Changes in the Diffuse $CO₂$ Emission and Relation to Seismic Activity in and around El Hierro, Canary Islands

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Abstract—Significant changes in the diffuse emission of carbon dioxide were recorded in a geochemical station located at El Hierro, Canary Islands, before the occurrence of several seismic events during 2004. Two precursory CO₂ efflux increases started thirteen and nine days before two seismic events of magnitude 2.3 and 1.7, which took place near El Hierro Island, Canary Islands, on March 23 and April 15, reaching a maximun value of 51.1 and 46.2 $g m^{-2} d^{-1}$, respectively, five and eight days before the two seismic events. Other similar increases started thirteen and five days before the occurrence of two seismic events of magnitude 1.3 and 1.5 which took place on October 15 and 21 respectively, reaching the maximum values four and one day before the earthquakes. These changes were not related to variations in atmospheric or soil parameters. The Material Failure Forecast Method (FFM), which analyzes the rate of precursory phenomena, was successfully applied to forecast the first seismic event that took place in El Hierro Island in 2004.

Key words: El Hierro Island, precursors, Material Failure Forecast Method, diffuse degassing, carbon dioxide.

1. Introduction

El Hierro Island (278 km^2) is one of the youngest and the southwesternmost of the Canary Islands and rises 4000 m above the sea floor (Fig. 1). The main characteristics of El Hierro consist of a truncated trihedron shape and three convergent ridges of volcanic cones. The older subaerial rocks of El Hierro have been dated at 1.12 Ma (GUILLOU *et al.*, 1996) and there is only one questionable report of a single volcanic eruption in El Hierro Island in the last 500 years, Lomo Negro volcano, in 1793 (HERNÁNDEZ PACHECO, 1982). The volcanic evolution of El Hierro can be divided into three successive volcanic edifices: Tiñor volcano, El Golfo volcano and Rift Volcanism (GUILLOU et al., 1996; CARRACEDO et al., 1997). The island has been covered in the last 37 ka by lavas erupted by the last stage of the volcanic evolution and deep embayment has been produced by giant landslides between the three rift zones, being the most recent El Golfo failure on the

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northwest flank of El Hierro, which occurred approximately 15 ka ago (MASSON, 1996; GEE et al., 2001).

Since fumarolic activity is absent at the surface environment of El Hierro, the study of the evolution of diffuse $CO₂$ emissions becomes an ideal geochemical tool for monitoring its volcanic activity (CHIODINI et al., 1998; HERNÁNDEZ et al., 2001a, b, c, 2003, 2006; SHIMOIKE et al., 2002; FRONDINI et al., 2004; NOTSU et al., 2005, 2006; GRANIERI et al., 2006). $CO₂$ is, after water vapor, the major gas species in basaltic magmas (BARNES *et al.*, 1988), and it is a good geochemical tracer of subsurface magma degassing, since its low solubility in silicate melts at low and moderate pressure (GERLACH and GRAEBER, 1985). Natural emissions of $CO₂$ have different sources: mantle, carbonate metamorphism, descomposition of organic matter and biological activity (IRWIN and BARNES, 1980) and active faults favor gas leaks because they are preferential paths for crustal and subcrustal gases (IRWIN and BARNES, 1980; SUGISAKI et al., 1983; KLUSMAN, 1993; GIAMMANCO et al., 1998; KING, 1996; KING et al., 2006). Areas with high $CO₂$ discharges can indicate high pore pressure at depth and might be a tool to identify potential seismic regions (ROJSTACZER et al., 1995; CASTAGNOLO et al., 2001; SPICAK and HORALEK, 2001). Relatively high $CO₂$ fluxes correlate with areas that show deep fractures or faults with emissions of CO2 from magmatic reservoirs or decarbonation processes (TOUTAIN and BAUBRON, 1999) and increases of diffuse $CO₂$ emissions related to seismic events and volcanic activity have been reported (HERNÁNDEZ et al., 2001b; ROGIE et al., 2001; SALAZAR et al., 2002; CARAPEZZA et al., 2004; PÉREZ et al., 2005).

