

Supplementary Data

This document contains (1) additional figures and tables, (2) detailed methods.

1- Additional figures and tables

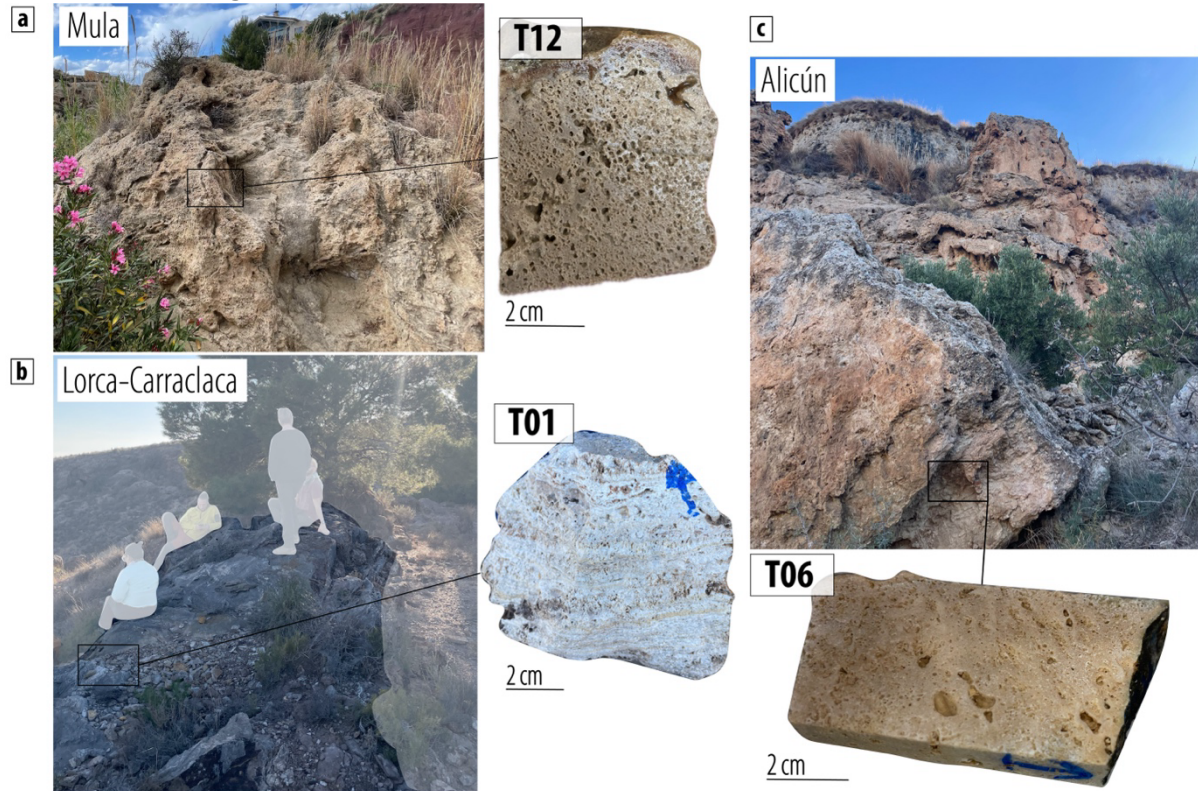


Figure S1: Additional samples travertines

9 Table S1: C and O isotope ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, VPDB) of travertines. No influence of petrographic heterogeneity on isotopic composition.

