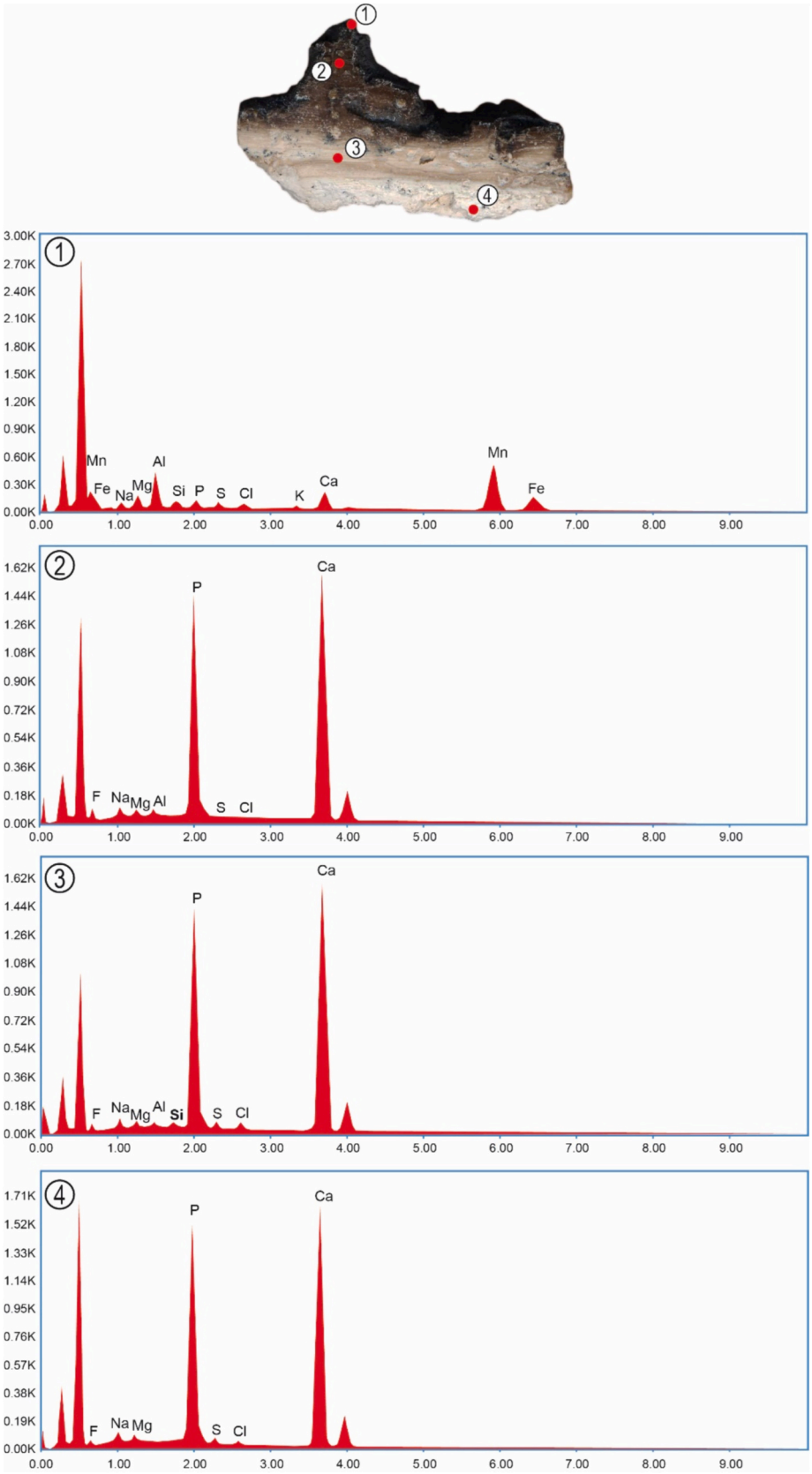

Fig. 8. EDS microanalyses. 1) Fe—Mn oxides of the external black cover of the crust. 2, 3, 4) Dark-brown, yellow and white areas of the crust showing homogeneous CFA composition; note decreasing intensity of the fluorine peak towards the base of the crust.

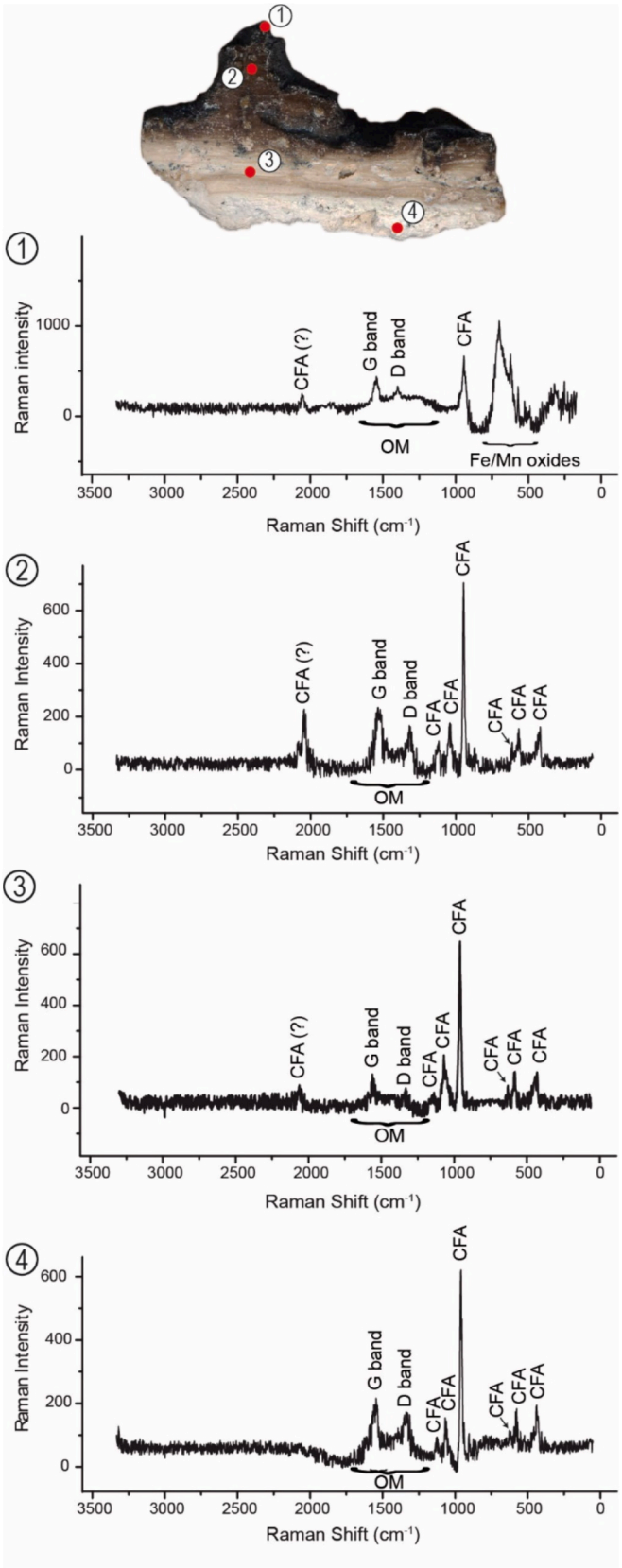

Fig. 9. Raman spectra of the Fe/Mn external cover (1), dark-brown CFA (2), yellow CFA (3), and white CFA (4). Note the CFA peak among the typical Fe/Mn oxide peaks on the spectra obtained from the external surface of the crusts. Independently, the Raman spectra denote a homogeneous presence of organic material (D and G bands) strictly related to the minerals.

