



# Geochemical constraints on the element enrichments of microbially mediated manganese and iron ores – An overview

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## ARTICLE INFO

### Keywords:

Biomining  
Cell mineralization  
EPS mineralization  
Ore-forming processes of Fe- and Mn  
Diagenesis

## ABSTRACT

The role of biogenicity in the mineral world is larger than many might assume. Biological processes interact with physical and chemical processes at the Earth's surface and far below underground, leading to the formation, for instance, of banded iron formations and manganese deposits. Microbial mats can form giant sedimentary ore deposits, which also include enrichment of further elements. Microorganisms play a basic role in catalyzing geochemical processes of the Earth and in the control, regularization and leading of cycles of elements. Microbial mats and other biosignatures can be used as indicators for environmental reconstruction in geological samples. This article reviews the many ways that microbially controlled or mediated processes contribute to mineralization and examines some published case studies for clues of what might have been missed in the analysis of sedimentary rocks when biogenicity was not taken into account. Suggestions are made for tests and analyses that will allow the potential role of biomineralization to be investigated in order to obtain a more complete view of formation processes and their implications.

## 1. Introduction

To understand the main and rare element content of sedimentary ore formations like iron and manganese ores, it is important to consider the role of microbial life (in particular bacteria and fungi) in the geological context of mineralization and mobilization processes, because the mechanisms governing such activities often supersede purely inorganic reactions. Microbially mediated mineralization is a special metabolic process resulting in the formation of particular minerals. This includes microbially controlled mineralization, a direct connection between microbes and minerals. However, indirect connections cannot be excluded; in this case the microbial activity acts on the environment, which then results in mineralization. This is called microbially induced mineralization. Microbially mediated minerals are very fine-grained ( $\mu\text{m}$  scale) and microbial processes are very effective when compared with chemical processes (up to  $10^5 - 10^6$  times more effective). Further details on geomicrobiological background on the mineral assemblage of ore deposits are given in Polgári et al. (2019) and in this volume.

Sources of metals and accompanying elements and the selective enrichment processes that result in the deposits of iron and manganese are often debated, leading to disharmony and controversy in the

interpretation of datasets. One typical approach is hydrothermal models that overlook the basic role of microbial processes in the sequestration of metal ions from geofluids into solid form as minerals and in the selective enrichments of particular elements. One example is huge formations of extreme K-rich altered pyroclastic rock masses (Varga, 1992; Nagy, 2006). Polgári et al. (2019) summarized the important role of microbially mediated ore-forming processes and cell mineralization in general. This is explained by case studies such as those of Úrkút in Hungary (Polgári et al., 2012a), Datangpo in China (Yu et al., 2019), and Urucum in Brazil (Biondi et al., 2020). Deposits are the result of complex diagenetic processes, which include the decomposition and mineralization of cell and extracellular polymeric substances of Fe and Mn bacteria and cyanobacteria. These processes supply bioessential elements depending on the store of elements, the type of metabolism, microbial species, and the mineralogical characteristics. The mineralization of the cells and the extracellular polymeric substances material contribute significantly to the material of ore deposits and other rock types, both in terms of quantity and of varied mineral composition.

This paper aims to call attention to the role of microbial processes and to provide a short overview of the role of microbial processes in the

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main and trace element content of sedimentary iron and manganese ores in general. These deposits have high economic value, and the information they can provide on the role and development of biomineralization is also valuable. Through re-examining some earlier case studies that overlooked microbial processes in different sedimentary environments, we also aim to demonstrate how the analysis of biomineralization – and particularly the roles of microbially mediated metallization – can contribute to and expand the original conclusions of the study.

## 2. Historical background

What happened before biomineralization spread over the planet and became an important factor in building up the crust? What are the results of biomineralization on the global level on the planet Earth?

### 2.1. Before the spread of biomineralization

In the beginning, reduced rocks and a reducing atmosphere (90% N<sub>2</sub>, 10% CO<sub>2</sub>, low amounts of H<sub>2</sub> and traces of O<sub>2</sub>, CH<sub>4</sub>, NH<sub>3</sub>, HCHO, and noble gases) characterized the conditions on the planet, but what happened before biomineralization spread on Earth? One of the most important factors is the appearance of elemental oxygen. As a first step, photodissociation resulted in oxygen accumulation in the atmosphere till the Urey level, 0.001 Present Atmospheric Level (PAL). The increase of oxygen concentration in the atmosphere is the result of biological activity; there are no other processes that could achieve this. Cyanobacteria, living in marine environments, are therefore responsible for the oxygen-bearing atmosphere. The genesis of life and the oxygenic atmosphere are strongly dependent on each other. This increase of oxygen in the atmosphere started around 3.5 Ga years ago, and reached a level at 2.4 Ga years ago, called the Great Oxygenation Event (GOE). The oxygenation of the planet caused dramatic changes in all geospheres.

The first biosignatures did not represent geologically important masses. After the appearance of oxygen the first biostructures were stromatolites. Stromatolites are geological structures of variable size (micrometer-scale to meter-scale) that are formed by microbial mediation (Fig. 1). These structures are common even today, and can involve signs of biomineralization. Though these structures are widespread in some environments they can mainly be considered as local occurrences. The most common mineral composition of stromatolites is carbonate, but economically important, specific metal-bearing travertine-stromatolites also occur (Fe-, Mn-oxides and carbonates, As-bearing stromatolites) (Polgári et al., 2012a; 2012b).

But what happened with the forming oxygen? At first it did not accumulate in the atmosphere; instead, it dissolved in seawater and oxidized the reduced compounds, which was an important role concerning elements with changing valence state. Looking at the Periodic Table, most of its elements are involved with biological cycles (Wackett et al., 2004). These biological cycles could begin only after the appearance of oxygen in the system, as this allows redox changes in many of the metals, which are favored by microbial metabolism. These cycles presented the right set of circumstances for biomineralization processes on a global level. This was followed by a complex diagenetic mineralization of cell and extracellular polymeric substances (EPS). The evolution of the metal utilization of biota is discussed in the following section.

What were these chemical compounds for oxidation, and what was the result of these processes?

- Fe(II) and Mn(II) in the rocks, sediments and oceans
- Compounds of atmosphere mineralized (precipitated) and formed rocks
- Composition of oceans changed

After the oxidation of giant amounts of Fe(II) and Mn(II), the accumulation of oxygen started in the atmosphere (GOE), around 2.4 Ga

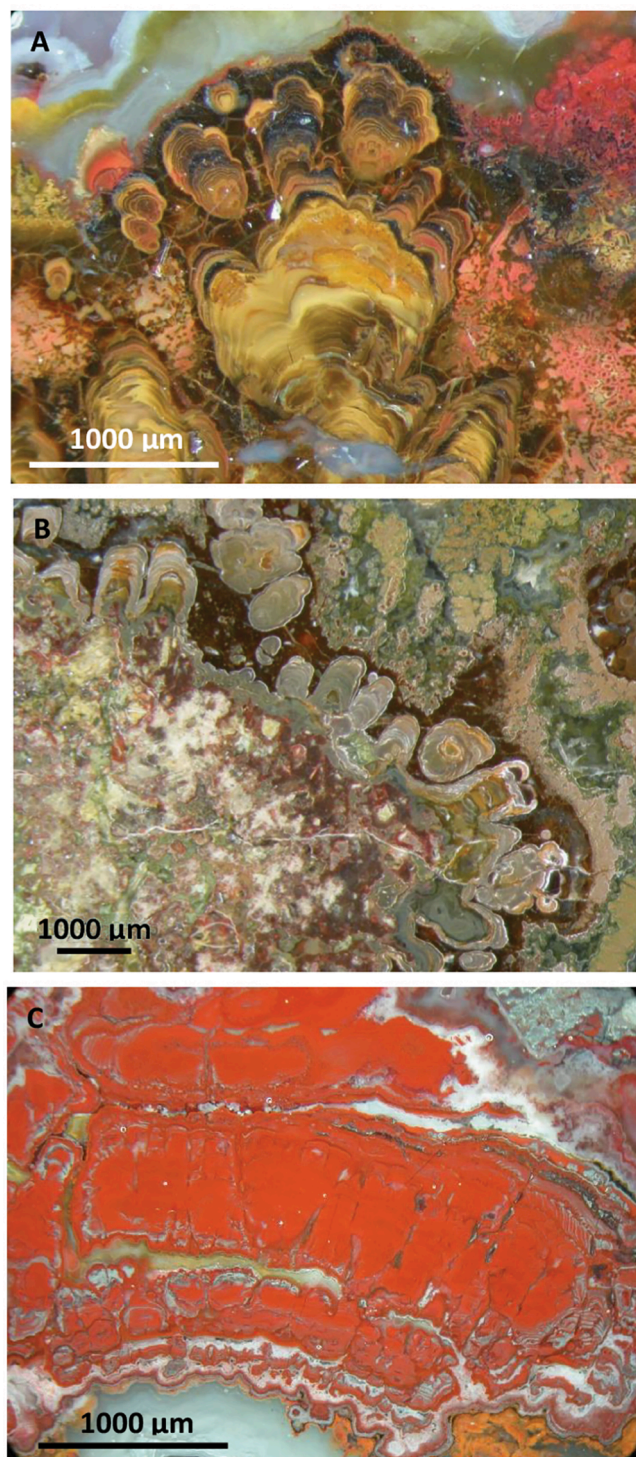


Fig. 1. Stromatolites. (A-C) Stromatolite in chalcedony and opal, in S-Mátra Mts., Hungary (thin section by optical rock microscopy, 1 N; Müller, 2009).

years ago (Lyons and Reinhard, 2009).

Why do Fe and Mn play such an important role? Fe is the most frequent heavy metal, with 5% crustal abundance, while Mn accounts for about 0.1% (Turekian, 1969). The answer is that Fe(II) and Mn(II) were oxidized to Fe<sup>3+</sup> and Mn<sup>4+</sup> forming solid phases (minerals), which precipitated fractionally depending on the available oxygen. Fe precipitation in the form of banded iron formations (BIF) started under suboxic conditions, while Mn precipitation continued to increase oxygen content when the dissolved oxygen level reached the obligatory oxic conditions

(2 mL/l dissolved oxygen). But what was the process of precipitation and accumulation? Numerous papers have presented evidence that banded Fe- and Mn-ores formed through variable forms of microbial mediation (e.g., Gutzmer and Beukes, 2008, and references therein; Biondi et al., 2020). During these processes giant geological reservoirs formed, creating mineral deposits with high economic value today.

Microbial Mn and Fe oxidation determine the global biogeochemical cycle of these elements in oxic environments. This process influences the concentration of Fe(II) and Mn(II) in the oceans, where they are critical nutrients for primary plankton productivity (Polgári et al., 2012a). These microbial processes catalyze important biogeochemical processes, which interact with C, N, Fe, U, and S element cycles (Myres and Neelson, 1988a; 1998b; Neelson et al., 1988; Parkers et al., 1994; Tebo et al., 1997).

## 2.2. Constraints on geochemistry of biomineralization

### 2.2.1. Metal utilization of biota

To understand the element content of microbially mediated geological formations (biominerals), a short historical overview of the metal utilization of biota is needed. Here we summarize based on Dupont et al. (2010). As molecular biology is not the subject of this paper, we mention only some aspects.

Molecular speciation and reactivity both within cells and the environment on a global scale is influenced by the fundamental chemistry of trace elements. The mechanisms that control intracellular metal concentrations and also the metal-binding proteins for catalyzing electron transport and redox transformations were absent at the time when life arose on Earth. Thus, the metal concentration of the Archean oceans determined the creation of metal-specific structures that belonged to the development of protein structures for metal homeostasis. These processes established the biogeochemical cycles of elements and this contributed to the diversification of developing system of *Archaea* and *Bacteria*. As the redox conditions determined the metal content of the ancient ocean, Cu and Zn binding structures evolved later. This is also evidence that environmental availability had a basic impact on selection of elements. The bioavailability of Zn – the essential element for Zn-binding proteins in eukaryotic cellular biology – was limited in the ancient reductive ocean.

Metalloproteins include one or more chemical elements in their structure, and approximately 30% of all proteins belong to this group (Rosenzweig, 2002). These metalloenzymes control numerous biological pathways to support life (Andreini et al., 2008), including among others Mg, K, Ca, Fe, Mn, and Zn (Williams and Fraústo da Silva, 2006). Besides these, other elements (Cu, Mo, Ni, Se, Co) are important for metabolic processes, and trace elements represent varied roles in different species (Williams and Fraústo da Silva, 2006).

Based on geological evidence the shift in the global redox state occurred during the development of Earth, and this basically determined the trace elements, among them metal contents (Williams and Fraústo da Silva, 2003; 2006; Anbar, 2008). The reducing Archean ocean was probably characterized by high Fe, Mn, and Co concentrations, while the content of Cu, Zn, and Mo was low (Saito et al., 2003; Anbar, 2008). Oxygenic photosynthesis resulted in an increase in dissolved O<sub>2</sub> in the ocean and also its accretion in the atmosphere, which reached a turning point at around 2.4 Ga years ago in the frame of Great Oxygenation Event (Anbar and Knoll, 2002; Arnold et al., 2004; Bekker et al., 2004; Lyons and Reinhard, 2009). Coexisting with this, starting at an early stage, microbially mediated oxidation and precipitation of Fe- and Mn-sequestration (solved ions into solid phase, into sediment) occurred in giant amounts. The previously reducing ocean turned to a generally oxic and oxidizing one, which resulted in the considerable enrichment of Cu, Zn, and Mo and the abrupt decrease of Fe, Mn, and Co (Saito et al., 2003).

This complex evolution and interaction among geospheres allowed the evolution of modern life, and this also affected the biological

exploitation of selected elements (Williams, 1997; Wang et al., 2007). The environmental availability of trace metals determined the type of emerging metal-binding proteins.

The evolution of metalloenzymes, as a whole, can be schematically matched with the generalized geochemical and physical fossil record at two points: (i) The GOE would result in a physiological need for the oxidative defense-enzymes superoxide dismutase and catalase; (ii) The first appearance of univocal physical fossils of eukaryotic life was found in rocks formed 1.6 Ga years ago (Knoll et al., 2006).

## 3. Biogeochemistry of sedimentary ores – Formation conditions

Sedimentary ores often include selective element enrichments like Si, Mg, P, As, Co, or Ce in addition to the ore-forming main elements (Fe, Mn). To understand the processes which result in these element enrichments, we need a general review.

Microorganisms are widespread everywhere on and also under the surface of Earth till some km depth (Stevens et al., 1993; Stevens and McKinley, 1995; Fyfe, 1996; Pedersen, 1993; 1997; Colwell et al., 1997; Ghiorse, 1997; Onstott et al., 1998; Banfield and Welch, 2000). Submarine microbial alteration of sediment and basalt is known to occur some hundreds of meters below the seafloor (Parkers et al., 1994; Stevens and McKinley, 1995; Thorseth et al., 1995; Fisk et al., 1998; Furnes and Staudigel, 1999; Banfield and Welch, 2000). These organisms survive boiling water, but they also tolerate extreme cold snow surfaces on Antarctica. Extremophiles tolerate extreme salt concentration like saturated NaCl solution or extreme radiation (1.0 – 1.5 Mrad gamma radiation), acidic conditions (pH ~ 3.6), metal concentrations (e.g. some 1000 ppm As), or intensive exsiccation in hot and icy deserts (Deming and Baross, 1993; Barns et al., 1994; Eisenberg, 1995; Minton and Daly, 1995; Onstott et al., 1998; Summit and Baross, 1998; Priscu et al., 1999; Sun and Friedmann, 1999; Edwards et al., 1999; 2000).

