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Geochemistry and mineralogy of travertine deposits of the SW flank of Mt. Etna (Italy): Relationships with past volcanic and degassing activity

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Abstract

Travertine deposits outcropping in the lower SW flank of Mt. Etna were studied for their mapping, as well as for their chemical, mineralogical and isotopic compositions. These deposits are dated to about 24 to 5 ka in the Adrano area, located at the western limit of the study area. In this area travertines show high Mg contents and are composed mostly of dolomite, thus apparently ruling out any primary deposition in favour of a diagenetic origin. Travertines outcropping near Paternò, in the east part of the study area, should be younger than 18 ka. Those located to the SSW of Paternò (Paternò–Diga) show high Sr contents and aragonite as dominant mineralogical phase, thus suggesting primary deposition. Those located to the W of Paternò (Paternò Simeto–Stazione) are instead poor both in Mg and in Sr and show calcite as dominant phase. Carbon isotope composition of travertines indicates a magmatic origin of CO_2 that formed them. Based on the estimated volume of travertines, between 10 and 20 Gg/a of CO_2 were involved in their formation. The time-span of travertine formation coincided with the eruptive cycles of Ellittico and the first part of Mongibello, which were probably characterised by a greater amount of CO_2 transported through groundwater circulation. Widespread travertine deposition probably ceased after the opening of the Valle del Bove depression that modified the volcanologic and hydrologic conditions in the summit crater area.
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1. Introduction

Travertine are chemically-precipitated continental limestones whose precipitation is mainly due to carbon dioxide degassing from a groundwater source leading to calcium carbonate supersaturation (Pentecost, 2005). Based on the origin of the CO_2 interacting with the groundwater, Pentecost (2005) subdivided travertines

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into meteogene and thermogene deposits. In the former CO_2 has a shallow origin from organic activity in the soil, whereas in the latter it has a deeper origin either from magmatic degassing or from decarbonation processes. Waters related to meteogene travertines have lower temperature (generally ambient), lower contents both of dissolved inorganic carbon (DIC < 10 mmol l^{-1}) and CO_2 partial pressure ($pCO_2 < 0.1$ atm) and higher pH values (7–8). Furthermore, while meteogene travertines display low deposition rates (< 10 mmol cm^{-2} a^{-1}) and generally show a negative carbon isotopic composition ($\delta^{13}C$ vs. PDB between −12 and 0‰), thermogene travertines, on the contrary, display deposition rates in the order of hundreds of mmol cm^{-2} a^{-1} and values of $\delta^{13}C$ vs. PDB in the range −1 to 10‰.

One of the best studied active travertine deposition site is the Huanglong Ravine (Sichuan, China). Many articles highlighted the hydrodynamic control on deposition rates (Liu et al., 1995) and on mineralogical composition (Lu et al., 2000) and demonstrated the prevailing contribution of endogenous CO_2 through the determination of the carbon isotopic composition of the travertine-forming carbonate minerals (Yoshimura et al., 2004).

The close relationship between CO_2 degassing at the surface and active travertine deposition or fossil travertine deposits has long been evidenced (Barnes et al., 1978) and is often related to active or recent volcanism. For example, Central Italy is an area of widespread CO_2 degassing and the abundant travertine deposits there outcropping have been the targets of recent geochemical and mineralogical studies (Pentecost, 1995; Minissale et al., 2002). The origin of CO_2 in this area has long been debated, but a mixing of two end-members (mantle degassing and limestones decarbonation) is the most probable explanation (Minissale et al., 2002).

The volcanic system of Mt. Etna is one of the major emitters of magmatic CO_2 on the Earth's surface (D'Alessandro et al., 1997), but in spite of its huge CO_2 emission, at present only very little active travertine deposition is known in the area. However, some fossil travertine deposits outcrop on the lower south-western flank of the volcano and in this study samples taken from the most representative sections of these deposits have been analysed for their mineralogical, chemical and isotopic composition.