These sequences were subjected to clustering using VSEARCH (Rognes et al., 2016) with a 97 % identity cutoff, resulting in the formation of eight clusters (Table S5). Among these clusters, six were represented by single sequences (sequences 1_1101_12708_3858, 1_1101_19647_8085, 1_1102_10515_27429, 1_1102_10571_6018, 1_1102_18680_3842, and 1_1102_26850_8327) (Table S5). One cluster (represented by the sequence 1_1101_9191_4740) contained two sequences, while another cluster (represented by the sequence 1_1102_23809_11866) included a total of 117 sequences. The representative 16S rRNA gene sequences from each identified cluster, the sequences of the genus "Ca. Manganitrophus", and the reference sequences of the genera *Leptospirillum*, *Nitrospira*, "Ca. Nitrospira", and *Thermodesulfovibrio* (Table S6) were used to generate a phylogenetic tree (Fig. 11).

As shown, six sequences (1_1101_19647_8085, 1_1101_9191_4740, 1_1102_10515_27429, 1_1102_18680_3842, 1_1102_23809_11866, 1_1102_26850_8327) were found to be phylogenetically close to the EZBioCloud sequence EU491114, while the sequence 1_1101_12708_3858 was phylogenetically close to a clade containing sequences EU491114, HM187074, and that of "*Ca.* M. noduliformans HYJII51-Mn-bac16s-1-B09". Notably, both EU491114 and HM187074 are annotated as belonging to the genus "Ca. Manganitrophus" (Fig. 11). Notably, all seven of these sequences, together with the reference sequences EU491114 and HM187074, form a phylogenetically related group closely associated with "*Ca.* M. noduliformans", while the isolates GAC1 and GAC2 are more distantly related. On the contrary, the sequence 1_1102_10571_6018 is phylogenetically more distant, occupying an intermediate position between the "Ca. Manganitrophus" and other bacteria of the phylum Nitrospirota. The analysis was then extended to the fasta sequences of the DSC-S, DCS-G, and SC datasets (Table S3). This analysis led to the identification of 79 and 28 sequences assigned to the genus "Ca. Manganitrophus" or the family "Ca. Manganitrophaceae" in the DSC-S and DSC-G datasets, respectively (Table S4). However, no similar sequences were found in the SC dataset.

Python-based analysis was then extended to other bacteria possibly involved in the manganese cycle. In particular, we focused on *Ramlibacter*, a genus of Gram-negative, aerobic, pleomorphic bacteria that exhibit peculiar features, including a complex cell cycle in which cyst-shaped cells resistant to desiccation alternate with mobile rod-shaped cells (Heulin et al., 2003). Although this genus of bacteria includes heterotrophic microorganisms, an autotrophic species of *Ramlibacter*, called "*R. lithotropichus*", has recently been isolated in co-culture with the "Ca. Manganitrophus" (Yu and Leadbetter, 2020; Yu et al., 2022). This bacterium is characterized by H_2- and O_2-dependent growth, possesses the Calvin-Benson-Bassham cycle and genes related to sulfur oxidation, and possibly performs anaerobic respiration through dissimilatory reduction of metals including oxidized iron and manganese. Indeed, "*R. lithotrophicus*" expresses *mtrCAB* genes when grown on Mn(II) in co-culture with "*Ca.* M. noduliformans" (Baker et al., 2021; Yu and Leadbetter, 2020; Yu et al., 2022). These genes are essential for conducting extracellular electron transfer and encode multi-heme proteins that assemble into nanowires, enabling bacteria to transport electrons to reduce extracellular substrates (Jiang et al., 2020; Baker et al., 2021).

The 16S rRNA gene sequences of *Ramlibacter* were searched in our datasets using the two custom Python scripts. For the initial filtering step (identity >90 %), three 16S rRNA gene sequences from the genus *Ramlibacter* were used as input (Table S2). 174 unique sequences meeting the criteria were identified in the Zinzulùsa Cave dataset and subsequently processed using the second script. This script used a reference database consisting of 21 sequences (Table S3, Ramlibacter_references fasta files; DOI:https://doi.org/10.5281/zenodo.10575873). 18 sequences from the Zinzulùsa Cave dataset were confidently assigned to the *Ramlibacter* genus, phylogenetically close to *R. cellulosilyticus* (Table S4, Ramlibacter_ZC.fasta; DOI:https://doi.org/10.5281/zenodo.10575873). Notably, sequences belonging to the *Ramlibacter* genus were also identified in the fasta sequences from the

