Sedimentary Geology 363 (2018) 221–234

Contents lists available at ScienceDirect

Sedimentary Geology

journal homepage: www.elsevier.com/locate/sedgeo

Invited research paper

Manganese carbonates in the Upper Jurassic Georgiev Formation of the Western Siberian marine basin

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ARTICLE INFO

Article history:
Received 16 September 2017
Received in revised form 16 November 2017
Accepted 17 November 2017
Available online 1 December 2017

Editor: Dr. B. Jones

Keywords:
Mn carbonates
Upper Jurassic
Western Siberia
Diagenesis
Geochemistry

ABSTRACT

Manganese (Mn) carbonate rocks are a common lithological constituent of the Upper Oxfordian to Lower Tithonian (Volgian) Georgiev Formation of the Western Siberian marine basin (WSMB). The Mn carbonates in the Georgiev Formation are present in the form of massive sediments, stromatolites, and oncolites, and are associated with glauconite and partly also phosphate-rich clay- and siltstones. Unlike most Mn carbonates, they are not directly associated with organic-rich sediments, but occur below an organic-rich succession (Bazhenov Formation). The Mn carbonate occurrences can be traced from the western central area of the WSMB to its center along a distance of at least 750 km. The thickness of the Mn carbonates and their Mn contents becomes reduced in an eastward direction, related to increased detrital input. The geochemical and mineralogical heterogeneity within the Mn carbonates indicates that they were deposited stepwise in a diagenetic regime characterized by steep gradients in Mn, Ca, and Mg. A first step consisted in the replacement of initial sediments within the microbialites during an early diagenetic stage, followed by a second step where massive sediments were transformed into Mn carbonate. During both steps, the decomposition of organic matter was an important source of the newly formed carbonate. During a further step, voids were cemented by Mn carbonates, which are rich in pyrite. This last generation may only have formed once the organic-rich sediments of the overlying Bazhenov Formation were deposited. Accumulation of the Mn carbonates in the Upper Jurassic WSMB was controlled by the proximity of Mn-enriched parent rocks, likely in the Ural, which were subjected to intense geochemical weathering during the Late Jurassic.

1. Introduction

The geochemical behavior of manganese (Mn) in marine environments is strongly dependent on redox conditions. In oxygenated bottom waters and sediments, Mn^{4+} tends to be precipitated in the form of Mn-oxyhydroxide, which dissolves once transferred into an anoxic environment (e.g., Hem, 1972). Mn is liberated in the form of Mn^{2+}, which may be transferred into a diagenetic carbonate phase or is recycled back into the bottom waters (Calvert et al., 1996; Calvert and Pedersen, 1996). The two main sources of Mn in marine sediments are hydrothermal activity and continental biochemical weathering (Kuhn et al., 2005; Hein and Koschinsky, 2014). Mechanisms leading to Mn enrichment include Mn delivery from oxygen-minimum zones by upwelling and Mn accumulation along the oxygenated margins of anoxic basins (Frakes and Bolton, 1984; Maynard, 2010, 2014).

Microbial activity was often described as instrumental in the formation of Mn carbonates (Polgári et al., 2004, 2012a, 2012b; Dubois et al., 2015), which is usually taken to be close to the sediment/water interface (Heiser et al., 2001). The scarcity in detrital supply and low accumulation rates in general is a further factor, which was implied in the precipitation of Mn carbonates (e.g., Mongelli et al., 2010). Finally, the frequently observed increased concentration of Mn in carbonate concretions may be related to the large difference in calcium (Ca) and Mn solubility under diagenetic conditions, with the effect that Mn^{2+} cations primarily bind with CO_3^{2-} anions, in spite of the generally lower concentrations of Mn^{2+} relative to Ca^{2+} (Strakhov et al., 1968; Yudovich et al., 1998; Yudovich and Ketris, 2013).

The occurrence of Mn carbonates hosted in organic-rich sediments is known from different parts of the world and different time periods (Polgári et al., 2004, 2016; Yudovich and Ketris, 2013). They are, for instance, present in sediments of the modern Baltic Sea, where periodic changes between oxic and anoxic conditions influence sedimentation pattern and the (re-)distribution of Mn (Huckriede and Meischner, 1996; Heiser et al., 2001; Emel'yanov, 2011). They occur also in Upper Miocene to Pliocene organic-rich sediments of the Japan Sea, where they resulted from the reduction of Mn oxyhydroxides under sulfate-reducing conditions and the re-precipitation in the form of rhodochrosite (Matsumoto, 1992; Johnson et al., 2016). A further example is provided by Mn carbonates present in organic-rich sediments of

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https://doi.org/10.1016/j.sedgeo.2017.11.012
0037-0738/

Early Toarcian age in the Úrkút Basin, Hungary. Their formation was associated with microbial activity under dysaerobic conditions (Polgári et al., 2000, 2003, 2004, 2012a, 2012b, 2016). Of great interest is also the occurrence of Mn carbonates in Paleoproterozoic, organic-rich sediments of Gabon, which were equally related to microbial activity and dysaerobic conditions (Dubois et al., 2015).