2. Study area and analytical methods

Mt. Etna, located in eastern Sicily, is the largest strato-volcano in Europe (3.3 km of altitude a.s.l. with an elliptical base of about 60 by 40 km) and one of the most active in the world. It grew in proximity to the collision boundary of the African and Eurasian continental plates, from repeated eruptions of alkali basalts–hawaiites over the last 200 ka.

Travertine deposits crop out on the lower south-western flank of the volcano near the towns of Adrano and Paternò (Fig. 1). The deposits closer to Adrano have been dated with ^{230}Th and ^{226}Ra methods (Romano et al., 1987) indicating that deposition started about 20 to 24 ka and ended about 5 ka before present. No geochronological dating is available for the deposits near Paternò, but an upper temporal limit for the onset of their deposition could be estimated considering that they overlay the 3rd fluvial terrace system of Simeto river dated at about 18 ka (Chester and Duncan, 1982). Etna travertines were deposited at the contact between volcanic rocks and the underlying impermeable sedimentary rocks, where most of Etna's aquifers emerge. Groundwaters in the area between Adrano and Paternò
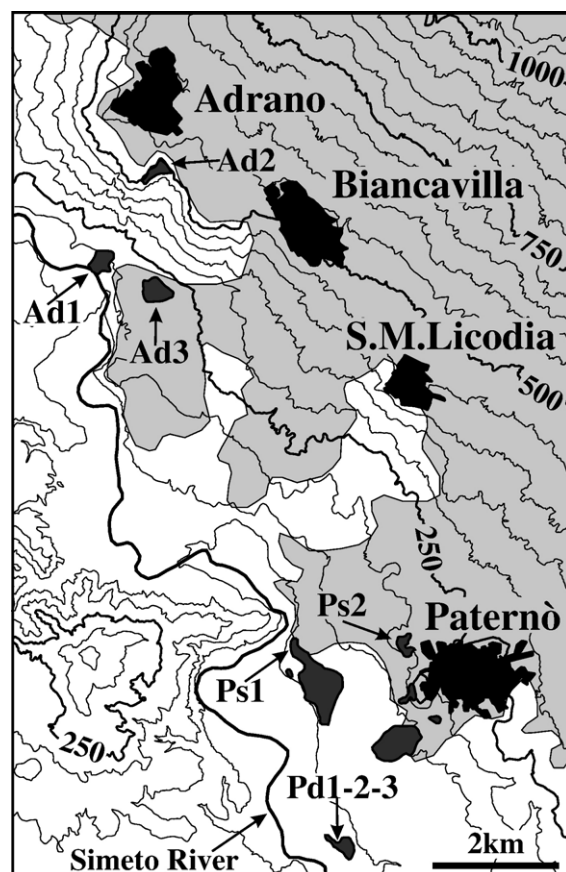

Fig. 1. Location of sampling points on the south-western flank of Mt. Etna. Etnean volcanic products are mapped in light grey, underlying sedimentary rocks in white and travertine deposits in dark grey. Towns are shown in black.

Table 1
Mineralogical, isotopic and chemical composition of the Etnean travertine samples

