

STUDY ON THE ORIGIN OF CO₂ IN THE GASEOUS EMISSIONS OF CENTRAL ITALY

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INTRODUCTION

Central Italy is characterized by widespread CO₂ gas emissions that occur in the absence of present-day volcanism. Many hypotheses have been put forward for the origins of the emissions: carbonate hydrolysis (Panichi & Tongiorgi, 1976), metamorphic decarbonation in Paleozoic basement (Gianelli, 1985; Duchi *et al.*, 1992), or magma degassing (Minissale, 1991). The CO₂ in the gas emissions of the peri-Tyrrhenian sector is in general considered to be a mixture of mantle degassing sources and the byproduct of decarbonation of crustal carbonates, present in variable proportions (Minissale *et al.*, 1997; Minissale, 2004; Chiodini *et al.*, 1995, 2000). In the pre Apennine - Apennine belt, the origin of CO₂, whose manifestation often occurs in solution in highly mineralized waters, is still subject to debate. Some authors (Italiano *et al.*, 2008; Heinicke *et al.*, 2006) have suggested a pure crustal origin of CO₂-dominated gases, which is released by mechanical energy during seismic events or microseismicity.

In this work a geochemical study was carried out on central Italy to understand the relationship between gas emission, tectonic activity, travertine outcrop and groundwater chemistry and circulation. This investigation involved the performance of isotopic and chemical data from gas vent and soil gas, groundwater and travertine. The elaborations of the data allow us to improve our knowledge about both the source of CO₂ in the gas emissions of central Italy and the relationship between the source of CO₂ and the different geological settings throughout Italy.

GEOLOGICAL AND HYROGEOLOGICAL SETTING

Central Italy is divided from West to East into three geographical regions: the peri-Tyrrhenian sector, the Apennine chain and the peri-Adriatic basin; this division is based on distinctive geological, geophysical, and geothermal features.

The peri-Tyrrhenian sector is characterized by a thin young crust, less than 25 km thick, by high values of heat flow (up to 200 mW/m²; Della Vedova *et al.*, 2001) and shallow earthquakes (< 7 km; Amato & Selvaggi, 1991); in this sector, the extensional regime, directly correlated with the opening of the Tyrrhenian Basin, led to crustal thinning that allowed the ascent of magma which in turn fed a volcanic complex with prevalently high-K melt.

The Apennine chain is characterized by a 25-50 km thick crust, normal heat flow (30 mW/m²; Della Vedova *et al.*, 2001), and deeper seismicity (10-30 km; Amato & Selvaggi, 1991). Small volcanic edifices younger than 0.6 Ma occurred, where carbonate-rich pyroclastic rocks are associated with ultra-alkaline rocks (Stoppa & Woolley, 1997; Peccerillo, 1998).

The Adriatic sector is the only domain of the Apennines where folding and thrusting are still active, associated with the progressive eastward shifting of the Adriatic foredeep and migration of the foreland peripheral bulge. The seismic activity is not frequent. Most hydrocarbon reservoirs occur here; oil and gas are trapped at the top of Middle Miocene and Mesozoic carbonates or in structural (thrust-faulted anticlines) and stratigraphic traps (pinch-outs) located within different Pliocene sand bodies in the Adriatic foredeep.

From the hydrogeological point of view, the Mesozoic carbonates of the Apennine area are the most permeable formation of central Italy; due to their wide areal extent, the high fracture permeability and the relatively high rainfall rate, they are a major regional groundwater aquifer (Boni *et al.*, 1986). In the Apennine

area the main water types are Ca-(Mg)-HCO₃ and Ca-Mg-SO₄; in a limited number of cases the water types are Na-HCO₃, Na-Cl and Na-SO₄ (Chiodini *et al.*, 2000). The presence of Ca-SO₄ water types is mainly attributed to their circulation through Triassic anhydrites layers, located at the base of Mesozoic carbonate unit. The Apennine chain is a watershed; in the western part, *i.e.*, in the peri-Tyrrhenian sector, small shallow aquifers are hosted in Quaternary volcanics, leading locally to significant reservoirs of thermal water. In contrast, the eastern part of the watershed is characterized by limestone covered by a thick layer of clay-rich Miocene-Quaternary foredeep sediments. Furthermore, water emerging from Plio-Pleistocenic, Messinian and alluvial plain of Adriatic sector can have anomalous chemistry due to the upward movement of mineralized waters (both connate and from solubilisation of evaporitic rocks) through tectonised belts with Apenninic and anti-Apenninic orientation or where they cross, whether outcropping or buried (Desiderio *et al.*, 2007).

