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High time resolution fluctuations in volcanic carbon dioxide degassing from Mount Etna - [DOI: 10.1016/j.jvolgeores.2013.11.014](https://doi.org/10.1016/j.jvolgeores.2013.11.014)

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12
13 **Abstract** - We report here on the first record of carbon dioxide gas emission rates from a
14 volcano, captured at ≈ 1 Hz. These data were acquired with a novel technique, based on the
15 integration of UV camera observations (to measure SO₂ emission rates) and field portable gas
16 analyser readings of plume CO₂/SO₂ ratios. Our measurements were performed at the North
17 East crater of Mount Etna, southern Italy, and the data reveal strong variability in CO₂
18 emissions over timescales of tens to hundreds of seconds, spanning two orders of magnitude.
19 This carries important implications for attempts to constrain global volcanic CO₂ release to
20 the atmosphere, and will lead to an increased insight into short term CO₂ degassing trends. A
21 common oscillation in CO₂ and SO₂ emission rates in addition to the CO₂/SO₂ ratios was
22 observed at periods of ≈ 89 s. Our results are furthermore suggestive of an intriguing
23 temporal lag between oscillations in CO₂ emissions and seismicity at periods of $\approx 300 - 400$
24 s, with peaks and troughs in the former series leading those in the latter by ≈ 150 s. This work

25 opens the way to the acquisition of further datasets with this methodology across a range of
26 basaltic systems to better our understanding of deep magmatic processes and of degassing
27 links to manifest geophysical signals.

28 **Carbon Dioxide; Passive Degassing; Volcanic remote sensing; Plume imaging; Volcano**
29 **seismology;**

30 **1. Introduction**

31 Carbon dioxide (CO₂) is among the most abundant constituents of volcanic gases (Carroll and
32 Holloway, 1994), and exsolves from magmas deeper than other common volatiles such as
33 sulphur dioxide (SO₂) and water vapour (H₂O) (Giggenbach, 1996). Knowledge of CO₂
34 emissions can therefore contribute significantly to our understanding of the movement of
35 magmas in deep volcanic plumbing systems. Hitherto, the measurement of CO₂ emission
36 rates has been challenging due to the difficulty of resolving volcanogenic CO₂ above high
37 background atmospheric levels. In consequence, attempts to routinely measure plume CO₂
38 emission rates, particularly at high time resolution, have been rather limited (Aiuppa et al.,
39 2006; 2010). Therefore, notwithstanding the significant contributions made in constraining
40 CO₂ emission rates of volcanic plumes at targets such as Mt. Erebus, Antarctica (Wardell et
41 al., 2004), Ol Doi Nyio Lengai, Tanzania (Koepnick et al., 1996), White Island, New Zealand
42 (Werner et al., 2008), Ruapehu, New Zealand (Werner et al., 2006), Redoubt, Alaska
43 (Werner et al., 2012a; 2012b), Stromboli, Italy (Aiuppa et al., 2010; 2011), Mt. Etna, Italy
44 (Allard, 1991) and Kilauea, USA (Poland et al., 2012), these data remain relatively spartan,
45 and in general lack information regarding temporal changes. This remains a fundamental
46 weakness in attempts to constrain global volcanogenic CO₂ emission rate budgets, in view of
47 which there is a pressing demand for the development and application of novel

48 methodologies to improve constraints on spatio-temporal volcanic CO₂ degassing and our
49 comprehension of volcanic systems.

50

51 Recently, the Multi-GAS technique (Shinohara, 2005; Aiuppa et al., 2005) has been
52 pioneered to enable rapid measurements of volcanic plume chemical compositions, including
53 CO₂/SO₂ gas ratios, leading to significant advances in our understanding of degassing
54 processes. Furthermore, in the last years, UV camera imagery has been applied in
55 volcanology, enabling acquisition of SO₂ emission rates with time resolutions of ≈ 1 Hz,
56 many orders of magnitude faster than possible in the past (e.g., Mori and Burton, 2006;
57 Tamburello et al., 2011a). Here we report on the first volcanic deployment of a novel
58 technique, by which volcanic CO₂ emission rates are captured with an acquisition frequency
59 of ≈ 1 Hz, based on the integration of the above two approaches. Such a capability will
60 increase the future potential of linking degassing to geophysical data on unprecedented
61 timescales with significant applicability in improving hazard analysis (Gerlach et al., 2002)
62 and eruption forecasting measures (Aiuppa et al., 2007; Poland et al., 2012).

63

64 The CO₂ emission rate data were captured during a field campaign on Mt. Etna (37.734°N,
65 15.004°E), an alkaline strato-volcano whose CO₂-rich magmas (Spilliaert et al., 2006) result
66 in the volcano being the largest time averaged contributor to global volcanic emissions of
67 CO₂ (Allard et al., 1991; Gerlach 1991). Etna currently has four degassing summit areas: the
68 South-East crater (SEC), the Central Craters (Bocca Nuova and Voragine), and the North-
69 East crater (NEC) (Fig. 1). Our study is based on passive emissions from the NEC, in recent
70 times one of the most actively degassing vents on Etna (Aiuppa et al., 2008) and the site of
71 recurrent eruptive activity in the last few decades (Allard et al., 2006).

72

73 2. Methodology

74 The SO₂ emission rates were captured using two Apogee Alta U260 cameras, fitted with 16
75 bit 512 x 512 pixel Kodak KAF-0261E thermo-electrically cooled CCD array detectors. A
76 Pentax B2528-UV lens of $f = 25$ mm was attached to the front of each camera, providing \approx
77 24° field of view. The lenses were fitted with filters of 10 nm FWHM (Asahi Bunko Inc.),
78 one centred around 310 nm, where plume SO₂ absorbs incident UV radiation, and the other at
79 330 nm, where no such absorption occurs. Qualitative plume absorbances captured in the
80 camera plume images were converted to column amounts via a calibration procedure
81 involving four quartz cells containing known SO₂ column amounts: 100, 200, 1000, 2000
82 ppm m; SO₂ values within the plume were always within this range. The calibrations were
83 performed at the time of measurement, by viewing clear sky adjacent to the plume, resulting
84 in R^2 values > 0.99 for the linear fitting. As the measurement conditions were favourable:
85 e.g., the plume was transparent, the background sky was cloudless and the plume was < 4 km
86 distant, additional DOAS based calibrations were not performed, as there is an excellent
87 match between DOAS and cell based calibrations under such conditions (Lübcke et al.,
88 2013). Under such circumstances we speculate that the measurement error was low, however,
89 as radiative transfer has yet to become a routinely considered element of UV camera
90 retrievals it is hard to provide an exact error budget in this case (e.g., Kern et al., 2009). For
91 full details on all data capture, retrieval and calibration procedures please see Kantzas et al.,
92 (2010). All of these protocols were executed using the Vulcamera code (Tamburello et al.,
93 2011b).

94

95 The UV camera was located at the Pizzi Deneri observatory which provided a clear vantage
96 point of the NEC plume, at a distance of ≈ 2 km (Fig. 1); the data were acquired between
97 08:45 and 09:45 GMT on the 12th of September 2012. Integrated column amount (ICA)

98 values were determined by summing SO₂ concentrations over the plume profile,
99 perpendicular to its transport vector (Fig. 1). The emission rates (kg s⁻¹) were then found by
100 multiplying ICAs by the plume transport speed, with the latter arising from cross-correlation
101 analysis of the propagation of the plume across the field of view over a sequence of camera
102 images (e.g. see McGonigle et al., 2005; Williams-Jones et al., 2006). The plume speed
103 varied very little over the acquisition period ($\approx 13.4 \text{ m s}^{-1}$ throughout). The camera capture
104 rate ranged between 0.5-1 Hz depending upon incident light levels, hence linear interpolation
105 was applied, where necessary, to produce a uniform 1 Hz SO₂ emission rates dataset.

