

1 Groundwater table fluctuations recorded in zonation of microbial
2 siderites from end-Triassic strata

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4 By Weibel, R.^{1*}, Lindström, S.¹, Pedersen, G. K.¹, Johansson, L.² Dybkjær, K.¹, Whitehouse, M.³,
5 Boyce, A.⁴, Leng, M.J.⁵

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8 ¹ GEUS, Geological Survey of Denmark and Greenland, Øster Voldgade 10, 1350 Copenhagen K, Denmark.

9 ² Department of Geology, Lund University, Sölvegatan 12, 223 62 Lund, Sweden.

10 ³ Department of Geosciences, Naturhistoriska Riksmuseet, 104 05 Stockholm, Sweden.

11 ⁴ NERC Isotope Geosciences Facilities, SUERC, Rankine Avenue, East Kilbride, G75 0QF, UK.

12 ⁵ NERC Isotope Geosciences Facilities (Stable Isotope Facility), British Geological Survey, Keyworth,
13 Nottingham, NG12 5GG, UK.

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15 *Corresponding author: Weibel, R., rw@geus.dk, Phone: +45 51513364

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18 **Keywords**

19 Siderite concretions; sphaerosiderite; spheroidal siderite; oxygen and carbon isotopic composition; microbial
20 activity; groundwater fluctuations

25 **Abstract**

26

27 In a terrestrial Triassic–Jurassic boundary succession of southern Sweden, perfectly zoned sphaerosiderites
28 are restricted to a specific sandy interval deposited during the end-Triassic event. Underlying and overlying
29 this sand interval there are several other types of siderite micromorphologies, i.e. poorly zoned
30 sphaerosiderite, spheroidal (ellipsoid) siderite, spherical siderite and rhombohedral siderite. Siderite
31 overgrowths occur mainly as rhombohedral crystals on perfectly zoned sphaerosiderite and as radiating
32 fibrous crystals on spheroidal siderite. Concretionary sparry, microspar and/or micritic siderite cement
33 postdate all of these micromorphologies. The carbon isotope composition of the siderite measured by
34 conventional mass spectrometry shows the characteristic broad span of data, probably as a result of multiple
35 stages of microbial activity. SIMS (secondary ion mass spectrometry) revealed generally higher $\delta^{13}\text{C}$ values
36 for the concretionary cement than the perfectly zoned sphaerosiderite, spheroidal siderite and their
37 overgrowths, which marks a change in the carbon source during burial. All the various siderite morphologies
38 have almost identical oxygen isotope values reflecting the palaeo-groundwater composition. A pedogenic /
39 freshwater origin is supported by the trace element compositions of varying Fe:Mn ratios and low Mg
40 contents. Fluctuating groundwater is the most likely explanation for uniform repeated siderite zones of
41 varying Fe:Mn ratios reflecting alternating physiochemical conditions and hostility to microbial life/activity.
42 Bacterially-mediated siderite precipitation likely incorporated Mn and other metal ions during conditions that
43 are not favourable for the bacteria and continued with Fe-rich siderite precipitation as the physico-chemical
44 conditions changed into optimal conditions again, reflecting the response to groundwater fluctuations.

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50 **Introduction**

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52 Siderite is a common early diagenetic mineral occurring with a variety of morphologies in different
53 depositional environments. Rhombohedral and spheroidal (ellipsoid-shaped) siderite are known from marine
54 mudstones and sandstones (e.g. Mozley and Carothers 1992; Mortimer et al. 1997; Wilkinson et al. 2000,
55 Weibel et al. 2010), whereas sphaerosiderite (with internal radial and/or concentric zonation) and spherulitic
56 siderite morphologies (with internal radial structures) and nodules/spheres of siderite (without clear internal
57 structures) are commonly of pedogenic origin (e.g. Browne and Kingston 1993; Retallack 1997; Driese et al.
58 2010; Robinson et al. 2010; Suarez et al. 2010; Rosenau et al. 2013) and are occasionally found in tidal flats
59 (Choi et al. 2003). A morphological change from spherulitic to rhombohedral siderite during diagenesis has
60 recently been suggested by Köhler et al. (2013) and renders the probability of other explanations for the
61 varying siderite morphologies. In a similar way to the changes during burial of marine sediments, the initial
62 microbial mediated fast precipitation may change into rhombohedral growth, as the supply of Fe becomes
63 slower during increased burial of continental deposits. Zonation is common in rhombohedral and spheroidal
64 siderite, and sphaerosiderites are characterized by internal radial-concentric microstructures. Siderite
65 zonation has previously been ascribed to mixing of meteoric and marine waters (Mozley 1989; Choi et al.
66 2003), diagenetic evolution of freshwater or brackish-marine pore water during burial (Matsumoto and Iijima
67 1981; Lim et al. 2004), or modification of the original marine pore waters during successive stages of
68 microbial decomposition of organic matter (Mozley and Carothers 1992; Wilkinson et al 2000; Lim et al.
69 2004). Despite the wide occurrence of sphaerosiderite, little is known of the pedogenetic conditions
70 (physical, chemical and biological) under which they form and when different siderite morphologies are
71 likely to precipitate (Driese et al. 2010). Precipitation of siderite, even within historical time (< 100 years)
72 shows that microbial degradation of organic contaminants can enhance siderite precipitation rate (Driese et
73 al. 2010). Hence, microbial activity in the pedogenic regime may have promoted precipitation of
74 sphaerosiderite. Siderite formation has been interpreted to be microbially mediated in various environments;
75 marine (Mozley and Carothers 1992; Wilkinson et al. 2000), tidal (Choi et al. 2003), and lacustrine (Fisher et

76 al. 1998). A wide range in carbon isotope composition ($\delta^{13}\text{C}$) of sphaerosiderites is interpreted to originate
77 from variations in the type of microbial activity in soils (e.g. Robinson et al. 2010), whereas a more narrow
78 range of oxygen isotope compositions ($\delta^{18}\text{O}$) is thought to reflect meteoric water compositions (e.g., Ufnar et
79 al. 2004b; Driese et al. 2010; Robinson et al. 2010; Suarez et al. 2010). The latter has therefore been used as
80 a palaeoproxy for the isotope composition of rainfall, primarily during the Cretaceous (Ludvigson et al.
81 1998; Ufnar et al. 2001, 2002, 2004a, 2004b, 2004c; Suarez et al. 2009, 2010; Robinson et al. 2010).