In order to improve the volcanic surveillance program of El Hierro Island and to provide a multidisciplinary approach, a continuous geochemical station to measure $CO₂$ efflux was installed on September 2003 in Llanos de Guillén, the interception center of the three volcanic-rift zones of the island, with the aim of detecting changes in the diffuse emission of $CO₂$ related to the seismic or volcanic activity. Monitoring of $CO₂$ efflux has demonstrated to be a useful tool to forecast precursory signals of volcanic eruptions and seismic events. HERNÁNDEZ et al., $(2001b)$ reported an increase from 120 to 240 t/d on the $CO₂$ efflux six months before the volcanic eruption of the Usu volcano, Japan, which occurred in 2000. CARAPEZZA et al. (2004) observed a significant increase of nearly double the maximum $CO₂$ efflux values measured previously by an automatic geochemical station one week before the 2002 Stromboli eruption, Italy. SALAZAR et al. (2002) observed anomalous changes in the diffuse emission of carbon dioxide before some of the aftershocks of the 13 February 2001 El Salvador earthquake.

PÉREZ and HERNÁNDEZ, 2005 and PÉREZ et al., 2006 have reported significant increases in a $CO₂$ efflux time series prior to seismic events, as the increase observed from approximately 16 g m⁻² d⁻¹ to 270 g m⁻² d⁻¹, in the carbon dioxide efflux values measured in an automatic geochemical station nine days before the January 2002 short temp unrest occurred at San Miguel volcano, El Salvdor.

In the last 15 years, the Instituto Geográfico Nacional (IGN) has reported the occurrence of several seismic events in and around El Hierro Island. Figure 2 shows the number of earthquakes registered in and around El Hierro Island since 1993. An anomalous increase in the seismic activity occurred in 2004. Unfortunately, no mechanism information is available for these earthquakes due to the characteristics of the seimic network of IGN in the Canary Islands.

2. Procedures and Methods

The automatic geochemical station (EHI01) to measure the $CO₂$ efflux was installed at Llanos de Guillén, in the center of El Hierro Island (Latitude: N 27° 42' 58.2"; Longitude: W 18° 01' 8.8") on September 25, 2003. Previous CO_2 efflux surveys covering the entire island indicated that the selected location for the automatic station shows one of the highest $CO₂$ efflux values measured in El Hierro Island (MART´INEZ-ZUBIETA, 2001 ; PADRÓN et al., 2006). Moreover, the place is located at the interception center of the three volcanic rifts of the El Hierro Island.

The station measures on an hourly basis the $CO₂$ and $H₂S$ efflux, the $CO₂$ and $H₂S$ air concentrations, the soil water content and temperature and the atmospheric parameters: wind speed and direction, air temperature and humidity and barometric pressure. The meteorological parameters together with the air $CO₂$ concentration are measured 1 m above the ground and the soil water content and soil temperature are measured 40-cm deep, and recorded contemporaneously with $CO₂$ efflux. On October 5, 2004, a rain gauge was also installed in the geochemical station. Both $CO₂$ and $H₂S$ diffuse fluxes are estimated according to the accumulation chamber method (PARKINSON, 1981) by means of a nondispersive specrtophotometer (LICOR Li-820) with a 2000 ppm span cell and a DRÄGER Polytron II, respectively. The geochemical station is powered by a solar cell panel and a battery. Each $CO₂$ and $H₂S$ efflux measurement starts when the open side of the chamber is placed onto a fixed collar in the soil surface. A pump allows the air contained in the chamber to circulate through the NDIR spectrophotometer and then back into the chamber. To verify the performances and the reliability of this method, several calibration tests were made in the laboratory and the accuracy was estimated to be $\pm 10\%$. Each hour the station also measures the soil temperature and water content and the meteorological parameters. All the data are stored on flash memory and radio-telemetered to ITER.

3. Results and Discussion

During 2004 a total of thirteen seismic events were registered by the seismic network of IGN in and around El Hierro Island. The locations of these seismic events are shown in Figure 3. A time series of the total 6,385 measured data of $CO₂$ efflux, wind speed, soil water content and temperature, air humidity and temperature and barometric pressure during 2004 is shown in Figure 4. A 48-hour moving average is also plotted for $CO₂$ efflux, wind speed, air humidity and temperature and barometric pressure time series.