106

107 The CO₂/SO₂ degassing ratios of the NEC were measured with a field portable Multi-GAS
108 unit (Shinohara, 2005; Aiuppa et al., 2005) located $\approx 100 \text{ m}$ downwind of the crater's vent, at
109 a site chosen to avoid signal contamination from low-temperature fumarolic discharges
110 (Shinohara et al., 2008). This unit extractively sampled the plume gases, providing CO₂ and
111 SO₂ concentration readings at $\approx 0.5 \text{ Hz}$ measurement frequency. The SO₂ concentrations
112 were measured with an electrochemical sensor (City Technology, sensor type 3ST/F), of
113 calibration range 0-200 ppm, and manufacturer quoted accuracy of $\pm 2\%$, repeatability of 1%
114 and a resolution of 0.5 ppmv. The CO₂ concentrations were measured with an infrared sensor
115 (Edinburgh Instruments, Gascard II), of 0-3000 ppmv range, and with an accuracy $\pm 2\%$ and
116 a resolution of 0.8 ppmv. Prior to the campaign, the Multi-GAS sensors were calibrated in the
117 laboratory using standard gas cylinders of concentrations within the sensor ranges (e.g., 10
118 and 100 ppm SO₂ and 3,000 ppm CO₂; all in nitrogen matrixes) and gas mixtures
119 corresponding approximately to plume conditions (e.g., 10-30 ppm SO₂ in air; e.g., with 380-
120 900 ppm CO₂). Pure nitrogen was used as zero reference in each case. These laboratory
121 characterisations confirmed a typical measurement error in the CO₂/SO₂ ratios of $\leq 15\%$.

122

123 An additional calibration test was performed to measure the response characteristics of the
124 Multi-GAS sensors to rapid changes in gas fumigation, under the range of conditions we
125 encountered during our field study. This was achieved by connecting three gas bottles of the
126 following compositions: 79% N₂, 21% O₂ (e.g., the eluent); 79% N₂, 21% O₂, 3010 ppm
127 CO₂; 79% N₂, 21% O₂, 100 ppm SO₂, via regulators to the Multi-GAS inlet, to provide an
128 overall flow rate of 1.2 l min⁻¹ into the instrument (e.g., as is typically the case for Multi-GAS
129 field sampling). Firstly, the typical plume conditions were mimicked by setting the eluent
130 flux to 0.72 l min⁻¹, and the CO₂ and SO₂ bottle fluxes to 0.24 l min⁻¹ each, which led to gas
131 concentrations at the sensor of 615 ppm and 20.4 ppm, respectively, for CO₂ and SO₂. The
132 registered Multi-GAS ratios for such conditions are shown in Fig. 2 for $t < 70$ s and $t > 130$ s,
133 leading to corresponding ratio errors of $< 5\%$. We also simulated rapid increases and
134 decreases in gas concentration at the sensor ($t \approx 80$ s, 125 s; Fig. 2) to correspond to those we
135 observed in the field, both in terms of timescale and magnitude, corresponding to the arrival
136 and departure of more intense volcanogenic gas parcels. This was achieved by switching the
137 eluent flux to/from 0.5 l min⁻¹ and the CO₂ and SO₂ fluxes concurrently to/from 0.35 l min⁻¹,
138 altering the concentrations to/from 29 ppm and 878 ppm, respectively for SO₂ and CO₂. As
139 shown in Fig. 2, the ratio in error remained within $\pm 15\%$ during these transitions, confirming
140 the ability of the Multi-GAS to respond rapidly to these changes in plume fumigation, given
141 typical $t_{90\%}$ values of ≈ 10 s for both the Multi-GAS SO₂ and CO₂ sensors ($t_{90\%}$ corresponds to
142 the time between standard gas injection and the instrumental signal reaching 90% of the
143 plateau value). Hence, this provides confidence that any field observed changes in gas ratios
144 could not be artefacts of differing instrumental response times. Indeed, Fig 3b shows a
145 zoomed section of the acquired Multi-GAS time-series showing the similar response
146 characteristics of the two sensors to volcanogenic changes in the concentrations of both
147 species. Atmospheric background CO₂ values were determined by plotting raw CO₂ values

148 with SO₂ on a scatter plot. The intercept of the regression line with the axis is taken as the
149 background level, in this case a value of ≈ 200 ppm. Temporal synchronicity with the UV
150 camera SO₂ emission rate data series, throughout the one hour observation period, was
151 ensured by time referencing both instruments' data series with GPS receiver outputs. Linear
152 interpolation was applied to the Multi-GAS ratio data to temporally match these data to the 1
153 Hz UV camera SO₂ emission rates.

154

155 The ICA determination for the NEC SO₂ emission rate calculation was made ≈ 180 m
156 downwind of the GPS receiver geo-referenced multi-GAS measurement location. The UV
157 camera derived plume speeds were then used to derive temporal lags between the gas
158 emission rate and gas ratio time series (≈ 13 s throughout the acquisition), enabling shifting
159 of the series relative to one another by this lag value to account for the slight offset between
160 the plume locations viewed/sampled by the two techniques. This procedure provided
161 excellent overlap between peaks and troughs in the gas concentration and emission rate series
162 as the volcanogenic source signal fluctuated (Fig. 3b) and also serves to offset the small
163 Multi-GAS sensor lag. A lag of ≈ 13 s is also achieved when cross-correlating the UV camera
164 SO₂ emission rate with Multi-GAS SO₂ readings, further corroborating our procedure.

165

166 **3. Results and Discussion**

167 The acquired NEC Multi-GAS CO₂ vs. SO₂ concentrations are plotted in Fig. 3a,
168 demonstrating a general trend (with a mean molar ratio of 0.5 ± 0.07 , based on the largest, e.g.,
169 $\pm 15\%$, uncertainty encountered during our laboratory sensor characterisations) between
170 emissions of the two species, with the exception of large spikes in CO₂ emissions within the
171 shaded grey oval. Since the Multi-GAS measurement location was chosen with great care to
172 completely avoid fumarolic discharges, we exclude the possibility that this feature could arise

173 from contamination by these sources. Given that these spikes were also closely temporally
174 aligned to peaks in seismicity, the source of which was located under the NEC at the time of
175 measurements, as discussed further below, this is also suggestive that these trends were
176 indeed related to activity at the NEC.

177

178 Each molar CO₂/SO₂ gas ratio datum (Fig. 3d), was converted to a mass ratio on the basis of
179 the species' relative molecular weights and then multiplied by the temporally coincident SO₂
180 emission rate (Fig. 3f) to deliver the CO₂ emission rate time series shown in Fig. 3e,
181 demonstrating significant variability in emissions, spanning two orders of magnitude (from ≈
182 0.1 to 12 kg s⁻¹), over timescales of tens to hundreds of seconds. These fluxes are subject to
183 errors of ±15% arising from the gas ratios, on the basis of our aforementioned experimental
184 characterisations, however errors arising from the SO₂ fluxes are not considered here for the
185 reasons detailed above. This observation of fluctuation in CO₂ degassing, in tandem with our
186 reported methodology, has the potential to add to our understanding of CO₂ degassing trends
187 and of their importance in volcanic loading of the atmosphere.