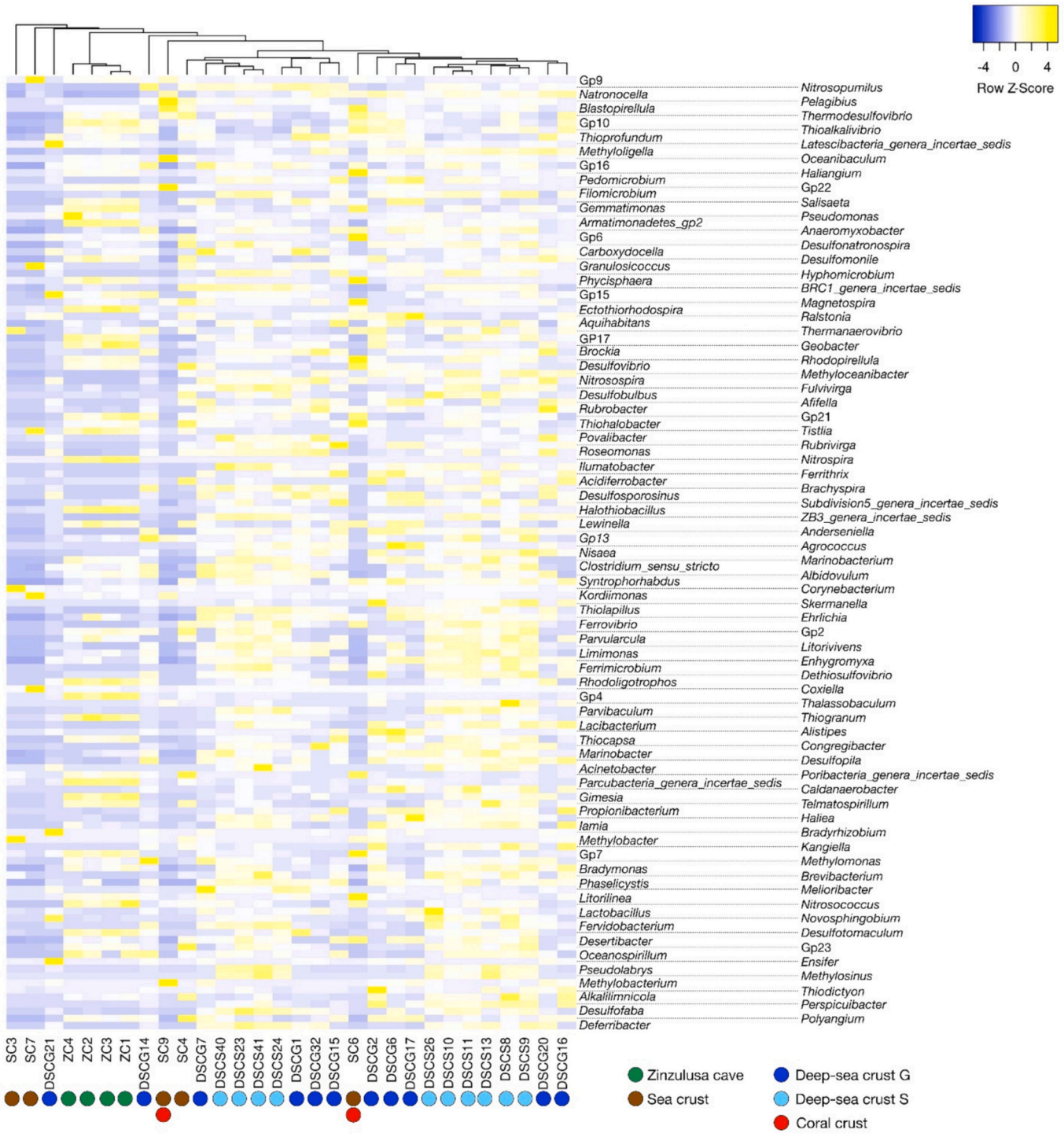

Fig. 10. Heatmap and hierarchical clustering of the 133 most abundant bacterial genera identified in the 16S rRNA gene metabarcoding dataset of Fe—Mn crusts/nodules from Zinzulùsa Cave (ZC) (Talà et al., 2021), Takuyo-Daigo Seamount (DSC-G) (Kato et al., 2018), Takuyo-Daisan Seamount DSC-S (Kato et al., 2018) and Southwestern Atlantic Ocean: Rio Grande Rise (SC) (Bergo et al., 2021) datasets. Only genera with a relative abundance >0.1 % in at least 10 out of 30 samples were reported. Clustering was obtained using the method Average Linkage (Euclidean) applied to rows.

DSC-G dataset (43 sequences) and the DSC-S dataset (1 sequence) (Table S4). Of the 43 sequences from the DSC-G dataset, 18 were phylogenetically close to *R. algicola*, 15 to *R. ginsenosidimutans*, 4 to *R. aurantiacus*, 3 to *R. alkalitolerans*, and 3 to *R. terrae*. The single sequence identified from the DSC-S dataset was phylogenetically close to *R. alkalitolerans* (Table S4).

The 18 sequences selected from the Zinzulùsa dataset were further clustered using VSEARCH. This resulted in two clusters (represented by the sequences 1_1101_15560_17993 and 1_1101_11098_8398) (Table S5). The first contained 4 sequences, while the second cluster comprised 14 sequences (Table S5). To generate a phylogenetic tree, the two representative sequences were used, along with sequences from various genera belonging to the Comamonadaceae family (*Variovorax*, *Semplicispira*, *Limnohabitans*, *Giesbergeria*, *Delftia*, *Polaromonas*, *Rhodoferax*, *Verminephrobacter*, *Vandammella*, *Pseudorhodoferax*, *Kinneretia*, *Tibeticola*, *Hydrogenophaga*, *Comamonas*, *Ottowia*, *Pelomonas*,