Samples	C	A	D	O	$\delta^{13}C$	$\delta^{18}O$	Mg	Ca	Mn	Fe	Sr	Ba
	(%)				(‰)		(mg/g)					
Ad.1a	27	0	0	73	−0.1	27.0	67.2	222	0.55	26.1	1.08	0.13
Ad.1b	34	0	28	38	1.9	24.9	68.5	296	0.12	4.29	2.57	0.14
Ad.1c	70	0	25	5	0.9	24.7	72.5	272	0.09	3.45	2.16	0.16
Ad.1d	48	0	42	10	1.6	26.3	110	227	0.12	5.41	1.33	0.11
Ad.1e	20	0	35	55	1.8	26.5	88.7	236	0.45	9.48	2.75	0.20
Ad.1f	15	0	35	50	2.4	25.2	92.2	215	0.97	39.1	2.52	0.31
Ad.1g	57	0	40	3	3.6	26.2	50.0	339	0.08	1.82	2.06	0.12
Ad.1h	20	0	30	50	2.0	25.0	83.7	175	0.95	38.7	2.12	0.31
Ad.1i	40	0	20	40	2.3	26.1	52.0	248	0.39	13.6	1.76	0.18
Ad.1j	10	0	78	12	2.3	25.8	115	244	0.12	3.47	2.91	0.22
Ad.1k	10	0	80	10	2.3	24.2	91.1	213	0.17	5.28	2.18	0.20
Ad.2a	20	0	70	10	3.2	25.8	84.3	296	0.02	0.60	2.14	0.10
Ad.2b	20	0	75	5	4.3	24.9	81.8	283	0.77	6.82	1.51	0.12
Ad.2c	25	0	70	5	2.4	25.4	55.7	330	0.25	1.88	2.02	0.15
Ad.3a	97	0	0	3	3.0	24.4	38.5	332	0.02	0.74	0.23	0.02
Ad.3b	80	0	20	0	2.7	23.8	52.3	344	0.07	1.53	0.99	0.06
Ad.3c	90	0	0	10	2.3	23.6	24.6	398	0.51	0.93	0.84	0.07
Pd.1a	98	0	0	2	1.0	24.6	11.4	395	0.11	0.91	1.05	0.21
Pd.1b	94	0	0	6	−1.9	24.3	17.5	342	0.19	5.09	1.68	0.33
Pd.1c	13	87	0	0	5.8	25.2	17.2	382	0.01	0.33	6.75	0.93
Pd.1d	18	82	0	0	5.0	25.1	28.9	361	0.02	0.51	5.33	0.61
Pd.1e	98	0	0	2	−0.7	23.8	18.3	339	0.03	0.94	1.46	0.26
Pd.2a	50	50	0	0	2.9	25.6	27.2	300	0.04	0.47	5.94	0.63
Pd.2b	54	20	23	3	2.5	26.0	64.4	314	0.14	6.30	4.50	0.42
Pd.2c	0	55	36	9	2.9	25.3	60.8	305	0.19	5.91	7.84	0.58
Pd.2d	0	30	63	7	2.3	27.2	89.5	240	0.21	6.80	3.57	0.29
Pd.3a	10	90	0	0	6.3	24.8	6.78	373	0.01	0.51	7.26	0.59
Pd.3b	71	29	0	0	5.2	24.8	23.9	357	0.07	1.11	2.40	0.50
Ps.1a	94	0	0	6	0.3	23.9	18.6	367	0.39	0.41	0.84	0.06
Ps.1b	96	0	0	4	4.4	23.0	14.3	364	0.48	0.85	0.77	0.07
Ps.1c	99	0	0	1	4.9	23.0	12.0	326	0.38	1.02	1.34	0.07
Ps.1d	99	0	0	1	4.7	23.0	14.8	366	0.60	1.82	0.98	0.07
Ps.1e	97	0	0	3	4.6	24.0	14.5	348	0.18	1.09	1.12	0.06
Ps.2a	99	0	0	1	5.6	24.0	13.7	322	0.28	0.95	1.00	0.06
Ps.2b	98	0	0	2	5.5	24.4	11.6	369	0.53	4.86	1.07	0.07
Ps.2c	98	0	0	2	6.1	24.6	12.8	355	1.70	6.76	0.54	0.14

Samples are identified by the initials of the area (Ad = Adrano; Pd = Paternò Diga; Ps = Paternò Simeto–Stazione) the number of the site as in Fig. 1 and a letter indicating the sequence in the profile, letter a being always the sample at the base. Mineralogic composition (C = Calcite; A = Aragonite; D = Dolomite; O = Other), semiquantitatively estimated following the method of Schultz (1964), is expressed in % of the whole rock. Isotopic composition is expresses as ‰ with respect to the standards V-PDB ($\delta^{13}C$) and V-SMOW ($\delta^{18}O$). Chemical composition, expressed as mg/g, was determined on the 0.5 N HCl soluble fraction.

are generally very rich in magmatic CO_2 and tend to be supersaturated with respect to calcite (Brusca et al., 2001; Aiuppa et al., 2002).