188

189 The acquisition averaged NEC CO₂/SO₂ molar ratio of 0.5±0.07 was low although not
190 unusual for this crater, where the degassing activity is often sourced by more evolved (e.g.,
191 more volatile-depleted) magmas than those supplying the central craters' (CCs) plumes
192 (Aiuppa et al., 2006; 2008). Likewise, the mean NEC CO₂ emission rate and SO₂ emission
193 rates captured in our dataset were also rather low, although not unprecedentedly so: at 2 kg s⁻¹
194 and 6 kg s⁻¹, respectively. On the day of the measurements the majority of Etna's degassing
195 arose from the CCs, with combined Voragine and Bocca Nuova CO₂ and SO₂ emission rates
196 of 86 kg s⁻¹ and 14 kg s⁻¹, respectively; these data were acquired by us with our Multi-GAS
197 and UV camera unit and are consistent with previous evaluations (e.g., Aiuppa et al., 2008).

198 Whilst this NEC contribution was only a fraction of Etna's gas budget, these observations do
199 provide the opportunity, for the first time, to characterise the short term CO₂ degassing
200 behaviour of an active volcano, and any periodicities observed therein. Studying this
201 behaviour for the other craters will be a key target of future work.

202

203 Periodicity in SO₂ release, on short timescales, has been reported from a few volcanoes
204 worldwide (e.g., Boichu et al., 2010; Nadeau et al., 2011; Tamburello et al., 2012, 2013).

205 Periodicity was investigated in our CO₂, SO₂ and contemporaneous geophysical data using a
206 continuous Morlet wavelet transform technique (see Fig. 4). This approach involves scaling a
207 defined oscillation (a Morlet wavelet), and mathematically assessing similarities between the
208 acquired data and the scaled wavelet. This signal processing technique is often used in the
209 analysis of environmental processes due to its effectiveness in detecting natural oscillations
210 (Morlet et al., 1982), such as climatic variability (Jevrejeva et al., 2003). This technique is
211 preferred to other time series analysis as information is gleaned on the stability of
212 periodicities present at a given time. Given the duration of our acquisition, the longest
213 resolvable oscillation period via this analysis was 512 s according to the Nyquist theorem
214 (Nyquist, 2002), hence the plots in Fig. 4 are cropped accordingly.

215

216 Fig. 4 shows non-stationary degassing behaviour in the NEC CO₂ and SO₂ Morlets with
217 characteristic periodicities between \approx 40-500 s. Oscillations in this period range are also
218 apparent in Morlet analysis of contemporaneously acquired seismic data (Fig. 4d). The
219 dominant modulation frequencies in the degassing data were assessed with power spectral
220 densities (PSDs) using Welch's method (Welch, 1967), applied after normalization of the
221 data. The resultant periodograms show the power of manifest oscillations across this period
222 range (see Fig. 4), revealing the dominant peak for CO₂ emission rates at \approx 89 s; a peak

223 matching this period is also evident in the SO₂ data, and the dominant peak in CO₂/SO₂ ratios
224 also falls here (≈ 85 s). The latter result strongly implies that the observed non-stationary
225 degassing signals are indeed volcanogenic in origin and not an artefact of atmospheric
226 transport processes which would not generate any modulation in sampled gas ratios.
227 Furthermore, the presence of the ≈ 89 s signal in both CO₂ and SO₂ emission rate PSDs
228 suggests that a common source process is generating the periodicity in both cases.

229

230 There are many physical processes which could potentially drive the observed modulations in
231 gas emission rates and ratios. These include: (1) convection of magma in the conduit and/or
232 the shallow to deep plumbing system (Kazahaya et al., 1994; Boichu et al., 2010); as
233 convection is likely a non-stationary process, this could involve varying overturn rate, leading
234 to modulation in gas release; (2) pulsatory supply of volatile rich magmas into the conduit; on
235 Mt. Erebus, this has been proposed to introduce a consequent periodicity in emissions at the
236 magma surface (Oppenheimer et al., 2009); (3) changes in the volatile content of the magma
237 or supply of volatiles from depth (Kazahaya et al., 2002), in which depressurisation based
238 exsolution of gases from the melt could, itself, lead to a periodicity in gas sourcing; (4) short
239 to long term changes in rheology of the magma (Koyaguchi et al., 1993); such trends in
240 magma viscosity would act to vary gas transit speed throughout the plumbing system; and (5)
241 interaction of magma and entrained volatiles with geometric discontinuities in the conduit or
242 shallow storage zones (James et al., 2006; Palma et al., 2011); such features could cause
243 periodic collection and release of bubbles, by analogy with the collapsing foam model for
244 strombolian activity (Jaupart and Vergnolle, 1988; Vergnolle and Brandeis, 1994). Further
245 work based on an expanded dataset is now required to investigate, in more detail, the
246 relevance of each of these models in this volcanic context, by assessing the variation and
247 stability of emission rate periodicities in time and their links to geophysical signals.

248

249 In the context of this study we investigated the relationship between periodicities manifested
250 in the various captured datasets. This was achieved by correlating the coefficients produced
251 by the Morlet wavelet analysis for the CO₂ and SO₂ emission rate and seismic data (Fig. 5), in
252 order to establish the degree to which oscillations at a particular period demonstrated
253 common strength and phase between the series. This is preferable to correlating the raw
254 signals as it eliminates rapid variability, hence more clearly resolves where dominant
255 fluctuations are shared across the data streams. There is a clear link between the periodicities
256 present in CO₂ and SO₂ emissions up to ≈ 250 s where the link breaks down for around 50 s,
257 before resuming, then peaking at ≈ 500 s (Fig. 5a). Note that discussion of a possible gas-
258 infrasonic relationship is not included here as any link, if present, was obscured by high wind
259 pollution in the acoustic dataset. The seismic vs. CO₂ emission rate analysis reveals an
260 intriguing negative correlation (< -0.5 ; Fig. 5b) for periods between 300 and 400 s, which
261 corresponds to the period range where the relationship between CO₂ and SO₂ emissions
262 breaks down (Fig. 5a).

263

264 This anti-correlation is suggestive of a possible temporal lag between oscillations at these
265 frequencies in the seismic and CO₂ emission rate series, which we investigated further by
266 performing, each second, a mathematical integration of the Morlet coefficients, between 300
267 and 400 s for the seismic, CO₂/SO₂ and CO₂ emission rate series, to generate the output
268 shown in Fig. 6b. These three traces all show distinctive peaks between $\approx 08:50$ and $\approx 09:00$
269 GMT, e.g., the time intervals shaded grey in Figs. 3 and 6, where elevated wavelet
270 coefficients in this period range (Figs. 4a, b and d) demonstrated strong oscillations therein,
271 and the CO₂/SO₂ ratios spikes to high values (Fig. 3a). The two gas peaks in the shaded area
272 of Fig. 6b preceded those in the seismic record by 100-150 s, and indeed, moving forward the

273 seismic record in time by 125 s and correlating led to a correlation coefficient of ≈ 0.9 in this
274 time window. Therefore, given the absence of any seismic events prior to these gas spikes,
275 this could well imply the existence of a process causing elevated CO₂ emissions to be
276 released from the vent some 150 s prior to peaks in seismicity. Transit time of gas from the
277 source to measurement location is < 30 s. Our observations might also be indicative of a
278 model of quite the opposite nature, in that a small NW displacement in tremor location
279 occurred at a depth of ≈ 500 -1000 m between $\approx 09:10$ - 09:15 (Personal Communication,
280 Giuseppe Di Grazia, INGV), is followed by several large peaks in gas emissions, ≈ 500 -900 s
281 later, which corresponds to realistic travel times for gas rise from such depths (Manga, 1996).

