

# Temporal variations of soil and fumarole gases at Mt. Etna Volcano (Italy) during 2000–2002

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**Abstract.** Gas samples collected during the period July 2000 – December 2002 from six sites on Mt. Etna volcano characterised by anomalous high ground degassing (mainly CO<sub>2</sub>) showed that the origin of CO<sub>2</sub> is largely magmatic and compatible with a source marked by  $\delta^{13}\text{C}$  values in the range –2 to –1‰. Concurrent He emissions are characterised by He isotope values in the range 1.02 to 7.61 Ra and suggest a variable contribution of a magmatic component. During the studied period significant variations of CO<sub>2</sub> efflux, CO<sub>2</sub>, He, CO, CH<sub>4</sub> concentrations and C and He isotopes were observed more or less at all sites. Anomalies were observed, in particular, between August and December 2000, between April and November 2001, and between March 2002 and the end of the same year. All of them preceded evident increases in the eruptive activity, including the two large lateral eruptions started in July 2001 and October 2002, respectively. The variations observed are coherent with magma accumulation at depth and its progressive degassing during migration toward the surface. The arrival of each batch of magma at depth (> 10 km) produces anomalies (mainly CO<sub>2</sub> efflux and CO concentration increases) that are best observed at the most peripheral sites (P39, VS). Migration of magma towards the surface (depth < 10 km) produces anomalies that are observed at sites closer to the summit craters (including P78). Short-term anomalies were recognised in anomalous increases of fumarole temperature, which occurred some weeks to some days Etna's eruptions and were due to greater input of high-enthalpy fluids (mainly water vapour) through the major fracture systems that cut the summit of Etna.

## 1 Introduction

Mount Etna is the largest volcano in Europe and one of the most active in the world. A prominent feature of Etna's activity is the persistent emission of a huge volcanic plume arising from its summit craters both during quiescent and eruptive

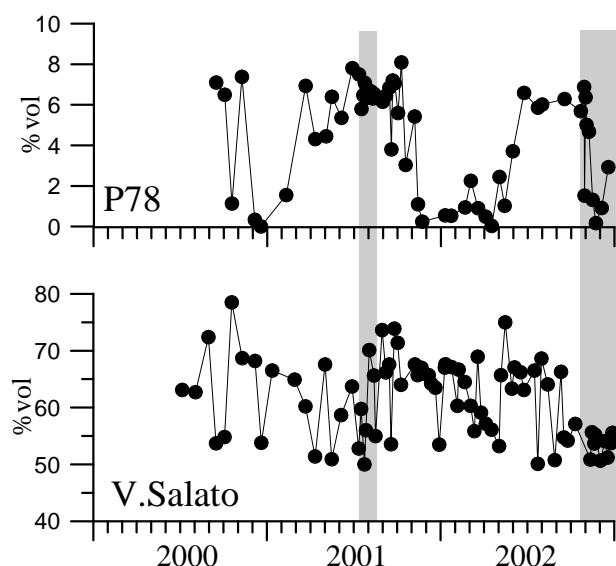
magma degassing (Allard et al., 1991). Other types of gas manifestations (fumaroles, mofettes, “mud volcanoes”, diffuse soil degassing, bubbling gases in surface and ground water) also occur in peripheral sectors of the volcano. Anomalous soil gas emissions in the Etna area occur mostly, if not exclusively, along active tectonic structures (Giammanco et al., 1998b). Among the magmatic gases issuing from Etna's flanks, carbon dioxide is the most abundant species emitted, but several other gases (CH<sub>4</sub>, He, H<sub>2</sub>, CO) can be found as well, with concentrations well above those in the air.

The aim of this work was to follow the temporal evolution of the chemical and isotope composition of gases issuing from different areas on the flanks of Mt. Etna, trying to correlate the eventual changes with the evolution of volcanic activity, after recognition of any interaction between magmatic volatiles and shallow crustal fluids.

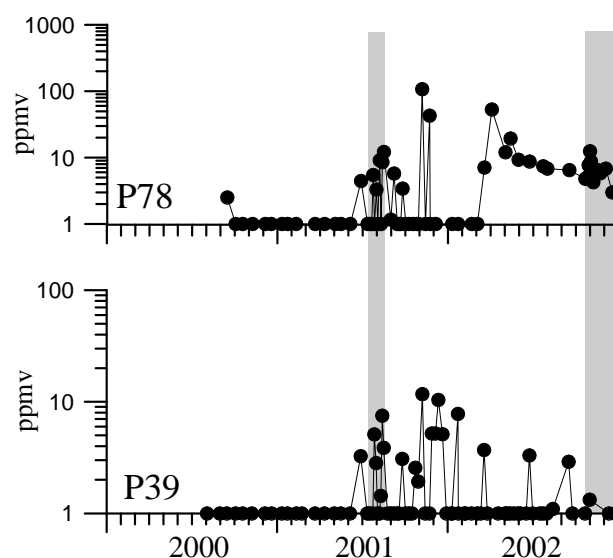
## 2 Results

Gas samples were collected in six sites, characterised by different types of gas emissions: three sites are close to Etna's summit (RNE on the north-east rift, TDF and Belvedere on the southern flank, close to the 2001 eruptive fissures) and are fumarolic emissions with outlet temperature lower than 100°C; two sites are characterised by high soil gas emissions at low altitude (P78, on the lower eastern flank of the volcanic edifice, and P39, on the lower southwestern flank); one site is characterised by gas bubbling in muddy and salty waters (Vallone Salato, located on the southwestern foot of Etna just a few kilometers east of site P39).