Due to instrumental and telemetry problems, the time series has a 27.1% of missing data, with the main lag of data occurring between June 8 to July 29. Table 1 summarizes the results of the total recorded data.

The CO₂ efflux ranged between nondetectable values to 53.1 g m⁻² d⁻¹, with an average value of 12.5 g $m^{-2} d^{-1}$. The detection limit of the automatic station has been estimated to be 0.5 g m⁻² d⁻¹. During the period of study, the H₂S efflux values were always below the detection limit of the instrument (<1.5 g m^{-2} d⁻¹). Inspection of the $CO₂$ efflux time series shows four main relatively anomalous increases in the degassing rate. The first increase (A in Fig. 4) began approximately on March 10 and reached a maximum value of 52.1 g m^{-2} d⁻¹ on March 18, five days before a seismic event of magnitude 2.3 occurred near El Hierro Island (Fig. 5). The earthquake was located 24-km deep and its epicenter at 12.6 km from EHI01. The second increase (B in Fig. 4) started approximately on April 6, 2004 and reached a maximum value of 46.3 g m^{-2} d⁻¹ on April 7 (Fig. 5). The third increase (C in Fig. 4) in the $CO₂$ efflux was recorded on October 5 and reached a maximum value of 43.8 g $m^{-2} d^{-1}$ on October 14, followed by a seismic event of magnitude 1.3 which occurred on October 15 (Fig. 6). The last increase (D in Fig. 4) started on October 16, 2004 and reached a maximum value of 43.3 g m^{-2} d⁻¹ on October 21, the same day as the occurrence of a seismic event magnitude 1.5 near El Hierro (Fig. 6).

Between April 15 and May 25, a total of ten seismic events occurred inside and near El Hierro Island, with magnitudes between 1.0 and 2.2. However, there was no significant increase in the $CO₂$ emission prior to these seismic events.

The observed increases in the $CO₂$ efflux at EHI01 seem uncorrelated with significant changes in any of the other parameters recorded by the automatic geochemical station. Short-temp. $CO₂$ efflux changes driven by meteorological fluctuations have been reported

Table 1

Statistical summary of the variables measured by the automatic geochemical station EHI0 in El Hierro during

Non detected values (n.d.) were bellow the detection limit of the instrument.

Figure 1 Geographical localization of El Hierro in the Canary Islands.

in other volcanic systems (SALAZAR et al., 2000, 2002; PADRÓN et al., 2001; ROGIE et al., 2001; GRANIERI et al., 2003). Semidiurnal fluctuations inversely correlated with the barometric pressure variation and small increases correlated with soil water content have

Figure 2 Evolution of the seismicity registered by Instituto Geogra´fico Nacional since 1993 in and around El Hierro Island.

Figure 3 Location of the seismic activity during 2004 in and around El Hierro Island.

been observed in the $CO₂$ efflux time series at the station site. Significant changes with the wind speed have not been observed, probably due to the relatively low wind speeds recorded at the station place. However, the observed changes in the $CO₂$ efflux cannot be explained in terms of such meteorological fluctuations.

Time series of the measured CO₂ efflux and soil and meteorological parameters recorded during 2004 at the geochemical station, El Hierro Island. Moving average of 48 h is also displayed. A, B, C and D dots lines indicate the start of the four significant $CO₂$ efflux increases recorded.

3.1. Filtering the Automatic Station Data

In order to check the temporal variability and its possible dependence with external variables, the soil $CO₂$ efflux was differenced one time to obtain a substantially greater stationary time series. Figure 7 shows the Fast Fourier Transform of the resulting time

Time series of the measured $CO₂$ efflux with a 48 h moving average and barometric pressure at the geochemical station together with the seismic activity during the first part of 2004, El Hierro Island. Arrows indicate the occurrence of seismic events.

series, with the typical diurnal and semidiurnal cycles (12 and 24 h-periods, respectively). Spectral coherences between the soil $CO₂$ efflux and barometric pressure and air temperature were also observed, yielding significant peaks at 12 and 24 h (Fig. 8). These coherences suggest that short-time fluctuations in the diffuse $CO₂$ emission in the observation site are partially driven by meteorological parameters. The observed fluctuations on the 24 h and 12 h periods shown in Figure 8 indicate that diurnal and

Time series of the measured $CO₂$ efflux with a 48 h moving average and barometric pressure at the geochemical station together with the seismic activity during the second part of 2004, El Hierro Island. Arrows indicate the occurrence of seismic events.

semidiurnal fluctuations in the $CO₂$ efflux time series are partially explained in terms of air temperature and barometric pressure fluctuations.