282
283 Regardless of the possible lag direction, a mechanism involving the movement of magma
284 and/or entrained volatiles, induced by changes in pressure or temperature, could be invoked.
285 Peaks in the gases' CO₂/SO₂ ratios could be caused by a deeper than average pressure base
286 i.e. a greater source depth. A system-wide increase in temperature could also drive a long-
287 term increase in ratios by facilitating the transport of volatiles from depth; a localised
288 temperature increase, through injection of fresh magma, might also therefore, in theory,
289 temporarily reproduce the same effect. Each of these processes could generate seismicity, due
290 to migration of magmas and/or volatiles, followed by elevated gas emissions. An opposite
291 hypothesis could involve a model based on readjustment of the magma level, with
292 corresponding seismic energy generation, following release of gases at the surface. These
293 tentative hypotheses, based on our initial observations, are presented as avenues for future
294 work, in which longer datasets are required to further investigate the direction of any
295 manifest lag between seismic and degassing data, with a view to better characterising the
296 associated underground magmatic processes.

297

298 **4. Concluding Remarks**

299 Here we report for the first time the combined use of a field portable Multi-GAS sensor and
300 UV camera imaging to produce a high time resolution (≈ 1 Hz) volcanic CO₂ emission rate
301 dataset, in this case from Mt. Etna's North East crater. The development of such a
302 methodology has significant implications for the study of short and long term degassing
303 trends and improved integration between degassing and geophysical datasets. We
304 demonstrate that CO₂ emissions are highly variable, spanning two orders of magnitude, on
305 timescales of tens to hundreds of seconds. This technique is therefore significant in respect of
306 attempts to assess global volcanogenic CO₂ emission rates. We furthermore establish that
307 both the CO₂ emission rates and SO₂ emission rates, in addition to the CO₂/SO₂ ratios, exhibit
308 prominent common periodicities at ≈ 89 s and that our results are suggestive of an intriguing
309 lag between CO₂ and seismic oscillations, with periods of around 300 – 400 s, possibly
310 indicative of a process involving the movement of magma in the conduit. This work paves the
311 way for further high time resolution investigations into degassing of CO₂ at Mount Etna and
312 other basaltic volcanoes worldwide to expand our understanding of degassing dynamics and
313 links to manifest geophysical signals.

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323 **References**

324 Aiuppa, A., Federico, C., Paonita, A., Giudice, G., Valenza, M., 2005. Chemical mapping of
325 a fumarolic field: La Fossa Crater, Vulcano Island (Aeolian Islands, Italy). *Geophys. Res.*
326 *Lett.* 13 (L13309), doi:10.1029/2005GL023207

327 Aiuppa, A., Federico, C., Giudice, G., Gurrieri, S., Liuzzo, M., Shinohara, H., Favara, R.,
328 Valenza, M., 2006. Rates of carbon dioxide plume degassing from Mount Etna volcano. *J.*
329 *Geophys. Res.* 111 (B09207), doi:10.1029/2006JB004307

330 Aiuppa, A., Moretti, R., Federico, C., Giudice, G., Gurrieri, S., Liuzzo, M., Papale, P.,
331 Shinohara, H., Valenza, M., 2007. Forecasting Etna eruption by real time evaluation of
332 volcanic gas composition. *Geology* 35 (12), 1115-1118

333 Aiuppa, A., Giudice, G., Gurrieri, S., Liuzzo, M., Burton, M., Caltabiano, T., McGonigle, A.
334 J. S., Salerno, G., Shinohara, H., Valenza, M., 2008. Total volatile flux from Mount Etna,
335 *Geophys. Res. Lett.* 35 (L24302), doi:10.1029/2008GL035871

336 Aiuppa, A., Burton, M., Caltabiano, T., Giudice, G., Guerrieri, S., Liuzzo, M., Mure, F.,
337 Salerno, G., 2010. Unusually large magmatic CO₂ gas emissions prior to a basaltic paroxysm,
338 *Geophys. Res. Lett.* 37 (L17303), doi:10.1029/2010GL043837

339 Aiuppa, A., Burton, M., Allard, P., Caltabiano, T., Giudice, G., Gurrieri, S., Liuzzo, M.,
340 Salerno, G., 2011. First observational evidence for the CO₂-driven origin of Stromboli's
341 major explosions. *J. Geophys. Res-Sol. Ea.* 2 (2), 135-142, doi :10.5194/se-2-135-2011

342 Allard, P., Carbonnelle, J., Dajlevic, D., Le Bronec, J., Morel, P., Robe, M. C., Maurenas, J.
343 M., Faivre-Pierret, R., Martin, D., Sabroux, J.C., Zettwoog, P., 1991. Eruptive and diffuse
344 emissions of CO₂ from Mount Etna. *Nature* 351, 387-391

345 Allard, P., Behncke, B., D'Amico, S., Neri, M., Gambino, S., 2006. Mount Etna 1993-2005:
346 Anatomy of an evolving eruptive cycle. *Earth-Sci. Rev.* 78, 85-114

347 Boichu, M., Oppenheimer, C., Tsanev, V., Kyle, P., 2010. High temporal resolution SO₂ flux
348 measurements at Erebus volcano, Antarctica. *J. Volcanol. Geotherm. Res.* 190, 325-336

349 Caltabiano, T., Burton, M., Giammanco, S., Allard, P., Bruno, N., Murè, F., Romano, R.,
350 2004. Volcanic gas emissions from the summit craters and flanks of Mt. Etna, 1987– 2000.
351 In: Bonaccorso, A., Calvari, S., Coletelli, M., Del Negro, C., Falsaperla, S. (Eds.), *Mt. Etna:*
352 *Volcano Laboratory*. AGU, Washington, D. C., pp. 111-128

353 Carroll, M. R., Holloway, J. R., (Eds.) 1994. *Volatiles in Magmas*. Mineralogical Society of
354 America *Reviews in Mineralogy* 30, Washington, D. C.

355 Gerlach, T. M., 1991. Present-day CO₂ emissions from volcanoes. *EOS Trans. AGU* 72
356 (249), 254-255

357 Gerlach, T. M., McGee, K. A., Elias, T., Sutton, A. J., Doukas, P., 2002. Carbon dioxide
358 emission rate of Kilauea Volcano: Implications for primary magma and the summit reservoir.
359 *J. Geophys. Res.* 107 (B9), 2189, doi:10.1029/2001JB000407

360 Giggenbach, W. F., 1996. Chemical composition of volcanic gases. In: Scarpa, R., Tilling, R.
361 I. (Eds.), *Monitoring and Mitigation of Volcanic Hazards*. Springer, New York, pp. 221-256

362 James, M. R., Lane, S. J., Chouet, B. A., 2006. Gas slug ascent through changes in conduit
363 diameter: Laboratory insights into a volcano-seismic source process in low-viscosity
364 magmas. *J. Geophys. Res.* 111 (B05201), doi:10.1029/2005JB003718

365 Jaupart, C., Vergnolle, S., 1988. Laboratory models of Hawaiian and Strombolian eruptions.
366 *Nature* 331, 58-60

367 Jevrejeva, S., Moore, J. C., Grinsted, A., 2003. Influence of the Arctic Oscillation and El
368 Niño-Southern Oscillation (ENSO) on ice conditions in the Baltic Sea: The wavelet
369 approach. *J. Geophys. Res. Atm.* 108 (D21), doi:10.1029/2003JD003417

370 Kantzas, E.P., McGonigle, A. J. S., Tamburello, G., Aiuppa, A., Bryant, R. G., 2010.
371 Protocols for UV camera volcanic SO₂ measurements. *J. Volcano. Geotherm. Res.* 194, 55-60

