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Origin of the Oligocene manganese deposit at Obrochishte (Bulgaria): Insights from C, O, Fe, Sr, Nd, and Pb isotopes

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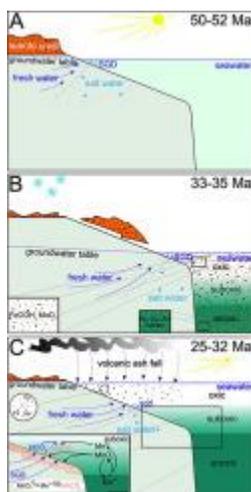
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Abstract :

The large manganese (Mn) deposit at Obrochishte (NE Bulgaria) is part of a cluster of similar Early Oligocene deposits located around present-day Black Sea. They collectively constitute the Earth's second largest endowment of Mn, after the Kalahari Manganese Field in Africa. We have employed a battery of isotopic techniques (C, O, Fe, Sr, Nd, Pb) to help understand the genesis of this deposit. Carbon isotope data indicates that some sections of the Mn-ore layer have diagenetic MnCO₃ mineralization, formed by reaction of Mn oxides with organic carbon (Corg), whereas other sections have MnCO₃ precipitated directly from the seawater column. Oxygen isotopes show that the high-grade Mn mineralization had seawater as the fluid source, whereas some lower-grade sections had a mix of ground water and seawater as fluid sources. Sr and Nd isotope values of ore leachates also indicate that the Mn deposition occurred in normal Early Oligocene seawater. Nd and Pb isotope values suggest that the clastic host sediments were sourced from continental bedrock rather than younger arc volcanic rocks to the west. Iron isotope composition of the Mn ore implies deposition in a redox-stratified basin, similar to the modern Black Sea, with much of the Fe sequestered in deep, anoxic-euxinic water as sulfides. Similar to the modern Black Sea, most of the detrital Fe was transferred from shallow oxic sediments into deep, anoxic-euxinic water by an "iron shuttle" and remobilized Mn sequestered in the upper suboxic water layer. However, during the Oligocene, the "iron shuttle" operated intermittently due to the chemocline falling mostly below the shelf break, thereby limiting the efficiency of the shuttle mechanism. We propose a model for the Lower Oligocene strata in which intense weathering during the Eocene weathering phase produced a thick lateritic crust on the southern European continent. The drastic sea-level drop at the end of the Eocene initiated downcutting of streams through this weathered material, transferring Fe- and Mn-oxides to the redox-stratified Western Black Sea. Here, these oxides were partly or entirely dissolved in the suboxic

(Mn-oxides partly, Fe-oxyhydroxides entirely dissolved) and anoxic-euxinic (Mn-oxides entirely dissolved, dissolved Fe²⁺ re-precipitated) water layers. Eventually, Fe was re-precipitated as sulfide in the deep anoxic-euxinic water, while Mn accumulated in the suboxic water layer. Transgression in the Early Oligocene brought this Mn-rich water onto the shallow shelf where it precipitated as Mn-oxide, then converted to Mn-carbonates during early diagenesis. Some Mn was also contributed by submarine groundwater discharge. Further transgression brought lower-oxygen water onto the shelf and Mn-carbonate precipitated directly from the water column. The findings from this work provide insights about the unique Oligocene geochemical event in the region that led to the formation of the 2nd largest cluster of Mn deposits in the world.

Graphical abstract



Highlights

► Mn-carbonate ore at the Obrochishte has dual origin: diagenetic and authigenic. ► Mn deposition was a result of the climatic events at the Late Eocene-Early Oligocene. ► Mn ore was deposited in a redox-stratified basin, similar to the modern Black Sea.

Keywords : Mn metallogenesis, C-O-Fe-Sr-Nd-Pb isotopes, Early Oligocene, submarine groundwater discharge, water column anoxia, proto-Black Sea geochemistry

61

62 **1. Introduction**

63

64 The Oligocene Mn deposit in north-east Bulgaria (known as Obrochishte, or in older
65 literature as Varna deposit) is one of a group of large deposits of Oligocene age that encircle the
66 Black Sea. These include the deposits from the Chiatura (Georgia), Laba (Russia), Nikopol and

67 Bol'shoy Tokmak deposits (Ukraine) and Binkiliç deposit (NE Turkey) (Varentsov, 2002;
68 Kuleshov, 2003, 2017). Collective reserves of all of these deposits are on the order of 600×10^6
69 metric tons of Mn making this region the world's second largest repository of Mn, after the
70 supergiant Kalahari Manganese Field of South Africa (Maynard, 2010; Beukes et al., 2016).
71 Recent information on reserves at Obrochishte itself is scarce. One source (GIS/GEODE 2016)
72 gives a figure of 16×10^6 metric tons at 28% Mn. Data in the USGS minerals yearbooks shows
73 cumulative production in 1963-2016 was 2.2×10^6 metric tons per year of ore with 28.6% Mn.

74 Mn-ore bed in outcrops (Vassilev et al., 1958; Stoyanov, 1961, 1963; Vangelova et al.,
75 2005), in drill cores (Aleksiev, 1959; Stoyanov, 1961, 1963; Gnoevaya et al., 1982), and in mine
76 sections (Obrochishte mine) in NE Bulgaria has been the subject of a number of studies aiming at
77 shedding light on its geology (Mandev, 1954; Vassilev et al., 1958; Stoyanov, 1961, 1963;
78 Bogdanova, 1968), sedimentology (Aleksiev, 1960b; Stoyanov, 1963; Aleksiev and Nacheva,
79 1966; Vangelova et al., 2005), mineralogy (Vassilev et al., 1958; Aleksiev and Nacheva, 1966;
80 Vassilev, 1967; Bogdanova, 1968; Puliev and Alexiev, 1972; Milakovska et al., 2006; Atanasova
81 et al., 2009), and major element geochemistry (Vassilev et al., 1958; Aleksiev and Nacheva, 1966;
82 Vassilev, 1967; Puliev and Alexiev, 1972; Vangelova et al., 2005; Milakovska et al., 2006).

83 The comprehensive mineralogy work of Vassilev et al. (1958) found that the only primary
84 Mn-minerals (and at the same time the major ore minerals) in the deposit were Ca-rhodochrosite
85 and Mn-calcite. Less abundant Mn-oxyhydroxides were secondary minerals formed as weathering
86 products on the primary Mn-carbonates (Vassilev et al., 1958). Thus, two Mn-ore types can be
87 distinguished on the basis of major Mn minerals determined in the ore bed: carbonate (primary)
88 and oxyhydroxide (secondary). Later studies (Aleksiev, 1960a; Aleksiev and Nacheva, 1966;
89 Puliev and Alexiev, 1972) claimed that a part of some of the Mn-ore layers was composed of Mn-

90 silicates (e.g., neotocite), but they did not provide any solid proofs for presence of these minerals
91 in the deposit. (Neotocite was determined on the basis of: three unclear peaks at the Debye-
92 Scherrer X-ray diffraction pattern, three peaks at the differential thermal curve, major element
93 concentrations measured through unknown method, optical microscopy, and hand specimen
94 description.) The results of these studies were accepted without any criticism by later workers and
95 this led to creation and wide circulation of incorrect classifications of the major ore types in this
96 deposit: e.g., Mn-carbonate, Mn-carbonate/Mn-silicate, Mn-silicate, and Mn-oxyhydroxide/Mn-
97 carbonate (Gnoevaya et al., 1982). In addition to the imprecise mineralogy determinations there
98 has been no attempt to investigate in detail the geochemistry (including radiogenic and stable
99 isotopes) of the Mn-ore bed in order to shed light on the fluid and metal sources. Therefore, the
100 suggested genetic models for this deposit (Vassilev et al., 1958; Aleksiev and Nacheva, 1966;
101 Vangelova et al., 2005) based on geological, mineralogical, and geochemical (major elements)
102 considerations were mostly speculative.

103 The size of the deposit at Obrochishte (largest in Europe), and its similarity to the group of
104 deposits of the same age around the Black Sea, makes it an ideal site to investigate the genesis of
105 the sedimentary Mn ores. Detailed trace element and isotope investigation can provide information
106 about why so much Mn was deposited over such a short period of time around Black Sea? The
107 answer must lie in the geochemistry of the basin seawater at this time and place. In this work, we
108 provide a comprehensive set of geochemical and isotopic (C, O, Fe, Sr, Nd, and Pb) data for
109 samples from the Obrochishte deposit and its host rocks, in order to decipher the processes that
110 lead to the formation of the largest European Mn mineralization.

111

112

113 2. Geological setting

114

115 Mn mineralization in NE Bulgaria and the adjacent Black Sea shelf is located within the
116 Ruslar Formation (Tenchov, 1993), which is a part of the Oligocene Series (Lower and Upper)
117 (Fig. 1A, B). Thickness of this Formation varies from a few tens of meters up to ~900 m (based
118 on drill core data). At the majority of the studied sites, it overlies both the Avren and Aladan
119 Formations (Tenchov, 1993) (Fig. 1B, lithostratigraphic core logs). The lower boundary of the
120 Ruslar Formation marks a hiatus stratigraphically interpreted to have varying time span: from
121 Late Cretaceous to Late Eocene. When the hiatus in sedimentation had been long (Fig. 1B,
122 uppermost lithostratigraphic core log) the lower boundary of the Formation is sharp. In the
123 southern part of the region the hiatus had likely been short (Fig. 1B, middle and lowermost
124 lithostratigraphic core logs) and the lower boundary of the Formation is gradational and unclear.
125 The Ruslar Formation is overlain by different stratigraphic units (with hiatus) of the Neogene
126 System (Fig. 1B, lithostratigraphic core logs).

127 Biostratigraphically, the Mn horizon was deposited in the Early Oligocene during the
128 Pshekian stage at the transition from Nannoplankton (NP) zone 21 to zone 22 (Sachsenhofer et
129 al., 2009, their Figure 2). At the Eocene-Oligocene boundary, which occurs in the NP zone 21,
130 there was a brief, but extensive regression that created an erosional unconformity. Following this
131 regressive episode, sea-level rapidly recovered and by the beginning of NP22, when Mn
132 deposition began, had returned close to pre-regression level (Mayer et al., 2017, their Figure 2).
133 Throughout the succeeding NP22 zone, sea-level fell, but slowly. Surface water salinity also fell
134 until brackish conditions developed at the beginning of the NP23 zone. This has been referred to
135 as the “Solenovian Event” (e.g., Sachsenhofer et al., 2017).

136 The Ruslar Formation is composed of clays, sandstones, siltstones, and marls (Aleksiev and
137 Nacheva, 1966). The dominance of clays makes it easily recognizable among the other
138 Formations. The clays are finely laminated, gray to brown, with varying silt component, and non-
139 calcareous. Siltstones are gray-green and often grade into silty clays and silty sandstones. Marls
140 are light-gray to green and show unclear laminations. They form a compact body at the middle of
141 the Ruslar Formation. Thus, the Formation is clearly divided into three units north of Varna:
142 under-marl unit (R1), marl unit (R2), and over-marl unit (R3) (Fig. 1B). South of Varna, the marls
143 are presented as single isolated layers. The Ruslar Formation contains also spongolites,
144 diatomites, and bentonites, which form scattered, single, isolated layers.

145 Manganese mineralization forms 1 to 4 beds within the lower part of the Ruslar Formation
146 (Gnoevaya et al., 1982). The thickest Mn-ore beds are within the siltstones and sandstones of the
147 under-marl unit (R1) north-east of Varna and within the clays of the lower part of the Formation
148 south of the Kamchia River. The ore bed thickness varies from 2 to 24 m, with 11.3 m within the
149 Obrochishte mine area.

150

151

152 **3. Samples and methods of investigation**

153

154 *3.1. Samples*

155

156 We investigated 27 samples from the Mn-ore bed and 5 samples from the host-rock (both
157 below and above the Mn-ore bed) all located at the basal part of the Ruslar Formation recovered
158 at 11 sampling sites (Fig. 1): 12 samples from 5 drill cores, 12 samples from 5 outcrops, and 8

159 samples from the Obrochishte mine (Table 1). The eight mine samples were collected across the
160 Mn-ore bed crossed and mined at shaft #1 (~320 m below the surface) of the Obrochishte mine
161 located near the Tzarkva village (Dobrich district, northeast Bulgaria). Drill core and outcrop
162 samples were collected by us. Samples from the Obrochishte mine were provided by the mine
163 geologist Mr. Plamen Neychev following our requirements based on the mine report description
164 of the Mn-ore bed. Pisoliths from 6 mine samples and the matrix among them from one sample
165 were selected by hand picking for further analyses.

166

167 *3.2. Methods of investigation*

168

169 Initial characterization of the samples was with a binocular microscope, followed by
170 examination of polished thin sections with an optical polarizing microscope (Eclipse LV100N
171 POL, Nikon; Department of Marine Resources and Energy, Tokyo University of Marine Science
172 and Technology). Subsequent qualitative X-ray fluorescence mapping of the thin sections was
173 performed on a Bruker Tornado μ XRF using a Rh source operating at 50 kV and 600 μ A under 20
174 mbar vacuum (Laboratory for Ocean Geosciences, European Institute for Marine Studies). Spot
175 size was 20 μ m and dwell times were 6 ms/pixel. Images of the areal distribution of elements along
176 the thin sections were produced using M4 Tornado software package with spectra deconvolution
177 and averaging every 3 pixels. All elements were represented by their K_{α} emission lines except for
178 Fe, for which K_{β} emission was chosen for imaging due to significant overlap of the K_{α} Fe emission
179 signal with the stronger K_{α} emission of Mn in the samples. Scanning electron microscope (SEM)
180 imaging and energy dispersive X-ray analysis (EDX) using a FEI XL30 ESEM and an associated
181 EDX system were performed in order to investigate mineral morphology and chemistry on a

182 smaller scale.

183 Bulk samples, separated pisoliths and matrix among the pisoliths were ground to fine powder
184 in an agate mortar and sieved to less than 200 mesh in acid-washed stainless-steel sieves prior to
185 the bulk mineralogy and geochemistry investigations.

186 Bulk mineralogy was determined by X-ray diffractometry (XRD) on the powdered samples
187 mounted on glass slides by dispersing grains in alcohol. This standard specimen preparation is
188 necessary when working with small amounts of samples. It provides an even coating of powder
189 that adheres to the sample holder and helps alleviate problems with preferred crystal orientation.
190 Instrumentation was a Siemens D500 X-ray diffractometer with Cu K_{α} radiation (Department of
191 Geology, University of Cincinnati). Scans were conducted from 5° to 55° 2θ with a step size of
192 0.2° 2θ and a count time of 10 s/step. Quantification of the X-ray diffraction patterns was done by
193 Rietveld refinement using the software Panalytical HighScore Plus and the reference patterns
194 stored in the ICSD 2013 database distributed by FIZ Karlsruhe.

195 Bulk chemistry of the samples was determined by X-ray fluorescence (XRF) using a Rigaku
196 3070 spectrometer (Department of Geology, University of Cincinnati). Sample powders were
197 pressed into thin pellets using a Spex 3624B X-Press 20-ton press. Samples were analyzed for
198 major and selected trace elements. Concentrations of major elements were calculated by multiple
199 regression using data from a set of USGS and NIST standards selected to bracket the range of
200 compositions in the samples. Trace elements were calibrated by simple regression after correcting
201 for peak overlaps (e.g., Sr K_{β} on Zr K_{α}).

202 A set of powdered sub-samples (~50 mg each; bulk and pisoliths) were dissolved with HF-
203 HCl-HNO₃ in clean Teflon vials for whole-rock elemental concentration and radiogenic isotopes
204 measurements (Department of Geological Sciences, University of Florida). According to the

205 previous studies (Vassilev et al., 1958), the Mn-ore bed is composed of both ore (Mn- carbonates
206 and oxyhydroxides) and detrital components. Therefore, we decided to investigate the chemical
207 composition of both components. For this reason, we prepared another set of powdered sub-
208 samples (bulk and pisoliths) for two-step dissolution. About 80 mg of sample powder was
209 dissolved with 2M HCl for 2 hours on a hot (100°C) plate aiming at leaching of the ore component
210 (Mn-carbonates and -oxyhydroxides) only. The resultant leachates were separated from the
211 residues in clean Teflon vials and evaporated to dryness. The remaining residues (supposed to be
212 detrital component) were further dissolved with HF-HNO₃. Chemical compositions of produced
213 solutions (bulk samples, leachates, and residues) were analyzed with Inductively Coupled Plasma
214 Mass Spectrometry (ICP-MS) using Thermo-Finnigan Element 2 instrument, and Re and Rh as
215 internal standards. Quantification of the results was done by external calibration using a
216 combination of USGS rock standards (AGV-1, BCR-2, and BIR-1) and following methods
217 described in Kamenov et al. (2008). The error for the trace elements was less than 5%.

218 Strontium, Nd and Pb isotopes were separated from bulk and pisolith samples (bulk,
219 leachate, and residue) using standard ion-exchange procedures and measured on a Nu Plasma
220 Multiple Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS) following
221 methods described in Kamenov et al. (2008). The reported ⁸⁷Sr/⁸⁶Sr ratios are relative to NBS 987
222 ⁸⁷Sr/⁸⁶Sr=0.71025 (+/-0.00003, 2σ). The Nd isotopic compositions are relative to JNdi-1
223 ¹⁴³Nd/¹⁴⁴Nd=0.512115 (+/-0.000018, 2σ). The Pb isotope data are relative to the following values
224 of NBS 981: ²⁰⁶Pb/²⁰⁴Pb=16.937 (+/-0.004, 2σ), ²⁰⁷Pb/²⁰⁴Pb=15.490 (+/-0.003, 2σ), and
225 ²⁰⁸Pb/²⁰⁴Pb=36.695 (+/-0.009, 2σ).

226 For C and O isotope analyses, bulk (carbonate) samples, separated pisoliths and standards
227 were reacted in He purged exetainer vials (10 min at 110 mL/min He flow) with 100% phosphoric

228 acid in a water bath at 25°C. The C and O isotopic composition of the CO₂ headspace gas was
229 analyzed on a Thermo Delta V Advantage isotope ratio mass spectrometer with a Thermo
230 Gasbench II connected via a Conflo IV interface (Department of Geology, University of
231 Cincinnati). The $\delta^{13}\text{C}$ values of carbonates were normalized to the VPDB scale using LSVEC (-
232 46.6‰) and NBS-19 (1.95‰). The $\delta^{18}\text{O}$ values were normalized to the VPDB scale with NBS-18
233 (-23.01‰) and NBS-19 (-2.2‰) following the recommendation of Kim et al. (2015). The O
234 isotope acid fractionation factors that were used for calcite and rhodochrosite were 1.01030 (Kim
235 et al., 2007) and 1.01012 (Friedman and O'Neil, 1977; amended from Sharma and Clayton, 1965),
236 respectively. Precision and accuracy were determined by analyzing an independent calcite
237 standard over the course of analyses (n=43). For $\delta^{13}\text{C}$, precision and accuracy were 0.11‰ (1 σ)
238 and 0.00‰, respectively. For $\delta^{18}\text{O}$, precision and accuracy were 0.09‰ (1 σ) and 0.01‰.

239 Stable Fe isotopes were studied in 20 samples according to the analytical protocol reported
240 in Rouxel et al. (2008) at Pôle de Spectrométrie Océan, IUEM/Ifremer. About 50 mg of each
241 powdered sample and georeference materials [BHVO-2 (Hawaiian basalt), Nod-A-1 (Atlantic Mn-
242 nodule), and Nod-P-1 (Pacific Mn-nodule)] were put in 15 mL PFA beakers. Powders were
243 dissolved in 2 mL concentrated (14.4M) ultrapure HNO₃ (obtained using TFE sub-boiling
244 distillation system, hereafter referred as SB grade) and between 1 to 2 mL of concentrated Trace
245 Metal™ (Fisher Scientific) grade HF. Solutions were evaporated to dryness on a hot plate at 80°C.
246 Then, we added 2 mL concentrated SB grade HNO₃ and 2 mL 6M SB grade HCl (thus forming
247 *aqua regia*). Solutions were evaporated to dryness on a hot plate at 90°C. After that, we added 1
248 mL 5M HCl with 10 μL of 30% (v/v) H₂O₂ in each beaker, closed the beakers and put them on a
249 warm (60°C) plate for 1 h. The beakers were cooled down (20°C) and the solutions were ready for
250 column load.

251 For Fe isotope separation we used 2.0 mL (wet volume) of anion-exchange resin AG MP-1
252 placed in polypropylene columns. All diluted acids were prepared from SB-grade concentrated
253 acids. Before the sample load, the resin was washed with 10 mL 3M HNO₃, 10 mL 18 MΩ cm⁻¹
254 H₂O, 5 mL 1.2M HCl, and conditioned with 2 mL 5M HCl. 1 mL of each sample solution was
255 loaded in the columns. The matrix fraction was eluted with 14.5 mL 5M HCl. Fe was eluted with
256 14 mL 1.2M HCl in PFA beakers. After evaporation of the Fe eluate at 90°C, we added 2 mL
257 0.28M HNO₃ in the beakers and transferred the solutions into 2 mL PFA vials.

258 Fe isotope compositions were determined with a Neptune (Thermo-Scientific) MC-ICP-MS
259 using medium or high-resolution mode. It involves both “sample-standard bracketing” and
260 “internal normalization” using Ni of known isotope composition (Weyer and Schwieters, 2003;
261 Poitrasson and Freydier, 2005; Rouxel et al., 2005). All analyses are reported in delta notation
262 relative to the IRMM-014 standard, expressed as δ⁵⁶Fe. Based on >50 replicate dissolutions,
263 purifications, and analyses of internal standard BHVO-2, we have obtained: δ⁵⁶Fe = 0.09 ± 0.07‰
264 (2 SD). Results for Mn-nodules Nod-A-1 and Nod-P-1 yielded δ⁵⁶Fe = -0.39 ± 0.06‰ (2 SD) and
265 -0.51 ± 0.06‰ (2 SD), respectively, which is indistinguishable, within analytical error, from
266 previously published values (Asael et al., 2013; Marcus et al., 2015; Rolison et al., 2018).

267

268

269 4. Results

270

271 4.1. Petrography

272

273 Most samples collected from the Mn-ore layer at the mine were highly pisolitic (Fig. 2)

274 comprising tan to brownish-red, concentrically-laminated pisoliths (Fig. 3A, B) set in a greenish-
275 tan matrix. Pisoliths are 1 to 2 cm in diameter and show some tendency to increase up-layer in
276 both size and abundance. Thin section microscope observations revealed that the grain size for
277 both the carbonate and the aluminosilicate components was exceeding small and the ore matrix
278 looked greyish-brown to light-brown (images not shown). Optical microscopy observations along
279 with X-ray fluorescence mapping showed that the pisolith concentric layers were of two types:
280 carbonate-rich and aluminosilicate-rich (Figs 3C, D; 4). Carbonate-rich layers were composed of
281 Mn- and Mn-Ca-carbonates (Fig. 4A, B, C). They alternated with layers enriched in elements
282 typical for detrital aluminosilicate component: Al, Si, Fe, Rb, and Zr (Fig. 4D, E, F, G, H). The
283 SEM imaging showed that the carbonate-rich layers contained large crystals of Mn-carbonate (Fig.
284 5A), whereas the aluminosilicate-rich layers were composed of sub-micron spheres of silica and
285 Mn-carbonate (Fig. 5B), and, possibly, clays.

286 An EDX survey of the composition of pisoliths and matrix showed (Table 2) the same
287 distribution as in the X-ray mapping: the matrix was primarily Al- and Si-rich, whereas the
288 pisoliths were composed predominantly of Mn and Ca.

289

290 *4.2. Mineralogy*

291

292 The strata below and above the Mn-ore layer are composed mainly of quartz, plagioclase,
293 and clay minerals (illite/smectite and kaolinite). Where carbonates are present, they are calcite or
294 dolomite rather than one of the Mn-carbonates (Table 1).

295 The Mn-ore layer and its low-grade equivalents also include the same detrital components.
296 They differ from the host strata in having Mn-carbonates as well. The amount and type of Mn-

297 carbonates varies laterally. In the area of the Obrochishte mine, the Mn-ore layer is mainly
298 composed of rhodochrosite (MnCO_3) with some kutnahorite [$\text{Ca}(\text{Mn}^{2+}, \text{Mg}^{2+}, \text{Fe}^{2+})(\text{CO}_3)_2$] at the
299 base and lesser amounts of detrital components (Table 1). This assemblage is consistent with the
300 results of Vassilev et al. (1958). However, northeast of the Obrochishte mine where the ore-
301 equivalent horizon is crossed by drill holes, kutnahorite dominates over rhodochrosite and non-ore
302 components roughly equal ore minerals. To the south and southwest of the Obrochishte mine
303 where the ore interval crops out (Fig. 1), it is mostly composed of quartz, plagioclase, and clays
304 with subordinate amounts of Mn-calcite [$(\text{Ca}, \text{Mn})\text{CO}_3$] and kutnahorite (Table 1). Our samples
305 are mostly free of Mn-oxides. Trace amounts of pyrolusite (MnO_2) and todorokite [$(\text{Na}, \text{Ca},$
306 $\text{K})_2(\text{Mn}^{4+}, \text{Mn}^{3+})_6\text{O}_{12} \cdot 3-4.5(\text{H}_2\text{O})$] were found in some samples (OBR-7-3178, OBR-7-4130,
307 OBR-8-A, OBR-9-3884) at amounts too low to be quantified by the Rietveld refinement (therefore,
308 not in Table 1). Rare thin (0.1-0.5 mm) pyrite veins cross the ore matrix (Figs 3E, F, G; 6). They
309 have thin rhodochrosite bands (Fig. 3E) and are altered along thin cracks at some places (Fig. 3H).