Thirty-six travertine samples (Table 1 and Fig. 1) were collected in 7 sites that can be grouped in three main areas (Adrano, Paternò Simeto–Stazione and Paternò Diga). At each site samples were collected along a profile from the base to the top of the travertine outcrop. The number of samples collected at each site varied from two to eleven, depending on the thickness of the travertine deposit.

Mineralogical analyses were performed with XRD methods, using a CuKα radiation Ni filtered, and scanning rate of 2° 2θ min^{-1} in the range 2° – 60°. Semi-quantitative estimation of the abundance of the identified mineralogical phases was performed using the method of Schultz (1964). Chemical analyses were performed by IC (Ca and Mg) and ICP-MS (Mn, Fe, Sr and Ba) on the 0.5 N HCl-soluble fraction and are expressed as mg per g of soluble fraction. Carbon and oxygen isotope compositions were determined by standard mass spectrometric analysis and are expressed

as $\delta^{13}C$ ‰ vs. V-PDB standard and $\delta^{18}O$ ‰ vs. V-SMOW standard, respectively.

All analytical results are displayed in Table 1.

3. Results

The three geographically distinct areas display different mineralogical compositions of travertines. In the Adrano area, travertines have generally higher contents of non-carbonate minerals (up to 73%) and calcite–dolomite as carbonate phases. Travertines of the Paternò Diga area display a calcite–aragonite association, with aragonite being sometimes prevalent, and minor amounts of other minerals (<9%). One sampling site in this area revealed also high amounts of dolomite (up to 63%). Lastly, travertines outcropping at Paternò Simeto–Stazione are composed of almost pure calcite, with minor non-carbonate phases (1–6%).

The chemical composition of the HCl 0.5 M soluble fraction evidences a great variability, especially in minor elements. Calcium and magnesium display the highest contents, ranging from 175 to 398 mg/g and from 6.8 to 115 mg/g, respectively. Magnesium contents display a fair positive correlation with the percentage of dolomite, thus indicating its preferential incorporation within this mineral phase. Iron and Manganese range from 0.33 to 39.1 mg/g and from 0.01 to 1.7 mg/g, respectively, and are often highly correlated each other (R^2 from 0.73 to 0,99), thus evidencing common processes that incorporate these elements in the travertine deposits. However, different sites show different Fe/Mn ratios, the highest being found at site Ad1 in the Adrano area (40). This site displays also a positive correlation between Fe (R^2 0.78) or Mn (R^2 0.57) contents and percentage of insoluble residue, thus indicating that Fe and Mn are probably not incorporated in the lattice of carbonate minerals. The highest Fe and Mn contents are actually found in the

levels collected close to the two ash layers incorporated in the travertine deposit and are probably related to secondary minerals derived from weathering of the volcanic glass. Strontium and Barium, which also display a wide range of concentrations (from 0.23 to 7.84 mg/g and from 0.02 to 0.93 mg/g), are also positively correlated, which underlines their similar geochemical behaviour during travertine deposition.

Looking at the spatial differences we note that travertines of Adrano are the most enriched in Mg (72.5 ± 24.6 mg/g) and those of Paternò Diga show the highest Sr contents (4.3 ± 2.5 mg/g), whereas those of Paternò Simeto–Stazione are the least enriched in both elements (14.0 ± 2.2 and 1.0 ± 0.2 mg/g, respectively).

The Carbon isotopes composition of the above travertines (Fig. 2) overall ranges from −1.9 to 6.3‰ vs. V-PDB, but more than 70% of the samples fall within a narrower range between 1‰ and 5‰. Their Oxygen isotope composition (Fig. 2) ranges from 23.0 to 27.2 ‰ vs. V-SMOW. Again, some spatial differences can be seen among the different sampling sites, because the deposits of Paternò Simeto-Stazione are the most enriched in ^{13}C and the most depleted in ^{18}O.

