WIDESPREAD FOSSIL CO_2 IN THE ANSANTO VALLEY (ITALY): DENDROCHRONOLOGICAL, ^{14}C, AND ^{13}C ANALYSES ON TREE RINGS

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ABSTRACT. The Ansanto Valley (southern Italy) is characterized by vents and boiling mud lakes that emit typical volcanic exhalations (mostly fossil CO_2). This fossil dilution spreads over the Ansanto Valley and its impact on local trees is investigated in this study. Six trees at increasing distance from the emitting sources and 2 aliquots of gas were sampled. Dendrochronological analysis was performed on tree cores in order to check the accuracy of the tree-ring sequences; the results indicate no anomalies in the curves of the analyzed trees. $\delta^{13}C$ and radiocarbon (^{14}C) analyses were performed on the α-cellulose extracted from some selected tree rings. The main aim of $\delta^{13}C$ analysis was to gain information about the origin of CO_2 arising from the source; the results support the hypothesis of a carbonatic origin, with respect to a volcanic origin. ^{14}C analysis was performed to evaluate the influence and to quantify the percentage of fossil dilution characterizing the local atmosphere and affecting the trees at different distances from the source during the years. The results show the presence of a strong fossil dilution affecting the trees, increasing toward the sources (from ~6% at 80 m distance to ~30% at 20 m from the nearest vent) with quite stable values over the examined period.

INTRODUCTION

This study investigates CO_2 emissions characterizing the area of the Ansanto Valley in the municipality of Rocca San Felice ("Mefite" area). This area contains some small lakes of boiling mud and cracks in the ground from which some gases arise (mainly CO_2 [98%], N_2 [1.3%], H_2S [0.33%], and CH_4 [0.23%]; [Chiodini et al. 2010]). Many animals and also some humans died in the valley because of the anoxic environment caused by the stratification of emitted gasses and fume toxicity (Gambino 1991). Over the years, many geologists have analyzed the phenomenon, reaching different conclusions. On one hand, some scholars support the hypothesis of volcanic phenomena with a post-volcanic origin (Manzi 1997) or with a secondary volcanism origin (Ortolani and Pagliuca 2008). On the other hand, the carbonate origin of the fumes is sustained by other scholars, either suggesting a deep CO_2 origin from the upper mantle (Frezzotti et al. 2009) or proposing a superficial origin from the Gessoso-Solfifera unit (an Italian geological formation; Selli 1960). In this last case, the formation of CO_2 is explained by the decomposition of limestone rock carbonates by sulfuric acid or with the presence of CO_2 in the superficial water as a constituent (Sinno 1969).

Regardless of the vent nature (volcanic or carbonatic), fossil CO_2 (dead ^{14}C) arises from the vents and spreads into the valley, inducing isotopic anomalies in atmospheric CO_2 and influencing (i.e. aging) the ^{14}C age of trees grown in the proximity of the vents. In fact, the CO_2 photosynthesized by trees (a mix between air and vent CO_2) is depleted in ^{14}C and leads to a ^{14}C age older than the real tree-ring age. This phenomenon is visible independently by the geological CO_2 origin (Sulerzhitzky 1970; Bruns et al. 1980; Saupé et al. 1980; Rubin et al. 1987; Calderoni and Turi 1998; Pasquier-Cardin et al. 1999; Cook et al. 2001; Marzaioli et al. 2005; Yoshikawa et al. 2005). On the contrary,

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Proceedings of the 21st International Radiocarbon Conference edited by A J T Jull & C Hatté
RADIOCARBON, Vol 55, Nr 2–3, 2013, p 1114–1122

the $\delta^{13}C$ values reflect different signatures depending on the origin of the geological phenomenon: the leaching of carbonate rocks, caused by the acid of the valley, should produce a CO_2 with a $\delta^{13}C$ towards positive values (West et al. 1988; Jenkyns et al. 1994; Chiodini et al. 2000; Wissler et al. 2003; Xu et al. 2006), while the volcanic origin of the gas should give $\delta^{13}C$ values similar to the normal $\delta^{13}C$ value of atmosphere ($\delta^{13}C_{atm}$ = –8‰; Craig 1953; Castrillo et al. 2004).