372 Kazahaya, K., Shinohara, H., Saito, G., 1994. Excessive degassing of Izu-Oshima volcano:
373 magma convection in a conduit. *B. Volcanol.* 56, 207-216

374 Kazahaya, K., Shinohara, H., Saito, G., 2002. Degassing process of Satsuma-Iwojima
375 volcano, Japan: Supply of volatile components from a deep magma chamber. *Earth Planets
376 Space* 54, 327-335

377 Kern, C., Deutschmann, T., Vogel, L., Wöhrbach, M., Wagner, T., Platt, U. 2009. Radiative
378 transfer corrections for accurate spectroscopic measurements of volcanic gas emissions. *B.
379 Volcanol.* 72, 233-247, doi: 10.1007/s00445-009-0313-7

380 Koepenick, K., Brantley, S., Thompson, J., Rowe, G., Nyblade, A., Moshy, C., 1996. Volatile
381 emissions from the crater and flank of Oldoinyo Lengai volcano, Tanzania. *J. Geophys. Res.*
382 10, 13,819-13,830

383 Koyaguchi, T., Hallworth, M. A., Huppert, H. E., 1993. An experimental study on the effects
384 of phenocrysts on convection in magmas. *J. Volcan, Geotherm. Res.* 55, 15-32

385 Lübcke, P., Bobrowski, N., Illing, S., Kern, C., Alvarez Nieves, J. M. Vogel, L., Zielcke, J.,
386 Delgado Granados H., Platt, U., 2013. On the absolute calibration of SO₂ cameras. *Atmos.*
387 *Meas. Tech.* 6, 677-696, doi:10.5194/amt-6-677-2013

388 Manga, M., 1996. Waves of bubbles in basaltic magmas and lavas. *J. Geophys. Res.* 101
389 (B8), 17,457-17,465

390 McGonigle, A. J. S., Hilton, D. R., Fischer, T. P., Oppenheimer, C., 2005. Plume velocity
391 determination for volcanic SO₂ flux measurements. *Geophys. Res. Lett.* 32 (L11302),
392 doi:10.1029/2005GL022470

393 Mori, T., Burton, M., 2006. The SO₂ camera: a simple, fast and cheap method for ground-
394 based imaging of SO₂ in volcanic plumes. *Geophys. Res. Lett.* 33 (L24804),
395 doi:10.1209/2006GL027916

396 Morlet, J., Arens, G., Fougéau, E., Giard, D., 1982. Wave propagation and sampling theory;
397 Part I, Complex signal and scattering in multilayered media. *Geophysics* 47 (2), 203-221

398 Nadeau, P.A., Palma, J. L., Waite, G. P., 2011. Linking volcanic tremor, degassing, and
399 eruption dynamics via SO₂ imaging. *Geophys. Res. Lett.* 38 (L01304),
400 doi:10.1029/2010GL045820

401 Oppenheimer, C., Lomakina, A. S., Kyle, P. R., Kingsbury, N. G., Boichu, M., 2009.
402 Pulsatory magma supply to a phonolite lava lake. *Earth Planet. Sci. Lett.*, 284, 392-398

403 Nyquist, H., 2002. Certain topics in telegraph transmission theory (Reprinted from
404 Transactions of the A. I. E. E., February, pg 617-644, 1928). Proceedings I. E. E. E. 90 (2),
405 280-305, doi:10.1109/5.989875

406 Palma, J. L., Blake, S., Calder, E. S., 2011. Constraints on the rates of degassing and
407 convection in basaltic open-vent volcanoes. *Geochem. Geophys. Geosy.* 12 (11),
408 doi :10.1029/2011GC003715

409 Poland, M. P., Miklius, A., Sutton, A. J., Thornber, C. R., 2012. A mantle-driven surge in
410 magma supply to Kilauea Volcano during 2003-2007. *Nat. Geosci.* 5 (4), 295-297,
411 doi:10.1038/NGEO1426

412 Shinohara, H., 2005. A new technique to estimate volcanic gas composition: Plume
413 measurements with a portable multi-sensor system. *J. Volcanol. Geotherm. Res.* 143, 319–
414 333.

415 Shinohara, H., Aiuppa, A., Giudice, G., Gurrieri, S., Liuzzo, M., 2008. Variation of H₂O/CO₂
416 and CO₂/SO₂ ratios of volcanic gases discharged by continuous degassing of Mount Etna
417 volcano, Italy. *J. Geophys. Res* 113 (B09203), doi:10.1029/2007JB005185

418 Spilliaert, N., Allard, P., Métrich, N., Sobolev, A. V., 2006. Melt inclusion record of the
419 conditions of ascent, degassing, and extrusion of volatile-rich alkali basalt during the
420 powerful 2002 flank eruption of Mount Etna (Italy). *J. Geophys. Res.* 111 (B04203),
421 doi:10.1029/2005JB003934

422 Tamburello, G., Kanzas, E. P., McGonigle, A. J. S., Aiuppa, A., 2011a. Recent advances in
423 ground-based ultraviolet remote sensing of volcanic SO₂ fluxes. *Ann. Geophys.* 54 (2), 199-
424 208

425 Tamburello, G., Kantzas, E. P., McGonigle, A. J. S., Aiuppa, A., 2011b. Vulcamera: a
426 program for measuring volcanic SO₂ using UV cameras. *Ann. Geophys.* 54 (2), 219-221

427 Tamburello, G., Aiuppa, A., Kantzas, E.P., McGonigle, A. J. S., Ripepe, M., 2012. Passive
428 vs. active degassing modes at an open-vent volcano (Stromboli, Italy). *Earth and Planetary
429 Science Letters* 359-360, 106-116

430 Tamburello, G., Aiuppa, A., McGonigle, A. J. S., Allard, P., Cannata, A., Giudice, G.,
431 Kantzas, E.P., Pering, T. D., 2013. Periodic volcanic degassing behaviour: The Mount Etna
432 example. *Geophys. Res. Lett.* 40 (1-5), doi:10.1002/grl.50924

433 Vergnolle, S., Brandeis, G., 1994. Origin of the sound generated by Strombolian explosions.
434 *J. Geophys. Res.* 21, 1959-1962

435 Wardell, L. J., Kyle, P.R., Chaffin, C., 2004. Carbon dioxide and carbon monoxide emission
436 rates from an alkaline intra-plate volcano: Mt. Erebus, Antarctica. *J. Volcan. Geotherm. Res.*
437 131 (1-2), 109-121

438 Welch, P.D., 1967. The Use of Fast Fourier Transform for the Estimation of Power Spectra:
439 A Method Based on Time Averaging Over Short, Modified Periodograms. *IEEE Transactions
440 on Audio Electroacoustics* AU-15 (2), 70-73

441 Werner, C., Christenson, B.W., Hagerly, M., Britten, K., 2006. Variability of volcanic gas
442 emissions during a crater lake heating cycle at Ruapehu Volcano, New Zealand. *J. Volcan.
443 Geotherm. Res.* 154 (3-4), 291-302

444 Werner, C., Hurst, T., Scott, B., Sherburn, S., Christenson, B. W., Britten, K., Cole-Baker, J.,
445 Mullan, B., 2008. Variability of passive gas emissions, seismicity, and deformation during
446 crater lake growth at White Island Volcano, New Zealand, 2002-2006. *J. Geophys. Res-Sol.
447 Ea.* 113 (B1), doi:10.1029/2007JB005094

448 Werner, C., Evans, W. C., Kelly, P. J., McGimsey, R., Pfeffer, M., Doukas, M., Neal, C.,
449 2012a. Deep magmatic degassing versus scrubbing: Elevated CO₂ emissions and C/S in the
450 lead-up to the 2009 eruption of Redoubt Volcano, Alaska. *Geochem. Geophys. Geosy.* 13 (3),
451 doi:10.1029/2011GC003794