310

311 4.3. Geochemistry

312

313 Similar to the distribution of minerals, the host strata below and above the Mn-ore layer lack
314 significant Mn content ($\text{MnO}=0.04-0.46$ wt.%; Table 3). Content of the most other elements in
315 bulk rock samples are similar in the ore layer and in the host strata except for Ca, Fe, Pb, and Zn,
316 which are higher in the host rocks, and Mn, Co, Mo, Ni, V, P and total rare earth elements (REE),
317 which are substantially higher in the ore interval. The ore interval shows considerable lateral
318 variation in geochemistry. In the Obrochishte mine area, the Mn-ore layer contains less SiO_2 ,
319 Al_2O_3 , Fe_2O_3 , K_2O , and S_{tot} , and more MnO, MgO, and C_{tot} than both the host rocks and the Mn-

320 ore interval sampled at the outcrops and drill holes outside the mine area (Table 3). Across the
321 Mn-ore layer CaO and Fe₂O₃ concentrations decrease upward (Table 3). Overall, the picture from
322 mineralogy and bulk geochemistry is that the sedimentary rocks are a mixture of a detrital
323 component of fixed composition and a (presumably) authigenic component that varies from Ca-
324 rich to Mn-rich.

325 Within the authigenic component, there are important variations that likely relate to
326 depositional conditions. The relationship between organic carbon (C_{org}) and total sulfur (S_{tot})
327 content is often used to characterize low-oxygen environments (e.g., Potter et al., 2005). Organic
328 carbon concentrations in the studied samples are low, ranging from 0.1 to 1.3 wt.% with an average
329 of 0.4 wt.% (Table 3). Total sulfur content ranges to higher values, with some exceeding 2 wt.%
330 (Table 3). Many of the studied samples show the typical correlation between C_{org} and S_{tot} that is
331 found in normal marine sediments (Fig. 7) (Berner, 1982; Raiswell and Berner, 1986; Morse and
332 Berner, 1995). There is another group of samples, however, that has excess S, which is usually
333 interpreted to indicate free H₂S in the water column (euxinic conditions). There is a tendency for
334 the S_{tot} concentration in these rich in S samples to increase upwards across the Mn-ore layer, but
335 there are exceptions.

336 Because the ore consists of a mixture of detrital components and authigenic material in two
337 contrasting textural forms (matrix and pisoliths), it is useful to view the geochemistry of major and
338 trace elements in terms of separate fractions. The concentrations of trace elements and some major
339 elements in the bulk, pisolith, leachate and residue fractions of the samples are reported in Table
340 4.

341 The chemistry of the studied sample fractions (leachates and residues) shows some
342 interesting features (Table 4). The major part (>50%) of the investigated elements (Mg, Fe, Mn,

343 Na, K, Li, Sc, Ti, V, Cr, Co, Zn, Ga, Rb, Zr, Nb, Cs, Ba, Hf, Ta, and Th) in the host rock (sample
344 OBR-8-A) are in the residual fraction (Table 4). Only P, Ni, Cu, Y, Pb, and U reside mostly (>50%)
345 in the leachate fraction of the host rock. REE and Sr are equally distributed in both fractions.

346 The residues of the Mn-ore layer (sampled in the mine and in a drill hole) and pisoliths (Table
347 4) contain the major part of K, Sc, Ti, Cr, Ga, Rb, Zr, Nb, Cs, Hf, and Ta. The leachate fraction of
348 this layer and of the pisoliths contains most (>50%) of Ca, Mg, Mn, Na, P, Li, V, Co, Ni, Zn, Sr,
349 Y, Ba, REE, Pb, Th, and U. Cu is almost in equal proportions in both fractions.

350 The vertical distribution of some elements across the Mn-ore layer sampled at the mine show
351 some correlation with the ore mineralogy. Major ore mineral in the lowermost two samples is
352 kutnahorite whereas rhodochrosite is the only ore mineral in the rest of the samples upward (see
353 sub-section 4.2 and Table 1). Li and V are mostly in the residue in the lowermost two kutnahorite-
354 containing samples and in the leachate in the upper rhodochrosite samples. Fe and Pb are mostly
355 in the leachate fraction of the pisoliths in the lower kutnahorite-containing samples and
356 progressively decrease upward through the rhodochrosite samples. Na is mostly in the leachate of
357 the pisoliths, but lower in the lowermost two kutnahorite-containing samples. Cu is mostly in the
358 leachate of pisoliths in the lower two kutnahorite samples and mostly in the residue in the upper
359 rhodochrosite samples.

360 In order to estimate the magnitude of elemental enrichment of the Mn-ore layer with respect
361 to the host rocks we compared the averages of the leachate compositions of the bulk samples from
362 the Obrochishte mine (samples OBR-11: Mn-ore layer), one drill hole (samples OBR-5: Mn-ore
363 layer), and a host rock sample (OBR-8-A), and of the pisoliths from the Mn-ore layer at the
364 Obrochishte mine (samples OBR-11-1.2P, -1.8P, -3.8P, -4.4P, -5.1P, -6.1P). This sample selection
365 is based on the assumption that the residues of all studied samples represent detrital component

366 delivered to the sedimentary basin from the same provenance and with similar composition.

367 Ca concentration in the leachates of the host rocks (~20%) is 3-5 times higher than that of
368 the leachates of the Mn-ore layer and its pisoliths (Table 4). In contrast, Mn, Mg, and Fe
369 concentrations in the leachates of both the Mn-ore layer and its pisoliths are higher than those of
370 the host rocks. Mn and Mg contents are even 2-3 and 1-2 (respectively) orders of magnitude higher
371 than those of the host rock. Only K, Ti, Cu, Nb, Hf, Ta, and Pb have similar concentrations in the
372 leachates of both types of samples: Mn-ore layer (and its pisoliths) and host rock. Contents of all
373 the other studied elements (V, Co, Ba, Na, Li, Ni, REE, Th, Zn, Ga, Cr, Rb, Sr, Y, Zr, Cs, and U)
374 are higher in the leachates of the Mn-ore layer (and pisoliths) than in those of the host rock. The
375 concentrations of Na, Li, Ni, REE, and Th are 1 and those of V, Co, and Ba are 1-2 orders of
376 magnitude higher than those of the host rock. Pisoliths are richer in P, Y, heavy REE (Ho-Lu), and
377 U than the Mn-ore layer (bulk) and host rock, but poorer in Th than the Mn-ore layer (Table 4).
378 They are richer in Mn, Ca, and (particularly) P than the matrix among them (Table 3).

379 The total content of REE (Σ REE) in the studied Mn-ore samples (Table 4) is slightly lower
380 than that of the average upper continental crust (UCC) (McLennan, 1989). Σ REE in the
381 background samples (below and above the Mn-ore bed) are even less than the Σ REE of the Mn
382 ores (Table 4, sample OBR-8-A). Over 60% of the content of each rare earth element in the studied
383 Mn ore samples is within the leachable by 2M HCl fraction and only <40% of the REE content is
384 in the residue supposed to be composed of detrital aluminosilicates (Table 4; Fig. 8A, B). Selected
385 pisoliths show similar REE composition with over 70% of the REE content being within the
386 leachable fraction (Table 4; Fig. 8C). The REE distribution patterns of the Mn ores and their
387 components (Fig. 8A-D; Table 4) are broadly similar to those of the upper continental crust (Fig.
388 8F; McLennan, 1989) with light REE (LREE) enrichment, flat heavy REE (HREE) distributions

389 and negative Eu anomaly ($\text{Eu}/\text{Eu}^* < 1$). The only difference between them and those of the upper
390 continental crust is the negative Ce anomaly ($\text{Ce}/\text{Ce}^* < 1$) (Fig. 8A-D; Table 4). The negative Ce
391 anomaly is well pronounced at the REE distribution patterns of both the bulk samples
392 ($\text{Ce}/\text{Ce}^*_{\text{average}} = 0.69$) and the 2M HCl leachates ($\text{Ce}/\text{Ce}^*_{\text{average}} = 0.79$), whereas it is negligible at the
393 REE distribution patterns of the residues ($\text{Ce}/\text{Ce}^*_{\text{average}} = 0.90$) (Fig. 8A-D; Table 4). REE
394 distribution patterns of the leachates of both the Mn ores and background rocks are similar with
395 the only difference that the REE contents in the Mn ores are about five times more than those in
396 the background rocks (Fig. 8A, B, F).

397

398 *4.4. Isotope geochemistry*

399

400 *4.4.1. C and O isotopes*

401 C and O stable isotope values of studied samples (Table 5), when plotted against one another,
402 fall into two groups (Fig. 9A). One has $\delta^{18}\text{O}_{\text{PDB}}$ of 0‰ to -4‰, and $\delta^{18}\text{O}_{\text{PDB}}$ is independent of
403 $\delta^{13}\text{C}_{\text{PDB}}$ (Fig. 9A). The other group has a strong correlation of $\delta^{18}\text{O}_{\text{PDB}}$ to $\delta^{13}\text{C}_{\text{PDB}}$, with lighter O
404 isotope values, ranging from -12‰ to -3‰. This second group comes from sample sites (##6, 7,
405 8, and 9) located in the southern part of the Ruslar Formation with larger content of detrital
406 component (clays and sandstones) (Fig. 1B). They plot along an array between typical fresh water
407 and seawater. Although mineralized, this sample group has lower MnO content: $\leq 10\%$. These
408 samples are strongly enriched in Cu, Pb, and Zn (3 to 8 times in bulk composition) compared to
409 the fully marine group, which in turn is strongly enriched in Cl, S, and V with lesser enrichment
410 in Co and Ni. The number of leachate samples for the first sample set was too small to make valid
411 comparisons.

412 Another aspect of C-O isotope geochemistry is seen in a plot of $\delta^{13}\text{C}_{\text{PDB}}$ against Mn content
413 of the studied samples (Fig. 9B). This pair of variables also shows two distinct trends, but involving
414 a somewhat different grouping of samples from the $\delta^{18}\text{O}_{\text{PDB}} - \delta^{13}\text{C}_{\text{PDB}}$ plot (Fig. 9A). One set of
415 samples (Group I) clusters around the value for seawater bicarbonate ($\delta^{13}\text{C}_{\text{PDB}} = 0\text{‰}$) and is
416 independent of Mn concentration. This set of samples is substantially larger than the other set and
417 comes from stratigraphically lower positions in the Mn-ore layer in the mine area. The other
418 sample set (Group II) has lighter C isotope values, -5‰ to -25‰ , and they correlate inversely to
419 the MnO concentration (Fig. 9B). The first array has $\delta^{13}\text{C}_{\text{PDB}}$ values consistent with derivation
420 from seawater HCO_3^- , whereas the second array has some to all of its C derived from decay of
421 organic matter, perhaps including some oxidized methane for samples with $\delta^{13}\text{C}$ in the -25 to $-$
422 32‰ range. The lightest $\delta^{13}\text{C}_{\text{PDB}}$ value, -25‰ , corresponds to modern C isotope values for organic
423 matter in sediments on the shelf off the mouth of the Danube River, -26‰ to -23‰ (Galimov et
424 al., 2002), so the second array spans the complete range from 100% organic-sourced C to 100%
425 seawater-sourced carbon. The bulk chemistry of the two populations identified on Figure 9B shows
426 enrichments in Group I in Pb and Zn when compared to Group II, which in turn shows strong
427 enrichments in Co, Ni, and S and smaller enrichments in V, Cr, and Cu. For the leachates, a smaller
428 sample set, the Co and Ni enrichments seen in the bulk chemistry do not appear, but V and Cu
429 remain higher in Group II samples compared to Group I. Pb continues to be enriched in Group I,
430 but Zn does not show enrichment.

431

432 4.4.2. Sr, Nd and Pb isotopes

433 $^{87}\text{Sr}/^{86}\text{Sr}$ in the bulk samples shows a range from 0.70826 to 0.70937 (Table 5). The leachates
434 show lower values compared to the bulk samples and cluster around the expected seawater Sr

435 isotopic composition at 31 My (Fig. 10). A t-test shows that the means of the two sets of data are
436 statistically different ($P = 0.001$). The residues show much more radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ when
437 compared to leachates and bulk, with values ranging from 0.70967 to 0.72038 (Table 5). Sample
438 size for the residues is too small for effective statistical evaluation.

439 Bulk samples show a relatively narrow range for ϵNd , between -6.7 and -8.1 (Table 5).
440 Leachates also show a narrow range for ϵNd , between -6.0 and -7.4. Again, the means are
441 significantly different ($P = 0.009$). A portion of the leachates overlap with the expected Nd isotopic
442 composition for Atlantic and Tethys seawater at 31My, although some leachates and most of bulk
443 samples extend to more negative ϵNd , towards the residues (Fig. 11). As can be seen from Figure
444 11, the residues show the most negative ϵNd as low as -12.1, from all of the analyzed samples
445 (Table 5).

446 In contrast to Sr and Nd isotopes, Pb isotopes have very similar median values for bulk and
447 leachate compositions and show the same modes on histograms. Statistically, the means for bulk
448 and leachate sample sets are the same for $^{206}\text{Pb}/^{204}\text{Pb}$ ($P = 0.33$) and for $^{207}\text{Pb}/^{204}\text{Pb}$ ($P = 0.83$),
449 whereas the means for $^{208}\text{Pb}/^{204}\text{Pb}$ are somewhat different ($P = 0.02$). The residence time of Pb in
450 seawater (unlike that of Sr and Nd) is very short (30-400 years) and Pb reflects local weathering
451 inputs (e.g., Basak and Martin, 2013). Thus, the dissolved and particulate Pb fractions should have
452 similar isotope composition. Means for the three isotope ratios are: $^{206}\text{Pb}/^{204}\text{Pb}$ of bulk samples,
453 18.95 and leachate samples, 18.89; $^{207}\text{Pb}/^{204}\text{Pb}$ – 15.661 and 15.663, respectively; $^{208}\text{Pb}/^{204}\text{Pb}$ –
454 38.80 and 38.70, respectively. Sample OBR-8-A departs significantly from others in Pb isotope
455 values, but it is mostly composed of CaCO_3 rather than of MnCO_3 . Therefore, we have excluded
456 it from the statistical analysis. We only have Pb isotopic data from 4 residues, so statistical
457 comparisons are difficult. However, the similarity of the whole-rock and leachate values implies

458 that the residues should also be similar. Also, the means for the residue isotopes are within 1% of
459 the means for the leachates and whole rock.

460

461 4.4.3. *Fe isotopes*

462 Iron isotope composition ($\delta^{56/54}\text{Fe}$) of the whole-rock samples from the Mn-ore layer at the
463 Obrochishte mine ranges from -0.16‰ to +0.16‰ (samples OBR-11-...; Table 5) and does not
464 clearly correlate to other geochemical parameters such as concentrations of Al_2O_3 and MnO
465 (Tables 3, 4). In the areas lateral to the mine, the whole-rock $\delta^{56/54}\text{Fe}$ range is greater: -0.33‰ to
466 +0.24‰. The pisolith $\delta^{56/54}\text{Fe}$ (analyzed at the Obrochishte mine only) has a distinct trend to lighter
467 values relative to the host whole-rock data and decreases upward within the Mn-ore layer (Table
468 5). The lower Mn-ore beds (samples OBR-11-1.2 to OBR-11-3.8) have average $\delta^{56/54}\text{Fe}_{\text{pisolith}} = -$
469 0.08‰ (Table 5), whereas the upper Mn-ore beds (samples OBR-11-4.4 to OBR-11-6.1) have
470 average $\delta^{56/54}\text{Fe}_{\text{pisolith}} = -0.36\text{‰}$.

471

472

473 5. Discussion

474

475 5.1. *Mineralogy of Mn-ore layer*

476

477 The absence of Mn-minerals in the host strata below and above the Mn-ore layer (Table 1)
478 suggests that precipitation was caused by an abrupt change in geochemical conditions. Maynard
479 et al. (1990) observed a similar abrupt appearance of Mn in the Molango deposit of Mexico and
480 related it to a rise in sea-level that allowed penetration of new water into the depositional basin.

481 For Obrochishte deposit, the occurrence of Mn-oxides mostly in the outcrop samples is in
482 accordance with the previous suggestion (Vassilev et al., 1958) that these are secondary minerals
483 formed as a weathering product of the primary Mn-carbonates. The Mn-ore layer crossed at the
484 Obrochishte mine is richer in Mn-minerals (rhodochrosite and kutnahorite) than at the other
485 studied sites (Table 1). We interpret this lateral variability in the mineralogical composition of the
486 Mn-ore layer as a result of different degree of dilution of the Mn-minerals with detrital component
487 (quartz, plagioclase, and clays). The area of the Mn deposit is relatively small (Fig. 1) and it does
488 not seem plausible to assume that the lateral variability in the mineralogy of the Mn-ore layer is
489 due to spatial variations in the conditions of Mn-mineral precipitation.

490

491 *5.2. REE constraints on redox conditions of Mn-carbonate precipitation*

492

493 The close resemblance of the REE distribution patterns of the Mn-ore residues (after 2M
494 HCl leaching) (Fig. 8A-D; Table 4) to those of the average UCC (Fig. 8F) suggests that the residues
495 are detrital (terrigenous) component. The negative Ce anomaly in the REE distribution patterns of
496 the 2M HCl leachable component of the Mn-ores is visible at the REE distribution patterns of the
497 bulk Mn-ore (Fig. 8A, B) as the latter is the sum of both leachable and residual (without Ce
498 anomaly) components. The 2M HCl leachable component is mostly composed of authigenic Mn-
499 carbonates and therefore, it is essential to understand the source of this anomaly and its
500 implications for the source of Mn in the ore layer.

501 The location of the Mn-ore layer within a sedimentary rock sequence (Oligocene Ruslar
502 Formation) suggests that it is a sedimentary formation (e.g., Johnson et al., 2016). Therefore, any
503 aspect of its deposition needs to consider the conditions in the depositional basin. The Ruslar

504 Formation in general, had formed at the western margin of the Western Black Sea basin, which
505 was progressively opening during the Oligocene (Nikishin et al., 2015). According to the
506 paleotectonic reconstructions (Nikishin et al., 2015) during this epoch, the uplift of the Pontides
507 orogenic area limited the open oceanic connection of the basin with the Tethys. This reduced the
508 ventilation of the Western Black Sea, which in turn led to suboxic to anoxic conditions in the water
509 column (Sachsenhofer et al., 2009; Mayer et al., 2017). Therefore, when discussing the
510 geochemistry of the Mn deposit formed at the western margin of the Oligocene Black Sea, it seems
511 reasonable to use as a proxy the recent anoxic Black Sea (see also Schulz et al., 2005).

512 The modern Black Sea water body is vertically stratified in three layers (from surface to
513 bottom): oxic, suboxic and anoxic (Lewis and Landing, 1991; German et al., 1991; Schijf et al.,
514 1991). The suboxic layer is the zone where sharp gradients of dissolved as well as particulate
515 elements (Mn, Fe, and REE) are found (German et al., 1991; Schijf et al., 1991). Its thickness
516 varies from a few meters up to as much as 80 m with an average of ~26 m (Glazer et al., 2006a,
517 b). Particulate Mn concentration is high throughout the suboxic layer, but its maximum occurs at
518 the top of this layer coincident with a minimum in dissolved total REE and a minimum in Ce/Ce^*
519 (German et al., 1991). The maximum of particulate Fe content is shifted down, at the transition
520 from the suboxic to the anoxic layer. Average Ce/Ce^* (chondrite-normalized) of dissolved REE is
521 0.39 in the oxic layer, 0.08 at the oxic-suboxic transition, 0.34 in the suboxic layer proper and 0.86
522 in the anoxic layer (calculated from the data reported by German et al., 1991). We have not found
523 any data for the REE composition of the corresponding particulate material. A rough estimate can
524 be calculated by assuming the observed dissolved values are the residual after extraction of
525 dissolved REE by adsorption to newly-formed Mn-oxide particles. The very low Ce/Ce^* value at
526 the oxic-suboxic boundary requires a positive particulate Ce anomaly of about 1.80, based on the

527 difference between the dissolved values of La, Ce, and Nd in the oxic and transition layers. Using
528 the same approach, the suboxic layer itself would produce particles with Ce/Ce* of about 0.84 (see
529 online data supplement for details). These numbers are sensitive to the exact choice of samples to
530 be included in each category, but they do give an indication of what is to be expected for different
531 levels in the water column.

532 The Ce/Ce* of the Mn-ore leachates (Fig. 8A-D) ranges from 0.61 to 1.03 with an average
533 of 0.77 with no apparent trend across the Mn-ore layer. For comparison, two other circum-Black
534 Sea deposits have reported REE data: Binkiliç, which averages 0.80 for Ce/Ce* and Nikopol,
535 which has 1.05 in oxide ore and 0.91 in carbonate ore [calculated from data of Gültekin and Balci
536 (2018) and Varentsov et al. (1997), respectively]. Thus, the REE in the Mn-ores around the
537 Oligocene paleo-Black Sea could reasonably have been acquired by scavenging of the dissolved
538 REE ions by particulate Mn-oxides, which then sank to the seafloor and were converted to MnCO₃
539 during diagenesis. The values seen suggest formation in the lower part of the suboxic zone. The
540 Ce/Ce* values are also consistent with a portion of the REE being directly incorporated in MnCO₃
541 in the seawater column (see model of Konovalov et al., 2006). The carbonate phase would not
542 have a preference for Ce⁴⁺ so its REE distribution pattern would be the same as that of the seawater
543 parcel where precipitation occurred. The amount of this authigenic MnCO₃ is hard to estimate
544 because of the uncertainty in the value for the Mn-oxides, but 20 to 30% could easily be
545 accommodated (see calculations in online data supplement). In summary, Ce/Ce* for the
546 Obrochishte Mn-ore layer is consistent with precipitation of Mn as Mn⁴⁺-oxide in the suboxic layer
547 of the seawater column in a euxinic basin similar to the modern Black Sea, with some Mn going
548 directly into MnCO₃ as Mn²⁺ at the top of the anoxic zone.

549

550 *5.3. Controls on the trace element content of the Mn-ore layer*

551

552 *5.3.1. Crystallography and mineralogy controls on the Sr and Ba concentrations in Mn-ore layer*

553 The lowermost part of the Mn-ore layer crossed at the Obrochishte mine (OBR-11-1.2 and
554 OBR-11-1.8) is richer in Sr and Ba than the middle-upper part of this layer sampled in the
555 Obrochishte mine (Table 4). The mineralogy studies did not reveal any single mineral phases of
556 Sr and Ba in any sample. Hence, Sr and Ba are either hosted in the crystal lattice of some minerals,
557 or they are adsorbed on the mineral surfaces. Chemistry of the acid-leached fraction (presumably
558 composed mainly of Mn-carbonates) and residual fraction (presumably composed mainly of
559 aluminosilicates) showed that Sr and Ba were mostly (>70%) hold in the Mn-carbonates
560 (excluding Ba in the lower part of the Mn-ore layer drilled at site #5) (Table 4). We have not
561 performed detailed partitioning chemistry analysis that would allow us to precisely determine the
562 carbonate-bound and adsorbed fractions of these two elements. Therefore, we may consider (at
563 first approximation) that a major part of the elements leached according to our protocol (see 3.2)
564 are carbonate-bound. Thus, the vertical distribution of Sr and Ba across the Mn-ore layer in the
565 mine (site #11) seems to be crystallographically controlled.

566 The lowermost Mn-ore layer contains kutnahorite as a major ore mineral along with
567 rhodochrosite, whereas the middle-upper Mn-ore layer contains only rhodochrosite (Table 1). The
568 only possible structural site for Sr²⁺ and Ba²⁺ substitution in rhodochrosite (MnCO₃) is that of Mn²⁺
569 in octahedral coordination, whereas the structural sites for Sr²⁺ and Ba²⁺ substitution in kutnahorite
570 [Ca(Mn, Mg, Fe)(CO₃)₂] are those of Ca²⁺, Mg²⁺ and Fe²⁺ in addition to that of Mn²⁺. According
571 to the Goldschmidt's rules of substitution of ions in crystals (Goldschmidt, 1954) from charge
572 considerations Sr²⁺ and Ba²⁺ might substitute for Mn²⁺, Ca²⁺, Mg²⁺ and Fe²⁺ in the crystal lattices

573 of both carbonates. Then, the governing control for such a substitution is the ionic radius of the
574 replacing and replaced ions. For an extensive substitution, the radius of the replacing ion must not
575 differ from the radius of the replaced ion by more than 15% (Goldschmidt, 1954). The ionic radius
576 of Mn^{2+} in six-fold coordination (like that in rhodochrosite) is 0.75-0.91 Å (depending on the low
577 or high spin, respectively), whereas the radii of Sr^{2+} and Ba^{2+} in the same coordination are 1.21
578 and 1.44 Å, respectively (Whittaker and Muntus, 1970). Hence, Sr^{2+} and Ba^{2+} substitution for Mn^{2+}
579 in rhodochrosite crystal lattice is difficult: r_{Sr} and r_{Ba} must be ≤ 1.05 Å (i.e., 115% of the Mn^{2+} -site
580 radius) for an extensive substitution. However, the theoretical possibilities of Sr^{2+} and Ba^{2+}
581 incorporation in the kutnahorite crystal lattice are different. In addition to the structural site of
582 Mn^{2+} , which obviously cannot easily accommodate these elements, there are also those of Ca^{2+} ,
583 Mg^{2+} and Fe^{2+} . The ionic radii of Mg^{2+} and Fe^{2+} in six-fold coordination are even smaller than that
584 of Mn^{2+} (0.80 and 0.86 Å, respectively), which means that their structural sites cannot easily
585 accommodate Sr^{2+} or Ba^{2+} . However, the structural site of Ca^{2+} ($r_{\text{Ca}} = 1.08$ Å; Whittaker and
586 Muntus, 1970) can easily accept substitution of ions up to 1.24 Å (within the 15% substitution
587 tolerance), which is perfect for Sr^{2+} accommodation ($r_{\text{Sr}} = 1.21$ Å), but more difficult for Ba^{2+}
588 accommodation ($r_{\text{Ba}} = 1.44$ Å). This explains the higher concentrations of Sr in the lowermost Mn-
589 ore layer containing kutnahorite than in the middle-upper Mn-ore layer having only rhodochrosite.
590 Barium may instead reside in small amounts (<4%, the detection limits of XRD) of single Ba-
591 mineral like barite that has not been detected during our XRD investigations. The lowermost Mn-
592 ore layer contains on average 190 ppm Ba, whereas the middle-upper Mn-ore layer (samples OBR-
593 11-4.4 to -6.1) has on average 160 ppm Ba (Table 4). Its enrichment in the lower Mn-ore layer
594 may reflect a more oxidizing depositional environment, which is supported by the presence of
595 excess S (i.e., S in excess of that predicted from the C_{org} content) in the middle-upper Mn-ore

596 layer: $S_{\text{excess lower}} = 100 \text{ ppm}$, $S_{\text{excess upper}} = 1300 \text{ ppm}$ (Table 3).

