TDFe(II) were observed. The increased TDFe(II) concentrations and the low associated pH_T values may be causing an important fertilization event in the seawater around the volcano near the Island of El Hierro, providing optimal conditions for the regeneration of the area.

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