452 Werner, C., Kelly, P. J., Doukas, M., Lopez, T., Pfeffer, M., McGimsey, R., Neal, C., 2012b.
453 Degassing of CO₂, SO₂, and H₂S associated with the 2009 eruption of Redoubt Volcano,
454 Alaska. *J. Volcanol. Geotherm. Res.* doi:10.1016/j.volgeores.2012.04.012

455 Williams-Jones, G., Horton, K. A., Elias, T., Garbeil, H., Mougini-Mark, P. J., Sutton, A. J.,
456 Harris, A. J. L., 2006. Accurately measuring volcanic plume velocity with multiple UV
457 spectrometers. *B. Volcanol.* 68, 328-332, doi:10.1007/s00445-005-0013-x

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460 **Figures and Captions**

461 Fig. 1: Map of the summit of Mount Etna showing the craters (NE – North East Crater,
462 Voragine, Bocca Nuova, SE – South East Crater), EBCN seismic station, the Multi-GAS
463 location and (a) the plume direction; the left inset shows the volcano location in Sicily; the
464 right inset shows the NE crater plume on the acquisition day as viewed with the UV camera
465 from Pizzi Deneri, with the colour scale indicating ppm m column amounts of SO₂ over the
466 image pixels; (b) shows the plume cross-section used to determine the Integrated Column
467 Amount (ICA) within this inset; and (c), within the main image, the viewing vector
468 corresponding to this profile with respect to the Multi-GAS location.

469 Fig. 2: Multi-GAS laboratory measurements characterising the passing of a cloud of elevated
470 concentration CO₂ (black line) and SO₂ (grey line) gases, simulating the plume “puffs” we
471 measured on Etna. The Multi-GAS derived CO₂/SO₂ molar ratio (blue line) and ratio error
472 (red line) demonstrate rapid instrumental responses to these transient changes with minimal
473 associated uncertainty (< 15%).

474 Fig. 3: a) Background air corrected CO₂ versus SO₂ concentrations, from the Multi-GAS
475 instrument observations; the mean molar gas ratio (0.5) is determined as the gradient of the
476 best fit regression line; the grey-filled area indicates a peak in CO₂; b) UV SO₂, Multi-GAS
477 CO₂ and SO₂ readings showing excellent overlap between peaks and troughs and
478 demonstrating equal temporal response characteristics to changes in the volcanogenic signal
479 from the two Multi-GAS sensors; c) Multi-GAS CO₂ and SO₂ time series captured over the
480 acquisition period; d) the molar ratio of CO₂/SO₂; e) the CO₂ emission rate and f) SO₂
481 emission rate across the acquisition period.

482 Figure 4: Morlet wavelets (normalised) for a) CO₂/SO₂ ratio; b) CO₂ emission rate; c) SO₂
483 emission rate and d) seismicity during the acquisition period showing periodicities in the

484 range 40-500 s; Welch power spectral density plots are also shown, indicating the dominant
485 frequencies in each case.

486 Fig. 5: Correlation matrices produced by calculating linear correlation between coefficients
487 extracted from the Morlet wavelets in SO₂ emission rate, CO₂ emission rate and seismicity, at
488 steps of 1 s. Strong correlation is evident between CO₂ and SO₂ emission in a); whilst
489 negative correlation for periods between 300 and 400 s is apparent in b); see main text for
490 further details.

491 Fig. 6: a) the RMS vertical component of seismicity from the EBCN station, in the 0.5-5.5 Hz
492 range; b) the wavelet components (integrated over the 300-400s period range) of the CO₂/SO₂
493 ratio, CO₂ emission rate and seismic RMS are compared, showing, between \approx 08:50 and
494 09:00 GMT (the grey shaded area), a lag of \approx 100-150 s between peaks and troughs in CO₂
495 emissions and seismicity.

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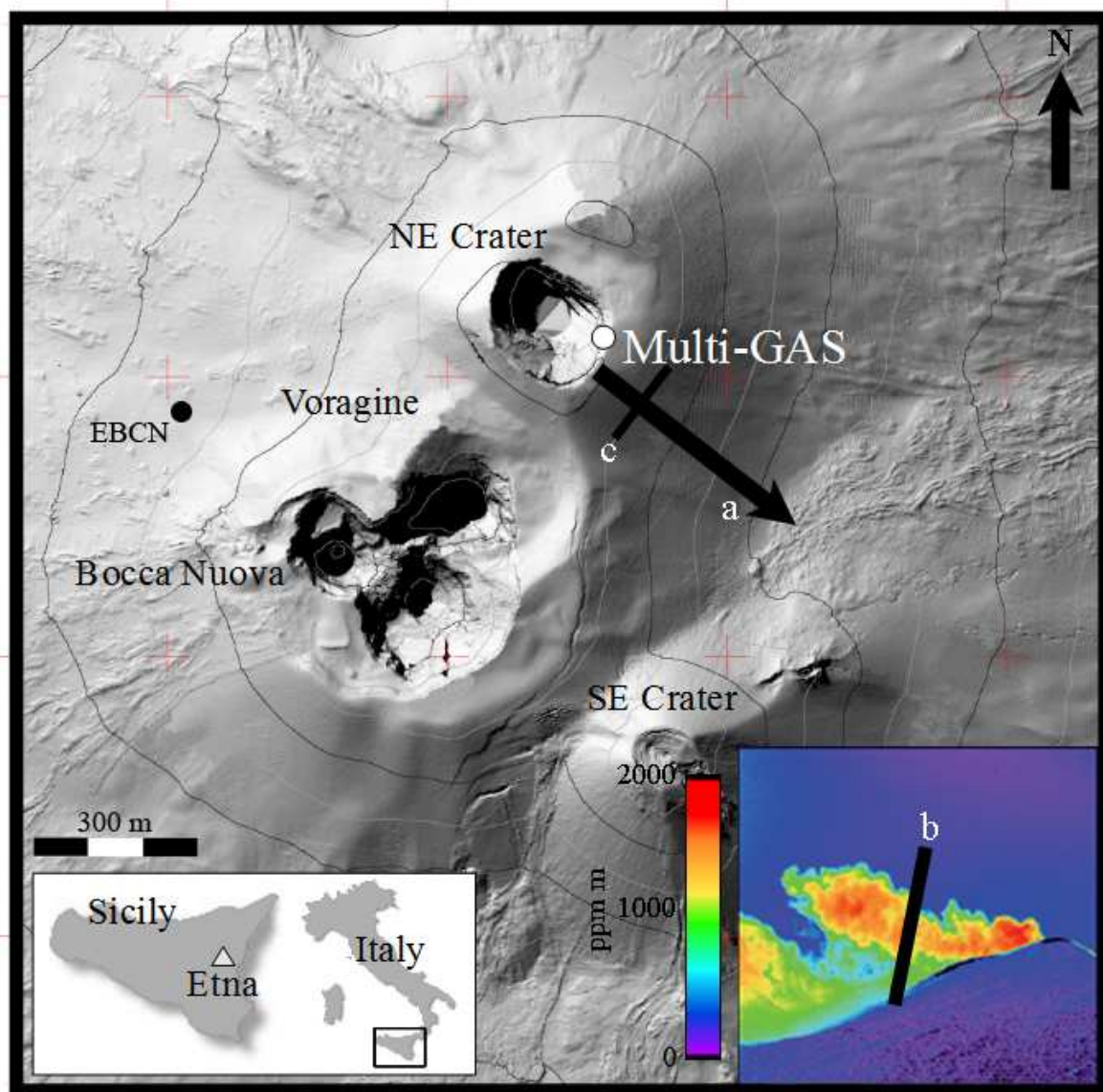
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505 **Figure 1**