82
83 The end-Triassic event is one of the five largest biotic crises during the Phanerozoic (Bond and Wignall
84 2014). It is temporally linked to the emplacement of intrusive and extrusive volcanic rocks during the
85 formation of the Central Atlantic Magmatic Province (Schoene et al. 2010; Blackburn et al. 2013), and
86 degassing from this volcanism is generally believed to have played a major part in the extinction scenario
87 (e.g., Hesselbo et al. 2002; Ruhl et al. 2011; Lindström et al. 2012). Organic $\delta^{13}\text{C}$ records across the
88 Triassic–Jurassic boundary show large negative perturbations in the carbon cycle interpreted as reflecting
89 input of light carbon from the volcanism or from methane release (e.g. Hesselbo et al. 2002). In the terrestrial
90 realm, physiological responses in fossil plants indicate intense global warming across the Triassic–Jurassic
91 boundary (McElwain et al. 1999). Increased storminess and lightning activity are further indicated by
92 charcoal records showing increased wildfire activity from Greenland, Denmark, Sweden and Poland
93 (Marynowski and Simoneit 2009; Belcher et al. 2010; Petersen and Lindström 2012). Sedimentary records
94 from the Danish Basin indicate increased reworking of palynological material (Lindström et al. 2012), and
95 marked changes in fluvial terrestrial successions in Sweden and Greenland seem to indicate an increased
96 water content in the hydrological cycle across the boundary (Lindström and Erlström 2006; Steinthorsdottir
97 et al. 2012).

98
99 Sphaerosiderites and other siderite morphologies have previously been reported from Triassic–Jurassic
100 boundary sediments (Höganäs Formation) in Scania, southern Sweden (Fig. 1; Troedsson 1951; Ahlberg
101 1994). Troedsson (1951) reported sphaerosiderites from early – middle Rhenish clayey sediments (Vallåkra
102 Member of the Höganäs Formation) in several old cored wells and outcrops in northwest and central Scania,

103 and concluded that sphaerosiderites were restricted to this particular interval. Here we show that
104 sphaerosiderites also occur within the latest Rhaetian sand and sandstones (Helsingborg Member of the
105 Höganäs Formation), although they are apparently absent from the intermediate part (Bjuv member of the
106 Höganäs Formation) (Fig. 1). The purpose of this study is to find explanations for the different siderite
107 morphologies and contribute to the understanding of sphaerosiderite formation, and its implications
108 regarding Triassic – Jurassic-boundary events. In northwest Scania, southern Sweden, the end-Triassic
109 terrestrial succession is characterized by a pronounced shift in depositional style and in occurrence of various
110 types of authigenic siderite. Mid to late Rhaetian forest mires and confined fluvial channel deposits are
111 completely free of authigenic siderite, whereas the overlying latest Rhaetian unconfined and probably
112 episodic braided river deposits are dominated by siderite concretions and authigenic siderite. In this sense,
113 the Albert-1 core, Norra Albert quarry and the Fleninge No. 266 core (Fig. 2), which together encompass
114 Norian–Hettangian strata, provide excellent opportunities for such investigations as perfectly zoned
115 sphaerosiderite occur juxtaposed with other siderite morphologies.

116

117 *Fig. 1: Stratigraphy*

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119 *Fig. 2: Map*

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121

122 **Geological setting**

123

124 During the Late Triassic – Early Jurassic the Norwegian–Danish Basin was situated on the margin of an
125 epicontinental basin covering NW Europe (e.g. Fischer and Mudge 1998; Nielsen 2003). Southern Sweden
126 was part of the Fennoscandian Border Zone, which is structurally defined by the Sorgenfrei-Tornquist Zone,
127 and marks the transition from the Fennoscandian Shield to the north-east and the gradually deepening
128 (epicontinental) basin towards the south-west (Fig. 1; Liboriussen et al. 1987; Mogensen and Korstgård,