A preliminary study on tree rings of plants grown in the Ansanto Valley demonstrated the strong presence of fossil dilution, as well as its variability depending on the distance from the vents and the years (Capano et al. 2012). This preliminary analysis was performed on a limited number of measurements (5 tree rings selected from 2 trees) in order to evaluate the presence of a possible contamination in the radiocarbon (^{14}C) dating of some archaeological wooden sculptures. The preliminary results motivated this study, where a more detailed characterization of the area influenced by the fossil CO_2 activity and the identification of the possible origin of the Ansanto Valley CO_2 fumes is investigated, in order to better describe the geological phenomenon. In this work, more trees and CO_2 gases were analyzed 1) to assess the variability of the dilution in tree rings, 2) to define its influence in the valley, and 3) to infer the geological origin of the exhalations.

SITE DESCRIPTION AND SAMPLING

The Ansanto Valley is located in the Apennine, near Avellino, in southern Italy (Figure 1). The area of our interest (Mefite) is located at the confluence of 2 streams: the Ansanto River and a rivulet from the north. This area has no vegetation but many crystals of sulfur and gypsum (Manzi 1997).

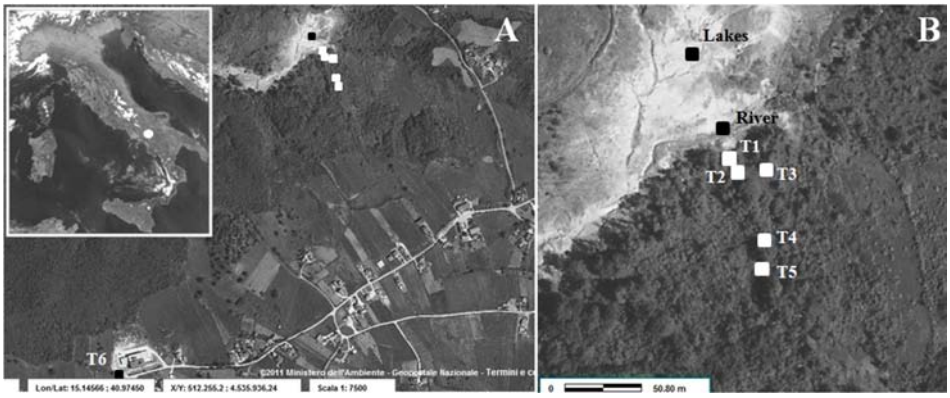

Figure 1 Aerial photographs of the Ansanto Valley (IGM map of Ministero dell'Ambiente – Geoportale Nazionale). A) Overview of the area indicating the T6 location; in the upper left, a map of Italy with the location of the Ansanto Valley. B) Area of sampling with the location of the other trees sampled.

Since ancient times, the Ansanto Valley has been of interest to scholars, both for the religious aspect and for the previously described geological characteristics. In fact, the area is a famous place of worship: the goddess Mephitis (*Mefite* in Italian) in the 1st millennium BC and Santa Felicita from the 4th century AD (Mele 2008).

In October 2012, 2 gas aliquots were taken by means of 2 vacuum-tight canisters (2 L volume), previously evacuated in the laboratory and opened near the emitting sources: one close to the main mud lake and the other close to a vent along the Ansanto River bed. In early March 2012, 6 trees (T1 to T6, named according to their distance from the emitting area) were sampled in the valley at an increasing distance from the vents, following a southeast trajectory, where the vegetation is mostly

concentrated (Table 1; Figure 1). Their geographic coordinates, the coordinates of the Ansanto River, at the point closest to the sampled trees, and the point in the middle between the 2 main lakes were recorded with a GPS system (~4 m of precision; Figure 1; Table 1). The sampled trees are all *Quercus* sp. (deciduous oak), with the exception of one (T1), an *Ulmus* sp. (elm), which is the closest tree to the emission area (Table 1). Tree T6 was sampled at a distance of 1 km, on the top of Santa Felicita Hill (Figure 1; Table 1), in order to have a control sample, which should be unaffected by the fossil dilution. Two cores 5 mm in diameter were taken from each tree at breast height with a Pressler increment corer from trees T3, T4, T5, and T6. Only 1 core was sampled from trees T1 and T2.

Table 1 Overview of the trees sampled in the Ansanto Valley, with the tree name, wood species, distance from the vent area, altitude (above sea level [asl]), and number of rings. The code is a progressive number related to the tree distance from the vent area. "FD1": means fossil dilution calculated comparing the values of the analyzed trees with the "clean air"; "FD2": means fossil dilution calculated comparing the values of the analyzed trees with T6 tree values. The FD standard deviations (SD) highlight the variability of the measurements due to different environmental factors.

