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CO_2 output and $\delta^{13}C(CO_2)$ from Mount Etna as indicators of degassing of shallow asthenosphere

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Abstract An estimated average CO_2 output from Etna's summit craters in the range of 13 ± 3 Mt/a has recently been determined from the measured SO_2 output and measured CO_2/SO_2 molar ratios. To this amount the CO_2 output emitted diffusely from the soil ($\approx$ 1 Mt/a) and the amount of CO_2 dissolved in Etna's aquifers ($\approx$ 0.25 Mt/a) must be added. Data on the solubility of CO_2 in Etnean magmas at high temperature and pressure allow the volume of magma involved in the release of such an amount of this gas to be estimated. This volume of magma ($\approx$ 0.7 km^3/a) is approximately 20 times greater than the volume of magma erupted annually during the period 1971–1995. On the basis of C-isotopic data of CO_2 collected in the Etna area and of new hypotheses on the source of Mediterranean magmas, significant contributions of CO_2 from non-magmatic sources to the total output from Etna are unlikely. Such large outputs of CO_2 and also of SO_2 from Etna could be due to an anomalously shallow asthenosphere beneath the volcano that allows a continuous escape of gases toward the surface, even without migration of magma.

Key words Etna · Carbon dioxide output · Magma degassing · Volcanic activity

Introduction

During the past few years, the output of gas from active volcanoes has received growing interest. This has mainly been the result of the development of techniques for remote measurement of gases emitted from active craters. In particular, measurements of the SO_2 flux, carried out using correlation spectrometry (COSPEC) methodologies, allowed the SO_2 output from the plume of some active volcanoes to be evaluated (Stoiber et al. 1987; Allard et al. 1991; Caltabiano et al. 1994). Estimates of the CO_2 flux in the plume have been made using C/S ratios in volcanic gases (Allard et al. 1991). More recently, direct measurements of the CO_2 emitted from the plume have been carried out using IR spectrophotometry (McGee et al. 1995).

Mt. Etna is one of the most active volcanoes in the world. Gerlach (1991), on the basis of the data from Allard et al. (1991), pointed out the large amounts of CO_2 being emitted from this volcano. The estimated total amount of CO_2, approximately 25 Mt/a (13 Mt/a from the summit craters and the rest from its flanks), represents approximately 15% of the global volcanic CO_2 emissions. However, Etna's contribution to the global CO_2 budget is only a small fraction compared with that from human activities, which amounts to approximately 22 Gt/a (Boden et al., cited in Gerlach 1991). As regards the origin of the gases released from the volcano, data gathered on the C-isotopic composition of CO_2 emitted (Allard et al. 1991; D'Alessandro et al., 1997; Giammanco and Inguaggiato 1996) indicate a primary deep source. Furthermore, the measured values of the $^3He/^4He$ ratio in fluid inclusions from Etnean lavas (Marty et al. 1994) and in free and dissolved gases from Etna's groundwaters (Allard et al., submitted) suggest a mantle origin, with minor crustal contamination.

In the present work an attempt is made to derive a model able to explain the origin of these emissions on the basis of the CO_2 emission data from Etna acquired in the past several years.

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Results and discussion

In an active volcanic system such as Etna, the transfer of deep gases (mainly CO_2) toward the surface occurs principally along zones of high permeability in the crust. Major pathways for this migration are the feeding conduits of the volcano. However, diffusive loss of CO_2 through the flanks of the volcano could be significant as well. From the available data, an attempt is made to estimate the total CO_2 output from Mt. Etna.

The output of CO_2 from the summit craters of Etna has been estimated from the measured flux of SO_2 (using the COSPEC method) and the CO_2/SO_2 molar ratio. Allard et al. (1991) estimated an average amount of 13 ± 3 Mt/a for the period 1975–1987. Similar results have been obtained using the measured SO_2 fluxes from Bruno et al. (1994) for the period 1987–1992.

The diffuse emissions can be estimated assuming that a part of the rising CO_2 dissolves in the Etna aquifers, whereas the rest is exhaled through the soil. Since 1987 data on the diffuse flux of CO_2 through the soil have been collected monthly at Paternò, on the southwestern flank, and at Zafferana Etnea–Santa Venerina, on the eastern slopes, where the soil emission is greatest (Giammanco et al. 1995). In these areas the contribution of CO_2 to the aquifers has been quantified. In fact, both measurements of the partial pressure of CO_2 and of bicarbonate contents in the ground waters are periodically carried out in 11 springs and 7 wells (Bonfanti et al. 1996).