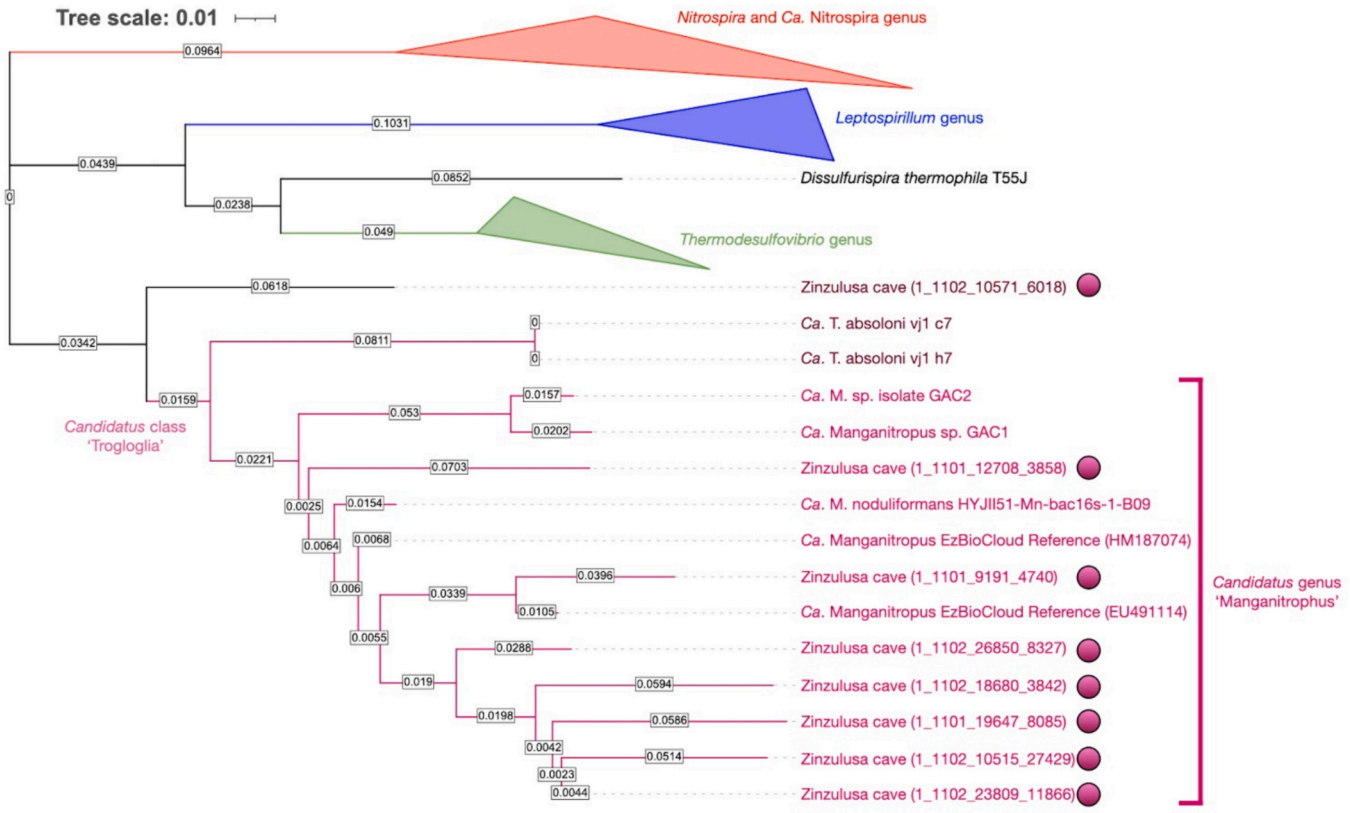

Fig. 11. Phylogenetic tree showing the sequences assigned to the genus "Ca. Manganutrophus" identified in the Zinzulùsa Cave sediment (ZS) samples. The tree shows representative sequences of 8 clusters obtained with VSEARCH which group a total of 125 sequences. 117 of these sequences are represented by the sequence 1_1102_23809_11866 and another two sequences are represented by the sequence 1_1101_9191_4740. The other clusters each contain only one sequence.

Lampropedia and *Ramlibacter*) (Table S6). As expected, the two representative sequences (1_1101_15560_17993 and 1_1101_11098_8398) were found to be phylogenetically close to the EZBioCloud sequence of *R. cellulosilyticus* (MN603953) (Fig. 12).

5. Discussion

5.1. Microbial ferromanganiferous mineralization

This report of ferromanganiferous crusts in anchialine caves extends the environments where these fabrics form. Similar structures, named Frutexites, were recently described from Pleistocene to Recent marine environments (Guido et al., 2016). Frutexites-like structures have been described in association with Fe—Mn oxyhydroxides coatings (Böhm and Brachert, 1993; Kershaw, 2000; Allouc and Harmelin, 2001; Mamet and Préat, 2006; Reolid and Molina, 2010; Reolid and Nieto, 2010; Rodríguez-Martínez et al., 2011a, 2011b; Jakubowicz et al., 2014; Guido et al., 2016).

Temperature, pH, solution chemistry, and redox changes have been suggested as the main factors controlling abiotic mineralization of ferromanganiferous deposits in caves (Northup and Lavoie, 2001; Engel et al., 2004; Barton and Northup, 2007). However, the involvement of microbes in mineral precipitation and numerous reports of microbial signatures found in ferromanganiferous structures (Horodyski, 1975; Lowenstam and Weiner, 1989; Chafetz et al., 1998; Buczynski and Chafetz, 1991; Frankel and Bazylinski, 2003; Rodríguez-Martínez et al., 2011a, 2011b; Jakubowicz et al., 2014) led to wide acceptance of the hypothesis that they are a result of microbial activity (Myrow and Coniglio, 1991; Böhm and Brachert, 1993; Northup et al., 1997; Jones, 2001; Melim et al., 2001; Barton and Luiszer, 2005; Spilde et al., 2005; Barton and Northup, 2007; de los Ríos et al., 2011; Reolid, 2011; Carmichael et al., 2013).

Mn oxides/hydroxides frequently associated with microbial activity include: i. vernadite ($Mn^{4+}_{0.6}Fe^{3+}_{0.2}Ca_{0.1}Na_{0.1}O_{1.5}(OH)_{0.5}{\cdot}1.4[H_2O]$), found in marine and freshwater Fe—Mn crusts and concretions, often in relict bacterial forms; ii. birnessite ($Na_{0.3}Ca_{0.1}K_{0.1}Mn^{4+}Mn^{3+}O_4{\cdot}1.5[H_2O]$), found in deep sea nodules; iii. todorokite ($Na_{0.2}Ca_{0.05}K_{0.02}Mn^{4+}_4Mn^{3+}_2O_{12}{\cdot}3[H_2O]$) primarily found as a constituent mineral in deep sea nodules (Tebo et al., 2004). Bacterial activity is also commonly associated with Fe oxide/hydroxide precipitation, e.g. magnetite (Fe_3O_4, Kooli et al., 2018); hematite (Fe_2O_3, Konhauser, 1997; Polgári et al., 2019); ferrihydrite ($Fe_2O_3{*}0.5H_2O$, Polgári et al., 2019); and goethite (α-FeO(OH), Polgári et al., 2019).

Metabolic activities and mutual relationships in microbial associations characterizing ferromanganiferous crusts have not been investigated previously at this site. Here we utilized a multidisciplinary approach, coupling morphological, mineralogical, biogeochemical and 16S rRNA gene metabarcoding analyses to elucidate the role of bacteria in the biomineralization of the ferromanganiferous cover on the Zinzulùsa anchialine cave crusts. SEM-EDS analyses are consistent with a microbial origin of these Fe—Mn coatings. The micromorphologies observed on the crust surfaces are very similar in size and morphology to those observed by Allouc and Harmelin (2001) in ferromanganiferous deposits of shallow cryptic marine environments, by Guido et al. (2016) in bioconstructions forming in Pleistocene to Recent submarine environments, and in Jurassic Fe—Mn macro-oncoids interpreted as microbial by Reolid and Nieto (2010). Very fine Nanometric filaments and coccoid corpuscles which form complex intricate heterogeneous textures, suggest a microbial origin (Figs. 5 and 6). For example, microspheroidal corpuscles up to ~1 μm in size that show external incrustation around empty centers could derive from the external mineralization of bacterial cell clusters.