Code	Tree	Species	Distance from the vent	Altitude asl	Ring nr	%FD1 ±SD	%FD2 ±SD
T1	U_Ansanto6	*Ulmus* sp.	~20 m	~662 m	27	32 ± 6	30 ± 2
T2	Q_Ansanto2	*Quercus* sp.	~31 m	~668 m	45	18 ± 2	17 ± 2
T3	Q_Ansanto1	*Quercus* sp.	~41 m	~678 m	20	31 ± 3	30 ± 3
T4	Q_Ansanto4	*Quercus* sp.	~70 m	~681 m	36	12 ± 3	10 ± 3
T5	Q_Ansanto5	*Quercus* sp.	~80 m	~682 m	47	7 ± 2	6 ± 2
T6	Q_Ansanto7	*Quercus* sp.	~1 km	~754 m	37	2 ± 1	–

MATERIALS AND METHODS

Dendrochronology

Dendrochronological measurement was performed to determine the correct dating of each tree ring. Ring widths were measured using a LINTAB™ instrument at the Dendrodata s.a.s. laboratory. Data processing was done using the TSAP® software, following standard dendrochronological procedures (Fritts 1976; Baillie 1982).

Chemical Pretreatment

After dendrochronological analysis, some rings (corresponding to years 1975, 1980, 1985, 1990, 1995, 2000, 2001, 2002, 2003, 2004, 2005, 2006, 2007, 2008, 2009, 2010, and 2011) were selected for stable isotope and ^{14}C analyses. The period of the last 10 yr, present in all the trees, was analyzed with 1-yr spacing, in order to infer the annual variability; moreover, a ring every 5 yr was selected going back to the pith, in order to have an idea also about the dilution variability in the time. The cores were sliced in annual tree rings, isolating the latewood of each growth ring. The wood of each ring was reduced to very small pieces and the α-cellulose was extracted following the Jayme-Wise method (Green 1963), with a modified procedure from Marzaioli et al. (2005):

- 4% HCl solution at 80 °C for 1 hr;
- A solution of 10 g of $ClNaO_2$ in 500 mL of HCl solution (pH 3) at 80 °C; the solution was changed each 2 hr for 4 times and afterwards left overnight at room temperature;
- 4% NaOH solution for 1 hr;
- 4% HCl solution for 1 hr.

The cellulose extracted was finally divided for ^{14}C analysis by AMS (accelerator mass spectrometry) and $\delta^{13}C$ analysis with IRMS (isotope ratio mass spectrometry).

Radiocarbon

For ^{14}C analysis, gas samples were cryogenically purified to CO_2 according to Bertolini et al. (2005), while about 3–4 mg of cellulose was oxidized to CO_2 by combustion. The reduction of CO_2 to graphite was later performed using Fe as catalyst and Zn and TiH_2 as reagents (Marzaioli et al. 2008). The graphite obtained was measured by the AMS facility of CIRCE (Terrasi et al. 2008). Several replicated standards and blanks were simultaneously processed with the same combustion and graphitization procedures as the unknown samples. The primary standard IAEA C3 was used for the normalization, the control standards NIST OXII and IAEA C5 for the evaluation of overall procedure accuracy and precision, while AESAR graphite and VIRI K wood (Scott et al. 2010) were used to estimate the background correction (Terrasi et al. 2008). $\Delta^{14}C$ values (Stuiver and Polach 1977) of the samples were compared with those obtained from the "clean air" signal, which is a mean of the Northern Hemisphere zone 1 data (Hua and Barbetti 2004), Jungfraujoch data (Levin et al. 2008), and data from the NOAA ESRL/GMD, Niwot Ridge Forest, Colorado (NOAA Cooperative Network 2008). The percentage of fossil dilutions for each tree and for each year was then calculated applying an isotopic mass balance (Capano et al. 2010). The annual fossil dilution % values of each tree were later averaged in order to have an estimation of the mean dilution of the trees and its variability with time, determined by the standard deviation, in order to sensitively estimate the individual fossil dilution oscillation.