METHODS

Chemical and isotopic analysis of gas samples

36 samples of gas vents and 86 samples of soil gas were collected in 25 ml stainless steel canisters sealed by two vacuum stop-cocks. The sampling locations are shown in Fig. 1.

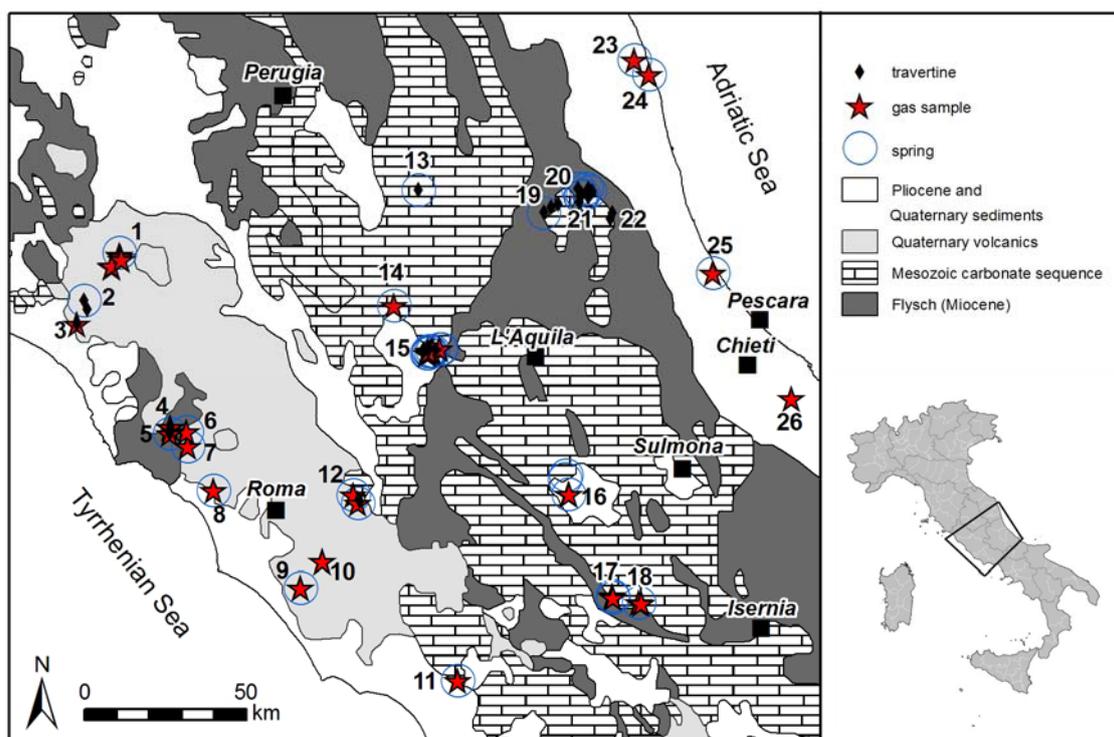


Fig. 1 - Geological map of central Italy and location of the sampling points: 1 - Latera, 2 - Canino, 3 - Mt. Rozzi, 4 - Tolfa, 5 - Stigliano, 6 - C. Monterano, 7 - C. Manziana, 8 - Palidoro, 9 - Zolfoforata Pomezia, 10 - Cava dei Selci, 11 - Laghi del Vescovo, 12 - Acque Albule, 13 - Triponzo, 14 - S. Susanna, 15 - S. Vittorino, 16 - Fucino, 17 - Posta Fibreno, 18 - Val Comino, 19 - Acquasanta Terme, 20 - Ascoli, 21 - C. Trosino, 22 - C. del Tronto, 23 - S. Marco, 24 - Porto S. Giorgio, 25 - Pineto, 26 - Frisa.