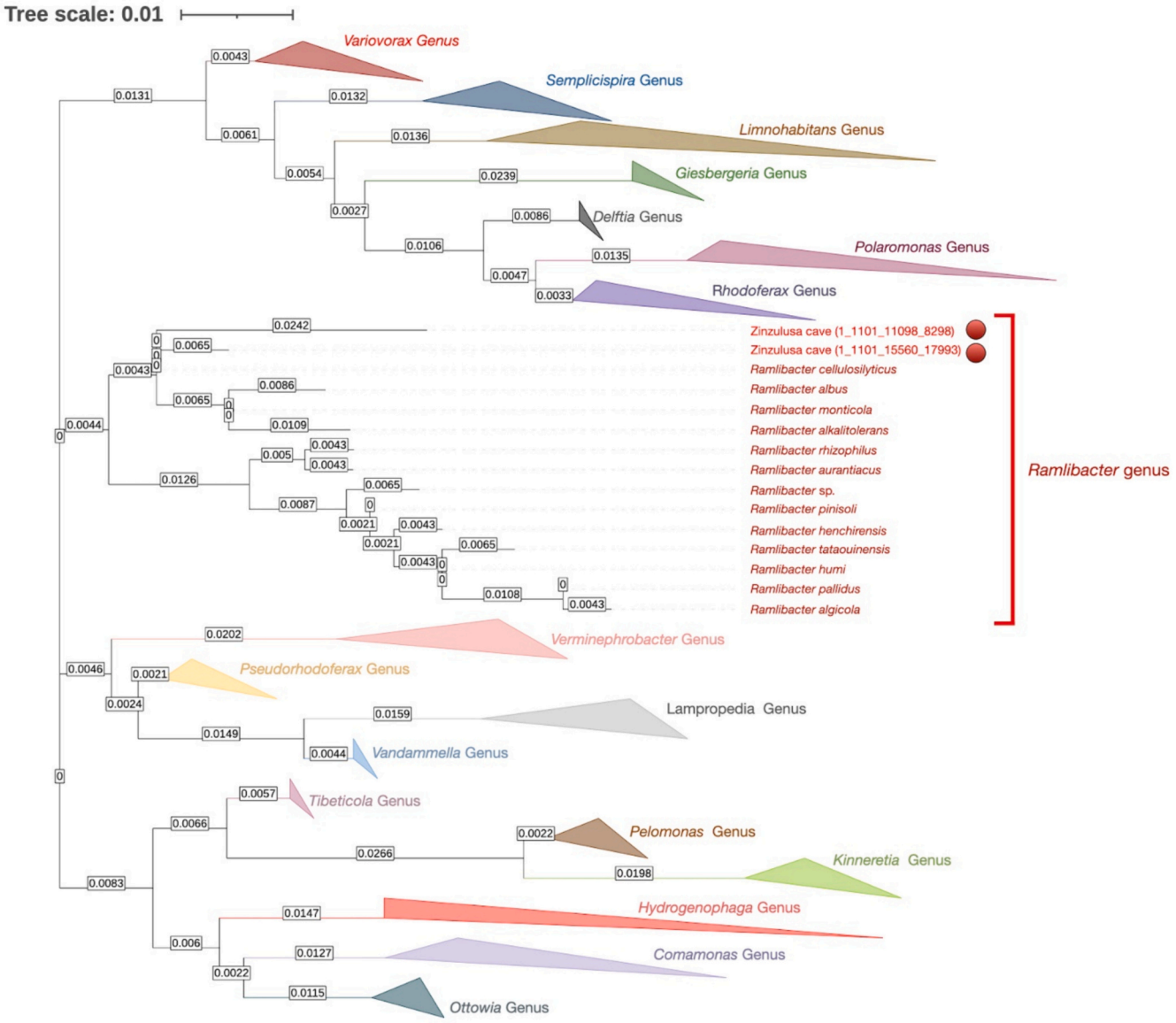

Fig. 12. Phylogenetic tree showing sequences assigned to the genus *Ramlibacter* identified in Zinzulùsa Cave Fe—Mn crust (ZC) samples. The tree shows representative sequences of 2 clusters obtained with VSEARCH which group a total of 18 sequences. 14 of these sequences are represented by the sequence 1_1101_11098_8398 and another 4 sequences are represented by the sequence 1_1101_15560_17993.

Microspheroidal corpuscles similar to those in the Zinzulùsa Cave were formed during long-term, on-site mineral precipitation experiments carried out at four locations (Kaikata, Daini-Bayonaise, Takuyo-Daigo, Takuyo-Daisan) at water depths of 900–4500 m near the western margin of the Pacific plate and the eastern margin of the Philippine Sea plate (Usui et al., 2020). A microbial origin for ferromanganiferous mineralization in the Zinzulùsa Cave is further supported by XRD data demonstrating the presence of hematite and vernadite, in addition to francolite (Fig. 7). Hematite and vernadite are among the Fe—Mn oxides/hydroxides more frequently associated with microbial activity (Tebo et al., 2004; Hoffmann et al., 2021).

In our study, comparative 16S rRNA gene metabarcoding analysis detected a "core microbiome", represented by 113 bacterial/archaeal genera and 20 candidate genera, shared by all analyzed samples from a variety of geographically widespread deep-water or cryptic habitats characterized by ferromanganiferous crusts (Fig. 10). This suggests the existence of a critical role of specific groups of microorganisms involved in the formation of these mineral phases. Comparison of 16S rRNA gene metabarcoding data from the Fe—Mn crusts of the various environments (DSC-G, DSC-S, SC, ZC) suggests a key role for nitrifying, sulfide/sulfur/thiosulfate-oxidizing sulfate/thiosulfate/sulfur-reducing, and iron/manganese-oxidizing/reducing bacteria in the biomineralization processes (Fig. 10). Nitrifying and sulfide/sulfur/thiosulfate-oxidizing bacteria characterized by chemolithotrophic metabolisms are believed to be major primary producers in dark deep-water and cryptic habitats. Haliangiales (fruiting body-forming bacteria), Hyphomicrobiales (stalked and budding bacteria) and Rhodospirillales (a *group of* spirilla with *diverse* metabolism) also occur in the core microbiome. Hyphomicrobiales, such as *Hyphomicrobium* and *Pedomicrobium*, are commonly involved in ferromanganiferous crusts biogenesis (Cox and Sly, 1997; Gebers and Beese, 1988).

At present, precise mechanisms by which microbes induce Mn oxide precipitation remain unclear (Tebo et al., 2005). Both passive (biologically-induced) and active (biologically-controlled) processes have been proposed (Ghiorse and Ehrlich, 1992; Skinner and Fitzpatrick, 1992; Adams and Ghiorse, 1987; Boogerd and de Vrind, 1987; Learman et al., 2011). In Recent environments, Mn precipitation can be linked to Mn-oxidizing microbes (Nealson and Stahl, 1997; Francis and Tebo, 2002;

Frankel and Bazylinski, 2003). Dissolved Mn^{2+} can be adsorbed onto negatively charged organic polymers on the bacterial surface and biofilm (Allouc and Harmelin, 2001). This allows the formation of organometallic compounds and the accumulation of supplementary Mn^{2+} that acts as nucleation sites. The subsequent oxidation of Mn^{2+} into Mn^{4+} induces Mn oxide precipitation associated with extracellular polymeric substances (Nealson et al., 1988; Dixon and Skinner, 1992; Nealson and Stahl, 1997; Allouc and Harmelin, 2001; Francis and Tebo, 2002; Carmichael et al., 2013; Frankel and Bazylinski, 2003).

Passive attraction of Fe^{2+} ions to negatively charged microbial cells or cation-binding exopolymeric substances produced by microbial communities could explain Fe enrichment of the crusts (Beveridge et al., 1997; Braissant et al., 2007). In subaerial cave environments, Fe^{2+} ion enrichment can be linked to freshwater input. Under these conditions, the Mn/Fe ratio can also be significantly increased by the addition of Mn provided by the seeping or flowing of continental waters (Allouc and Harmelin, 2001). These observations are consistent with the distinctive anchialine conditions in the submerged sector of the Zinzulùsa Cave; a water body with restricted exposure to the open air, subterranean connections to the sea, and a combination of significant marine as well as terrestrial influences.