Lat.	Long.	Site	Samples	Comments	$\delta^{13}\text{C}$ (‰VPDB)	$\delta^{18}\text{O}$ (‰VPDB)
37°41'48.92"N	1°39'50.69"W	Carraclaca	T1.1	Light zone	7.09	-5.55
			T1.2	Iron-rich band	4.47	-5.67
			T2.1	Light zone	7.28	-5.72
			T2.2	Iron-rich band	5.51	-5.87
			T3	Homogeneous travertine	10.01	-4.82
37°30'35.10"N;	3° 6'33.95"W	Alicún de las Torres	T4	Homogeneous travertine	0.56	-9.74
			T5	Homogeneous travertine	0.28	-9.57
			T6	Homogeneous travertine	0.8	-6.24
			T7.1	Matrix band	-0.36	-9.38
			T7.2	Calcite band	-0.46	-9.84
37° 1'12.67"N	2°27'16.58"W	Tabernas	T8.1	Darker matrix band	4.02	-5.05
			T8.2	Whiter matrix band	1.86	-6.48
			T8.3	Calcite bands	3.07	-5.47
			T9.1	Darker porous zone	0.56	-4.89
			T9.2	Whitest more compact zone	0.46	-5.78
38° 2'15.82"N	1°25'35.14"W	Baños de Mula	T12.1	Porous area	-6.05	-7.25
			T12.2	Compact area	-7.03	-6.94
36°54'21.71"N	2° 5'38.27"W	Carboneras	T13.1	Closer to the fault plan	-7.94	-4.1
			T13.2	Closer to the matrix	-8.48	-4.73
			T13.3	Matrix with clast	-6.38	-4.4
37°13'53.13"N	3°43'12.36"W	Sierra Elvira	T14	Crystalline phase	-10.35	-7.32

10

11

Table S2: Uncorrected version of Table 2 showing raw gas compositions prior to atmospheric air correction. Oxygen concentrations and analytical uncertainties for all measured gas species are included.

12

13

14

Site gas-phase concentration, non air-corrected	N ₂ (vol%)	O ₂ (vol%)	CO ₂ (vol%)	CH ₄ (vol%)	⁴ He (ppmv)
ALFACAR (B)	77.5 ± 0.9	14.64 ± 0.04	0.443 ± 0.002	4.9 ± 0.5	6.5 ± 0.2
ARCHENA (B)	88 ± 2	7.05 ± 0.03	2.04 ± 0.01	0.50 ± 0.09	1000 ± 10
ARCHENA (D)	80 ± 1	0.76 ± 0.01	8.55 ± 0.03	1.2 ± 0.2	710 ± 10
CAPUCHINA (Lanjarón) (B)	27.9 ± 0.4	7.71 ± 0.02	62.4 ± 0.2	0.03 ± 0.04	7.1 ± 0.2
EL FRONTIL (B)	81.5 ± 1.0	15.75 ± 0.05	0.323 ± 0.001	0.012 ± 0.003	18.4 ± 0.2
LORCA-CARRACLACA (B)	43.4 ± 0.7	3.44 ± 0.01	51.1 ± 0.2	0.03 ± 0.02	229 ± 4
PUERTOBLANCO (RONDA) (B)	83 ± 1	3.85 ± 0.01	0.0463 ± 0.0007	10.1 ± 0.7	13.6 ± 0.2
(Sierra) ALHAMILLA (B)	85 ± 1	6.9 ± 0.9	4.2 ± 0.3	0.4 ± 0.1	327 ± 3
ZÚJAR (B)	93 ± 1	2.179 ± 0.007	1.577 ± 0.006	0.11 ± 0.02	434 ± 5

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29 Table S3: Air-corrected gas compositions of gas and water samples from partial pressure. Gas- and water-phase compositions should not be interpreted as
 30 directly equivalent, as gas-water partitioning was not assumed to be at equilibrium. These values are therefore used only for visualization in the ternary
 31 diagram shown in Figure 6a.
 32

Site	Phase	N ₂ (%)	CH ₄ (%)	CO ₂ (%)	⁴ He ppmv
Alfacar	Gas	81	17	1.5	10
Alicún de las Torres	Water	95	0.02	4.9	139
Archena	Water	89	1.4	9.8	812
Archena	Gas	92	0.81	7.0	1434
Capuchina	Water	3.3	0.08	97	5
El Frontil	Gas	99	0.05	1.3	63
Graena	Water	95	0.14	4.4	64
Lorca-Carraclaca	Gas	37	0.03	63	280
Mula	Water	93	0.02	6.8	146
Pórtugos	Water	5.9	0.05	94	4
Puerto Blanco	Gas	87	13	0.05	16
Retamar–Carboneras	Water	95	0.96	4.1	703
Salado	Water	5.1	0.05	95	4
Santa Fe	Water	99	0.06	1.3	214
Sierra Alhamilla	Gas	93	0.57	6.6	503
Zújar	Water	92	0.12	7.6	784
Zújar	Gas	98	0.13	1.8	498

