Microbial action formed Jurassic Mn-carbonate ore deposit in only a few hundred years (Úrkút, Hungary)

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ABSTRACT

The Úrkút (Hungary) manganese (Mn) ore, hosted by Jurassic black shale, was studied using high-resolution mineralogical, microtextural, and chemical methods. Two independent superimposed biostatigraphic methods were identified consisting of rhythmic laminations that provide important proxies for paleoenvironments and duration of ore formation. Millimeter-scale laminae reflect a depositional series of Fe-rich biostromes, mineralized microbial produced sedimentary structures. These biostromes formed at the sediment-water interface under dysoxic and neutral pH conditions by enzymatic Fe³⁺ oxidizing processes that may have developed on a daily to weekly growth cycle. The early diagenetic sedimentary ore is composed of Ca rhodochrosite, celadonite, and smectite, and also shows a 100–1000-Å-scale element oscillation that produces Mn(OH)₂-rich and Si(Fe-clay)–rich microlaminae. This microlamination may reflect a 10 to 100 year rhythmicity produced by the growth of microbial communities. If true, then the giant Úrkút ore deposit may have formed over hundreds of years, rather than hundreds of thousands of years as previously thought.

INTRODUCTION

Extensive microbial mats colonize many sandy tidal flats along coasts (e.g., Noffke et al., 2003, 2006; Eriksson et al., 2007). This biophysical interaction gives rise to characteristic microbially induced sedimentary structures considered as important biosignatures for ancient microbial communities. Microbial mats also occur in a wide variety of present-day, shallow- to deepwater environments. Modern Fe-rich biostromes occur in various neutrophilic environments, and the microbial precipitation of ferric hydroxide is widespread (Fortin et al., 1997; Riding and Awwramik, 2000; Baede et al., 2008). Regardless of geologic age and geographic location, Fe-rich structures are interpreted to be associated with microbes and a paleoenvironment that often showed gradients in dissolved oxygen and Fe²⁺ at the seabed over extensive areas (tens of square kilometers; Pétai et al., 2000). An areal extent of 10⁶ km² was estimated for the Precambrian Hamersley Group (Australia) banded iron formation, which was proposed to have formed via microbial Fe³⁺ oxidation (Konhauser et al., 2002).

STUDY AREA AND ORE DESCRIPTION

We propose that the Jurassic manganese (Mn) carbonate ore deposit of the Úrkút Basin, Hungary, is an example of a series of ancient biostromes (Fig. 1). A new genetic model proposed for the Mn deposit shows that two cycles of bacterial activity existed during ore formation (Polgári et al., 1991, 2012). However, the mechanism for the laminae formation that characterizes the ore is still controversial and one of the main issues we address here. The original Mn deposit was an ore giant, with ~300 × 10⁴ t of ore (32 × 10⁴ t of Mn metal, 26 × 10⁴ t of Fe, 5 × 10⁴ t of SiO₂), with an areal extent of tens of square kilometers. The ore deposit consists of 3 ore beds (10, 3, and 1 m thick), separated by a 20-m-thick black shale (Fig. 1B). The duration of ore formation was not more than 500 k.y., based on ammonite zones (Géczy, 1973).

The black-shale-hosted Mn-carbonate ore deposit is laminated (millimeter scale; Fig. 1C). This has been attributed to variations in mineralogy. The ore ore shows a millimeter-scale brown (goethite) lacework texture. The matrix is compositionally dominated by Mn-carbonate and clay minerals, and supports the Fe lacework over distinct intervals. We interpret the Fe lacework as a biosignature for Fe-rich biostromes, similar to those reported to be a robust indicator for biostromes (e.g., Chan et al., 2011). If this interpretation is correct, then this series of Fe-rich biostromes characterizes the entire thickness of the ore over its areal extent (now ~8 km²). Laminated sedimentary rocks are generally attributed to deposition in an anoxic environment (Wignall, 1994). However, we propose that Úrkút ore-deposit laminae formed from biostromes at the sediment-water interface. Here we show that the paleoenvironment and duration of ore formation can be constrained by determining the mechanism of laminae formation.

SAMPLES

Oriented samples of an almost continuous section of the Mn-carbonate ore were collected and described (Fig. DR1 in the GSA Data Repository¹). Evidence for erosion was not found. We collected 112 samples from 5 sections in the Úrkút Mn mine. The Mn-carbonate samples included a total of 757 cm for lamina analyses; because of the variability in the thickness of the section, 800 cm was used for all calculations.

