# Emissions of Fe(II) due to the undersea volcano of El Hierro and its kinetic of oxidation

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## ABSTRACT

The eruptive process and the subsequent hydrothermal stage which took place in the undersea volcano at the southeast of the El Hierro Island, have increased the concentration of TDFe(II) (Total dissolvable iron(II), unfiltered) in the waters nearest to the main cone. Three cruises were carried out in October 2013, March 2014 and May 2015 in order to detect any variation in concentrations of TDFe(II) due to hydrothermal emissions, two years after the eruptive process. Flow injection chemiluminescence using luminol as the reagent was used to determine the concentrations of TDFe(II). The results confirm positive anomalies in TDFe(II) which coincide with negatives anomalies in $pH_T$ in a secondary cone during these cruises. Temporal studies in the stations located over the main cone and two secondary cones with positively anomalies in TDFe(II) concentrations and negative anomalies in pH values were carried out during hours to days. These showed an important variability in both $pH_T$ and TDFe(II) concentrations which indicated that the volcanic area was affected by intermittent events of hydrothermal fluid emissions. These anomalies were present in the volcanic cone three years after the eruptive phase had ceased. The increased TDFe(II) concentrations and the low associated $pH_T$ values may be triggering an important fertilization event in the seawater around the volcano at the Island of El Hierro providing optimal conditions for the regeneration of the area.

## INTRODUCTION

Hydrothermal vents are an important source of material of different size, texture and chemical composition, such as gases and metals particularly reduced species.. The emission of gas and reduced species in hydrothermal vents modifies the carbonate system, decreasing the dissolved oxygen concentrations and reducing pℰ and pH which favour the presence of Fe(II) and decrease its oxidation rate [1].

It is known that the Fe(II) is thermodynamically unstable and is rapidly oxidized in oxic waters (seconds to minutes) to Fe(III) by $O_2$ and $H_2O_2$ [2-4]. The concentration of Fe(II) dissolved in shallow and deep waters, depends on the rate of oxidation of Fe(II) which is a function of $O_2$ and $H_2O_2$ concentration, pH, temperature, $[HCO_3^-]$ concentrations and ionic strength and nutrient concentration [4-10].

In hydrothermal vents, the Fe(II) oxidises in the presence of $O_2$ and precipitates in various mineral forms, mainly oxy-hydroxide [11] forming massive deposits of iron. Moreover reduced species of Fe and S form a FeS colloidal complex, which remains suspended in the water and is changing as the pH changes [12]. These nanoparticles can stay suspended in the deep sea for years with slow settling rates [13] and will solubilize and release the Fe(II).

The presence of shallow hydrothermal vents in the post-eruptive phase of the submarine volcano close to the coastal area gives us the opportunity to study the emissions of dissolved Fe(II), changes in the pH of the surrounding waters and the correlation with the dissolved Fe(II) concentration. This provides information about both the kinetics of oxidation of Fe(II) and natural Fe(II) fertilization process taking place in the area.

## MATERIAL & METHODS

The study was conducted in the region of the undersea volcano, south of the island of El Hierro (Canary Islands, Spain, at 27º37'07''N – 017º59'28''W).

In order to determine the concentration of Fe(II) in seawater the FeLUME system (Waterville Analytical) was selected. The FIA-chemiluminescence technique uses luminol as the reagent [14]. Dissolved, colloidal and labile phases of Fe(II) are determined and expressed as TDFe(II). The Software executed in the chemiluminescence was provided by Waterville analytical (WA CONTROL V105, PHOTO COUNTER CONTROL). The detection limit obtained was 0.09nM (LD= 3xSTD $[Blank]$, n =4), with correlation coefficients of $r^2$= 0.999.

The pH was measured in the whole the water column using an SBE18 pH sensor that provides values expressed in the NBS scale. Additionally, discrete samples were measured on the total scale at a constant temperature of 25ºC ($pH_{T,25}$) by the UV-Vis spectrophotometric technique [15] that used m-cresol purple as an indicator [16].

The kinetic studies were undertaken in a thermo regulated cell connected to a thermostatic bath (PolyScience). For each study the seawater was tempered to the temperature

chosen. When the temperature was equilibrated the pH was measured and also the Tris buffer.

## RESULTS & DISCUSSION

Important deviations were observed in the proximities of the volcano during the October 2013, March 2014 and May 2015 cruises. TDFe(II) positive anomalies were followed by negative anomalies in $pH_T$ along the full profiles and for the bottom samples for October 2013, March 2014 and May 2015 cruises.