33

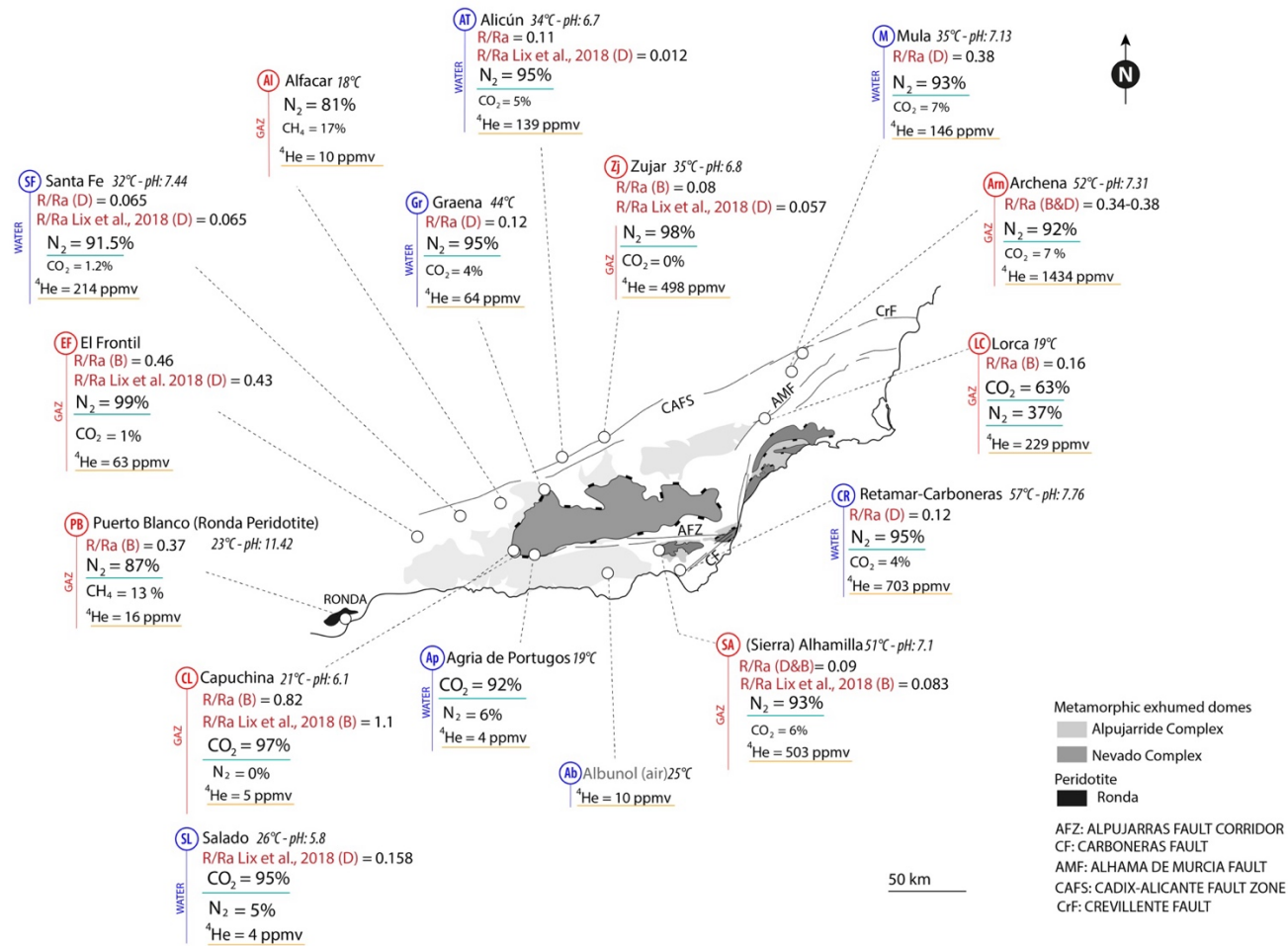