Earlier it was thought that the quantity, activity and diversity of microorganisms below the surface is low, but based on recent studies their number is significant ( $10^5 - 10^8$  cells/cm<sup>3</sup>; Balkwill, 1989; Fredrickson et al., 1989; Onstott et al., 1998). Their quantity does not reduce even under deep solid crust conditions (Havemann et al., 1999). The cell number in surface waters in oceans is  $10^4 - 10^7$  cells/ml, while in mud and biogenic laminae it can reach  $10^{12}$  cells/g. In soils it is  $10^6 - 10^9$  cells/cm<sup>3</sup>, and on mineral surfaces there can be 1 cell/μm<sup>2</sup>. Microorganisms represent an important source of reactive surfaces of the environments because of their small size and enormous number. Furthermore, their essential element components, which are needed by every cell, as a whole represent significant element enrichments and element reservoir pools.

### 3.1. Biogeochemical cycles

The bioessential elements such as O, N, C, H, Si, Mg, P, Na, Ca, K, S, I, Cl, Fe, Mn, Cr, V, Se, Zn, Cu, Sn, and Mo are very important for biogenic processes (Ehrlich, 2002). In addition to biologically controlled mass and energy transfer in the environment, purely chemical or purely physical actions also take place.

Cycles of elements occur in nature. The atoms are spread in the spheres of Earth continuously, transferring and forming bonds with other atoms following strict rules, resulting in billions of new combinations, separating and then combining again. The same atom journeys across geological times and the bodies of uncountable organisms, and through very different abiotic environments, and moves in an unpredictable but seriously determined way through its endless motion (Ehrlich, 2002).

The biogeochemical cycles (gas and sedimentary nutrient cycle) refer to the fact that in the cycle of elements the living organisms (bio), the geological environments and objects like minerals (geo), and the chemical reaction networks are interlocked and proceed without disruption. The general features of these cycles are (1) the wandering of

elements from the abiogenic side toward the living organisms and back; (2) the presence of giant “geological reserve depos (pools)”, element stores, and element resources that are transitionally indifferent, non-reactive; and (3) the wandering of elements via cycles from organic bonds to inorganic and back, while the oxidation state of their atoms changes permanently (Ehrlich, 2002).

Biogenic and abiogenic phases can be distinguished. In biogenic phases the wandering of elements is biologically controlled, in abiogenic phases it is not. The longer their way via biogenic systems, and the shorter via abiogenic ones, the more participation of elements in the material transfer in ecosystems is ensured. Biogeochemical cycles are closely linked to the hydrological cycle and energy transfer via the biosphere. Biogeochemical cycles carry out alternation of nutrient elements among different ecosystems on a global scale. The transportation of nutrient elements in the ecosystem is termed the “inner nutrient budget” (Odum, 1971).

Microorganisms play a basic role in catalyzing the geochemical processes of Earth. Oxidation and reduction caused by microorganisms, the contribution of metabolic materials to abiogenic reactions, and the accumulation of cell remnants can form variable geological formations. Microorganisms play a basic role in nature in the precipitation of S, Fe, Mn, Mg, and Ca (as minerals), among others, and in the dissolution of P, S, Fe, K, Ca, Si, Mn, Mg, Al, Cu, Zn, Co, etc.

*Microbial oxidation* affects mainly C, N, P, S, H, Fe, Mn, As, and Se. Some microbially mediated oxidation is connected to cell energy metabolism. Heterotrophic organisms for example oxidize organic matter, while chemoautotrophic ones oxidize N, S, H, Fe, Mn, etc. Other types of oxidation do not have a direct relationship to the energy metabolism and energy demand of microbes or only a slight connection with it.

There are three types of microbial oxidation of inorganic compounds:

1. Metabolism of chemoautotrophic organisms using the chemical oxidation energy of ammonium, nitrite, sulfur,  $\text{H}_2\text{S}$ , metal-sulfides,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ , or  $\text{H}_2$  gas. Here, cells produce large amount of products (minerals), because only a small part of these processes can be used for energy supply.
2. Some heterotrophic fungi and bacteria oxidize certain elements by enzymatically catalyzed processes (e.g., sulfate production from organic sulfur in soil, nitrate production).
3. Some oxidation occurs indirectly, when the products of microbial metabolism and inorganic ions react without enzymatic reactions resulting in minerals.

The most important elements taking part in *microbial reduction* processes are C, N, P, S, Fe, Mn, and Cl. A number of reductive processes are connected with energy taking and conservation mechanisms. The capability of reduction of organic and inorganic material of microorganisms occurs everywhere and its three main mechanisms are the following:

1. Reduction is directly bound to energetic metabolism and the oxidant serves as an electron acceptor. The aerobe forms reduce oxygen to water (sulfate to sulfide, denitrificants reduce nitrate and nitrite to dinitrogen or nitrogen-oxides, some anaerobes reduce  $\text{CO}_2$  to  $\text{CH}_4$ , but bacteria also belong to this group that use  $\text{Fe}^{3+}$  or  $\text{Mn}^{4+}$  as terminal electron acceptors burning organic matter, which results in  $\text{Fe}^{2+}$  or  $\text{Mn}^{2+}$  forms.
2. Reduction occurs via consumption of oxygen, resulting in Eh decrease or formation of reductive compounds, or both (non-enzymatic reductions, e.g. oxygen-depleted muds in oceans or lakes belong to this group).
3. Reduction is the result of acid formation (e.g., decrease in pH causes spontaneous  $\text{Fe}^{2+}$  -  $\text{Fe}^{3+}$  and  $\text{Mn}^{2+}$  -  $\text{Mn}^{4+}$  transformations).

There are elements (e.g. P, Si) that are stable in their oxidative

compounds, like phosphates and silicates under anaerobe conditions. On the contrary, N, Fe, Mn, etc. can reduce easily if important oxygen-consuming microbial processes become dominant. Further, there are elements that occur under anaerobe conditions in both reductive and oxidative forms, e.g.,  $\text{CO}_2$  -  $\text{CH}_4$ , sulfate - sulfide, or organic acids - alcohols. The ratio of these compounds depends on numerous factors.

Microorganisms change the pH of their surrounding environment, which can have important geochemical effects. Some autotrophic organisms produce  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ , etc., while others produce organic acids or  $\text{H}_2\text{CO}_3$ . Algae and cyanobacteria influence water dynamics by photosynthetic activity, adsorbing  $\text{CO}_2$ , but also release it via respiration, which influences the buffer system of  $\text{CO}_2$ -bicarbonate-carbonate.

The forming acids attack, consume, decompose and dissolve the originally insoluble phosphates, silicates, clay minerals, K, Al, Mg, Ca, Fe, Mn, and via these processes microorganisms decompose rocks, while in other places they form mineral accumulation on a local or global level.

The physical effect of microorganisms and the change of the physical structure of the environment belong to secondary weathering processes, but simply their occurrence in the environment can have major effects (e.g. bioturbation - algae, clearing of vegetation - increase of erosion). Moving microorganisms can transport elements on a considerable level. Via the life and death of microorganisms organic matter is released and secondary-diagenetic processes occur, which are important in the transportation of metals, mobilization, adsorption, in the formation of CH and coal, and also of ores, and which offer an active surface for other primary biogeochemical processes.

### 3.2. Biomineralization

Microorganisms can induce mineral precipitations. These can occur as the result of cell metabolism, but can occur in the case of inactive cells, too (bacterially controlled mineralization (BCM) and bacterially induced mineralization (BIM), Pósfai et al., 2013). Minerals can occur both inside and around the cells ( $\text{CaCO}_3$  formation in coccolith, magnetite, and/or greigite magnetosome in bacteria for navigation purposes) (Devouard et al., 1998; Pósfai et al., 1998a, 2013; 1998b;; Pósfai and Arató, 2000). Another example is  $\text{SiO}_2$  precipitation by microorganisms in diatoms. Mineral precipitation can happen if microbial activity creates favorable conditions in a geochemical environment, e.g. the very common  $\text{CaCO}_3$  precipitation (Ferris et al., 1986; 1994;; de Vrind-de Jong and de Vrind, 1997). Benzerara et al. (2014) studied 68 cyanobacterial strains and concluded that Ca-carbonate biomineralization is widespread, formed by the cyanobacteria, which are scattered as amorphous phase in cytoplasm or linked to the septum of cells. Ca-carbonate can be produced extracellularly by metabolism of cyanobacteria.

Couradeau et al. (2012) found that cyanobacteria occurring in marine, terrestrial and freshwater environments, typically alkaline have affected the carbon, nitrogen and oxygen cycles for billions of years. The carbonate produced by biomineralization includes Ca-Mg-Sr-Ba inclusions, such as aragonite, calcite, Ca-substituted strontianite, and a mixed carbonate phase benstonite including all of the mentioned cations in stoichiometric formulae. The intracellular carbonates imply that the alkalinity excess produced by cyanobacteria during photosynthetic carbon fixation acts as a pH buffering system.

Li et al. (2016) proposed that extracellular carbonate mineralization of cyanobacteria is the result of saturation of a solution of calcite, Mg-calcite, aragonite, hydromagnesite. In some cases calcite could be produced intracellularly by sulfur bacteria, as well. Li et al. (2016) concluded that cyanobacteria produce not only carbonates but polyphosphates with C, K, and Mg.

An important category of biomineralization is the group of enzymatic redox reactions that supply energy. The biological oxidation of  $\text{Mn}^{2+}$  to  $\text{Mn}^{4+}$  is  $10^5$  times quicker than inorganic oxidation, and results in the precipitation of vernadite, buserite, todorokite (Tebo et al., 1997).

This can occur also in the inactive condition of cells. In contrast, the usage of  $\text{Mn}^{4+}$  as a terminal electron acceptor results in the dissolution of Mn minerals.

Microorganisms can get energy for their metabolism from other sources, such as S and N components, oxidation of  $\text{H}_2$ , forming or degrading methane, or reduction of U. Biomineralization of Fe and the usage of Fe oxide minerals as terminal electron acceptors for respiration are also very important (Konhauser, 1998). These metabolic processes influence the chemical composition of water, increasing  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ , and  $\text{S}^{2-}$  concentration in pore water, which leads to the precipitation of metal sulfides like greigite and mackinawite and also the mineral composition of sediments.

In the sulfate reduction zone of the sediments, numerous metal-sulfides form as main or trace minerals ( $\text{FeS}_2$ ,  $\text{ZnS}$ ,  $\text{CuS}$ ). These processes are responsible for giant, economically important deposits. In certain cases redox biogeochemical processes result in significant adsorption and precipitation of toxic elements (U, As, Se).

### 3.3. Bioindicator minerals

The occurrence of certain minerals in the sediment pile can indicate important microbially mediated processes. These minerals are called bioindicator minerals, after Skinner (2005). The most common bioindicator minerals are the following:

**Fe-minerals** – pyrite, amorphous Fe-oxide-hydroxides (ferrihydrite, lepidocrocite), goethite, and magnetite (magnetotactic or  $\text{Fe}^{3+}$  microbial reduction), although sulfides like greigite and mackinawite are also common. Reutilization of Fe in the environment is the result of biological activity. Pyrite occurs in the sulfate reduction zone with  $\text{Fe}^{3+}$  reducing microorganisms. Total Fe content shows the upper limit of available Fe for microbial metabolism. The ratio of different types of microorganisms (aerobe, anaerobe,  $\text{Fe}^{3+}$ -reducing,  $\text{SO}_4^{2-}$  reducing, etc.) and the maximum activity in the sediment can be estimated.

**Mn-minerals** – Mn oxides and hydroxides are bioindicator minerals and also paleoenvironmental indicators of obligatory oxic conditions, which is a requirement for enzymatic Mn oxidation. Eh and pH sensitivity of Mn minerals is high, and Mn is a basic bioessential element. Microbially mediated Mn oxides occur in desert varnish in stromatolites (Raymond et al., 1992), in hot hydrothermal vents (Ferris et al., 1987a, b), and in deep sea nodules (Ehrlich, 2002).

As observed in recent biomats, both reduction of sulfur compounds and oxygenation of metal cations like Fe and Mn are prevalent. This transformation influences the proton balance, inducing chemolithoautotrophic oxidation, which generates acidity. This can directly affect carbonate dissolution (Engel, 2008).

The positive anomaly of Mo and Li has been proposed for marine hydrothermal discharge systems. Mo is characteristic in sulfidic systems as an enzymatic element (Orberger et al., 2007). In contrast, the Úrkút black shale-hosted diagenetic Mn-carbonate deposit represents obligatory oxic conditions via ore formation (and also via “black shale” formation (Polgári et al., 2012a; 2016a; 2016b) with basically different microbial systems. The main and trace element enrichments of ore deposits depend on the Eh features of the environment (Southam and Sanders, 2005).

**Ca-phosphate** – apatite – low T apatite grains are fine grained and poorly crystallized. P is a basic bioessential element of life, is highly concentrated in the environment, and in normal cases it is reused. When an organism dies, organic P is released and is reused by the metabolism of biota. If reutilization does not happen immediately, P forms local enrichments reacting with Ca, and highly dissoluble apatite precipitates. This apatite is very fine-grained, pelletal, concretionary, noduliferous or enriched in crusts. It can be disseminated or can accumulate in layers as amorphous Ca-phosphate-carbonate (francolite, collophane) and the P content can reach  $\text{P}_2\text{O}_5 > 18\%$ . Distribution of P in soils and sediments is directly bound to biological activity. Phosphorites can include high amounts of REE, Th, U and organic matter. Important phosphorite

deposits in a sedimentary environment probably represent the kind of time and location where P accumulation was accompanied by lower biological activity or dissoluble apatite-bearing material separated from normal biological cycles and reutilization. In general, P does not substitute other elements e.g. in clay minerals, or in other low T phases, but instead, it forms independent phases, like Al- or Fe-phosphate (variscite  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ , vivianite  $\text{Fe}^{2+}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ , strengite  $\text{Fe}^{3+}\text{PO}_4 \cdot 2\text{H}_2\text{O}$ , or struvite  $(\text{NH}_4)\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ ) (Skinner, 1993). Cl-apatite does not form in a marine environment, in spite of its high Cl content. In F-apatites the  $\text{OH}^-$  is substituted by F.

In summary, living organisms use numerous mechanisms in growing and surviving, and after their death they also contribute to the structure, element distribution, and chemical variability of the sediment. Fe, Mn, S and P are important elements of the energy and electron fluxes of living systems (Skinner, 1993).

#### 3.3.1. Consequence of very small grain size

A basic feature of low T biominerals is their very small grain size ( $\mu\text{m}$  or a few hundredths of nanometers). This is caused by the quick nucleation of oversaturation. The small core size will remain because of the low solubility of ions, which limit diffusion-based crystal growth. According to researchers of material science, the small grain size results in peculiar material features. Unusual optical electric behavior and modified structure and activity of the surface is characteristic. This is important in environmental science, as nano-scale microbial material is very frequent in fluids, sediments and soils. These features cause incredible difficulties in research, as physical separation is impossible and investigations need high-resolution in-situ methods (SEM, TEM, LAICPMS, FTIR, Raman spectroscopy, etc.).

#### 3.3.2. Biological behavior of some selected elements

**Mg** – a bioessential element, occurring as MgATP and MgADP molecules, which are very important “energy molecules” (Nisbet et al., 1996). It has an important role also in enzymes (Volbeda et al., 1995). This is essential in cycles of nitrogen and hydrogen. Another aspect is bacterial photosynthesis, where Mg is in the center of bacteriochlorophyll (McDermott et al., 1993; Hartman and Harpel, 1994).

**Zn, Cu, Mo, Ni** – also used expansively as metalloproteins. Zn-proteins are typical, with numerous functions. Zn is generally present in bacteria (Coleman, 1992). Zn is also essential for animals and plankton groups. Cu-proteins are similar to Zn-proteins. Mo is a rare element in most rocks and sediments, but is a typical hydrothermal element, and its biological usage is also widespread (Wolle et al., 1992; Howard and Rees, 1994). The enzymatic role of Ni is also essential (Ehrlich, 2002; Dupont et al., 2010). The role of Ni (Mg) in the transformation of sheet manganate ( $\text{MnOOH}$ -birnessite-buserite) to tecto manganate ( $\text{MnOOH}$ -todorokite) is documented (Bodei et al., 2007).

