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Origin and significance of hydrocarbons in CO_2-rich gases from Central Italy seismic areas

A. Ricci, Y. Oliveri, D. Buttitta, G. Capasso, L. Chiaraluce, E. Serpelloni, A. Caracausi

Supplementary Information

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- Materials and Methods
- Extended Description of the Results
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Materials and Methods

Seven cold ($T^{outlet} \leq T^{air}$) gas vents (Fungaia, Uppiano, Nogna, Umbertide, Vibio, Montenero, Montecchie), located in Central Italy roughly along a N-S axis (Figure 1 in the main text), were sampled in December 2018, April 2019 and October 2023. At Fungaia, Umbertide, Vibio, Montenero and Montecchie, deeply derived gases vigorously bubble in surficial waters forming bubbling pools as large as 2-3 meters in diameter (*e.g.*, Umbertide). Such sites are characterized by intense CO_2 degassing, with estimated CO_2 fluxes of tens of tons/day. On the contrary, Uppiano and Nogna sites are characterized by lower fluxes and more gentle gas bubbling in water.

Pre-evacuated 150 mL glass flasks filled with 50 mL of a 4 M Na(OH) solution (Giggenbach, 1975; Giggenbach and Goguel, 1989) and equipped with a Teflon stopcock were used in line with silicone/tygon tubes connected to a plastic/steel funnel to sample gases for the determination of the stable isotopic composition of methane, ethane, propane and n-butane. At each sampling sites, three further gas aliquots were collected using 20-60 mL flow-through glass flasks equipped with two Teflon stopcocks for measuring the chemical gas composition, the $^{13}C/^{12}C$ ratio of CO_2 and the helium isotopic composition. Chemical and isotopic analyses were carried out at the laboratories of the Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo (INGV-PA).

Concentration of inorganic and organic gas species was determined using a gas chromatograph (GC, Agilent 7890B equipped with PPU and MS5A columns) associated with a MicroGC module (equipped with a PPU column) and a double detector (TCD and FID) and using argon as carrier gas. The analytical error was better than 3 %.

The carbon isotopic composition of CO_2 was measured using a Delta Plus XP isotope ratio mass spectrometer equipped with a Thermo TRACE GC and a Thermo GC/C III interface. The ^{3}He and ^{4}He were measured by a Helix SFT-GVI double collector while a multicollector Thermo-Helix MCPlus mass spectrometer was used to measure ^{20}Ne after applying standard purification procedures to the gas samples (Rizzo *et al.*, 2015, 2018).

The $^{13}C/^{12}C$ ratios of CO_2 are reported in delta notation (‰) relative to VPDB (*i.e.*, $\delta^{13}C$-CO_2), while helium isotope compositions are given as R/Ra (*i.e.*, $^3He/^4He$ of the sample versus the atmospheric $^3He/^4He$ ratio of 1.39×10^{-6}), with analytical errors lower than 0.1 ‰ and 0.3 %, respectively.

The analyses of the $^{13}C/^{12}C$ and $^2H/^1H$ ratios of CH_4 (expressed as $\delta^{13}C$-CH_4, ‰ *vs*. VPDB and δ^2H-CH_4, ‰ *vs*. VSMOW, respectively) were performed on CH_4 enriched in the headspace of the sampling flasks using a Thermo Delta Plus XP IRMS coupled with a Thermo TRACE GC and equipped with a GC/C III and a GC/TC interface for determining carbon and hydrogen isotopic composition, respectively. Methane was separated using a GC system equipped with a Poraplot-Q column (length = 30 m, i.d. = 0.32 mm) held at 50 °C and using a constant flux of helium (carrier gas) of about 1.3 cm^3/min. After separation, methane was converted to CO_2 at 950 °C using an oxidation furnace (NiO-CuO). For the H-isotope analysis, methane was instead converted to H_2 at 1450 °C using a pyrolysis furnace. The CO_2 and H_2 thus obtained were then introduced in the IRMS using the system of injection split/splitless described in Grassa *et al.* (2010). The C-isotope analysis of ethane, propane and n-butane was performed following the same procedures used for methane. The analytical error for carbon and hydrogen isotope analysis was usually better than 0.2 ‰ and 5 ‰, respectively.