129 2003; Nielsen 2003). Therefore, minor sea-level changes played a significant role in controlling the lateral
130 facies distribution (Ahlberg et al. 2003). In Scania, the southernmost part of Sweden, typical continental red
131 beds of the Norian Kågeröd Formation, deposited under a semi-arid regime, are succeeded by claystones,
132 sandstones and coals belonging to the Rhaetian-Hettangian Höganäs Formation (Fig. 1). The oldest member
133 of the Höganäs Formation, the Vallåkra Member, consists of variegated smectitic clays and sands which
134 constitute a transition from the underlying red beds of the Kågeröd Formation to the kaolinite-rich
135 underclays, mature sands and coals of the Bjuv Member (Ahlberg et al. 2003). The Norwegian–Danish Basin
136 was transgressed in two steps (indicated on Fig. 1) during the Rhaetian, culminating with a maximum
137 transgression (MFS7) that can be traced all over the Danish part of the Norwegian–Danish Basin (Figs 1 and
138 3; Nielsen 2003; Lindström and Erlström 2006). The marine transgression reached as far in Scania as the
139 localities Helsingborg and Lunnom, and at Norra Albert an incursion of marine dinoflagellates probably
140 represents marine waters entering the rivers during storm episodes (Fig. 1; Lindström and Erlström 2006).
141 The precursor mires, resulting in the Bjuv Member coals/coaly beds, were formed on a low-relief coast
142 affected by a transgressive event in the mid-late Rhaetian (Petersen et al. 2013). The change from a semi-arid
143 climate during the Norian to more humid conditions during the Rhaetian has been attributed to effects of the
144 marine inundation of the Central European Basin from the Tethys (Ahlberg et al. 2002). Climatic changes at
145 the Triassic–Jurassic boundary that forced supraregional deforestation in NW Europe, (van de Schootbrugge
146 et al. 2009) which severely affected the forest mires (Petersen and Lindström 2012), may have triggered the
147 changes in continental deposits from mire forests and wetlands with confined fluvial channels (Bjuv
148 Member) to braided streams of the Boserup beds (Helsingborg Member) (Lindström et al. 2015). The
149 Boserup beds constitute the basal part of the Helsingborg Member (Sivhed 1984, Troedsson 1951). Some
150 authors have placed the boundary between the Bjuv Member and the Helsingborg Member at the top of coal
151 bed A, i.e. at c. 3 m in Fig. 3A (Sivhed 1984). In the Norra Albert quarry the boundary of the Boserup beds
152 has not been formally defined. In the present paper it is placed at 6 m in Fig. 3A based on sedimentological
153 considerations. The Bjuv Member is characterized by mudstones and coal beds with subordinate sandstones
154 interpreted as fluvial deposits. The overall depositional environment is interpreted as a floodplain. The coal
155 bed A is overlain by carbonaceous mudstone and with strongly deformed sand beds 5.0–6.2 m (Fig. 3A).

156 This succession comprises thin beds of fine-grained sand with graded bedding separated by mud-drapes. The
157 sand shows ripple-cross-lamination, indistinct lamination and locally parallel bedding. The sedimentary
158 structures suggest episodic, non-channelized deposition of sand in a flood-plain environment. Two phases of
159 soft-sediment deformations are interpreted caused by seismic shocks (Lindström et al. 2015). They are
160 erosionally overlain by the Boserup beds, which are a distinct association of facies dominated by structure
161 less, parallel bedded and trough cross-bedded sand, with several large concretions. The Boserup beds are
162 interpreted as braided stream deposits.

163

164 At the Norra Albert quarry and in the Fleninge No. 266 well this terrestrial ecosystem change is marked by a
165 gradual loss of Taxodiacean/Cupressacean gymnosperm pollen (*Perinopollenites elatoides*) from trees that
166 thrived in mires in favour of the enigmatic gymnosperm pollen tetrad *Ricciisporites tuberculatus*,
167 representing an unknown habit, perhaps ruderal / scrubby (Kürschner et al. 2014). A similar shift in
168 dominating pollen-type is recorded in marine sediments (the Stenlille-1 well – see Fig. 2) representing a
169 sediment source-area larger than that of the investigated terrestrial localities (Lindström et al. 2012). In
170 addition, repeated intervals of seismites occur at the Triassic-Jurassic transition at the Norra Albert quarry
171 (Lindström et al. 2015) coinciding with the occurrence of perfectly zoned sphaerosiderite (Fig. 2).

172

173 *Fig. 3: Sedimentary logs from Norra Albert quarry, Albert-1 and Fleninge No. 266 cores.*

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175

176 **Methodology and terminology**

177

178 The samples comprise outcrop rock samples taken during field work in the Norra Albert quarry 2009 - 2012
179 and core samples from the Albert-1 and the Fleninge No. 266 wells, which were drilled in 2009 and 1935,
180 respectively. Consequently, the samples from the Fleninge No. 266 well were restricted by the limited
181 remaining core samples.

182

183 Petrography was evaluated from polished thin sections using a Zeiss Axioplane for transmitted and reflected
184 light microscopy. Supplementary studies of crystal morphologies, dissolution features and paragenetic
185 relationships were performed on gold coated rock chips mounted on stubs and on carbon coated thin sections
186 using a Phillips® XL 40 scanning electron microscope (SEM) operated with secondary electron detector
187 (SE) and back-scatter detector (BSE), respectively. The SEM was equipped with an energy dispersive X-ray
188 analysis (EDX) system Thermo Nanotrace® 30 mm² detector surface window and a Pioneer Voyager® 2.7
189 10 mm² window Si(Li) detector. The electron beam was generated by a tungsten filament operating at 17 kV
190 and 50-70 µA. One sample was partially dissolved in hydrochloric acid heated at 30°C in 2 hours under
191 agitation in order to enhance visibility of growth structures in the SEM.

192

193 Bulk samples for X-ray diffraction (XRD) analysis were mounted with random orientation. Samples were
194 scanned on an automated Philips® PW 3710 X-ray diffractometer with automatic divergence slit, using
195 graphite monochromated CuKα radiation. Quantification of major mineral phases based on bulk samples
196 was done by Rietveld analysis of X-ray diffractograms.

197

198 Total abundances of the major oxides and several minor elements were analysed by ICP-ES (inductively
199 coupled plasma-emission spectrometry) and the rare earth elements were determined by ICP-MS
200 (inductively coupled plasma-mass spectrometry) at ACME laboratory. The samples were fused by lithium
201 metaborate/ tetraborate and digested in dilute nitric acid. Total S and C were analysed by LECO. The major
202 elements were applied for calculation of mineral abundances.

203

204 Quantitative chemical analyses of the carbonates were performed on a JEOL® JXA-8200 electron
205 microprobe operated at an acceleration voltage of 15 kV, a beam current of 8 nA and a spot size of 10 µm.
206 Carbon coated thin section were applied.