**Co** – found in vitamin  $\text{B}_{12}$ , which is why numerous bacteria are Co demanding. In this sense the Co enrichment can originate from the vitamin demand of the organisms. Sedimentary Mn deposits are characterized by elevated Co content (Polgári et al., 2012a, Biondi and Lopez, 2017). It may be that as a first step, Mn oxidizing bacteria oxidize Co and enrich it in solid but amorphous mud;  $\text{MnOOH}$  can adsorb also metals on surface or in structure as stabilizing ions. When Co is in the system, a vitamin B producer can get it as nutrient from the mud, and the filamentous FeOB (Fe oxidizing bacteria) can use this vitamin B. In brief, Mn can be an important precursor in primary Co fixing; if there is a vitamin B producer, it will use this Co and offer vitamin B for the blooming of for example filamentous FeOB in the system. This can support formation of filamentous Fe-biomats. The biologically bound Co is released during the decomposition of cells and can then bind into the structure of ferrihydrite or other mineral phases, causing trace element enrichment in the ore (Hiemstra and Riemsdijk, 2009; Song, 2013; Hiemstra, 2013).

Co is also an essential element of nitrogen-fixing organisms, along with Mo, and stimulates growth. Moffett (1990; 1994;); Moffett and

Ho (1996) investigated the uptake of Co, Mn and Ce in Waquoit Bay (Massachusetts) and in the Sargasso Sea to separate biological and chemical redox reactions. They found that the uptake of Co mainly took place by microbial oxidation (Moffett and Ho, 1996). Further, there was a strong relationship between Mn(II) and Co(II) oxidation, with a 7–10 times more frequent ratio of Mn(II), and competitive behavior of Co and Mn for microbial oxidation (Moffett and Ho, 1996). The results show that both elements oxidize together by the same microbial catalytic process, which is probably an important mechanism in the uptake of Co into Mn oxides (Moffett and Ho, 1996).

Ce – oxidizes together with Mn via microbially mediated processes, where the specific oxidation ratio of Ce/Mn is constant in a wide range of littoral and oceanic environments (Moffett, 1990; 1994; Moffett and Ho, 1996).

Sr – the role of Sr is emphasized in connection with a function of Fe bacteria, referring to the affinity between the two elements (Couradeau et al., 2012).

As – highly toxic for humans, animals with a central nervous system, plants and also for certain simple organisms (Wood, 1975). Arsenite (AsIII) is more toxic than arsenate (AsV). Numerous microbes reduce arsenate to arsenite, or oxidize As(III) to As(V). Numerous fungi liberate As-bearing gases on As-bearing material. Volatilization of As happens in soils, too. With missing oxygen and nitrate ions, analogous to energy getting processes via the burning of nitrate and sulfate reduction, the reduction of arsenate occurs. In this case arsenate serves as a terminal electron acceptor and provides the energy supply of heterotrophic metabolism. Arsenic appears in microbial catalytic redox processes, many of which result in biomineralization. It is well known that in acid mine waste waters considerable enrichment is detected of As, Cu, Pb and other heavy metals, which are toxic for most living organisms. Chemolithotrophic microorganisms utilizing inorganic chemical compounds as energy sources catalyze reactions. Sulfo-arsenides and arsenides are also important ore-forming minerals (Mandl et al., 1992; Ahmann et al., 1994). Recent microbial ferrihydrite and carbonate precipitation was reported in Cézallier Spring in Massif Central (France). The trace element (mainly arsenic) trapping effect of these precipitates was also reported (Casanova et al., 1999; Le Guern et al., 2003). In a French mine at Carnoulès, Fe<sup>3+</sup> precipitation was detected, a stromatolitic travertine in which there was 20 wt% As content. In such environments *Thiobacillus ferrooxidans* occurs in extremely acid waters (pH < 3), where it catalyzes the oxidation of Fe<sup>2+</sup> and precipitates Fe<sup>3+</sup> oxide-hydroxide, or Fe<sup>3+</sup> sulfate-jarosite, if there is a high amount of sulfate ions in the environment (Leblanc et al., 1996). This bacterium exists in As-bearing waste water in mines, meaning that As-bearing conditions are not toxic for it. In the studied waste water As (280 mg/l) occurs in the form of As(III) as arsenite, and migrates in the form of H<sub>3</sub>AsO<sub>3</sub> under pH = 2.2–2.8, Eh (0.2–0.3 V) conditions. The oxidation of Fe<sup>2+</sup>/Fe<sup>3+</sup> and As (III) to As(V), and precipitation of Fe<sup>3+</sup>-arsenate is biologically catalyzed (Leblanc et al., 1996). It has great environmental-geochemical importance because it sequesters minerals in 2 orders of magnitude higher concentration, in which microbial processes separate this dangerous, toxic element from hydrological systems in the form of solid material as minerals. Pb can also be absorbed in As-bearing microbial colonies.

Si – Laboratory experiments indicate that FeOB consumes silica against stress, and it is also used for protection by microbes (Mioszewska et al., 2018). The amorphous silica transforms into more stable phases, like quartz (Herdianita et al., 2000), or takes part in clay mineral formation (Konhauser, 1998).

Radionuclides (U, Th, Ra) – Iron and manganese hydroxides precipitate as characteristic discharge features influencing radioactivity of microbial mats and water. Iron hydroxide precipitate as an effective radium (Ra) reservoir was hypothesized inside the aquifer near to the St. Placidus spring outlet (Switzerland) by Gainon et al. (2007a) as an explanation for the high radon levels (average of 650 Bq/l) measured in the spring water. According to their study, iron hydroxides, which can be formed for instance by mixing of uprising anoxic deep waters and

oxygenated freshly infiltrated waters, adsorb radium efficiently. Afterwards, decay of the adsorbed radium may lead to locally high radon concentrations in water (Schott and Wiegand, 2003; Gainon et al., 2007a; 2007b).

Tazaki (2009) proposed that heavy metals and radionuclides can be accumulated in microbial mats by precipitation on EPS in hot springs in Japan. Accumulation of radium causes high radioactivity of the hot springs (Fujisawa and Tazaki, 2003). The accumulation of iron, manganese, arsenic, and other trace elements was also reported. The green microbial mats found on the surface at spring outlets consist of *Cyanobacteria*, which are associated with ferrihydrite, calcite, and Mn-oxide minerals. Deeper zones of the microbial mats are characterized by bacilliform and coccoid types of bacteria encrusted with calcite, whereas accumulation of spherical grains can be observed also around the cells, which are biominerals containing Fe, As, and other metals. Carboxyl and hydroxyl groups of the bacterial cell surface have important roles in the precipitation and complexation of heavy metals and radionuclides in microbial mats (Tazaki, 2009).

From the element substitutions of the above section it is clear that in the case of certain bacteria the catalytic locality is not selective for any particular element, e.g. Mn. Metal substitution generally occurs in microbial uptake processes. For example in Zn deficient cases Co(II) can substitute Zn(II) as a micro-nutrient of phytoplankton (Price and Morel, 1990; Sunda and Huntsman, 1987; Moffett and Ho, 1996). The ability to substitute an important but rare element with another similar one can be a major advantage for a microorganism. In other cases it can lead to toxicity.

### 3.3.3. Mechanisms in the background of element enrichments

To investigate the question of what mechanisms affect element enrichments, we can discuss it from the side of microbes and from the side of the ore forming system. There are different mechanisms in the background of microbial element enrichment. These include:

- (1) Direct oxidation of main ore-forming metals to sequester giant masses of biominerals (Fe-, Mn-oxidizing microbial activity); direct oxidation can include trace elements as well (e.g. Co and Ce are oxidized by Mn-oxidizing bacteria);
- (2) Structure (mineral) stabilizing role, such as Mg bound from seawater (sinking process) by EPS (Mandernack et al., 1995), or mineral stabilization through a structure stabilizing ion via transformation from instable sheet MnOOH (buserite, birnessite) to stable tecto MnOOH (todorokite) (Bodeř et al., 2007);
- (3) Adsorption, as in Ni adsorption from seawater or hydrothermal fluids (biogenic signature-decay of organic matter-plankton) by sheet MnOOH (birnessite) resulting in Ni–Mn(II)–sheet MnOOH (birnessite-buserite). Some Ni adsorption is later released via todorokite formation (55% Ni release; the fate of the released Ni is unknown, but it must lead to recycling or stabilization somehow). The oceanic Ni cycle is determined by these processes. In another example, U, Th, Ra, Rh adsorption on active Fe-biomats is common (Tsezos et al., 1987).
- (4) Detoxication, for instance Ce(III) to Ce(IV) by MnOB, on MnOOH – which is a microbial oxidation path with P.
- (5) Vitamin demand, such as the need for Co for vitamin B<sub>12</sub> (Knoll et al., 2012).
- (6) Enzymatic demand (Dupont et al., 2010). As an example, we have the case of Cu in the multicopper oxidase enzyme, which is essential for Mn(II) microbial oxidation. Although its name refers to the Cu content of this enzyme, the Cu content of giant manganese carbonate deposits is generally low, or this element is lower than its standard crustal abundance. There are three types of this enzyme, determined by the Cu binding motif: mononuclear, binuclear and combined binuclear. In addition, there are a lot of proteins which are related to multicopper oxidase, which lost its Cu-binding capability via evolution. In bacteria the loss of

Cu binding occurs, which will not be substituted by other elements. These are not real multicopper oxidase enzymes, they are very similar only on a sequence level. This is a typical structure versus function question in the biology of proteins.

- (7) Protection against UV radiation and high Fe concentration (such as Si) - FeOB consumes silica against stress, and it is also used for protection by microbes (Mioszewska et al., 2018).
- (8) Energy aspects. An important category of biomineralization is the group of enzymatic redox reactions that supply energy (Konhauser, 1998). Fe, Mn, S and P are important elements of the energy and electron fluxes of living systems (Skinner, 1993).

Element content has great economic importance: first of all the main element(s) as mineable material(s); but also accompanying main and minor or trace elements that make a positive contribution, increasing the economic value of the sedimentary ores. On the other hand there may be minor or trace elements that make the processing difficult, causing extra fees, or have harmful effects that can totally exclude the processing of ores (e.g. high P content in Mn ores).

#### 4. Biomineralization on the global scale during geological history

##### 4.1. Giant Fe accumulations

Giant Fe ore geological reservoirs formed across the world that are of global importance and major economic value. Banded ironstone formations (BIFs) are peculiar sedimentary rock types that are mainly of Precambrian age (Rosing et al., 1996). The most characteristic features of this formation are the alternating laminae (bands) of mm to few cm scale. The laminae consist of black iron oxides, generally magnetite ( $\text{Fe}_3\text{O}_4$ ) or hematite ( $\text{Fe}_2\text{O}_3$ ), and red, iron-poor shales and cherts (Katsuta et al., 2012). Ferrihydrite, goethite, and also siderite are also common syngenetic and diagenetic minerals.

One hypothesis for the formation of BIFs is microbial (e.g., Gutzmer and Beukes, 2008). In this scenario, Fe-oxidizing bacteria forming Fe-rich biomats had a fundamental role in the genesis of BIFs. Microtextural evidence is available in the form of mineralized filaments encrusted by Fe oxide minerals, an important biosignature. Four types of microbial metabolisms are known that can oxidize  $\text{Fe}^{2+}$  forming Fe-oxide minerals (Ehrenreich and Widdel, 1994; Straub et al., 1996; Konhauser, 1998; Ehrlich, 2002; Knoll et al., 2012). They are the following microbial Fe(II) oxidizing metabolisms:

- acidophilic and oxic
- driven by light, occurring in anoxic/anaerobic and neutrophilic conditions (photoferrotroph)
- suboxic/anaerobic, where neutrophilic  $\text{NO}_3^-$  reducers coupled with Fe(II) oxidizers contribute to the biochemical milieu
- suboxic and neutrophilic *Gallionella* (*Mariprofundus*)-like Fe-oxidizing microbes, which are generally common in many environments.

All cases can be characterized and determined concerning environmental conditions based on mineral assemblages. An indirect role for bacteria in the oxidation of Fe can also be supposed, as microbial activity can change the geochemical conditions of the environment, which results in the chemical oxidation of Fe.

These metabolic processes are determined by environmental proxies (Eh, pH, light), which offer paleoenvironmental considerations based on microbial mineralization as "paleoenvironmental indicators". Fine, cyclic mineral lamination in rocks also offers an opportunity for the estimation of formation time duration based on microbial growth population cycles (Polgári et al., 2012b; Gyollai et al., 2015).

The primary microbially-mediated minerals are ferrihydrite and lepidocrocite, poorly crystallized minerals that transform to more stable

minerals like goethite and hematite (in its reduced form as magnetite) over time via silica segregation. These processes occur quickly – several months to years – by dehydration–dissolution (Konhauser, 1998; Schwertmann and Cornell, 2007; Gyollai et al., 2015). Later, during diagenesis, Fe oxide and the segregated silica react with cations and anions released via cell and EPS material decomposition, and complex mineralization occurs. Aegirine, celadonite, chamosite, etc. can be mentioned as examples (Biondi et al., 2020). These processes are often overprinted by diagenetic microbially mediated mineralization, which results in the mineralization of organic carbon in the form of metal carbonates; in the case of Fe in the form of siderite or mixed carbonates like ankerite.

##### 4.2. Giant Mn accumulations

Giant Mn ore geological reservoirs formed when the conditions became more oxic, and also are of global importance and high economic value.

The first product of microbial enzymatic Mn(II) oxidation is a biologically formed Mn oxide (e.g. vernadite, birnessite, buserite), as was reported by Villalobos et al. (2003), Bargar et al. (2005), Morgan (2005), and Bodei et al. (2007). This enzymatic Mn oxidation can be referred to as Cycle I in Mn ore formation, in the frame of which chemolithoautotrophic microbes sequester and precipitate Mn(II) from geofluids in the form of variable Mn oxide-hydroxides. For microbial (enzymatic) Mn(II) oxidation, oxic conditions ( $>2$  mL/L dissolved oxygen) are obligatory. The forming bio-oxide is poorly crystallized, thermodynamically unstable 7-Å-vernadite (hexagonal phyllosmanganate) (Villalobos et al., 2003). Surplus Mn(II) in the system serves as a reductant, and plays a role in the stabilization of secondary abiotic mineral products (manganite, see  $\text{Mn}^{2+}$  Polgári et al. (2012a) on components in minerals of Úrkút, and Biondi et al. (2020) for evidence from Urucum). Cation binding, like Mg and Ni, supports phyllosmanganate transformation to stable tectomanganate (Bodei et al., 2007). Mg adsorption on the cells is caused by reaction with extracellular polymers; experimental studies support this mechanism (Mandernack et al., 1995). This sheds light on the complex processes, which include not only direct microbial oxidation of Mn(II) to Mn(IV), but also determine the cation composition of the forming Mn oxide minerals. As a result, variable Mn minerals form ( $\text{Mn,Fe,Mg,Ca,K,Na}$ ) $_2$ \*( $\text{Mn}_5\text{O}_{12}$ )\* $3\text{H}_2\text{O}$  as todorokite, which is the general, fine grained poorly crystallized biomineral in marine Fe- and Mn deposits.

Via diagenesis, the stabilization of the syngenetic Mn oxide hydroxides takes place, and pure forms such as pyrolusite, ramsdellite, nsutite, hausmannite, manganite are formed, as well as variable cation bound forms (e.g., Na, K, Ca, Mg, Ba, Fe) such as cryptomelane, jacobsonite, romanèchite, and manjorite (Giovanoli, 1980; Mandernack and Tebo, 1993; 1995; Villalobos et al., 2003; Bargar et al., 2005; Bodei et al., 2007; Johnson et al., 2016). In accordance with findings in Polgári et al. (2012a), Maynard (2014), and Johnson et al. (2016), rhodochrosite can be mentioned as the result of early diagenetic sporadic heterotrophic, sub-oxic microbial activity (representing Cycle II in Mn ore formation). Diagenetic interaction of Mn oxide with segregated silica results in braunite and serandite (Biondi et al., 2020).

