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ORIGINAL PAPER

Geochemical characterization of clastic sediments sheds light on energy sources and on alleged anthropogenic impacts in cave ecosystems

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Abstract

Caves are usually oligotrophic ecosystems, where the organic matter represents a limiting factor to the hypogeal community and sediments are often a significant energy source. With a view to identifying the energy input influencing the ecological processes occurring in caves, as well as the potential alteration sources of the natural equilibriums, geochemical features of several typologies of clastic sediments from the Pertosa-Auletta Cave (Italy) were investigated. The collected sediments, analyzed for a number of chemical (organic matter, Al, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Si, Sr, Ti, V, Zn concentrations) and mineralogical (quartz, calcite, dolomite, clay minerals) characteristics, showed a different composition. Overall, their origin is supposed to be allochthonous, related to the important fluviokarst activities interesting the cave in the past, whereas the abundance of calcitic and dolomitic compounds can be autochthonous, being the carbonate the main host rock. The highest concentrations of organic matter, together with C, Cu, Mo, N, P, Pb, S and Zn, highlighted in one sample composed mainly of bats guano, revealed an important bioavailable energy input as well as a pollutant accumulation, mainly of anthropogenic origin.

Keywords Cave sediments · Geochemistry · Mineralogy · Karst ecosystem · Pertosa-Auletta Cave

Introduction

Sediments represent a significant energy source in caves, being these ecosystems generally poor in nutrients, mainly due to the absence of organic matter deriving from the photoautotrophic primary producers, limited only to the lighted entrance areas (Gillieson 1996; Mammola and Isaia 2018) or to the lit trails of tourist caves (Mulec and Kosi 2009). In some cases, also cave confinement restricts the organic supplies from the external environment, but if a substantial degree of connectivity and interaction with the surface environment exist, cavities can be considered a perfect snare for detrital and organic matter, which accumulate in underground environments due to gravity fall or carried inside by water (Gillieson 1996; Arriolabengoa et al. 2015; Kováč 2018). Such deposits, commonly called clastic sediments, can be autochthonous, originating from inner cave local inputs (guano, phosphate minerals, speleothem fragments, clays…), or allochthonous, carried from outside by surface water, which represents the main matter carrier in underground environments, hauled inside the cave by shafts or overlying soils through the epikarst and vadose zone (Gillieson 1996; White 2007; Kováč 2018).

External pollutants from surface anthropogenic activities or visitors in show caves may represent further energy sources altering the natural nutrient-poor ecological equilibrium of underground ecosystems (Chelius et al. 2009; Dredge et al. 2013; Smith et al. 2013). Allochthonous particles, such as dust, fibers, hair, but also bacteria, spores and seeds can constitute organic and inorganic inputs emanated in the cave (Russell and MacLean 2008) and depositing on the floor and wall surfaces.

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Besides their ecological importance in the cave food chain, sediments may preserve valuable information about the environmental, geomorphological, sedimentological, hydrological and paleo-climatological history of the underground spaces in which they originated or deposited (White 2007; Arriolabengoa et al. 2015).

The goal of this study was to investigate the geochemical nature of clastic sediments collected in the Pertosa-Auletta Cave (Campania Region, southern Italy), which represents an excellent model of a heterogeneous cave system (Addesso et al. 2019, 2021). Indeed it presents a different fruition between the trails (tourist and closed to the public paths), as well as a diversification of the environmental conditions in the same system (fossil areas where water is present only as dripping, and active trails where dripping is active and water pools seasonally change in extent, or cave branches with a large river flowing through). Throughout an extensive geochemical sediment characterization, from pristine to disturbed states, this research aims to shed light on the energy sources in caves, helping also to identify potential anthropogenic impacts in the karst ecosystem.

Materials and methods

Sediment sampling

Samples were manually collected in May 2020, using plastic tools to avoid metal contamination, in several places along the three principal paths (Fig. 1) of the Pertosa-Auletta Cave (WGS84: 40°53′62″ N; 15°45 ′ 48″ E), extensively described in Addesso et al. (2019). In particular, 6 samples were taken from the tourist trail (Ts), 5 from the fossil trail (Fs) and 5 from the active trail (As), collecting them from accumulations found on rock recesses (triangles in Figs. 1 and 2a) or those deposited on the floor (circles in the Figs. 1 and 2b), left there by intense water currents when the cave passages were still active. In the actual active trail, crossed by a perennial underground stream, called Negro, samples were collected on both above the water (filled symbols in Fig. 1) and underwater (empty symbols in Fig. 1).

Sediment geochemical characterization

Fine sediments (< 2 mm) were dried in a stove at 75 °C to constant weight and then turned to dust using a pulverizing mill endowed with jars and agate balls (PM4, Retsch, Germany). Organic matter (OM) was determined (in triplicate) by calcination in a muffle furnace (B150, Nabertherm, Germany), at 550 °C for 4 h, and expressed as percentage of dry weight.

For elemental analysis, total C and N were determined (in triplicate) by a CHSN-O Analyzer Flash EA 1112 (Thermo Fisher Scientific Inc., MA, USA), weighing ~ 3 mg in little tin capsules, with the blank and standards (holm oak leaves with a known concentration of C and N) used in the calibration curve. In addition, samples (125 mg) were mineralized (in triplicate) by a microwave oven (mls 1200, Milestone