This model was implemented following the discovery of bacterial chemolithotrophy via manganese oxidation (LaRowe et al., 2021). Although the oxidation of manganese by various groups of heterotrophic bacteria has long been recognized (Stein et al., 2001), evidence for manganese oxidation by chemolithotrophs has long remained an open question. In heterotrophic bacteria manganese oxidation can be generally associated with a stationary phase, during which some bacterial Mn (II)-oxidant proteins catalyze Mn(II) oxidation on the cell surface, forming a tiny layer of insoluble Mn oxides (MnOx) (Tebo et al., 2010). This layer may protect the bacteria from protozoan predation and viral attack (Geszvain et al., 2012), radiation (Daly et al., 2007), toxic compounds (Blöthe et al., 2015), or oxidative stress (Banh et al., 2013). However, the very thin layer of MnOx produced by heterotrophs can hardly explain the formation of extensive Fe—Mn crusts which may, instead, be better explained by the presence of Mn(II)-oxidizing chemolithotrophs that can be capable of forming MnOx nodules, even in laboratory conditions (Yu and Leadbetter, 2020). This was discovered in "*Candidatus* Manganitrophus noduliformis" which can couple extracellular Mn(II) oxidation to aerobic energy conservation and CO_2 fixation by the reverse tricarboxylic acid cycle (Yu and Leadbetter, 2020; Yu et al., 2022).

"*Ca.* M. noduliformis" was discovered using enrichment cultures based on municipal tap water (Yu and Leadbetter, 2020; Yu et al., 2022). In the enrichment cultures, growth of "Ca. M. noduliformis" in co-culture with "*Rhamlibacter lithotrophicus*" generated small MnOx nodules (20–500 μm in diameter) (Yu and Leadbetter, 2020). So far as we are aware, our report here is the first time that the genetic trace of "Ca. M. noduliformis" has been recognized in environments characterized by the presence of Fe—Mn crusts, although based on phylogenetic inferences, close relatives of "Ca. M. noduliformis" may reside in many subsurface and karst environments (Yu and Leadbetter, 2020).

Python-based analysis of 16S rRNA gene metabarcoding data allowed us to identify the gene sequences of this microorganism in 3 of the 4 sediment samples of the Zinzulùsa Cave, and in Fe—Mn crusts from two deep-sea sites in Pacific Ocean: Takuyo-Daigo Seamount (DSC-G samples) and Takuyo-Daisan Seamount (DSC-S samples) (Fig. 11; Table S4; Table S7). This indicates that at these sites, chemolithotrophy via manganese oxidation may influence the formation and/or remodeling of the ferromanganese crust, and that "*Ca.* M. noduliformans" is probably a key player in this process. In Zinzulùsa Cave the 16S rRNA gene sequences of "*Ca.* M. noduliformis" were only found in the sediments, and not in the Fe—Mn crusts on the rock wall of the cave. This may suggest that the niche occupied by this microorganism is mainly localized in the oxic-anoxic transition zones of the sediments, as supposed by Yu and Leadbetter (2020).

5.2. Microbial francolite mineralization

Microstructures interpreted as fossil bacteria in phosphorites of various ages and origins (e.g., Cosmidis et al., 2013a, 2013b) suggest that microbial communities play an important role in Ca-phosphate precipitation (Föllmi, 1996; Omelon and Grynpas, 2008; Crosby and Bailey, 2012; Cosmidis et al., 2015). Orthophosphate (Pi) liberation following hydrolysis of organic P during microbial degradation of organic matter (Föllmi, 1996; Paytan and McLaughlin, 2007) has often been invoked as a mechanism by which bacteria drive phosphogenesis in marine sediments. Soluble Pi reacts with Ca^{2+} ions to forms carbonate-fluoroapatite (francolite) when supersaturation with respect to these minerals is reached. Laboratory experiments on the microbial biomineralization of Ca-phosphates (Hirschler et al., 1990; Blake et al., 1998; Benzerara et al., 2004a) or U-phosphates (Beazley et al., 2007; Nilgiriwala et al., 2008; Shelobolina et al., 2009) suggest that alkaline phosphatases are key enzymes involved in bacterially-driven phosphogenesis. These enzymes, responsible for the release of Pi by organic matter remineralization (Cosmidis et al., 2013a, 2013b, 2015), can be located in the cytoplasm and/or extracellular in the periplasmic space (Luo et al., 2009). These membrane delimited compartments, characterized by a variety of physico-chemical conditions (ion concentrations, protein concentrations, pH, etc.), may present very different levels of supersaturation with respect to Ca-phosphates. Furthermore, bacterial membranes can act as nucleation templates for mineral precipitation (Fortin et al., 1997). The variety of possible nucleation processes involved in Ca-phosphate precipitation suggests that this biomineralization occurs in a complex heterogeneous biological system (Cosmidis et al., 2015).

Microbial involvement in recent and fossil phosphorite formation has also been inferred from the presence of microstructures morphologically similar to microorganisms (Lucas and Prévôt, 1985; Mullins and Rasch, 1985; Soudry and Lewy, 1988; Lamboy, 1994; Purnachandra Rao et al., 2000; Soudry, 2000; Benzerara et al., 2004a, 2004b; Bailey et al., 2013; She et al., 2013). Phosphatized microbes can be preserved as capsules with apertures oriented towards open pore space (Krajewski et al., 1994), and as phosphatized filaments (e.g., Martin-Algarra and Vera, 1994; Vera and Martín-Algarra, 1994). In phosphorite deposits, a close relation between microbes and phosphogenesis is also demonstrated by the occurrence of phosphatized stromatolites (Krajewski, 1983; Krajewski, 1984; Krajewski et al., 1994).

Bacilli-like microstructures and metabarcoding data reveal a rich microbial community in the Zinzulùsa crusts, suggesting a role of bacteria in francolite mineralization, in addition to biomineralization of the ferromanganiferous crusts. Similar bacilli-like microstructure has been reported in various phosphorite deposits (Bréhéret, 1991; Lamboy, 1994; Mullins and Rasch, 1985; O'Brien et al., 1981; Purnachandra Rao et al., 2000; Soudry and Lewy, 1988; Soudry, 2000; Toporski, 2002). Other morphologies interpreted as bacterial remains include cocci-like structures (Álvaro and Clausen, 2010; Bréhéret, 1991; Krajewski et al., 1994; Lamboy, 1994; Lundberg and McFarlane, 2011; O'Brien et al., 1981; Purnachandra Rao et al., 2008, 2000, 1992; Soudry and Lewy, 1988; Soudry, 1992, 2000; Toporski, 2002) and filaments (Álvaro and Clausen, 2010; Bréhéret, 1991; Lundberg and McFarlane, 2011; Purnachandra Rao et al., 2008, 1992; Soudry, 2000; Toporski, 2002).