##### 4.3. Mineralogical interpretation – Source of elements

Ore microbialites contain ore minerals (syngenetic and simply stabilized) but at the same time they contain a variety of other minerals.

As shown in Table 1, both Mn and Fe ore microbialite systems occur. Separated mineralogy helps to follow the processes. Syngenetic Mn (S-Mn, vernadite, todorokite, birnessite, manganite) and Fe minerals (S-Fe, ferrihydrite, lepidocrocite) form via direct microbial enzymatic processes as different lines of mineralization, but in intimately bound form. After burial decomposition of cell and EPS material starts, cations and anions release, forming an element reservoir (pool) for complex

**Table 1**  
Mineral assemblage in selected microbially mediated ore systems and typical minerals indicative of Eh-pH ranges based on environmental mineralogy (syngenetic (Mn and Fe system), diagenetic (Mn and Fe system and combined) and others).

Minerals/Processes	Chemical formula	Urucum Mn Biondi et al. (2020) Neoproterozoic	Urucum Fe Polgári et al. (2021) Neoproterozoic	Datangpo Mn Yu et al. (2019) Neoproterozoic	Masi Mn Yu et al. (2021) Carboniferous	Xinglong Mn Yu et al. (2021) Permian	Úrkút Mn Polgári et al., 2012a Jurassic
Mn mineral assemblage		Brazil	Brazil	China	China	China	Hungary
<i>Oxides and hydroxide</i>							
Pyrolusite	$Mn^{4+}O_2$	*	*		*	*	*
Ramsdellite	$Mn^{4+}O_2$	*			*	*	
Nsutite	$(Mn^{4+}Mn^{2+})(O,OH)_2$	*					
Hausmannite	$Mn^{3+}_3O_4$	*					
Cryptomelane	$KMn^{4+}_6Mn^{2+}_2O_{16}$	*			*		*
Jacobsite	$Mn^{2+}_{0.6}Fe^{2+}_{0.3}Mg_{0.1}Fe^{3+}_{1.5}Mn^{3+}_{0.5}O_4$	*	*		*	*	
Manganite	$Mn^{3+}OOH$	*	*	*	*	*	*
Vernadite $\delta MnO_2$ (wad)	$(Mn^{4+}Fe^{3+}CaNa)(OOH)_2 \cdot nH_2O$	*					*
Todorokite	$Na_{0.2}Ca_{0.05}K_{0.02}Mn^{4+}_4Mn^{3+}_2O_{12} \cdot 3(H_2O)$	*	*		*	*	*
Birnessite	$Na_{0.7}Ca_{0.3}(Mn^{3+}Mn^{4+})_7O_{14} \cdot 2.8H_2O$	*					
Romanèchite (psilomelane)	$[(Ba,H_2O,Mn_5O_{10}, Ba(Mn^{4+}, Mn^{3+})O_{10} \cdot 1.4H_2O)]$	*			*	*	
Hollandite*	$Ba(Mn^{4+}, Mn^{2+})_8O_{16}$	*			*		*
Manjiroite	$Na(Mn^{4+}_7Mn^{3+})O_{16}$	*	*		*	*	
Pyrophanite	$MnTiO_3$				*	*	
<i>Carbonates</i>							
Rhodochrosite	$MnCO_3$	*	*	*	*	*	*
Mn- Calcite	$Mn-CaCO_3$		*		*	*	
Kutnohorite	$(Ca,Mn)(CO_3)_2$		*	*	*	*	*
<i>Oxides-silicates</i>							
Serandite	$NaMn^{2+}_{1.5}Ca_{0.5}Si_3O_8(OH)$	*			*	*	
Braunite	$Mn^{2+}Mn^{3+}_6SiO_{12}$	*	*		*	*	
<i>Sulfides</i>							
Alabandite	$MnS$		*			*	
Rambergite	$MnS$				*	*	
Fe mineral assemblage							
<i>Oxides and hydroxides</i>							
Ferrihydrite	$FeOOH$	*	*	*	*	*	
Lepidocrocite	$Fe^{3+}O(OH)$	*		*	*	*	
Hematite	$Fe_2O_3$	*	*	*	*	*	*
Goethite	$FeOOH$	*	*		*	*	*
Magnetite	$Fe_2O_3$	*			*	*	
Anatase	$TiO_2 - Fe_xTi_{(1-x)}O_{(2-x)}OH_x$		*		*	*	
<i>Carbonates</i>							
Siderite	$FeCO_3$		*	*	*	*	*
Ankerite	$Ca(Fe^{2+},Mg)(CO_3)_2$	*	*	*	*	*	
<i>Sulfides</i>							
Pyrite	$FeS_2$	*		*	*	*	*
Marcasite	$FeS_2$		*			*	*
<i>Sulfates</i>							
Na-jarosite	$NaFe^{3+}_3(SO_4)_2(OH)_6$				*	*	
<i>Silicates</i>							
Aegirine	$Ca_{0.75}Na_{0.25}Mg_{0.5}Fe^{2+}_{0.25}Fe^{3+}_{0.25}(Si_2O_6)$	*	*			*	
Riebeckite	$Na_2(Fe^{2+}_3Fe^{3+}_2)Si_8O_{22}(OH)_2$	*					
Celadonite	$KMg_{0.8}Fe^{2+}_{0.2}Fe^{3+}_{0.9}Al_{0.1}Si_4O_{10}(OH)_2$	*				*	*
Nontronite	$Ca_5(Si_7Al_8Fe_2)(Fe_{3.5}Al_4Mg_{0.1})O_{20}(OH)_4$					*	*
Chlorite	$Mg_{3.75}Fe^{2+}_{1.25}Si_3Al_2O_{10}(OH)_8$	*					*

(continued on next page)

Table 1 (continued)

Minerals/Processes	Chemical formula	Urucum Mn Biondi et al. (2020) Neoproterozoic	Urucum Fe Polgári et al. (2021) Neoproterozoic	Datangpo Mn Yu et al. (2019) Neoproterozoic	Masi Mn Yu et al. (2021) Carboniferous	Xinglong Mn Yu et al. (2021) Permian	Úrkút Mn Polgári et al., 2012a Jurassic
Chamosite	(Fe <sup>2+</sup> Mg) <sub>5</sub> Al(AlSi <sub>3</sub> O <sub>10</sub> )(OH) <sub>8</sub>	*					
Others							
<i>Oxides - hyydroxides</i>							
Quartz	SiO <sub>2</sub>	*	*	*	*	*	*
<i>Carbonates</i>							
Dolomite	CaMg(CO <sub>3</sub> ) <sub>2</sub>	*	*	*	*	*	
Strontianite	Sr(CO <sub>3</sub> )	*					
<i>Silicates</i>							
Orthoclase	KAlSi <sub>3</sub> O <sub>8</sub>	*		*			
Albite	NaAlSi <sub>3</sub> O <sub>8</sub>	*	*		*	*	*
Kaolinite/dickite	Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>	*					
Muscovite	KAl <sub>3</sub> Si <sub>3</sub> O <sub>10</sub> (OH) <sub>1.8</sub> F <sub>0.2</sub>	*	*			*	
Montmorillonite	(Na,Ca)(Al,Mg) <sub>2</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub> xnH <sub>2</sub> O		*		*	*	*
Illite	(K,H <sub>3</sub> O)(Al,Mg,Fe) <sub>2</sub> (Si,Al) <sub>4</sub> O <sub>10</sub> [(OH) <sub>2</sub> , (H <sub>2</sub> O)]			*			
Zeolite							*
<i>Silicate-carbonate- sulphate</i>							
Cancrinite	(NaCa...) (Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> )(CO <sub>3</sub> ,SO <sub>4</sub> ) <sub>2</sub> *2H <sub>2</sub> O	*					
<i>Phosphates</i>							
Apatite	[(Ca <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH, F, Cl) <sub>2</sub> ]	*	*	*	*	*	*
<i>Sulphates</i>							
Barite	Ba(SO <sub>4</sub> )	*			*	*	*
Gypsum (anhydrite)	CaSO <sub>4</sub> .2H <sub>2</sub> O	*					*
Johannite	Cu(UO <sub>2</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>2</sub> 8H <sub>2</sub> O	*			*	*	
Organic material		*	*	*	*	*	*

Minerals/Processes	Chemical formula	Eh	pH		Microbially	S	Mn	Fe	D	Mn	Fe	C	EPS
Mn mineral assemblage		oxic	suboxic	anoxic	acidic	neutral-slightly alkaline	alkaline	mediated					
<i>Oxides and hydroxide</i>													
Pyrolusite	Mn <sup>4+</sup> O <sub>2</sub>	*							*	*			
Ramsdellite	Mn <sup>4+</sup> O <sub>2</sub>	*							*	*			
Nsutite	(Mn <sup>4+</sup> Mn <sup>2+</sup> )(O,OH) <sub>2</sub>	*					*		*	*			
Hausmannite	Mn <sup>3+</sup> <sub>3</sub> O <sub>4</sub>	*							*	*			
Cryptomelane	KMn <sup>4+</sup> <sub>6</sub> Mn <sup>2+</sup> <sub>2</sub> O <sub>16</sub>	*							*	(*)			
Jacobsite	Mn <sup>2+</sup> <sub>0.6</sub> Fe <sup>2+</sup> <sub>0.3</sub> Mg <sub>0.1</sub> Fe <sup>3+</sup> <sub>1.5</sub> Mn <sup>3+</sup> <sub>0.5</sub> O <sub>4</sub>	*							*	(*)	*	*	
Manganite	Mn <sup>3+</sup> OOH	*					*	*	*	*			
Vernadite δMnO <sub>2</sub> (wad)	(Mn <sup>4+</sup> Fe <sup>3+</sup> CaNa)(OOH) <sub>2</sub> *nH <sub>2</sub> O	*					*	*	*	*			
Todorokite	Na <sub>0.2</sub> Ca <sub>0.05</sub> K <sub>0.02</sub> Mn <sup>4+</sup> <sub>4</sub> Mn <sup>3+</sup> <sub>2</sub> O <sub>12</sub> •3(H <sub>2</sub> O)	*			*		*	*	*	*			
Birnessite	Na <sub>0.7</sub> Ca <sub>0.3</sub> (Mn <sup>3+</sup> Mn <sup>4+</sup> ) <sub>7</sub> O <sub>14</sub> .2.8H <sub>2</sub> O	*			*		*	*	*	*			
Romanèchite (psilomelane)	[(Ba,H <sub>2</sub> O,Mn <sub>5</sub> O <sub>10</sub> , Ba(Mn <sup>4+</sup> , Mn <sup>3+</sup> )O <sub>10</sub> .1.4H <sub>2</sub> O)]	*							*	(*)			
Hollandite*	Ba(Mn <sup>4+</sup> ,Mn <sup>2+</sup> ) <sub>8</sub> O <sub>16</sub>	*							*	(*)			
Manjiroite	Na(Mn <sup>4+</sup> ,Mn <sup>3+</sup> ) <sub>7</sub> O <sub>16</sub>	*							*	(*)			
Pyrophanite	MnTiO <sub>3</sub>	*											
<i>Carbonates</i>													
Rhodochrosite	MnCO <sub>3</sub>		*		*		*		*	(*)			
Mn- Calcite	Mn-CaCO <sub>3</sub>		*										
Kutnohorite	(Ca,Mn)(CO <sub>3</sub> ) <sub>2</sub>		*						*	(*)			
<i>Oxides-silicates</i>													
Serandite	NaMn <sup>2+</sup> <sub>1.5</sub> Ca <sub>0.5</sub> Si <sub>3</sub> O <sub>8</sub> (OH)								*			*	
Braunite	Mn <sup>2+</sup> Mn <sup>3+</sup> <sub>6</sub> SiO <sub>12</sub>		*			*	*		*			*	
<i>Sulfides</i>													
Alabandite	MnS			*			*		*	*			
Rambergite	MnS								*	*			

(continued on next page)

Table 1 (continued)

Minerals/Processes	Chemical formula	Eh	pH	Microbially	S	Mn	Fe	D	Mn	Fe	C	EPS
Fe mineral assemblage												
<i>Oxides and hydroxides</i>												
Ferrihydrite	FeOOH	*		*	*		*					
Lepidocrocite	Fe <sup>3+</sup> O(OH)	*		*	*		*					
Hematite	Fe <sub>2</sub> O <sub>3</sub>	*	*	*				*		*		
Goethite	FeOOH	*	*					*		*		
Magnetite	Fe <sub>2</sub> O <sub>3</sub>	*	*	*				*		*		
Anatase	TiO <sub>2</sub> - Fe <sub>x</sub> Ti <sub>(1-x)</sub> O <sub>(2-x)</sub> OH <sub>x</sub>	*		*				*		*		
<i>Carbonates</i>												
Siderite	FeCO <sub>3</sub>	*		*				*		*		
Ankerite	Ca(Fe <sup>2+</sup> ,Mg)(CO <sub>3</sub> ) <sub>2</sub>	*						*		*		*
<i>Sulfides</i>												
Pyrite	FeS <sub>2</sub>		*	*				*		*		
Marcasite	FeS <sub>2</sub>		*	*				*		*		
<i>Sulfates</i>												
Na-jarosite	NaFe <sup>3+</sup> <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>		*	*				*		(*)		
<i>Silicates</i>												
Aegirine	Ca <sub>0.75</sub> Na <sub>0.25</sub> Mg <sub>0.5</sub> Fe <sup>2+</sup> <sub>0.25</sub> Fe <sup>3+</sup> <sub>0.25</sub> (Si <sub>2</sub> O <sub>6</sub> )	*			*			*		(*)		
Riebeckite	Na <sub>2</sub> (Fe <sup>2+</sup> <sub>3</sub> Fe <sup>3+</sup> <sub>2</sub> )Si <sub>8</sub> O <sub>22</sub> (OH) <sub>2</sub>							*		(*)		
Celadonite	KMg <sub>0.8</sub> Fe <sup>2+</sup> <sub>0.2</sub> Fe <sup>3+</sup> <sub>0.9</sub> Al <sub>0.1</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub>	*		*				*		(*)		
Nontronite	Ca <sub>5</sub> (Si <sub>7</sub> Al <sub>8</sub> Fe <sub>2</sub> )(Fe <sub>3.5</sub> Al <sub>4</sub> Mg <sub>1</sub> )O <sub>20</sub> (OH) <sub>4</sub>			*				*		(*)		
Chlorite	Mg <sub>3.75</sub> Fe <sup>2+</sup> <sub>1.25</sub> Si <sub>3</sub> Al <sub>2</sub> O <sub>10</sub> (OH) <sub>8</sub>		*					*		(*)		
Chamosite	(Fe <sup>2+</sup> Mg) <sub>5</sub> Al(AlSi <sub>3</sub> O <sub>10</sub> )(OH) <sub>8</sub>		*					*		(*)		
<i>Others</i>												
<i>Oxides - hydroxides</i>												
Quartz	SiO <sub>2</sub>		*	*				*		*		
<i>Carbonates</i>												
Dolomite	CaMg(CO <sub>3</sub> ) <sub>2</sub>	*		*				*				*
Strontianite	Sr(CO <sub>3</sub> )	*		*				*				*
<i>Silicates</i>												
Orthoclase	KAlSi <sub>3</sub> O <sub>8</sub>			*				*				*
Albite	NaAlSi <sub>3</sub> O <sub>8</sub>			*				*				*
Kaolinite/dickite	Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>	?	?	*				*				*
Muscovite	KAl <sub>3</sub> Si <sub>3</sub> O <sub>10</sub> (OH) <sub>1.8</sub> F <sub>0.2</sub>							*				*
Montmorillonite	(Na,Ca)(Al,Mg) <sub>2</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub> xnH <sub>2</sub> O	*		*				*				*
Illite	(K,H <sub>3</sub> O)(Al,Mg,Fe) <sub>2</sub> (Si,Al) <sub>4</sub> O <sub>10</sub> [(OH) <sub>2</sub> (H <sub>2</sub> O)]							*				*
Zeolite								*				*
<i>Silicate-carbonate-sulphate</i>												
Cancrinite	(NaCa...)(Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> )(CO <sub>3</sub> ,SO <sub>4</sub> ) <sub>2</sub> *2H <sub>2</sub> O							*				*
<i>Phosphates</i>												
Apatite	[(Ca <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH, F, Cl) <sub>2</sub> )]	*		*	*			*				*
<i>Sulphates</i>												
Barite	Ba(SO <sub>4</sub> )	*		*				*				*
Gypsum (anhydrite)	CaSO <sub>4</sub> ·2H <sub>2</sub> O	*	*	*				*				*
Johannite	Cu(UO <sub>2</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>2</sub> ·8H <sub>2</sub> O							*				*
Organic material					*							