597

598 *5.3.2. Euxinia control on Fe, Zn, Cu, Cr, Ni, Co, and Mo contents of Mn-ore layer*

599 Principal minerals in the Mn-ore layer are rhodochrosite and kutnahorite (Table 1).
600 Reasonably, major part of Mn, Ca, and Mg in this layer (and in the extracted pisoliths) is in the
601 leachate fraction (Table 4), i.e., mostly in the Mn-carbonates. In addition to these major elements,
602 a number of trace elements (Na, P, Li, V, Co, Ni, Zn, Sr, Y, Ba, REE, Pb, Th, and U) is also mostly
603 contained in the leachate fraction of the Mn-ore layer (Table 4). The enrichment of the Mn-ore
604 layer in these trace elements relative to the host rocks is likely a result of the processes that led to
605 the deposition of this layer in the Western Black Sea during the Early Oligocene.

606 Major accumulations of sedimentary Mn are thought to require the presence of a large body
607 of anoxic seawater to provide a sufficient reservoir of dissolved Mn (e.g., Maynard, 2014). The
608 required anoxia can develop in two ways: a restricted marine basin, or an intense oxygen-minimum
609 zone in the open ocean (Maynard, 2010). In the former case, the basin becomes euxinic: i.e., there
610 is free H_2S dissolved in the bottom water. In both cases, the Mn deposit forms above the anoxic
611 water where suboxic conditions impinge on the seafloor.

612 Consistent with this model, REE evidence from studied deposit suggests that the Mn-ore
613 layer formed in suboxic seawater conditions (see 5.2). Euxinic conditions offshore from the area
614 of deposition are indicated by several studies of the petroleum potential of the Ruslar Formation
615 (e.g., Sachsenhofer et al., 2009; Mayer et al., 2017). We also see some evidence for euxinic
616 conditions at the area of Mn deposition, based on the excess S found in some of the samples (Fig.
617 7). It would appear that seawater in the deeper Early Oligocene Western Black Sea basin was
618 anoxic, while on the shallow shelf it was generally suboxic (see Mayer et al., 2017, their Figures

619 11 and 12), but with occasional intervals when the chemocline rose to cover the shallow shelf.
620 Deposition of several Mn-carbonate layers (up to 4; Gnoevaya et al., 1982) during Early Oligocene
621 suggests for intermittent euxinic conditions, like those in the modern Baltic Sea deeps (Lenz et al.,
622 2015).

623 This model is also supported by the Mo content of the Mn-ore layer (Table 3). Molybdenum
624 concentrations of this layer are generally below 10 ppm (except for sample OBR-5-1262; Table
625 3). Studies on modern euxinic basins (Scott and Lyons, 2012) showed that Mo concentrations
626 exceeding 100 ppm in sediments are a strong indicator for the presence of H₂S in the water column
627 overlying the sediment. It has also been demonstrated that Mo/Al ratio of the sediments increases
628 in euxinic conditions (Algeo and Lyons, 2006). Low Mo content of the Mn-ore layer yields Mo/Al
629 ratios (not shown) below those typical for the euxinic Black Sea sediments (Eckert et al., 2013).
630 All this is in line with the hypothesis that the Mn-ore layer formed above the deep euxinic waters.

631 To understand the distribution of trace elements in the Ruslar Formation, it is necessary to
632 consider processes in the suboxic seawater layer and in the underlying anoxic (euxinic) layer.
633 Again, using the modern Black Sea as an analog of the Early Oligocene Western Black Sea,
634 particulates in the euxinic (sulfidic) deep seawater should be enriched in elements that form highly
635 insoluble sulfide minerals, whereas the overlying suboxic seawater should be enriched in those
636 elements that bind strongly to Mn-oxides. From the data reported by Lewis and Landing (1991;
637 1992), particulate Fe, Pb, and Zn are strongly enriched in deep Black Sea anoxic seawater.
638 Particulate Mn, Cu, and Ni have highest concentrations in the suboxic layer. Yigitheran et al.
639 (2011) also reported a correlation of Fe and Pb in the particulate fraction of the deep Black Sea
640 anoxic seawater. Zn did not correlate well to Fe, possibly owing to anthropogenic contributions,
641 but the authors attributed Zn removal to the formation of sulfides. Particulate Co was strongly

642 associated with Mn, as were U and V. Particulate Cr, Mo, and Ni were strongly correlated to each
643 other, but not to Mn or Fe, and they tended to have irregular vertical distributions. Cu had no
644 associations (Yigitheran et al., 2011). In summary, the euxinic deep seawater has particulates rich
645 in Fe, Pb, and Zn, whereas the suboxic shallow waters have high particulate Mn, Co, U, and V
646 concentrations. The elements Cr, Cu, Mo, and Ni can be with either seawater layer.

647 For the Ruslar Formation, using leachate compositions as representative of the non-detrital
648 component (Table 4), Mn-rich samples show a strong enrichment in Mg and V and moderate
649 enrichments in Ba, Co, Ni, and P compared to low-Mn samples, but are depleted in Ca, Fe, Pb,
650 and Zn. This pattern is consistent with deposition in the suboxic zone of an euxinic basin like the
651 modern Black Sea.

652 Strata deposited under anoxic to euxinic conditions are reported from Lower Oligocene
653 sections in various parts of Parathethys, for example the eastern Carpathians (Sachsenhofer et al.,
654 2015), Georgia (Pupp et al., 2018), Azerbaijan (Bechtel et al., 2014). We can hypothesize that the
655 euxinia in the deeper basin sequestered a substantial amount of the dissolved metals that bind to
656 S, most importantly Fe. Manganese does not make easily an insoluble sulfide, which allowed the
657 separation of Mn^{2+} dissolved in the water column from Fe^{2+} , which was incorporated in bottom
658 sediments as Fe-sulfides. The Early Oligocene transgression over the Western Black Sea shelf
659 promoted the deposition of Mn-oxides, which in turn absorbed Ba, Ce, Co, Cu, Ni, and V. During
660 early diagenesis, these Mn-oxides were converted to the Mn-carbonate layers and would have
661 retained most of this array of trace elements (e.g., Johnson et al., 2016). However, as shown by the
662 C isotope patterns described in sub-section 4.4.1, this scenario of diagenetic formation of
663 carbonates only applies to a portion of the Mn-ore beds. Other portions formed authigenically by
664 direct precipitation from the seawater of the basin as carbonates, and thus would have been less

665 prone to incorporation of those elements that bind to Mn-oxides. In modern Mn-nodules, the most
666 strongly enriched trace elements are $\text{Co} > \text{Ni} > \text{Mn} > \text{Cu}$ (Li 2000). These elements, plus Cr and V,
667 are enriched in the diagenetically formed Mn-carbonate layers compared to the authigenic ones,
668 which provides support for our model of Mn-carbonate formation by dual pathways.

669

670 *5.4. Sr, Nd, and Pb isotope constraints*

671

672 McArthur and Howarth (2004) report the following Oligocene seawater $^{87}\text{Sr}/^{86}\text{Sr}$ values
673 (error ± 0.00002): 0.707915 at 32 Ma, 0.70795 at 31 Ma, and 0.70798 at 30 Ma. The average
674 $^{87}\text{Sr}/^{86}\text{Sr}$ observed in our samples leachates is 0.707966 (± 0.00012), and excluding one outlier
675 (leachate OBR-5-1264 with $^{87}\text{Sr}/^{86}\text{Sr}=0.70837$), the average $^{87}\text{Sr}/^{86}\text{Sr}$ is 0.707941 (± 0.00006).
676 Both average leachate values (with and without the outlier) are indistinguishable from the
677 Oligocene seawater at 31 Ma, suggesting that all of Sr in the 2M HCl leachable fraction was most
678 likely derived from seawater. The slightly elevated values observed in the OBR-5-1264 sample
679 are likely due to minor incorporation of Sr from the residual, detrital fraction during the 2M HCl
680 leaching. In contrast to the leachates, the highly radiogenic Sr observed in the residues (presumably
681 representative of the terrigenous input) indicates input from continental source.

682 Peucker-Ehrenbrink et al. (2010) reported ϵNd of about -7.9 for modern Aegean Sea, which
683 is the source for the underflow entering through the Bosphorus in Black Sea. Lericolais et al. (2012)
684 reported slightly more negative ϵNd , from -8.0 to -9.0, for Danube River-derived sediments in the
685 western Black Sea. Nd isotopes in the leachates and bulk samples overall show less negative values
686 when compared to modern day input from Danube and/or Bosphorus. However, the less negative
687 values observed in our leachates and bulk samples overlap with the expected values for

688 Atlantic/Tethys seawater at 31 Ma. The leachates showing lower ϵNd compared to Atlantic/Tethys
689 (Fig. 11) can be explained either with contribution of Nd from paleo-Danube River or Nd
690 contribution from the residues. Either way, the more negative ϵNd values indicate contribution
691 from continental source. As can be seen on Figure 11 the leachates and bulk samples extend
692 towards the more negative values represented by the residues. This suggests that Nd (and
693 presumably the REE) is controlled by boundary exchange processes (mixing between seawater
694 and regionally derived detrital input), given the proximity of the sediment deposition area to nearby
695 landmasses.

696 Based on the regional geological setting, the most likely regional sources for the detrital
697 materials to the Oligocene Western Black Sea was the eastern part of the Moesian Platform (to the
698 west and north-west), the Eastern Balkanides (including eastern Stara Planina and eastern
699 Srednogorie to the west), Strandzha Mountains and Eastern Rhodope Mountains to the south-west.
700 Erosion of Cretaceous-age volcanic cover rocks from the Srednogorie Arc would have supplied
701 detrital material with low $^{87}\text{Sr}/^{86}\text{Sr}$ (~ 0.7045 ; Georgiev et al., 2009). The pre-Mesozoic basement
702 of the Srednogorie Arc, however, would have yielded more radiogenic values, ~ 0.7076 - 0.7081
703 (Georgiev et al., 2009). Detrital material from the Eastern Rhodope Mountains would likely have
704 been blocked from reaching the studied part of the Oligocene Western Black Sea by the
705 Srednogorie Arc, but explosive volcanism could have supplied the tephra component. There are
706 several contemporaneous volcanic centers, but most show either less-radiogenic Sr (0.7073 -
707 0.7078), or much higher ϵNd (-2.8 to -3.8) (Ivanova et al., 2002; Kirchenbau et al., 2012) to explain
708 the trend observed in Sr-Nd isotopes of our samples. Only Mesta volcanics, which contain acidic
709 extrusives with a large component of assimilated crust, can be a possible source as Marchev et al.
710 (2014) reported initial $^{87}\text{Sr}/^{86}\text{Sr}$ in the range of 0.71080 - 0.71521 and initial ϵNd of -6.1 to -8.1 .

711 However, even the Sr-Nd isotopic composition of the Mesta volcanics does not extend to the
712 observed high $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (as high as 0.72038) and low ϵNd (as low as -12.1) in the residues,
713 representing the detrital input to the studied area. Therefore, based on the observed data for the
714 sample residues we can rule out volcanoclastic input from the Srednogorie and/or Eastern Rhodope
715 Mountains as a major contributor of the detrital component in the studied area. The high $^{87}\text{Sr}/^{86}\text{Sr}$
716 and low ϵNd observed in the sample residues point to an older, non-arc related source for detrital
717 component, possibly lithologic units in Stara Planina and/or Moesian Platform.

718 Pb isotopes of the studied samples show a wide range of compositions with no particular
719 relationships observed between leachates and residues (Fig. 12). Overall, the Pb isotope data plot
720 above the mantle evolution line, indicating that Pb was sourced from rocks with continental crust
721 affinity. The overall linear spread in the Pb isotope data can be interpreted as Pb derivation from
722 two sources. The most plausible sediment sources in the region are the Mesozoic Srednogorie Arc
723 and the orogenic belt of Stara Planina, located between the arc terranes and the Moesian Platform.
724 As can be seen on Figure 12, the available data from Srednogorie Arc can explain some of the less
725 radiogenic Pb isotope values in the Obrochishte samples. In particular, 3 out of the 4 residues plot
726 in Srednogorie field close to Vitosha Mountain, a volcano-magmatic complex related to the
727 Mesozoic subduction. In contrast, Stara Planina detritus shows more radiogenic Pb isotopes, close
728 to the bulk and a number of leachates (Fig. 12). It is highly unlikely that the 3 samples available
729 in the literature from Stara Planina represent the full spread of Pb isotope values in the orogenic
730 belt. In addition, it is possible that some of the radiogenic Pb isotopes observed in Obrochishte
731 were derived from suspended sediments carried by proto-Danube River. Overall, the Pb isotopes
732 in the Obrochishte samples indicate continental source for the sediments, consistent with the
733 observed Sr-Nd isotopes in the residues.

734

735 *5.5. Source of Fe to the Mn-ore layer: Fe isotope constraints*

736

737 Our data argue for Mn-ore deposition at suboxic conditions in a redox-stratified marine basin
738 representative of the Oligocene Western Black Sea. Studies on the Fe cycle in a modern redox-
739 stratified marine basin (e.g., Black Sea) showed that Fe_{solid} from the oxic shelf is eventually
740 exported to the deep anoxic basin via a benthic shuttle mechanism (Severmann et al., 2008, 2010).
741 It was demonstrated that reduction of the sedimentary Fe deposited at the oxic shelf fractionates
742 Fe isotopes and produces an isotopically light Fe flux to the deep basin (Severmann et al., 2010;
743 Chever et al., 2015). Whereas $\delta^{56/54}Fe$ of the oxic shelf sediments (0.07‰) is close to that of the
744 weathering input (0‰; Dauphas et al., 2017), $\delta^{56/54}Fe$ of the anoxic-euxinic sediments is typically
745 negative, reflecting the value of the Fe shuttle ($\delta^{56/54}Fe = -1.2$ to -0.7 ‰; Severmann et al., 2008;
746 Rolison et al., 2018) and Fe isotope fractionation during diagenetic pyrite formation (Guilbaud et
747 al., 2011).

748 Iron isotope composition of the investigated Mn-ore layer is slightly negative: $\delta^{56/54}Fe_{bulk} =$
749 -0.05 ‰ (average of 14 measurements; Table 5). Pisoliths from the Mn-ore layer have more
750 negative Fe isotope composition, which is comparable to that of the modern Black Sea anoxic-
751 euxinic sediments: $\delta^{56/54}Fe_{pisolith} = -0.22$ ‰ (average of 6 measurements; Table 5), $\delta^{56/54}Fe_{Black\ Sea}$
752 $euxinic\ sediments} = -0.22$ ‰ (Severmann et al., 2008). These Fe isotope values imply: (i) significant Fe
753 isotope fractionation during diagenesis, such as dissimilatory Fe reduction leading to isotopically
754 lighter Fe in the sediment porewaters, which is then recorded in the pisoliths; (ii) a significant
755 portion of total Fe in the Mn-ore layer has been supplied through a benthic shuttle mechanism
756 (Severmann et al., 2008, 2010) from the shallow oxic shelf sediments.

757 Compared to the oxic shelf sediments of the modern Black Sea (taken as a prototype of the
758 background oxic sediments of the Oligocene Western Black Sea) that have Fe/Al ratio ranging
759 from 0.5 to 0.6 (Severmann et al., 2008), the studied Mn-ore layers display a large range of Fe/Al:
760 from 0.14 (OBR-11-6.1P) to 2.49 (OBR-11-1.2). This suggests that Fe is depleted in some Mn-ore
761 layers while being enriched in others. The large variation in the excess of Fe content is consistent
762 with a variable efficiency of the Fe shuttle. The lack of relationships between $\delta^{56/54}\text{Fe}_{\text{bulk}}$ and Fe/Al
763 further suggests that Fe enrichment/depletion processes produced only a limited Fe isotope
764 fractionation.

765 Because Mn oxidizes more slowly than Fe in seawater, and does not easily form insoluble
766 sulfides in euxinic conditions, a geographic separation of Mn and Fe deposits is often observed in
767 sedimentary Mn deposits. The lack of relationship between Fe/Mn ratio and $\delta^{56/54}\text{Fe}$ is consistent
768 with a strong decoupling between Fe and Mn enrichment processes, leading to important
769 constraints on the depositional setting of Mn-ore layers. We propose that the limited enrichment
770 of Fe in the Mn deposits result from the combined effect of (i) the efficient trapping of Fe in the
771 deeper part of the basin under euxinic conditions, which is also consistent with limited enrichment
772 in Mo in the deposits (see section 5.3.2.) and (ii) a deepening of the chemocline (suboxic/euxinic
773 interface) below the shelf edge, leading to a decreased efficiency of the Fe shuttle (e.g., Eckert et
774 al., 2013). Considering that Fe requires lower redox potential than Mn to be solubilized, the
775 expansion of suboxic conditions on the shelf would further promote the input of Mn in the water
776 column, which can then be incorporated in Mn deposits either through direct precipitation in the
777 water column, or through co-precipitation of Mn oxides and organic matter and further diagenetic
778 reactions [see below and Maynard (2014)].

779

780 *5.6. Mechanisms of Mn-carbonate deposition: C and O stable isotope constraints*

781

782 The studied bulk samples from the Mn-ore bed are mostly composed of Mn-carbonates
783 (Table 1). Hence, the C and O isotope composition of these samples (Table 5) reflects the C and
784 O isotope composition of the Mn-carbonates, the major ore component.

785 C-O-isotope data distribution along two distinct trends (Fig. 9A), suggests two different
786 mechanisms of Mn-carbonate precipitation at the studied region. All samples from the southern
787 part (south of Obrochishte mine, sites ##6, 7, 8, 9, 10; Fig. 1B) as well as some samples from the
788 north-eastern part of the Ruslar Formation (sites ##1, 2, 3; pisoliths from the lower part of the Mn-
789 ore bed at site #11; Fig. 1B) lie along the mixing line between the modern Danube River water and
790 Oligocene seawater (Fig. 9A). This suggests that C and O in the Mn-carbonates of the ore bed
791 derived from two distinct sources: fresh water and seawater. Oligocene seawater is a reasonable
792 source of C and O in carbonates deposited in the Oligocene marine basin. Questionable remains
793 the fresh water source of C and O in Mn-carbonate deposits, which are interpreted to be submarine
794 based on lithostratigraphic evidence (Aleksiev, 1960a; Stoyanov, 1963). The only possible
795 submarine source of fresh water at continental margins is the submarine groundwater discharge
796 (SGD) (Moore, 2010; Santos et al., 2012). SGD comprises terrestrial fresh groundwater mixed
797 with seawater that has infiltrated coastal aquifers, and flows from the seafloor to the coastal ocean
798 (Moore, 2010). It has recently been recognized as a global phenomenon (and also widespread in
799 the Black Sea; Schubert et al., 2017), which is an important source of fresh water and dissolved
800 elements to the ocean, comparable to the riverine input (Moore, 2010). This water flux contains
801 high concentrations of dissolved inorganic carbon (DIC), Fe, and Mn (Windom et al., 2006;
802 Szymczycha and Pempkowiak, 2016). Thus, the precipitation of Mn-carbonates, which plot along

803 the mixing line between the fresh water and Oligocene seawater C-O-isotope composition (Fig.
804 9A), is explained by SGD at the Oligocene Western Black Sea shelf. According to the
805 paleogeographical reconstructions (e.g., Nikishin et al., 2015), the area of deposition of the Ruslar
806 Formation was a wide shelf (Western Black Sea basin) bounded by the Balkan High to the south
807 and Moesian High to the north-west during the Oligocene. The elevated landmasses could have
808 provided a sufficient hydraulic head difference to overcome the pressure from seawater and allow
809 groundwater to discharge onto the seafloor.

810 The proportions of two end-members of the SGD, fresh water and seawater, vary spatially
811 and temporally due to a number of factors (Moore, 2010; Santos et al., 2012). Thus, the spread of
812 the data points between both end-members (Fig. 9A) reflects the different contribution of fresh
813 water and seawater to the C and O isotope composition of the Mn-carbonates. Mn-carbonates in
814 the southern part of the Ruslar Formation (associated with ~400 m thick clays and sandstones; Fig.
815 1B) formed at higher proportion of fresh SGD than the Mn-carbonates from the north-eastern part
816 of the Ruslar Formation (associated with ~100-250 m thick clays, sandstones, and marls; Fig. 1B)
817 (Fig. 9A).

818 Mn-carbonates that show precipitation at submarine groundwater discharge with varying
819 contribution of its two components (fresh water and seawater, Fig. 9A) cluster along a trend at the
820 $\delta^{13}\text{C} - \text{MnO}$ space (Fig. 9B) suggesting precipitation by direct reaction with HCO_3^- . The second
821 group of Mn-carbonate samples comprising those from the upper part of Mn-ore bed at site #11
822 and lower part of Mn-ore bed at site #5 form distinct arrays at both C-O-isotope diagrams (Fig.
823 9A, B), suggests they formed by oxidation of organic matter within the sediment. Thus, the Mn-
824 carbonates from the studied Mn-ore bed likely formed via two different mechanisms: (1)
825 precipitation through reaction of dissolved inorganic species (e.g., Mn^{2+} and HCO_3^-), and (2)

826 diagenetic precipitation mediated by oxidation of organic matter. Whereas the second mechanism
827 operated within the sediment, the first may have worked either in the water column or in the near-
828 seafloor sediment pore space.

829 The average range for C isotopic compositions in sediment-hosted Mn-carbonate ores is -1
830 to -16‰ (based on a survey of 17 deposits with isotopic data compiled at
831 http://www.sedimentaryores.net/Index_Mn.html). Some samples from the Obrochishte deposit
832 have $\delta^{13}\text{C}$ values outside this range, both positive and negative (Table 5). $\delta^{13}\text{C}$ values in the range
833 0 to +5‰ are reported for 6 of the 17 deposits listed in the database cited above, so this is a common
834 situation. Almost all are associated with high Ca/Mn ratio, as are most of the positive values for
835 Obrochishte samples. Such values could result from slight evaporation of seawater, or be from
836 residual CO_2 left from CH_4 fermentation during early diagenesis, with the CH_4 escaping. Two
837 samples from the Obrochishte deposit have very light $\delta^{13}\text{C}$ values (Table 5). Similar values have
838 been reported for 3 of the 17 deposits in the database, so this situation is not common, but also not
839 unusual. These values could result from CO_2 totally sourced from oxidation of marine organic
840 matter or, more likely, from oxidation of CH_4 .

841 The long-standing debate on the source of Mn to the Oligocene Western Black Sea and,
842 eventually, to the deposited Mn-carbonates was recently summarized by Vangelova et al. (2005).
843 We will just underline the earlier observations of Aleksiev (1959) on the lithology and stratigraphy
844 of the Oligocene Series in NE Bulgaria and his interpretations about the Mn source to the
845 Oligocene Black Sea basin. He described three (in some sections four) sets of rhyolite tuff layers
846 across the Oligocene Series in NE Bulgaria and noticed that the Mn ore layers either immediately
847 overlie the tuff layers, or are intercalated in them (Aleksiev, 1959; Huff et al., 2014). Based on
848 lithology, mineralogy, and geochemistry studies, Aleksiev (1959) assumed that the tuff layers were

849 a result of submarine volcanic activity within the Oligocene Western Black Sea. He suggested that
850 post-volcanic submarine hydrothermal activity was the source of Mn to the Mn-ore deposits
851 around the modern Black Sea. Later work has not added anything meaningful to this problem
852 except for far-going “exotic” hypotheses about the Mn source and origin of the Mn-ore bed
853 [summarized in Vangelova et al. (2005)].

854 Based on the interpretation of our C and O isotope data we suggest that in addition to or
855 instead of the inferred submarine hydrothermal source of Mn (Aleksiev, 1959), the submarine
856 groundwater discharge may be another possible Mn source in the Oligocene Western Black Sea.
857 Studies on the redox conditions in the SGD show that they vary from oxic to anoxic depending on
858 the proportions of fresh water and recirculated seawater, and local conditions at the seafloor
859 (Moore, 2010; Santos et al., 2012). Transportation of Mn in dissolved state within the SGD and its
860 input into the marine basin generally requires suboxic to anoxic conditions. Further, the
861 precipitation of Mn in solid phase and deposition at the seafloor requires either high Eh ($E_h > 530$
862 mV at pH=7 and $T=25^\circ\text{C}$, and preliminary precipitation as Mn-oxyhydroxides), or high alkalinity,
863 or very high dissolved Mn concentrations (direct precipitation as Mn-carbonates).