Three models have been proposed to explain the formation of authigenic phosphate minerals (Cosmidis et al., 2013a, 2013b and reference therein): 1) organic matter remineralization; 2) iron redox pumping; and 3) polyphosphate metabolism. In the organic matter remineralization model, phosphate precipitation is a consequence of microbial hydrolysis of organically bound P (Arning et al., 2009; Burnett, 1977; Föllmi, 1996; Jaisi and Blake, 2010; Jarvis et al., 1994; Krajewski et al., 1994; Soudry, 2000). In this model P is released from organics and converted to Pi, which is accomplished by hydrolytic cleavage catalyzed by phosphatases (Ehrlich and Newman, 2009; Omelon and Grynpas, 2008). Soluble Pi released into interstitial

sediment pore solution reacts with calcium ions from seawater to form insoluble carbonate-fluorapatite.

In the iron redox pumping model, P is produced by dissolution of Fe- and Mn-(oxyhydr)oxides, releasing Pi absorbed on their surface (Hongve, 1997; Sundby et al., 1992) which reacts with calcium ions from seawater to form carbonate-fluorapatite (Delaney, 1998; Heggie et al., 1990; Jarvis et al., 1994; März et al., 2008; Schuffert et al., 1998; Scopelliti et al., 2010). Microorganisms may participate in this process by coupling Fe or Mn reduction with organic carbon oxidation (e.g. Nealson and Saffarini, 1994). Moreover, the reduction of Fe- and Mn-(oxyhydr) oxides can be enhanced under conditions of intense sulfate reaction (Zoss et al., 2019), by reaction with sulfide species produced by sulfate-reducing bacteria (Glasauer et al., 2003; Jensen et al., 1995; Li et al., 2014; Mortensen et al., 1993).

In the polyphosphate metabolism model, Ca-phosphate precipitation is induced by polyphosphate-accumulating bacteria (Crosby and Bailey, 2012) that can accumulate Pi as intracellular polyphosphate inclusions under oxic conditions. Subsequently, they gain energy by hydrolyzing stored polyphosphates, releasing Pi as a byproduct, which may promote Ca-phosphate mineralization.

The presence of Ca-phosphate mineralized bacilli-like microstructures supports a role for bacteria and (poly)phosphate metabolism in the Ca-phosphate mineralization of Zinzulùsa crusts. This model is suggested by the presence of polyphosphate-accumulating bacteria among detected genera by 16S rRNA gene metabarcoding (Fig. 10), and, in particular, the enrichment of *Gemmatimonas* in the samples ZC, DSC-G, DSC-S (Fig. 11).

Polyphosphate may have been introduced in the Zinzulùsa system by degradation of bat guano. Until the 1940's the subaerial part of the cave floor was covered by >3.0 m of bat guano which filled the large dome at the end of the cave, the resting site of a large bat population. Changes in water level and humidity dissolved the guano and carried it to the submerged part of the cave, down a steep slope about 5 m below the dome floor. The guano was subsequently completely removed during the 1950s for fertilizer production (Ciccarese, personal communication). It is conceivable that two processes could be involved in the formation of the Ca-phosphate crusts: 1) organic matter remineralization, by which bacteria degraded the bat guano, releasing Pi into the system; 2) polyphosphate metabolism, in which bacteria accumulated polyphosphate, releasing Pi following hydrolyzation.

With regarding to the first process, there may be a possible role for bacteria belonging to *Ramlibacter* genus, whose 16S rRNA gene sequences were found on Zinzulùsa Cave wall rock (Fig. 12; Table S4; Table S7). *Ramlibacter tataouinensis* is characterized by an unusually high diversity of phosphatases, facilitating hydrolysis of a broad range of organic P substrates, and is known to biomineralize Ca-phosphates in a variety of environmental contexts and laboratory conditions (Skouri-Panet et al., 2018). *R. tataouinensis* phosphatases play a critical role in this process, as their release of orthophosphate is key to achieving high saturation levels with respect to hydroxyapatite and the induction of phosphatogenesis. Heterologous expression of *R. tataouinensis* PhoD and PhoX phosphatases in recombinant *Escherichia coli* cells induced the precipitation of Ca-phosphate mineral phases, identified as poorly crystalline hydroxyapatite (Skouri-Panet et al., 2018).

SEM images from the Zinzulùsa crusts show filaments with longitudinal strings (about 20–40 nm wide) along the entire filaments, resembling cable bacteria (Fig. 5B). Cable bacteria (Deltaproteobacteria; family Desulfobulbaceae) are multicellular filamentous bacteria that transport electrons along long filaments for distances up to centimeters, coupling sulfide oxidation in deeper anoxic sediment layers to the reduction of oxygen or nitrate near the sediment-water interface (Bjerg et al., 2018; Pfeffer et al., 2012; Meysman, 2018; Meysman et al., 2019). Their metabolic activity locally strongly influences seafloor geochemistry. Sulfide oxidation acidifies pore water, promoting mineral dissolution of minerals, thus affecting the cycle of elements such as Ca, Fe, Mn and P (Meysman et al., 2015; Risgaard-Petersen et al., 2012). The genomes of "*Candidatus* Electronema" and "*Candidatus* Electrolux" suggest that cable bacteria fix CO_2 using the Wood-Ljungdahl pathway, assimilate smaller organic acids and alcohols, fix N_2, and synthesize polyphosphate and polyglucose, and storage compounds in the sulfidic anoxic zone, while in the suboxic/oxic zone they hydrolyze these compounds (Kjeldsen et al., 2019). Based on these characteristics, it is possible that cable bacteria have a role in Ca-phosphate precipitation, although the genetic signature of these bacteria was not detected during 16S rRNA gene metabarcoding in the microbiome of the Zinzulùsa Cave.

5.3. Microbial biomineralization model of the Zinzulùsa crusts

Comparison of 16S rRNA gene metabarcoding data from the Fe—Mn crusts of the various environments (DSC-G, DSC-S, SC, ZC) provides information regarding key microbial processes involved in the crust biomineralization. These data indicate that nitrifying bacteria and sulfide/sulfur/thiosulfate-oxidizing bacteria are major players in primary production in the Zinzulùsa Cave. We infer that oxidation of sulfide/sulfur/thiosulfate in the upper layers of the microbial biofilm and sediments led to acidification of pore water and mineral dissolution, thus affecting the cycling of elements such as Ca, Fe, Mn and P. The activities of nitrifying and fermentative bacteria also contribute to acidification. As a result, iron and manganese dissolution increases pore water concentrations of Fe(II) and Mn(II). Subsequent oxidation by iron- and manganese-oxidizing bacteria in the oxic zone forms iron and manganese oxides that precipitate in the Fe—Mn biofilm crusts.