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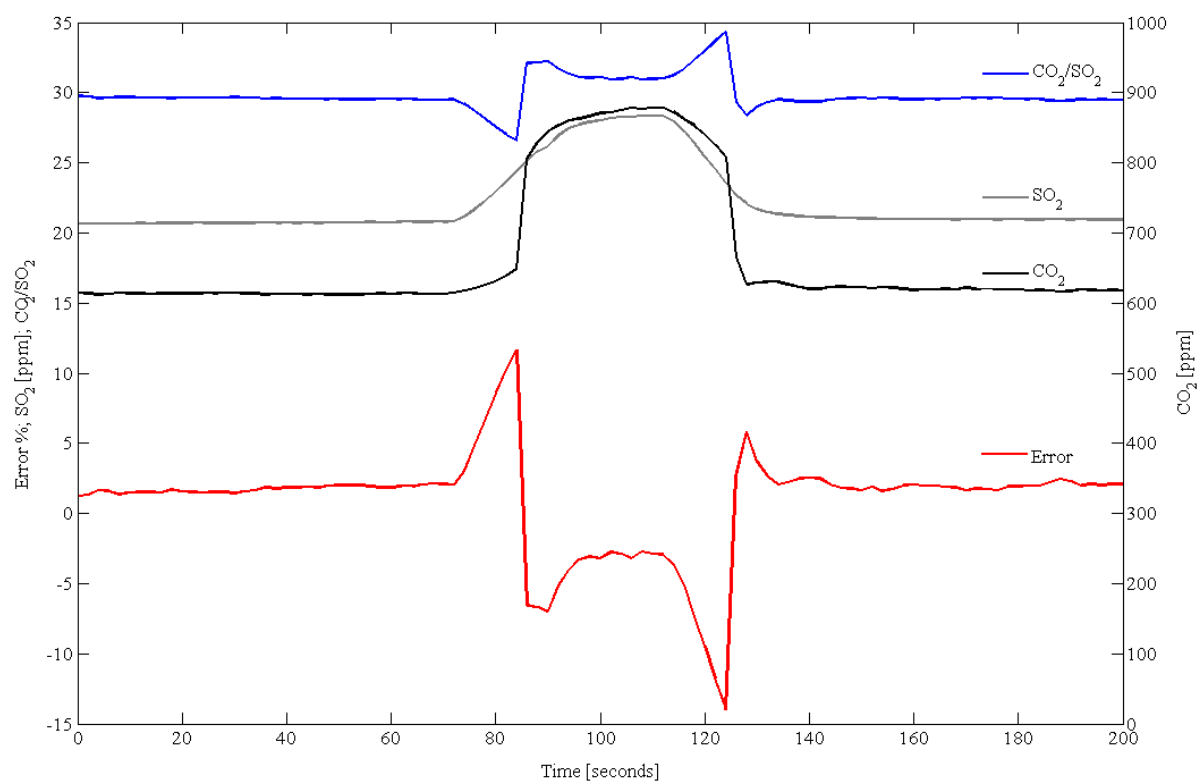
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512 **Figure 2**