4. Discussion

The saturation index defined as:

$$SI = \log(IAP/K) \tag{1}$$

where IAP is ionic activity product and K is the equilibrium constant of the mineral forming reaction, indicates if a mineral phase at a known temperature is undersaturated (SI<0), in equilibrium (SI=0) or oversaturated (SI>0) with respect to the aqueous solution with which it is in contact. Previous studies (Parello et al., 2001) evidenced that most of the Etna
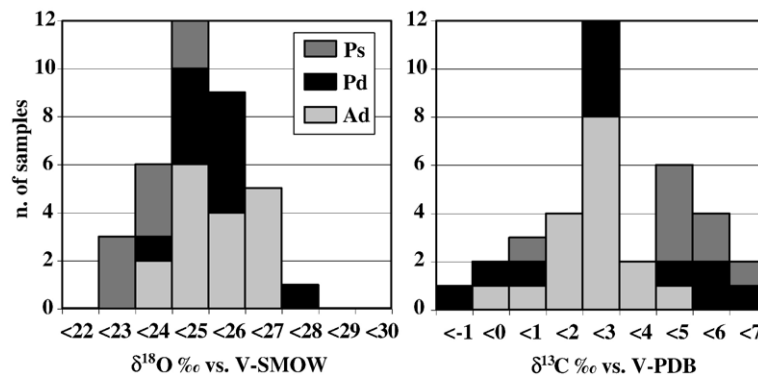
Fig. 2. Histograms of oxygen and carbon isotopic composition of the sampled travertines, subdivided by geographic area (Ad = Adrano; Ps = Paternò Simeto–Stazione; Pd = Paternò Diga).
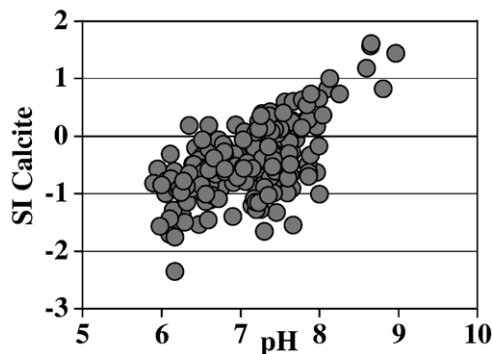
Fig. 3. Calcite saturation index vs pH binary diagram of Etnean groundwater samples (data from Parello et al., 2001).

groundwater are undersaturated with respect to calcite (Fig. 3). Only groundwaters from the most peripheral areas of the volcanic edifice, and especially those from the area between Adrano and Paternò, display positive values of the saturation indexes for calcite. Furthermore, groundwaters of the latter area are at present often supersaturated with respect to CO_2 and show a free CO_2-rich gas phase. Loss of CO_2 from water in turn determines supersaturation also with respect to solid carbonate phases. Notwithstanding calcite supersaturation, at present there is no widespread travertine deposition. A reason for this evidence could be that often calcite precipitation does not start, or proceeds at a very low rate, until the SI of the solution exceeds the value of 1 (Dandurand et al., 1982; Bono et al., 2001; Drysdale et al., 2002). Actually, SI values higher than 1 have been only found in a restricted area close to the town of Paternò, where limited travertine deposition is still active.
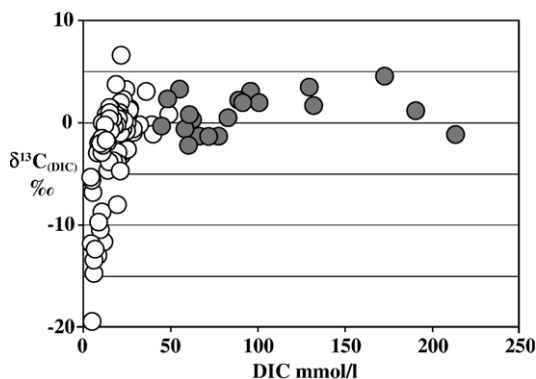