$\delta^{13}C$

Stable isotope analyses have been performed at CIRCE with the Delta Plus™ isotopic ratio mass spectrometer (IRMS, Thermo Finnigan). For cellulose analyses, the Delta Plus was coupled to a Flash EA1112 elemental analyzer (EA), according to the method first presented by Preston and Owens (1985). About 0.04–0.06 mg of cellulose was weighed in tin capsules for stable isotope analysis. The reference material used to calibrate the analyses was IAEA-CH3, cellulose ($\delta^{13}C_{VPDB}$ = –24.72 ± 0.04‰ and IAEA-CH_6, sucrose, $\delta^{13}C_{VPDB}$ = –10.45 ± 0.03‰ according to Coplen et al. 2006). The accuracy and precision of the analyses were assessed using various cellulose standards: IAEA C3, Sirfer cellulose, and cellulose extracted by VIRI K. The variability of the measurements (±0.5‰) was estimated by the standard deviation of the IAEA C3 replicates. $\delta^{13}C_{VPDB}$ measurements of purified CO_2 gas aliquots were determined by dual-inlet IRMS calibrated against RM-8562 and RM-8564 reference materials (Verkouteren and Klinedinst 2003).

RESULTS AND DISCUSSION

Dendrochronology

The examined samples show a number of rings ranging from 20 (T3) to 47 (T5), with no core reaching the pith (Table 1). A mean curve was built only from 3 curves (T4, T5, and T6), because the others did not show good matching among them and with the mean curve (Figure 2). However, the overlap between the individual sequences of T2 and T3, on one hand, and the mean curve, on the other hand, shows the absence of missing-ring or false-ring problems (Figure 2), testifying to the accuracy of the tree-ring measurements and of sequence elaboration. Despite the possible heteroconnection between oak trees and elm trees (Lambert and Lavier 1991; Martinelli and Kromer 2002), the matching between our elm curve with the main curve of oak trees gives poor results. However, the presence of pointer years confirms the validity of the T1 tree-ring sequence.

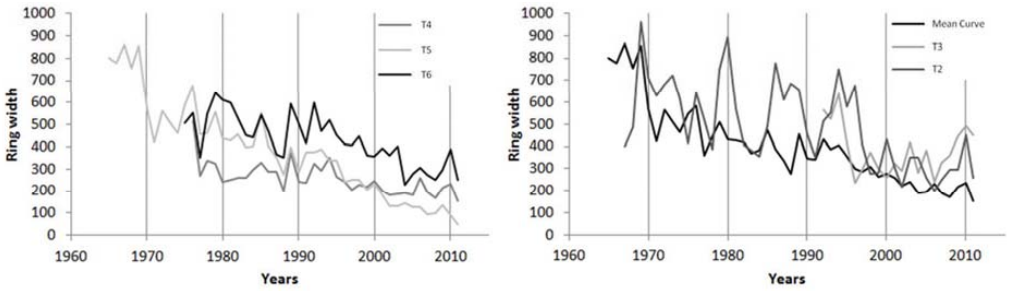

Figure 2 Dendrochronological curves: at left, the tree sequences averaged in the mean curve; at right, the mean curve compared with the other *Quercus* sp. tree sequences, not included in it.

Radiocarbon

^{14}C analysis on gas aliquots collected from the Ansanto Valley confirms the fossil origin of CO_2 (Table 2). In fact, the ^{14}C age of both samples statistically agrees with the experimental blank. The tree-ring results show a diffuse fossil dilution, quite constant over time, but variable in relation to the distance from the fossil source: increasing when approaching the emission area, as is highlighted by the adherence of each tree's values to the trend line (obtained by scaling a factor, proportional to the fossil dilution, to the "clean air" curve; Figure 3).

Table 2 Results of ^{14}C and $\delta^{13}C$ measurements of CO_2 sampled near the main lake and the river in the Ansanto Valley.

Lab code	Sample	^{14}C age BP	$\delta^{13}C$
DSH4438	CO_2_lake	51,722 ± 4190	2.59 ± 0.02
DSH4439	CO_2_river	49,380 ± 3147	1.56 ± 0.05