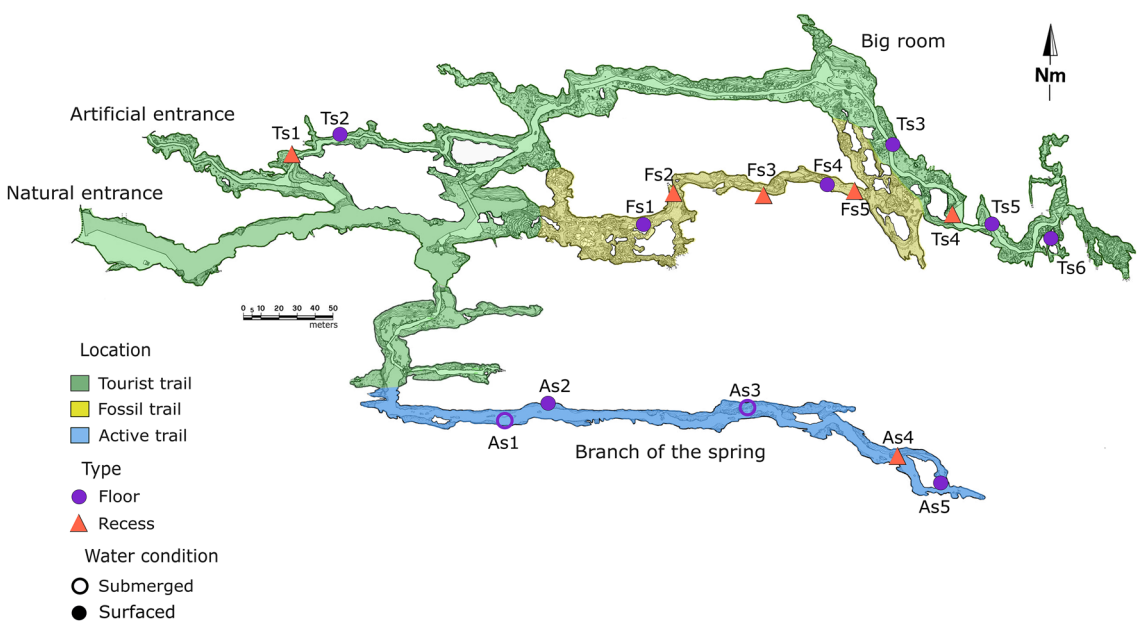

Fig. 1 Pertosa-Auletta Cave (Campania, southern Italy) map, with the three main paths: active (A, blue), tourist (T, green) and fossil (F, yellow). Sediments sampling sites are also reported, distinguishable in deposits collected to the floor (circles) and accumulated in the rock recesses (triangles). Empty circles in the active trail indicate submerged sediments collected underwater

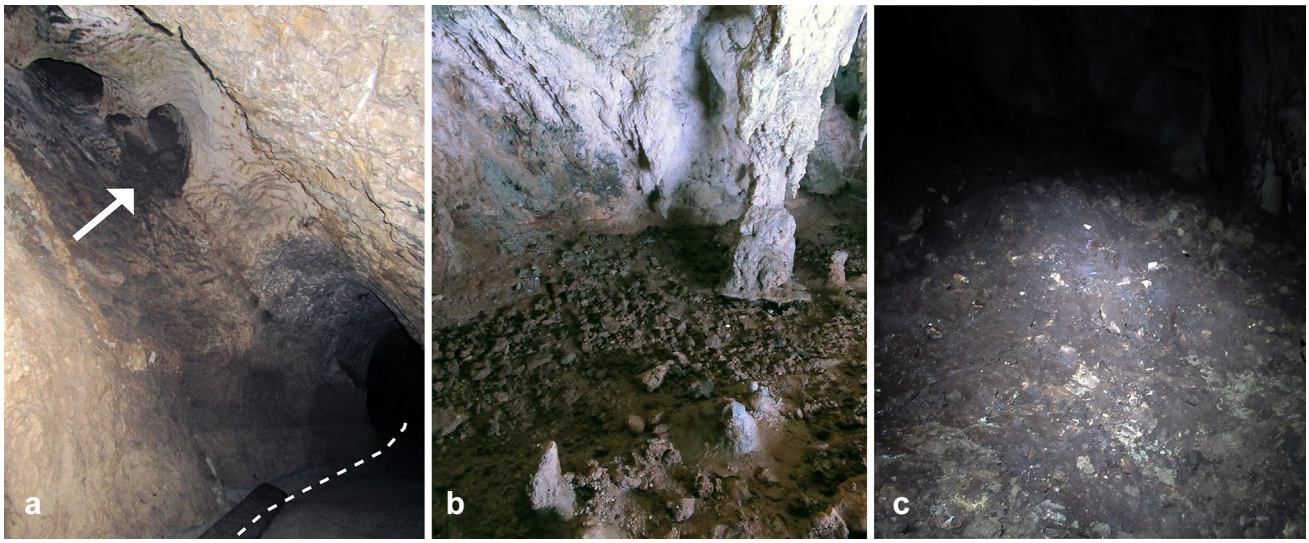

Fig. 2 Photographs of sediments from the Pertosa-Auletta Cave. **a** Ts4 sample: sediments deposited in the rock recess (white arrow; dotted line indicates the tourist pathway). **b** Ts2 sample: sediments to the floor. **c** Ts3 sample: sediments visibly constituted by bats guano

Microwave Laboratory Systems, Shelton, CT, USA), using a mixture of hydrofluoric acid and nitric acid (50% HF: 65% HNO_3 = 1:2 = v: v). After digestion, deionized water was used to dilute the solution up to a final volume of 25 mL. Al, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Si, Sr, Ti, V and Zn concentrations were analyzed using an Optima 7000 DV ICP-OES (PerkinElmer, Krakow, Poland). To estimate the analytical accuracy and possibly correct the analyzed element concentrations in the single samples, the Standard Reference Material NCS soil DC 73321 was also analyzed with the same procedure.

Sediment mineralogy was determined by X-ray diffraction, using a D2 PHASER diffractometer (Bruker, Massachusetts, USA), equipped with a Cu tube (λ = 1.54184 Å, 10 mA, 30 kV, 5°–45° 2θ with a step angle of 0.02°, analysis time = 1.5 s per step, variable rotation = 10/min). The open-source software Profex 4.0.2 using the BGMN database (Doebelin and Kleeberg 2015), through Rietveld refinement, according with Taylor and Rui (1992) method, was used for the identification and abundance estimation of the main minerals.