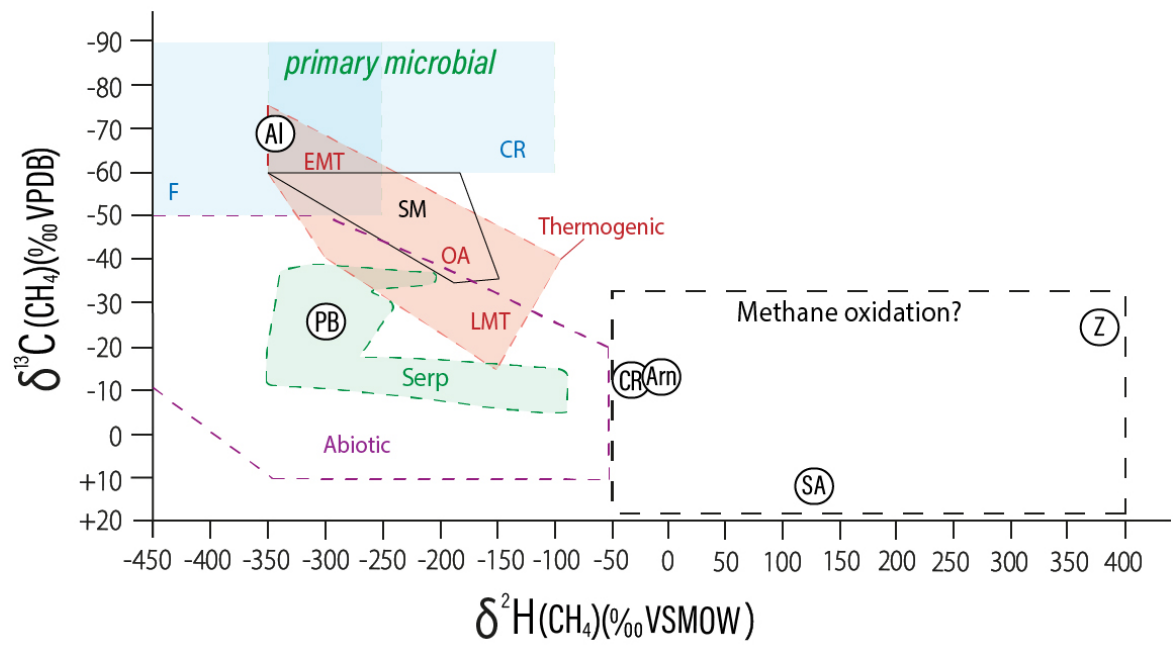


