

Scientific highlights (2013-2016)

2013

Celadonite and smectite formation in the Úrkút Mn-carbonate ore deposit (Hungary) – Synsedimentary and early diagenetic oxygen levels are estimated by evaluating celadonite-smectite formation in marine Jurassic black shale-hosted manganese-carbonates. Celadonite formed under suboxic-dysaerobic conditions, Al-rich Fe-smectite formed at suboxic-anaerobic conditions, and nontronite formed at anoxic-anaerobic conditions during sedimentary burial. A genetic pathway by direct precipitation from solution is proposed for the enormous mass of celadonite, based on mineral and textural evidence. Lamination of the manganese ore is independent of clay-mineral composition and was given by a series of mineralized microbial Fe-rich biomats.

Clay minerals constrain the paleoenvironmental conditions during formation of the Úrkút Mn ore deposit. The clay minerals formed synchronously in different parts of the sediment column under different redox conditions, celadonite at the sediment/water interface or very close to it, and smectite in the deeper, more reducing parts. A pathway of celadonite formation is proposed by direct precipitation from solution en masse. Nontronite formed in the reducing part of the sediment column. These results show that celadonite and nontronite indicate palaeo-oxygen level fluctuations in the environment. Biomats reflect suboxic conditions, which changed to anoxic with increasing burial. Color in the Úrkút deposit does not reflect oxygen conditions as commonly thought; for example, brown can be anoxic (nontronite) and green suboxic (celadonite), so color as a paleoproxy must be used with caution.
Estimated formation conditions of the clay minerals in the black shale-hosted Mn carbonate ore deposit (Ürküt), zone of microbial Fe(II) oxidation (+0.3 V Eh using recent analogs; Konhauser, 1998; Hallbeck and Pedersen, 1990; Emerson et al., 2010), and the results of nontronite synthesis laboratory experiments (by dashed lines, Harder, 1976, 1978). Note: in general oxidizing conditions mean high oxygen concentration (high Eh values up to +0.4V), while reduced conditions reveal a lack of oxygen (low Eh down to -0.2V. Eh estimation is based on Wignall, 1994).
Geological profile with sample locations of the Úrkút Mn-carbonate deposit (Sampling 2009, Úrkút Mine, Shaft No. III, deep level, +180 m; total No. of samples 112 spanning 917 cm from the base to the top of the three ore layers and the intervening black shale). Key: fragm-fragmented sample; cont.-continuous sampling; not cont.-not continuous sampling; numbers on the stratigraphic columns are sample numbers; * indicates samples for XRD; 0 indicates samples for thin sections (in brackets the number of thin sections, total 90); Profiles 1, 3, 4, 5 are from main ore bed, Profile Za and Zb are from second ore bed. Patterns show only color varieties and not sedimentary structures; (C1) green (C2) brown Mn-carbonate ore.
2015
The presence of anomalous terrestrial radioisotopes must be suspected in black shale-hosted manganese ore deposits, based on high organic matter content, which is useful tool in genetic, among them paleoenvironmental investigations. Our work aims at the characterization of the paleoredox conditions of the Úrkút Manganese Formation based on terrestrial radioisotopes. Paleoredox indicators were estimated and interpreted for the whole profile using U/Th, δU, rare earth element (REE) patterns, and other trace elements, enrichment factors (EF) and excess (EX) of elements. The results of paleoredox indicator element ratios show, that these methods must be used with caution (microbial selective element enrichments, mobilizations), and the complex interpretation using mineralogy and microtexture can be recommended.