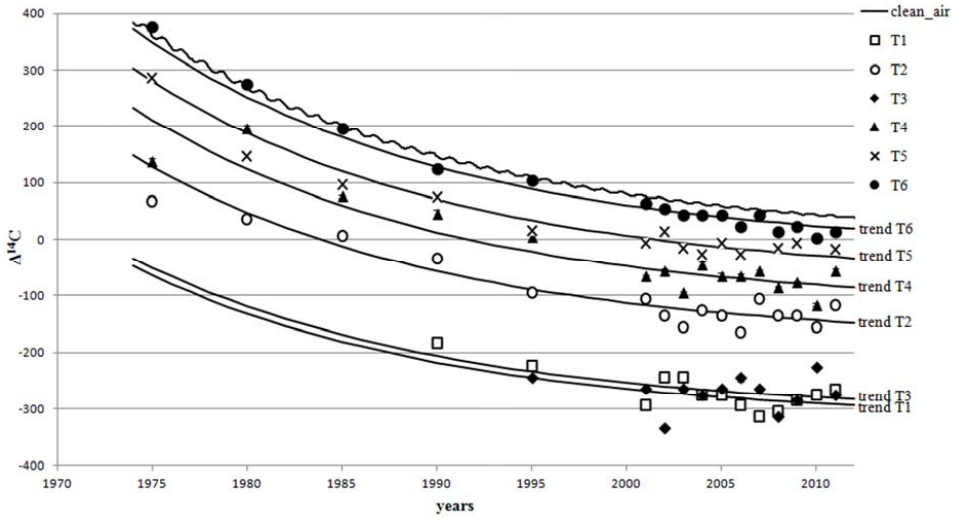

Figure 3 Results of ^{14}C measurement. The full curves (trend) are obtained by scaling a factor, proportional to the fossil dilution, to the "clean air" curve.

Looking at the dilution (Figure 3), one anomaly is evident: tree T3 is ~41 m away from the emitting source, while T2 is ~31 m away, though the fossil dilution is greater in the first than in the second tree (Figure 3; Table 1; Table S1, supplemental online-only file). This anomaly is probably attributable to the presence of other trees between tree T2 and the river and to the absence of other trees before T3, or it can be explained by the wind preferential direction/hillside geomorphology. Tree T6, 1 km from the Ansanto Valley emission (Figure 1), was chosen as the blank for this analysis, so no fossil dilution was expected in its rings. However, a small fossil dilution is observable beginning from 2002 (Figure 3; Table S1). Because of the presence of this effect only since the last decade, this fossil ^{14}C dilution can be attributable to local anthropogenic factors more than to the Ansanto Valley gases, otherwise present independently along the analyzed period. Because of the probable diffuse presence of the anthropogenic dilution in the whole area, the estimation of fossil dilution percentage was done comparing $\Delta^{14}C$ of T1, T2, T3, T4, and T5 with the $\Delta^{14}C$ of T6 (FD2 in Tables 1 and S1), instead of the "clean air" signal (see Materials and Methods).

In order to estimate to what extent the fossil dilution affects the atmosphere of the valley, the mean fossil dilution of each tree was correlated with the distance of the tree from the nearest emitting source (Figure 4). A simple power law fit for a point source (Figure 4) shows that the fossil dilution contribution is negligible within the experimental error for distances beyond 300 m from the source.

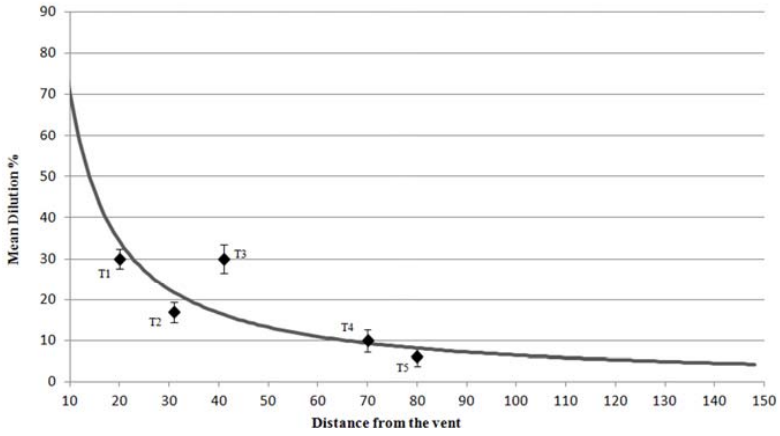

Figure 4 Estimation of the tree distance from the emitting source where the fossil dilution stops. The gray line represents the simple power law fit for a point source.