The chemical composition of all samples from the high-altitude sites, as well as those from site P78, results mainly from mixing between air (N<sub>2</sub> + O<sub>2</sub>) and CO<sub>2</sub>. This is due to the combined effect of high soil permeability and relatively low, although anomalous, gas flux through the ground. In addition, CH<sub>4</sub>, H<sub>2</sub> and CO can be found sometimes. The source of gas from these sites should be a relatively shallow magma reservoir (< 10 km, according to Giammanco et al., 1998;



**Fig. 1.** Temporal evolution of CO<sub>2</sub> concentrations in the samples from sites P78 and Vallone Salato. These sites were chosen as examples of the different behaviour of CO<sub>2</sub> between air-rich and CO<sub>2</sub>-rich samples. The vertical gray bands indicate the lateral eruptions during the studied period.



**Fig. 2.** Temporal evolution of CO concentrations in the samples from sites P78 and P39. These sites were chosen as examples of the different behaviour of CO between air-rich and CO<sub>2</sub>-rich samples. The vertical gray bands indicate the lateral eruptions during the studied period.

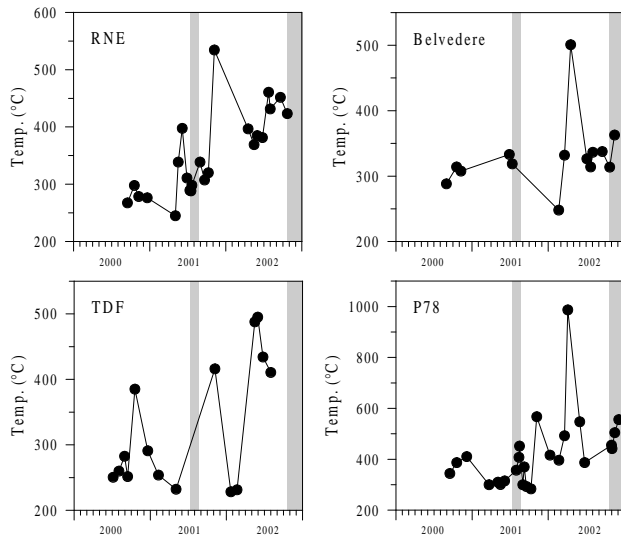
Bruno et al., 2001). The gas samples from sites P39 and Vallone Salato are characterised by high concentrations of CO<sub>2</sub>, CH<sub>4</sub> and He and their source is likely a deep magma reservoir (> 10 km, according to Giammanco et al., 1998a; Bruno et al., 2001; Caracausi et al., 2003). Some samples, however, show a slight N<sub>2</sub> enrichment due to air contamination. As for the air-rich sites, sometimes CO and H<sub>2</sub> have also been detected. The high He concentrations relative to CO<sub>2</sub> result from interaction between deep CO<sub>2</sub>-rich gases and shallow CO<sub>2</sub>-unsaturated groundwaters (Giammanco et al., 1998a). The methane enrichment relative to CO<sub>2</sub> can be in part explained with similar interactions between magmatic gas and CO<sub>2</sub>-unsaturated groundwater as those inferred for the He enrichment. However, interactions between magmatic gas and relatively shallow hydrocarbon reservoirs can also be invoked, as deduced by Parello et al. (1995) and Giammanco et al. (1998a) and confirmed by the isotopic composition of carbon and deuterium of CH<sub>4</sub> (−47‰ and −183‰, respectively).

Isotope analyses on He and on  $\delta^{13}\text{C}_{\text{CO}_2}$  showed values ranging from 1.2 to 7.5 Ra and from −19 to +2‰, respectively. The isotopic signature of He dissolved in Etna magma is around 7 Ra (Marty et al., 1994). Values lower than 2 Ra indicate a marked mixing between deep and atmospheric He. According to Giammanco et al. (1998a), the deep magmatic gas of Etna volcano is marked by  $\delta^{13}\text{C}_{\text{CO}_2}$  values ranging from −2 to −1‰. The variability observed in our samples may be a consequence of C isotope fractionation processes caused by shallow interactions between magmatic CO<sub>2</sub> and shallow fluids (thermal and/or cold groundwaters, organic matter, hydrocarbon reservoirs), and/or kinetic fractionation

processes. Besides, an important role is played by the intensity of the flux of CO<sub>2</sub> coming from depth (the higher the flux of CO<sub>2</sub>, the lesser is the interaction between magmatic CO<sub>2</sub> and surrounding environment; Giammanco et al., 1998a).