Mineral assemblage is based on Raman and FTIR spectroscopy analyses

Eh-pH ranges and microbially mediated mineralogy based on: Listova (1961); Harder (1976); (1978); Trudinger & Swaine eds. (1979); Berner (1980); Giovanoli (1980); Sung & Morgan (1981); Cole & Shaw (1983); Ewers (1983); Maynard (1983); Coleman (1985); Skinner (1993); Ehrenreich & Widdel (1994); Wignall (1994); Mandernack et al. (1995); Straub et al. (1996); Banfield & Nealson (1997); Konhauser (1998); Herdianita et al. (2000); Ehrlich (2002); Bazylinski & Frankel (2003); Lee et al. (2003); Villalobos et al. (2003); Bargar et al. (2005); Dupraz & Visscher (2005); Morgan (2005); Bodei et al. (2007); Lemos et al. (2007); Schwertmann & Cornell (2007); Dupraz et al. (2009); Chan et al. (2011); Polgári et al. (2012a,b, 2013, 2016); Biagioni et al. (2014); Johnson et al. (2016); Gyollai et al. (2017); Mloszewska et al. (2018)

\* Hollandite (empirical) Ba<sub>0.8</sub>Pb<sub>0.2</sub>Na<sub>0.1</sub>Mn<sup>4+</sup><sub>6.1</sub>Fe<sup>3+</sup><sub>1.3</sub>Mn<sup>2+</sup><sub>0.5</sub>Al<sub>0.2</sub>Si<sub>0.1</sub>O<sub>16</sub>

S: syngenetic

D: diagenetic stabilization (diagenetic on EPS influence)

C: Fe + Mn combined diagenesis

EPS: non-ore mineral formation on cell and EPS decomposition element reservoir

diagenetic mineralization. At the same time the stabilization of poorly crystallized Mn and Fe minerals occurs in the form of minerals such as pyrolusite, hematite, goethite and segregated quartz. These minerals represent the clear (simple) diagenetic line of stabilization of Mn and Fe minerals. In the case of diagenetic Mn minerals a highly variable cation-determined mineral group forms because of the favorable crystal structure of Mn oxide (Table 1, D-Mn), affected by the element pool of cell and EPS decomposition (designated by brackets). Further, with the mineralization of organic matter, carbonate minerals like rhodochrosite, kutnohorite, Mn-calcite form. In the case of Fe the crystal structure does not allow such variability, and Fe carbonate forms such as siderite, ankerite and variable silicates (pyroxene/aegirine, amphibol-/riebeckite, Fe-bearing clay minerals-celadonite, nontronite, chamosite) (Table 1, D-Fe).

The two systems can influence each other and combined diagenetic minerals also form, like serandite and braunite, where Mn oxide and segregated silica interact (stabilization process of ferrihydrite) (Table 1, D-C).

Besides the diagenetic lines of Mn and Fe (+combined) other minerals also form that do not contain the ore metals (Mn, Fe), but whose formation is also the result of complex mineralization (quartz, apatite, feldspar, etc.). In the case of these minerals, previously a debris origin was postulated, but more recent studies support authigenic formation based on their CL features. It is worth mentioning that quartz, anatase, and silicates like feldspars, clay minerals, and mica can form in this way. The formation of microbialites took place in starving basins, and this means that the element source of minerals was the element pool of cell and EPS decomposition. This interpretation explains the highly variable mineral assemblage of Mn and Fe ore microbialites, and the fact that diagenetic ore minerals are highly variable, as well as explaining the numerous other mineral phases that occur in these deposits.

One approach is to use summary tables on mineral assemblages and embedded organic matter ( $C_{org}$ ) on individual deposits, including interpretation on environmental mineralogy aspects elaborated in ore microbialites. Another useful approach is to create process tables in a deductive way from recent mineral assemblages and indicate also the syngenetic processes (paleoenvironmental considerations) (Biondi et al., 2020).

We note that although we do not discuss other biogenicity indicators like isotope datasets here, because this section focuses on element composition and mineralogy, such datasets are also important.

#### 4.4. Biomineralization in sedimentary environments forming variable rocks

While this study focuses on ore-forming biominerals, we should not ignore the fact that microbially mediated processes also contribute to the formation of other minerals. These include calcite, dolomite, or clay minerals, and also those that built up giant masses such as mountains from ancient times, such as limestone, dolostone, claystone, etc. These minerals also accompany ore minerals. These microbially mediated processes have been active from ancient times (Dupraz and Visscher, 2003; Dupraz et al., 2009).

### 5. Revisiting case studies: Evidence of biomineralization

The work on sedimentary Mn- and Fe microbialites concerning formation conditions and diagenesis outlined above demonstrates that microbially controlled and microbially induced mineralization is a phenomenon that is perhaps more common than some people in the earth sciences might expect. As much of this work has emerged in the past two decades or so, it is perhaps understandable that not all analyses of geosites include a survey of biomineralization factors and effects. Here we take a second look at some earlier case studies from Qatar, Graefenthal Horst (Germany), Lower Saxonian Basin (NW Germany), and finally Fe-bearing oolitic Wabana (Paleozoic) and Minette

(Jurassic) ironstones in which biomineralization was not taken into account, in an attempt to identify whether the conclusions still hold when microbially controlled or mediated mineralization is also considered. We also intend to point out the types of data that should be gathered in order to determine the role of biomineralization.

Here, a set of four case studies with Dill as the leading author is reviewed, looking at how Fe can be interpreted on (1) description of sabkha, a depositional environment of microbial features, which is the meso- to macrotidal environment, where many features are found in calcareous rocks (Dill et al. 2005); (2) anoxic pyritiferous environments, more specifically (2a) deeper or shallow reducing environments where the so-called framboidal pyrites developed from the Paleozoic to the Cretaceous anoxia, the metallogenesis of the Early Paleozoic graptolite shales from the Graefenthal Horst (Germany) (Dill 1986) and (2b) crystallographic and chemical variations during pyritization in the Upper Barremian and Lower Aptian dark claystones from the Lower Saxonian Basin (NW Germany) (Dill and Kemper, 1990); and finally (3) from the general depositional environment move into Fe-bearing oolitic Wabana (Paleozoic) and Minette (Jurassic) ironstones deposits (Dill 2010).

From a preliminary overlook, it is obvious that in the four studies reviewed here, mineralized microbial microtexture was not studied; the dimension of investigations did not fall into the microbial scale; bulk mineralogy was given instead of in situ mineral assemblage; detailed characterization of some mineral phases such as clay minerals was not given; clarification of syn- or diagenetic anoxia was not provided; Fe mineral phase was not exactly described; the origin of minerals as authigenic or debris contribution was not studied; and the source of ore and trace elements were given in graptolite shales and Barremian/Aptian claymarlstone, but not in the sabkha.

Based on information on the different environments offered by the cited papers as case studies, we focus on proposing possible microbial interpretations (Fe) and call attention to missing information, which would contribute to a more comprehensive interpretation of the sedimentary and diagenetic systems.

#### 5.1. Meso- to macrotidal environment with calcareous rocks

Dill et al. (2005) summarize sedimentary facies, mineralogy and geochemistry of the sulphate-bearing Miocene Dam Formation in Qatar, providing stratigraphy, lithology, sedimentology, and mineral composition of the Miocene sedimentary rocks with their depositional environment from the inorganic data and biodata (cited in Tables 1 and 2 of Dill et al., 2005), element correlations (cited in their Table 3) and a complex profile (cited in their Fig. 2). The case study interprets the stromatolitic features in detail, showing their types concerning the energy conditions of the system; biodata include foraminifers, bivalves, gastropods, echinoids, ostracodes and bryozoans, which are not on the microbial level.

Restricted platform sedimentation shows the transitional character of rock color, red and green for varying oxidizing and reducing

**Table 2**  
Mineralogy of formation (Dill, 1986).

Mineral type	Description
Overlying rocks	contact zone between graptolite shale and overlying rocks contain Fe chlorite and 10–14 Å mixed layer clay minerals
Graptolite shale	quartz, white mica, rare albite, anatase, rutile, calcite, dolomite, palagonite-muscovite mixed layered minerals organic matter is finely disseminated phosphate occur as complex aggregates of (i) collophane (carbonate-rich hydroxyl-apatite) as isotropic phosphate I, and (ii) anisotropic phosphate II. (F-apatite). Does not form continuous layers, and sulfides intersect it
Footwall	elongated quartz clasts, thüringite- $(MgFe)_3(SiAl)_4O_{10}(OH)_2 \cdot (MgFe)_3(OH)_6$ , ripidolite- $(MgFeAl)_6(SiAl)_4O_{10}(OH)_8$ , varieties of chlorite minerals of chamosite-clinocllore series

**Table 3**

Paragenesis of ore minerals (Dill, 1986).

Ore mineral type	Description	Paragenesis
Pyrite I	framboidal dissemination	early diagenesis
Pyrite II	resulted from enlargement of Fe sulfides	later diagenesis
Pyrite III	massive pyrite developed within joints sometimes associated with marcasite	later diagenesis
Sphalerite I	cements pyrite II aggregates along fractures	later diagenesis
Sphalerite II	minute crystals of ruby sphalerite	later diagenesis
Sphalerite III	with II and with U oxide	later diagenesis
Sphalerite IV	Fe-rich marmatitic	later diagenesis (metamorphism)
Galena I	lacks any sulfantimonide exsolution, rare	later diagenesis
Galena II	together with sphalerite III, also containing black U oxide ore	later diagenesis (metamorphism)
Galena III	massive with anomalous Ag enrichment	later diagenesis (metamorphism)
Chalcopyrite I, II, III	minute grain size, not investigated in detail	later diagenesis (metamorphism)
U	predominantly was adsorbed onto C <sub>org</sub> (carburan) rarely poorly crystallized sooty pitchbende + Zn, Cu, Pb sulfides+U-Fe-Al-phosphates via pyritiferous alteration of black shale	secondary alteration

conditions. Red parts contain goethite and hematite. Green parts are attributed to Fe<sup>2+</sup>-bearing fillosilicates, but the exact determination of clay mineral types was not provided. Fe-bearing green clays have an important role in environmental (paleoenvironmental) characterization, e.g. celadonite (Fe-mica) forms under suboxic neutrophylic conditions, while nontronite (Fe smectite) represents anoxic/anaerobic neutrophylic formation conditions (Polgári et al., 2013 and references therein). Microtextural observation and description of samples at high magnification, which is adequate to detect microbial contribution based on mineralized microbial biosignatures, was also not provided.

Case study interpretation presumed fluvial and aeolian contribution based on mineral assemblages, mentioning lithoclasts of metamorphic, igneous, sedimentary origin, but detailed investigations were not made. Further, among authigenic particles, which are an important group in characterization of environmental conditions, gypsum, celestite, dolomite, goethite, hematite, bassanite, anhydrite, halite, and iron disulfide are mentioned. Their Table 1 also mentions limestone particles like calcite and dolomite. A third group of minerals belong to terrestrial particles, namely quartz, plagioclase, orthoclase, palygorskite (smectite), kaolinite, muscovite, illite, zircon, rutile, and epidote-clinozoisite s.s.s.

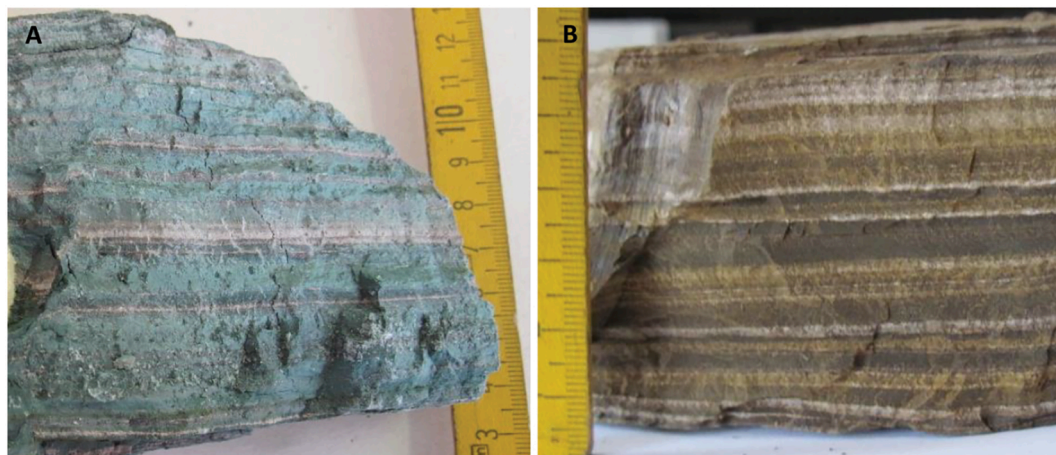
Limestone, marly limestone, marlstone, limemarl, are given as rock type, but the clay mineral type is not determined, nor its origin – whether this clay mineral assemblage is the result of debris contribution or is authigenic (and/or early diagenetic) as the result of microbial contribution or microbially mediated diagenesis (also an important aspect in description of the system).

Experience based on ore microbialites shows that minerals that are known as being of magmatic, metamorphic origin can also occur as unusual authigenic minerals. Examples are quartz, feldspar, pyroxene, amphibole. This fact should call attention to the fact that some peculiar mineral assemblages can form via authigenic and/or early diagenetic processes, often reflecting microbially mediated processes and the important role of the element reservoir offered by the decomposition of cell and EPS material (Polgári et al., 2019). At this point we arrive at the main focus of this study, the element source of minerals. We have to keep in mind that the element composition of the authigenic and/or early diagenetic microbially mediated minerals is the same as debris components of fluvial or aeolian source, for instance, and this means that the element correlations are also the same. Therefore, the detailed study of minerals concerning a possible authigenic formation is highly suggested, and cathodoluminescence features or microtextural evidence can help in this study (Yu et al., 2019; Biondi et al., 2020).

Stromatolites are concerned as geological structures of microbial activity, not necessarily including direct microbial mineralization. Fe minerals, goethite and hematite can reflect suboxic, neutrophylic conditions, resulting in microbially mediated ferrihydrite as a syngenetic biooxide formed via Fe(II) oxidizing microbial activity, and stabilized as goethite and hematite accompanying silica segregation, well known from the literature. This segregated silica can result in quartz, in clay minerals of variable element composition, and also in special Fe-bearing clay mineral formation. Further, this silica can form other silicates such as feldspar, pyroxene or amphibole (Polgári et al., 2012a; Molnár et al., 2017; Yu et al., 2019; Biondi et al., 2020, and the papers of this special volume). Supposing microbial Fe(II) oxidation, we can give its type (acidophylic aerobe, photophoretrophie can be excluded), but nitrate-reducing Fe oxidizers can also contribute in such an environment. Microtextural evidence can clarify this and give further details on clay mineral formation (or debris contribution) in the case of marl-type rocks. In the case of Fe-clay minerals there is not enough information.