864 We may speculate about the mechanisms of Mn-carbonate precipitation at the Oligocene
865 Western Black Sea floor. The REE evidence shows that the eventual Mn-carbonates had formed
866 at suboxic seawater conditions (see 5.2). Suboxic conditions can exist throughout large volumes
867 of seawater column: suboxic and anoxic marine basins, and oxygen-minimum zone at continental
868 margins. Although we are not aware of existence of highly alkaline conditions in large seawater
869 masses in the modern ocean, we cannot completely rule out the temporary establishment of
870 alkaline conditions in isolated and semi-isolated marine basins. Hence, direct precipitation of Mn-
871 carbonates in the seawater column seems likely when a high flux of dissolved Mn into a suboxic

872 seawater layer is combined with increased alkalinity. In modern times this process has been
873 reported only in lakes (Havig et al., 2018; Herndon et al., 2018).

874 Could this high Mn flux have been caused by purely sedimentary processes? It is tempting
875 to view the diagenetic Mn as forming from Mn-oxide particles settled in the suboxic water layer,
876 where the highest particulate Mn occurs (e.g., Lewis and Landing, 1991), whereas the authigenic
877 Mn is formed in the underlying anoxic euxinic layer, where the highest dissolved Mn is found
878 (Lewis and Landing, 1991). If this was the case, we would expect to see higher S in the authigenic
879 Mn (deeper water, below the H₂S interface). Furthermore, there should be a weak Ce anomaly in
880 the authigenic Mn precipitates, but a large one in the diagenetic Mn phases. Our results show that
881 the reverse is true for both parameters: S_{tot} averages 0.21% in the authigenic beds compared with
882 0.54% in the diagenetic beds. Ce/Ce* of the leachate is 0.75 in the authigenic beds, 0.81 in the
883 diagenetic. (We excluded the fresh water-influenced samples from these calculations). Thus, the
884 authigenic beds that dominate the ore body have geochemical properties inconsistent with a
885 deposition in anoxic euxinic deep waters. The only reasonable possibility that remains is
886 precipitation of authigenic Mn-carbonates in the suboxic water column. To have this process
887 working and producing ore-grade Mn deposit there should be high dissolved Mn flux and alkalinity
888 in the suboxic zone.

889 The group of samples that were strongly affected by SGD (with the highest fresh water
890 contribution), based on C-O-isotopes, have sub-economic concentrations of Mn in all cases (Fig.
891 9). Hence, it would appear that, at least for the Obrochishte case, an inferred Mn flux from SGD
892 alone was not sufficient to produce a major Mn deposit. Considering the high-Mn samples, all
893 have O-isotopes consistent with precipitation from seawater with a minor fresh water component
894 (presumably SGD) (Fig. 9A). Those, whose C-isotopes indicate diagenetic conversion of Mn-

895 oxide to Mn-carbonate, have trace element signatures suggestive of primary deposition as Mn-
896 oxide. By contrast, the samples whose C-isotopes indicate direct precipitation in seawater column
897 are enriched in Ba, Pb, and Zn, elements that are mobilized and released from the sediment during
898 organic matter-driven diagenesis (Gobeil and Silverberg, 1989; Kerner and Wallmann, 1992;
899 McManus et al., 1994; Hendy, 2010).

900

901 *5.7. Model of formation of the Obrochishte Mn deposit*

902

903 There is virtually no direct evidence for hydrothermal Mn input in the Oligocene Western
904 Black Sea other than the tuff layers associated with the deposit. Bulk chemistry of the Obrochishte
905 Mn-ores is the same as background sediment, except for Mn and C. Oxygen isotopes do not suggest
906 a hydrothermal component. Nd, Pb, and Sr isotopes reflect seawater, or local clastics. Textures
907 and sequence stratigraphy seem more or less like any other Phanerozoic deposit. But the mass of
908 Mn contained in this narrow time interval is at least 600×10^6 tons (Maynard, 2010), more than all
909 of the rest of the Phanerozoic deposits combined, and precipitated in only about 500,000 years.
910 This truly remarkable geochemical event suggests some special circumstances at this time interval.
911 The Earth climate was coming off an exceptionally high temperature and high P_{CO_2} at the Early
912 Eocene Climatic Optimum (EECO) (50-52 Ma, Zachos et al., 2001). This event was followed by
913 the initiation of glaciation in Antarctica at the end of Eocene and beginning of Oligocene,
914 accompanied by one of the sharpest drops in temperature and sea level in the Phanerozoic. It is
915 likely that the intense chemical weathering during the Eocene produced a thick residuum enriched
916 in kaolinite and Fe- and Mn-oxyhydroxides on the continents and these processes peaked ~ 35 Ma,
917 during the Late Eocene (see for example Retallack, 2010) (Fig. 13 A). The Early Oligocene sea

918 level fall caused rapid erosion of these lateritic deposits, while at the same time producing
919 restricted basins and anoxic euxinic conditions (Fig. 13 B). The hypothesis of erosion of the
920 Eocene laterites is supported by a recent study (Dekoninck et al., 2019) of the weathering of
921 primary Mn-rich sedimentary rocks (Ordovician) and formation of supergene Mn-deposits (Late
922 Oligocene – Late Neogene) in the Central and Western Europe. It concluded that the old
923 weathering series/systems (e.g., Eocene) must have been removed (at least partly) from the
924 geological record. The erosion products that found their way to the open ocean remained as stable
925 detrital sediments. Fe- and Mn-oxyhydroxides deposited into anoxic euxinic basins (like the
926 Western Black Sea) were dissolved and released Fe and Mn in the seawater. The Fe was
927 reprecipitated as Fe-sulfides while the Mn accumulated as dissolved Mn^{2+} in the anoxic euxinic
928 water column (Fig. 13 B). Suboxic water layer formed as a transition zone between the deep anoxic
929 and surface oxic waters. Steep concentration gradient of dissolved Mn across the suboxic-anoxic
930 interface caused Mn diffusion towards the suboxic layer where it oxidized and sank back into the
931 anoxic waters (Fig. 13 C). The amount of oxidized Mn^{2+} in the suboxic layer was controlled by
932 the available dissolved O_2 . Due to the general depletion of O_2 in this layer part of the dissolved
933 Mn supplied from below remained as Mn^{2+} . The weathering-related Mn flux to the Western Black
934 Sea was supplemented by SGD Mn flux. Volcaniclastic layers below and among the Mn-ore layers
935 (Aleksiev, 1959) imply that ash fall dissolution in seawater (e.g., Frogner et al., 2001; Randazzo
936 et al., 2009; Censi et al., 2010) may have additionally supplied Mn in the basin before and during
937 Mn-ore deposition (Fig. 13 C). Alteration of this ash would also have increased alkalinity and
938 raised the dissolved silica level in sediment pore waters (e.g., Lyons et al., 2000).

939 Was the dissolved Mn stored in the Oligocene Black Sea enough to produce the Mn ores
940 deposited there? The dissolved Mn inventory of the modern Black Sea is about 220×10^6 metric

941 tons (5.03×10^5 km³ seawater below chemocline with 8 μ M dissolved Mn). This amount compares
942 to 550×10^6 tons of Mn in high-grade ores in all Oligocene deposits combined (Maynard, 2014).
943 Assuming an equal mass for low-grade ore, the total resource is about 1000×10^6 tons of Mn. Even
944 if all of the dissolved Mn in the modern Black Sea could be precipitated at once, it would still fall
945 short by a factor of five. How often is this mass of Mn renewed? In the fluxes of Mn to the Black
946 Sea, particulate-borne Mn in river suspended solids dominates substantially over dissolved
947 transport, and the Danube dominates all other river sources. Annual suspended load for the Danube
948 before dam construction was about 47×10^6 tons/year (Oaie et al., 2005) with 1380 mg/kg Mn
949 (Yigiterhan and Murray, 2008). Deep-water sediments contain approximately 620 mg/kg of Mn
950 (Brumsack, 1989) so the net contribution of Mn from the Danube flux is 760 mg/kg or 3.6×10^4
951 tons/year of Mn. Using the same concentration values for other rivers entering the Black Sea would
952 add another 0.6×10^4 tons, based on suspended loads from Mikhailova (2009). Total river sources
953 would then be 4.2×10^4 tons/year. Some of this river flux is lost to the Mediterranean Sea via the
954 net outflow through the Bosphorus Strait, but the amount is very small compared to the river flux.
955 At 4.2×10^4 tons/year it would take only 24000 years to supply all of the Mn in the Oligocene
956 economic deposits. Even if the efficiency were only 10%, there would be adequate supply to
957 account for the existing deposits. But there are no large accumulations of Mn forming in the Black
958 Sea today, suggesting that there must be additional factors beyond the existence of a large euxinic
959 basin responsible for the formation of the ore bodies.

960 Eocene-Oligocene glaciation had led to an increased ocean alkalinity on a global scale
961 (Coxall et al., 2005). Ephemeral glacial ice (Greenland) and sea ice (Arctic) formed in the Northern
962 Hemisphere (Tripathi and Darby, 2018). We can assume that there may have been at least
963 permafrost in northern Europe (the drainage area of the big rivers emptying in Oligocene Black

964 Sea). This would mean that the groundwater table had lowered in the northern Europe during the
965 cooling event at Eocene-Oligocene boundary.

966 Early Oligocene warming and sea level rise must have led to a marine transgression over the
967 Western Black Sea shelf. The suboxic layer of vertically stratified seawater would have impinged
968 on the shelf. From what we know from the modern Black Sea, this layer contained both suspended
969 MnO_2 and dissolved Mn^{2+} . Settled MnO_2 particles had diagenetically transformed into MnCO_3 :
970 MnO_2 dissolution, Mn^{4+} reduction to Mn^{2+} , and Mn^{2+} re-precipitation as MnCO_3 (Fig. 13 C).

971 Early Oligocene warming had caused permafrost/glacier melting in northern Europe, which
972 would have increased the groundwater volume and led to groundwater table rise (e.g., Liljedahl et
973 al., 2017). As a result, the SGD flux should have increased and this would bring HCO_3^- and
974 alkalinity directly in the Western Black Sea shelf. Eocene rocks (potential groundwater aquifer
975 during Early Oligocene) that underlie Obrochishte Mn-layer are mostly carbonates. Hence, high
976 HCO_3^- and alkalinity supply (through SGD and as a result of previous glaciation) to the shelf seems
977 possible.

978 Thus, dissolved Mn^{2+} precipitation as Mn-carbonates in suboxic water layer overlaps with
979 diagenetic Mn-carbonate precipitation from MnO_2 precursor in the sediment (Fig. 13 C). Dissolved
980 Mn precipitation will draw down its content in the suboxic layer and this will cause pumping of
981 dissolved Mn from the deeper anoxic Mn store due to sharp concentration gradient and molecular
982 diffusion, eddy diffusion and turbulent mixing (e.g., Podymov et al., 2017). This pumping
983 mechanism will supply high dissolved Mn flux to the shelf where it will meet high alkalinity flux
984 and this will result in authigenic precipitation of Mn-carbonates in the seawater column.

985

986 *5.8. Comparison of Obrochishte Mn-deposit to other Oligocene Mn-deposits around the Black Sea*

987

988 Although the Oligocene Mn-deposits around the Black Sea have been studied for many
989 years, data is still spotty and incomplete, except for major elements (Table 6). Isotopic data for
990 radiogenic isotopes are not available that we know of, but some information on stable isotopes of
991 C and O has been published [see Kuleshov (2017) for a summary]. However, there is a lack of
992 systematic data where major, trace element, and isotopic data were acquired on the same samples.
993 There is only enough systematic data for us to make comparisons for C and O isotopes for three
994 deposits: Binkiliç (Turkey), Chiatura (Georgia), and Mangyshlak (Kazakhstan). The detailed
995 datasets for each of these deposits are available at
996 <http://www.sedimentaryores.net/Manganese/Black%20Sea%20index.html>.

997 Binkiliç Mn-deposit shows a pattern of stable isotopes with a cluster tightly grouped around
998 $-6.6\text{‰ } \delta^{13}\text{C}_{\text{VPDB}}$ and $-7\text{‰ } \delta^{18}\text{O}_{\text{VPDB}}$ (Fig. 14 A). The C isotopes do not show a correlation with
999 the amount of Mn (Fig. 14 B), which is not consistent with the formation of MnCO_3 by reaction
1000 of MnO or MnO_2 with organic matter during early diagenesis. Instead, direct precipitation in the
1001 water column is more likely. Ozturk and Frakes (1995) interpreted the uniformly light oxygen
1002 isotope values as indicating an important role of meteoric water in ore genesis. We speculate that
1003 Binkiliç Mn-deposit could have formed in a large freshwater lake.

1004 The Mn-deposits at Chiatura have isotopic values that are strongly overprinted by a late
1005 diagenetic event, one that added considerable Ca and some Mn from a fluid with $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$
1006 close to 0‰ (Fig. 14 C,D) [see Kuleshov (2017) for a discussion].

1007 Of the three deposits for which we have sufficient data, Mangyshlak is closest in isotope
1008 behavior to Obrochishte. A plot of MnO content vs $\delta^{13}\text{C}$ (Fig. 14 E) shows the same two
1009 populations as at Obrochishte: (1) has constant $\delta^{13}\text{C}$ at all MnO contents, indicating direct

1010 precipitation of MnCO_3 in the water column (This data population has low R^2 (0.30) and high p
1011 (0.17), which suggests there has to be some significant additional factor at work for these samples:
1012 likely an irregular component of diagenetic addition of lighter $\delta^{13}\text{C}$.), and (2) has a negative
1013 covariance of MnO content and $\delta^{13}\text{C}$, indicating production of MnCO_3 via reaction of MnO_2 with
1014 organic matter during early diagenesis (This data population has R^2 of 0.82 and a p value of 0.01
1015 for the regression, which suggests that this group of samples is well-explained by our model.). A
1016 plot of $\delta^{18}\text{O}$ vs $\delta^{13}\text{C}$ (Fig. 14 F) shows a linear trend to sharply lighter $\delta^{18}\text{O}$ at nearly constant $\delta^{13}\text{C}$,
1017 suggestive of groundwater-seawater mixing, as at Obrochishte, but this time, only calcite is
1018 involved.

1019

1020

1021 6. Conclusions

1022

1023 Isotope geochemistry of the Obrochishte Mn-deposit revealed surprising complexity in the
1024 details of Mn precipitation. The data indicate involvement of normal seawater and meteoric water
1025 (presumably from submarine groundwater discharges onto the seafloor). There was authigenic as
1026 well as diagenetic precipitation of the main ore minerals, Mn-carbonates. We present a general
1027 model of the formation of the Obrochishte Mn-deposit (Fig. 13) that we believe is applicable to
1028 the series of deposits of this age that encircle the present-day Black Sea and explains the peculiar
1029 concentration of Mn ores at this time and place. Intense weathering during the Eocene weathering
1030 phase produced thick lateritic soils enriched in Fe and Mn. The dramatic sea level fall at the
1031 Eocene-Oligocene boundary caused flushing of the lateritic residue into marginal basins while at
1032 the same time led to isolation of these basins from the global ocean which fostered anoxic

1033 conditions. The sea level fall also produced a much greater head difference between groundwater
1034 recharge areas and the continental shelf, which intensified submarine discharge of Mn-bearing
1035 groundwater. Continent-derived Fe and Mn were transferred to a redox-stratified Western Black
1036 Sea basin, similar to the modern Black Sea. Most of the Fe was sequestered in deep anoxic-euxinic
1037 water as sulfides, while Mn accumulated in the suboxic water layer. Transgression of this Mn-rich
1038 seawater onto the shallow shelf, and some Mn contribution from submarine ground water
1039 discharge, led to the formation of the Oligocene Mn deposits. This unique sequence of events and
1040 the configuration of the continental masses around the depositional basin produced the exceptional
1041 accumulations of Mn around the Black Sea.

1042

1043

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1045

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1052

1053

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1354 **Figure captions**

1355

1356 **Fig. 1.** (A) Simplified geological map of the tectonic framework of Bulgaria (after Ivanov, 1988)
 1357 with the location of the studied north-eastern region (B). Each tectonic unit includes several
 1358 geomorphology structures. Some of them (not all) are mentioned in the paper: e.g., the Balkan
 1359 Zone includes Stara Planina Mountains, Sredna gora Zone includes Sredna gora (Srednogorie) and
 1360 Vitosha Mountains, Sakar-Strandzha Zone includes Strandzha Mountains, and Rhodope Massif
 1361 includes Rhodope Mountains and Mesta Basin. (B) Map of the distribution of the Ruslar Formation
 1362 in the NE Bulgaria and adjacent Black Sea shelf (based on unpublished data of Juranov and
 1363 Valchev from 338 drill holes) with the sample sites: white circles = drill holes, black circles =
 1364 outcrops, black star = mine. Legend: I = Ruslar Formation, in general; II = under-marl unit with
 1365 the Mn-ore bed at the base; III = marl unit; IV = over-marl unit; V = boundaries of extension of
 1366 the lithostratigraphic units (LSU), a – proven, b – extrapolated; VI = edge of the continental shelf;
 1367 VII = fault. Sample site numbers: 1 = C-258a Dobruja drill hole (sample OBR-1-3270), 2 = C-
 1368 140a Dobruja drill hole (sample OBR-2-1601), 3 = C-170a Dobruja drill hole (sample OBR-3-
 1369 1622), 4 = C-3a Makedonka drill hole (sample OBR-4-1413), 5 = C-138a Dobruja drill hole
 1370 (samples OBR-5-1261, -1262, -1263, -1264, -1265, -1266, -1267; -1302), 6 = NE of Pripek village
 1371 (sample OBR-6-3186), 7 = Kalimanski dol (samples OBR-7-3178, -3205, -4130, -4131), 8 = E of
 1372 Pripek village (samples OBR-8-4136, -3193, -A, -B), 9 = Ichme kulak (samples OBR-9-3884, -
 1373 3885), 10 = Kondulak cheshme (sample OBR-10-164), 11 = Obrochishte mine (samples OBR-11-
 1374 1.2, -1.8, -2.8, -3.8, -4.4, -5.1, -5.7, -6.1). Summary lithostratigraphic core logs representative for
 1375 different areas (arrows) are shown at the right-hand side.

1376

1377 **Fig. 2.** Chunk of Mn-ore with concentrically-laminated pisoliths of Mn-carbonates within matrix
 1378 of Mn-carbonates and clays (sample OBR-11-5.7).

1379

1380 **Fig. 3.** Photomicrographs (optical polarizing microscope; sample OBR-11-1.2) of: (A) pisolith
 1381 layers (transmitted light, $\parallel N$); (B) the same as at (A) at $\times N$, note the carbonate-rich layers (high
 1382 interference colors) alternating with carbonate-poor layers (light to dark brown); (C) rhodochrosite
 1383 (rh) layers in pisolith (transmitted light, $\parallel N$); (D) the same as at (C) at $\times N$; (E) veins of pyrite
 1384 (black; py) in matrix of Mn-carbonate and clays, note the thin rims of rhodochrosite (white; rh)
 1385 along the pyrite veins (transmitted light, $\parallel N$); (F) the same as at (E) in reflected light at $\parallel N$; (G)
 1386 pyrite vein (white; py) (close up) with rhodochrosite rhombic crystals (greyish-black; rh) (reflected
 1387 light, $\parallel N$); (H) pyrite vein (white; py) (close up) with secondary alterations along cracks and
 1388 rhodochrosite rhombic crystals (greyish-black; rh) (reflected light, $\parallel N$).

1389

1390 **Fig. 4.** X-ray fluorescence maps of the distribution of elements across a pisolith within the ore
 1391 matrix (sample OBR-11-6.1): (A) microphotograph (thin polished section) of the pisolith, general
 1392 view; (B) X-ray fluorescence scan in Mn K_{α} ; (C) X-ray fluorescence scan in Ca K_{α} ; (D) X-ray
 1393 fluorescence scan in Al K_{α} ; (E) X-ray fluorescence scan in Si K_{α} ; (F) X-ray fluorescence scan in
 1394 Fe K_{β} ; (G) X-ray fluorescence scan in Rb K_{α} ; (H) X-ray fluorescence scan in Zr K_{α} . Brighter colors
 1395 correspond to higher concentrations.

1396

1397 **Fig. 5.** SEM photomicrographs (SEI; sample OBR-11-6.1) of: (A) laminae of carbonate
 1398 (composition is consistent with Ca-rhodochrosite: $Mn_{80}Ca_{11}Mg_7Fe_2$ (mole %)) in pisolith; (B) sub-
 1399 micron spheres (Si/Mn = 3/1) likely composed of silica and rhodochrosite.

1400

1401 **Fig. 6.** X-ray fluorescence maps of the distribution of elements across a pyrite vein within the ore
 1402 matrix (sample OBR-11-1.2): (A) microphotograph (thin polished section) of the pyrite (py) vein
 1403 (black), general view; (B) X-ray fluorescence scan in Fe K_{β} ; (C) X-ray fluorescence scan in S K_{α} .
 1404 Brighter colors correspond to higher concentrations.

1405

1406 **Fig. 7.** Correlation between S_{tot} and C_{org} concentrations in the studied samples.

1407

1408 **Fig. 8.** C1 chondrite-normalized (Sun and McDonough, 1989) REE distribution patterns of
 1409 samples: (A) OBR-11-1.8 (Mn-ore bed); (B) OBR-11 (Mn-ore bed): bulks, 2N HCl leachates,
 1410 residues; (C) OBR-11 (Mn-ore bed): 2N HCl pisolith leachates, pisolith residues; (D) OBR-5 (Mn-
 1411 ore bed): 2N HCl leachates, residues; (E) oxic (50 m water depth), suboxic (100 m water depth)
 1412 and anoxic (2185 m water depth) seawater from Black Sea (German et al., 1991); (F) OBR-8-A
 1413 (above Mn-ore bed) and average UCC (McLennan, 1989).

1414

1415 **Fig. 9.** C and O stable isotope correlation diagrams of studied carbonates from Ruslar Formation:
 1416 (A) $\delta^{18}\text{O} - \delta^{13}\text{C}$ correlation diagram. Note, the two arrays of the data point distribution: one at
 1417 constant $\delta^{18}\text{O}$, the other with linear $\delta^{18}\text{O} - \delta^{13}\text{C}$ correlation. Oligocene seawater data from
 1418 Armstrong-McKay et al. (2016); modern Danube River water data from Povinec et al. (2013) and
 1419 Rank et al. (2014). (B) $\delta^{13}\text{C} - \text{MnO}$ correlation diagram. Note, the two trends in data point
 1420 distribution suggesting two sources of C in Mn carbonates. Squares = samples from the southern
 1421 part of Ruslar Formation (sites ##6, 7, 8, 9, 10; Fig. 1B); circles (open, blue and green) = samples

1422 from the northern part of Ruslar Formation (sites ##1, 2, 3, 5, 11); blue circles = upper part of Mn-
1423 ore bed at site #11; green circles = lower part of Mn-ore bed at site #5.

1424

1425 **Fig. 10.** Comparison of Sr isotopic compositions of bulk, leachate and residue samples with
1426 seawater Sr isotope curve. Note, the residue for sample OBR-5-1264 ($^{87}\text{Sr}/^{86}\text{Sr}=0.72038$) plots
1427 beyond the scale of the plot. Seawater Sr curve from McArthur and Howarth (2004).

1428

1429 **Fig. 11.** Comparison of Nd isotopic compositions of bulk, leachate and residue samples with
1430 Atlantic and Tethys seawater. Seawater field after Stille et al. (1996).

1431

1432 **Fig. 12.** Pb isotopic compositions of bulk, leachate and residue samples compared to Srednogorie
1433 Arc (including Vitosha volcano-magmatic complex) and Stara Planina detritus. Note that there is
1434 no particular trend between leachates and residues. Overall, Obrochishte Pb isotopes do not show
1435 any significant mantle input and indicate derivation from crustal sources. Srednogorie Arc data
1436 from Georgiev et al. (2009), Vitosha and Stara Planina from Kamenov (2008), Continental crust
1437 and Mantle evolution lines from Stacey and Kramers (1975).