207

208 Carbon and oxygen isotopes were analysed on bulk rock samples by IRMS (isotope ratio mass spectrometry)
209 and *in situ* by SIMS (secondary ion mass spectrometry) on thin sections. Bulk rock carbon and oxygen
210 isotope analyses using a VG SIRA II dual inlet mass spectrometer were performed on carbon dioxide
211 released from the carbonates after reaction with phosphoric acid at 25°C for 3 hours (calcites) and at 100°C
212 for 96 hours (siderites) at the SUERC facility in the UK. This way the major part of carbon dioxide produced
213 at 25°C will be from calcite, ensuring that the subsequent produced (at 100°C) carbon dioxide was
214 dominantly from siderite. The fractionation factors used were from Friedman and O'Neil (1977) (calcite) and
215 Rosenbaum and Sheppard (1986) (siderite). Carbon and oxygen isotope data ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) are presented
216 in the standard δ notation relative to PDB, Pee Dee Belemnite (Craig 1957). *In situ* carbon and oxygen
217 isotopes measurements, were performed at the NORDSIM facility, Stockholm, using a CAMECA®
218 IMS1280 large-geometry ion microprobe using a 20 kV, ca. 10 μm Cs^+ primary beam, a low-energy
219 electron-flooding gun to compensate for charge build-up and simultaneous detection in either two Faraday
220 detectors (for ^{16}O and ^{18}O) or a Faraday together with an ion-counting electron multiplier (for ^{12}C and ^{13}C
221 respectively). All analyses were performed in automated chain sequences that regularly interspersed analyses
222 of unknowns with those of standards. Because there is no universally accepted siderite standard we
223 developed our own through the Stable Isotope Facility (SIF) at the BGS using a VG Optima dual inlet mass
224 spectrometer and the Isotope Community Support Facility (ICSF) at SUERC using a VG SIRA II dual inlet
225 mass spectrometer). These two laboratories have slightly different analytical methods but agreed on the
226 preferred value for our principal standard, to which we compare our data. The siderite standard is from
227 Ivigtut cryolite deposits, Ivigtut, Greenland. It was reacted under vacuum with anhydrous phosphoric acid
228 at a constant 100°C for 96 hours (SIF) and at 70°C for one week (ICSF). The CO_2 liberated was
229 cryogenically separated from water vapour under vacuum and analysed using IRMS. The mineral-gas
230 fractionation factor used for siderite was 1.00881 (derived from Rosenbaum and Sheppard, 1986). The
231 oxygen and carbon isotope composition of the siderite ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) are reported as per mil (‰) deviations
232 of the isotope ratios ($^{18}\text{O}/^{16}\text{O}$ and $^{13}\text{C}/^{12}\text{C}$) calculated to the V-PDB scale. The SIF derived value for the
233 siderite standard was -21.97‰ (0.09 1SD) $\delta^{18}\text{O}$ and -8.08‰ (0.02 1SD) for $\delta^{13}\text{C}$. The ICSF derived value
234 for the siderite standard was -22.13‰ (0.23 1SD) $\delta^{18}\text{O}$ and -8.51‰ (0.17 1SD) for $\delta^{13}\text{C}$. Consequently,

235 average values of -22.04‰ (0.17 1SD) for $\delta^{18}\text{O}$ and -8.25‰ (0.24 1SD) for $\delta^{13}\text{C}$ were achieved when
236 compiling all standard measurements and were applied for correcting the SIMS data.

237

238

239 **Results, sedimentology and petrography**

240

241 **Occurrence of siderite in the sediments**

242

243 At the Norra Albert quarry siderite concretions are confined to the coarse-grained, poorly sorted, fluvial
244 sandstones of the Boserup beds and sporadic siderite cement in the uppermost part of the Bjuv Member (Fig.
245 3A), whereas their absence is notable in the underlying more clayey floodplain sediments of the Bjuv
246 Member. In general, the siderite concretions (ranging in size from 20 cm – 2 m) are developed preferentially
247 along the stratification (Fig. 4A, 4C and 4D). In some cases, the concretions appear to have initiated locally
248 in the most coarse-grained undulating intervals followed by continued siderite growth into the surrounding
249 finer-grained sand intervals, which cuts the sedimentary structures (Fig. 4E and 4F). In rare cases, petrified
250 wood occurs in the centre of siderite concretions (Fig. 4B). pure siderite occurs. The pure siderite can be
251 either detrital, very early siderite, or a late infilling in the centre of the concretion (cf. Bojanowski et al.
252 2016). Siderite may comprise a relatively large proportion of the concretions, suggesting that siderite
253 precipitation took place as displacive growth (Fig. 5).

254

255 The Albert-1 core (Fig. 3B) shows that authigenic siderite is absent in the Bjuv Member, though present in
256 the underlying Vallåkra Member. Core samples from the Fleninge No. 266 well (Fig. 3C) verify the presence
257 of perfectly zoned sphaerosiderite and other authigenic siderite morphologies in the lower part of the
258 Boserup beds; and confirm that authigenic siderite is absent in the Bjuv Member, though present at the
259 boundary to Vallåkra Member (Fig. 3C).

260

261 *Fig. 4: Siderite concretions at N Albert quarry*

262

263 *Fig. 5: Calculated mineral abundance*

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266 **Siderite micromorphology**

267 The siderite micromorphologies are divided into the following types that precipitated in successive order:

- 268 1. Zoned sphaerosiderite and spheroidal siderite, which is subdivided into: 1A perfectly zoned
269 sphaerosiderite: 1B poorly zoned sphaerosiderite (and spherulites); and 1C zoned spheroidal siderite.
- 270 2. Radial siderite overgrowths, which exhibit variable habits according to their substratum: from
271 mainly rhombohedral on the perfectly zoned sphaerosiderite (A) to preferentially fibrous, when
272 growing on the spheroidal siderite (B).
- 273 3. Microcrystalline, anhedral or subhedral, randomly orientated pervasive siderite cement that forms
274 concretionary cements. Rhombohedral single siderite crystals dispersed in the sandstones are
275 considered initial precipitations in ‘immature concretions’ (compare with Bojanowski et al. 2016).