## 5.2. Anoxic pyritiferous environments

This section looks at deeper or shallow reducing environments where the so-called framboidal pyrites developed from the Paleozoic to the Cretaceous anoxia, the metallogenesis of the Early Paleozoic graptolite



**Fig. 2.** Mineralized cycles as micro-lamination. (A) celadonite-bearing and (B) goethite-bearing fine-laminated Mn carbonate ore (Ca-rhodochrosite) (Jurassic), Úrkút Mine, Hungary, scale: 1 cm.

shales from the Graefenthal Horst (Germany) (Dill 1986) and (2b) crystallographic and chemical variations during pyritization in the Upper Barremian and Lower Aptian dark claystones from the Lower Saxonian Basin (NW Germany) (Dill and Kemper, 1990).

#### 5.2.1. Metallogenesis of early Paleozoic graptolite shales and ochre limestone

Let us first discuss the metallogenesis of Early Paleozoic graptolite shales from the Graefenthal Horst (Northern Bavaria, Germany) (Dill 1986). Psammo-pelitic sediment in a metamorphic series hosts graptolite shale of two horizons as bioliths (Silurian and Devonian), including phosphatites, alumshales and organic matter-bearing chert. Ore indication of V and U and also Zn, Pb, Cu, formed under reducing conditions in the outer shelf in the presence of abundant  $H_2S$ , is supposed to have a basic role, and invites economic interest. During formation the sedimentary basin was starving in the sense of debris contribution. Based on mineralogy and chemistry there was no volcanic matter contribution. Two element sources are proposed: (i) from underlying strata into bottom water enriched in  $H_2S$ , or (ii) coastward upwelling along the shelf abundant in P. The two black shale layers are separated by ochre limestone, which is not characterized, but based on its name it is Fe-bearing (siderite and pyrite and probably Fe oxide-bearing).

The case study distinguishes two periods of diagenesis, early diagenesis and the more important late diagenesis resulting in sulfide ore minerals (sphalerite, galena, chalcocopyrite, and tetraedrite). Dynamothermal metamorphism of very low grade regional and lower green schist facies occurred.

Strata-bound fault-hosted Fe-Cu-Zn-Pb-U indications are realized in pyrite, marcasite, sphalerite, galena, and point to low T conditions and element derivation from embedded organic matter. Ag-enriched galena and marmatitic sphalerite formed via contact metamorphic processes. Subsequent superegene alteration during the Pliocene/Pleistocene caused U-bearing Fe-Al-phosphate formation, concentrated along fractures by decomposition of pyrite of black shale. The case study classified the formation as syngenetic-metamorphic polymetallic, low T, fault hosted deposits formed by mobilization.

Bioliths were deposited on a fairly thick sialic crust. Ordovician clastic formations are rimmed by argillaceous rocks with interbedded oolitic Fe seams (Wabana type oolitic Fe indication, Dill, 2010). The black shale thickness is around 30 m. Upper alumshale contains phosphate-bearing and pelitic arenaceous intercalations, while bituminiferous limestone and the lower chert alumshale also occur with thin dolomite intercalations. There is no information on the type of clay minerals of the black shale.

The case study provides information on the mineralogy of the foot-wall rock (elongated quartz clasts, thuringite -  $(MgFe)_3(SiAl)_4O_{10}(OH)_2 \cdot (MgFe)_3(OH)_6$ , ripidolite -  $(MgFeAl)_6(SiAl)_4O_{10}(OH)_8$ , varieties of chlorite minerals of chamosite-clinochlore series) (Tables 2 and 3). Graptolite shale consists of quartz, white mica, rare albite, anatase, rutile, calcite, dolomite, palagonite-muscovite mixed layered minerals. Metamorphic minerals did not occur (illite crystallinity and vitrinite reflectance data were used). Organic matter is finely disseminated. Phosphate occurs as complex aggregates of (i) colophonite (carbonate-rich hydroxyl-apatite) as isotropic phosphate I, and (ii) anisotropic phosphate II. (F-apatite). It does not form continuous layers, and sulfides intersect it. The contact zone between graptolite shale and overlying rocks contains Fe chlorite and 10–14 Å mixed layer clay minerals.

Dill concluded that metallic evolution probably occurred in sedimentation – middle Ordovician – on a shallow marine platform in a lagoonal pond which temporally was terminated, or in the open sea near a sand bar. From late Ordovician to Silurian there was basin deepening, which is supported by the increase of V/Cr and decrease of C/S (tectonically active region).

Sedimentation changed from an environment of biogenic precipitation (chert and dolomite) into an environment with limited clastic

sedimentation rate within a starved basin (alumshales), a situation in which clay can be authigenic via distal hydrothermal discharge and the boom of microbial activity on nutrient sources.

The true sapropelic environment or  $H_2S$  zone during which the ferruginous graptolite shales were deposited is shown by the preponderance of metals like V, Mo, Cu, Zn, Ni and by the frequent occurrence of high S and C content. But the question is whether anoxia was syngenetic or diagenetic. What proves syngenetic conditions?

Any contribution of Ba halo and volcanic tuff is missing, which excludes volcanic contribution. A poor sedimentary element supply by upwelling streams rich in P has to be discussed for the graptolite shales. A model on the migration of Fe, Cu, Zn, Pb bearing fluids from underlying sediments into the basin with poorly aerated bottom waters with  $H_2S$  was proposed by Dill (1986) (the “outer shelf” model). For P a microbial source can be proposed. Fe enrichment refers to a local source of ore forming fluids. U has peculiar behavior, a bond microbial mediation with Fe bacteria (and also Mn bacteria) in enrichment (Gál et al. 2020), which suggests a microbial origin for the U-Be-P-Mn-Fe deposit. Concerning element enrichments, an important role of the element reservoir offered by the decomposition of cell and EPS material can also be proposed (Polgári et al., 2019), as the conditions were starving. Furthermore, Fe in probably oxide form contributes to ochre limestone. Ochre formation occurs in the vicinity of exhalation (hydrothermal discharge) zones. Enrichment of Fe is caused most probably by microbial Fe oxidation under suboxic and neutrophilic conditions. Unfortunately, microtextural evidence was not studied. An assumption of microbial Fe oxidation makes the information on formation conditions more exact.

In the ochre limestone Fe was fixed in siderite, rather than pyrite, which indicates that the basin had been once again brought into the  $CO_2$  zone. The sea level proposed in the original case study was based on lithological variation from black shale to limestone and vice versa (low stand is calcite, high stand is shale). The case study (Dill, 1986) came to the conclusion that a bathymetric situation based on Fe distribution supports this scenario. Based on ore microbialite research, we have to raise the question of whether the siderite is syngenetic or diagenetic after microbial Fe oxide (ferrihydrite) formation and its microbially mediated reduction. This is a key point, which can be proven by microtextural observations and a stable C isotope study. Concerning paleoenvironmental proxies like element ratios (e.g. V/Cr), our experience has shown that their reliability is questionable, as found for on the black shale-hosted Úrkút manganese carbonate deposit (Bíró et al. 2015). Further information on black shale and ore microbialite element distribution also supported formation under a suboxic-oxic water column and diagenetic anoxia caused by a high amount of buried organic matter (microbial organic matter originating from the microbial boom on nutrient rich ore forming fluids), with a characteristic authigenic/early diagenetic clay mineral formation supported by starving conditions (Polgári et al., 2016a, 2016b), which is also the case here. We mentioned earlier the importance of the suboxic zone. In this case study the siderite of the ochre limestone could be the result of this zone.

Early diagenetic processes resulted also in phosphate I, another reference to suboxic conditions. As the content of metal oxides (e.g. Fe) was limited and/or a high amount of organic matter was preserved and became the source of sulphate reducing microbial activity, pyrite I formed under anoxic diagenetic conditions. As organic matter is supposed to be the source of elements (Table 4), after decomposition of organic matter (cell and EPS) an element reservoir was formed in the pore water, which provided elements for variable sulfide mineralization (ore indication). The types of element enrichments in the organic matter vary and are summarized in Tables 3 and 4.

Concerning mineral assemblage, some of the minerals (quartz, feldspar, etc.) can form as authigenic and the rock texture can be similar to that of debris-like rocks, because these authigenic mineral grains can grow to mm dimension, which is also described in the cited ore microbialites.

Later diagenesis and metamorphic events influenced the distribution

**Table 4**  
Chemistry (Dill, 1986).

Element	Source	Notes	Comment
Zr	detrital	increase from pelitic to psammitic, less in biogenic chert	no fine grained silty or sandy material was contributed to this typical environment of silica precipitation – STARVING
Ce		does not follow lithology, because co-precipitated with phosphates and not concentrated in heavy mineral monazite which is more characteristic for detrital sediments in an environment of deposition.	microbial element
Cr + V		potential redox indicators, V/Cr < 2 → oxygenated conditions V/Cr > 2 → sapropelites Cr <sup>3+</sup> bond on allochthonous clay V <sup>3+</sup> is related to authigenic C <sub>org</sub> (porphyrin not soluble) graptolite shale-sapropel footwall rocks-better oxidized overlying rocks-negative Eh-pyritiferous	authigenic
Ni, Co		in porphyry and via diagenesis bond in pyrite Ni/Co increase via prograding metamorphism Co in pyrite	microbial enzymatic element
Mo		typical element in bituminiferous sediments, bond in C <sub>org</sub> (microbial enzymatic element) sulfides with Cu trend	microbial enzymatic element authigenic
Zn		little here, no volcano-sedimentary system	microbial enzymatic element
Ba		normal range of common black shales, not affected by hydrothermal processes	microbial enzymatic element
C		C-U + correlation, C <sub>org</sub> diagenesis and metamorphic affect is basic in U enrichment	microbial enzymatic element
U		carburan	microbial enzymatic element authigenic
S		in sulfides, but can substitute P in phosphate S and C <sub>org</sub> connection genetic relationship between C <sub>org</sub> metabolization and sulphate reduction by bacteria + correlation of S and C in pyrite low C/S ratios in alumshale and chert show 1.3–3.9 → euxinic character of depositional environment fairly high ratios of phosphatization (4.4–7.4) refer to higher oxygen content	microbial enzymatic element
Se		in pyrite, no selenide because of low Eh which govern the Se/S ratio in mineralization	microbial enzymatic element
As, Sb		in pyrite, and in diagenetic pyrite	microbial enzymatic element
Au		+ corr. Au-Sb in pyrite + corr Au-Se in pyrite originally on C <sub>org</sub>	microbial enzymatic element

and features of mineral phases, increasing the concentration of Fe, Cu, Zn, Pb, Sb, As in sulfide layers, and also trace element content like Ag, Fe in sphalerite, Bi, Sb in galena. Secondary alteration determined U-Fe-Al phosphate formation.

### 5.2.2. Crystallographic and chemical variations during pyritization

Upper Barremian/lowermost Aptian pyritic claystones and marls were studied. Six types of pyrite were distinguished based on morphology, which are associated with subordinate amounts of Fe carbonate, chalcopyrite, sphalerite and wurtzite. All types of pyrite are early to late diagenetic. Conversion of crystal habits was accompanied by a striking variation in trace element contents (Au, Se, Te, Tl, Co). The case study found the role of As and Ni important in establishing the sequence of pyritization, which may help define a basin zonation for these argillaceous sedimentary rocks, categorized as normal facies-oxygenated bottom waters, interrupted by short episodes of bottom water oxygen depletion (bituminous facies). The cube to octahedron in Fe bisulfide aggregates suggests led to a continuous removal of As and Ni from pyrite, referring to the decrease of these elements in the pore fluids with time. On the other hand, in each type of pyrite As and Ni contents increase from the margin towards the center of the basin, which is interpreted as being due to more abundant organic matter content in the basinal sediments. This reveals the organic matter source of these elements. Other elements like Mn, Cu, Sb, and Ag do not follow this trend. Their high quantities are controlled by host rock chemistry (the presence of volcanoclastic material). Microbial mineralized forms, tubular hollows of burrowing organisms occur with pyrite. This pyrite formation is due to microbial sulphate reduction and Fe<sup>3+</sup> reduction resulting first in siderite, then the formation of H<sub>2</sub>S resulting in pyrite. The base of Aptian Mn is enriched in pyrite, which does not influence the crystal habit; it is stratigraphically controlled. Syngenetic Mn oxidation on the active surface of microbially mediated Fe oxide-hydroxide (ferrihydrite)

(active surface catalysis model, Morgan 2005) may be responsible for this elevated Mn content (as a remnant feature).

Periodic low oxygen conditions led to the deposition of well-laminated shales. The lack of benthic fauna or trace fossils indicates a decrease in oxygen content in the bottom water zone. In the case of laminated sediments we have to take into consideration the overwhelming impact of e.g. microbial boom on nutrient supply, resulting in high amounts of organic matter under oxic conditions, which will also result in laminated sediments.

### 5.3. Fe-bearing oolitic Wabana (Paleozoic) and Minette (Jurassic) ironstone deposits

This is also a coastal environment but more wave-dominated. The Wabana (Minette) type Fe formations are related to the above detailed metallogenesis of the Early Paleozoic graptolite shales from the Graefenthal Horst (Dill 1986). Ordovician Wabana ironstones are intercalated between highly tectonized pencil slates.

Most marine and fluvial minette-type ironstones consist of reworked ferruginous coated grains deposited in agitated water, but there are also indicative structural features of in situ formation in the supporting medium of lateritic and hydromorphic environments. In the zone of oscillating groundwater, repeated leaching and subsequent concretionary precipitation of hydrated ferric oxides take place, according to the prevailing Eh/pH-conditions and microbial activity.

The moderate Al substitution of goethite from hydromorphic environments corresponds to the observed range in oolitic ironstones. Dill (2010 and references therein) therefore assumes erosion, reworking and subsequent fluviomarine redeposition of soil derived oxids to be the major processes of generating minette-type ironstones.

Oolitic ironstones (Minette/Wabana-types) are formed under favorable bathymetric and geodynamic conditions on shallow marine shelves

or in epicontinental basins on stable cratons. They are controlled by facies but not necessarily time-related. An ironstone ore seam is interpreted as having formed in a maximum flooding zone (MFZ) between a transgressive system tract and highstand system tract. There is a sequence stratigraphy of oolitic ironstones (Wabana-type) interbedded with siliciclastic units in the Saxothuringian zone (Dill, 2010).

The environment of deposition of the Ordovician Fe ores appears to have been characterized by atmospheric  $\text{PCO}_2$  values, which were 16–18 times higher than the present-day ones. The association of comparatively low tropical temperatures (and an ice sheet at high palaeolatitude) with high atmospheric  $\text{PCO}_2$  might have been a result of lower solar luminosity in the late Ordovician (Yapp, 1991; 1998).

The well-known Minette ores are associated with shales, sandstones and limestones that formed in brackish waters in a shallow basin. Deposition of oolitic ironstones with other leptochlorites in addition to chamosite and thuringite occurred at the top of a coarsening and shallowing upward megasequence that reflects a regression of the sea (Teyssen, 1989). Silica-rich ferric oxides may be converted during diagenesis in a reducing environment into siderite and Fe chlorite (Siehl and Thein, 1989). Microbial activity probably played also a key role during Fe accumulation in the near-shore environments (Burkhalter, 1995).

Ironstones of marine origin – oolitic ironstones (Minette/Wabana types and detrital iron ore deposits) – may contain considerable amounts of phosphate in the form of apatite. Unlike many marine phosphorites caused by upwelling processes along the shelf edge, ironstones and phosphatic bone-beds developed in shallow marine settings where the prevailing sediment accumulation rates are very low (Macquaker et al., 1996).