During the period July 2000 – December 2002 most of the studied geochemical parameters showed evident temporal variations (Figs. 1 and 2). The largest variations were observed in the concentrations of CO, CH<sub>4</sub> and CO<sub>2</sub>, as well as in the efflux of CO<sub>2</sub> through the soil. Anomalous changes were also recorded in the outlet temperature of the sampled fumaroles, and in the C<sub>CO<sub>2</sub></sub> and He isotopic compositions. CO<sub>2</sub> concentrations (Fig. 1) showed quite stable values at the CO<sub>2</sub>-rich sites (P39 and Vallone Salato), with only minor variations that occurred in late 2000, in July–August 2001 and in April 2002. In the other sites increases of soil CO<sub>2</sub> were observed mostly between April and September 2001 and from about April 2002 to the onset of the 2002 eruption (late October). A similar indication was obtained from the values of dynamic concentration of soil CO<sub>2</sub>, a parameter that is proportional to the flux of CO<sub>2</sub> according to the method proposed by Gurrieri and Valenza (1988). The main difference was in the data from P39 site, where CO<sub>2</sub> dynamic concentrations showed a strong increase in early 2001 and then a further increasing trend from July 2001 until February 2002. Values then dropped to a low level until a new strong increase occurred in mid-November 2002, that is after the beginning of the 2002–03 eruption. It is noteworthy that the decrease in CO<sub>2</sub> dynamic concentrations observed at P39 corresponded to the increase at the high-altitude sites, as above described.

Soil CO concentrations showed different temporal evolu-



**Fig. 3.** Temporal evolution of apparent equilibrium temperatures calculated with the  $\text{CO-CH}_4\text{-CO}_2$  geothermometer (Giggenbach, 1987) in the samples from sites RNE, Belvedere, TDF and P78. The vertical gray bands indicate the lateral eruptions during the studied period.

tion as a function of the sampling sites and also as a function of the period. Actually, at all of the sites no important CO emission was recorded before April 2001. Afterwards, CO concentrations showed frequent spike-like increases at the  $\text{CO}_2$ -rich sites until the end of our period of observation, whereas at the other sites this kind of behaviour was observed only during the second half of 2001. Since March–April 2002 soil CO values at these sites were constantly high, with a strong increase at the beginning of this anomalous period followed by a slow decrease (Fig. 2). In general, the anomalous emission of CO indicates that magmatic gases have a lesser interaction with shallow fluids, likely due to increased velocity of gas transfer from depth to the surface.

Anomalous increases of fumarole temperature were observed at site Belvedere in particular during the periods October – December 2000, April – May 2001, July 2001 and during most of 2002 until the onset of the 2002–03 eruption. Similar increases were measured also at RNE in April – May 2001 and from November 2001 to May 2002. Due to the location of these sites, such variations can be ascribed to greater input of high-enthalpy fluids (mainly water) through the major fracture systems that cut the summit of Etna. Equilibrium temperatures of gases were calculated at sites RNE, TDF, Belvedere and P78 using the  $\text{CO-CH}_4\text{-CO}_2$  geothermometer of Giggenbach (1987). The temporal plots of these values (Fig. 3) show that apparent equilibrium temperatures at all of the above sites increased significantly in early November 2001 and in April–May 2002. Site RNE showed an increasing trend of this parameter during 2002 until the 2002–03 eruption. A somewhat similar trend can be inferred for site P78, although in this site the very high value calculated in April 2002 (about  $950^\circ\text{C}$ ) is clearly an indica-

tion that gases did not attain equilibrium.

As regards the isotopic data, He Ra values clearly indicated a general increase that started just before the July–August 2001 eruption and continued for some weeks after. During the period of observations, values of  $\delta^{13}\text{C}_{\text{CO}_2}$  from all sites indicated a trend towards values compatible with the inferred magmatic end-member of Etna's gas.

### 3 Discussion and conclusions

The three main periods of marked anomalies were observed between August and December 2000, between April and November 2001 and between March 2002 and the end of the same year. The first anomalous period seems to be related to the increase of eruptive activity observed at Etna from November 2000 to July 2001; the second seems to correlate at least in part with the July–August 2001 lateral eruption; the anomalies of the third period preceded and accompanied the 2002–2003 lateral eruption.

Impulsive increases in the emission of reduced gas species may be explained as due to disequilibrium conditions in the gas phase dissolved in the magma, imposed by a rapid migration of magma toward shallower and more oxidised portions of crust (e.g. Sato and McGee, 1981; Giammanco et al., 1998a). Increases in the efflux of  $\text{CO}_2$ , especially when observed at all or most of the sampling sites, indicate increases in the gas pressure at depth due to arrival of fresh gas-rich magma. Sudden decreases in  $\text{CO}_2$  efflux, such as that observed at site P39 in early March 2002, followed by increases at the high-altitude sites (P78, Belvedere, RNE and TDF) can be ascribed to depressurisation of the deep gas source likely due to rapid magma migration towards the surface (Giammanco et al., 1995, 1998a; Bruno et al., 2001).

In conclusion, our data proved useful in indicating magma accumulation at depth and its migration toward the surface before the last two large lateral eruptions of Mt. Etna (July–August 2001 and October 2002 – January 2003).

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