Data analysis

Differences among samples based on their overall geochemical characteristics, considering three fixed variables, location (tourist, fossil and active trails), type of sampling (from the ground or from recesses), water conditions (at the surface or underwater), were evaluated using permutational multivariate analysis of variance (PERMANOVA), based on the Manhattan distance metric and 999 permutations. Non-metric multi-dimensional scaling (NMDS), based on the same distance metric and on 2 axes, with the superimposition of confidence ellipses (α = 0.05), was also performed. Subsequently, differences according to the single analyzed parameters, considering the same fixed variables as in PERMANOVA, were evaluated by three-way analyses of variance (three-way ANOVAs), followed by Tukey's *post hoc* tests. Finally, for the different sediment characteristics, a network based on the Pearson's correlation coefficients was obtained.

All the analyses were carried out in the R 4.0.0 programming environment (R Core Team 2020), with functions from the "vegan", "agricolae", "ggplot2" and "q graph" packages.

Results and discussion

The Pertosa-Auletta Cave presents several sediment accumulations along the three main trails, individuated based on their different fruition and environmental conditions (Addesso et al. 2019), evidence of its hydrological history, characterized by intense past floods. These different types of debris, carried in from outside (allochthonous) or deriving from near the sampling site (autochthonous), deposited on the ground or on the rock wall recesses depending on their dimensional and physical features (Dykes 2007). Parts of these sediments were altered, moved and reused to build the path for tourists, such as in the long passage before the "Great Room" (Fig. 1), where the sediments solidified, making the sampling difficult. In the other sectors, they resulted in a pristine state, object of collection for this study. All the 16 collected sediments (Fig. 1) had a fine-grained texture and a brown coloring with different gradations, in one case

(Ts3, Fig. 2c) tending to black, probably because of the presence of bats guano.

Chemical composition of the analyzed sediments (Table 1) highlighted a broad variability among the samples, with differences in element concentrations of one, and, in some cases, of two orders of magnitude. The observed mean values of Ba, C, Co, Cu, Ni, Pb, Sr and V are however comparable with the average concentrations of the same elements measured in sediments from the Modrić Cave (Croatia), reported by Miko et al. (2002); conversely, Cd and Zn showed lower concentrations in sediments from the Pertosa-Auletta Cave. Ts3 sample, visibly composed for the most part by guano (Fig. 2c), diverged from the others for the higher concentrations of several elements, in particular Cu (4269 µg/g d.w.), Mo (87 µg/g d.w.), P (40 mg/g d.w.), Pb (41 µg/g d.w.), S (5.8 mg/g d.w.) and Zn (428 µg/g d.w.). Also for C, N and organic matter, presenting average values of 0.1, 2.9 and 5.0% d.w., respectively, Ts3 sample displayed the highest concentrations, equal to 3.0, 16.9 and 46.0% d.w., respectively (Table 1), confirming its organic origin (Miko et al. 2001).

Guano deposits can be classified as autochthonous clastic sediments (White 2007), representing an important energy source for several cave species, therefore called guanobites and guanophiles (Deharveng and Bedos 2018). These deposits are primarily constituted of organic matter, such as chitin from insects and other not digested compounds, combined over time with autochthonous inorganic materials, such as quartz, calcite and clay (Putra et al. 2019). Anyway, not only the high concentrations of organic matter and chemical elements (C, N, P, S) associated to its composition may be related to bat guano, but also elements of abiotic origin (Miko et al. 2001), similarly found in the Ts3 sample in high concentrations (particularly Pb). In this case, a bioaccumulation of persistent contaminants from the predation habitats may be expected, being bats excellent environmental biomonitors (Zukal et al. 2015; Wurster et al. 2015).

Mineralogical features of sediments from the Pertosa-Auletta Cave are reported in Table 2 and in Fig. 3, showing the estimated relative abundances of minerals composing the sediments and the diffractograms for each sample, respectively. As1, As2, As3, As5, Ts5, Ts6, Fs1 and Fs4 showed a similar mineralogical composition, with average values of α-quartz, calcite and dolomite equal to 61.4, 17.6 and 21.0%, respectively. As4 displayed only α-quartz and calcite minerals (81.3 and 18.7%, respectively). Ts1, Ts3, Ts4 and Fs3 were composed, in their entirety, of α-quartz. Also Fs2 showed the main percentage of α-quartz (96.3%), associated to lime (3.7%), not contained in any of the other samples, certainly related to unreacted residual of calcium carbide, used for acetylene burners by speleologist illuminating caves (Abdyzhaparova et al. 2021). Ts5 and Ts6 presented different amounts of α-quartz (65.5 and 83.4%, respectively), calcite (18.2 and 6.1%, respectively) and dolomite (16.3 and 10.5%, respectively). Ts2 and Fs5, unlike the others, were mainly composed of calcite (88.1 and 97.3%, respectively) with a low amount of α-quartz (11.9 and 6.3%, respectively). It was not possible to quantify clay minerals due to the limits of the protocol chosen for this investigation, but they were also detected in traces (Table 2). Especially, smectite, muscovite and kaolinite, indicated by diffraction peaks around 6°, 8.8° and 12.5° 2θ, respectively, according to Moore and Reynolds (1997), were identified in most samples (As1, As1, As3, As5, Ts2, Ts3, Ts5, Fs1 and Fs4). As4, Ts1, Fs2 and Fs3 sediments showed traces of kaolinite and muscovite; while Ts6 and Fs5 presented traces of kaolinite and muscovite, Ts4 of kaolinite and smectite, and Ts6 and Fs5 only of muscovite.