Figure S2: Spatial distribution of air-corrected gas compositions across the Betic Cordillera (cf Table S3). Blue symbols (D) represent dissolved-gas measurements and red symbols (B) bubbling-gas samples. N₂ and CO₂ are reported in % from partial pressure, and ⁴He in ppmv. Gas- and dissolved-phase compositions should not be interpreted as directly equivalent, as gas–water partitioning was not assumed to be at equilibrium; dissolved-gas compositions are shown here only to facilitate spatial comparison.

40



41
42
43
44
45
46
47

Figure S3: Carbon and hydrogen isotope compositions of methane ($\delta^{13}\text{C-CH}_4$ and $\delta\text{D-CH}_4$) from Betic springs. Alfacar exhibits a microbial methane signature, whereas Puerto Blanco is consistent with methane generated from serpentinization of the Ronda peridotite (Etiope et al., 2016). Most samples plot outside the established genetic fields, consistent with methane oxidation (Milkov and Etiope, 2018).

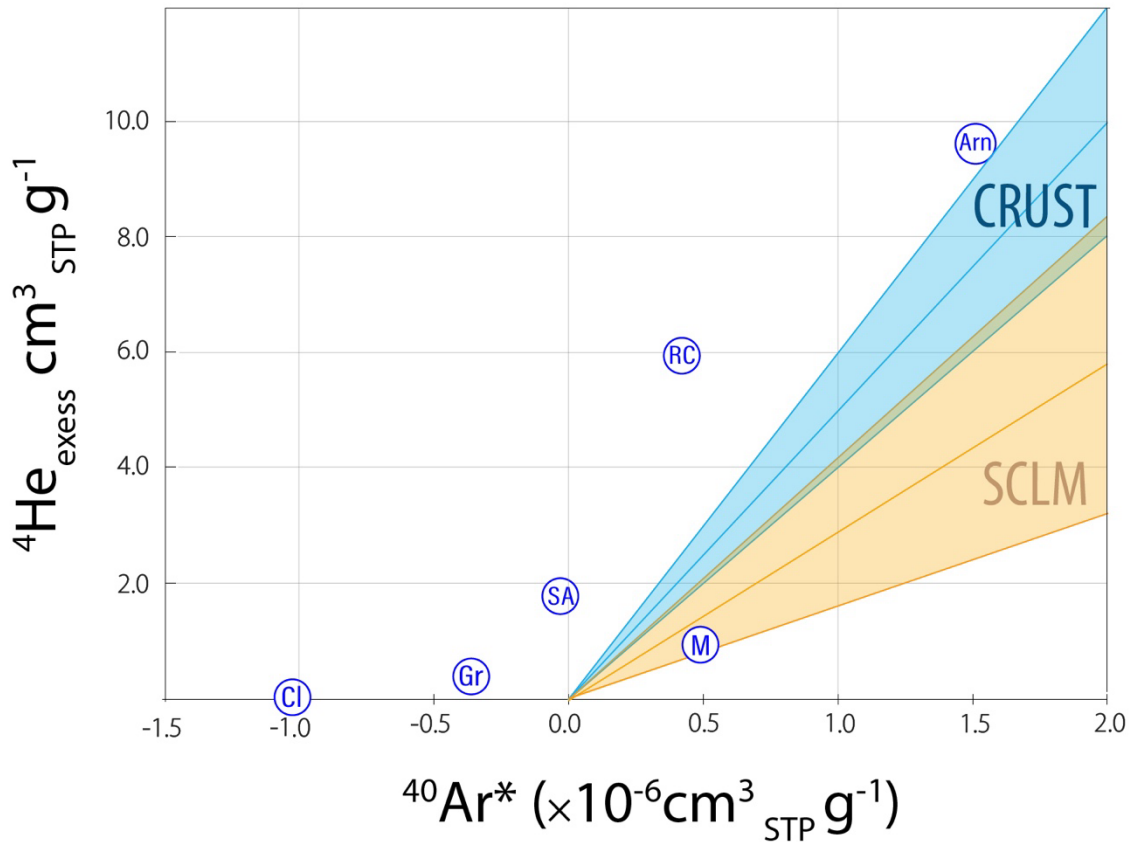


Figure S4: ${}^4\text{He}^*_{\text{excess}}$ vs ${}^{40}\text{Ar}^*$ in Betic spring waters, adapted from the approach of Brown et al. (2026). Excess concentration refers to non-atmospheric component. Because ${}^{38}\text{Ar}$ was not measured, ${}^{40}\text{Ar}^*$ was approximated from total Ar and measured ${}^{40}\text{Ar}/{}^{36}\text{Ar}$ ratios, assuming atmospheric ${}^{36}\text{Ar}$. ${}^4\text{He}_{\text{excess}}$ was estimated by subtracting the atmospheric He component inferred from dissolved Ne and equilibrium He/Ne ratios. Colored fields represent expected crustal (4-6) and MORB/SCLM (1.6-4.2) ${}^4\text{He}/{}^{40}\text{Ar}$ production ratio.