Fig. 4. Carbon isotopic composition of DIC (dissolved inorganic carbon) vs. total DIC content of the Etnean groundwaters (data from Parello et al., 2001). Waters exsolving a free CO_2-rich gas phase are evidenced in grey.
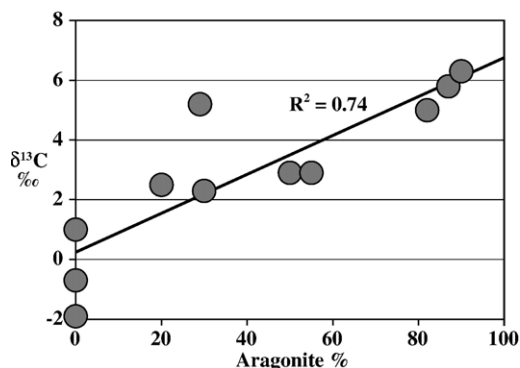

Fig. 5. Bulk carbon isotopic composition of travertine vs. aragonite content in the samples colleted at the Paternò diga (Pd) site.

During the period of widespread travertine deposition in the study area, strong supersaturation of the issuing waters must have been the rule. Usdowski et al. (1979) indicate that in such conditions the carbon isotope composition of travertines should be very close to the isotope composition of dissolved inorganic carbon (DIC). The present day $\delta^{13}C_{(DIC)}$ values in CO_2-supersaturated waters of the study area are in the range from -1 to 5‰ (Fig. 4), hence perfectly overlapping the range of most of our travertine samples. This indicates that the CO_2 involved in the deposition of travertines had the same magmatic origin as present day DIC (Parello et al., 2001). Carbon isotope values lower than 0‰ were generally measured either at the top or at the bottom of the travertine sequences, thus suggesting instead diagenetic processes that involved fluids with a lighter organic marker of carbon. Diagenetic processes are also confirmed by the mineralogical composition of travertines. Aragonite in travertines is always related to primary deposition processes and the strong positive correlation between $\delta^{13}C_{(CARB)}$ values and aragonite content ($R^2 = 0.74$; Fig. 5) strongly suggests that the more positive values of $\delta^{13}C_{(CARB)}$ are characteristic of primary deposition.

The abundant presence of dolomite in the Adrano area could be related to higher Mg contents in the waters that deposited the travertines. At present, groundwaters in the Adrano area display an average Mg/Ca molar ratio of about 5, that is much higher than that in the groundwaters of the Paternò area (Mg/Ca of about 1 — Parello et al., 2001). Dolomite is generally related to secondary diagenetic processes, therefore conditions allowing primary deposition (i.e. high salinity, high alkalinity and Mg/Ca ratios higher than 10) seem unlikely.

A rough estimate of the CO_2 involved in the deposition of the studied travertines was made on the

basis both of the estimated volumes of the deposits (45×10^6 m^3 — Burgio, 2005) and of the deposition interval (Chester and Duncan, 1982; Romano et al., 1987). The estimate of the CO_2 mass involved in the travertine deposition takes in account that for each $CaCO_3$ molecule deposited one CO_2 molecule is released by the system. The results indicate that on average about 10–20% of the present day CO_2 budget in Etna's groundwater (50 Gg/a, according to D'Alessandro et al., 1997) was involved in the deposition of the studied travertines (Burgio, 2005). This is a strong indication of an increased CO_2 flux through the volcanic aquifer at the time of travertine deposition. Since at present there is no widespread travertine deposition, conditions inside or outside the volcanic system must have changed with time, and some hypothesis can be made to explain this change. During the main deposition period there may have been some reasons for an enhanced magmatic gas uprise in the area, which can be ascribed to volcanic (higher magma uprise rate or higher CO_2 contents), structural (increased crustal permeability possibly due to tectonic stress) or hydrologic processes (lesser volume of the aquifer, different geometry of pathways for water drainage).