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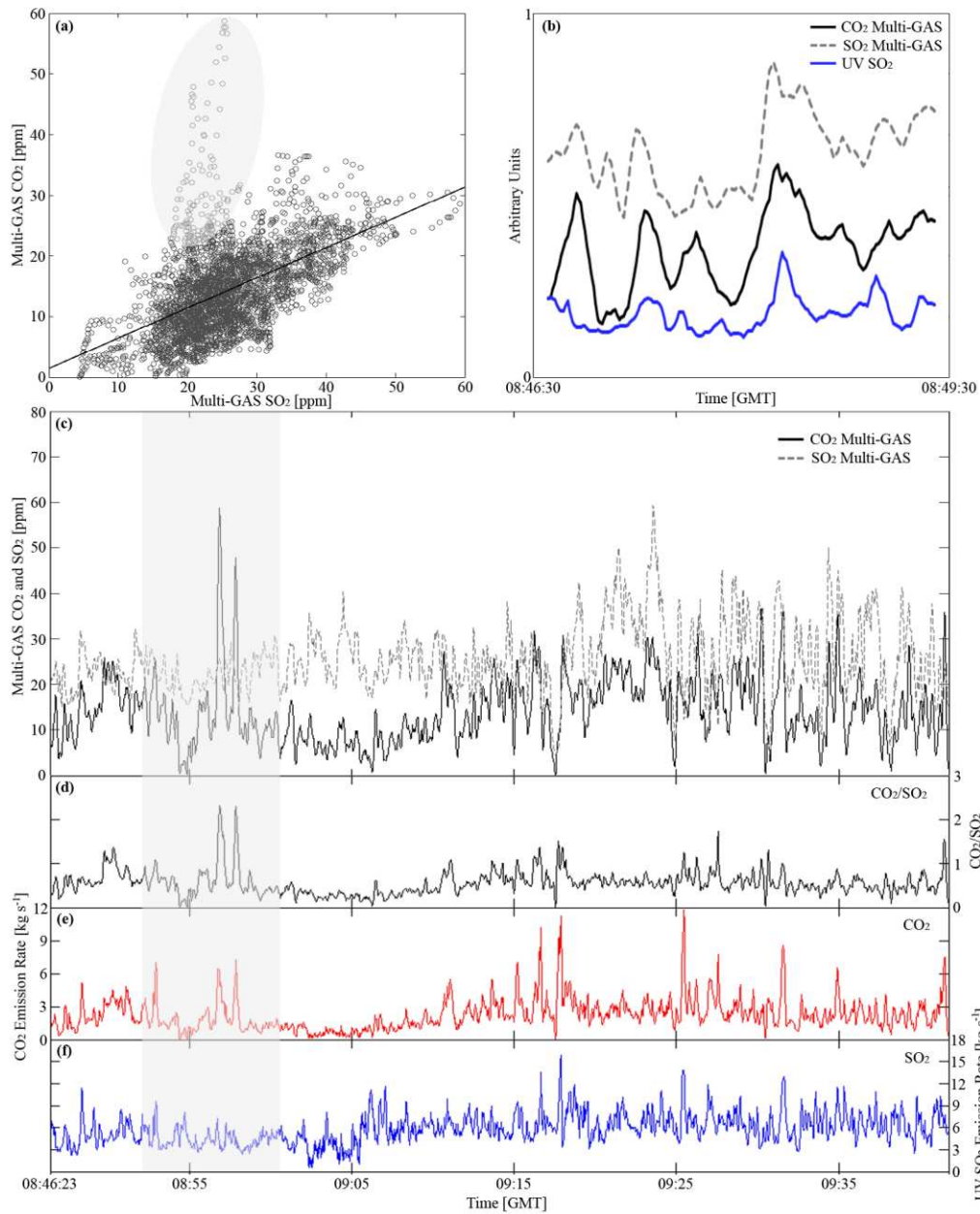
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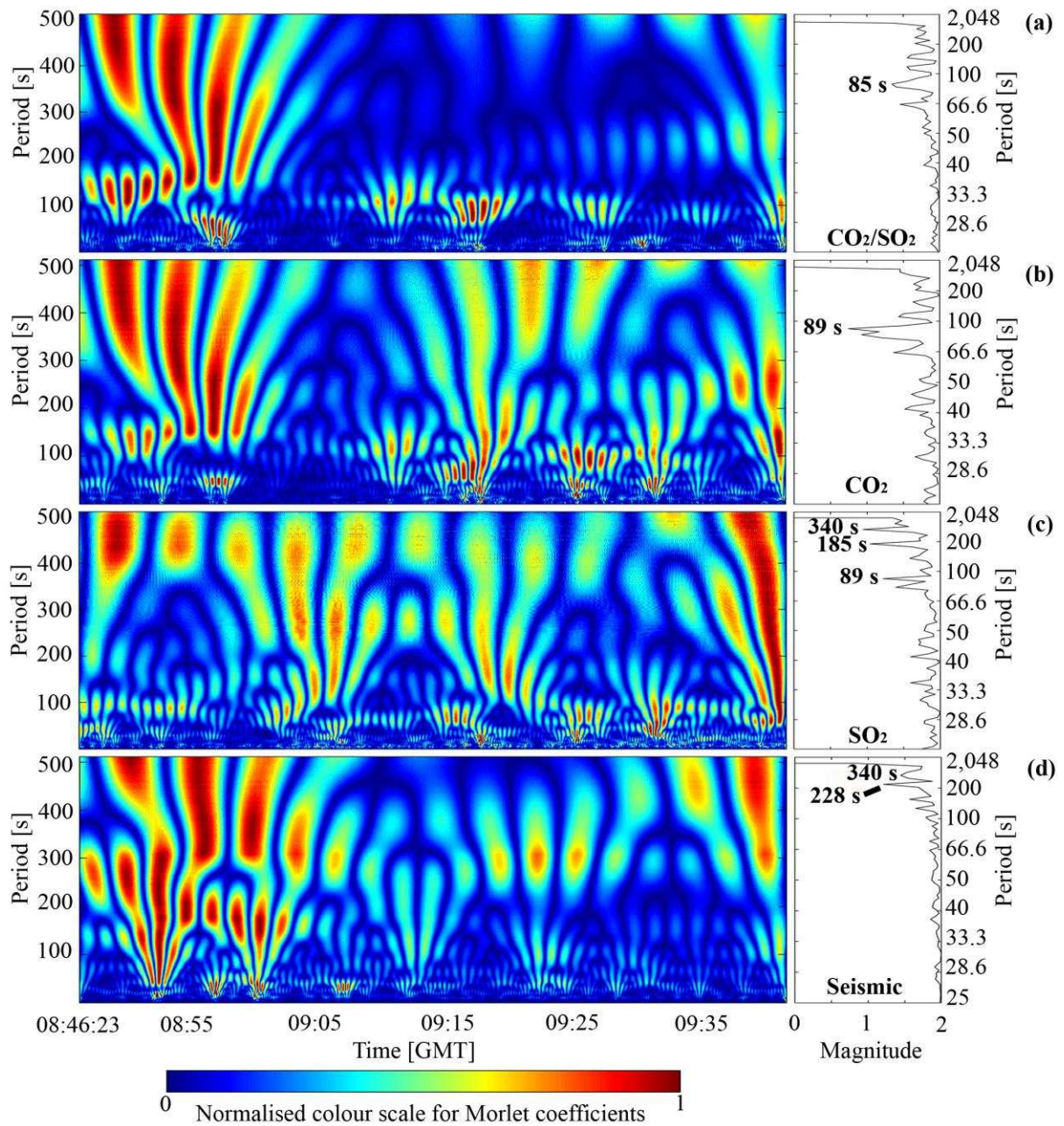
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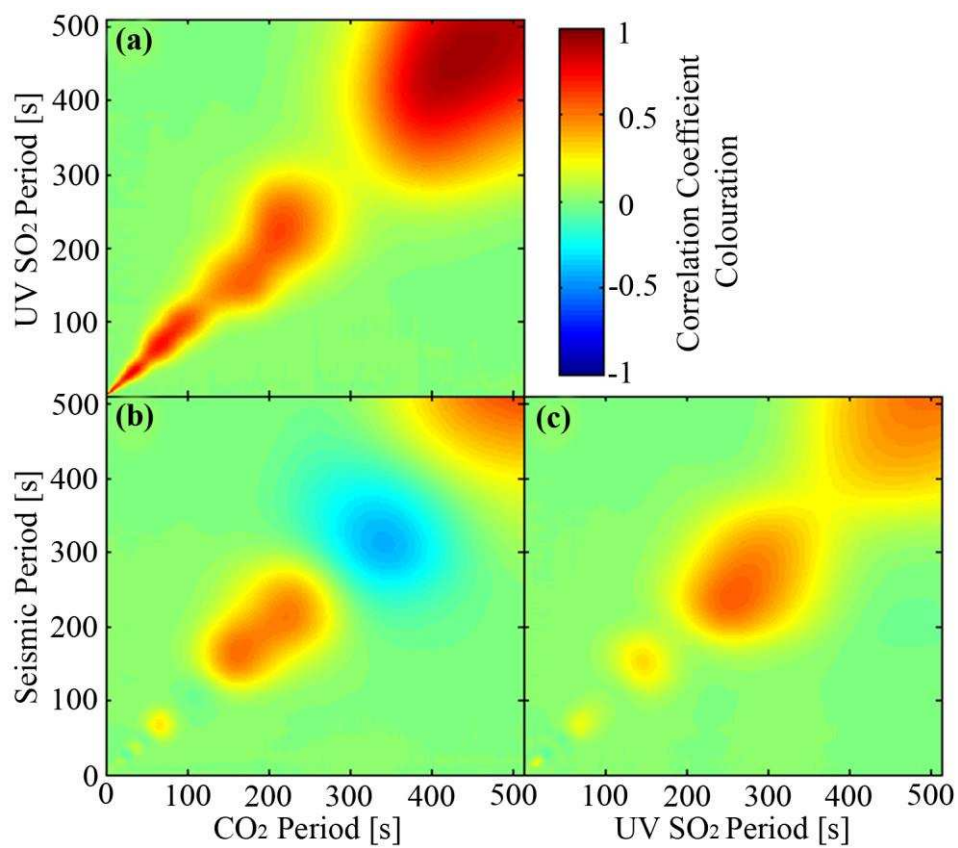
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535 **Figure 5**



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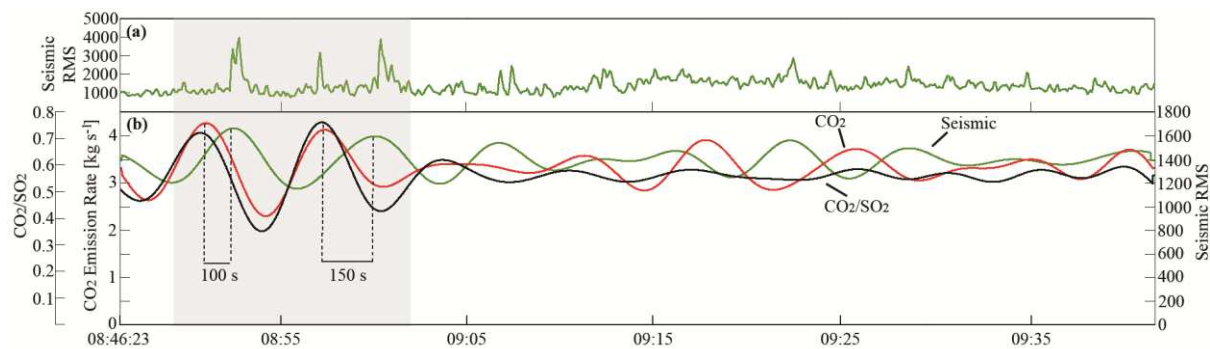
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546 **Figure 6**



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