The presence of quartz, calcite and clay minerals in cave sediments is worldwide reported (Miko et al. 2002; Zupan Hajna et al. 2008; Arriolabengoa et al. 2015); anyway, the analyses carried out on the Pertosa-Auletta Cave sediments show a mineralogical variability among the samples. Calcite and dolomite are the most abundant and important carbonate minerals, deriving from the host rock. The Pertosa-Auletta Cave is one of the most important basal springs of the Alburni karst system, extending for a total length of 3000 m. It is divided into three main branches (Fig. 1), which mark the border fault of the carbonate massif with NW–SE orientation. Previous stratigraphic and sedimentological studies allowed identifying different bauxite horizons marking episodes of continental emersion of the Cretaceous limestone (Cafaro et al. 2010). The underground water flow inside the Alburni karst system, instead, is still poorly known, but part of the waters coming from the NW portion of the plateau have the Pertosa-Auletta Cave as their final destination (Celico et al. 1994; Cozzolino et al. 2015a, b; Pedrali et al. 2015; Pastore et al. 2017). In particular, the Pertosa-Auletta Cave is crossed by an underground river, named "Negro", which is currently present only in the southern branch. Nevertheless, there are several morphological evidences, such as residual fluvial sediments placed at different elevations in all the branches, which suggest the presence of water flow all along the cave in the past.

Quartz found in sediment samples from the Pertosa-Auletta Cave might be attributed to both allogenic material or to impurities in the carbonate series, being silica, as well as clay minerals, the most common insoluble impurities in carbonate rocks. Together with silt, they represent the most widespread clastic deposits in caves. Because they are transported in suspension, these deposits may coat walls and even the ceiling, although most accumulation is on the floor. Their sources are diversified: allogenic material including fluvial and lacustrine sediments, infiltrates from soils overhead and windborne dust are the most common. There is often a significant autogenic component from the weathering of walls

Table 1 Chemical composition (mean values ± standard deviations) of each sediment sample from the Pertosa-Auletta Cave