Both sediment types cap coarsening upward successions and are commonly developed in mudstone-dominated settings. In bone beds cement comprises early apatite, glauconite and later calcite and pyrite produced in suboxic pore waters where there was limited Fe reduction. From the sequence stratigraphic point of view, phosphatic bone beds formed on marine flooding surfaces and ironstones formed at sequence boundaries, major flooding surfaces or maximum flooding surfaces. Since any aquatic milieu with appropriate fluctuations of Eh and pH can produce ferruginous coated grains, marine iron ooids associated with hardgrounds and areas of low sediment input can also occur. But in such a case, release of ferrous iron, transport in saline interstitial waters, and fixation of ferric hydroxides – usually with very low Al-substitution – take place on a much smaller scale and are incapable of generating the huge iron accumulations of Minette-type ore deposits (Siehl and Thein, 1989).

**Mineralogy and geochemistry** – oolitic iron deposits, commonly called Minette-type deposits, contain oolites of siderite, a siliceous iron mineral known as chamosite, and goethite. Ooids made up of Fe chlorite from the nearshore marine ironstones are also common (Dill, 2010).

Postdepositional diagenetic changes may convert the aluminous, silica-rich ferric oxides into berthierine ( $\text{Fe}^{2+}, \text{Fe}^{3+}, \text{Al}, \text{Mg}$ ) $_3(\text{Si}, \text{Al})_2\text{O}_5(\text{OH})_4$ , a member of the kaolinite-serpentine group (septe-chamosite) in reducing environments if the chemical bulk composition of the primary goethite is similar.

According to Zitzmann (1977), the Wabana ores are normally hematitic Fe ore with siderite and chamosite (51% Fe, 12%  $\text{SiO}_2$ , 1% P). Also representative of this type of Fe ore is Fe chlorite (thuringite). These Ordovician oolitic Fe ores, containing siderite, thuringite, chamosite and magnetite, were formed during transgressions in a shallow-marine environment (Bach et al., 1976).

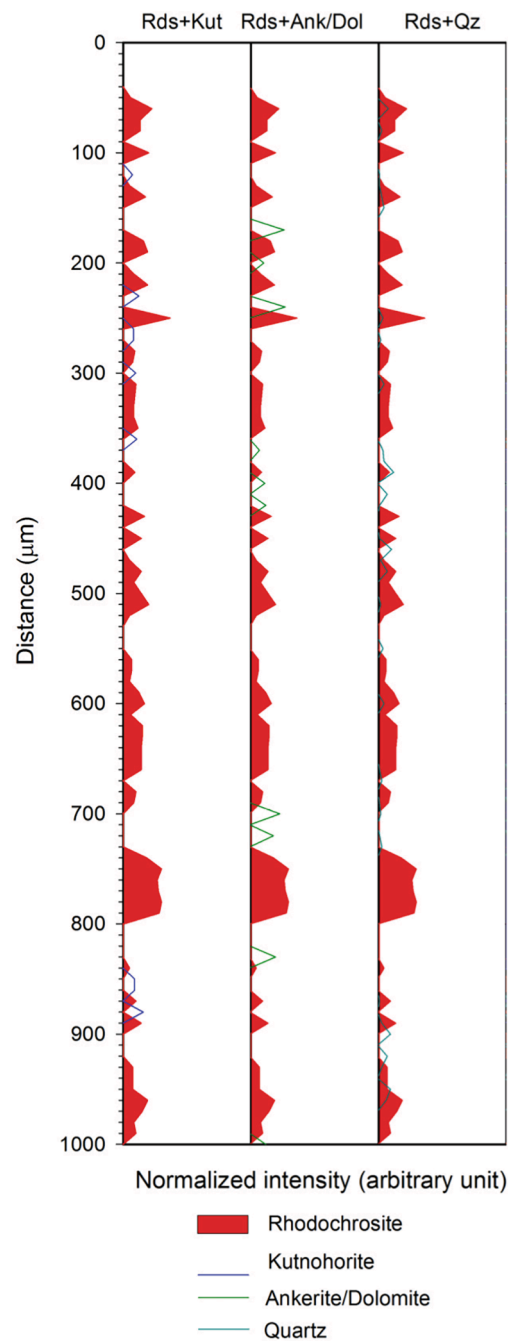
Siderite eroded during the Cretaceous was converted into goethite. Accessory minerals are smectite, phosphates, glauconite, Mn calcite and rhodochrosite. Ironstone formation occurred in a shallow-marine high-energy zone (Kolbe, 1962).

Vanadates and the vanadiferous analogue of goethite, called mon-troseite, with as much as 45% V develop under oxidizing conditions. Among vanadium deposits, V–Fe ironstones (Minette and Pebble Fe ore)

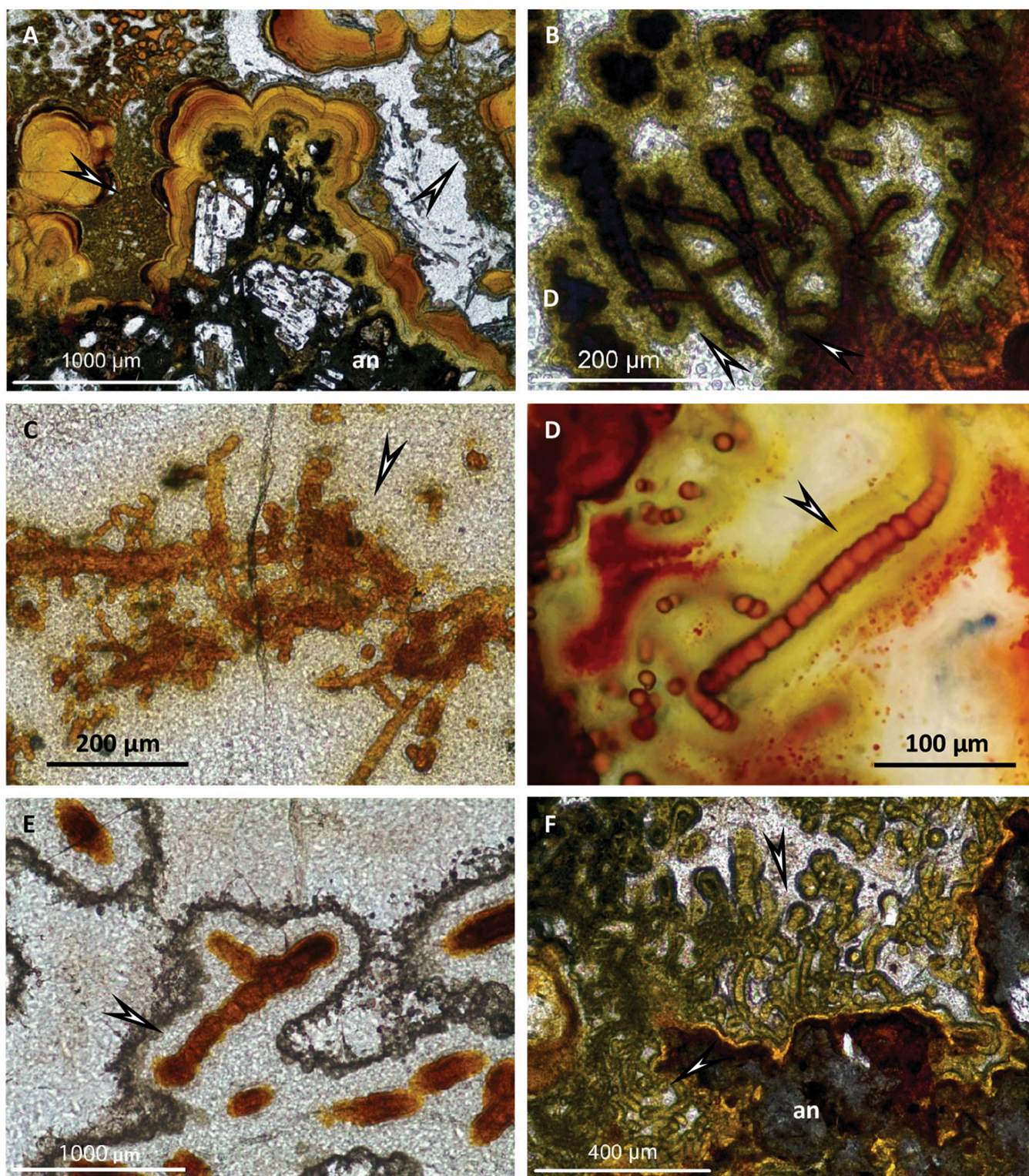
represent a subgroup.

Taking into account microbially controlled/mediated mineralization processes, we may consider the evidence from a different aspect. The moderate Al substitution of goethite from hydromorphic environments corresponds to the observed range in oolitic ironstones. Al is an organic-supported element (Maliva et al., 1999; Biondi et al., 2020). Similar to the Al demand of chamosite ( $(\text{Fe}^{2+}\text{Mg})_5\text{Al}(\text{AlSi}_3\text{O}_{10})(\text{OH})_8$ ) mentioned above, the mobility of aluminum is enhanced by complexation with organic acids. In such systems, aluminum is released and hence available for clay-mineral precipitation when the organo-aluminum complexes are destabilized (Maliva et al., 1999).

Based on Biondi et al. (2020), in shallow marine condition evaporitic alkaline sodium-rich conditions cannot be ruled out and indeed, are



**Fig. 3.** Mineralized cycles as micro-lamination determined by micro-Raman spectroscopy, Ghaoyang Mn deposit, China (600 My). Abbrev: Rds–rhodochrosite, Kut–kutnohorite, Ank–ankerite, Dol–dolomite, Qz–quartz.



**Fig. 4.** Mineralized microbially produced micro-textures (MMPT). (A, F) stromatolitic biotite on microbially weathered andesite (an) and filamentous microbially mediated micro-texture (biosignatures) (arrows) (rock consuming and rock forming evidence; (B, C, D, E) mineralized extracellular polymeric substance (EPS) around the mineralized filamentous micro-texture (arrows), in case of (B, D) green clay mineralization (celadonite) occur (15 My, Müller, 2009). Thin sections by optical rock microscopy, 1 N.

preferred for aegirine formation in the Urucum Mn deposit. The high silica concentration favors aegirine formation instead of clay minerals (Decarreau et al., 2004, 2008), which only sporadically occur in the samples studied here (celadonite, chamosite). Chamosite formation is favored by seawater solutions at low temperatures with a relatively reduced pH, a low amount of  $\text{SiO}_2$ , high content of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ , and a relatively high amount of Al and Mg. Aluminum may be donated to the system by organic matter, as reported by Maliva et al. (1999), who showed that the aluminum content is greatly increased by complexation with organic acids. Low silica concentration in solution is the most important condition for low-temperature synthesis of clay minerals, as high silica concentration in solution inhibits their formation (Harder, 1976). The silica source may result from the well known transformation and segregation of ferrihydrite. Harder (1978) noted that "...the silica content of sedimentary iron ores is found in quartz and different iron-containing clay minerals. Chamosite, greenalite, cronstedtite, nontronite, glauconite, and thuringite are common minerals in sedimentary iron ores. In general, all these minerals are extremely fine-grained."

P and V are organophil elements and their enrichment is microbially mediated on organic matter source. Other accompanying elements are described in detail above.

Concerning mineralogy: ferric hydroxides, goethite, hematite, magnetite, siderite, chamosite, berthierine, Fe-chlorite, thuringite, apatite, Fe-Al-phosphate are common. These minerals can be interpreted by microbial  $\text{Fe}^{2+}$  oxidizing and reducing system via diagenesis and complex mineralization, reported in detail by Polgári et al. (2012a); Yu et al. (2019); Biondi et al. (2020).

Starving conditions take place, and in the zone of oscillating groundwater repeated leaching and subsequent concretionary precipitation of hydrated ferric oxides occur, according to the prevailing Eh/pH-conditions and microbial activity (Dill 2010). A shallow marine environment and transgression-regression phases caused Eh/pH changes, which resulted in ore deposits.

#### 5.4. Suggestions for including a biomineralization dimension in studies

The study of ore microbialites teaches us numerous connections and facts that can also be useful in the interpretation of non-ore systems or in other types of ore indication-bearing sedimentary systems. Among others we can mention the following examples, which are well known but still not routinely used in many cases: (i) lamination is not equal to anoxia; (ii) mass balance aspects; (iii) the importance of the suboxic diagenetic zone; (iv) the influence of microbial element enrichments

(isotope effect) on element (isotope) ratio analyses; and (v) sources of elements.

To summarize, the four case studies reviewed here, while quite thorough in many ways, did not include sufficient attention to the possibility of biomineralization. Mineralized microbial microtexture was not examined in any of them. In some studies detailed characterization of mineral phases was lacking, and consideration of the origin or sources of enrichment minerals was missing. The data collected (or reported) was not always sufficient to analyze the potential role of microbially mediated processes. Thus, the description of the rocks in the case studies is somewhat incomplete. The detailed description and interpretation of microbially mediated processes offer a more plausible coherent picture by including identification of formation conditions, syn- and diagenetic processes, and also element enrichments based on mineral assemblages.

If a through study of a geological site is planned, a complete interpretation can be made only if sufficient data is available, including evidence of potential microbial mediation. We recommend the following methods for collecting samples and data so that an analysis on microbially mediated formation can be carried out to inform comprehensive analysis and interpretation.

1. Dimension of investigations must fall into microbial size dimension (e.g. there is a need for high magnification microtextural observations as a first step to investigate the possible occurrence of microbial mediation)
2. Besides bulk analyses, in situ determination of mineral assemblage and embedded organic matter is needed.
3. If the possibility of microbial mediation can be raised in a formation (through microtextural evidence), the choice of appropriate methods is essential. For instance, XRD does not "see" X-ray amorphous poorly crystallized microbially mediated minerals, furthermore, attention is needed concerning excitation energy, which can convert minerals like ferrihydrite to more stable hematite. Thus, along with Raman spectroscopy, FTIR spectroscopy at lower excitation energy is also suggested.
4. Debris character can be a "virtual" outlook (large minerals of authigenic processes), influencing textural features, which can be clarified easily by using cathodoluminescence microscopy.
5. Authigenic formation of minerals that are well known as being of a particular origin may actually appear as authigenic materials. One example is with magmatic or metamorphic conditions (quartz, feldspar-earlier known), but also, pyroxene as aegirine,

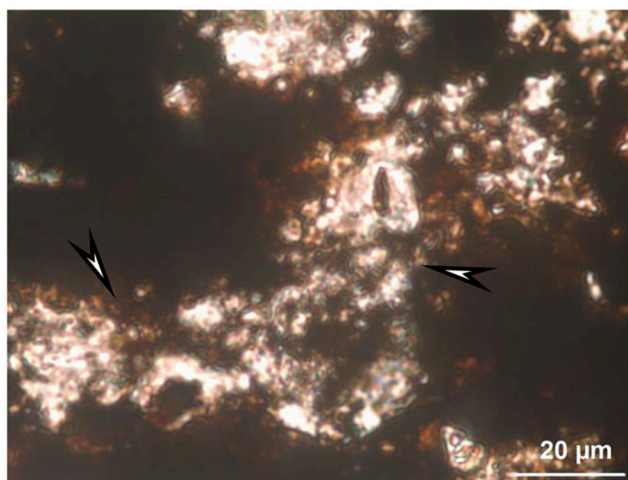
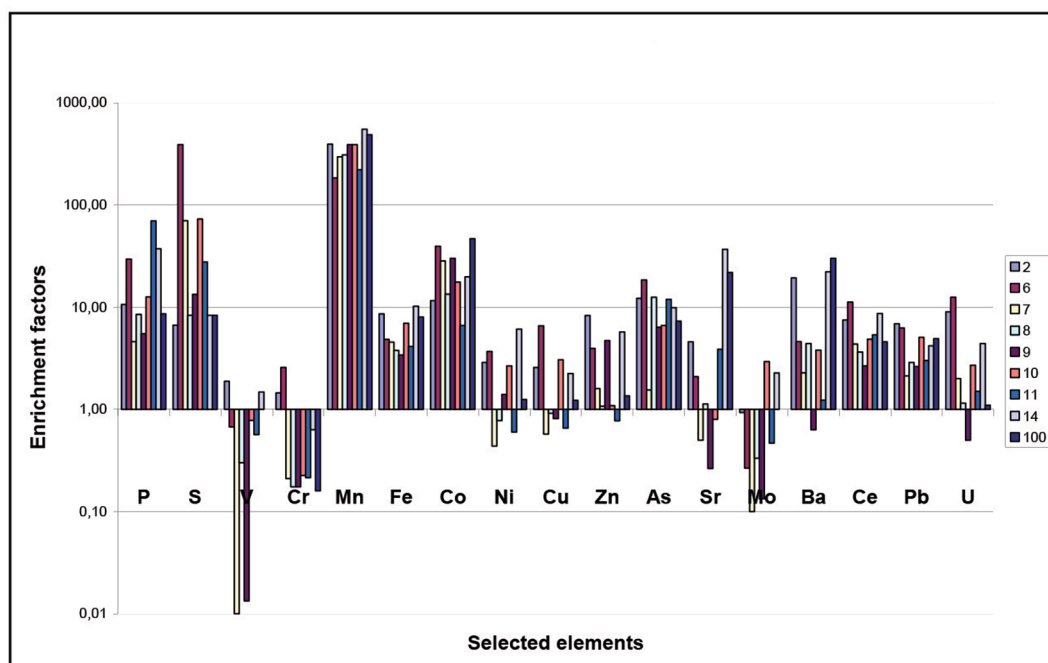


Fig. 5. Mineralized microbially produced micro-textures (biosignatures)(arrows)(MMPT), high magnification optical rock microscopy, 1 N. Ghaoyang Mn deposit, China (600 My).



