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Mineral and chemostratigraphy of a Toarcian black shale hosting Mn-carbonate microbialites (Úrkút, Hungary)

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ABSTRACT

Toarcian black shale that hosts Mn-carbonate microbialites at Úrkút, Hungary was investigated by mineralogical, inorganic, and organic geochemical methods for characterization and comparison with other European black shales representative of the Toarcian Oceanic Anoxic Event. Based on the authigenic mineral composition, calculations were made to estimate environmental conditions during sediment accumulation and early diagenesis. Geochemical and petrographic results of organic, carbonate, and REE multiple-proxy analyses revealed a strong congruence between the host black shale and the Mn-carbonate ore beds. The Úrkút black shale is really a gray shale with moderate to low TOC contents that accumulated in a starved basin. The organic matter and anoxic characteristics resulted from rapid accumulation of organic matter from microbial booms, accompanied by a geothermally generated hydrothermal circulation system, and a high rate of authigenic mineral formation (clay minerals and proto-ore minerals). The inferred enzymatic Mn and Fe oxidation blocked carbonate formation by decreasing the pH. The system remained suboxic via syngenetic mineral accumulation (Fe-rich biomats), and became anoxic during diagenesis in conjunction with pyrite generation. The separation of black shale beds and Mn-ore beds is not distinct through the section. Instead, a distal hydrothermally induced clay-rich authigenic assemblage (marlstone) best describes the black shale, in which Mn-oxide proto-ore beds (Mn-rich laminae) formed from 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 was transformed to Mn-carbonate ore during microbially mediated processes during early diagenesis. The drivers for Mn-bearing organic matter-rich marlstones were most probably a combination of regional and local processes, with generation of a tectonic rift system that promoted geothermally generated hydrothermal fluids, which initiated microbial blooms. Black shale mineralogy, geochemistry, and organic matter at Úrkút differ from those of the epicontinental shelf black shales of the Tethyan Ocean.

1. Introduction

Organic geochemistry of black shales has been widely studied (e.g. Wignall, 1994; Jenkyns, 2010) because of their key role in understanding global changes, for example the Toarcian Ocean Anoxic Event (T-OAE). Black shales are of enormous economic importance because they are source rocks for the bulk of the World's hydrocarbons, and metalliferous black shales form ore deposits for many metals (e.g. Fe, Cu, Ni, Pb, V, Mo, Mn), and yet they are among the least understood sedimentary rock (e.g., Coveney and Chen, 1991;

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Pašava, 1993; Loukola-Ruskeeniemi, 1999; and others). The identification of paleo-oxygen levels is therefore of critical importance in the paleoenvironmental reconstruction and understanding the genesis of black shales (Wignall, 1994).

In the early Toarcian, global environmental change caused considerable mass extinction of terrestrial and marine organisms (Jenkyns, 1985, 1988; Pálfy and Smith, 2000; Pálfy et al., 2002). At the same time, a ~5–7‰ negative $\delta^{13}C$ excursion of carbon reservoirs was identified (marine organic matter, marine carbonate, terrestrial plants), as well as an abrupt increase of ocean water temperature (Küspert, 1982; Jenkyns and Clayton, 1997; Hesselbo et al., 2000; Rosales et al., 2004; Kemp et al., 2005). As a consequence of global, regional, and local effects, the accumulation of organic material increased resulting in a global distribution of black shales (Jenkyns, 1985, 1988; Haas, 2012).

For interpretation of the enriched organic matter accumulation and the negative $\delta^{13}C$ excursion, models were established. Among those models, some key global and local ones include: (i) Volcanism (Karoo–Ferrar continental plateau basalt formation) as a global catastrophe was the driving force for climate change that triggered black shale deposition. The global response to considerable volcanic CO_2 emission resulted in changes of sea level and current systems, which led to increased biomass productivity in upwelling zones (Jenkyns, 1985, 1988; Jenkyns and Clayton, 1997; Vető et al., 1997; Pálfy and Smith, 2000; Röhl et al., 2001; Schmid-Röhl et al., 2002; McArthur et al., 2008). (ii) Massive dissociation of methane hydrates caused by the warm climate was also proposed (Hesselbo et al., 2000; Kemp et al., 2005). (iii) Water stratification in silled basins may have obstructed oxygen supply, a local process without invoking global drivers (e.g., salinity differences, Röhl et al., 2001; Schmid-Röhl et al., 2002; Schwark and Frimmel, 2004; van de Schootbrugge et al., 2005). (iv) Mixed scenarios of global events, e.g. reduced levels of atmospheric oxygen and global ocean changes (Hallam, 1967, 1981). Early Toarcian black shales occur worldwide, although their onset and decline are potentially diachronous (Wignall et al., 2005). Understanding the conditions of formation and paleoenvironments of the black shales is important; clarification of global, regional, and local drivers is a great challenge (Haas, 2012).