1438

1439 **Fig. 13.** Schematic representation of our hypothesis for the sources of Mn, accumulation of
1440 dissolved Mn in the Oligocene Western Black Sea water, modes of Mn deposition at the shelf, and
1441 formation of Obrochishte Mn deposit (Ruslar Formation, Oligocene Series). (A) Enhanced
1442 chemical weathering during the Eocene weathering phase (EECO, 50-52 Ma) resulted in thick
1443 laterite crusts rich in Fe- and Mn-oxyhydroxides in the drainage basin of the Western Black Sea.
1444 World Ocean (including Western Black Sea) was characterized by a high sea-level stand during

1445 this warm epoch. Groundwater table in the drainage basin was high. (B) Late Eocene cooling that
1446 peaked at the Eocene-Oligocene transition (33-35 Ma) led to glaciations (continental ice sheets
1447 and sea ice) in both hemispheres. This resulted in low (global) sea-level stand, isolation of the
1448 small marine basins (e.g., Black Sea) which in turn provoked onset of anoxia conditions. Sea-level
1449 fall drew down the erosional basis of the rivers that led to increased erosion of the laterite crusts.
1450 Residually accumulated Fe- and Mn-oxyhydroxides in the laterites were swept away into the
1451 ocean. In vertically stratified anoxic marine basins (with oxic, suboxic and anoxic water layers)
1452 they remained in suspended state in the oxic and suboxic water layers, but were dissolved in the
1453 anoxic deep waters when they sank down. In anoxic-euxinic waters (with free HS⁻) dissolved Fe
1454 and other chalcophile elements (e.g., Cu, Zn, Pb) were immobilized as sulfides, which settled on
1455 the seafloor while dissolved Mn was accumulated in seawater. (C) Early Oligocene warming (25-
1456 32 Ma) caused glacier and sea ice melting, and rise of both sea-level and groundwater table. In the
1457 anoxic Western Black Sea the suboxic layer migrated upward (synchronously with sea-level rise)
1458 and impinged on the shelf. Steep gradient of the dissolved Mn²⁺ concentration across the suboxic-
1459 anoxic interface and turbulent mixing caused dissolved Mn flux (molecular diffusion and eddies)
1460 from the deep Mn storage to the suboxic water layer. Part of dissolved Mn²⁺ precipitated as MnO₂
1461 and the amount of immobilized Mn²⁺ was controlled by the available O₂ in this layer. Sinking
1462 MnO₂ particles could either fall back in the anoxic water where they re-dissolved (Mn²⁺), or settle
1463 on the seafloor in the suboxic layer. The last could be reduced in the presence of organic matter in
1464 the sediment and liberated Mn²⁺ may react with CO₂ and precipitate as MnCO₃ (diagenetic
1465 precipitation). High groundwater table would produce high SGD flux through the seafloor which
1466 will supply HCO₃⁻ and alkalinity to the suboxic water layer. Excess dissolved Mn²⁺ in the suboxic
1467 layer would react with HCO₃⁻ in the alkaline environment and precipitate as MnCO₃ in the water

1468 column (authigenic precipitation). Volcanic ash fall contemporary of MnCO_3 precipitation had
 1469 supplied additional amount of Mn (through partial dissolution of ash particles) to the basin.
 1470 Manganese diffusion-turbulent pump from the deep anoxic Mn storage to the suboxic water layer
 1471 would supply Mn enough for formation of large Mn deposits around the Oligocene Black Sea.

1472

1473 **Fig. 14.** $\delta^{18}\text{O} - \delta^{13}\text{C}$ and $\delta^{13}\text{C} - \text{MnO}$ correlation diagrams of Mn-ore samples from Binkiliç (A,
 1474 B) [data from Öztürk and Frakes (1995)], Chiatura (C, D) [data from Kuleshov and Dombrovskaya
 1475 (1997)], and Mangyshlak (E, F) [data from Kuleshov (2003, 2017)] deposits.

- 1476 • Mn-carbonate ore at the Obrochishte has dual origin: diagenetic and authigenic
- 1477 • Mn deposition was a result of the climatic events at the Late Eocene-Early Oligocene
- 1478 • Mn ore was deposited in a redox-stratified basin, similar to the modern Black Sea

1479

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1482

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1490

1491 November 14, 2019

1492

1493 Dear Sirs,

1494

1495 I, on behalf of my co-authors, declare that there is no conflict of interests in our work submitted to
 1496 your Journal as manuscript entitled "Origin of the Oligocene manganese deposit at Obrochishte (Bulgaria):
 1497 Insights from C, O, Fe, Sr, Nd, and Pb isotopes" by V.M. Dekov, J.B. Maynard, G.D. Kamenov, O. Rouxel, S.
 1498 Lalonde and S. Juranov. The manuscript is an original work, not published elsewhere or under
 1499 consideration for publication elsewhere.

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Sincerely Yours

Vesselin Dekov

1506
1507**Table 1**

Investigated samples from the Oligocene Mn-ore layer in NE Bulgaria.

Sample ID	Sample type	Sample site	Stratigraphic position	Position, m above base	Mineralogy ^a								
					Rhodochrosite	Kutnahorite	Mn-calcite	Dolomite	Apatite	Quartz	Plagioclase	Illite-smectite	Kaolinite
OBR-1-3270 ^b	drill core	C-258a Dobruja	lower part of Ruslar Fmn	below Mn-rich layer	-	2	49	-	-	18	-	31	-
OBR-2-1601	drill core	C-140a Dobruja	lower part of Ruslar Fmn	Mn-rich layer	32	16	-	31	-	14	7	-	-
OBR-3-1622	drill core	C-170a Dobruja	Ruslar Fmn	-	-	-	-	-	-	-	-	-	-
OBR-4-1413	drill core	Makedonka	lower part of Ruslar Fmn	4.4 above Mn-rich layer;	-	-	-	-	-	8	14	77	-
OBR-5-1261	drill core	C-138a Dobruja	lower part of Ruslar Fmn	13.8 uppermost Mn-rich layer;	-	1	-	-	-	17	28	52	3
OBR-5-1262	drill core	C-138a Dobruja	lower part of Ruslar Fmn	12.4 Mn-rich layer;	32	32	36	-	-	-	-	-	-
OBR-5-1263	drill core	C-138a Dobruja	lower part of Ruslar Fmn	11.3 Mn-rich layer;	-	7	-	-	-	18	-	75	-
OBR-5-1264	drill core	C-138a Dobruja	lower part of Ruslar Fmn	9.3 Mn-rich layer;	15	46	-	-	-	25	14	-	-
OBR-5-1265	drill core	C-138a Dobruja	lower part of Ruslar Fmn	6.3 Mn-rich layer;	22	56	-	-	-	22	-	-	-
OBR-5-1266	drill core	C-138a Dobruja	lower part of Ruslar Fmn	0.9 base Mn-rich layer;	13	24	-	-	-	41	22	-	-
OBR-5-1267	drill core	C-138a Dobruja	lower part of Ruslar Fmn	0.1 Mn-rich layer	-	26	-	-	-	74	-	-	-
OBR-5-1302	drill core	C-138a Dobruja	lower part of Ruslar Fmn	NE of	-	-	-	-	-	-	-	-	-
OBR-6-3186	outcrop	Pripek village	lower part of Ruslar Fmn	-	-	-	-	-	-	-	-	-	-
OBR-7-3178	outcrop	Kalimanski dol	lower part of Ruslar Fmn	-	-	23	-	-	-	60	-	17	-
OBR-7-3205	outcrop	Kalimanski dol	lower part of Ruslar Fmn	-	-	-	-	-	-	-	-	-	-

OBR-7-4130	outcrop	Kalimans ki dol	lower part of Ruslar Fmn	- below Mn- rich layer below	1	-	16	-	-	34	31	17	1
OBR-7-4131	outcrop	Kalimans ki dol	lower part of Ruslar Fmn	rich layer below	-	-	-	-	-	42	31	22	5
OBR-8-3193	outcrop	E of Pripek village	lower part of Ruslar Fmn	rich layer	-	-	-	-	-	36	-	64	-
OBR-8-4136	outcrop	Pripek village	Avren Fmn	-	-	-	35	-	-	60	-	5	-
OBR-8-A	outcrop	E of Pripek village	lower part of Ruslar Fmn	rich layer	-	-	73	-	-	24	3	-	-
OBR-8-B	outcrop	E of Pripek village	lower part of Ruslar Fmn	rich layer	-	-	-	-	-	-	-	-	-
OBR-9-3884	outcrop	Ichme kulak	lower part of Ruslar Fmn	rich layer above	-	-	27	-	-	14	28	31	-
OBR-9-3885	outcrop	Ichme kulak	lower part of Ruslar Fmn	rich layer	-	-	-	-	-	-	-	-	-
OBR-10-164	outcrop	Kondulak cheshme	Ruslar Fmn	7.4 Mn- rich layer;	-	-	-	-	-	-	-	-	-
OBR-11-1.2 ^c	mine	Obrochish te	Ruslar Fmn	1.2 Mn- rich layer;	29	39	-	32	-	-	-	-	-
OBR-11-1.8	mine	Obrochish te	Ruslar Fmn	1.8 Mn- rich layer;	73	24	-	-	-	1	-	2	-
OBR-11-2.8	mine	Obrochish te	Ruslar Fmn	2.8 Mn- rich layer;	95	-	-	-	-	-	-	5	-
OBR-11-3.8	mine	Obrochish te	Ruslar Fmn	3.8 Mn- rich layer;	95	-	-	-	-	5	-	-	-
OBR-11-4.4	mine	Obrochish te	Ruslar Fmn	4.4 Mn- rich layer;	97	-	-	-	-	2	-	1	-
OBR-11-5.1	mine	Obrochish te	Ruslar Fmn	5.1 Mn- rich layer;	100	-	-	-	-	-	-	-	-
OBR-11-5.1P ^d	mine	Obrochish te	Ruslar Fmn	5.1 Mn- rich layer;	100	-	-	-	-	-	-	-	-
OBR-11-5.7	mine	Obrochish te	Ruslar Fmn	5.7 Mn- rich layer;	-	-	-	-	-	-	-	-	-
OBR-11-6.1	mine	Obrochish te	Ruslar Fmn	6.1 Mn- rich layer;	61	11	-	-	-	-	-	28	-
OBR-11-6.1M ^e	mine	Obrochish te	Ruslar Fmn	6.1 Mn- rich layer;	49	-	-	-	-	2	-	49	-
OBR-11-6.1M ^e	mine	Obrochish te	Ruslar Fmn	Mn- rich layer;	90	-	-	-	9	-	-	-	-

11- te rich
6.1P layer;
6.1

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^a %, X-ray diffraction with Rietveld refinement quantification.

^b The last four digits of the drill core sample IDs denote the depth (m) below surface.

^c The last two digits of the mine sample IDs denote the distance (m) from the lower boundary of the Mn-ore layer.

^d Pisolith.

^e Matrix.

1514 **Table 2**

1515 EDX data for sample OBR-11-4.4.

	Matrix	Pisolith
SiO ₂ , wt.%	19.2	6.40
Al ₂ O ₃	3.57	0.19
CaO	2.80	4.09
MgO	5.44	2.24
Fe ₂ O ₃	1.80	0.79
MnO	35.6	52.9
CO ₂ ^a	31.5	33.7
Total	100.0	100.4

1516 ^a Measured C_{tot} (C_{inorg}+C_{org}) recalculated as CO₂ considering that 88% of C_{tot} is as C_{inorg} in
1517 carbonates (bulk sample analyses; Table 3).
1518

1519 **Table 3**

1520 Chemical composition (XRF) of bulk samples and separated pisoliths.

Sample ID ^a	Si O ₂ wt. %	Al ₂ O ₃	Ca O	Mg O	Fe ₂ O ₃	Mn O	K ₂ O	Na ₂ O	Ti O ₂	P ₂ O ₅	L OI	H ₂ O ⁻	H ₂ O ⁺	C _{to} t ^b	C _{or} g ^b	C _{ino} r ^b	S _{tot} ^b ppm	Total wt. %	Mo ppm
<i>Detection limits</i>	0.4	0.5	2	0.1	2	2	1	0.2	1	0.1	0.2	0.2	0.2	2	2	2	20		3
OBR-1-3270	30.1	13.0	16.8	2.9	8.1	0.0	1.8	0.2	0.6	b.d.	26.4	3.5	22.8	4.3	0.5	3.8	479	100	b.d.
OBR-2-1601	24.0	12.4	14.1	1.1	1.3	18.9	1.5	0.6	0.1	0.2	25.6	1.1	24.5	5.8	0.2	5.6	430	99.	b.d.
OBR-3-1622	53.9	8.8	1.6	1.1	3.2	8.8	2.4	1.3	0.1	0.2	16.4	2.4	14.1	3.6	0.1	3.5	685	98.	b.d.
OBR-5-1261	55.8	15.8	0.4	1.8	8.0	0.0	2.4	1.6	0.7	0.1	12.3	2.9	9.3	1.1	1.1	0.0	422	99.	3.3
OBR-5-1262	54.9	14.5	0.4	1.7	8.6		2.4	1.6	0.8	0.1	13.0	3.1	9.8	1.2	1.3		573	98.	81.
OBR-5-1263	20.7	12.7	2.7	2.5	1.5	21.6	1.2	1.1	0.2	0.5	33.8	1.2	32.6	8.1	0.4	7.6	132	99.	11.
OBR-5-1264	51.5	16.4	0.4	1.8	8.1	0.2	2.6	1.1	0.9	0.1	15.7	3.8	11.8	0.8	0.7	0.1	388	99.	b.d.
OBR-5-1265	47.4	15.5	0.4	1.7	8.0	0.2	2.4	1.0	0.9	0.1	21.3	0.3	20.9	6.3	0.2	6.1	375	99.	b.d.
OBR-5-1266	23.0	12.6	13.3	3.2	4.6	15.6	1.3	0.8	0.2	0.3	24.1	1.1	22.9	6.1	0.3	5.7	256	99.	b.d.
OBR-5-1267	48.7	11.0	15.5	4.1	4.5	5.1	2.2	1.5	0.5	0.2	4.9	0.4	4.5	3.0	0.3	2.7	341	98.	b.d.
OBR-5-1302	67.1	4.0	3.6	1.7	2.6	4.8	1.4	0.7	0.0	0.0	12.9	2.0	10.1	2.2	0.2	1.9	218	100	27.
OBR-6-3186	40.7	12.7	10.8	2.1	3.7	7.1	2.1	0.6	0.5	0.2	18.2	2.0	16.1	2.2	0.1	2.1	459	99.	17.
OBR-7-3178	34.9	14.1	2.9	1.5	2.9	15.4	2.0	0.5	0.2	0.3	24.5	5.5	18.7	0.5	0.1	0.4	416	99.	b.d.
OBR-7-3205	40.6	13.7	8.6	2.0	6.2	1.5	2.4	b.d.	0.5	0.1	23.4	4.9	18.1	2.8	0.3	2.4	503	99.	19.

OBR-7-4130	41.	13.	7.2	2.2	3.2	8.0	2.4	0.6	0.5	0.2	20.	3.8	16.	1.5	0.1	1.3	101	99.	4.3
OBR-7-4131	60.	15.	3.2	0.5	3.9	0.2	2.2	0.8	0.6	0.1	11.	2.5	9.1	1.4	0.5	0.9	120	99.	4.6
OBR-8-3193	53.	18.	0.2	2.4	4.3	0.7	b.d.	0.1	b.d.	19.	2.0	17.	0.1	0.1	b.d.	640	99.	b.d.	
OBR-8-4136	39.	13.	9.6	1.9	3.8	8.1	1.8	0.4	0.5	0.2	20.	3.4	16.	1.8	0.1	1.7	620	99.	3.2
OBR-8-A	21.	4.9	41.	0.4	2.1	0.4	0.3	0.2	0.5	0.1	27.	0.4	26.	6.3	0.1	6.2	890	99.	b.d.
OBR-8-B	63.	10.	0.8	0.1	1.6	9.7	1.3	0.9	0.1	0.2	8.2	1.8	6.4	0.1	0.1	b.d.	267	97.	11.
OBR-9-3884	26.	11.	15.	1.5	2.8	7.9	1.5	0.3	0.4	0.2	30.	2.8	27.	5.4	0.6	4.8	224	98.	5.7
OBR-10-164	20.	14.	6.5	1.4	5.1	17.	1.9	b.d.	0.3	1.2	31.	7.4	23.	2.3	0.1	2.1	885	99.	b.d.
OBR-11-1.2	6.9	1.5	22.	1.5	2.9	29.	0.1	0.2	0.0	0.1	34.	-	-	9.7	0.2	9.4	935	99.	3.9
OBR-11-1.2P ^d	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1	-	681	-	-
OBR-11-1.8	8.0	4.0	11.	4.2	2.2	36.	0.5	0.6	0.1	0.2	33.	-	-	7.7	0.2	7.4	922	100	11.
OBR-11-1.8P	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.2	-	877	-	-
OBR-11-2.8	3.8	3.8	3.9	6.7	1.7	45.	0.6	0.8	0.1	0.2	32.	-	-	7.5	0.2	7.3	815	99.	8.0
OBR-11-3.8	23.	7.5	3.0	11.	1.6	17.	0.9	1.5	0.3	0.2	32.	-	-	6.1	0.3	5.8	907	99.	12.
OBR-11-3.8P	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.2	-	819	-	-
OBR-11-4.4	2.1	4.1	2.8	7.5	1.5	43.	0.4	1.0	0.1	0.4	37.	-	-	7.7	0.3	7.3	870	100	b.d.
OBR-11-4.4P	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1	-	124	-	-
OBR-11-5.1	15.	5.5	2.9	8.1	1.3	32.	0.7	1.2	0.2	0.1	32.	-	-	6.9	0.3	6.6	211	100	b.d.
OBR-11-5.1P	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1	-	150	-	-
OBR-11-5.7	16.	4.7	1.6	9.5	0.4	24.	0.3	1.2	0.2	0.0	40.	-	-	2.3	-	-	100	100	b.d.
OBR-11-6.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.4	-	102	-	-
OBR-11-6.1P ^e	18.	4.6	1.9	9.1	0.7	21.	0.4	1.4	0.2	0.3	40.	-	-	3.8	-	-	99.	99.	b.d.
OBR-11-6.1P	9	7	7	4	8	5	1	4	9	0	3	-	-	8	-	-	200	99.	b.d.
OBR-11-6.1P	-	4	8	2	9	5	1	7	1	2	-	-	-	-	0.2	-	00	99.	b.d.

^a In bold italic, samples from the host strata; in regular, samples from the Mn-ore layer.

^b Elemental analyser data.

^c Below detection limit.

^d Pisolith.

^e Matrix.

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Table 4

Chemical composition (ICP-MS) of the investigated samples.

Sample ID ^a	OBR-11-1.2								OBR-11-1.8								OBR-11-2.8							
	bu	leachat	residue	% in the leachate	pisolith	pisolith residue	% in the leachate	bulk	leachat	residue	% in the leachate	pisolith	pisolith residue	% in the leachate	bulk	leachat	residue	% in the leachate						
Al, wt.%	0.77	1.38	35.8	0.60	0.75	44.2	1.20	2.05	36.9	0.94	1.27	42.4	1.26	1.38	47.7									
Ca	8.32	1.91	81.3	19.5	1.93	91.0	8.04	1.14	87.6	9.52	1.27	88.2	3.11	0.29	91.5									
Mg	0.43	0.26	61.8	0.40	0.09	81.2	1.23	0.61	66.7	0.72	0.27	73.1	1.88	0.34	84.5									
Fe	1.09	0.93	54.0	0.97	0.36	73.2	1.12	0.91	55.0	0.69	0.51	57.7	0.76	0.57	56.9									
Mn	21.6	4.95	81.4	16.0	1.13	93.4	17.9	2.34	88.4	22.6	1.95	92.1	25.5	1.86	93.2									
Na	0.20	0.12	61.8	0.13	0.09	59.4	0.42	0.15	73.7	0.25	0.12	67.2	0.43	0.13	76.3									
K	0.03	0.14	17.4	0.02	0.05	30.0	0.09	0.30	22.6	0.05	0.12	29.8	0.07	0.21	24.7									
P	0.07	0.02	78.3	0.04	0.004	90.5	0.09	0.02	85.0	0.08	0.01	90.9	0.08	0.01	91.0									
Li, ppm	13.	5.73	8.70	39.7	3.07	2.13	59.1	88.	40.8	55.2	42.5	20.6	19.8	51.0	34.	20.7	14.4	58.9						

	6						3						0					
	1.7						3.6						2.6					
Sc	9	0.23	1.04	17.9	0.11	0.24	30.8	8	1.10	2.15	33.8	0.37	0.78	32.4	8	0.80	1.28	38.5
	69							11							89			
Ti	3	105	437	19.4	81.3	164	33.1	25	176	768	18.6	132	359	26.8	4	201	513	28.1
	70.							20							49.			
V	7	22.1	56	28.4	13.0	1.76	88.1	0	88.3	95.3	48.1	42.6	13.9	75.4	8	42.2	9.31	81.9
	13.							26.							18.			
Cr	3	4.33	10.9	28.4	3.02	3.31	47.7	8	9.46	17.0	35.7	5.62	6.44	46.6	4	9.06	10.6	46.0
	13.							36.							26.			
Co	3	7.94	3.54	69.2	4.73	1.77	72.8	1	26.6	7.98	76.9	20.5	4.78	81.1	8	20.1	4.81	80.7
	29.							11							60.			
Ni	1	20.9	11.2	65.2	15.7	6.37	71.1	8	84.2	37.5	69.2	63.0	21.3	74.8	8	46.6	16.6	73.7
	12.							23.							13.			
Cu	6	8.20	8.04	50.5	7.11	2.88	71.2	1	15.3	12.2	55.6	13.0	7.41	63.7	3	10.2	7.63	57.2
								30.							16.			
Zn		10.0	8.27	54.8	10.2	4.34	70.2	8	28.8	13.0	68.9	19.0	7.76	71.0	7	22.7	9.36	70.9
	2.4							4.9							3.7			
Ga	9	0.62	2.16	22.4	0.47	0.79	37.2	5	1.38	3.66	27.4	0.84	1.75	32.4	4	1.46	2.42	37.6
	13.							27.							20.			
Rb	4	2.12	10.4	16.9	0.92	2.99	23.5	1	4.64	20.1	18.7	2.72	8.38	24.5	4	3.93	14.5	21.4
	19							21							10			
Sr	6	147	42.4	77.6	296	34.3	89.6	3	174	32.3	84.3	194	32.0	85.9	2	86.8	15.3	85.0
	12.							15.							14.			
Y	6	8.97	2.66	77.1	5.34	0.49	91.7	2	11.3	2.85	79.8	8.72	1.57	84.7	4	10.8	1.68	86.5
	11.							26.							20.			
Zr	4	1.06	10.4	9.3	0.84	3.77	18.2	4	2.85	20.8	12.1	1.43	9.14	13.5	7	2.22	15.3	12.6
	1.3							2.6							1.9			
Nb	4	0.06	1.27	4.7	0.04	0.37	10.0	4	0.07	2.64	2.5	0.05	1.00	4.7	7	0.04	1.90	2.3
	0.8							1.7							1.2			
Cs	6	0.13	0.68	15.7	0.06	0.19	23.8	0	0.22	1.34	14.0	0.13	0.56	19.3	5	0.20	0.92	17.6
	22							23							17			
Ba	2	146	53.7	73.1	183	23.1	88.8	7	156	54.9	74.0	177	37.0	82.7	2	111	33.9	76.7
	10.							15.							11.			
La	5	7.42	2.92	71.8	3.30	0.77	81.0	3	11.3	3.92	74.3	7.14	1.86	79.3	5	8.08	2.31	77.8
	14.							20.							15.			
Ce	2	11.1	4.77	69.9	4.67	1.18	79.9	5	15.3	6.47	70.3	10.1	2.33	81.3	5	11.6	3.59	76.4
	2.0							3.0							2.5			
Pr	8	1.26	0.55	69.7	0.56	0.16	77.4	8	2.05	0.82	71.6	1.33	0.38	77.7	0	1.54	0.48	76.3
	8.4							12.							10.			
Nd	5	5.14	2.09	71.1	2.42	0.63	79.3	3	8.48	3.16	72.9	5.42	1.45	78.9	1	6.47	1.81	78.2
	1.8							2.6							2.2			
Sm	7	1.04	0.38	73.0	0.48	0.11	81.0	2	1.69	0.56	75.0	1.13	0.26	81.1	1	1.30	0.33	79.9
	0.4							0.6							0.5			
Eu	8	0.26	0.09	74.7	0.15	0.02	86.0	3	0.40	0.12	77.4	0.29	0.06	82.3	3	0.32	0.07	82.1
	1.9							2.7							2.3			
Gd	8	1.19	0.37	76.2	0.61	0.11	85.3	3	1.83	0.51	78.3	1.20	0.25	82.6	1	1.44	0.27	84.1
	0.3							0.4							0.3			
Tb	1	0.19	0.06	75.7	0.10	0.02	86.3	2	0.28	0.08	78.5	0.20	0.04	82.9	6	0.23	0.05	83.0
	1.8							2.4							2.1			
Dy	9	1.14	0.38	75.0	0.64	0.11	85.9	1	1.57	0.46	77.5	1.18	0.26	82.0	4	1.36	0.26	83.9
	0.4							0.5							0.4			
Ho	1	0.25	0.08	75.6	0.14	0.02	86.5	0	0.33	0.10	76.7	0.24	0.05	81.8	5	0.30	0.06	83.3
	1.2							1.4							1.3			
Er	1	0.75	0.26	74.0	0.42	0.07	85.4	3	0.92	0.30	75.4	0.71	0.18	80.2	3	0.85	0.20	81.0
	0.1							0.2							0.2			
Tm	8	0.11	0.04	73.2	0.06	0.01	84.3	1	0.13	0.05	73.7	0.10	0.03	78.6	0	0.13	0.03	80.4
	1.0							1.2							1.2			
Yb	7	0.61	0.24	71.6	0.34	0.07	83.9	8	0.73	0.29	71.6	0.61	0.18	77.5	2	0.72	0.21	77.3
	0.1							0.1							0.1			
Lu	7	0.09	0.04	70.0	0.05	0.01	86.1	9	0.10	0.04	69.8	0.09	0.02	78.0	9	0.11	0.03	76.9
	44.							63.							50.			
ΣREE	8	30.5	12.3		14.0	3.29		7	45.1	16.9		29.7	7.36		6	34.5	9.69	
(Ce/Ce*)	0.7							0.6							0.6			
^b	0	0.81	0.86		0.77	0.77		9	0.72	0.84		0.75	0.64		7	0.76	0.80	
(Eu/Eu*)	0.7							0.7							0.7			
^c	6	0.73	0.71		0.85	0.68		1	0.69	0.65		0.75	0.72		1	0.70	0.69	
La _{CN} /Lu	6.6							8.6							6.5			
_{CN}	3	8.84	8.13		6.79	9.87		6	11.9	9.52		8.72	8.05		9	7.89	7.48	
	0.2							0.6							0.4			
Hf	2	0.04	0.28	12.0	0.03	0.10	20.2	0	0.07	0.55	11.4	0.05	0.24	16.5	4	0.05	0.40	10.8
	0.0							0.1							0.1			
Ta	7	0.00	0.08	2.0	0.001	0.02	6.4	7	0.001	0.16	0.4	0.001	0.04	2.5	0	0.001	0.09	0.6
	2.3							6.1							3.3			
Pb	7	2.30	0.69	76.9	9.42	0.29	97.0	4	5.95	0.40	93.7	5.30	0.29	94.8	3	5.29	0.30	94.6
	0.9							2.5							1.9			
Th	5	0.58	0.52	52.4	0.20	0.17	54.5	5	1.54	0.98	60.9	0.79	0.42	65.1	6	1.09	0.66	62.3
	3.2							3.7							1.9			
U	5	2.58	0.84	75.5	2.31	0.30	88.4	4	3.13	0.84	78.9	1.66	0.37	81.9	3	1.51	0.43	77.7