RESULTS

Thin-section microscopy of Mn-carbonate samples showed structures resembling Fe-rich biostromes (Fig. 1D; Fig. DR2). The brown laminae are variable in thickness and frequency of occurrence; however, they define an approximately regular, millimeter-scale rhythmic laminations in the ore bed. Thin sections show a fabric-like lacework texture within the clay (celadonite, nontronite) and Mn-carbonate matrix described previously as an interwoven, filamentous meshwork (see Polgári et al., 2012, for a detailed description of biogenicity). Mineralized filamentous structures range in thickness from ~1 to 10 μm. Solitary carbonate, clay clusters, and quartz grains float or are embedded within the laminated matrix without grain to grain contact. These intervals show generally sharp upper and lower contacts macroscopically, but microscopically the contacts are more diffuse.

Bulk samples and individual laminae were analyzed using X-ray powder diffraction (XRD; Fig. DR3). The XRD showed five main components in the ore beds in variable amounts: Ca rhodochrosite, celadonite, nontronite, and goethite, and, in the upper bed, siderite (Figs. 1E and 1F). The clay minerals are authigenic (Weiszburg et al., 2004). Less abundant components include bioclastic quartz, Mn-bearing calcite, apatite, feldspar, pyrite, barite, manganese, katoahorite, clinoptilolite, and gypsum.

On the basis of fine-scale Raman spectroscopic analyses, the distribution of minerals did not show major differences between laminae, but the goethite- or pyrite-bearing brown laminae show a 500–750 μm rhythmicity (Figs. 1G and 1H; Fig. DR4). Three representative thin sections were analyzed for Mn, Fe, Si, Al, Mg, Ca,

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¹GSA Data Repository item 2012255, supplement Figures DR1–DR6, is available online at www.geosociety.org/pubs/tt2012.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.
and K on a micrometer scale by scanning electron microscopy—energy dispersive spectrometry. Line-profile analyses showed Mn(Ca)-rich and Si(Fe clay + biocalyca)-rich oscillations on a 100–300 μm scale, called here microlaminae (Fig. DR5). Comparing the element distribution with the XRD mineralogy, Ca-rhodochrosite-rich and celadonite-smectite-rich microlaminae alternate (Figs. II and J).

For a more quantitative analysis of periodicity, a Lamb-type calculation was used together with element-correlation analyses that support the XRD mineralogy (Figs. DR5 and DR6; correlation of Si-K-Al-Mg in clay). Periodicity analyses resulted in a 750 μm periodicity for all thin sections and for all the major elements (Mn, Fe, Si). On the basis of this ~750 μm periodicity, the total Mn-carbonate sequence contains 10,667 brown laminae (used in all calculations). There is also a shorter microlamination periodicity (100–300 μm).

DISCUSSION

Millimeter- and Micrometer-Scale Rhythmicities

Laminated sediments have been shown to form during more or less continuous sediment accumulation, with variation in some characteristics such as mineralogy, color, and grain size. The Ürküt samples show the same variations, but in contrast, the Ürküt deposit is a chemical and diagenetic-authigenic mineral deposit that shows a distinct interwoven texture. We propose that microbial mats, reflected now as brown goethite, produced the millimeter-scale lamina in the Mn-carbonate ore. In general in the ocean basins, most varved sediments in 100–1000 m water depths reflect annual or seasonal changes in climate, productivity, detrital input, and other drivers (Chambers et al., 2000). In the Early Jurassic, the Ürküt Basin was a tropical zone; a warm and humid climate was characteristic, with wet and dry seasons, for all of the Jurassic. The Ürküt was a starved basin and isolated from sources of terrigenous debris (Polgári et al., 2012). Transport of detrital minerals was mainly by wind seasonally, but that input is not distributed in a way that would produce millimeter-scale rhythmicity. The mineralogy of the Ürküt clays indicates a predominantly authigenic rather than wind-blown origin. The dominance of Mn-carbonates and authigenic clay minerals masked the background sedimentation to such a degree that seasonal changes are not discernible.

Significant changes in grain size are usually accompanied by changes in mineralogy. In the Ürküt deposit, the grain size is uniformly fine grained throughout, interrupted only over some distinct intervals where coarser bioclastic debris occurs (Mn-bearing calcite or apatite). However, the distribution of bioclastic debris does not produce the millimeter-scale rhythmicity. Nutrient supply is a key issue, but a seasonal or annual nutrient proxy cannot be identified in these samples. Consequently, our new approach to estimate the duration of ore formation is based on microbial layering.