The genetic signature "*Ca.* M. noduliformans" in the sediments of the Zinzulùsa Cave suggests that chemolithotrophy via manganese oxidation may have an important role in the Fe—Mn crusts. This microorganism occupies an ecological niche mainly localized in sediment oxic-anoxic transition zones (Yu and Leadbetter, 2020). At these interfaces, manganese can be cycled between aerobic Mn(II)-oxidizing chemolithotrophs and anaerobic manganese oxide-respiring (reducing) chemotrophs, and the bacteria produce extracellular polymers on the rock wall (including Hyphomicrobiales of the genus *Pedomicrobium*) that can serve as scaffolds that trap and deposit MnOx produced by the Mn(II)-oxidizing chemolithotrophs.

Within the internal layers, below the Fe—Mn crust, acidification leads to calcium carbonate dissolution. Dissolved carbonate is utilized by chemolithotrophs and the dissolved calcium interacts with phosphate, produced by hydrolysis of polyphosphate by polyphosphate-accumulating bacteria in the biofilm, to produce francolite. It is well known that phosphogenesis occurs in sediments beneath some oceanic upwelling zones that harbor polyphosphate-accumulating bacteria. These bacteria concentrate phosphate in sediment pore waters, creating supersaturated conditions with respect to apatite precursors. In the Zinzulùsa Cave, the abundance of bat guano may have favored selection of the polyphosphate-accumulating bacteria. *Ramlibacter*, whose genetic signature occurs in the microbial biofilm on the wall of the Zinzulùsa Cave, may have an important role in this process, since it can hydrolyze a wide range of organic P substrates and can be particularly effective in Ca-phosphate biomineralization (Skouri-Panet et al., 2018).

The formation and remodeling of Fe—Mn crusts, and the replacement of carbonate by phosphate to form francolite, may have been accelerated by the presence of particular groups of microorganisms, such as cable bacteria which characteristically generate extended redox and pH gradients along their filaments. In the lower anoxic sulfidic zone of the filament, sulfide oxidation leads to sulfuric acid production, acidification of pore water, and dissolution of carbonate and non-carbonate minerals such as iron and magnesium oxides. Simultaneously, they accumulate polyphosphate that is hydrolyzed in upper suboxic and oxic zones of the filaments. The presence of these living and fossil bacteria is suggested by SEM images of Zinzulùsa Cave crusts.

5.4. Interconnections between Fe—Mn oxides and francolite mineralization and diagenetic evolution of the crusts

In natural environments, Fe—Mn oxide and francolite mineralization often occur in the presence of nitrifying bacteria and sulfide/sulfur/thiosulphate-oxidizing bacteria (Jørgensen et al., 2019). The metabolic activities of these groups generate pH, redox and chemical gradients that play crucial roles in biomineralization. This "core microbiota" is responsible for creating the essential conditions for the episodic growth of specific groups of microorganisms which can interact with each other also through synergistic interactions. The presence of "*Ca.* M. noduliformans" in Zinzulùsa sediments, and bacteria belonging to the genus *Ramlibacter* on the wall of the cave, may represent syntrophic interactions and require further study.

Our results suggest that the change from Ca-phosphate mineralization to Fe—Mn mineralization in these cave crusts can be directly related to anthropogenic influence. In this view, water chemistry and microbial associations were transformed by the change in chemical conditions in the cave that resulted from guano removal in the 1950s. Prior to this date, the abundant supply of phosphorus derived from bat guano allowed the development of rich polyphosphate-accumulating bacteria communities able to induce francolite precipitation. Removal of the guano allowed iron- and manganese-oxidizing bacteria to become the dominant association. As a result, Fe—Mn mineralization superceded apatite production. Future studies, including dating of the various components, should test this hypothesis.

Petrographic observations indicate that francolite crusts experienced dissolution-recrystallization. Carbonate-fluorapatite tends to transform into fluorapatite ($Ca_{10}(PO_4)_6F_2$) with the loss of CO_2 and fluorine due to geological ageing (McClellan, 1980) and meteoric deterioration (Lueas et al., 1980; Flieoteaux and Lucas, 1984). Color transition from yellow to white, increase in intrastructural porosity, and decrease in fluorine content from upper (younger) to lower (older) parts of the crust, would be consistent with early diagenetic, mainly dissolution processes, likely responsible of the periodic detachment of the crust from the submerged carbonate walls of the cave. These processes might in part reflect freshwater input from fractures in the cave walls and subsequent interaction with the francolite crusts.

6. Conclusions

Localized anchialine conditions in part of the Zinzulùsa Cave allowed the development of a unique microbial consortium that may represent novel biomineralization processes. This diverse microbial community occurs in submerged centimeter-thick carbonate-fluoroapatite (francolite) crusts, covered by ferromanganiferous oxides (hematite and vernadite). High fluorescence under UV-excitation, and organic bands in Raman spectra, demonstrate the organic nature of both mineral components, which are mixed with amorphous organic matter and coccoid and filamentous bacteria. Comparative 16S rRNA gene-based metabarcoding analyses identify a "core microbiota" similar to other ferromanganiferous and Ca-phosphate mineralizers in the geomicrobiological record. Nitrifying, sulfide/sulfur/thiosulfate-oxidizing and sulfate/thiosulfate/sulfur-reducing bacteria occur in this microbiota. These include "*Ca.* M. noduliformans", a manganese-oxidizing bacterium, together with abundant bacteria, able to produce extracellular polymers that trap iron and manganese oxides. These belong to the Planctomycetes-Verrucomicrobia-Chlamydiae (PVC) superphylum as well as Haliangiales (fruiting body-forming bacteria) and Hyphomicrobiales (stalked and budding bacteria), suggesting a direct role for microbial consortia in the vernadite and hematite mineralization. Similarly, the presence of bacteria able to utilize many organic P substrates, including those belonging to *Ramlibacter* genus, and traces of fossilized microorganisms resembling 'cable bacteria', support a microbial role in francolite biomineralization.

The discovery of a specific core microbiome associated with the unusual biomineralization observed in Zinzulùsa Cave, underscores the need for conservation and protection of this unique site, characterized by its rare and pristine biology, unusual chemistry and well-preserved mineralogy. Zinzulùsa Cave represents a valuable natural laboratory for the elucidation of fundamental geomicrobiological processes.

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CRediT authorship contribution statement

Adriano Guido: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Matteo Calcagnile:** Writing – original draft, Software, Methodology, Investigation, Formal analysis, Data curation. **Adelfia Talà:** Writing – original draft, Visualization, Methodology, Investigation, Formal analysis. **Salvatore Maurizio Tredici:** Validation, Methodology, Investigation, Formal analysis, Data curation. **Genuario Belmonte:** Writing – original draft, Visualization, Conceptualization. **Pietro Alifano:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Project administration, Methodology, Funding acquisition, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

All the sequences and codes used in this document are available online. The input sequences, codes, and sequences identified as 'Ca. Manganitrophus' or 'Ramlibacter' can be found on Zenodo (DOI: https://doi.org/10.5281/zenodo.10575873). The raw sequences resulting from the 16S metabarcoding analysis of the Zinzulùsa Cave samples (ZC and ZS) are accessible through the SRA database (PRJNA1026609).

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