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^b Ce/Ce* = 2Ce_{CN} / (La_{CN} + Pr_{CN})

^c Eu/Eu* = 2Eu_{CN} / (Sm_{CN} + Gd_{CN})

Table 4 (continued)

Sample ID	OBR-11-3.8						OBR-11-4.4								
	Element	bulk	leachate	residue	% in the leachate	pisolith leachate	pisolith residue	% in the leachate	bulk	leachate	residue	% in the leachate	pisolith leachate	pisolith residue	% in the leachate
Al, wt.%		1.48	1.61		47.9	1.45	1.58	47.9		1.18	1.25	48.5	0.85	0.80	51.5
Ca		2.80	0.32		89.9	3.32	0.22	93.8		2.40	0.12	95.1	2.81	0.18	93.9
Mg		2.31	0.50		82.2	2.36	0.42	84.9		1.40	0.26	84.3	0.88	0.23	79.5
Fe		0.82	0.68		54.4	0.82	0.67	54.8		0.53	0.51	50.7	0.33	0.33	50.4
Mn		20.7	1.89		91.6	23.1	1.20	95.1		28.8	1.28	95.8	32.8	1.45	95.8
Na		0.57	0.16		78.2	0.58	0.14	80.7		0.43	0.12	77.7	0.24	0.10	70.1
K		0.10	0.30		25.3	0.09	0.29	22.7		0.06	0.17	26.1	0.03	0.04	39.6
P		0.09	0.01		88.5	0.09	0.01	91.1		0.06	0.01	89.9	0.09	0.005	94.6
Li, ppm	40.9	23.9	18.1		56.9	23.3	19.0	55.2	22.3	13.8	9.28	59.7	7.10	2.50	74.0
Sc	3.58	1.06	1.76		37.6	0.94	1.97	32.2	2.12	0.51	0.99	34.1	0.10	0.11	48.0
Ti	1143	226	656		25.7	228	705	24.5	741	188	397	32.1	125	147	46.1
V	214	133	35.1		79.1	118	31.5	79.0	118	152	34.3	81.5	75.2	2.11	97.3
Cr	26.9	11.7	13.3		47.0	11.3	14.7	43.4	15.0	8.11	9.72	45.5	2.91	2.52	53.5
Co	41.3	27.5	9.15		75.1	25.7	10.4	71.1	33.3	21.1	9.26	69.5	8.45	8.13	51.0
Ni	118	82.9	32.2		72.0	85.3	35.5	70.6	70.2	46.2	21.2	68.6	24.4	27.4	47.1
Cu	27.2	13.9	15.0		48.1	13.4	15.8	45.8	18.3	11.0	10.9	50.1	4.97	6.66	42.7
Zn	30.9	26.9	12.3		68.5	27.2	12.3	68.8	9.48	18.6	8.77	67.9	10.4	5.07	67.3
Ga	4.90	1.47	3.27		31.0	1.50	3.50	30.0	2.98	1.13	2.10	35.1	0.67	0.78	46.3
Rb	29.5	5.00	21.2		19.1	4.28	23.1	15.7	17.3	3.09	12.4	19.9	1.17	2.95	28.4
Sr	112	87.2	18.9		82.2	92.1	16.3	85.0	87.4	74.8	11.5	86.7	67.9	9.48	87.8
Y	20.9	14.6	2.99		83.0	15.7	2.79	85.0	12.7	9.65	1.03	90.3	10.5	0.57	94.8
Zr	33.4	2.62	20.7		11.2	2.15	23.2	8.5	15.0	1.88	11.2	14.3	1.81	4.31	29.5
Nb	2.78	0.05	2.52		2.0	0.03	2.76	0.9	1.47	0.04	1.42	2.9	0.03	0.33	9.1
Cs	1.85	0.23	1.39		14.5	0.18	1.48	10.8	1.11	0.17	0.79	17.6	0.07	0.19	26.9
Ba	201	117	47.9		71.0	120	46.8	71.9	143	89.3	26.0	77.4	78.9	9.01	89.7
La	16.0	10.8	3.66		74.6	10.9	3.51	75.6	9.41	6.77	1.77	79.3	6.80	0.82	89.3
Ce	21.7	14.6	5.51		72.6	15.6	5.80	73.0	11.0	8.71	2.98	74.5	8.92	1.19	88.2
Pr	3.31	2.02	0.77		72.3	2.12	0.73	74.4	1.99	1.19	0.38	76.1	1.00	0.15	87.3
Nd	13.4	8.55	2.97		74.2	8.83	2.76	76.2	8.21	5.02	1.38	78.5	4.13	0.57	87.9
Sm	2.80	1.72	0.53		76.4	1.83	0.48	79.2	1.83	1.03	0.21	82.8	0.85	0.10	89.2
Eu	0.68	0.42	0.10		80.3	0.44	0.10	81.8	0.44	0.26	0.05	84.6	0.21	0.02	90.9
Gd	3.08	1.97	0.46		81.0	2.07	0.43	82.6	1.93	1.21	0.20	85.7	1.06	0.10	91.7
Tb	0.47	0.31	0.07		80.9	0.33	0.07	82.1	0.31	0.19	0.03	85.2	0.18	0.02	91.0
Dy	2.82	1.87	0.45		80.6	2.00	0.44	81.9	1.88	1.17	0.21	85.0	1.24	0.11	91.5
Ho	0.61	0.40	0.10		80.8	0.43	0.10	81.5	0.40	0.26	0.05	84.7	0.28	0.03	91.2
Er	1.79	1.17	0.31		78.8	1.26	0.30	80.6	1.16	0.75	0.14	84.0	0.84	0.09	90.6
Tm	0.27	0.18	0.05		77.7	0.19	0.05	78.5	0.18	0.10	0.02	81.0	0.14	0.01	90.6
Yb	1.65	1.02	0.33		75.5	1.13	0.33	77.5	1.07	0.64	0.15	80.7	0.80	0.08	90.7
Lu	0.25	0.15	0.05		75.4	0.17	0.05	77.2	0.17	0.09	0.03	78.9	0.12	0.01	90.4
ΣREE	68.8	45.2	15.4		47.3	15.2	47.3	40.0	40.0	27.4	7.60	26.6	26.6	3.30	
Ce/Ce*	0.69	0.72	0.76		0.75	0.84	0.60	0.69	0.85	0.74	0.78	0.74	0.78		
Eu/Eu*	0.71	0.69	0.62		0.68	0.63	0.72	0.70	0.68	0.66	0.62	0.66	0.62		
La _{CN} /Lu _{CN}	6.96	7.61	7.91		6.93	7.57	6.02	7.70	7.53	6.00	6.77	6.00	6.77		
Hf	0.77	0.06	0.54		9.8	0.05	0.63	7.4	0.30	0.04	0.31	12.5	0.04	0.12	24.4
Ta	0.19	0.001	0.13		0.9	0.001	0.15	0.8	0.06	0.001	0.07	0.8	0.001	0.01	4.9
Pb	7.45	5.69	0.35		94.3	11.3	0.72	94.0	1.96	3.21	0.47	87.2	2.65	0.33	88.9
Th	2.71	1.40	1.03		57.6	1.44	1.09	57.0	1.48	0.86	0.48	64.5	0.28	0.16	64.2
U	4.08	3.25	0.78		80.6	2.95	0.69	81.0	3.88	3.44	0.49	87.5	1.78	0.19	90.3

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Table 4 (continued)

Sample ID	OBR-11-5.1						OBR-11-5.7			OBR-11-6.1						
	Element	bul k	leachate	residu e	% in the leachate	pisolith leachate	pisolith residue	% in the leachate	bul k	leachate	residu e	% in the leachate	bul k	pisolith bul k	pisolith leachate	pisolith residue
Al, wt.%		1.14	1.29		47.0	1.13	1.04	52.1		2.08	1.43	59.3		1.26	1.05	54.4
Ca		2.08	0.43		82.9	2.35	0.19	92.7		0.93	0.14	86.8		4.46	0.52	89.5
Mg		1.47	0.50		74.7	1.11	0.26	81.1		2.85	1.19	70.6		1.92	0.49	79.7
Fe		0.77	0.93		45.4	0.51	0.61	45.6		0.62	0.81	43.3		0.49	0.64	43.6
Mn		27.8	3.80		88.0	30.4	1.94	94.0		17.3	0.99	94.6		23.8	2.68	89.9
Na		0.42	0.16		72.1	0.38	0.13	75.3		0.82	0.16	83.6		0.47	0.14	76.9

K		0.06	0.20	24.6	0.05	0.09	33.6		0.10	0.23	29.7		0.06	0.11	35.4	
P		0.05	0.01	87.0	0.05	0.01	89.2		0.06	0.01	89.2		1.08	0.12	89.8	
Li, ppm	22.							28.				33.				
	0	13.9	11.8	54.2	8.19	5.94	57.9	2	19.8	12.8	60.6	7	23.2	18.4	7.37	71.4
	2.1							2.8				3.1				
Sc	4	0.58	1.23	32.2	0.28	0.49	35.9	3	0.53	2.00	21.0	3	1.62	0.58	0.56	50.6
								112				105				
Ti	799	171	480	26.2	162	245	39.8	0	231	790	22.6	2	635	189	323	36.9
V	111	104	16.6	86.2	86.0	6.98	92.5	227	232	26.8	89.7	553	329	306	51.1	85.7
	16.							17.				30.				
Cr	0	7.78	7.93	49.5	4.33	4.93	46.7	6	7.89	11.0	41.8	9	11.9	8.04	7.48	51.8
	31.							22.				65.				
Co	7	19.1	11.8	61.8	12.9	7.42	63.4	1	17.9	3.86	82.3	5	44.5	32.2	10.3	75.7
Ni	129	79.4	68.7	53.6	53.6	47.1	53.2	107	98.6	24.7	80.0	151	127	79.5	48.8	61.9
	20.							15.				36.				
Cu	6	7.82	15.8	33.1	6.68	8.82	43.1	3	8.60	9.82	46.7	1	27.7	11.2	19.7	36.3
	5.1							17.				42.				
Zn	7	16.4	10.0	62.0	12.8	7.82	62.0	4	21.8	12.7	63.3	7	12.7	23.3	7.49	75.7
	3.0							4.7				4.9				
Ga	5	1.07	2.38	31.0	0.82	1.36	37.7	9	2.82	2.47	53.4	7	2.52	1.75	1.49	54.1
	17.							20.				23.				
Rb	6	3.04	14.5	17.3	1.83	6.95	20.8	2	3.36	16.2	17.2	7	11.7	2.89	8.00	26.6
	77.							84.								
Sr	3	66.7	20.4	76.6	63.1	11.4	84.7	3	81.4	13.6	85.7	113	399	326	44.6	88.0
	14.							13.				22.				
Y	1	11.0	3.15	77.8	9.87	1.05	90.4	4	10.2	2.75	78.8	2	64.9	54.9	6.73	89.1
	18.							24.				31.				
Zr	6	1.70	14.3	10.6	1.91	7.58	20.1	1	2.21	20.5	9.8	7	14.4	4.17	8.64	32.5
	1.6							2.9				2.7				
Nb	4	0.03	1.75	1.8	0.03	0.81	3.8	3	0.04	3.26	1.2	8	1.13	0.11	1.30	7.8
	1.1							0.9				1.5				
Cs	1	0.16	0.84	15.8	0.09	0.45	16.5	2	0.12	0.75	14.2	6	0.76	0.18	0.52	25.7
Ba	143	85.9	42.3	67.0	77.2	16.9	82.0	191	95.2	84.3	53.0	159	261	192	37.7	83.6
	9.2							11.				18.				
La	4	6.46	3.32	66.1	5.33	1.70	75.8	5	8.78	2.94	74.9	1	52.5	48.3	6.62	88.0
	11.							18.				25.				
Ce	6	8.80	4.26	67.4	7.25	2.81	72.1	5	14.2	5.80	71.0	3	62.0	58.2	8.73	87.0
	2.0							2.8				3.4				
Pr	7	1.24	0.70	63.9	0.94	0.36	72.3	1	1.86	0.78	70.5	2	7.17	6.23	0.96	86.6
	8.6							11.				13.				
Nd	3	5.22	2.68	66.1	3.95	1.37	74.2	2	7.33	3.13	70.0	9	28.9	25.8	3.89	86.9
	1.9							2.4				2.8				
Sm	6	1.11	0.49	69.5	0.82	0.25	76.8	3	1.48	0.67	68.7	8	5.69	5.03	0.72	87.5
	0.4							0.5				0.6				
Eu	9	0.27	0.11	71.9	0.21	0.04	85.2	5	0.32	0.12	73.1	8	1.41	1.19	0.16	87.9
	2.0							2.4				3.2				
Gd	8	1.33	0.47	74.0	1.00	0.21	82.7	6	1.49	0.55	73.1	6	7.28	6.28	0.84	88.1
	0.3							0.3				0.4				
Tb	5	0.22	0.07	75.8	0.18	0.03	84.9	8	0.24	0.09	73.4	9	1.12	0.97	0.13	88.5
	2.1							2.1				2.9				
Dy	3	1.39	0.45	75.3	1.20	0.20	85.5	7	1.37	0.51	72.9	3	6.98	6.13	0.83	88.0
	0.4							0.4				0.6				
Ho	6	0.31	0.10	76.0	0.28	0.04	86.7	6	0.29	0.10	74.0	2	1.54	1.37	0.18	88.3
	1.4							1.3				1.8				
Er	0	0.95	0.32	74.7	0.89	0.14	86.7	4	0.85	0.31	73.5	1	4.48	4.02	0.55	88.0
	0.2							0.2				0.2				
Tm	1	0.14	0.05	74.3	0.14	0.02	86.5	1	0.13	0.05	73.4	6	0.62	0.58	0.08	88.1
	1.3							1.2				1.5				
Yb	0	0.83	0.33	71.8	0.83	0.14	86.0	4	0.77	0.29	72.9	6	3.83	3.31	0.48	87.4
	0.2							0.2				0.2				
Lu	0	0.12	0.05	71.1	0.12	0.02	86.1	0	0.12	0.04	73.2	3	0.54	0.47	0.07	86.9
	42.							55.				75.				
ΣREE	1	28.4	13.4		23.1	7.32		5	39.2	15.4		5	184	168	24.2	
	0.6							0.7				0.7				
Ce/Ce*	2	0.71	0.65		0.73	0.84		7	0.82	0.92		4	0.68	0.71	0.75	
	0.7							0.6				0.6				
Eu/Eu*	4	0.68	0.67		0.70	0.47		8	0.65	0.58		8	0.67	0.65	0.64	
	4.9							6.3				8.2				
La _{CN} /Lu _{CN}	4	5.74	7.27		4.59	9.05		3	8.02	7.33		5	10.4	10.9	9.89	
	0.4							0.6				0.6				
Hf	1	0.04	0.39	8.9	0.04	0.20	16.2	2	0.05	0.62	7.8	8	0.30	0.09	0.25	26.5
	0.1							0.1				0.3				
Ta	0	0.001	0.08	1.3	0.001	0.05	2.1	9	0.001	0.20	0.6	1	0.06	0.005	0.09	4.8
	2.7							10.				9.3				
Pb	5	2.85	0.30	90.6	3.14	0.45	87.4	7	12.0	0.39	96.8	1	6.06	5.22	1.66	75.9
	1.5							4.6				2.4				
Th	1	0.88	0.74	54.2	0.47	0.52	47.4	6	3.83	1.00	79.3	4	1.43	0.85	0.46	64.6
	3.9							2.8				10.				
U	2	3.24	1.12	74.3	2.17	0.37	85.5	5	2.96	0.42	87.7	9	10.5	9.88	1.31	88.3

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Table 4 (continued)

Sample ID	OBR-5-1263	OBR-5-1264	OBR-5-1265	OBR-5-1266	OBR-5-1267	OBR-5-1302	OBR-8-A
Element	leachate residue %						
wt. %	0.92	0.97	0.8	0.9	0.9	0.8	0.7
Ca	8.78	0.20	5	9	4	2	3
Mg	0.83	0.22	8	3	1	0	4
Fe	1.37	1.48	5	6	9	6	9
Mn	25.8	0.28	5	0	4	7	3
Na	0.48	0.45	2	2	3	8	4
K	0.07	0.12	6	7	5	8	0
P	0.33	0.03	2	9	7	1	2
Li, ppm	17.0	8.08	1	0	0	7	0
Sc	0.54	3.62	9	3	5	2	1
Ti	106	102	25	2.2	103	8	7
V	51.4	10.5	2	6.5	2	9	7
Cr	5.32	7.36	2	6.7	6	7	9
Co	14.5	10.7	7	7	6	3	7
Ni	87.8	26.9	9	5	7	4	3
Cu	45.6	21.8	4	1	1	4	1
Zn	34.4	46.7	5	3	7	5	1
Ga	1.00	1.31	9	6.2	8	1	9
Rb	3.44	7.50	9	2	3	4	7
Sr	360	62.1	6	5	234	3	2
Y	14.6	15.4	4	8	9	2	2
Zr	2.00	3.21	9	2.9	4	4	9
Nb	0.05	0.04	0	0.3	5	3	3
Cs	0.14	0.36	8	2	9	6	7
Ba	632	61.4	7	8	3	6	3
La	12.4	15.7	7	4	2	1	9
Ce	17.6	35.5	5	3	8	0	5
Pr	2.14	4.41	0	8	0	3	7
Nd	8.98	18.2	9	7	7	8	4
Sm	1.81	3.92	5	7	8	1	7
Eu	0.51	0.84	2	3	6	1	9
Gd	2.06	3.60	9	2	6	7	1

Tb	0.31	0.0	79.	0.0	87.	0.2	0.0	86.	0.3	0.0	83.	0.3	0.1	79.	0.4	0.0	89.	0.0	0.0	60.	
		8	7	0.55	8	9	6	4	2	7	1	9	0	9	3	5	8	6	4	2	
		0.4	81.	0.4	86.	1.4	0.2	85.	1.8	0.3	82.	2.1	0.5	78.	2.4	0.2	89.	0.3	0.2	57.	
Dy	1.87	3	2	3.00	9	0	5	4	8	1	9	4	9	9	6	8	8	2	3	9	
		0.0	81.	0.1	83.	0.3	0.0	85.	0.3	0.0	82.	0.4	0.1	79.	0.5	0.0	90.	0.0	0.0	58.	
Ho	0.39	9	5	0.54	1	1	0	5	2	8	8	3	4	2	0	1	5	4	7	5	
		0.2	80.	0.3	79.	0.8	0.1	84.	1.0	0.2	81.	1.1	0.3	76.	1.4	0.1	89.	0.1	0.1	53.	
Er	1.14	8	3	1.46	7	7	5	5	7	8	5	3	9	6	9	7	8	3	7	4	
		0.0	79.	0.0	74.	0.1	0.0	83.	0.1	0.0	79.	0.1	0.0	74.	0.2	0.0	88.	0.0	0.0	49.	
Tm	0.16	4	7	0.20	7	9	2	2	8	5	4	2	6	6	2	1	3	9	2	2	
		0.2	77.	0.4	71.	0.7	0.1	83.	0.8	0.2	76.	0.9	0.3	72.	1.2	0.1	87.	0.1	0.1	46.	
Yb	0.93	7	5	1.18	7	4	0	4	3	3	5	9	1	5	0	0	7	5	4	6	
		0.0	75.	0.0	69.	0.1	0.0	79.	0.1	0.0	77.	0.1	0.0	70.	0.1	0.0	86.	0.0	0.0	44.	
Lu	0.13	4	7	0.17	7	2	0	3	9	2	4	1	3	6	5	7	3	4	2	7	
		17.		12.		43.	9.2		48.	15.		59.	20.		58.	13.		9.1	8.7		
ΣREE	50.4	9		89.2	5	1	7		5	9		4	6		6	4		2	8		
		0.8		1.5	0.8	0.9		0.8	0.9		0.8	0.9		0.8	0.9		0.8	0.9	0.6	0.9	
Ce/Ce*	0.77	6		1.03	0	2	0		5	2		3	1		8	5		1	1		
		0.6		0.8	0.6	1.1		0.6	0.8		0.6	1.0		0.6	1.0		0.5	1.0	0.5	1.0	
Eu/Eu*	0.81	0		0.67	7	7	9		6	4		5	2		5	6		9	6		
La _{CN} /Lu _{CN}	10.	8		9.98	9	0	2		7	9		3	7		1	2		1	7		
		0.5		3.0	0.0	0.3		12.	0.0	0.6		0.0	0.8		0.0	0.6		0.0	0.4		
Hf	0.05	1	9.1	0.13	2	4.2	5	4	9	7	6	9.8	8	5	8.4	4	2	6.3	2	0	4.7
		0.1		0.8	0.0	0.1		0.0	0.1		0.0	0.1		0.0	0.3		0.0	0.1	0.0	0.1	
Ta	0.001	7	0.7	0.001	5	0.1	0.1	0.9	0.1	8	0.4	0.1	1	0.3	0.2	6	1.1	0.1	4	0.4	
		1.4	86.	8.3	69.	4.9	5.3	48.	6.5	4.4	59.	6.3	7.7	45.	3.9	4.4	47.	4.7	3.7	55.	
Pb	9.75	9	7	19.0	0	5	8	5	2	0	8	2	7	2	2	1	1	0	0	5	
		0.8	54.	1.9	74.	0.9	0.4	68.	1.3	0.7	63.	2.0	1.0	65.	1.6	0.7	68.	0.1	1.2	10.	
Th	1.03	7	2	5.67	5	5	0	2	0	6	9	2	1	6	4	4	9	5	4	6	
		0.5	79.	1.4	41.	1.0	0.3	75.	1.7	0.5	76.	2.5	0.8	75.	1.6	0.4	78.	0.8	0.4	68.	
U	1.98	0	7	1.00	2	2	6	4	7	0	2	7	7	2	9	8	5	7	7	0	

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Table 5

Isotope composition of the investigated samples.