Samples	As1	As2	As3	As4	As5	Ts1	Ts2	Ts3	Ts4	Ts5	Ts6	Fs1	Fs2	Fs3	Fs4	Fs5
Type	Soil	Soil	Soil	Recess	Soil	Recess	Soil	Soil	Recess	Soil	Soil	Soil	Recess	Recess	Soil	Recess
Water condition	Submerged	Surfaced	Submerged	Surfaced	Surfaced	Surfaced	Surfaced	Surfaced	Surfaced	Surfaced	Surfaced	Surfaced	Surfaced	Surfaced	Surfaced	Surfaced
Al (mg/g d.w.)	35.8 ± 2.9	44.2 ± 6.4	42.7 ± 3.4	81.9 ± 1.6	33.0 ± 2.2	66.6 ± 2.3	20.3 ± 2.2	35.3 ± 1.6	93.4 ± 5.4	52.8 ± 2.5	29.8 ± 2.7	25.8 ± 2.8	67.2 ± 2.3	57.2 ± 2.4	36.6 ± 2.6	1.5 ± 0.1
B (µg/g d.w.)	58.5 ± 3.2	74.1 ± 6.9	62.3 ± 7.0	99.7 ± 1.4	61.2 ± 0.3	76.9 ± 4.8	81.3 ± 4.5	53.3 ± 2.2	108.6 ± 4.0	89.5 ± 5.0	35.0 ± 2.0	65.2 ± 6.7	77.0 ± 2.4	47.7 ± 2.7	61.3 ± 1.8	15.5 ± 1.4
Ba (mg/g d.w.)	0.142 ± 0.001	0.359 ± 0.045	0.502 ± 0.014	0.274 ± 0.037	0.002 ± 0.023	0.369 ± 0.051	0.040 ± 0.008	0.478 ± 0.030	0.298 ± 0.020	0.296 ± 0.025	0.362 ± 0.040	0.375 ± 0.050	0.397 ± 0.025	0.331 ± 0.024	0.388 ± 0.006	0.240 ± 0.001
C (% d.w.)	0.090 ± 0.005	0.104 ± 0.006	0.093 ± 0.002	0.113 ± 0.001	–	–	0.126 ± 0.004	3.054 ± 0.036	0.090 ± 0.001	0.147 ± 0.001	–	0.112 ± 0.009	0.044 ± 0.002	0.051 ± 0.002	0.071 ± 0.002	0.109 ± 0.003
Ca (mg/g d.w.)	63.9 ± 3.0	52.8 ± 6.3	45.6 ± 8.4	20.4 ± 1.5	39.1 ± 3.3	10.6 ± 1.3	84.7 ± 15.1	13.9 ± 0.9	8.1 ± 0.8	44.4 ± 1.6	49.8 ± 3.7	17.6 ± 1.5	5.3 ± 0.3	9.8 ± 0.1	26.7 ± 7.7	11.6 ± 0.8
Cd (µg/g d.w.)	0.064 ± 0.002	0.067 ± 0.008	0.059 ± 0.008	0.070 ± 0.006	0.057 ± 0.001	0.079 ± 0.006	0.112 ± 0.001	0.355 ± 0.010	0.074 ± 0.002	0.070 ± 0.002	0.061 ± 0.007	0.053 ± 0.005	0.050 ± 0.002	0.062 ± 0.003	0.050 ± 0.004	0.043 ± 0.003
Co (µg/g d.w.)	13.6 ± 1.0	15.0 ± 0.4	13.3 ± 0.7	20.7 ± 1.5	11.8 ± 0.6	20.2 ± 1.1	13.6 ± 0.2	15.9 ± 0.3	23.8 ± 0.8	18.0 ± 0.7	9.4 ± 0.4	11.9 ± 0.8	18.4 ± 0.7	16.7 ± 0.7	11.2 ± 0.3	2.0 ± 0.1
Cr (µg/g d.w.)	91.7 ± 4.5	120.0 ± 9.6	100.9 ± 8.3	170.3 ± 8.3	83.7 ± 4.5	125.8 ± 7.3	78.5 ± 1.9	94.6 ± 2.5	147.4 ± 5.2	156.4 ± 8.5	41.5 ± 3.1	76.4 ± 8.1	95.9 ± 3.4	70.9 ± 0.5	80.5 ± 1.2	12.9 ± 0.5
Cu (µg/g d.w.)	38.6 ± 2.1	46.0 ± 3.8	37.3 ± 2.9	68.1 ± 2.4	27.2 ± 0.7	35.0 ± 1.2	121.6 ± 4.5	4268.6 ± 110.6	133.0 ± 4.3	74.5 ± 2.7	15.5 ± 0.4	71.5 ± 5.1	40.7 ± 2.0	28.8 ± 1.2	26.1 ± 1.6	73.9 ± 4.5
Fe (mg/g d.w.)	25.0 ± 1.6	28.5 ± 3.2	26.6 ± 2.0	46.8 ± 1.2	19.7 ± 0.6	35.9 ± 0.3	18.4 ± 0.5	28.5 ± 0.9	58.9 ± 2.9	35.1 ± 1.7	14.7 ± 1.1	25.1 ± 1.2	39.8 ± 1.5	38.5 ± 1.8	27.4 ± 1.1	2.8 ± 0.3
K (mg/g d.w.)	11.1 ± 1.2	11.7 ± 1.2	12.0 ± 1.8	15.8 ± 0.3	11.6 ± 0.5	13.6 ± 0.2	7.0 ± 0.2	11.7 ± 0.6	16.7 ± 0.8	12.0 ± 0.6	13.9 ± 0.7	9.9 ± 0.4	15.9 ± 1.3	15.4 ± 1.3	12.6 ± 0.9	2.4 ± 0.2
Li (µg/g d.w.)	31.1 ± 1.8	37.5 ± 4.0	33.4 ± 3.6	72.3 ± 2.2	32.3 ± 3.5	57.4 ± 3.7	33.4 ± 0.6	13.5 ± 0.8	75.0 ± 3.2	48.8 ± 3.0	23.3 ± 3.3	30.7 ± 3.2	58.4 ± 2.3	45.2 ± 2.4	30.2 ± 1.6	2.5 ± 0.1
Mg (mg/g d.w.)	9.5 ± 0.6	13.1 ± 1.0	10.0 ± 0.1	10.5 ± 0.8	11.1 ± 1.1	6.8 ± 0.5	5.6 ± 0.7	2.9 ± 0.1	9.4 ± 0.9	10.1 ± 0.9	7.1 ± 1.1	13.0 ± 0.8	7.2 ± 0.2	5.9 ± 0.2	14.1 ± 0.6	1.0 ± 0.1
Mn (mg/g d.w.)	1.58 ± 0.05	1.00 ± 0.06	0.87 ± 0.04	1.68 ± 0.09	0.99 ± 0.04	1.87 ± 0.11	6.67 ± 0.06	0.08 ± 0.00	1.22 ± 0.09	1.31 ± 0.03	0.55 ± 0.02	1.17 ± 0.08	0.77 ± 0.01	5.51 ± 0.27	0.81 ± 0.02	1.15 ± 0.03
Mo (µg/g d.w.)	0.39 ± 0.18	0.93 ± 0.09	0.39 ± 0.11	0.67 ± 0.14	0.29 ± 0.06	-	3.13 ± 0.32	87.12 ± 4.07	1.00 ± 0.04	0.65 ± 0.20	-	0.46 ± 0.26	0.31 ± 0.18	0.35 ± 0.17	0.45 ± 0.25	0.11 ± 0.05
N (% d.w.)	3.25 ± 0.10	2.72 ± 0.02	2.60 ± 0.03	1.17 ± 0.02	2.70 ± 0.15	0.23 ± 0.02	6.90 ± 0.09	16.90 ± 0.28	0.76 ± 0.05	2.36 ± 0.06	1.48 ± 0.30	3.92 ± 0.12	0.45 ± 0.03	0.73 ± 0.03	3.15 ± 0.03	10.53 ± 0.16
Na (mg/g d.w.)	3.84 ± 0.06	2.79 ± 0.10	3.24 ± 0.27	1.80 ± 0.08	5.32 ± 0.20	7.88 ± 0.39	0.78 ± 0.08	2.76 ± 0.11	1.53 ± 0.15	2.21 ± 0.03	9.36 ± 0.64	4.21 ± 0.23	5.21 ± 0.21	4.80 ± 0.67	3.54 ± 0.24	0.07 ± 0.01
Ni (µg/g d.w.)	22.8 ± 2.3	23.2 ± 1.7	20.3 ± 4.1	48.3 ± 1.9	18.4 ± 0.8	13.6 ± 3.9	52.3 ± 5.5	19.3 ± 0.8	47.2 ± 1.5	40.8 ± 2.0	-	28.1 ± 2.6	33.7 ± 1.3	27.1 ± 0.8	26.6 ± 0.5	8.4 ± 0.8
P (mg/g d.w.)	1.55 ± 0.05	1.29 ± 0.05	1.39 ± 0.10	2.43 ± 0.18	1.98 ± 0.09	1.55 ± 0.10	10.97 ± 0.52	40.25 ± 1.03	1.75 ± 0.10	2.01 ± 0.07	0.70 ± 0.05	7.70 ± 0.44	0.76 ± 0.03	1.92 ± 0.19	1.29 ± 0.03	10.74 ± 0.61
Pb (µg/g d.w.)	14.2 ± 4.0	7.6 ± 5.2	9.2 ± 2.4	12.1 ± 0.4	11.4 ± 6.2	0.1 ± 0.1	2.1 ± 3.2	40.8 ± 3.9	24.1 ± 0.6	35.1 ± 5.0	9.9 ± 5.4	16.0 ± 1.4	20.7 ± 1.5	17.2 ± 1.2	13.2 ± 2.2	0.2 ± 0.1
S (mg/g d.w.)	0.30 ± 0.03	0.25 ± 0.01	0.23 ± 0.06	0.34 ± 0.01	0.23 ± 0.01	0.12 ± 0.02	1.23 ± 0.05	5.79 ± 0.12	0.33 ± 0.01	0.48 ± 0.02	0.08 ± 0.01	0.45 ± 0.03	0.14 ± 0.01	0.26 ± 0.04	0.22 ± 0.01	0.62 ± 0.04
Si (mg/g d.w.)	259.3 ± 13.7	300.5 ± 25.6	278.4 ± 17.3	281.2 ± 21.5	325.8 ± 13.7	518.2 ± 32.0	171.7 ± 7.7	198.8 ± 7.5	185.6 ± 7.2	315.8 ± 6.5	446.8 ± 36.6	189.6 ± 12.5	263.5 ± 12.4	394.0 ± 101.5	377.8 ± 8.6	53.4 ± 3.0
Sr (µg/g d.w.)	133.1 ± 6.3	138.5 ± 8.4	123.9 ± 6.9	102.3 ± 5.8	120.3 ± 7.6	104.6 ± 13.3	36.0 ± 1.9	92.6 ± 6.1	86.6 ± 5.5	107.5 ± 9.2	135.1 ± 24.3	63.9 ± 7.1	106.5 ± 17.8	144.1 ± 20.7	105.3 ± 6.1	10.4 ± 2.3
Ti (mg/g d.w.)	4.4 ± 0.3	6.1 ± 0.7	4.7 ± 0.8	6.3 ± 0.0	4.5 ± 0.2	8.7 ± 0.6	4.1 ± 0.3	4.2 ± 0.2	4.5 ± 0.2	6.1 ± 0.2	1.8 ± 0.1	4.1 ± 0.3	4.8 ± 0.1	3.4 ± 0.2	4.1 ± 0.1	1.1 ± 0.1
V (µg/g d.w.)	115.4 ± 1.2	142.3 ± 11.1	125.6 ± 12.2	204.8 ± 7.8	115.7 ± 7.5	174.6 ± 8.9	118.4 ± 5.9	93.4 ± 4.5	207.1 ± 6.6	187.9 ± 10.7	54.0 ± 3.6	100.4 ± 9.1	149.5 ± 4.2	102.0 ± 4.2	95.5 ± 1.7	30.0 ± 2.3
Zn (µg/g d.w.)	90.9 ± 4.9	99.2 ± 4.8	90.4 ± 5.2	153.3 ± 9.9	81.1 ± 2.2	163.0 ± 3.7	292.3 ± 10.6	427.7 ± 9.8	180.3 ± 7.0	140.9 ± 5.0	55.5 ± 1.4	151.8 ± 8.5	115.2 ± 2.5	114.0 ± 4.2	82.2 ± 3.1	211.3 ± 9.1
OM (% d.w.)	4.56 ± 0.12	5.74 ± 0.01	5.24 ± 0.20	7.88 ± 0.19	3.74 ± 0.04	3.82 ± 0.03	6.66 ± 0.20	45.99 ± 0.05	7.68 ± 0.12	9.20 ± 0.05	1.61 ± 0.08	4.39 ± 0.06	4.29 ± 0.07	3.92 ± 0.13	3.45 ± 0.04	2.90 ± 0.08