Multivariate Regression Analysis (MRA) was also used to isolate the response of the CO2 efflux to the externally measured variables. MRA is used to predict the dependent variable value as a function of relevant explanatory variables. In this case, we used as external variables the barometric pressure, wind speed and direction, air temperature and relative humidity, soil temperature and water content and power supply

Figure 7 Fast Fourier Transform of the resulting $CO₂$ efflux time series recorded during 2004 at the geochemical station, El Hierro Island.

voltage. MRA is useful to delineate the relations between the $CO₂$ efflux and external factors measured on the geochemical station site. The analysis built a linear model in which the dependent variable is the $CO₂$ efflux and the independent variables are the external factors measured at the station. Results of MRA provide an understanding of the percentage of the variability in the dependent variable which is explained by the selected set of independent variables. For the selected independent variables, the square of the multiple regression coefficients was 0.19, which means that about 19% of the variability in the estimated soil $CO₂$ efflux was explained by the regression model. The statistical significance level of the regression model $(p$ value) showed a value lower than 0.0001 for all the variables less wind speed, indicating a highly significant model. Figure 9 shows the original time series predicted and the residuals data. An inspection of the residual time series shows the four increases of the original $CO₂$ efflux time series, indicating that these increases are not explained by changes in the external parameters measured in EHI01. The maximum values given in the predicted time series are related to meteorological parameters and changes in the soil properties, such as soil water content increases.

3.2. Forecasting the Seismic Events

Since the observed changes in the $CO₂$ efflux always occurred a few days or hours before the seismic events, an attempt to forecast the seismicity was done by means of the Material Failure Forecast Method (FFM) (VOIGHT, 1988, 1989; CORNELIUS and VOIGHT, 1995). VOIGHT (1988, 1989) proposed the FFM, based on his work during the Mount St. Helens eruption in 1981. The method uses the rock failure as a fundamental cause for

Spectral coherences calculated using a 41 elements Tukey-Hamming window for diffuse $CO₂$ emission rate and (A) air temperature and (B) barometric pressure.

most precursory activity, which can lead to a volcanic eruption or seismic event, and is based on the empirical failure material model: The rate of change of some observable parameters before a volcanic eruption or a seismic event follows the following equation:

MRA results for the 2004 $CO₂$ efflux data recorded at the geochemical station of El Hierro with a 48 h moving average.

$$
\left(\frac{d^2\Omega}{dt^2}\right) = A \left(\frac{d\Omega}{dt}\right)^{\alpha},\tag{1}
$$

where Ω is any characteristic parameter (strain, rotation, traslation, seismic energy released,...) and A and α are two different constants. The method finally describes terminal failure of rocks, metals, etc. If a time series of a precursor seems to be representative of a solution for equation (1), it would be possible to determine the time of the event extrapolating the descending section of the inverse precursor time series to the time axis (CORNELIUS and VOIGHT, 1995). The time of a volcanic eruption or a seismic event is derived from the time of failure implied by the accelerating rate of the measured precursor. VOIGHT (1988) applied this method successfully to forecast volcanic eruptions (Mount St. Helens, USA, September 1981 and March 1982, and Bezymianny, Russia, April 1960), and for large landslides (Mount Toc, Italy, 1963). The method has also been applied by other authors on other volcanic systems (YAMAOKA, 1993; DE LA CRUZ-REINA and REYES-DÁVILA, 2001 ; ENDO and MURRAY, 1991; ORTÍZ et al., 2003). The application of the FFM method to the $CO₂$ efflux time series was firstly reported by Pérez *et al.* (2005). Pérez and HERNÁNDEZ (2007) successfully applied the FFM to a precursory $CO₂$ efflux increase prior to a seismic event of magnitude 2.7 at Tenerife, Canary Islands. Similar results can be obtained applying the FFM to the data reported by HERNÁNDEZ et al. (2001b), where the authors measured the total diffuse emission of $CO₂$ released by the Usu volcano in September 1998 and September 1999, showing an increase from 120 to 340 t/d. The results obtained by the application of the FFM method for the possible eruption date agree excellently with March 2000, when the Usu eruption took place. For this case, the release of volcanic gases and mainly carbon dioxide, seems to control the eruption process.