Extended Description of the Results

Chemical and isotopic compositions of gas discharges analyzed in the present study are reported in Tables S-1 through S-4. Most of the investigated gas discharges has a chemical composition dominated by CO_2 (765,000-975,000 µmol/mol). The only exception is Nogna gas emission which shows a CH_4-dominated chemical composition, with CH_4 and CO_2 concentrations of 919,000-927,000 and 2800 µmol/mol, respectively. Nitrogen (N_2) and helium (He) contents extend from 11,500 to 161,300 µmol/mol and from 4 to 378 µmol/mol, with the highest values measured at Uppiano gas emission. Methane contents in the CO_2-dominated gases are between 1848 and 4900 µmol/mol, except for Uppiano gases where they reach up to 53,900 µmol/mol. Oxygen (O_2) concentrations are always lower than 7500 µmol/mol, indicating that the investigated gas samples are generally not affected by significant air contamination. Molecular hydrogen (H_2) and carbon monoxide (CO) concentrations range from 1.4 to 247 µmol/mol and from 2.1 to 3.9 µmol/mol, respectively. The ethane (C_2H_6) concentrations are 0.2-293 µmol/mol and 268-391 µmol/mol in the CO_2-dominated emissons and Nogna site, respectively. The propane (C_3H_8) contents vary between 0.5 and 22 µmol/mol. The n-butane (nC_4H_{10}) concentration was only measured at the Fungaia site and is equal to 4 µmol/mol.

The $\delta^{13}C$-CO_2 values of the CO_2-rich gas discharges vary in a relatively narrow range, from -4.6 to +0.3 ‰, whereas those of the CH_4-rich gases emitted at Nogna show the lowest measured values, equal to -11.7 ± 1.4 ‰. Most of the CO_2-rich gases have $\delta^{13}C$-CH_4 and δ^2H-CH_4 values ranging from -38.9 to -17.8 ‰ and from -175 to -104 ‰, respectively. Methane discharged at Uppiano is instead characterized by a significantly more negative isotope signature, with $\delta^{13}C$-CH_4 and δ^2H-CH_4 of around -48.3 ‰ and -190 ‰, respectively. Finally, the CH_4-rich gases discharged at Nogna have $\delta^{13}C$-CH_4 and δ^2H-CH_4 values of around -75 ‰ and -201 ± 7 ‰, respectively. The carbon isotopic compositions of C_2H_6 and C_3H_8 for most of the investigated CO_2-rich gases vary from -28.8 to -21.8 ‰ and from -28.2 to -21.9 ‰, respectively. The only exception is Uppiano, where C_3H_8 shows a more ^{13}C-enriched isotopic composition, with $\delta^{13}C$ value of around -10.1 ± 0.4 ‰. The $\delta^{13}C$ of n-butane was only determined at the Fungaia site and has a value of -22.5 ‰. Methane-rich gases from Nogna show a highly variable isotopic composition of C_2H_6, with $\delta^{13}C$ of -31.6 ± 11.5 ‰.

The analyzed gas samples have helium isotope ratios (R/Ra) ranging between 0.01 and 0.7 and are characterized by high $^4He/^{20}Ne$ ratios (up to 3276).

Supplementary Tables

Table S-1 Name, geographical coordinates, and sampling dates (day/month/year) of the cold gas vents collected in Central Italy in December 2018, June 2019 and October 2023. The estimated distance (in km) of the gas emissions from the 100 mW/m^2 heat flux reference isoline are reported. The estimated heat flux at the gas emission site is also reported.

Sample name	**Sampling date**	**Coordinates (WGS84)**		**Distance from the 100 mW/m^2 heat flux isoline**	**Estimated heat flux**
	dd/mm/yyyy	Latitude (°)	Longitude (°)	km	mW/m^2
Fungaia	05/12/2018	43.628826	12.040583	55	70
Fungaia	04/06/2019	43.628826	12.040583	55	70
Fungaia	03/10/2023	43.628826	12.040583	55	70
Uppiano	05/12/2018	43.452101	12.202398	57	80
Uppiano	04/06/2019	43.452101	12.202398	57	80
Uppiano	03/10/2023	43.452101	12.202398	57	80
Nogna	04/12/2018	43.402869	12.459584	73	60
Nogna	04/06/2019	43.402869	12.459584	73	60
Umbertide[a]	05/12/2018	43.308252	12.305686	53	80
Umbertide	05/06/2019	43.308252	12.305686	53	80
Umbertide	02/10/2023	43.308252	12.305686	53	80
Vibio[b]	04/12/2018	42.823449	12.359266	25	40
Vibio	05/06/2019	42.823449	12.359266	25	40
Vibio	02/10/2023	42.823449	12.359266	25	40
Montenero	05/06/2019	42.712868	12.457389	27	35
Montecchie	04/12/2018	42.48792	12.378119	7.5	45
Montecchie	04/06/2019	42.48792	12.378119	7.5	45
Montecchie	02/10/2023	42.48792	12.378119	7.5	45

Table S-2 Chemical gas composition of the studied gas emissions from Central. Concentrations of the inorganic and organic gas species are reported in µmol/mol.