or the winnowing or decomposition of older deposits (Ford and Williams 2007).

Few studies have emphasized clay minerals and their ratios (Foos et al. 2000; Sasowsky, 2007) in cave sediments: although there is much variation, abundant kaolinite tends to indicate warm conditions either in the source rocks or during their weathering. Illite and chlorite are usually the most prominent clay minerals in glaciated regions, while the presence of smectite or montmorillonite suggests a drier climate. Based on the knowledge of the geology and the geomorphological evolution of this portion of the southern Italian Apennines, we have assumed various hypotheses that can explain the presence of clay sediments inside the cave. Considering the geomorphological evolution of the area, the sediments might have been transported by the water flows that over time have invaded the cavity. The sediments may derive from:

the erosion of the Miocene terrigenous deposits that once covered the inner plateau, and which are now only preserved in small depressions;

sediments of the Pleistocene lake that once existed in the Vallo di Diano basin, which could have had as its outflow the Polla cave, after the last ice age;

the residue of the clay-intercalations present within the carbonate succession.

Overall, PERMANOVA did not highlight significant differences among samples on the basis of their geochemical characteristics, considering the three fixed variables: location (tourist, fossil and active trail; $P = 0.727$), type of sampling (to the ground or in the recesses; $P = 0.178$), water conditions (in the surface or underwater; $P = 0.965$). According to these results, the NMDS multivariate ordination, with the superimposition of confidence ellipses, did not show differentiations among the locations nor between the typology and environmental (water) conditions of the sampled deposits (Fig. 4). Only Ts3 and Fs5 samples were separated from the others for the higher concentrations of C, Cu, Mo, N, P and S. In the univariate domain, the three-way ANOVAs highlighted significant differences for Al ($P < 0.05$) and Ca ($P < 0.001$) in relation to the type of sampling, as well as for dolomite mineral in relation to the three fixed variables: $P < 0.05$ for the location and water conditions, $P < 0.001$ for the type of sampling.

The relationships between the studied parameters in the 16 analyzed samples are shown in Fig. 5, displaying a network based on Pearson's correlation coefficients (Online Resource 1). Positive and negative correlations ($0.001 < P < 0.05$) among several parameters were observed, highlighting two big clusters of variables that can have a similar origin, including roughly elements of abiotic or biotic origin. Investigating the characteristics of cave clastic sediments pointed out several evidences about the inorganic and organic available energy, basics for the organization of ecological communities (influencing their structure and function), and highlighted modifications due to the human presence (introducing exogenous materials), potentially altering the natural chemico-physical energy balance of the underground system (Chelius et al. 2009). In this context, bat colonies play a fundamental role in the enrichment in manures of the cave ecosystem, representing not only an important organic input, but also a key factor revealing environmental alterations and anthropogenic impacts (Putra et al. 2019). Future efforts will focus on the endokarst and top soil characterization, to understand

Table 2 α–quartz, calcite, dolomite and lime estimated relative abundances (mean values ± estimated standard deviations) of each sediment sample from the Pertosa-Auletta Cave