The temporal study in station 55 during 4 days during the October 2013 cruise, in stations 56 and 61 during 5 days and four and a half hours, respectively, and in station 56 during 2 hours in May 2015, showed an important variability in both $pH_T$ and TDFe(II) concentration. This indicated that the volcanic area was affected by intermittent events [17] of hydrothermal fluids in vents that remain in the volcanic cone three years after the eruptive phase has ceased.

During May 2015 kinetic studies were done with two seawater samples at salinity 35.457 and 36.924. In all the cases the oxidation of iron (II) followed a pseudo-first order behaviour. For each salinity sample the oxidation became faster as the temperature increased. Moreover, the oxidation of iron (II) was faster in surface waters with salinity 36.924 and $pH_T$ over 8 than in deeper seawater (at 341dbar) with salinity 35.457.

Kinetic studies carried out in the volcanic area show Fe(II) oxidation faster than expected in natural seawater. In general, a kinetic behaviour similar to that in in high nutrient seawater was observed. González et al.[7] have demonstrated the effect of high nutrient seawater increasing the Fe(II) oxidation rate, particularly the silicate.

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## REFERENCES

1 - Santana-Casiano, J.M., et al., The natural ocean acidification and fertilization event caused by the submarine eruption of El Hierro. Scientific Reports, 2013. 3: p. 1-8.

2 - Kustka, A.B., et al., Extracellular production of superoxide by marine diatoms: Contrasting effects on iron redox chemistry and bioavailability. Limnology and Oceanography, 2005. 50(4): p. 1172-1180.

3 - Millero, F.J. and M. Izaguirre, Effect of ionic strength and ionic interactions on the oxidation of Fe (II). Journal of Solution Chemistry, 1989. 18(6): p. 585-599.

4 - Santana-Casiano, J.M., M. González-Dávila, and F.J. Millero, The oxidation of Fe (II) in NaCl–HCO 3− and seawater solutions in the presence of phthalate and salicylate ions: a kinetic model. Marine chemistry, 2004. 85(1): p. 27-40.

5 - González-Davila, M., J.M. Santana-Casiano, and F.J. Millero, Oxidation of iron (II) nanomolar with H 2 O 2 in seawater. Geochimica et Cosmochimica Acta, 2005. 69(1): p. 83-93.

6 - González-Dávila, M., J.M. Santana-Casiano, and F.J. Millero, Competition between O2 and H2O2 in the oxidation of Fe (II) in natural waters. Journal of solution chemistry, 2006. 35(1): p. 95-111.

7 - González, A.G., et al., Oxidation of Fe (II) in natural waters at high nutrient concentrations. Environmental science & technology, 2010. 44(21): p. 8095-8101.

8 - King, D. and R. Farlow, Role of carbonate speciation on the oxidation of Fe (II) by H 2 O 2. Marine Chemistry, 2000. 70(1): p. 201-209.

9 - Miller, W.L., et al., Photochemical redox cycling of iron in coastal seawater. Marine Chemistry, 1995. 50(1): p. 63-77.

10 - Shi, D., et al., Effect of ocean acidification on iron availability to marine phytoplankton. Science, 2010. 327(5966): p. 676-679.

11 - de Baar, H.J.W. and J.T.M. de Jong, Distributions, sources and sinks of iron in seawater, in The biogeochemistry of iron in sea water, D.R. Turner and K.A. Hunter, Editors. 2001, John Wiley & Sons Ltd. p. 123.

12 - Luther, G.W., et al., Chemical speciation drives hydrothermal vent ecology. Nature, 2001. 410(6830): p. 813-816.

13 - Yücel, M., et al., Hydrothermal vents as a kinetically stable source of iron-sulphide-bearing nanoparticles to the ocean. Nature Geosci, 2011. 4(6): p. 367-371.

14 - King, D.W., H.A. Lounsbury, and F.J. Millero, Rates and mechanism of Fe (II) oxidation at nanomolar total iron concentrations. Environmental science & technology, 1995. 29(3): p. 818-824.

15 - Clayton, T.D. and R.H. Byrne, Spectrophotometric seawater pH measurements: total hydrogen ion concentration scale calibration of m-cresol purple and at-sea results. Deep Sea Research Part I: Oceanographic Research Papers, 1993. 40(10): p. 2115-2129.

16 - González-Dávila, M., et al., Seasonal and interannual variability of sea-surface carbon dioxide species at the European Station for Time Series in the Ocean at the Canary Islands (ESTOC) between 1996 and 2000. Global Biogeochemical Cycles, 2003. 17(3): p. 1-5.

17 - Fraile-Nuez E., Santana-Casiano J. M. and González-Dávila M., 2016. Cyclic thermal behavior associated to the degassing process at El Hierro submarine volcano, Canary Islands (In preparation).