2016
The genesis of a suite of Jurassic (Lias) microbialites at the Úrkút black shale-hosted manganese carbonate ore body (central Hungary) is described by a two-step microbial formation model that uses mineral chemistry combined with whole-profile (up section) textural context and sulfur isotopic compositions of associated pyrite and barite. Petrogenetic analysis and paleoenvironmental reconstructions show that the sedimentary regime of the Úrkút microbialites mostly behaved as an open system during deposition of black shale under early diagenetic conditions. Sulfur isotopes and other chemostratigraphic indicators, however, reveal that the Mn ore bed horizons reached semi-closed/closed conditions which modulated sedimentation rate and organic matter burial. Barite formation occurred under semi-closed/closed conditions at diagenesis, and the Ba source is attributable to the decomposition of organic matter derived from plankton and other marine organisms, as well as transformation of biogenic silica. Pyritiferous horizons host equant, framboidal and euhedral morphotypes. The distribution and size of euhedral and framboidal sulfide habits is consistent with later diagenetic sulfate reduction under an oxic water column; more equant types occur at the contact zone of black shale and Mn-carbonate horizons. The microbialites of Úrkút bear strong similarities to ore bodies at Molango (Upper Jurassic, Mexico) and Tao Jiang (Middle Ordovician, China). Manganese supply and trace metal contents (Co, Ni, Zn, Cd and As) of the sulfides also point to the effects of distal hydrothermal fluid sources to the system.
Sulfur isotope distribution of barite and pyrite in the black shale-hosted Mn-carbonate deposit, Úrkút.
Thin section optical microscopy photos. Thin section photos showing Fe-rich biomat structures for different representative samples and magnifications (sample numbers are on the photos), and pyrite. The thickness of the thin sections and the density of biomats are variable (A, B, C, G by transmitted light). Arrows show representative parts of mineralized filamentous structures, partly pyritized on (A) and (B). (D, E, F, H) Reflected light photos of samples, showing euhedral (C, D, E), equant (G, H) and framboidal (F - arrow) pyrite. (D) is reflected light photo of (C); (H) is reflected light photo of (G).
A mineralogical and geochemical multiple proxy study of the Toarcian black shale that hosts a microbially mediated Mn-carbonate ore deposit at Úrkút in central Hungary was undertaken to determine its petrogenesis and paleoenvironmental setting.

The main conclusions are:
1. The Úrkút black shale is a gray shale, lean in organic matter.
2. The dominant mineralogical assemblage is authigenic rather than detrital.
3. The depocentre was a starved basin during accumulation of the black shale in the sense of diminished input of mineral detritus.
4. The organic matter content and diagenetic anoxic features were the result of rapid accumulation of microbial organic matter that resulted from microbial booms accompanied by geothermally generated hydrothermal circulation systems, and the high rate of accumulation of authigenic minerals (clay minerals and proto-ore minerals). The organic matter was trapped and degraded in a suboxic-anoxic diagenetic environment where pyrite was produced, decreasing the abundance of organic matter.
5. The sharp contact between the limestone/marlstone footwall and black shale unit Bs1 and the Mn-ore deposit reflect the initiation of hydrothermal vent systems in the marine basin. The inferred enzymatic Mn and Fe oxidation blocked carbonate formation by decreasing pH.
6. Even though Mn-oxide accumulation started very close to the contact with the underlying unit, accumulation of proto-ore did not initially predominate probably because of oxygen deficiency, because Mn(II) enzymatic oxidation is obligatory to this process. But the system remained suboxic via syngenic mineral accumulation (Fe-rich biomats), and became anoxic through diagenesis.
7. The separation of black shale beds and ore beds is not distinct throughout the section. Instead, a distal hydrothermally induced clay mineral-rich authigenic assemblage (marlstone) best describes the black shale, in which distinct Mn-oxide proto-ore beds (Mn-rich laminae) formed from nearly the beginning of black shale deposition, when the oxygen supply in the sedimentary basin was insufficient for enzymatic Mn(II) oxidation. Mn-oxide proto-ore transformed into Mn carbonate ore via microbially mediated processes during early diagenesis. Ore beds resulted where these Mn-rich laminae in the BS were highly enriched and abundant.
8. The drivers of Mn-bearing, relatively low organic matter, marlstone formation, compared to other Toarcian black shales, were most probably a combination of regional and local processes. Generation of a tectonic rift system promoted geothermally generated circulation cells and hydrothermal fluids and also initiated microbial blooms. The TR, and other regions of the Tethyan realm supported formation of black shales under this complex set of processes. These black shale-hosted Mn-carbonate deposits are indicators of ancient failed rift systems.
9. The Úrkút black shale and Mn ore paleoenvironmental proxies are very similar. Mineralogy, geochemistry, and organic matter are consistent with previous results of the Úrkút, but differ from those of the Tethyan epicontinental shelf occurrences.
Representative samples. Arrow shows to top of sample according to profile; no arrow: not oriented.

XRD mineralogy
Contributions from various sources and processes on black shale mineralogy. Bold black lines represent ore horizons, bold dashed lines represent hiatus in black shale sections.