Understanding the biochemistry of biotite formation is key to determining the type of Fe-rich biotite that may have been involved in formation of the Ürküt ore deposit, and to defining the environmental conditions. There are various types of microbial metabolisms that can oxidize FeIII. All of these occur only under varying states of oxygen-deficient conditions. Three types of Fe-rich biotites are considered for the Ürküt; all are neutrophilic and consistent with seafloor conditions determined for the Ürküt Basin: (1) Gallionella-like microbial neutrophilic, microaerobic FeIII oxidizing bacteria with photosynthetic metabolism (Konhauser, 1998); (2) Gallionella-like nonphotosynthetic neutro-
philic, microaerobic microbial Fe$^{III}$ oxidizing bacteria (Konhauser, 1998; Hallbeck and Pedersen, 1990); and (3) non-Fe-oxidizing microbes later overgrown by Fe oxides via microbial processes (Konhauser, 1998). Of the three types of microbial Fe$^{III}$ oxidation, photosynthetic metabolism produces a daily rhythmicity with growth only during daylight. Biomat growth would have been in competition with authigenic sediment formation. If the bacterial mats were photosynthetic, then the water depth of formation was shallower than earlier thought, but nonetheless deeper than the influence of storms; however, definitive evidence is lacking regarding the paleobathymetry of the Ūrkút deposit (Polgári et al., 2012). Alternatively, nonphotosynthetic microbial Fe$^{III}$ oxidizing bacteria can also produce rhythmic developmental stages. Free-living Fe$^{III}$ oxidizing bacteria exist in the lag and log phases, and stalk formation (Fe-rich biomat) occurs during the stationary (stat) phase under optimal conditions (pH > 6, aerobic, cell number > 6 x 10$^4$ ml$^{-1}$, low organic C content, 1–3 week whole microbial population growth period; e.g., Gallionella-like freshwater types) (Hallbeck and Pedersen, 1990; Chan et al., 2011). Lag, log, stat, and declining (dec) phases represent microbial population growth phases (Fig. DR2). When biominereralization occurs only during some phases of microbial growth, the microbial layering can be used as a time scale. Fe and Mn are widespread at the Earth's surface and both have strong and variable associations with microbial activity, making them ideal for this type of analysis.

A marine Gallionella-like microbe, Marineprofundus feroxoxidans (neutrophilic Fe$^{III}$ oxidizing bacteria), is similar morphologically and physiologically to Gallionella, although 16S RNA gene phylogeny shows that they are not closely related genetically (Emerson et al., 2010). Filaments of Marineprofundus are characteristically 1.7 μm thick, but can be as long as 70 μm. Doubling time at 23 °C is 12–24 h, and the population growth curve shows a 96 h lag phase, 144 h log phase, and a stationary phase that occurs only in the first 48 h (Emerson et al., 2010); according to these data, population growth fits well with a 3 week rhythmicity. Stalks can grow as long as 60–400 μm per cell per day (Chan et al., 2011).

Non-Fe-oxidizing microbes may have been the sole microbiota involved in mat formation. The main difficulty with this scenario, however, is the uniformity of the Fe lacework structures throughout the section, which would not be expected through inorganic processes.

Understanding the microbial processes would be easier if organic biomarkers were directly associated with the Fe-rich biomat structures. Raman data show organic matter in the goethite lacework, but is not diagnostic as to the type of organic matter. Biomarkers cannot be isolated because of multiphase microbial activity and extensive diagenetic overprinting, during which the degradation of the organic carbon was involved in the formation of carbonate ore.

Nutrient supply for rapid biomat formation is a key requirement and nearly everywhere in modern shallow-water environments is seasonal. However, a nonseasonal nutrient supply is proposed for the Ūrkút Basin. Chemolithoautotrophic metabolism requires chemically produced nutrients supplied by chemical gradients in the sediment. Fluid migration probably occurred via geothermal-driven discharge (Polgári et al., 2012).

A daily to weekly rhythmicity of biomat formation for the Ūrkút laminae would require that the deposit formed over only a few centuries, during which an estimated 58 x 10$^4$ t of metals (Mn plus Fe) accumulated. Even larger accumulations of Fe (253 x 10$^4$ t) have been proposed to have formed over ~700 yr in banded iron formations (Morris, 1993). It is clear that under certain unique conditions, such as density brines in the Red Sea (Atlantic II deposits), large low-grade metal deposits can form over short periods of time, i.e., thousands of years. The Ūrkút Basin may also have had a unique mechanism to concentrate metals over even shorter time periods, but direct evidence for that mechanism has not been preserved.

Duration of Ore Formation Based on Millimeter-Scale Laminae

The duration of ore accumulation is estimated based on the number of biomat laminae that formed with a daily to weekly rhythm. A daily minimum and a three-week maximum rhythm were used to calculate the range of possibilities assuming photosynthetic and nonphotosynthetic scenarios for Fe$^{III}$ oxidizing biota. For 1 biomat lamina formed per day (or several days duration for the photosynthetic case), then 10,667 lamina would have formed in ~27 yr. The length of a day in the Jurassic was ~22 h and the year was ~398 days. For the nonphotosynthetic case, 10,667 coupllets would yield 563 yr for the duration of ore formation based on an estimated 3 weeks for a microbial population growth cycle.