Helium concentrations were measured using a Varian Mass 4 spectrometer (analytical error ± 20 ppb). Nitrogen (N₂), oxygen (O₂) and carbon dioxide (CO₂) concentrations were determined using a Fisons GC-8000 Series gas-chromatograph coupled to a Thermal Conductivity Detector (TCD; analytical error $\pm 1\%$). For methane (CH₄) the instrument was coupled to a Flame Ionization Detector (FID) (analytical error ± 100 ppb). Chemical concentrations were corrected for air contamination.

After offline purification of CO₂ in a vacuum line, carbon isotope composition of CO₂ ($\delta^{13}\text{C-CO}_2$) was analyzed on a Finnigan MAT 252 (analytical error $\pm 0.1\%$). In 14 gas vent samples, carbon ($\delta^{13}\text{C-CH}_4$) and hydrogen ($\delta\text{D-CH}_4$) isotope compositions of CH₄ were measured by GC-C/TC-IRMS (analytical error $\pm 0.5\%$ and $\pm 5\%$, respectively). The system consists of a gas chromatograph (Trace GC ultra) coupled via an interface (GC-C/TC III) to a Thermo Finnigan Delta plus XP. Separation of the gases was performed on a CP PoraPLOT Q column. $\delta^{13}\text{C}$ and δD are expressed in delta notation relative to VPDB and VSMOW, respectively.

Helium isotope ratios were measured in 11 gas vent samples using a static vacuum mass spectrometer VG-5400TFT, following the method described by Caracausi *et al.* (2005). Typical uncertainties for low ^3He samples are below $\pm 5\%$. The $^3\text{He}/^4\text{He}$ isotope ratio is expressed as R/R_A , where R is $^3\text{He}/^4\text{He}$ ratio in the sample and R_A is the same ratio in the air ($R_A = 1.4 \times 10^{-6}$; Mamyrin & Tolstikhin, 1984).

Chemical and isotopic analysis of water samples

40 water samples were collected for chemical and isotopic analysis. The sampling locations are shown in Fig. 1. Temperature, pH, Eh and Electrical Conductivity were measured in the field. The samples were analyzed using an ion-chromatography (Metrom) for cations (Ca, Mg, Na, K) and anions (F, Cl, Br, NO₃, SO₄). $^{18}\text{O}/^{16}\text{O}$ isotopic ratios on water samples ($\delta^{18}\text{O-H}_2\text{O}$) were performed by equilibration technique (Epstein & Mayeda, 1953) with a Finnigan MAT 252. The isotopic composition of dissolved inorganic carbon ($\delta^{13}\text{C-DIC}$) was measured following the procedure of Kroopnick *et al.* (1970). The sample was acidified inside a vacuum line with concentrate phosphoric acid (H₃PO₄); the evolved CO₂ was purified and trapped with liquid nitrogen and analyzed on a Finnigan MAT 252. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ were expressed in delta notation relative to VPDB and VSMOW, respectively.

Isotopic analysis of travertine samples

69 travertine samples were collected in 10 sites; at each site the 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 one to eight, depending on the thickness of the travertine deposit. The sampling locations are shown in Fig. 1.

The travertine samples were analyzed for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ using standard procedures with a Finnigan MAT 252. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ are expressed in delta notation relative to VPDB and VSMOW, respectively.

RESULTS AND DISCUSSION

Sources of CO₂ in gas vents

As shown in Fig. 2A, the $\delta^{13}\text{C-CO}_2$ of gas vents suggests that CO₂ derived from different sources. Relatively negative $\delta^{13}\text{C-CO}_2$ values imply a CO₂ contribution from plant soil respiration and degradation of organic matter (Cerling *et al.*, 1991); less negative $\delta^{13}\text{C-CO}_2$ values involve thermo-metamorphic reactions in carbonate formation (from -3 to +2‰; Iannace, 1991), although a contribution from mantle ($\delta^{13}\text{C} = -4$ to -7% ; Pineau *et al.*, 2004) cannot be ruled out. Finally, contamination by atmospheric CO₂ ($\delta^{13}\text{C} =$ around -8% ; GLOBALVIEW-CO2C13, 2009) is possible in samples with very low concentration of CO₂. In order to estimate the proportion of CO₂ derived from distinct reservoirs, the carbon isotopic signature of CO₂ is often used. However, given the overlap in the isotopic fields of limestone and mantle end-member (Fig. 2a), the $\delta^{13}\text{C}$ values alone can lead to ambiguous results. Sano & Marty (1995) proposed to assess the mixing relations for carbon of various origins using the combination of $\delta^{13}\text{C}$, $^3\text{He}/^4\text{He}$ and He and C concentrations. The respective contributions from the different end-members: mantle (M), limestone (L) and organic-rich sedimentary (S), to the CO₂ gas emissions can be estimated by the following equation system:

$$\begin{aligned} \delta^{13}\text{C}_{\text{sample}} &= \text{M} * (\delta^{13}\text{C}_{\text{mantle}}) + \text{L} * (\delta^{13}\text{C}_{\text{limestone}}) + \text{S} * (\delta^{13}\text{C}_{\text{sedimentary}}) \\ 1/({}^{12}\text{C}/{}^3\text{He})_{\text{sample}} &= \text{M}/({}^{12}\text{C}/{}^3\text{He})_{\text{mantle}} + \text{L}/({}^{12}\text{C}/{}^3\text{He})_{\text{limestone}} + \text{S}/({}^{12}\text{C}/{}^3\text{He})_{\text{sedimentary}} \quad (1) \\ \text{M} + \text{L} + \text{S} &= 1 \end{aligned}$$

The isotopic end-member used for calculation were: $\delta^{13}\text{C}_{\text{mantle}} = -4/-7\text{‰}$ (Pineau *et al.*, 2004); $\delta^{13}\text{C}_{\text{limestone}} = +2.2\text{‰}$ (Cardellini, 2003); $\delta^{13}\text{C}_{\text{sedimentary}} = -23\text{‰}$ (Cerling *et al.*, 1991). Considering $^{12}\text{C}/^{3}\text{He}$ ratios of 2×10^9 for the mantle and 1×10^{13} for the carbonate rocks and for sedimentary sources (Sano & Marty, 1995), a progressive mixing between mantle and continental fluids was observed (Fig. 2b). The results strongly suggest that while the thermo-metamorphic reaction of Mesozoic limestone is the major source of CO_2 (average of 80%), a significant contribution arises from the mantle, particularly in the gas vents of “Laghi del Vescovo”, “Acque Albule” of Tivoli, “Val Comino”, “San Vittorino” plain and “Posta Fibreno” lake. The contribution of organic matter (1 to 30%) is not negligible in almost all of the samples.