276

277 **Zoned sphaerosiderite and spheroidal siderite**

278 Perfectly zoned sphaerosiderite and zoned spheroidal siderite are common in the siderite concretions in a
279 specific interval in the Boserup beds partly coincident with the interval of soft sediment deformation
280 structures (Fig. 3A). Poorly zoned sphaerosiderite generally occurs scattered, though is occasionally
281 abundant in concretions, immediately below this interval, i.e. in the uppermost part of the Bjuv Member (Fig.
282 3A and 3C). Scattered poorly zoned sphaerosiderites are common in concretions in the overlying Boserup
283 beds (Fig. 3A). Poorly zoned sphaerosiderite occurring in the basal part of the Bjuv Member (Fig. 3C) never
284 encloses detrital grains and are oversized compared with sphaerosiderite in the Bjuv and Helsingborg
285 members, though similar to those occurring in the Vallåkra Member analysed by Troedsson (1951) and

286 slightly resembling the cemented areas of the Vallåkra Member in the Albert-1 well (AL1-09.28 in Fig. 3B).
287 These oversized sphaerosiderite may not have been formed *in situ* within the Bjuv Member deposits, but
288 probably precipitated in older strata (e.g. Vallåkra Member) and were redeposited.

289

290 Poorly zoned sphaerosiderite has an inner core surrounded by a rim of rhombohedral or irregular crystals
291 (Fig. 6). Perfectly zoned sphaerosiderite has an inner core of radiating growth (which gives rise to a
292 characteristic extinction pattern) in few to several concentric zones (Fig. 7). The outermost rim of
293 rhombohedral crystals is partly coalescent with the cement filling the shrinkage fracture between the detrital
294 grains and sphaerosiderite. Sphaerosiderite commonly occurs in clusters (Figs 7E and 8B) forming a coccoid
295 morphology (compare Driese et al. 2010). Sphaerosiderite zonation is caused by variation in mineralogy and
296 chemistry. Rhodochrosite zones in sphaerosiderite seem to be more affected by dissolution than siderite (Fig.
297 8A). Rhodochrosite abundance of up to 25% of the cement of one concretion is documented by XRD. In
298 other concretions, ankerite dolomite and/or rhodochrosite are occasionally present in XRD detectable
299 amounts. Poorly zoned sphaerosiderite occur with dissolution voids next to poorly zoned sphaerosiderite
300 having a core of increased Ca, Mn and Si contents, suggesting that dissolution preferentially occurred in
301 other carbonate phases and low Fe siderite (Fig. 6B and 6D). Zonation enhanced by weathering in other
302 sphaerosiderites (Fig. 7C) may also originate from other carbonate minerals or incorporation of varying
303 amounts of Ca, Mn (Mg?) and Zn in the siderite structure (Fig. 8A and 8C). Zonation patterns are uniform
304 within concretions, though vary between different concretions (Figs 7D and 8A).

305

306 Zoned spheroidal siderite has an inner core of radiating crystals similar to the perfectly zoned
307 sphaerosiderite, and only few but regular spheroidal zones (Fig. 9). The spheroidal siderite has a more
308 uniform size (30 – 80 µm) than the size of the perfectly zoned sphaerosiderite (20 – 350 µm) and the usual
309 size of poorly zoned sphaerosiderite (3 – 170 µm) (Fig. 3).

310

311

312

313 **Overgrowths on siderite morphologies**

314 Perfectly zoned sphaerosiderite is typically surrounded by a rim of rhombohedral siderite crystals (Fig.
315 7). The outermost rim of rhombohedral crystals is partly coalescent with fracture-healing cement between the
316 detrital grains and perfectly zoned sphaerosiderite (Fig. 7A, 7B and 7D). The overgrowths on the zoned
317 spheroidal siderite preferentially consist of radiating crystals (Fig. 9A).

318

319 **Concretionary siderite cement**

320 Sparry, microspar or micritic siderite cement encloses perfectly and poorly zoned sphaerosiderite and
321 spheroidal siderite to form concretions. Dispersed rhombohedral siderite and poorly zoned sphaerosiderite
322 characterise the weakly-cemented sandstones in the lower part of the exposed Boserup beds at Norra Albert,
323 whereas the upper exposed part of the Boserup beds have concretions with poorly zoned sphaerosiderite
324 (Fig. 3A). The dispersed siderite occurs preferentially in the most coarse-grained intervals.

325

326

327

328 **Siderite in relation to other minerals**

329 Siderite is typically non-corrosive against detrital grains, which support a displacive growth of the siderite
330 cement. However, siderite crystals and spheres grow along cleavage planes in mica and feldspar and more
331 rarely in secondary porosity after feldspar and altered Fe-Ti oxides. Few authigenic phases predate siderite.
332 Rare pyrite, enclosing micro-spheres of siderite, is enclosed in the centre of sphaerosiderite so pyrite mainly
333 predates siderite. Kaolinite (crystal sizes: 2 – 4 µm) occur enclosed in rhombohedral siderite and partly
334 dissolved feldspar, and are enclosed in sparry siderite cement. Other authigenic phases, such as kaolinite
335 (crystal size: 5 – 10 µm), anatase and possibly quartz, occur in the central dissolution voids after poorly
336 zoned sphaerosiderite (Fig. 6C) and consequently postdate siderite. The authigenic origin of quartz is
337 suggested from its euhedral shape and from the ubiquitous initial quartz overgrowths on detrital quartz, in
338 general.