Here we describe Mn carbonates, which were discovered in sediments of different regions of the Western Siberian marine basin (WSMB; Fig. 1). Unlike the before-mentioned examples, they do not occur in direct association with organic-rich sediments, but underneath an organic-rich succession (Bazhenov Formation). They are primarily present in stromatolites and oncolites, but occur also in sediments hosting the microbialites. They belong to the Upper Oxfordian to Lower Tithonian (Volgian) Georgiev Formation. These occurrences were first described by Yasovich (1971), Ushatinsky and Zaripov (1971), Ushatinsky and Yasovich (1985), Zubkov (2001) and Zanin et al. (2003). According to those authors, the Mn enrichments occur mainly in the form of concentric concretions, with sizes varying between 1 and 2 mm and 6–10 cm. The MnO content in the concretions ranges from 2.95 to 27.01 wt%. These concretionary levels can be traced along distances of at least 750 km.

A detailed sedimentological and geochemical research of these occurrences was not carried out yet. Here we provide new data on the composition, mineralogy, and trace- and rare earth element (REE) geochemistry of the Mn carbonates and forward a model on the genesis of these rocks, in which the Mn carbonates were formed in different

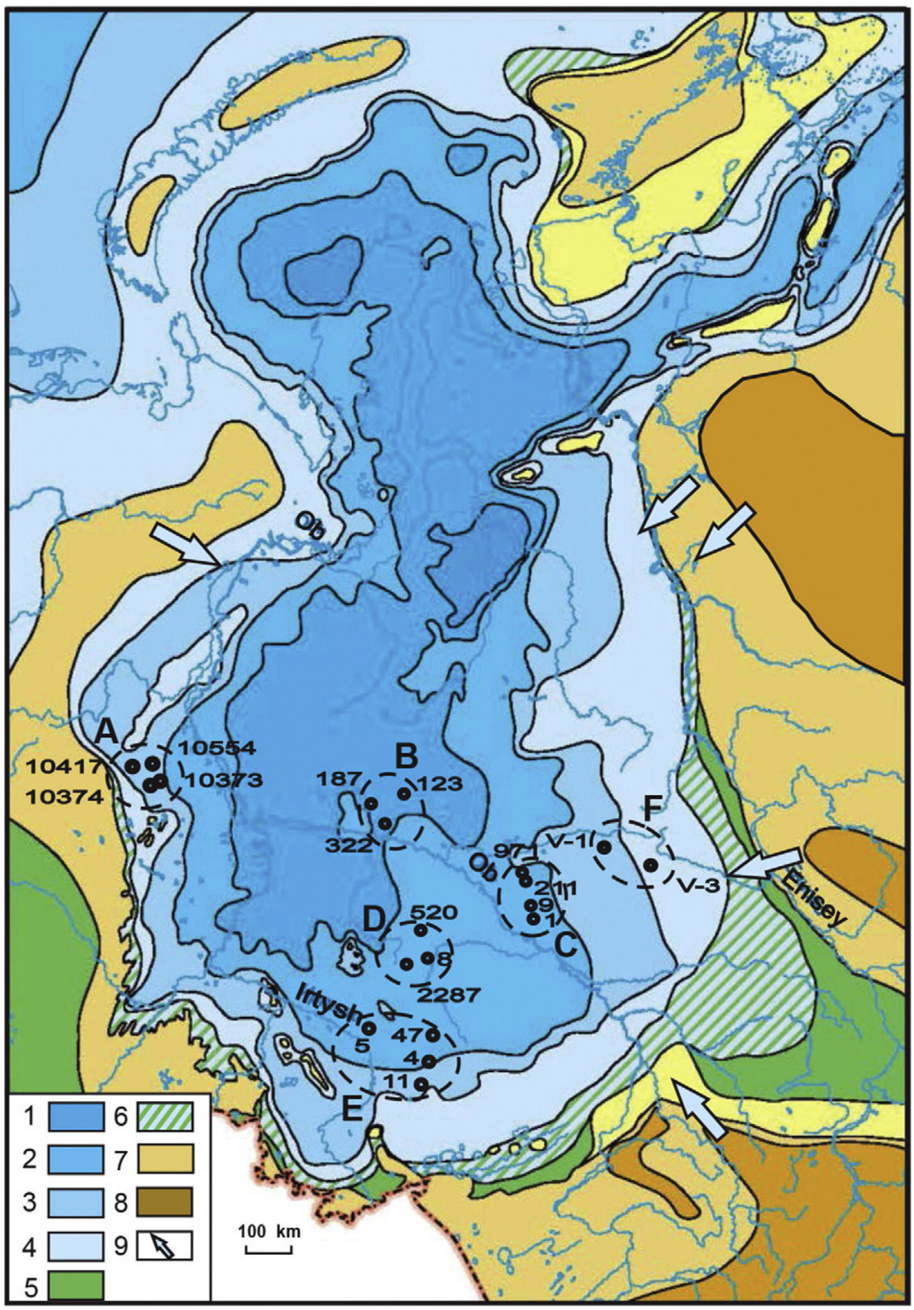

Fig. 1. Palaeogeographic reconstruction of the Western Siberian marine basin (WSMB) during the Tithonian with indication of the locations of the studied wells and reconstructed palaeobathymetric zones, modified after Kontorovich et al. (2013). Legend: 1 – <400 m; 2 – 200–400 m; 3 – 100–200 m; 4 – 25–100 m; 5 – coastal plain, periodically flooded by the sea; 6 – alluvial plain; 7 – hilly land; 8 – low mountains; 9 – main transport directions of detrital materials. A–D: regions of the WSMB in which Mn carbonates were recovered; A – western central region; B – northern central region; C – eastern central region; D – southern central region; E–F: regions of the WSMB in which Mn carbonates have not been detected; E – southern region; F – eastern region.