In the case of $CO₂$ efflux, the term of the equation (1) is the change with time of the diffuse degassing rate. The FFM graphical technique is based on an inverse representation of the characteristic parameter rate $(1/\Phi_{\rm CO_2})$ versus time. The volcanic eruption or seismic event time is found by simple extrapolation of the data set or linear fit towards the time axis. At this time the parameter would reach an infinite value.

In this work the FFM method was only successfully applied to the first anomalous $CO₂$ emission rate increase. To filter the external atmospheric influence in the time series, we used the difference between the predicted values by the MRA model and the observed (real) values of the $CO₂$ efflux time series. These differences can be negative if the data predicted by the MRA model is higher than the real value. The fluctuations in the residual data are essentially produced by variables which are not being measured in the automatic station; such as the deep contribution from the volcanic-tectonic environment of the island. This deep contribution in the negative residual data is negligible because it is considered to be completely explained in terms of the atmospheric and the soil parameters that have been monitored. Inspection of the residual data shows that the increase started on March 12th at 9:00 hours (Figure 10). The negative values were excluded from the analysis since they are completely explained in terms of the atmospheric parameters. Figure 10(B) depicts the inverse rate of $CO₂$ efflux data during the selected period toward the time axis. A least-squareslinear fit is extended toward the time axis showing an interception approximately on March 23 at 18:00 h, which means only three hours of delay with the occurrence of the magnitude 2.3 seismic event. These results suggest that the residually selected period of the $CO₂$ efflux time series obtained after MRA can be taken as a solution of the differential equation (1). The upper and lower 95% confidence limits of the linear fit are

Application of the FFM for the forecasting of the seismic events which occurred in and around El Hierro Island during 2004. (A) Residuals of the MRA for the March 8–23 period. (B) Inverse rate of the $CO₂$ efflux data during the selected time period toward the time axis. The upper and lower 95% confidence limits of the linear fit are also shown. Arrows indicate the interception of the linear fit and 95% confidence limits.

also shown in Figure $10(B)$. The interception of the confidence limits with the time axis allows us to compute a 95% confidence time interval of the interception between March 22, at 9:30 h and March 25, at 21:00 h.

3.3. Relation between Seismic Events and the Precursory $CO₂$ Efflux Signals

Figure 11(A) shows a plot of the time lag between the start of the anomalous increase in the $CO₂$ efflux and the occurrence of the seismic events versus the epicentral distances. An inverse correlation between both parameters is observed. Figure 11(B) offers a positive correlation between the maximum $CO₂$ efflux value measured at each precursory signal and the ratio Magnitude/Epicentral Distance (M/Ed) for each related seismic event. These results agree with the idea that the geochemical station should be more sensitive for closer and higher magnitude seismic events. TOUTAIN and BAUBRON (1999) did not observe a similar result when they studied the correlation between the amplitude of different geochemical precursors and the epicentral distance of earthquakes. A positive correlation between the time lag (difference between the start of the $CO₂$ efflux increase and the occurrence of the seismic events) and the ratio M/Ed is also observed (Fig. 11 (C)).

In the case of shorter epicentral distances and higher magnitude earthquakes, the increase in the $CO₂$ efflux should start earlier. However, no correlation was found between the duration of the precursory geochemical signal and the epicentral distance neither seismic magnitude. On the contrary, TOUTAIN and BAUBRON (1999) found a positive correlation between maximum duration of long-term anomalies and both magnitudes and epicentral distances.