2- Detailed methods and protocols

2.1 O-C Stable isotopes

Stable carbon and oxygen isotope analyses ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, VPDB) were performed on all travertines ($n = 12$; Table 1). Where distinct textural heterogeneities were observed (e.g., color variations or banding), multiple microdrilled subsamples were analyzed ($n=21$; Table S1). Carbonate powders ($\sim 40\text{-}50\ \mu\text{g}$) were extracted from travertine samples using a Dremel 3000 rotary tool and collected in plastic capsules at the LFCR. Powders were reacted with anhydrous 100% phosphoric acid at 70°C in individual vessels in an automated cryogenic distillation system (Kiel IV carbonate device), coupled with a Delta V-Advantage isotope ratio mass spectrometer (IRMS-Thermo Fisher Scientific) at the the IStEP laboratory (Sorbonne Université, Paris, France). The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values (V-PDB scale) were normalized to the international NBS-19 ($\delta^{18}\text{O} = -2.20\text{‰}$; $\delta^{13}\text{C} = 1.95\text{‰}$) standards. Isotopic ratios are reported in per mil (‰) relative to the VPDB standard, with analytical accuracy of $\pm 0.03\text{‰}$ for $\delta^{13}\text{C}$ and $\pm 0.06\text{‰}$ for $\delta^{18}\text{O}$.

2.2 Major Gaz isotopes (Isolab)

Chemical and carbon isotope compositions were performed by Isolab (Netherlands). The composition of gas samples is analyzed on two GCs. The H_2 , O_2 , Ar, N_2 , CO and methane are analyzed on an Agilent 7890A GC (Agilent Technologies, Santa Clara, US) equipped with a 25m, 0.32mm molsieve 5A column (Agilent) and a TCD detector. Hydrocarbons and CO_2 are analyzed on an Agilent 7890B GC equipped with a 50m, 0.32mm Porabond-Q column (Agilent), coupled to a TCD detector (for CO_2 and H_2S) and a 30m 0.32mm Gaspro column (Agilent), coupled to an FID detector (for hydrocarbons). Both GCs are equipped with a heated valve for injection of the samples and on both GCs Helium is uses as carrier gas. One complete composition is calculated from the results of the three detectors. Detector responses are calibrated several times a day using various reference standards. Detection limits are ca. 1ppm for hydrocarbons, ca. 400 ppm for H_2 and ca 100 ppm for CO_2 , O_2 and N_2 .

Carbon isotope of methane: Carbon isotopes of methane are analyzed with an Agilent 6890N GC (Agilent Technologies, Santa Clara, US) interfaced to a Finnigan Delta S IRMS (Finnigan is now part of Thermo Scientific, Bremen, Germany) using a Finnigan GC-C II interface. The GC is equipped with a 12m, 0.32mm molsieve column (Agilent) and an injection valve. Samples are calibrated regularly against a calibration standard and results are reported in promille vs. vPDB. Limit of concentrations required are: 25-50 ppm.

Carbon isotopes of ethane-pentane are analyzed on an Agilent 7890A GC (Agilent Technologies, Santa Clara, US) interfaced to a 253 plus IRMS (Thermo Scientific, Bremen, Germany) using a GC-Isolink interface from Thermo. The GC is equipped with a 25m, 0.32mm Porabond-Q column (Agilent) and an

injection valve. Cold trapping is used to pre-concentrate the sample when necessary. Samples are run at least 3 times after which the average of the results is calculated. The system is calibrated at least once a day using an in-house natural gas standard and results are reported in promille vs. vPDB.