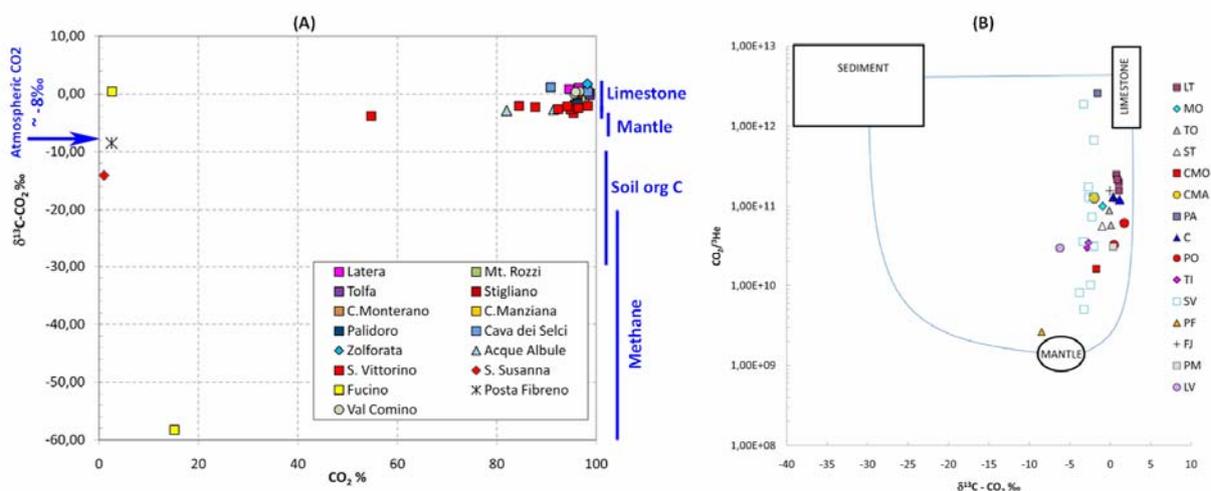


Fig. 2 - a) CO_2 concentration vs. $\delta^{13}\text{C}$ of gas vents, and value of $\delta^{13}\text{C}$ from various sources; b) Correlation diagram of Sano & Marty (1995) plotting $\text{CO}_2/^{3}\text{He}$ and $\delta^{13}\text{C}$ of the sampled gas vents: LT - Latera, MO - Mt. Rozzi, TO - Tolfa, ST - Stigliano, CMO - C. Monterano, CMA - C. Manziiana, PA - Palidoro, C - Cava dei Selci, PO - Zolforata Pomezia, TI - Acque Albule, SV - S. Vittorino, PF - Posta Fibreno, FJ - Fosso Janni, PM - Polla Monticchio, LV - Laghi del Vescovo. Lines show the theoretical mixing between a mantle end-member and two crustal end-members represented by marine limestone and sedimentary carbon.

Sources of CO_2 in soil gas

Through carbon isotope ratios it was possible to identify three different sources of CO_2 in soil gas (Fig. 3):

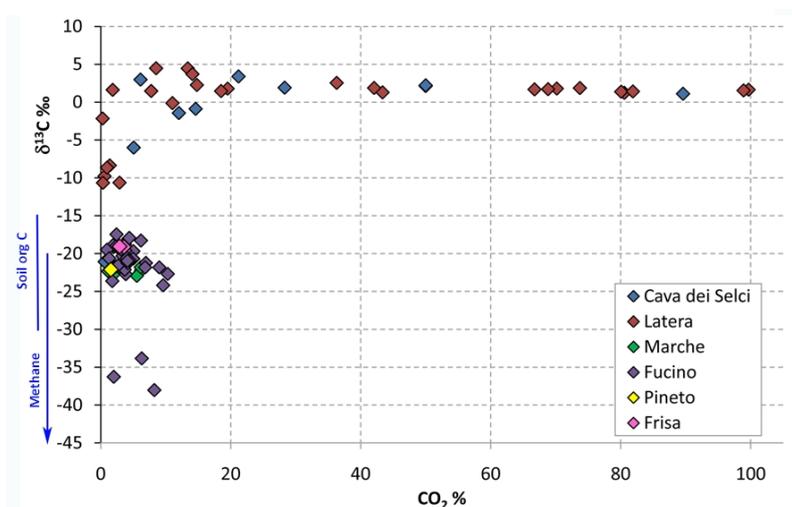


Fig. 3 - CO_2 concentration vs. $\delta^{13}\text{C}$ of soil gas, and value of $\delta^{13}\text{C}$ from various sources.

i) CO_2 from an inorganic source, such as the alteration of marine carbonates and/or degassing from mantle, characterized by $\delta^{13}\text{C}$ (from -5 to +5‰) in Cava dei Selci and Latera sites; *ii)* CO_2 produced from organic material by biological processes, characterized by $\delta^{13}\text{C} \sim -20\text{‰}$, in the majority of samples from the Fucino plain and from Adriatic sector sites; *iii)* CO_2 produced from CH_4 oxidation in unsaturated soil, with $\delta^{13}\text{C} \sim -33\text{‰}$, in some samples from the Fucino plain. The presence of high concentration (up to 10%) of CO_2 of biological origin in correspondence

with the major faults of the Fucino plain is particularly interesting. It suggests that CO₂ does not ascend through the fault from deep but is produced in the shallow soil. It is probable that, as faulting increases, the circulation of water and air along fractures is promoted, and therefore biological activity in them also increases. On the other hand, a biogenic CO₂ was found also in soil gas across the San Andreas fault (Shapiro *et al.*, 1982; Lewicki *et al.*, 2003) and across the Atotsugawa fault, in Japan (Sugisaki *et al.*, 1983). This result also shows that the values of the background gas concentration with respect to which of the relevant anomalies were detected (typically through various statistical methods; see Sinclair, 1991; Beaubien *et al.*, 2003) may be misleading without the confirmation of the isotopic data, at least as regards the determination of the anomalies of CO₂.

Sources of Dissolved Inorganic Carbon (DIC)

In the western Tyrrhenian sector of central Italy, CO₂ degassing occurs mainly from emission, such as gas vent or diffuse degassing and thermal springs; on the contrary, in the eastern Apennine area the CO₂ can be dissolved in the "cold" groundwater of regional aquifers hosted by Mesozoic carbonate formation (Chiodini *et al.*, 2000).