Widespread measurements of the diffuse CO_2 flux through the soils of Etna within this project and by Giammanco et al. (1995) led to an estimate of the average soil degassing in the range 0.01–0.1 $m^3/km^2 \times s$. These two flux values, if referred to a surface of 1000 km^2, which is the surface affected by Etnean activity, give an amount of diffusely emitted CO_2 in the range 0.6–6 Mt/a. The highest value is probably overestimated, given that part of it can be ascribed to CO_2 of organic origin; thus, a reasonable value is 1 Mt/a. The amount of CO_2 dissolved in the aquifers of Mt. Etna has been calculated considering a mean HCO_3^- value of 550 mg/l (Anzà et al. 1989; D'Alessandro et al., 1997 and unpublished data) and a mean annual rainfall of 0.86 km^3, of which 0.7 km^3 effectively infiltrate (Ogniben 1966). The contribution of bicarbonate from the rain water due to its equilibration with the atmospheric CO_2 can be neglected; therefore, an amount of dissolved CO_2 of approximately 0.25 Mt/a is obtained. Considering the above estimates, so that it is clear that the major contribution to the total output of CO_2 on Etna can be attributed to degassing from the summit craters. The amount of diffuse CO_2 emitted from the flanks of the volcano, estimated by Allard et al. (1991) to be comparable to that emitted from the summit craters, has been greatly overestimated.

Estimates of the energy budget during the 1991–1993 Etna eruption (Bonfanti et al. 1996) give a similar indication. The temperature of groundwaters increased by approximately 3 °C, as compared with mean seasonal values, starting 6 months before the eruption. The heat input responsible for the significant positive anomaly in groundwater temperature before the 1991–1993 eruption has been evaluated taking into account the average volume of water stored in the aquifers of the areas of Zafferana–S. Venerina and Paternò, the heat required to cause a thermal anomaly of approximately 3 °C in these water bodies, the thermal energy released by the eruption, and the estimated volume of emitted lavas and their mean temperature at the emission point (Table 1). The obtained value ($\approx 2 \times 10^{15}$ J, according to Bonfanti et al. 1996) indicates that the thermal energy necessary to produce the observed anomaly in groundwaters represents less than 0.3% of the total thermal energy released during the eruption.

Since the variation in temperature occurred over a relatively short time, the contribution from thermal conductivity of rocks can be neglected. Thus, the transfer of energy from the magma to these aquifers must be due to the ascent of the gases released from the magma itself. The estimated energy transported by these gases during the 1991–1993 eruption is at least one order of magnitude greater than that which produced the thermal anomaly (Bonfanti et al. 1996). This means that only a fraction of the volatiles released by the magma caused the observed temperature increase.

Based on the CO_2 budget, an attempt is made to estimate the volume of magma required to produce this amount of gas. Recent petrological studies (Clocchiatti et al. 1992), based on the analysis of fluid inclusions in olivines, have shown that Etnean magmas become saturated in CO_2 at approximately 7 kbar (at 1200 °C), corresponding to a minimum exsolution depth of approximately 24 km. Armienti (1994) estimated that at such pressures Etnean magmas contain approximately 0.7 wt% of CO_2. From this solubility value we calculated that approximately 0.7 km^3/a are involved in generating the estimated CO_2 emission rate. However, the lava emission rate on Etna during the period 1971–1995 is of the order of 0.035 km^3/a (Azzaro and Neri 1992; Barberi et al. 1993; Calvari et al. 1994), only approxi-

Table 1 Estimated values of the parameters considered in Mt. Etna mass and energy budgets