Sample name	Sampling date (dd/mm/yyyy)	CO_2	He	N_2	CH_4	O_2	H_2	CO	C_2H_6	C_3H_8	nC_4H_{10}
Fungaia	05/12/2018	908000	35	65700	1848	4800	247	2.9	56	16	
Fungaia	04/06/2019	933000	36	55000	1890	337	235	3.9	50	14	
Fungaia	03/10/2023	938600	36	50100	1887	413	247		52	11	4
Uppiano	05/12/2018	810000	316	122000	45000	1300			223	13	
Uppiano	04/06/2019	765000	378	161300	53900	1600	4	2.1	293	16	
Uppiano	03/10/2023	831700	310	119600	42700	1100					
Nogna	04/12/2018	2800	36	70200	927000	2000	2.5		391		
Nogna	04/06/2019	2800	33	60300	919000	721			268		
Umbertide	05/12/2018	886000	40	84000	2236	4900	2.2	2.6	35	4.3	
Umbertide	05/06/2019	912000	40	68600	2241	82	12		35	4	
Umbertide	02/10/2023	911800	43	73200	2322	1900	9		39	3.8	
Vibio	04/12/2018	962000	13	15000	2455	7300	1.4		1.3	1.3	
Vibio	05/06/2019	973000	13	14500	2392	947	7		2.1	1.7	
Vibio	02/10/2023	975000	13	11500	2429	548	8		3.2		
Montenero	05/06/2019	960000	11	26400	4900		6		2.8	22	
Montecchie	04/12/2018	951000	8	24000	2590	1500	2.9		0.2	0.5	
Montecchie	04/06/2019	960000	7	19300	2400		2.2				
Montecchie	02/10/2023	968300	3.9	11400	1856	208					

Table S-3 Carbon and hydrogen isotopic compositions of CO_2 and light hydrocarbons of the investigated cold gas vents from Central Italy. Isotopic compositions of H and C are reported in delta notation (‰) relative to VSMOW and VPDB, respectively.

Sample name	Sampling date (dd/mm/yyyy)	$\delta^{13}C$-CO_2	$\delta^{13}C$-CH_4	$\delta^{13}C$-C_2H_6	$\delta^{13}C$-C_3H_8	$\delta^{13}C$-nC_4H_{10}	δ^2H-CH_4
Fungaia	05/12/2018	-4.6	-36.3	-27.7	-24.4		-153
Fungaia	04/06/2019	-4.5	-36.9	-28.5	-24.4		-136
Fungaia	03/10/2023	-4.6	-38.9	-26.5	-24	-22.5	-175
Uppiano	05/12/2018	-3.2	-48.3	-21.8	-9.7		-190
Uppiano	04/06/2019	-3.1	-48.3	-22.5	-10.5		-191
Uppiano	03/10/2023	-3.4					
Nogna	04/12/2018	-10.3	-75.0	-43.1			-194
Nogna	04/06/2019	-13.1	-75.9	-20.1			-208
Umbertide	05/12/2018	-3.6	-25.1	-25.7	-21.9		-128
Umbertide	05/06/2019	-3.2	-25.6	-26.5	-22		-104
Umbertide	02/10/2023	-3.5	-27.6	-24.8			-140
Vibio	04/12/2018	-1.2	-22.7	-28.8	-28.2		-137
Vibio	05/06/2019	-0.4	-21.9	-28.5	-26.2		-157
Vibio	02/10/2023	-1.2	-20.0				-134
Montenero	05/06/2019	0.3	-23.0	-28.1	-26.6		-157
Montecchie	04/12/2018	-0.8	-21.4				-119
Montecchie	04/06/2019	-0.4	-18.8				-171
Montecchie	02/10/2023	-1.1	-17.8				-142

Table S-4 Noble gas isotopes of the studied cold gas vents from Central Italy. Helium isotopic compositions are reported as R/Ra values, with R and Ra being the $^3He/^4He$ ratios measured in the samples and of the atmosphere (1.39×10^{-6}), respectively.

Sample name	Sampling date (dd/mm/yyyy)	$^3He/^4He$	$^4He/^{20}Ne$
Fungaia	05/12/2018	0.02	3276
Fungaia	04/06/2019	0.02	645
Fungaia	03/10/2023	0.02	300
Uppiano	05/12/2018	0.02	2377
Uppiano	04/06/2019	0.02	1009
Uppiano	03/10/2023	0.03	946
Nogna	04/12/2018	0.01	113
Nogna	04/06/2019	0.01	103
Umbertide	05/12/2018	0.03	1638
Umbertide	05/06/2019	0.03	205
Umbertide	02/10/2023	0.03	247
Vibio	04/12/2018	0.10	1143
Vibio	05/06/2019	0.10	89
Vibio	02/10/2023	0.10	144
Montenero	05/06/2019	0.17	62
Montecchie	04/12/2018	0.64	441
Montecchie	04/06/2019	0.61	53
Montecchie	02/10/2023	0.70	35

Supplementary Information References

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