339

340 Alteration products, such as manganese oxides/hydroxides and iron-oxides/hydroxides, are common in most
341 sandstones. Iron-oxide/hydroxides (hematite in one sample) occur in altered zones of sphaerosiderite and
342 spheroidal siderite and as alteration rims around rhombohedral siderite. Manganese oxides/hydroxides occur
343 as authigenic rims around detrital and authigenic phases, though without any specific petrographic
344 relationship to the chemistry of the carbonate phases.

345

346 *Fig. 6: Poorly zoned sphaerosiderites (spherulites, spherulitic siderite)*

347

348 *Fig. 7: Perfectly zoned sphaerosiderites*

349

350 *Fig. 8: Varieties of zoned sphaerosiderites*

351

352 *Fig. 9: Spheroidal siderite (pseudomorphs after organic matter?)*

353

354 **Chemical composition**

355 Low CaMg siderites (Fig. 8) dominate all siderite morphologies with typically < 5 % CaCO₃ and < 3 %
356 MgCO₃. Maximum 11 % MgCO₃ (sample 516816), 10 % CaCO₃ (sample 516814) and up to 0.9 % ZnCO₃
357 occur in some samples. MnCO₃ is more common with up to 10 %. Poorly zoned sphaerosiderite has a
358 tendency of slightly higher content of CaCO₃, up to 10 %, than other siderite micromorphologies. Zoned
359 spheroidal siderite, perfectly zoned sphaerosiderite and their overgrowths have the highest content of
360 MnCO₃, up to 35 % (Fig. 8).

361

362 *Fig. 10: Chemical composition*

363

364 **Isotope composition**

365 The $\delta^{18}\text{O}$ of siderite is mostly unrelated to the siderite morphology, because concretions and weakly
366 cemented sandstones containing perfectly zoned and poorly zoned sphaerosiderite, spheroidal and
367 rhombohedral siderites appear with similar oxygen isotopic compositions (SIMS: -4.7 to -5.1‰ $\delta^{18}\text{O}$ and
368 IRMS: -4.8 to -5.3‰ $\delta^{18}\text{O}$) (Table 1; Fig. 11). Sphaerosiderite with rhodochrosite zones group together with
369 other perfectly zoned sphaerosiderites (Fig. 11A). Samples containing small rhombohedral siderites, which
370 are more prone to alteration, have relatively lower $\delta^{18}\text{O}$ values (down to -7.5‰). One intensively altered
371 sample with even lower values has been left out, as the high amounts of iron-oxide/hydroxides affected the
372 oxygen isotopic composition.

373

374 The SIMS measurements show clearly more positive $\delta^{13}\text{C}$ values for the concretionary cement (-5.5 to
375 $+7.8\text{‰}$) than for the siderite micromorphologies, such as perfectly zoned sphaerosiderite (-17.3 to -2.4‰),
376 spheroidal siderite (-101.1 to -5.1‰) and their overgrowths (-13.0 to $+3.0\text{‰}$) (Fig. 11B). The somewhat
377 wider span in $\delta^{13}\text{C}$ values (-17.3 to $+7.8\text{‰}$) for the *in situ* SIMS measurements compared to bulk rock IRMS
378 measurements (-11.6 to $+6.0\text{‰}$ $\delta^{13}\text{C}$) is a result of different mixtures of sphaerosiderite and spheroids and
379 concretionary cement in the bulk rock samples.

380

381 *Fig. 11: Isotopic composition*

382

383 *Table 1. Isotopic composition*

384

385

386

387

388

389 **Discussion**

390

391 **Microstructural growth pattern**

392

393 A wide spectrum of siderite morphologies is represented in the Norra Albert quarry. It is remarkable to find
394 perfectly concentrically-zoned sphaerosiderite, spheroidal siderite, rhombohedral siderite and poorly-zoned
395 sphaerosiderite occurring together. Poorly zoned sphaerosiderite could be the precursor to perfectly zoned
396 sphaerosiderite, which forms only under specific conditions.

397

398 Poorly-zoned sphaerosiderite and spherulites with central dissolution voids cannot, strictly speaking, be
399 distinguished. Internal dissolution voids in rhombohedral siderite and spherulites may origin from siderite
400 growths around a core of different chemistry or carbonate mineralogy, an episode of crystal poisoning
401 (Wilkinson et al. 2000) or it may be explained by areas ('eyes') of less stability within the spherulites
402 originating from its primary growth pattern (Gránásy et al. 2005). In the latter case no chemical or
403 mineralogical zonation is necessary in order to explain the central instability.

404

405 Radiating growth patterns are characteristic of the centre of perfectly zoned sphaerosiderite and spheroidal
406 siderite (Figs 7 and 9), but are more difficult to discern within the spherulites and poorly zoned
407 sphaerosiderites. The growth begins from a nucleus that seems very small in the sphaerosiderite. The
408 constrained spheroidal shape suggests some kind of growth control, possibly of organic origin, for example
409 within spheroidal pollen grains or within stomata of leaf cuticles (compare stomata of leaf of *ginkgoites* or
410 *anomozamites* known from a Rhaetian flora in Scania reported by Pott and McLoughlin (2011)). Siderite
411 precipitation may have started along the inside of the pollen wall as the spore-cell material decayed, or along
412 the guard cells of the open pores of the stomata, with subsequent continued growth inwards towards the
413 centre of the pollen grain/ stomata. As the organic matter degraded, growth of siderite radiating outwards
414 from the original location of the guard cells followed. Other types of organic matter may have acted as

415 nucleation sites for the sphaerosiderite growth. The growth pattern changes from radial to rhombohedral, as
416 spherulites were enclosed in sparry or rhombohedral siderite, and as rhombohedral crystals rimmed the
417 perfectly zoned sphaerosiderite (Fig. 7C and 7D). This change in growth pattern could reflect biogenically
418 facilitated, radially- and concentrically-zoned siderite, succeeded by a relatively slower precipitation of
419 siderite, beginning with rhombohedral crystals and ending with sparry and/or microsparry cement. A
420 diagenetically-induced change of spherulitic to rhombohedral siderite morphology is advocated by Köhler et
421 al. (2013), but it seems less likely that only the outermost part of the sphaerosiderite and spherulites should
422 be diagenetically altered prior to enclosure in sparry or microsparry siderite cement. In this case, a more
423 reasonable explanation would be continued growth under changed conditions and hence with different
424 precipitation rates, from bacterially-mediated Fe^{3+} reduction to microbial fermentation of organic matter in
425 the methanogenic zone (e.g. Hicks et al. 1996; Ludvigson et al. 1998; Krajewski et al. 2010).