Volume of water in the aquifers of the eastern and southwestern flanks of Etna	0.15 km^3
Heat required to raise groundwater temperature by 3 °C	2×10^{15} J
Energy released by the 1991–1993 eruption	$700–1400 \times 10^{15}$ J
Energy carried by magmatic gases during the 1991–1993 eruption	$2.5–5 \times 10^{15}$ J
CO_2 output from summit craters	13 ± 3 Mt/a
Average diffuse CO_2 output from soils	1 Mt/a
CO_2 dissolved in groundwater (assuming an infiltration value of 0.7 km^3/a)	0.25 Mt/a
Saturation conditions for CO_2 in magma	P = 7 kbar; T = 1200 °C
CO_2 content in Etna's magma	0.7 wt. %
Volume of magma required to produce the released CO_2	0.7 km^3/a
Volume of lava emitted annually from 1971 to 1995	0.035 km^3/a

mately 1/20 of the estimated volume of degassing magma. This estimated magma budget has been obtained assuming that, excluding the organic contribution, all the CO_2 emitted by the volcano is of only magmatic origin. However, some authors (e.g. Allard et al. 1991) explained the huge amount of CO_2 emitted from Etna by postulating a significant contribution due to thermal decarbonatation of limestones present in Etna's sedimentary basement.

Isotopic data on carbon in CO_2 reported recently (Allard et al. 1991; Anzà et al. 1989; D'Alessandro et al., 1997; Giammanco and Inguaggiato 1996) provide constraints on its origin in the Etna area. Values of $\delta^{13}C(CO_2)$ in gas from both the lower flanks and the summit craters area of Etna, generally fall in the range of –6 to +1‰ vs PDB. However, a –4 to –2‰ range may be considered typical for CO_2 of deep origin on Mt. Etna, although the values commonly accepted for the magmatic CO_2 are slightly more negative, generally in the range –6 to –8‰ (Craig 1953). The more positive values measured (–1 to +1‰) may be due to isotopic fractionation caused by diffusion processes or interaction with thermal aquifers (D'Alessandro et al., 1997) and characterize samples collected in peripheral areas (Paternò). The apparent shift toward more positive values can be explained in two different ways. Firstly, recent studies (Hoernle et al. 1995) pointed to the presence of a wide mantle plume underneath western and central Europe, including the Mediterranean sea, that is probably the source of all the volcanic rocks erupted in these areas. An interesting feature of volcanic products in these areas is the $^3He/^4He$ ratio (5.8–7 R/R_a), which is slightly lower than ratios typical of a MORB source (8 ± 1 R/R_a according to Lupton 1983), and have been explained by contamination with radiogenic He. If this hypothesis is correct, the isotopic values of CO_2 measured on Etna, which also diverge from typical MORB values, could be explained by a marked crustal contamination of the magmatic source as well. Secondly, as already pointed out by Gerlach (1991), Etna is also a strong emitter of SO_2, whose output alone would account for a huge amount of degassing magma. Further, its S-isotopic composition ($\delta^{34}S(SO_2) \approx +0.8$‰ vs Canyon Diablo Troilite) indicate a mantle source (Allard 1986). Therefore, the hypothesis that a significant part of the CO_2 is due to thermal decarbonation is very unlikely. The high output of both CO_2 and SO_2 might be typical of alkaline volcanoes such as Etna.

In the past several years, studies on gas output and thermal regime of volcanoes revealed for many of them (e.g. Stromboli, White island, Piñatubo and Popocatepetl) very low ratios between erupted and degassed magma (down to less than 1/1000; Francis et al. 1993; Allard et al. 1994 and references therein). This was explained by the intrusion of huge amounts of magma and/or with convective movements of the magma within the conduits and magma chambers. At Mt. Etna, the large volume of magma involved in the degassing process cannot be simply viewed as intruded magma at some depth beneath the volcano, because there is no geological or geophysical evidence for such an intrusion. A model that in our opinion is conceptually consistent with the observed phenomena suggests that the asthenosphere beneath Etna rises to a depth where reduced lithostatic pressure allows exsolution of CO_2 from the magma. This hypothesis is supported by recent seismic refraction studies that showed a significant upwarp of the lower-crust boundary beneath the eastern flank of Etna (Nicolich et al. 1996). These authors suggest that the deep magma chamber of Etna is a lens atop an upwarped mantle. Convective movements into this mantle lens can continuously transport gas-rich magma from deeper to shallower parts, thus making the source of gas practically infinite. This mechanism could explain why Etna's gas output is so much larger than that at other active volcanoes in the world (Gerlach 1991; McGee et al. 1995).

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