Chemical and isotopic composition of Dissolved Inorganic Carbon (δ¹³C-DIC) was used to discriminate the origin of CO₂ in studied groundwater, because this parameter represents the results of interaction among water, carbonate rocks and CO₂ coming from different sources, following the geochemical modeling proposed by Chiodini *et al.* (2000):

$$\delta^{13}C_{DIC} * DIC = (\delta^{13}C_{carb} * C_{carb}) + (\delta^{13}C_{ex} * C_{ex}) \quad (2)$$

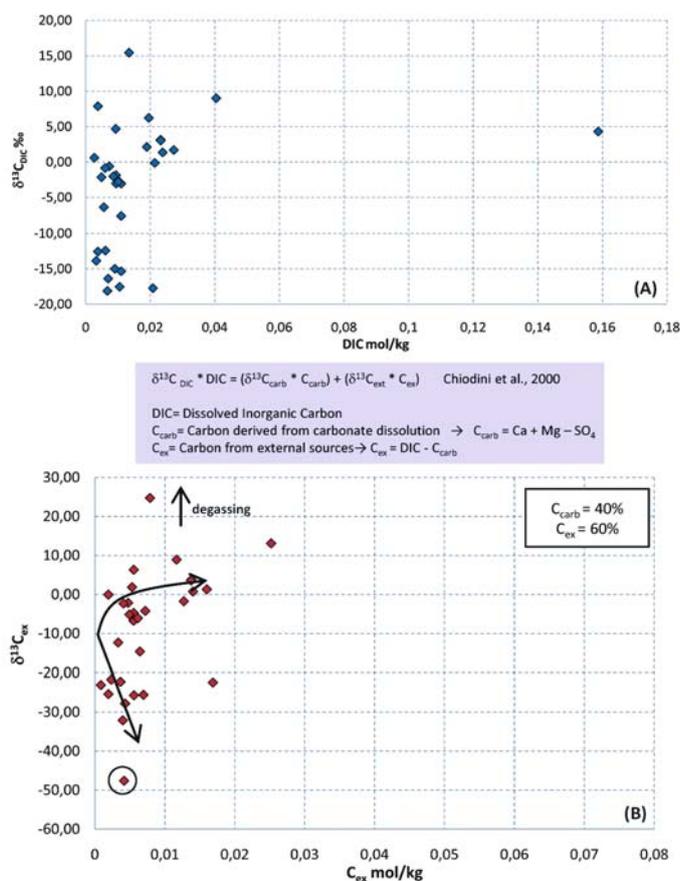


Fig. 4 - a) Dissolved Inorganic Carbon (DIC) contents vs. δ¹³C-DIC; b) Contents of dissolved carbon which derives from sources different from carbonate dissolution (C_{ex}) vs. its isotopic composition (δ¹³C_{ex}).

The amount of DIC that derives from the dissolution of the carbonate rocks (C_{carb}), limestone and dolostone, was computed as:

$$C_{carb} = Ca + Mg - SO_4 \quad (3)$$

The remaining fraction of carbon that derives from other sources (C_{ex}) is given by DIC - C_{carb}. In order to investigate the origin of C_{ex}, its isotopic composition (δ¹³C_{ex}) was computed by the equation (2) setting the isotopic composition of carbon, derived from dissolution of carbonate rocks (δ¹³C_{carb}), at 2.2‰ (Cardellini, 2003), *i.e.*, the average of carbon isotope composition of limestone of central Apennine.

δ¹³C-DIC in groundwater samples ranged from -18.2‰ to 15.4‰ (Fig. 4a), suggesting, through the large variation in DIC concentration, that the input of C_{ex} derived from more than one source. In particular, according to the equation (3), 40% of the carbon of DIC derived from the dissolution of carbonate rocks, 60% of carbon derived from other sources, on average. As shown in Fig. 4b, the calculated C_{ex} and δ¹³C_{ex} indicate the presence of two C_{ex} sources. The samples with δ¹³C_{ex} more negative

than -10‰ have received the input of soil CO₂ of organic origin, up to the case of samples collected along the Adriatic sector in which δ¹³C_{ex} reflects the organic CO₂ derived from decomposition of hydrocarbons. The samples with more positive δ¹³C_{ex} are compatible with an input of inorganic sources of CO₂.