The dD measurements are done on an Agilent 7890A GC (Agilent Technologies, Santa Clara, US) interfaced to a MAT 253 IRMS (Thermo Scientific, Bremen, Germany) using a GC-Isolink interface from Thermo. The GC is equipped with a 25m, 0.32mm molsieve column (Agilent) and an injection valve. Samples are calibrated regularly against a calibration standard and results are reported in promille vs. vSMOW. Minimum concentration: ca. 300ppm

2.3 MiniRUEDI

The concentration of O₂, N₂, CO₂, CH₄, H₂, ⁴⁰Ar, ³⁶Ar, and ⁴He were quantify using a quadrupole mass spectrometer, the MiniRuedi (Gasometrix, Switzerland). This portative spectrometer is equipped with a Faraday cup and an electron multiplier detector (in order to better detect low concentration). The detection limit is about parts per million by volume (ppmv) range and require very low gas flow rate (6mL/hr). For dissolved-gas measurements, water was pumped through a GE-MIMS membrane at ~1L min⁻¹, allowing dissolved gases to permeate through the membrane and be transferred continuously to the MiniRUEDI.

Element exceeding 1,000ppm were analyzed with the MiniRUEDI using a Faraday cup detector (cite the precise elements (integration time 6s per [m/z]. Species with lower concentration were measured using an electron multiplier (with integration time of 12 s per [m/z] ratio). Detector selection was therefore adapted to the expected concentration of each gas species.

Mass scale on involved measuring ambient air at m/z value of 14,18,28,32,40,44 and 84. We also used 2 different standards bags on 2 different inlet capillaries.

As we didn't know what to expect on the field, standards bags were prepared few days before the departure in hermetic bag from *calibrated instruments* (caliBond) to cover large range of concentration. Concentration of the first bag: He=2,6%; H₂= 1,7%; CH₄=2,6%; CO₂= 2,3%. The second bag: He=176 ppm; H₂=168 ppm (26/03/2025 – at Totalenergies). Ambient air and the two standards were measured regularly during field analyses to account for instrumental drift.

For measurements, samples were analyzed over three replicate cycles of ten analyses and were performed after stabilization of the gas signal. Further details on the operating principle and analytical setup of the miniRUEDI are provided in Brennwald et al. (2016).

2.4. Noble gas analysis

Noble gas analyses followed the general procedure described by Beyerlee et al. (2000). Dissolved gases were analyzed at ETH Zürich (Switzerland), whereas bubbling gases were analyzed at UPPA (Pau, France). In both cases, samples were collected in sealed copper tubes and connected directly to an ultra-high-vacuum extraction and purification line. For water samples, dissolved gases were extracted under vacuum before purification. The extracted gas has been purified using cryogenic traps and SAES getters operating at 700°C to remove all the reactive species. Then, the remaining noble gas fraction has been introduced in a Jarvis coldhead to separate He, Ne and Ar prior the introduction into the mass spectrometers (Argus VI for Ne and Ar; Hélix SFT for He).

For bubbling samples, the gas phase was introduced directly into the vacuum line and underwent the same purification and noble gas separation, without the water-extraction step.

Helium and Neon isotopes were measured after cryogenic separation of He from Ne, whereas Ar was analyzed from the heavier noble-gas fraction. Noble-gas concentrations and isotope ratios were calibrated using international standards (HESJ for He) and atmospheric inhouse standards (for Ar and Ne).

Supplemental references

- Brennwald, M. S., Schmidt, M., Oser, J., & Kipfer, R. (2016). A portable and autonomous mass spectrometric system for on-site environmental gas analysis. *Environmental science & technology*, 50(24), 13455-13463.
- Brown, G. A., Love, A. J., Banks, E. W., Broadley, M. W., Tyne, R. L., Chambers, T. E., ... & Seltzer, A. M. (2026). Integrated groundwater noble gas and isotope tracers constrain hydroclimate variability and subsurface volatile sources. *Earth and Planetary Science Letters*, 690, 120173.
- Etioppe, G., Vadillo, I., Whiticar, M. J., Marques, J. M., Carreira, P. M., Tiago, I., & Urresti, B. (2016). Abiotic methane seepage in the Ronda peridotite massif, southern Spain. *Applied Geochemistry*, 66, 101-113.
- Milkov, A. V., & Etioppe, G. (2018). Revised genetic diagrams for natural gases based on a global dataset of > 20,000 samples. *Organic geochemistry*, 125, 109-120.