Sample ID ^a	Sample type	$\delta^{13}\text{C}_{\text{PDB}}$ (‰)	$\delta^{18}\text{O}_{\text{PDB}}$ (‰)	$\delta^{56/54}\text{Fe}_{\text{IRMM14}}$ (‰)	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{143}\text{Nd}/^{144}\text{Nd}$	ϵNd	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$
OBR-1-3270	bulk	2.04	-1.50	-	-	-	-	-	-	-
OBR-2-1601	bulk	0.12	-0.53	-	-	-	-	-	-	-
OBR-3-1622	bulk	-2.76	-1.50	-	-	-	-	-	-	-
OBR-5-1261	bulk	-	-	-	-	-	-	-	-	-
OBR-5-1262	bulk	-	-	0.24	-	-	-	-	-	-
OBR-5-1263	bulk	-0.13	-1.13	-0.25	-	-	-	-	-	-
OBR-5-1263	leachate	-	-	-	0.70791	0.512296	-6.7	18.553	15.632	38.415
OBR-5-1264	bulk	-	-	0.16	-	-	-	-	-	-
OBR-5-1264	leachate	-	-	-	0.70837	0.512289	-6.8	18.337	15.596	38.318
OBR-5-1264	residue	-	-	-	0.72038	0.512193	-8.7	18.668	15.614	38.680
OBR-5-1265	bulk	-9.02	-1.57	-0.19	-	-	-	-	-	-
OBR-5-1265	leachate	-	-	-	0.70788	0.512277	-7.0	18.868	15.660	38.669
OBR-5-1266	bulk	-8.42	-1.02	-0.06	-	-	-	-	-	-
OBR-5-1266	leachate	-	-	-	0.70794	0.512291	-6.8	19.253	15.706	38.896
OBR-5-1267	bulk	-5.81	-3.23	0.04	-	-	-	-	-	-
OBR-5-1267	leachate	-	-	-	0.70795	0.512285	-6.9	19.339	15.709	38.940
OBR-5-1267	bulk	-9.01	0.02	-0.33	-	-	-	-	-	-

1302										
OBR-5-1302	leachate	-	-	-	0.70796	0.512260	-7.4	18.823	15.654	38.659
OBR-5-1302	residue	-	-	-	0.71336	0.512018	-	18.697	15.648	38.762
OBR-6-3186	bulk	-1.86	-6.13	-	-	-	-	-	-	-
OBR-7-3205	bulk	-1.28	-3.69	-	-	-	-	-	-	-
OBR-7-4130	bulk	-0.24	-7.31	-	-	-	-	-	-	-
OBR-7-4131	bulk	0.45	-4.62	-	-	-	-	-	-	-
OBR-8-3193	bulk	-0.96	-3.19	-	-	-	-	-	-	-
OBR-8-4136	bulk	-2.39	-6.08	-	-	-	-	-	-	-
OBR-8-A	bulk	-4.26	-9.19	-	-	-	-	-	-	-
OBR-8-A	leachate	-	-	-	-	0.512281	-7.0	18.262	15.597	38.039
OBR-8-B	bulk	-10.5	-12.2	-	-	-	-	-	-	-
OBR-9-3884	bulk	-1.79	-2.32	-	-	-	-	-	-	-
OBR-10-164	bulk	-0.60	-2.17	-	-	-	-	-	-	-
OBR-11-1.2	bulk	-0.60	-2.17	-0.12	0.70826	0.512297	-6.7	-	-	-
OBR-11-1.2	leachate	-	-	-	0.70791	0.512319	-6.2	-	-	-
OBR-11-1.2	residue	-	-	-	0.70967	0.512265	-7.3	18.534	15.622	38.405
OBR-11-1.2p	pisolith separate, bulk	3.60	-2.77	-0.35	-	-	-	-	-	-
OBR-11-1.2p	pisolith separate, leachate	-	-	-	0.70788	0.512324	-6.1	18.420	15.605	38.258
OBR-11-1.8	bulk	2.10	-2.31	0.16	0.70861	0.512233	-7.9	18.862	15.649	38.956
OBR-11-1.8	leachate	-	-	-	0.70789	0.512297	-6.7	18.794	15.654	38.703
OBR-11-1.8p	pisolith separate, bulk	-1.54	-2.12	0.13	-	-	-	-	-	-
OBR-11-1.8p	pisolith separate, leachate	-	-	-	0.70787	0.512288	-6.8	18.721	15.641	38.609
OBR-11-2.8	bulk	-0.80	-0.81	-0.15	0.70901	0.512279	-7.0	18.833	15.646	38.756
OBR-11-2.8	leachate	-	-	-	0.70812	0.512329	-6.0	18.785	15.653	38.690
OBR-11-3.8	bulk	0.82	-1.07	0.00	0.70937	0.512279	-7.0	-	-	-
OBR-11-3.8	leachate	-	-	-	0.70798	0.512306	-6.5	-	-	-
OBR-11-3.8p	pisolith separate, bulk	1.20	-1.01	-0.02	-	-	-	-	-	-
OBR-11-3.8p	pisolith separate, leachate	-	-	-	0.70798	0.512304	-6.5	18.459	15.614	38.329
OBR-11-4.4	bulk	-1.02	-1.05	-0.07	0.70902	0.512271	-7.2	18.922	15.662	38.776
OBR-11-4.4	leachate	-	-	-	0.70793	0.512282	-6.9	18.885	15.668	38.723
OBR-11-4.4p	pisolith separate, bulk	-0.66	-1.18	-0.42	-	-	-	-	-	-

OBR-11-4.4p	pisolith separate, leachate bulk	-	-	-	0.70793	0.512317	-6.3	18.889	15.658	38.669
OBR-11-5.1	bulk	-4.91	-2.09	-0.16	0.70917	0.512293	-6.7	18.938	15.662	38.750
OBR-11-5.1	leachate	-	-	-	0.70796	0.512327	-6.1	18.915	15.672	38.728
OBR-11-5.1p	pisolith separate, bulk	-7.43	-2.03	-0.44	-	-	-	-	-	-
OBR-11-5.1p	pisolith separate, leachate bulk	-	-	-	0.70793	0.512314	-6.3	18.846	15.655	38.651
OBR-11-6.1	bulk	-20.3	-3.34	0.08	0.70921	0.512224	-8.1	18.974	15.671	38.788
OBR-11-6.1	leachate	-	-	-	0.70796	0.512282	-6.9	19.017	15.687	38.755
OBR-11-6.1p	pisolith separate, bulk	-24.8	-2.09	-0.24	0.70808	0.512263	-7.3	19.050	15.679	38.777
OBR-11-6.1p	pisolith separate, residue	-	-	-	-	0.512205	-8.4	19.153	15.685	38.873

1565 ^a In bold italic, samples from the host strata; in regular, samples from the Mn-ore layer.

1566

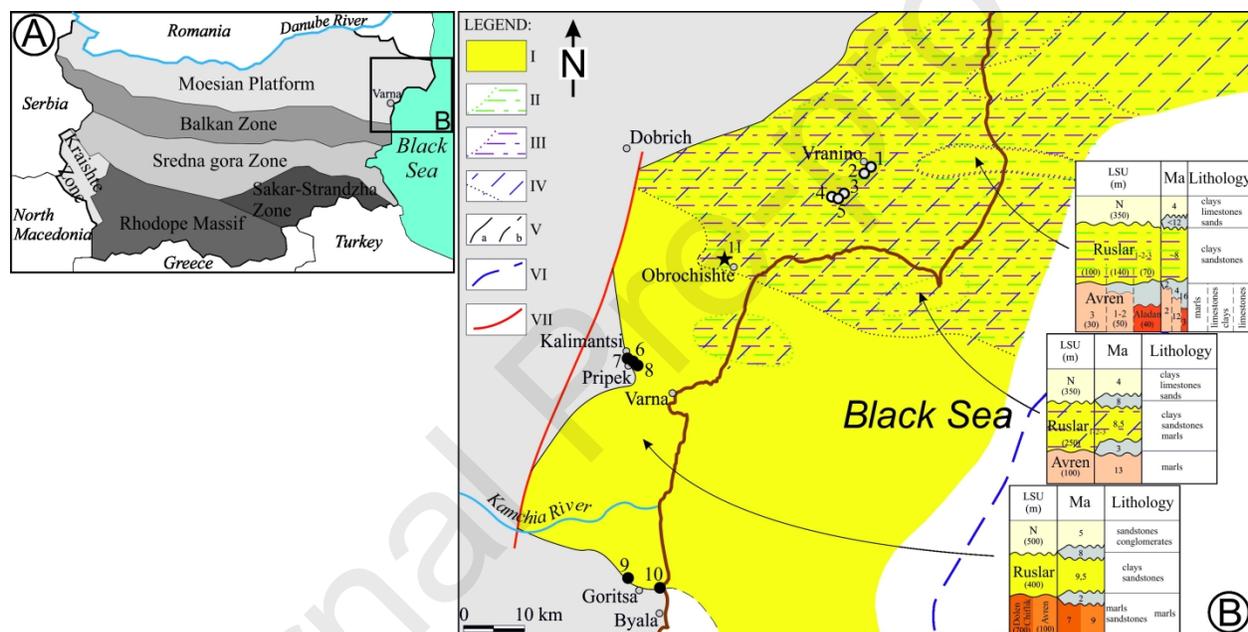
1567 **Table 6**

1568 **Geochemistry of Oligocene Mn-deposits around the Black Sea.**

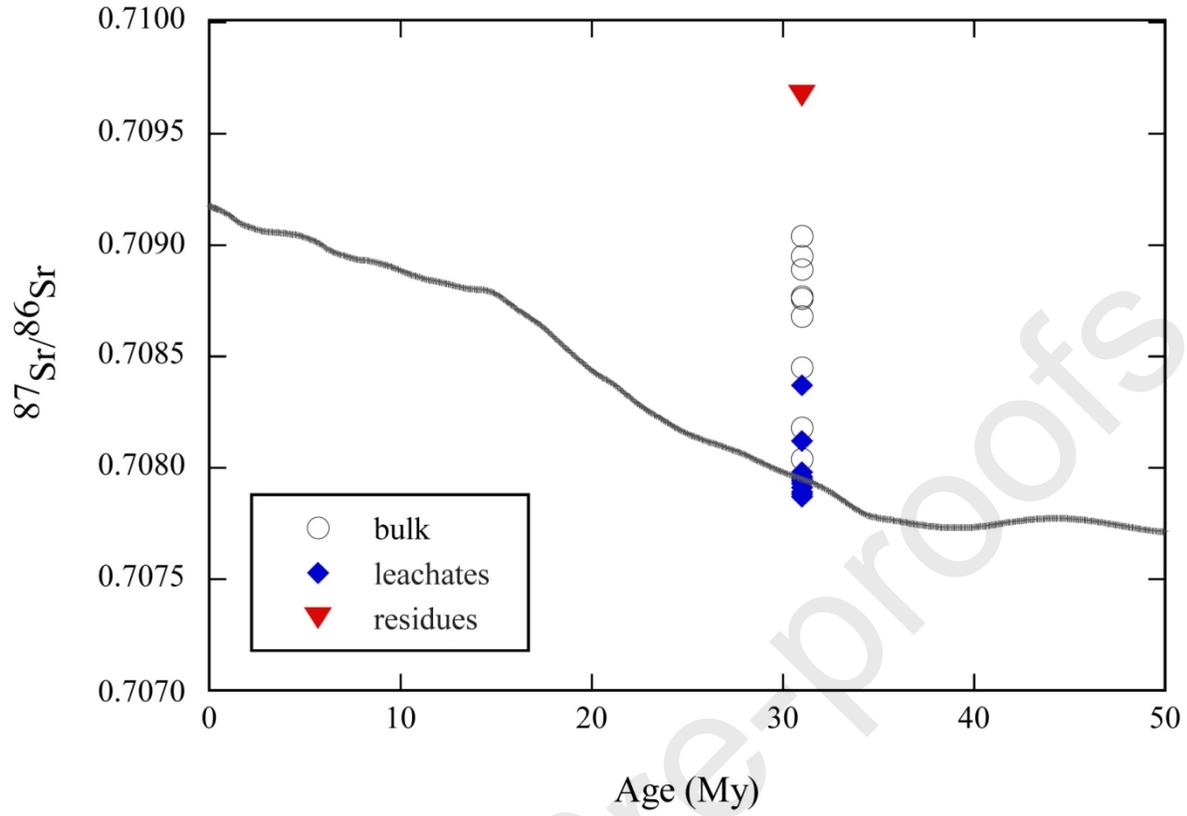
deposit facies	Binkiliç		Chiatura-Kvirila		Labá (Labinsk)	Mangyshlak	
age (Ma)	oxide	carbonate	oxide	carbonate	carbonate	oxide	carbonate
country	Turkey	Turkey	Georgia	Georgia	Russia	Kazakhstan	Kazakhstan
host rock	limestone	limestone	sandstone	sandstone	sand	calcareous sandstone	calcareous sandstone
predominant mineral	ore cryptomelane	rhodochrosite	manganite	rhodochrosite	rhodochrosite	pyrolusite	rhodochrosite
# of analyses	19	11	11	30	24	15	24
MnO (wt.%)	53.5	35.3	48.4	30.6	32.9	39.8	29.2
Fe ₂ O ₃ tot (wt.%)	2.92	5.92	1.63	3.33	3.88	3.48	2.61
SiO ₂ (wt.%)	7.47	8.26	14.7	18.6	-	-	35.5
Al ₂ O ₃ (wt.%)	2.47	2.27	3.52	3.59	-	-	5.72
CaO (wt.%)	15.1	18.4	5.25	9.56	9.85	-	11.6
MgO (wt.%)	0.94	1.05	1.86	3.07	1.39	-	1.22
K ₂ O (wt.%)	0.33	0.49	0.50	0.55	-	-	1.70
Na ₂ O (wt.%)	0.43	0.27	0.49	0.55	-	-	1.91
P ₂ O ₅ (wt.%)	0.74	0.32	0.22	1.14	0.04	0.09	0.48
TiO ₂ (wt.%)	0.56	0.38	0.17	0.24	-	-	0.17
LOI (wt.%)	13.4	25.3	16.6	26.8	39.6	-	13.8
Ba (ppm)	4249	5505	9578	785	-	-	-
Co (ppm)	85	72	21	49	13	68	8
Cr (ppm)	15	7	-	-	19	20	21
Cu (ppm)	93	64	24	69	22	60	18
Ni (ppm)	195	203	527	401	151	175	36
Pb (ppm)	46	43	26	22	-	-	-
Sr (ppm)	2232	2719	-	-	-	-	-
V (ppm)	44	91	-	-	37	86	-
Y (ppm)	14	17	-	-	-	-	-
Zn (ppm)	60	57	102	142	53	-	-
Zr (ppm)	53	35	-	-	-	-	-
Ce/Ce*	0.77	0.74	-	-	-	-	-

Eu/Eu*	2.78	1.62	-	-	-	-
Ce/Ce* (at Al=0)	0.80	0.81	-	-	-	-
Eu/Eu* (at Al=0)	3.33	1.78	-	-	-	-
C _{carb} (wt.%)	-	-	8.03	18.5	-	5.79
C _{org} (wt.%)	-	-	-	-	-	0.29
$\delta^{13}\text{C}_{\text{cct}}^{\text{a}}$ (‰ PDB)	-	-5.10	-7.10	-12.5	-	-5.98
$\delta^{13}\text{C}_{\text{rhod}}^{\text{b}}$ (‰ PDB)	-	-6.61	-10.1	-10.5	-	-10.3
$\delta^{18}\text{O}_{\text{cct}}$ (‰ PDB)	-	-8.05	-7.11	-4.32	-	-2.51
$\delta^{18}\text{O}_{\text{rhod}}$ (‰ PDB)	-	-6.39	-5.32	-4.40	-	-0.99
References	Öztürk and Frakes, 1995; Gültekin, 1998; Gültekin and Balçı, 2018	Varentsov and Rakhmanov, 1980; Dombrovskaya, 1997	Kalinenko et al., Kuleshov and 1965	Kuleshov, 2003; 2017		

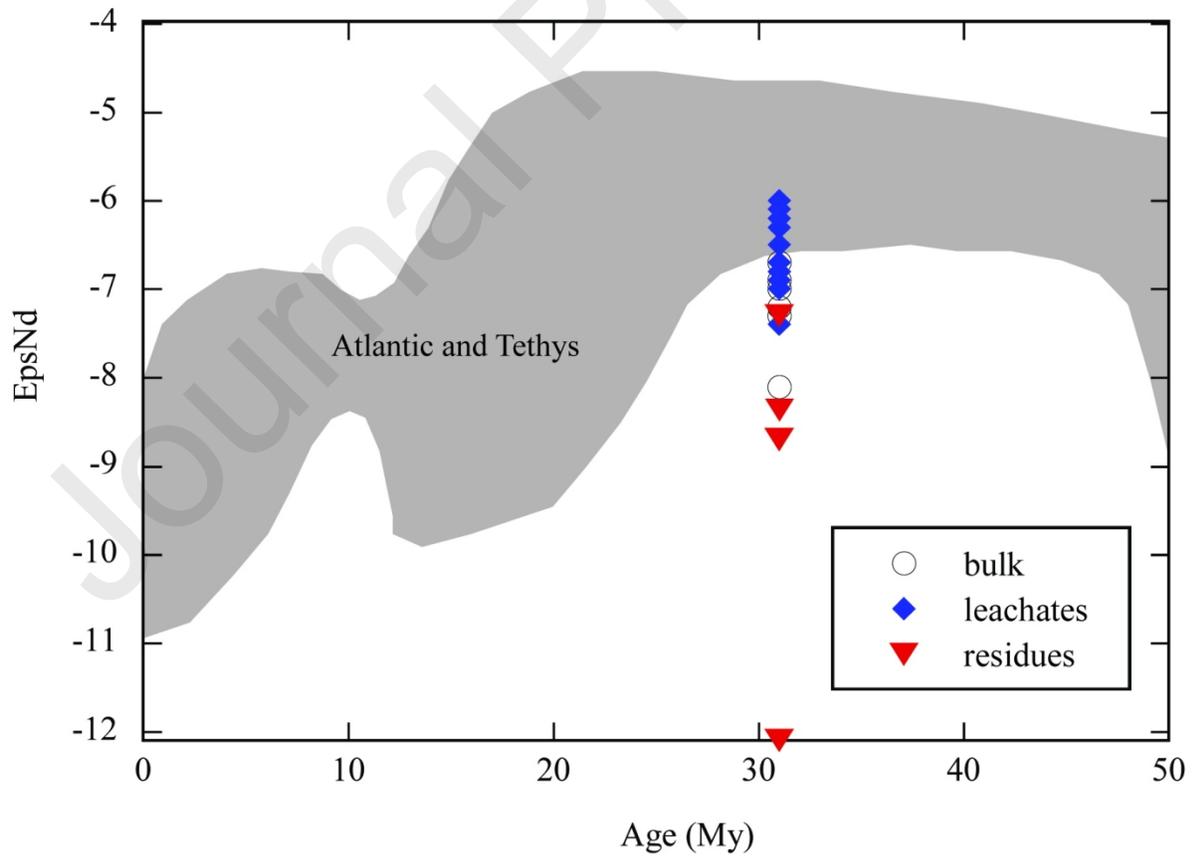
1569 ^a $\delta^{13}\text{C}_{\text{cct}} = \delta^{13}\text{C}_{\text{calcite}}$ (similarly, $\delta^{18}\text{O}_{\text{cct}} = \delta^{18}\text{O}_{\text{calcite}}$)
 1570 ^b $\delta^{13}\text{C}_{\text{rhod}} = \delta^{13}\text{C}_{\text{rhodochrosite}}$ (similarly, $\delta^{18}\text{O}_{\text{rhod}} = \delta^{18}\text{O}_{\text{rhodochrosite}}$)
 1571



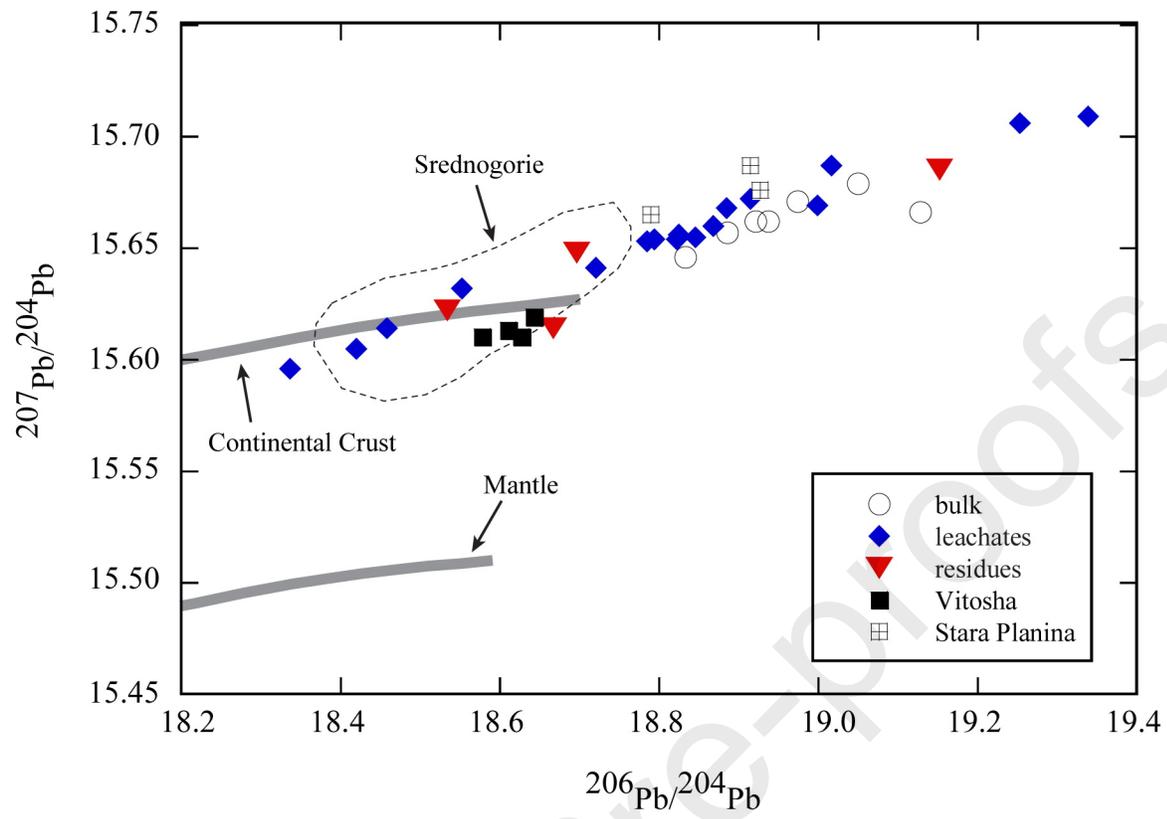
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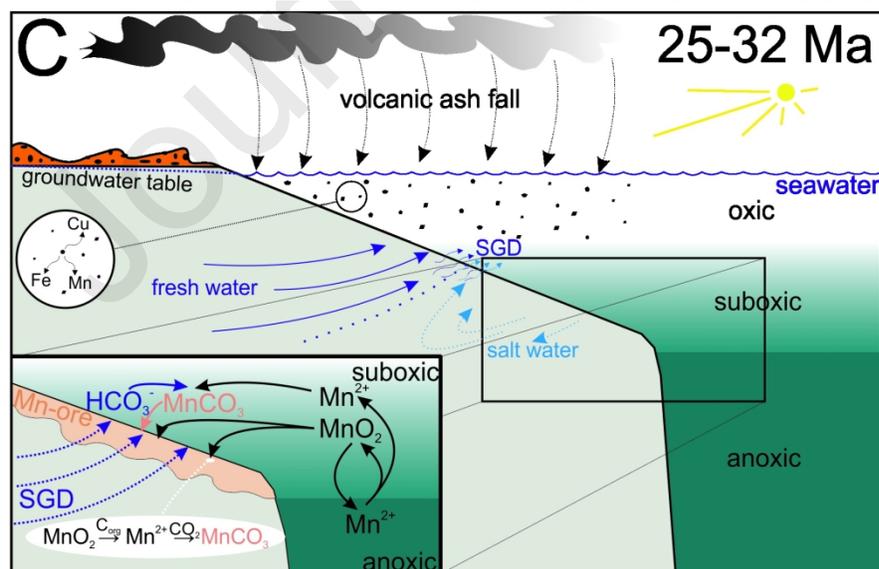
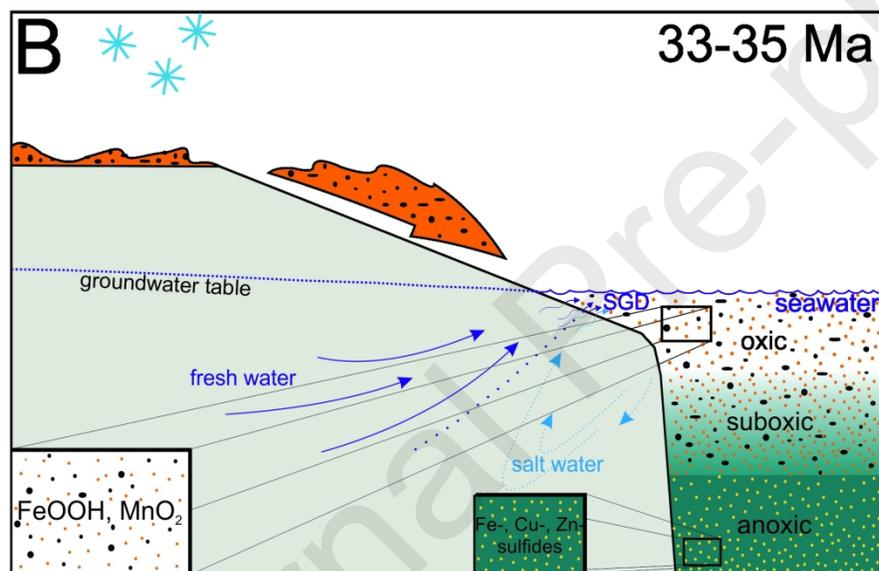
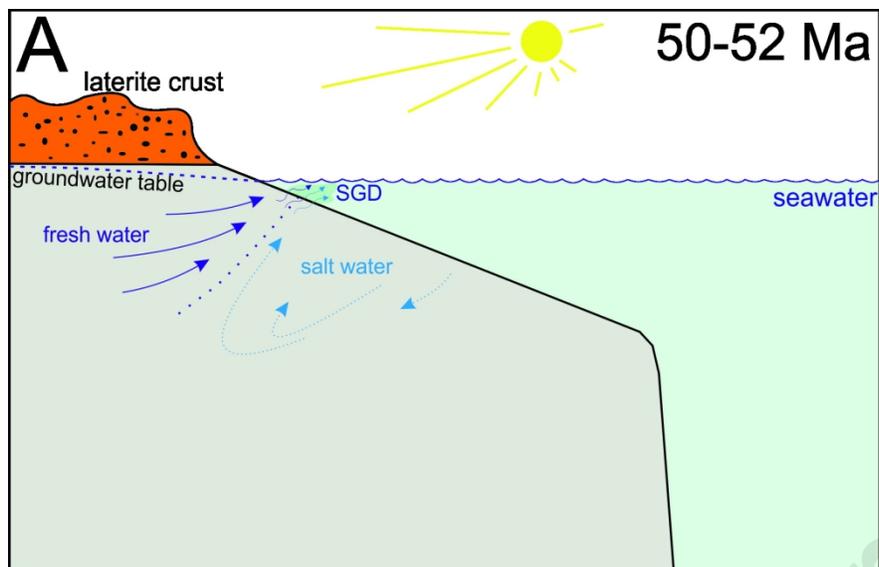
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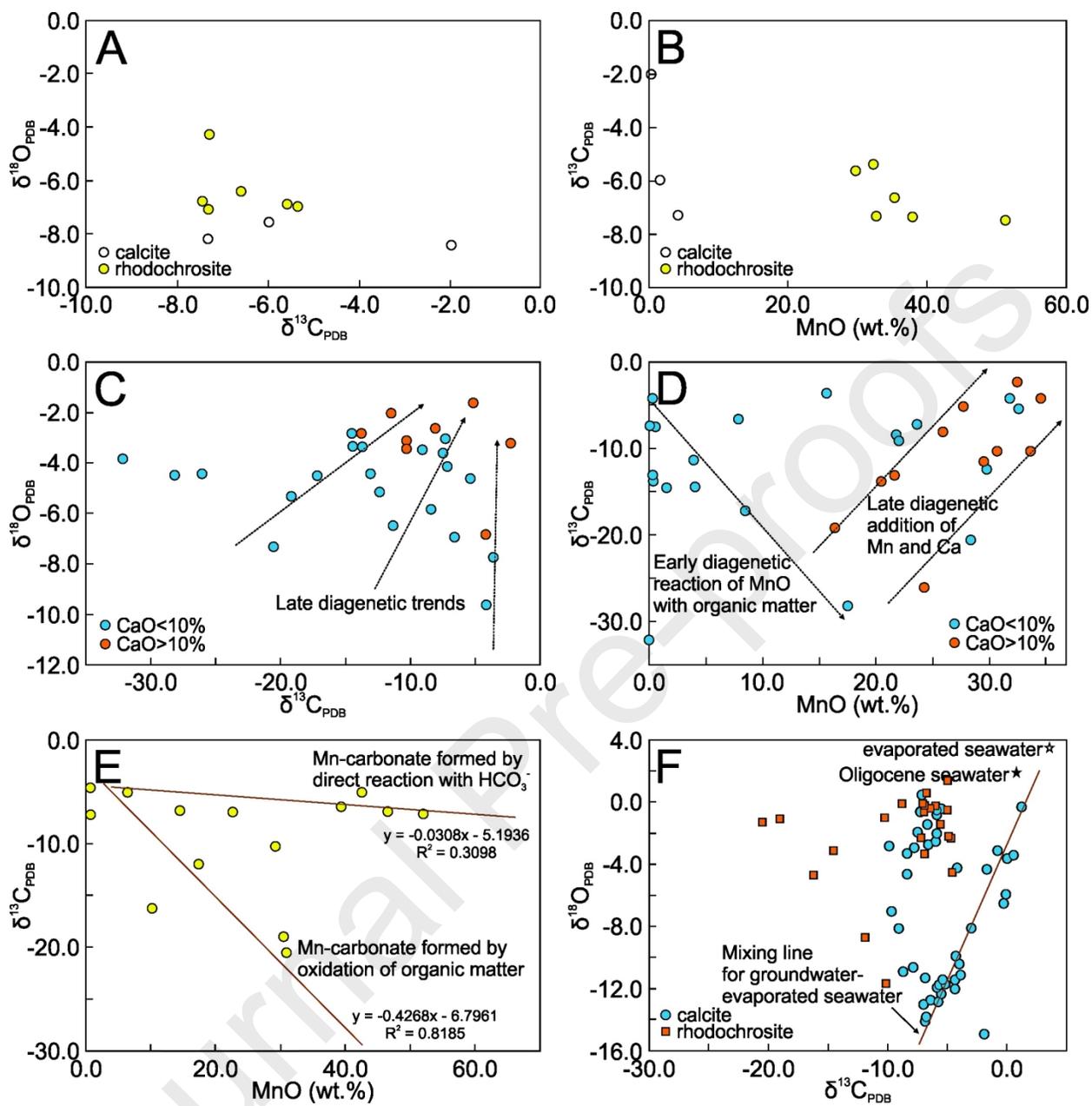