Sources of carbon in travertine

In Fig. 5, carbon and oxygen isotopic compositions of travertine are shown, compared to those from other sites in central Italy (Manfra *et al.*, 1976; Minissale *et al.*, 2002). According to the equation of Panichi & Tongiorgi (1976)

$$\delta^{13}C_{CO_2} = 1.2 * \delta^{13}C_{trav} - 10.5 \quad (4)$$

obtained from the carbon isotopic compositions of CO₂ and travertine at the orifice of 11 active travertine-depositing springs, the ¹³C/¹²C ratio of parental CO₂ was recalculated from the measured δ¹³C values in fossil travertine.

Travertine from the Acquasanta site could have precipitated from fluids with δ¹³C of a mean value of -2.3‰, although it's not possible to rule out a nonequilibrium isotopic exchange during CO₂ degassing and travertine precipitation. δ¹³C_{CO2} calculated through equation (4) for travertines connected to Salinello and Castellano rivers valley (ranging from -16 to 1.7‰) seems to indicate a precipitation from fluids rich in CO₂, partly of biological origin and partly inorganic, probably from the decarbonation of limestone. Only travertines from the Triponzo site have frankly meteogene characteristics.

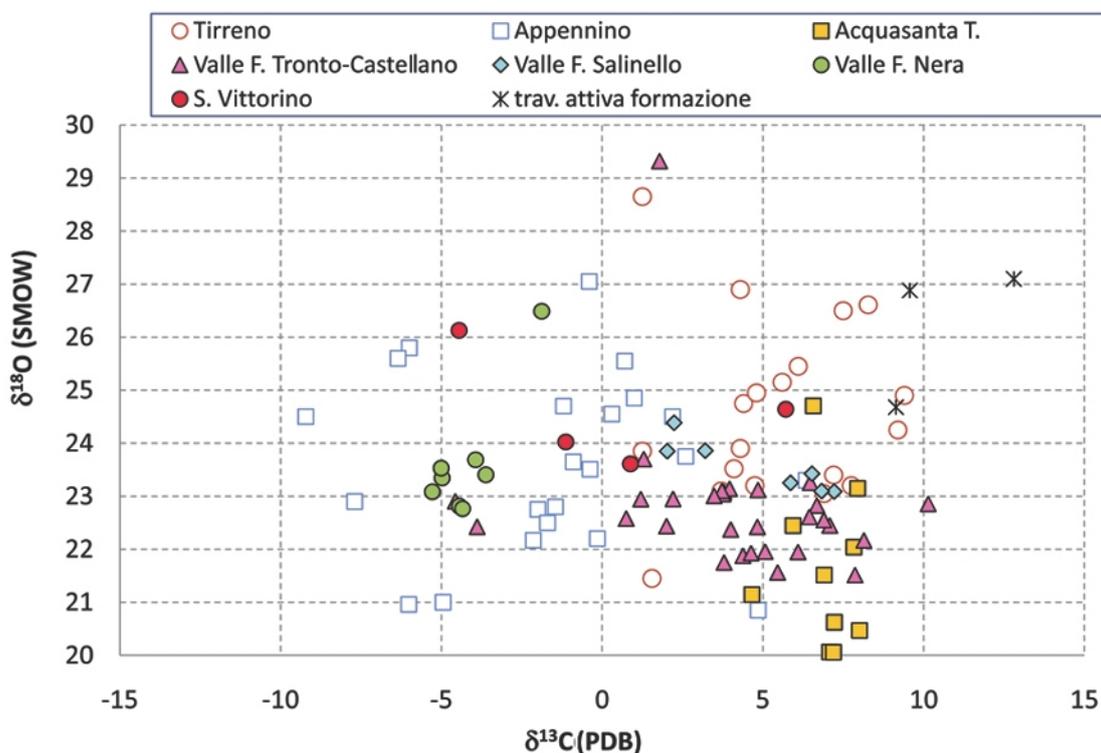


Fig. 5 - δ¹⁸O and δ¹³C plot for travertine sampled.