Two types of lower Toarcian black shales of the western Tethyan Ocean can be distinguished (Jenkyns, 1985, 1988): (i) accumulation on an epicontinental shelf [(boreal, Jet Rock, Great Britain (Sælen et al., 2000); Schistes Cartons, Paris Basin, France (Hollander et al., 1991; Katz, 1994); Posidonia Shale, Germany (Röhl et al., 2001); Lusitanian Basin, Portugal (Jenkyns, 1985, 1988; Duarte, 1998)] and (ii) Alpine–Mediterranean Tethyan Region [(Umbria–Marche Basin, Italy (Jenkyns, 1985, 1988; Duarte, 1998); Úrkút basin, Hungary (Polgári, 1993; Vető et al., 1997; Polgári et al., 2012a)]. The boreal type occurs as shallow-water shelf sediments 15–30 m thick, with 5–15 wt.% TOC and a Hydrogen Index (HI) of 300–600 mg HC/g TOC. The Alpine Mediterranean type occurs in pelagic limestone, in rifted areas of Atlantic-type continental margins, with TOC between 1 and 3 wt.% (up to 10 wt.%), and a generally low HI, 200–300 mg HC/g TOC (Jenkyns, 1985, 1988). Transitional types exist, which show mixed features [(Mecsek Réka Valley Óbánya Siltstone Formation (MRV-ÓSF), Hungary (Varga et al., 2007; Raucsik and Varga, 2008a); Basque-Cantabrian Basin, northern Spain (Rosales et al., 2004)] (Fig. 1). Besides these typical Toarcian black shales, another classification differentiates between the pure non-ore bearing and an ore-bearing, namely Mn-carbonate types.

Sedimentary Mn deposits have a wide distribution in time and space (Roy, 1981). Their formation extends through more than half of geological history and they are extensively distributed both in the geological record on the continents and on the bottom of the present-day oceans, shallow seas, and lakes. The Jurassic (Toarcian) was an important time of Mn-carbonate mineralization and different ideas about the controls on deposit formation have been put forward, including tectonic activity, volcanism, climatic variations, and combinations of these. Mn-carbonate deposits are typically associated with organic carbon-rich beds (Roy, 1981). Black shale-hosted Mn-carbonate deposits are numerous and most deposits have large reserves of manganese ore with grades of 20–30 wt.% Mn. Numerous subeconomic black shale-hosted Mn deposits occur along with the giant Úrkút deposit in the Alpine–Mediterranean Tethyan Realm (Transdanubian Range: TR) (Jenkyns, 1988; Jenkyns et al., 1991). Stratiform black shale-hosted Mn-carbonate deposits reached maximum development during the Toarcian *tenuicostatum–falciferum* ammonite zones in the Strubberg and Allgäu deposits of the Northern Calcareous Alps and Eastern Alps, the Úrkút deposit in the TR of the Southern Alps, in the Tatra unit, and lower Carpathians (Polgári et al., 2012a and references therein).

At different locations, the black shale-Mn associations show similarities and differences: (1) contemporaneous oxic deposits formed under similar environmental conditions occur in some locations (Jenkyns, 1988); (2) not all black shale sections are enriched in manganese (Jenkyns, 1988; Jenkyns et al., 1991, 2001); (3) if they are Mn-rich, the TOC content is relatively low, only 4–5 wt.%, which may support a microbial origin for the Mn-carbonate deposits (Jenkyns, 1988; Polgári et al., 2012a); (4) negative $\delta^{13}C$ values of early diagenetic $MnCO_3$ support a contribution from organic carbon to the dissolved carbon reservoir (Polgári et al., 1991); (5) Mn(IV, III) oxides characterized the proto-ore because initial metal enrichment took place in an oxic seafloor environment (Polgári et al., 2012a). This oxic depositional environment contrasts with the generally accepted explanation for the formation of a laminated black shale, assumed to result from very limited benthic infauna. (6) High primary productivity occurred during black shale deposition (Jenkyns, 1988, 2010; Jenkyns et al., 1991, 2001; Vető et al., 1997) and biomarker studies indicate that organic matter in all these lower Toarcian black shales is dominantly of marine origin, derived from algal and bacterial sources (Farrimond et al., 1989; Polgári et al., 1992; Polgári, 1993; Jenkyns et al., 2001). (7) Formation of $MnCO_3$ immediately pre-dated deposition of the TOC-rich shales in the majority of localities suggesting that their deposition was characteristic of environmental conditions immediately preceding the anoxic event (Jenkyns et al., 1991). (8) Black shale formation was structurally confined to rifted continental margins of the developing Tethyan Ocean (Bernoulli and Jenkyns, 1974; Channell et al., 1992). Wignall (1994) stressed the possibility that abundant organic carbon deposition overwhelmed the benthos, thereby promoting formation of laminae even with oxic bottom waters.

Diagenetic processes overprinted the seabed manganese depositional signals and caused significant transformations, such as formation of early diagenetic rhodochrosite (e.g. Polgári et al., 1991). The large mass of bacteria living in and on the surface of the sediment provided a large pool of reactive organic matter after death that promoted a series of diagenetic reactions. During decomposition, the consumption of the organic matter by other microbial consortia may have played a key role in diagenesis through formation of the Mn-carbonate ore. Those anaerobic bacterial cycles were different from the syndepositional aerobic bacterial cycle, although both occurred contemporaneously at different depths in the sediment column (Polgári et al., 2012a).

The black shale-hosted stratiform Mn-carbonate deposits were reported to have mainly a hydrothermal metal source and microbial processes were thought to have occurred in some of the deposits (Cornelius and Plöchinger, 1952; Gruss, 1956; Polák, 1957; Andrusov, 1965; Germann and Waldvogel, 1971; Germann, 1971; Bernoulli and Jenkyns, 1974; Faupl et al., 1982; Beran et al., 1983; Jenkyns, 1988; Krainer et al., 1994; Krajewsky et al., 2001; Rantitsch et al., 2003; Polgári et al., 2012a,b). During the past 100 years, numerous studies have addressed the complex formation of the Jurassic black shale-hosted Mn-carbonate ore at Úrkút. The ore beds are now thought to have resulted from a two-step, microbially mediated process that produced a microbialite (Polgári et al., 2003a,b, 2012a,b, 2013a,b, 2016). This important deposit is among the 10 largest Mn deposits in its type with