426

427 The perfect zonation of sphaerosiderite is so pronounced and systematic (Fig. 7D) that it cannot merely have
428 formed from alteration processes. Rather, the alteration processes have enhanced the visibility of the detailed
429 zonation (Fig. 8A) with *in situ* alteration products of iron-oxide/hydroxide and dissolution voids after less
430 stable phases such as Ca or Mn-rich siderite and rhodochrosite. Dissolution voids begin within the pure
431 rhodochrosite zones rather than in the siderite, so rhodochrosite zones dissolve faster than siderite (Fig. 9A).
432 Rhodochrosite forms under suboxic conditions whereas siderite precipitates under anoxic conditions
433 (Bojanowski et al. 2016), hence rhodochrosite is likely to be more stable under oxidizing conditions.
434 However, dissolution products of rhodochrosite are removed faster from points of dissolution since Mn^{2+} is
435 slightly more soluble than Fe^{2+} (Sholkovitz and Copland 1981). The central part of the spherulites and
436 poorly zoned sphaerosiderites is commonly dissolved; but when present the central part generally has higher
437 contents of Mn, Ca, and occasionally Si. It is therefore probable that the dissolution zones/centres are located
438 where the siderite has incorporated relatively high amounts of Mn and Ca. This would explain the common
439 occurrence of *ex situ* manganese-oxides/hydroxides as alteration rims covering both detrital grains and
440 authigenic phases, though without any petrographic association with siderite or rhodochrosite.

441 **Bacterial mediated perfect zonation?**

442

443 The growth of sphaerosiderite started on organic or detrital grains and continued in spherical zones around
444 the nuclei as the bacterial colony continued its reduction of Fe and Mn, which reacted with HCO_3^- , liberated
445 from the degradation of organic matter and precipitated as siderite (and rhodochrosite). Spheroidal siderite
446 started as impregnation of voids in organic tissue, for example pollen or stomata, and continued with zonal
447 growth of siderite crystals on the pollen wall or the guard cells and gradually filled the void (Fig. 12). This
448 could explain the uniform size of spheroidal siderite (Fig. 4A). After degradation of the surrounding organic
449 matter, the siderite growth continued outwards with larger radiating crystals, possibly reflecting more slowly
450 sourced iron.

451

452 Most investigations of sphaerosiderite record large variations in $\delta^{13}\text{C}$ (Table 1; e.g. Ludvigson et al. 1998;
453 Driese et al. 2010; Robinson et al. 2010; Suarez et al. 2010). The range in $\delta^{13}\text{C}$ values of sphaerosiderite and
454 spheroidal siderite, in general, and in this investigation, is large (-17.3 to -2.4% for sphaerosiderite and $-$
455 10.1 to -5.1% for spheroidal siderite) (Table 1; Fig. 11). This may reflect either a variety in the microbes
456 (bacteria and fermenters), which produced $\text{CO}_2 / \text{HCO}_3^-$ for siderite precipitation, or it could represent a
457 mixture of two different end-members of bicarbonate. Bicarbonate from the decomposition of organic matter
458 in the suboxic zone represents the low $\delta^{13}\text{C}$ values of sphaerosiderite and spheroidal s, whereas bicarbonate
459 originating from methanogenic fermentation of organic matter is responsible for the relatively high $\delta^{13}\text{C}$
460 values of the concretionary cement (Fig. 11; e.g. Irwin et al. 1977; Mozley and Wersin 1992; Ludvigson et
461 al. 1998; Krajewski et al. 2010). The shift in $\delta^{13}\text{C}$ values (Fig. 11) is accompanied by a change in crystal
462 morphology from radiating growth in sphaerosiderite to rhombohedral overgrowths and cement (Figs 7),
463 which also may be explained by a shift from bacterially-mediated growth in the iron reduction zone to
464 precipitation in the methanogenic zone.

465

466 The zonation within the perfectly zoned sphaerosiderites is caused by variation in carbonate mineralogy and
467 chemistry, and reflects availability of Fe, Mn, Ca and Mg in the neighboring/local environment. The rate of
468 iron reduction, and hence the availability of Fe^{2+} , is the limiting factor on precipitation of microbial siderite
469 (Mortimer et al. 1997). In addition to Fe, Mn, Mg, Zn and Ca abundance in the fluids, variation in nutritional
470 stress and physical conditions, for example temperature, also influence the iron reduction rate and hence the
471 incorporation of other elements, like Mn (Mortimer et al. 1997). Coccoid morphology/clusters of
472 sphaerosiderite and areas of sphaerosiderite with identical zonation pattern (Figs 7E and 8A) probably mark
473 the outline of microbial communities. The zonation pattern within one microbial community may represent
474 minor episodes of drying-out or harsh/hostile conditions for the microbes. During such dry periods,
475 shrinkage, partial dissolution and alteration of the protruding outgrowths may ensure its spherical/rounded
476 shape (Fig. 12).