CONCLUSION

The elaboration and interpretation of the analytical data allowed us to identify the source of CO₂ in the following studied sites:

- free gas related to the S. Susanna spring (Rieti plain): the source of CO₂ is atmospheric/biological;
- soil gas in the Fucino plain (AQ): CO₂ is of biological origin, due to soil respiration and in some places by CH₄ oxidation;
- gas vent in the Fucino plain (AQ): CO₂ has inorganic origin, produced by alteration of buried limestones;
- gas vent sampled in Roman Comagmatic Province, along the Tyrrhenian margin, in the sites of Latera, Canino Mt., Tolfa, Stigliano, Caldara di Manziana, Palidoro, Cava dei Selci and Zolfo di Pomezia: CO₂ is the result of a mixing between a CO₂ produced by thermo-metamorphic reaction of carbonatic rocks and a mantle CO₂ (in a percentage of 1-5%);
- gas vent of L. del Vescovo (LT), Acque Albule of Tivoli (RM), Val Comino (FR), S. Vittorino plain (RI): CO₂ is the result of a mixing between a CO₂ produced by thermo-metamorphic reaction of carbonatic rocks and a mantle CO₂ (in a percentage of 5-20%);
- free gas related to Posta Fibreno Lake (FR): more than 50% of CO₂ seems to derive from mantle degassing.

The chemical and isotopic data of water samples highlighted that 40% of dissolved inorganic carbon is produced, on the average, by the dissolution of calcium-magnesium carbonates and gypsum (or anhydrite). The remaining 60% of dissolved inorganic carbon can be representative of infiltrating water in equilibrium with soil gases or of an input of CO₂ deriving from metamorphic decarbonation of local marine limestones.

The source of CO₂ has been related to tectonic setting of central Italy. In fact, on a regional scale, in the central Italy the Tyrrhenian margin is characterized by extensional tectonics whereas the foredeep Adriatic sector can be considered to be in a compressive regime.

In this work, the geochemical data has allowed us to identify a relationship between the normal faults and the CO₂ produced by thermo-metamorphic reaction of carbonatic rocks and 1-5% of mantle-derived CO₂ along the Tyrrhenian margin. In the central Apennine sector, that overlaps with the Umbria-Marche-Abruzzi Apennines Ridge, Lavecchia *et al.* (1994) have described the concurrent existence, during the Quaternary, of extensional structures and transfer faults in the Apennines ridge, and the thrust fault in Adriatic off-shore, that represent the active front of Apennine chain.

In particular, Faccenna *et al.* (1994) identified a set of middle-upper Pleistocene N-S shear zones that display a strike-slip component of motion. In this shear zones (Acque Albule area, the western border of the Lepini Mountains, and the San Vittorino plain), the source of CO₂ is the result of a mixing between a CO₂ produced by the thermo-metamorphic reaction of carbonatic rocks and mantle CO₂ in the range of 5-20%. Of particular importance is the contribution of CO₂ from the mantle (estimated at around 75%) in the free gas related to Posta Fibreno lake.

This seems to confirm the interpretation of several authors (Scarascia *et al.*, 1994; Ciotoli *et al.*, 1993) about the Val Roveto fault, *i.e.*, a crustal discontinuity corresponding with a step in the Moho. Higher rates of carbon coming from the mantle can therefore be found in the Apennines than in the peri-Tyrrhenian volcanic areas. In the latter areas, however, the reservoirs of CO₂ are larger than those of the Apennine tectonic basins because the isotopic signal of carbon from the mantle may be diluted by the large amount of CO₂ produced mainly by thermal metamorphism.

Finally, the internal sector of the Apennines in extension is “separated” from the external compression by several thrusts, like the Olevano-Antrodoco-Mts. Sibillini thrust and the Gran Sasso thrust (Calamita *et al.*, 1997).

These structures constitute barriers either for the migration of fluids (Ghisetti *et al.*, 2000) and for the CO₂ produced in the west of these structures. In fact, the data of carbon isotopic composition of travertine and the

DIC of Acquasanta Terme, and the data of the isotopic composition of helium (Minissale *et al.*, 2002), demonstrates that CO₂ is mainly due to processes caused by the dissolution of CaCO₃ during long and deep water circulation. Even the travertine confirms the relationship between structural setting and the origin of CO₂. The thermogenic travertine, associated with thermal springs, are common in the peri-Tyrrhenian coast, whereas meteogene travertine are characterized by average values more negative of carbon isotopic composition (deposits associated with Castellano, Salinello and Corno River), because they come from CO₂ produced by the alteration of soil organic matter.

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