Strain-induced vertical fluids flow might be the origin of these anomalous increases in the $CO₂$ efflux, as was proposed by KING (1978), for the soil radon anomalies found in the San Andreas fault. It has been widely accepted that fluids play an important role in the faulting mechanism (S_{HI} and WANG, 1984/85; SPICAK and HORALEK, 2001). Crustal discontinuities with relatively high vertical permeability are preferential paths for crustal and subcrustal gases to escape towards the surface. This fluid circulation could explain the release of seismic energy through the occurrence of seismicity some days or even hours after these observed increases in the $CO₂$ efflux. The deformation of the crust in the tectonic generation of an earthquake may force the fluids contained in the pores and fractures to move to different locations, sometimes increasing the gas concentration and its flux in a sensitive point (KING et al., 2006). This movement of chemical compounds may originate anomalous concentrations of that chemical specie, as was observed by TSUNOGAI and WAKITA (1995) for the disastrous magnitude 7.2 Kobe earthquake in 1995. The distance from the earthquake to the sensitive point has a direct relation with the time lag between the gas anomaly reaching the sensitive point and the quake, as can be observed in Figures 11(A) and (C) in the case described here. The greater deformation generated during the earthquake and the closer to the sensitive point, the greater this gas emission anomaly would be (Fig. 11B). Increasing the high pore pressure confined within a seismogenic zone can also enhance the stress concentration beneath a seismogenic layer. Similar phenomena were described by SALAZAR et al. (2002) at San Vicente volcano, El Salvador, Central America, where a significant increase in $CO₂$ efflux rate was mainly driven by strain changes prior to a 5.1 magnitude earthquake which occurred

b

Figure 11

(A) Plot of the time lag between the start of the anomalous increase in the $CO₂$ efflux and the occurrence of the seismic event, versus the epicentral distances, (B) maximum $CO₂$ efflux value measured at each anomalous increase versus the ratio magnitude/epicentral distance for each related seismic event and (C) time lag between the start of the anomalous increase in the $CO₂$ efflux and the occurrence of the seismic event versus the ratio magnitude/epicentral distance.

25 km away from the monitoring point and by PEREZ et al. (2006) where a significant CO₂ efflux increase was observed in an automatic geochemical station nine days before a short-time unrest occurred at San Miguel volcano, El Salvador.

However, remarks on the observed relation between seismicity and diffuse degassing at El Hierro island must be made because there are unsuccessfully explained facts regarding the results shown here:

— The absence of diffuse degassing precursors for the earthquakes occurred between April 15 and May 25. The short temporal window data at EHI01 geochemical station and the lack of information about the triggering mechanism of the earthquakes make it difficult to reach a satisfactory explanation regarding this absence of precursors. One possible explanation would result if the second increment of $CO₂$ registered at the geochemical station is considered as a precursor of this seismic swarm which occurred in May. It is important to note that at this moment there are not enough available data that allow us to build satisfactory relationships between diffuse degassing precursors and the volcano-tectonic environment of El Hierro Island.

— Although the results shown here indicate that diffuse degassing studies are promising tools for seismic monitoring studies, additional and more extensive studies are needed to validate the application of the FFM method to forecast a seismic event with the diffuse degassing studies. In fact, there are only such good results for the first earthquake of 2004 at El Hierro. The relatively low magnitude of the few earthquakes registered at El Hierro Island could be related to this unsuccessful approach.

4. Conclusions

Four significant increases in the diffuse $CO₂$ emission rate were observed few hours before various seismic events which occurred during 2004 in and around El Hierro Island. The results obtained after the application of MRA to the time series which were recorded at the automatic geochemical station EHI01, and the successful application of the FFM model to forecast the first seismic event, together with the correlation observed between the four anomalous increases with the magnitudes and epicentral distances of the seismic events, seem to indicate a close relationship between the diffuse $CO₂$ efflux and the seismicity which occurred in and around El Hierro Island. Although short-temp fluctuations in the diffuse $CO₂$ emission at the observation site are partially driven by meteorological parameters, the main $CO₂$ efflux changes were not driven by fluctuations

of meteorological variables such as wind speed or barometric pressure and seem clearly to be associated with fluid pressure fluctuations in the volcanic system. Intrusion of fluids and its migration through porous rocks might cause changes in pore pressure and trigger the seismicity. These results demonstrated the potential of applying continuous monitoring of soil $CO₂$ efflux to improve and optimize the detection of early warning signals of future seismic events at El Hierro as well as in other active volcanic systems. Further observations are needed to verify the existence of a close relationship between the diffuse $CO₂$ emission rate and the occurrence of earthquakes.

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