**Fig. 6.** Enrichment factors of maximum concentrations of selected elements for the Úrkút deposit relative to the Earth's crust (Turekian, 1969). Logarithmic scale. Legend: 2—metalliferous clay; 6—black shale; 7—green-gray Mn-carbonate ore; 8—brown Mn-carbonate ore; 9—green Mn-carbonate ore; 10—gray Mn-carbonate ore; 11—bed No. II, Mn-carbonate ore; 14—cherty, Fe-rich Mn-oxide ore; and 100—contact Mn-oxide ore.

amphibol like riebeckite, and others, like dickite as high T and p minerals also common as authigenic minerals. Thus further study may be needed concerning mineral type, and a complex approach is proposed to avoid a false interpretation.

6. Selective element enrichment (isotopes) resulting from microbial processes means that we have to use geochemical ratio methods with caution. This enrichment can indicate a microbially influenced element source, which often does not even appear as a possible interpretation, and also demonstrates the need for a multi-methodology approach and complex interpretation.
7. It is very important to distinguish whether clay-size dimensions or clay minerals occur. If size dimension is under discussion, what are the minerals in that fraction? If clay mineral, then what is the origin? Is it detrital, hydrothermal, or microbial? It can indeed be microbial, and often this is the case. So in the case of marls or claystones (other clay-bearing rocks) this must be studied. Why? Generally the interpretation of clay-rich rocks is simply assumed to be increased wet weathering and run off from terrestrial parts, but in many cases that may be a false interpretation.
8. It is important to distinguish between syngenetic anoxia and diagenetic, since it determines original formation conditions.
9. Mass balance considerations should not be ignored, because the ratio of accumulating metal oxides, organic matter, and other components will influence the diagenetic processes.
10. Identifying suboxic zones is important due to consumption of organic matter by metal oxides and hydroxides and forming diagenetic mineral types.

If these factors are overlooked, and therefore it is not recognized that a system is microbially mediated (or evidence of microbial mediation is studied but not convincingly excluded), the conclusions will be incomplete.

There is no doubt that the dimension of investigations is different when we consider also microbial evidence, and in many cases

comparison between a case study's conclusions and microbial features cannot be made, because they are not comparable or data are missing. In most datasets the interpretation is made based on hydrothermal or debris contribution or sea level stands, while the enrichment factor is not mentioned, although microbial mediation is a vital factor in sedimentary environments. The outlook of the rocks will depend on complex factors, which can be described based on high-resolution multi-methodological characterization. In sedimentary systems the possibility of microbial contribution must be considered and the appropriate data must be collected on the appropriate scale in order for this factor to be convincingly excluded or verified.

## 6. Biogenicity

How can we prove that microbial mediation has occurred in the formation of minerals in geological samples? There are recent analogies, but geological time scale (My), overprinting and diagenetic influence can make the picture more complicated. Nowadays there is consensus on biogenicity aspects (Cady et al., 2003), which are summarized in Polgári et al. (2019). The main key is to find mineralized biosignatures. Complex methodological interpretation, adequate methods for poorly crystallized minerals and structural hierarchical interpretation can be used to verify microbial contribution.

**Macro- and micro-textural evidence** – Macroscopic observations of samples support fine lamination and a stromatolite-like structure, which is robust evidence. There are several criteria for the identification of biogenic signatures: one of the most important is morphology observation, another is identification of biogenic minerals that survive geological timescales, and also alteration of initial amorphous phases to more stable minerals (ferrihydrite to goethite, silica to quartz) (Baele et al., 2008). Mineralized microbially produced textures (MMPT) are characteristic of series of biomats. To identify this, high resolution optical rock microscopy and in situ detection and determination of micro-minerals (bioindicator minerals) and embedded organic matter are suggested

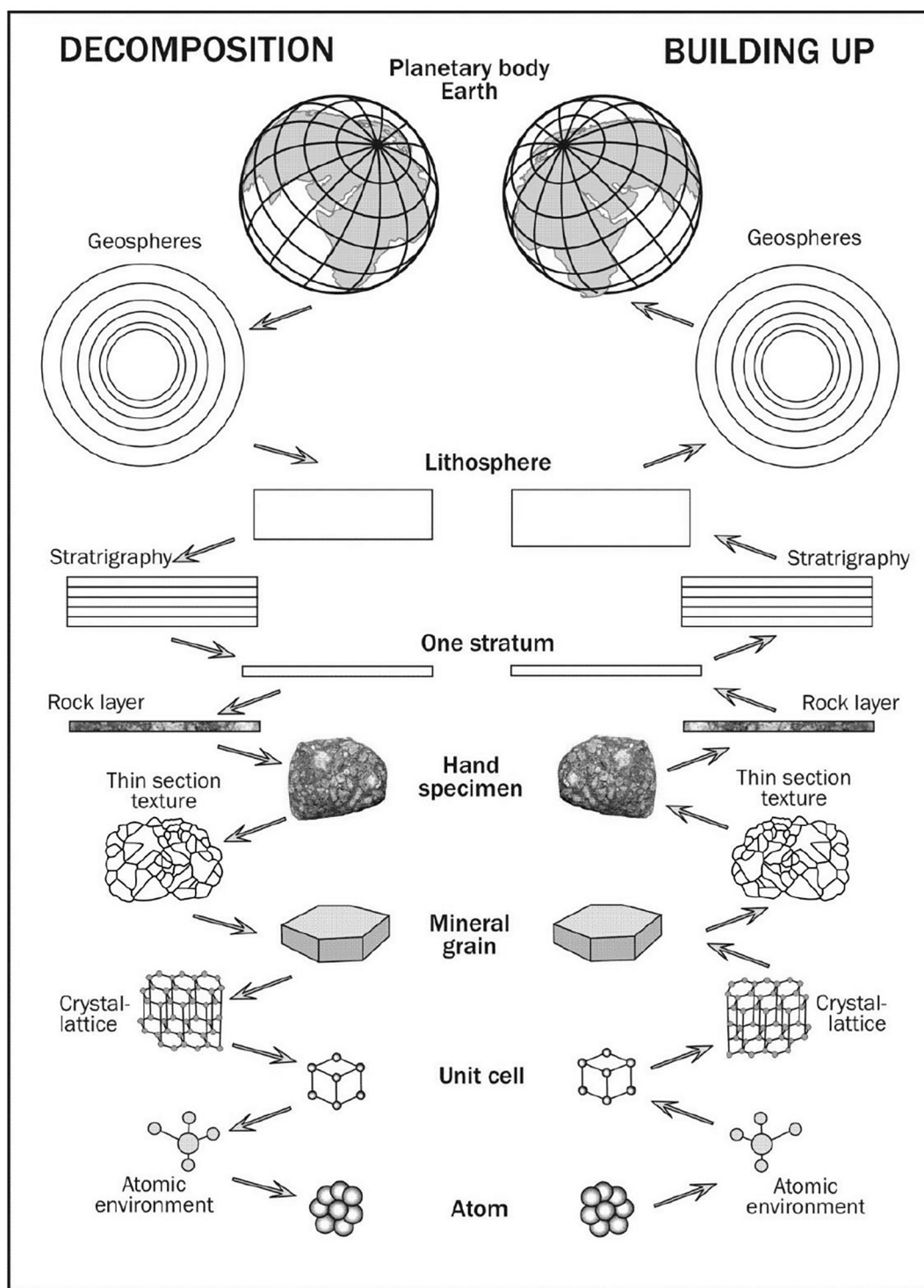


Fig. 7. Structural hierarchical levels (Bérczi, 2018).

using FTIR and Raman spectroscopy and also SEM (Polgári et al., 2012b; Gyollai et al., 2015; Molnár et al., 2017; Yu et al., 2019, 2021a, 2021b; Biondi et al., 2020). These datasets support mineralized cycles as microlamination (Figs. 2–5).

**Main and trace element composition** – ICP MS and EPMA-EDS are good enough but not great methods for shedding light on selective element enrichments, among them bioessential elements (Fig. 6).

**Isotope signals** – Vital effects are preserved as light isotope signals of C, S (Fe) and can be determined by GC–MS (Polgári et al., 2012a). Selective enrichment of light isotopes of the given elements accompanies

microbially mediated processes.

**Complex interpretation in the frame of structural hierarchy** – To understand the formation of microbial mats, the structural hierarchy method is the best by panning investigations and for interpretations. The structural hierarchy contains hierarchy levels and sequences of structures. This means that the investigation starts from the topmost structure to isotope dataset (here: morphology toward mineralogy toward elements toward isotope data) (Figs. 7, 8).

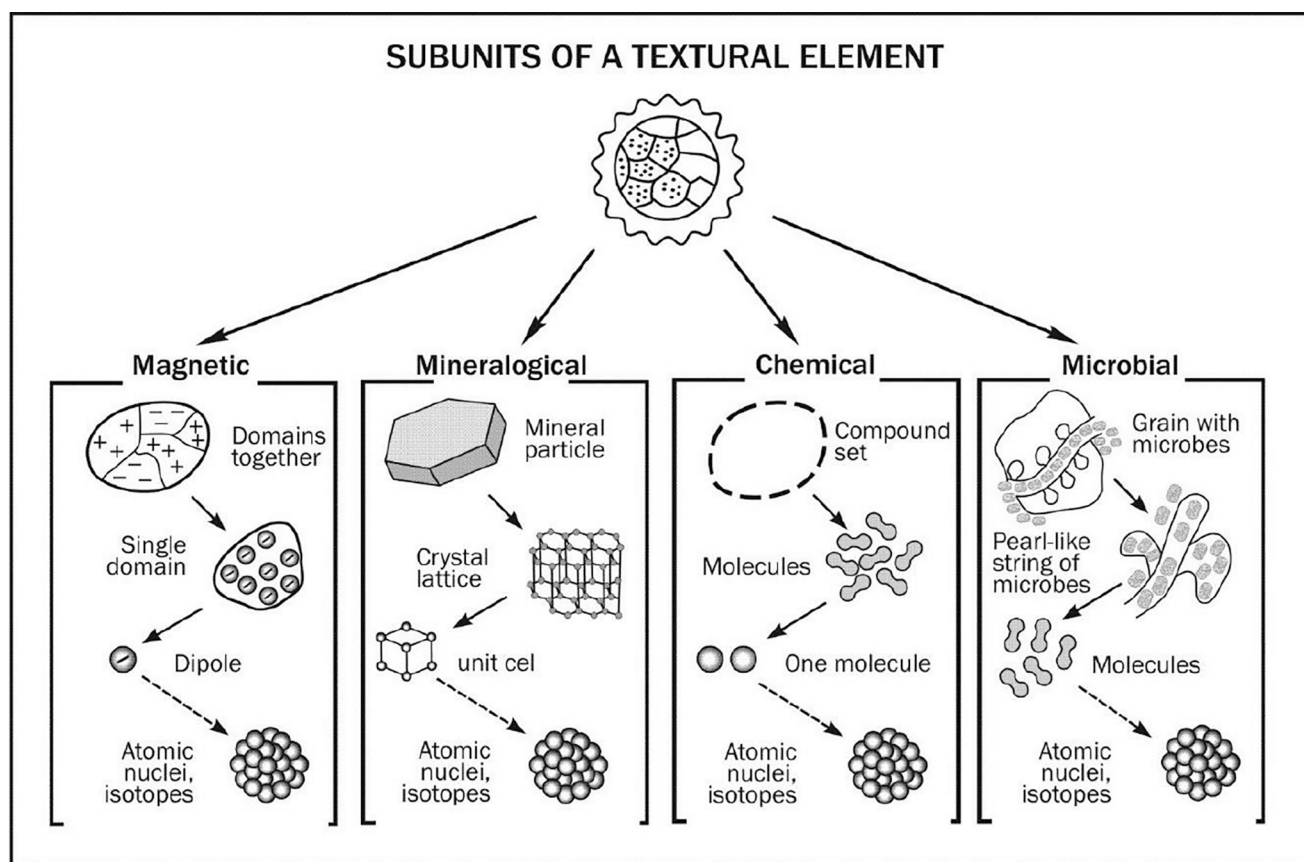


Fig. 8. Subunits of a textural element (Bérczi, 2018).

## 7. Conclusions

It is important to consider the role of microbial life (in particular, bacteria and fungi) in the geological context of mineralization and mobilization processes, because the mechanisms governing such activities often supersede purely inorganic reactions. It is also useful to have an overview of the evolution of biomineralization as a global control factor of diluted chemical constituents in the oceans and in the solid phase.

In this paper a detailed summary on biogeochemical cycles, biomineralization, and sedimentary ore formations has been provided. Microbially mediated mineralization and biomineralization, including organic matter accumulation (cell and EPS offering element reservoir pools) and diagenetic processes, are important factors in the stabilization of ore minerals. Complex mineralization of cell material and EPS occur with the accumulated minerals acting also as bioindicator minerals. This complex mineralization results in the highly variable mineral assemblage of Mn- and Fe ore microbialites, in spite of their similar syngenetic formation processes. This paper reviewed not only the authors' own research results on ore microbialites but also studies of other formations. Besides a geochemical and mineralogical summary, high resolution methodology and interpretation were also summarized. Recent conditions (rock, ore) and knowledge of biomineralization offer paleoenvironmental estimations.

The case studies reconsidered here show that overlooking the role of biomineralization can lead to incomplete conclusions. It is clear that making use of the experience and knowledge gained from research on ore microbialites and the possibilities for high resolution multi-methodology data collection and complex interpretation offer a more plausible and comprehensive interpretation with fewer contradictions in given depositional environments.

The synthesis of well known knowledge on new aspects can provide basically new results in the identification of formation conditions,

syngenetic and diagenetic processes, and also element enrichments based on mineral assemblages. The development of methods and instruments offers new horizons for investigation. Important analogies (Fe, Mn) for research of extraterrestrial life as robust biosignatures can also be proposed.

Documentation is deposited in the Archive of the Research Centre for Astronomy and Earth Sciences, Institute for Geological and Geochemical Research, Budapest.

## 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.

## Acknowledgments

The authors thank the support of National Research, Development and Innovation Office, National Scientific Research Fund Hungary, No. 125060. The authors are grateful to the comments made by two anonymous reviewers and by the guest editor H. G. Dill. The authors thank the support of authors of published papers on the subject, and the consultations with Gergely Szarkándi (University of Debrecen, Hungary) and Zsombor Molnár (Pannon University, Veszprém, Hungary).

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