$\delta^{13}C$

The results highlight the presence of 2 sets of $\delta^{13}C$ values: 1) a more depleted set (from about −29‰ to −25‰) and 2) a less-depleted one (from about −25‰ to −21‰; Figure 5), as clearly shown by the mean values represented in the upper graph. The trees far from the emitting sources (T4 and T5) show the more depleted values, with the exception of T6; while the trees closer to the vent area (T1, T2, and T3) show the less-depleted values of $\delta^{13}C$ (Figure 5; Table S1). These results confirm the carbonatic origin of the Ansanto Valley CO_2; in fact, a volcanic origin of CO_2 should have shown depleted values also in the trees closest to the vents, making the signature on ^{13}C similar to that of the normal atmosphere. The $\delta^{13}C$ values of the gas are close to 0‰ (Table 2), indicating a carbonatic origin of CO_2 and more generally of the vents characterizing the Ansanto Valley.

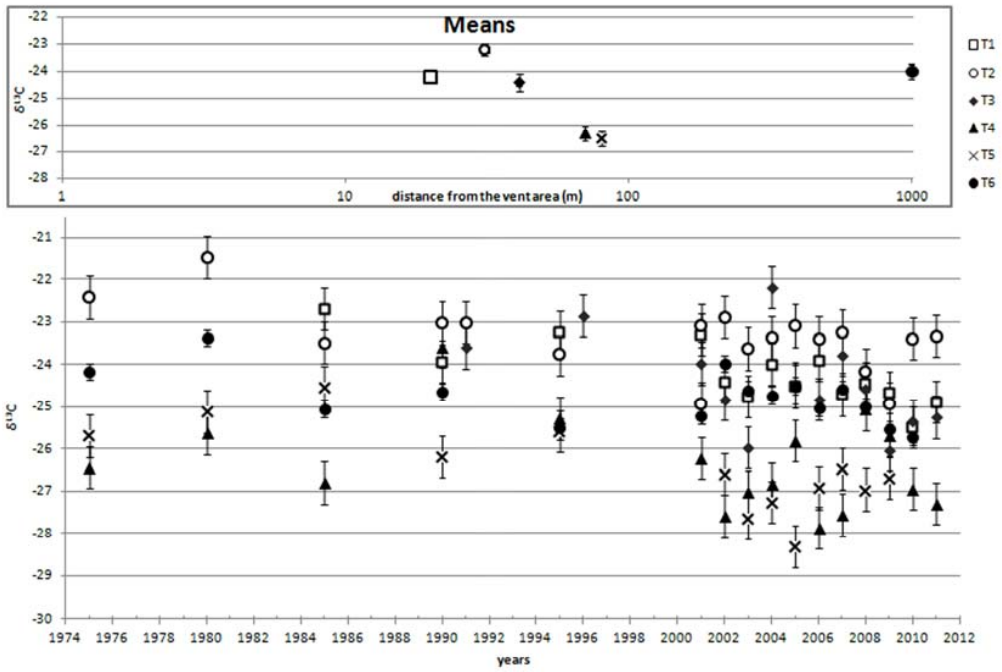

Figure 5 $\delta^{13}C$ results. Lower plot: raw data. Upper plot: the means of each tree's values with the corresponding standard error are reported in a logarithmic scale for a clear graphic rendering.

CONCLUSION

The presence of fossil CO_2 arising from some vents in the Ansanto Valley is confirmed by the ^{14}C measurement of CO_2 sampled close to the vents (^{14}C content = 0) and of trees grown in the valley. The $\Delta^{14}C$ of tree rings indicates a strong fossil dilution spread over the valley, variable in relation to the distance from the emitting sources and quite constant over about 4 decades. The dating of more rings with respect to the preliminary analysis gave a larger view of the fossil dilution diffusion over time, contradicting the conclusion of Capano et al. (2012), where the variability of emissions during the years was highlighted.

$\delta^{13}C$ analyses of tree rings seem to strengthen the suggestion of a carbonatic origin of the CO_2 exhalations of interest in the Ansanto Valley, with less depleted values in the trees nearest to the vents. However, the number of trees in which $\delta^{13}C$ was measured is too small to exclude a coincidence of the correspondence between the less-depleted $\delta^{13}C$ values and the proximity to the vents. On the contrary, the measurements of CO_2 clearly indicate a carbonatic origin of the vents (the δ^{13} of CO_2 is positive), excluding the volcanic origin, for which the stable isotope of carbon should have been more depleted.

ACKNOWLEDGMENTS

We wish to thank the municipality of Rocca San Felice, especially Mr Lucio Di Vito, who guided us in the valley during the sampling.

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