Sample	α – quartz (%)	Calcite (%)	Dolomite (%)	Lime (%)	Kaolinite	Smectite	Muscovite
As1	59.6 ± 2.0	20.4 ± 1.0	20.0 ± 1.0	–	*	*	*
As2	57.3 ± 2.0	12.4 ± 0.9	30.3 ± 1.0	–	*	*	*
As3	59.2 ± 1.0	19.5 ± 0.9	21.3 ± 0.9	–	*	*	*
As4	81.3 ± 9.0	18.7 ± 9.0	–	–	*	–	*
As5	55.8 ± 2.0	25.0 ± 1.0	19.2 ± 0.9	–	*	*	*
Ts1	100.0	–	–	–	*	–	*
Ts2	11.9 ± 4.0	88.1 ± 4.0	–	–	*	*	*
Ts3	100.0	–	–	–	*	*	*
Ts4	100.0	–	–	–	*	*	–
Ts5	65.5 ± 4.0	18.2 ± 2.0	16.3 ± 2.0	–	*	*	*
Ts6	83.4 ± 1.0	6.1 ± 0.6	10.5 ± 1.0	–	–	–	*
Fs1	44.7 ± 1.0	27.8 ± 0.9	27.4 ± 0.9	–	*	*	*
Fs2	96.3 ± 0.7	–	–	3.7 ± 0.7	*	–	*
Fs3	100.0	–	–	–	*	–	*
Fs4	65.6 ± 1.0	11.5 ± 0.6	22.9 ± 0.9	–	*	*	*
Fs5	6.3 ± 0.2	93.7 ± 0.2	–	–	–	–	*

Presence of clay minerals is also reported (*)

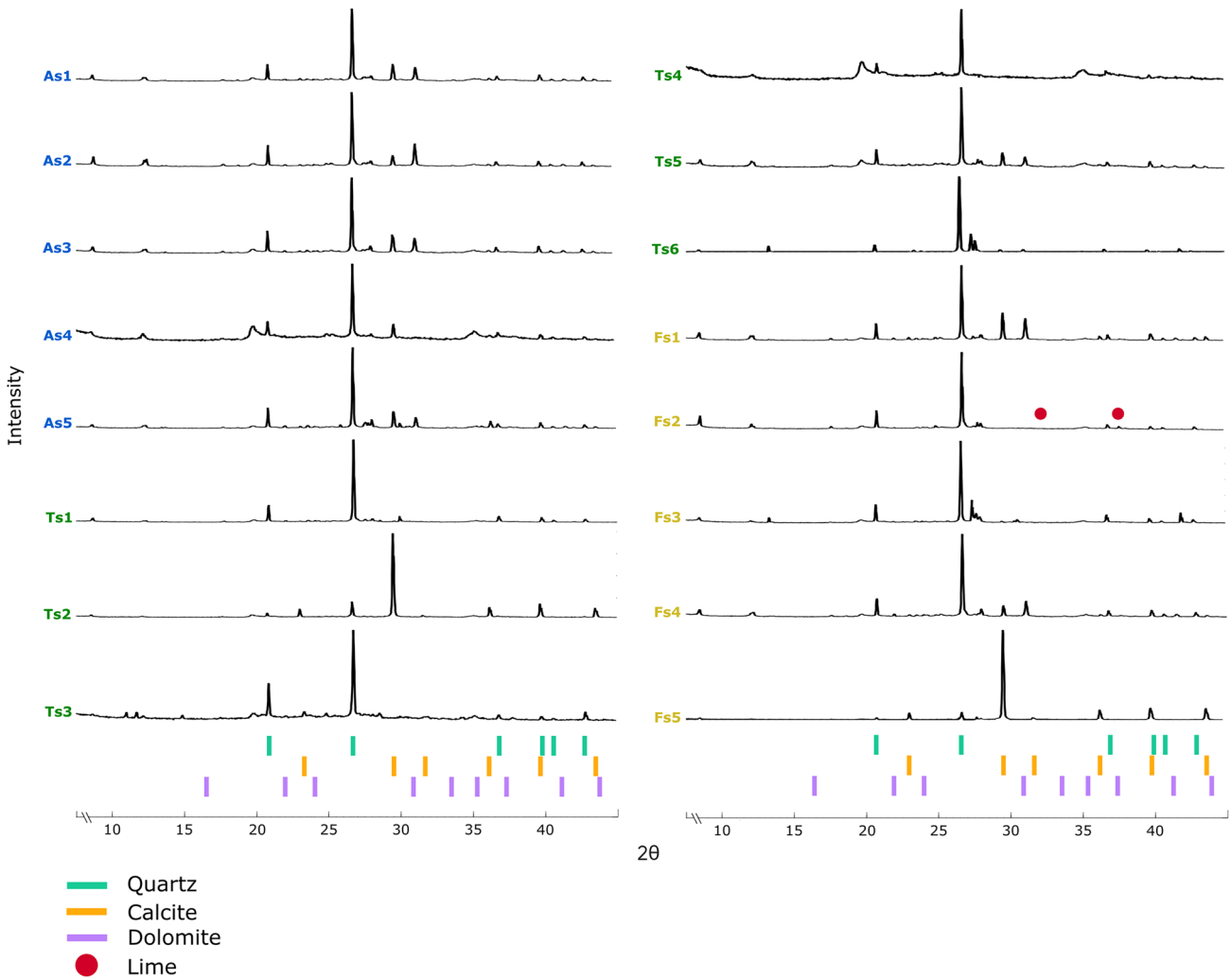

Fig. 3 Stacked diffractograms of cave sediments from the active (A, blue), tourist (T, green) and fossil (F, yellow) trails. α- quartz (teal), calcite (orange), dolomite (violet) diffraction lines are also reported. Lime phase occurring in F sample is indicated by red points

the genesis process of cave sediments, clarifying their provenance, such as their autochthonous or allochthonous origin, due to the past fluviokarst activity interesting the karst system.