The onset of travertine deposition in the Adrano area dates back to about 20–24 ka (Romano et al., 1987). This period corresponds to the first stages of formation of the Ellittico volcano, which belongs to the last evolutionary phase of volcanism in the Etna area (Branca et al., 2004). The Ellittico activity marked a WNW migration of the axis of the main magma system feeding volcanism in the Etna area and built a large stratovolcano that was much higher than the previous Etnean volcanic edifices (belonging to the Valle del Bove Centers that were active between about 120 and 60 ka — Branca et al., 2004). Development of the Ellittico volcanic edifice probably marked also the formation of an important volcanic aquifer on its western flank, which is still existing today as the largest hydrogeologic basin of Mt. Etna. Oversaturated CO_2-rich waters of this basin, issuing along the southwestern boundary of the volcano at the contact between the volcanic rocks and the underlying impermeable sedimentary rocks, produced the travertine deposits.

The major period of travertine deposition straddles the last two main eruptive cycles, which define the stratigraphic units of Ellittico and Mongibello (Branca et al., 2004). The Ellittico cycle, which ended about 15 ka BP with a series of caldera-forming plinian eruptions, was characterized by the emplacement of highly differentiated volcanic products (Del Carlo et al., 2004). The following Mongibello cycle was charac-

terised, in the period between 12 and 7.5 ka, by phreatomagmatic activity within the Ellittico caldera depression, which was likely filled by surface water or snow (Del Carlo et al., 2004). At present most of the CO_2 released by the Etna volcanic system escapes through open-conduit degassing, while only about 1% is transported as DIC by groundwater circulation (D'Alessandro et al., 1997; Aiuppa et al., 2004). The period of travertine deposition was probably characterised by closed conduit conditions within the volcano's upper feeding system, which impeded the degassing through the main summit craters and, consequently, increased significantly the amount of CO_2 released through the volcano's flanks and hence dissolved into groundwater.

The top of the travertine sequence at Site 1 of the Adrano area is characterized by an ash bed, known as TV, that is a marker bed dated at about 5 ka BP and deposited on the whole Etnean area following the formation of the Valle del Bove (Del Carlo et al., 2004). This collapse event deeply modified the summit area of Etna and altered both its volcanologic and hydrologic characteristics. Presence of the TV marker bed at the top of Adrano travertines indicates that this ash layer was deposited in the waning stage of travertine deposition, thus providing an approximate date for it. Dating of travertines made by Romano et al. (1987) confirms the age of the TV ash layer and highlights that travertine deposition in the other two sites of the Adrano area ceased between 8 and 9 ka BP. Unfortunately, our data do not allow us to date the end of travertine deposition in the Paternò area.

5. Conclusions

Our study on travertines outcropping in the south-western flank of Mt. Etna highlighted the unique features of those deposits. Carbon isotopic composition, generally in the range 1–5‰, confirms the endogenous (magmatic) origin of the dissolved inorganic carbon involved in travertine deposition. Their formation reflects a period (24–5 ka b.p.) of increased CO_2 release through the volcano's lower flanks likely due to peculiar conditions within the main magma feeding system (i.e., closed conduit). The remarkable amount of CO_2 involved in their formation, about 10 – 20 Gg/a, suggests that should the same closed-conduit conditions occur again at Mt. Etna, peripheral areas such as that of Adrano–Paternò could be affected by an intense diffuse degassing that would certainly have a strong impact on local populations in terms of gas-hazard. Carbon dioxide accumulation in poorly ventilated places below and immediately above ground such as caves,

galleries, cellars, water wells, etc. can be very dangerous. Such natural hazard has brought in the recent past to lethal incidents (D'Alessandro, 2006) and to damage to vegetation (Platania, 1916). Together with the area of Zafferana–S. Venerina on the lower eastern flank of the volcano, the area of Paternò–Adrano is prone to this type of hazard displaying high CO_2 fluxes from the soil (Aiuppa et al., 2004) and an increase in CO_2 emission would certainly bring to higher danger levels.

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