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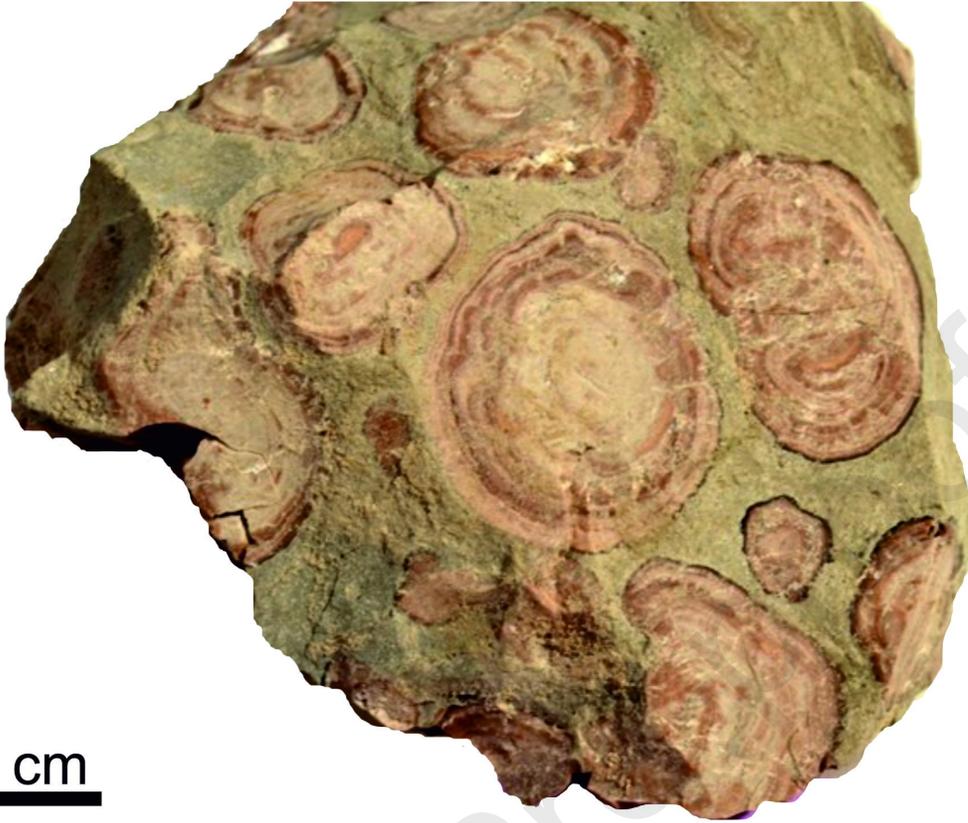


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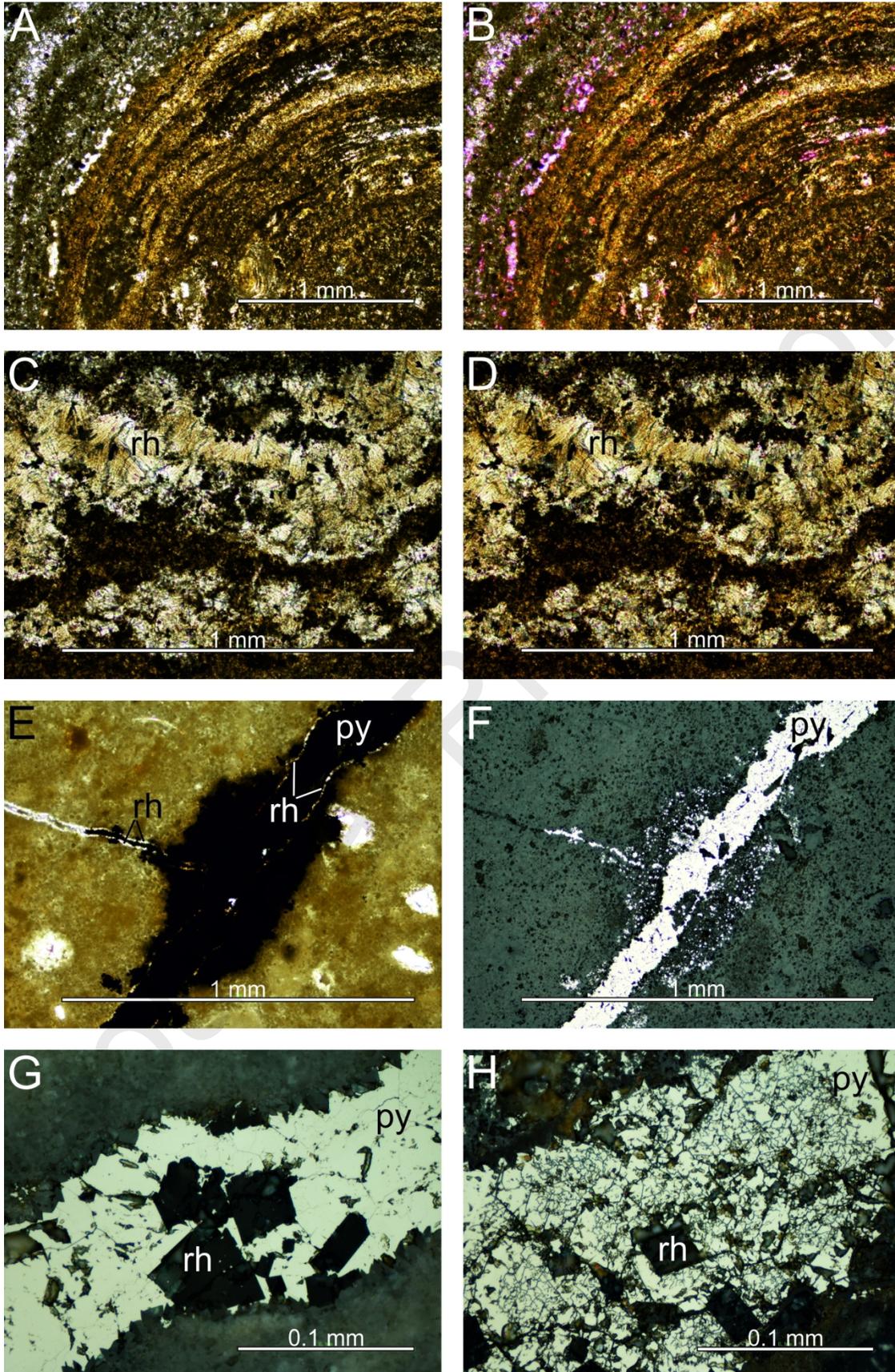
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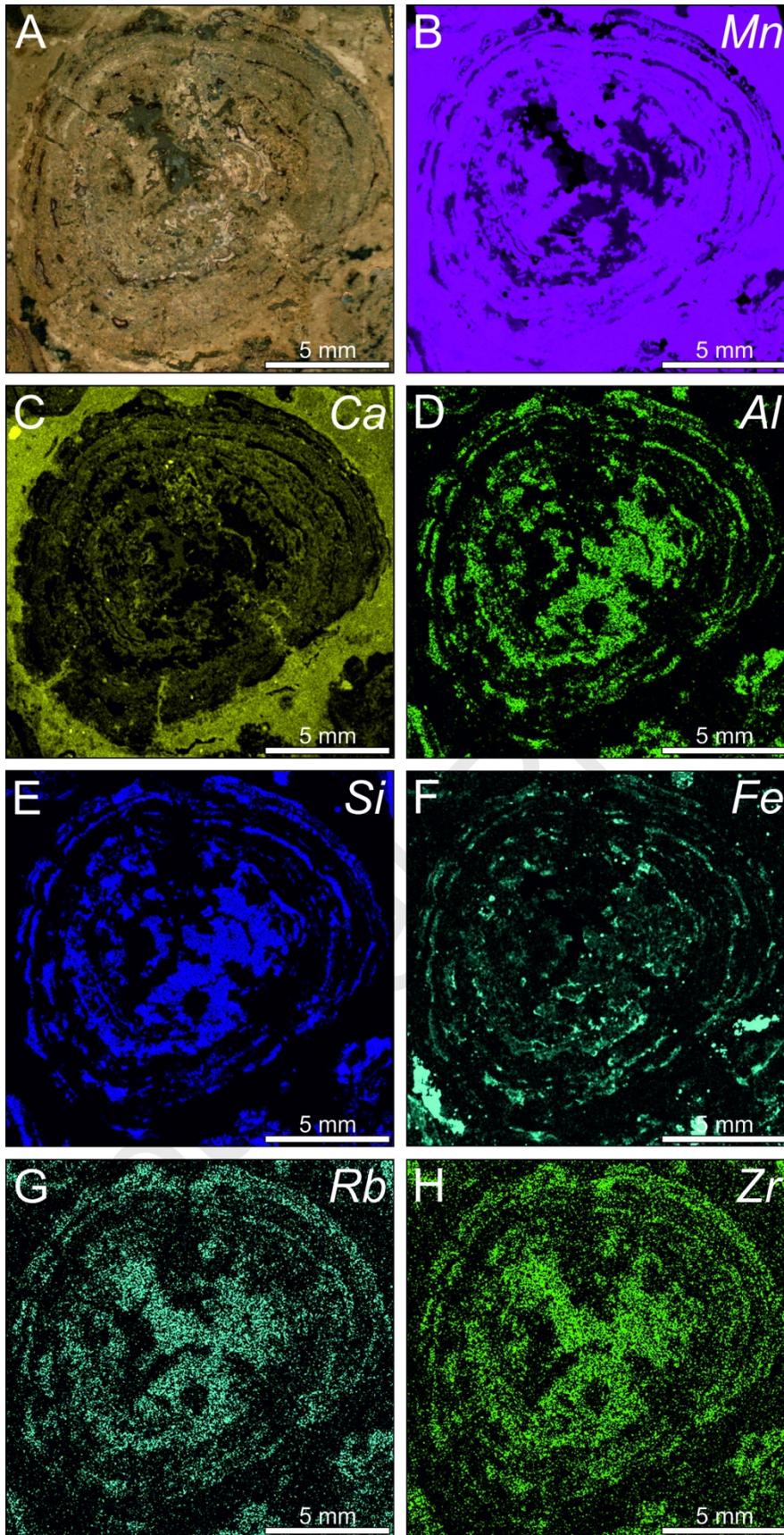


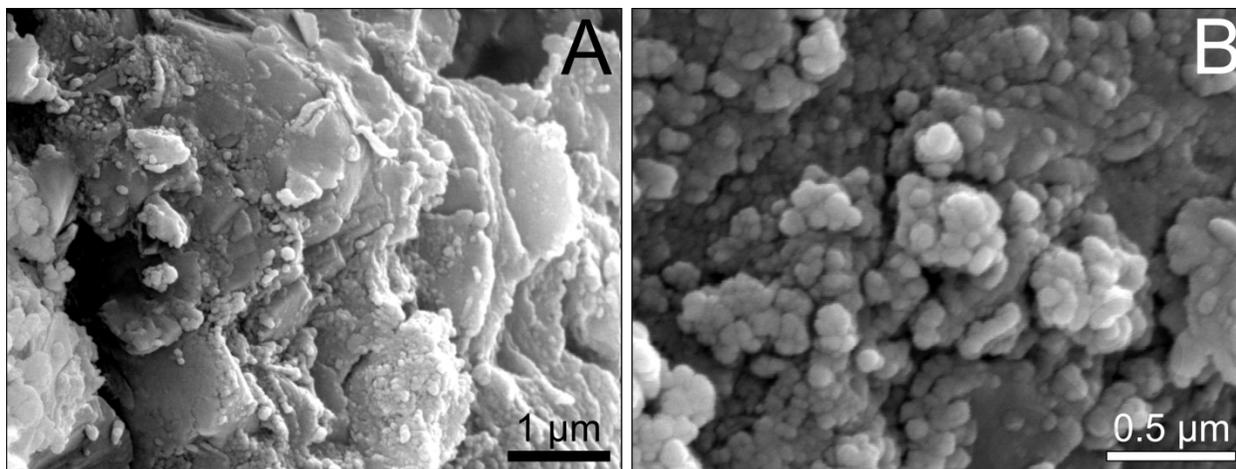
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Journal Pre-proofs

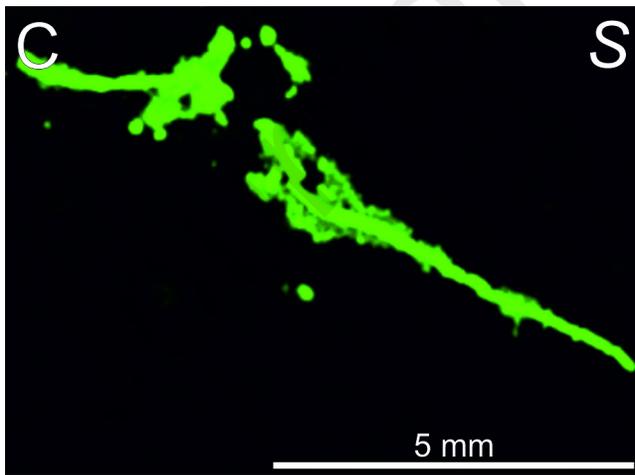
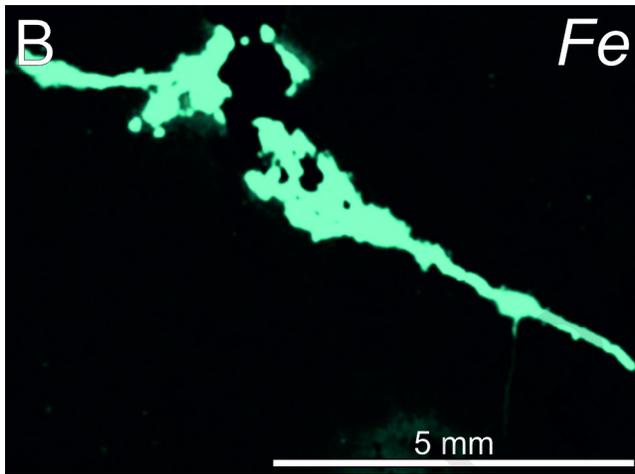
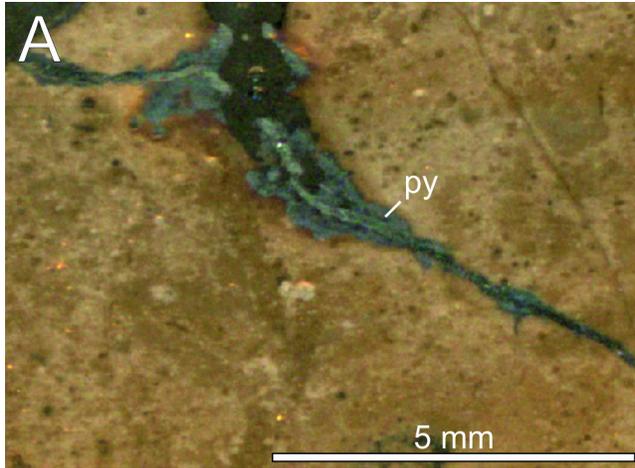




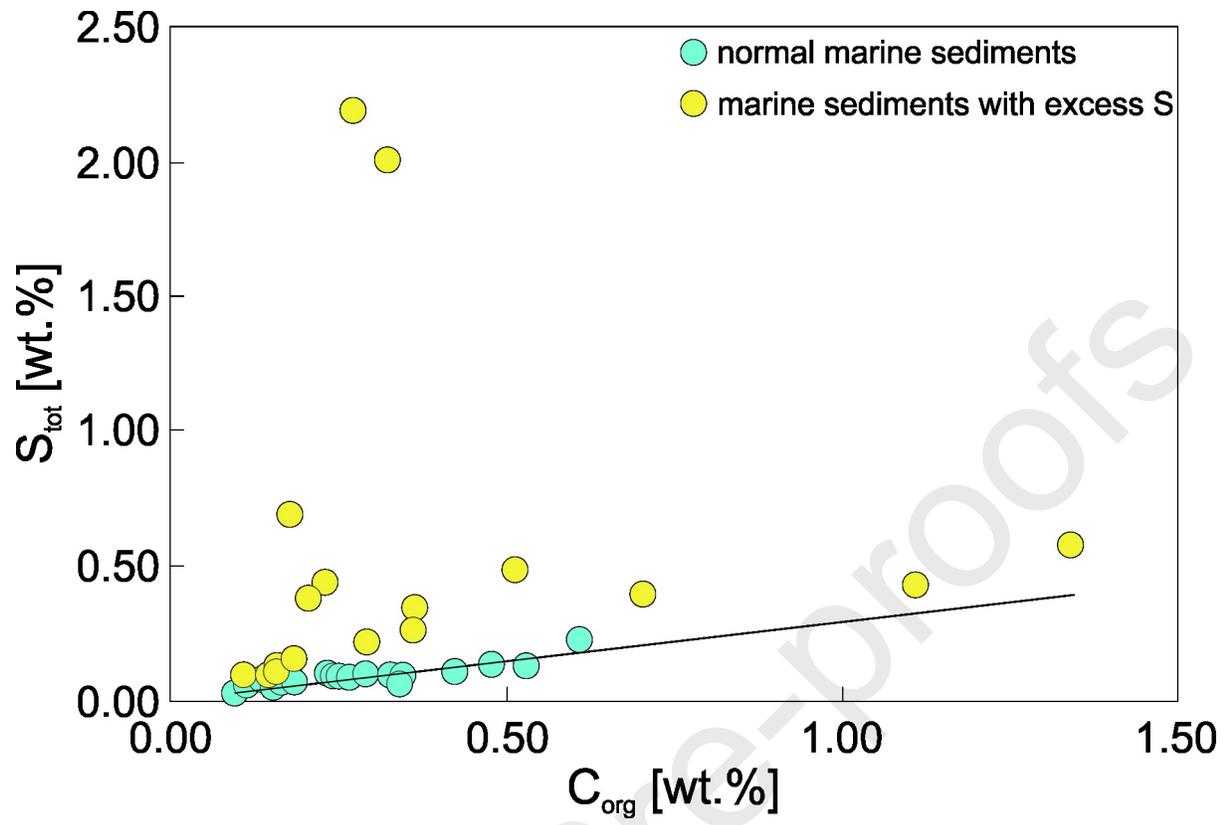


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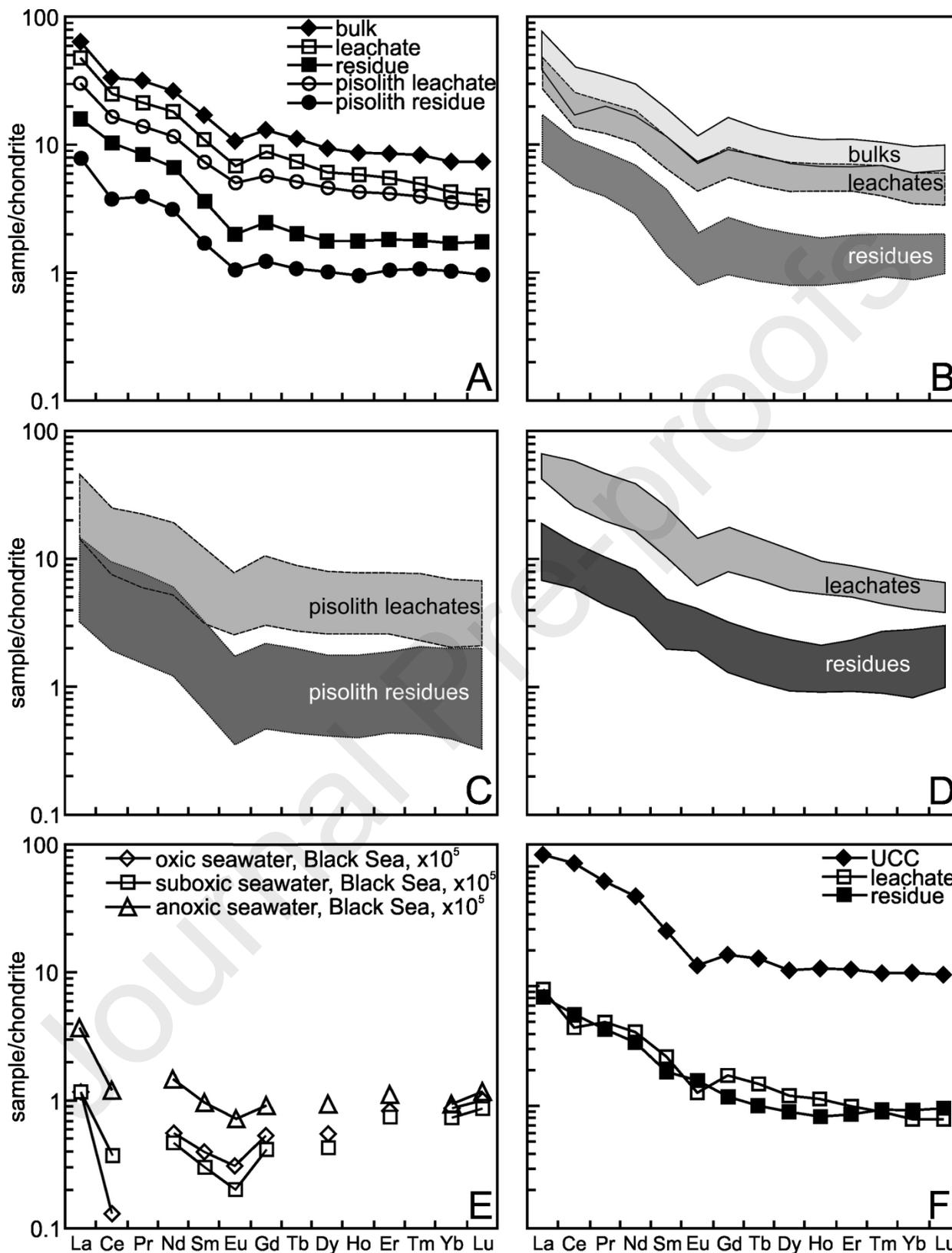
Journal Pre-proof



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