Conclusion

The extensive geochemical characterization of clastic sediments from the Pertosa-Auletta Cave, in Italy, provided a whole knowledge of their chemico-physical features, describing one of the most important cave compartments, which influence the fragile ecological equilibrium, taking place in underground ecosystems. The clastic sediments, belonging to different typologies, showed variable compositions, with a clear differentiation of one sample, in particular, contaminated by bat guano. It revealed the highest concentration of organic matter and of several chemical elements (C, Cu, Mo, N, P, Pb, S, Zn), proving not only the important support of guano in terms of energy source for cave communities, but also an accumulation of pollutants from the external environments, likely related to the bat food chain.

Three main pathways about sediment provenances were drawn: (i) the autochthonous origin likely related to the cave host rock constituted by carbonate, dolomite and limestone, justifying the presence of calcitic and dolomitic minerals; (ii) the allochthonous origin related to the past cave hydrological activity, where water flow carried underground quartz compounds; (iii) the accumulation of guano, from bat colonies inhabiting the cave.

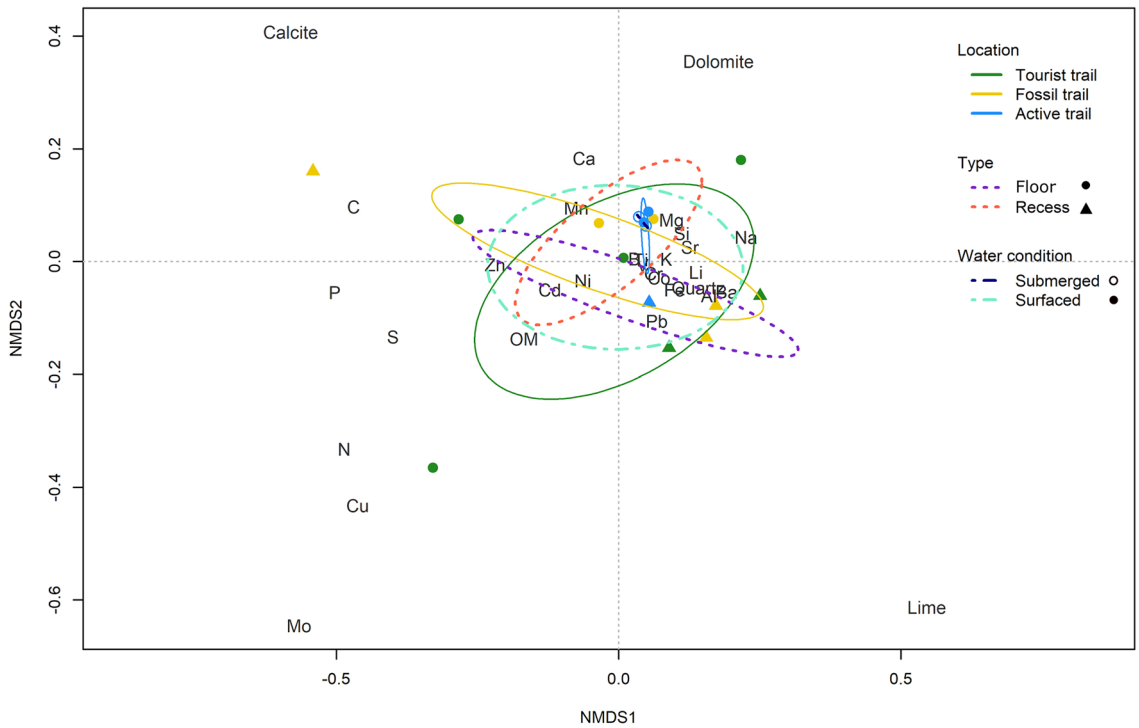

Fig. 4 NMDS bi-plot, with the superimposition of confidence ellipses for $\alpha = 0.05$, based on chemical element, organic matter and mineral concentrations in cave sediments from the active (A, blue), tourist (T, green) and fossil (F, yellow) trails of the Pertosa-Auletta Cave

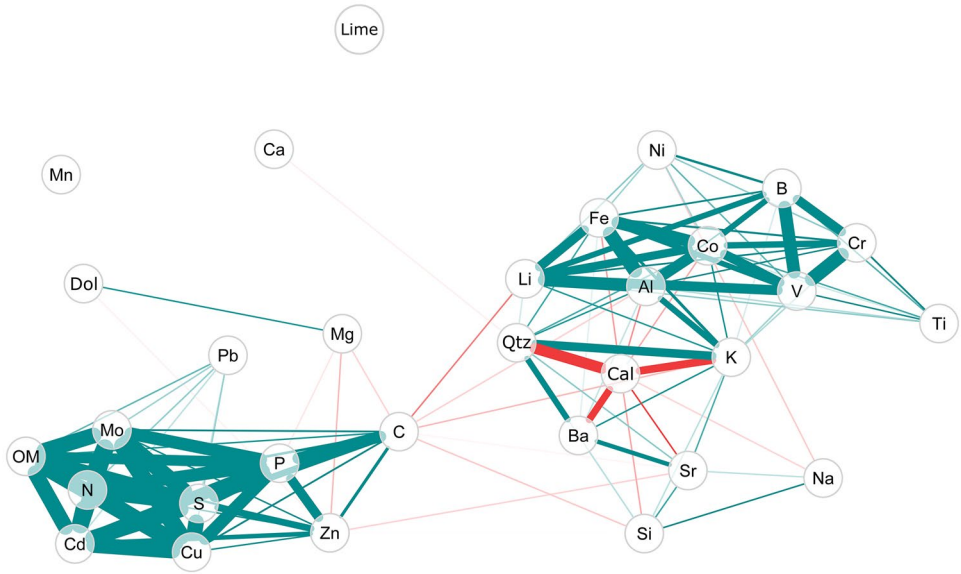

Fig. 5 Network based on Pearson's correlation coefficients. Negative (red) and positive (green) correlations are reported; lines more or less thick indicate correlations more or less strong between the variables. For minerals, the following abbreviations (according to Kretz 1983) have been employed: *Cal* calcite, *Qtz* α–quartz, *Dol* dolomite

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Declarations

Conflicts of interest None declared.

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