Duration of Ore Formation Based on Micrometer-Scale Oscillations

Two cases are considered in the interpretation of (Mn(α)-rich and Si(Fe clay)-rich) (100–300 μm) microlaminae rhythms. Two seasons per year most likely characterized the paleoenvironmental tropical climate. That would mean that a Mn(α)-rich and Si(Fe clay)-rich (clay + bisilica) couplet represents 1 yr. Based on 100 μm, the 8 x 10-μm-thick Mn-carbonate section would include 80,000 microlaminae, and one-half of that yields 40 kyr for Mn ore accumulation. Mnf$^{III}$ oxidizing microbial metabolism in general can also be considered for the Ūrkút Mn ore. The bacterial population growth period for the freshwater Mn$^{III}$ oxidizer *Leptothrix discophora* SS1 is 80 h (3.3 day; lag + log phases 20 h; stat phase 20–70 h; dec phase 10 h) with the start of Mn$^{III}$ oxidation in the early stationary phase (Zhang et al., 2002; Dworkin et al., 2006). Taking Mn$^{III}$ oxidizing microbial growth stages from the literature (assuming that marine forms have similar growth periods), and the minimum 100 μm lamina rhythmicity, the 40,000 coupllets represent a duration of 332 yr for ore formation.

Combination of Cycles

A combination of the two independent rhythm processes can provide further understanding of the complex development of the Mn-carbonate ore.

(1) The first process entails calculations based on the brown Fe-rich biomat interwoven sections that represent periods of sunlight: a thickness is 0.4 mm (about one-half the 750 μm rhythmicity); this thickness includes four microlaminae (based on 100 μm thickness), and daylight is 11 h (660 min). During that time four microlaminae formed, one-half Mn(α) rich and half Si(Fe clay) rich; 1 microlamina formed during ~165 min (for the coupllets 330 min or 15 h). Taking the 15 h couplet formation time and the minimum 100 μm lamina rhythmicity, the 40,000 coupllets represent 69 yr for the duration of ore formation.

(2) For the nonphotosynthetic case, 10,667 brown Fe-rich laminae and 3 weeks duration for microbial Fe$^{III}$ oxidizer population growth yield 123 h (5.6 days) per couplet of micrometer-scale rhythmicity. For the 123 h couplet formation time and the minimum 100 μm lamina rhythmicity, the 40,000 coupllets yield a duration of ore formation of 562 yr.

All these time intervals fit well with prokaryote generation times and cyclicality of microbial populations, but the best fit with literature data (Zhang et al., 2002) is version 2. On the basis of these hypotheses of daily to weekly rhythmities, and seasonal or microbial population growth periods, the duration of ore formation ranges from ~27 yr to ~40 kyr. All estimated durations indicate remarkably rapid accumulation of some sedimentary ores.

Paleoenvironmental Considerations

Formation of the Ūrkút main Mn ore bed occurred under aerobic conditions, where microbial Mn$^{III}$ enzymatic oxidation (with reactive organic matter) resulted in fine-grained accumulation of Mn oxides (cycle I), which later transformed to Ca-rodochrosite via bacterially mediated processes during suboxic early diagenesis (cycle II; Polgári et al., 1991, 2012). These redox conditions supported celadonite formation from mixing of geological fluids with seawater at the sediment-water interface or close to it during sedimentation and very early
diagenesis. The formation of celestolite reflected slight changes in redox conditions, from an oxidizing water-dominated environment (microbial Mn⁺ enzymatic oxidation, aerobic system with dissolved oxygen, DO > 2 mL/L), through dysoxic (DO 0.2–2.0 mL/L), to suboxic (DO 0–0.2 mL/L) conditions. Authigenic celestolite formed at low temperatures (17–23 °C; Polgári et al., 2012) and was colonized by Fe²⁺ oxidizing microbes (Fe-rich biomats) in a neutrophilic dysoxic-suboxic environment. The conditions changed to a more reducing environment after burial, when smectite and later nontronite formed and locally pyritization of goethite-replaced biomats took place (Fig. 2; Fig. DR2).

CONCLUSION

Independent but superimposed biostrokes can be important indicators for paleoenvironments, not only in laminated sediments but also in sedimentary ore deposits, offering the opportunity for novel approaches to determination of ore genesis and duration of ore formation. Millimeter-scale (0.7 mm) Fe-rich biomats can form daily or weekly and may give rise to the rapid accumulation of giant ore deposits such as the Úrkút Mn deposit. Based on our analyses of laminae in the Úrkút deposit, it is hypothesized that the upper limit for the duration of ore formation was 40 k.y., but it is more likely that ore formation took only several hundred years.

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REFERENCES CITED


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