477 478 479 **Microscale variations reflecting groundwater fluctuations**

480
481 Causes of zonation can be divided into two general explanations/hypotheses: 1) mixing of meteoric and
482 marine waters (Mozley 1989; Choi et al. 2003) and 2) modification of the original pore waters during
483 successive stages of microbial decomposition of organic matter (Mozley and Carothers 1992; Lim et al.
484 2004). The latter is almost identical to the explanation by Wilkinson et al. (2000) that siderite precipitation
485 takes place during gradual burial within the Fe and Mn reduction zones, while dissolution takes place in the
486 sulphate reduction zone, and siderite growth in the methanogenic zone.

487 The siderite morphologies found in the Boserup beds at Norra Albert provide two important contributions to
488 this dispute on the origin of zonation due to their microscale and macroscale variations in morphology and
489 stable isotope geochemistry. The observed microscale variations in siderite zonation pattern in the
490 sphaerosiderites (Figs 7A, 7E, 8A, 8C) cannot be explained by either of the hypotheses described previously.
491 Though marine excursions may have occurred in the Boserup beds during storm episodes, similar to the

492 marine occurrences in the Bjuv Member at other localities in Scania (Lindström and Erlström 2006), marine
493 influxes in a meteoric-dominated environment ought to have affected all sphaerosiderites. The chemical
494 composition is typically low in Mg and Ca for all siderite micromorphologies (Fig. 10), which suggests
495 meteoric water composition (Matsumoto and Iijima 1981; Mozley 1989; Browne and Kingston 1993). Pyrite
496 occurs rarely, and when present as a very early phase enclosed in the centre of the sphaerosiderite. This
497 indicates that sulphate was limited from the time of deposition and that iron reduction took over instead of
498 sulphate reduction. Furthermore, the $\delta^{18}\text{O}$ values in all siderite morphologies from Norra Albert are very
499 consistent, close to the meteoric water composition, and show no influence from marine water (Fig. 11).

500

501 If the zonation pattern reflects depth-controlled burial processes (as suggested by Mozley and Carothers
502 1992; Wilkinson et al. 2000), then repeated small tectonic movements or variations in sedimentation
503 rate/erosion would be required to explain the numerous changes through the Fe-reduction, Mn-reduction,
504 sulphate reduction and methanogenic zones. These possibilities seem unlikely as the fluvial style of the
505 Boserup beds does not change over this interval. Groundwater fluctuations seem a more likely explanation
506 and are supported by additional features besides the perfectly zoned sphaerosiderite. Siderite cementation in
507 shrinkage-fractures between detrital grains and sphaerosiderite could either be a result of mechanical
508 compaction or caused by a period of shrinkage occurring during drying-out, either due to subaerial exposure
509 or to lowering of the water table before siderite was again precipitated in the shrinkage fractures (Figs 7A,
510 12). The possibility that it could have been caused by mechanical compaction seems less likely, since
511 fractured sphaerosiderites only occur in one concretion. Fluctuations in groundwater table would result in
512 multiple changes in the physiochemical condition and the microbial life conditions. A longer growth period
513 could explain the numerous zones and the necessity of using other metals, e.g. Mn and Zn, as the Fe source
514 for the bacterial metabolism was exhausted. The presence of hematite suggests that siderite precipitation
515 was followed by its alteration to iron-oxide/hydroxides in the unsaturated zone prior to burial diagenesis, as
516 hematite replaced iron-oxide/hydroxides (not siderite) either due to aging (Van Houten 1961), which is less
517 likely in Triassic – Jurassic sediments, or at enhanced temperatures ($> 56^\circ\text{C}$) (Weibel 1999). The Triassic–
518 Jurassic-boundary strata in Scania have been subjected to moderate burial temperatures $< 85^\circ\text{C}$ (inferred

519 from vitrinite reflectance by Ahlberg 1994) and $> 65^{\circ}\text{C}$ (due to restricted quartz diagenesis, in comparison
520 with Weibel et al. 2010). Hence, fluctuations in groundwater level during deposition of the Boserup beds is
521 the most plausible explanation for both sphaerosiderites with numerous zones of slightly varying
522 composition, formation of hematite, and healing shrinkage cracks.

523

524 As elsewhere in NW Europe, the Danish part of the Norwegian–Danish Basin was subjected to major sea-
525 level changes at this time, the “regression–transgression couplet” that may have been linked to tectonic
526 movements during the formation of the Central Atlantic Magmatic Province (Hallam 1997; Hallam and
527 Wignall 1999). The underlying Bjuv member is interpreted to have been deposited during a transgression
528 and as part of a highstand systems tract (Petersen et al. 2013), with the maximum flooding surface MFS7 of
529 Nielsen (2003) situated between coal seams B and A, whereas the Boserup beds, in contrast, were formed
530 during a lowstand systems tract. However, these sea-level changes would not necessarily have caused
531 repeated fluctuations in groundwater level during the deposition of the Boserup beds. The high proportion of
532 structure less sandstones in the Boserup beds suggests rapid deposition, possibly from flash floods, rather
533 than through bedform migration, and associated liquefaction/fluidization processes. A more extreme climate
534 with increased humidity and storminess in the late Rhaetian (Petersen and Lindström 2012), strong
535 seasonality with episodic storms of heavy rain, alternating with periods of enhanced drought, could be
536 responsible for a fluctuating groundwater table. The co-occurrence of humid habitats and floral elements
537 with xeromorphic features, i.e. features that may be linked to physiological drought, in the Rhaetian flora in
538 Scania (Pott and McLoughlin 2011) may possibly also be ascribed to groundwater fluctuations or seasonal
539 drought. There is also the possibility that the fluctuations in ground-water table were linked to increased
540 repeated seismicity during this time (Lindström et al. 2015), because changes in groundwater levels are a
541 common effect during earthquakes (Wang and Manga 2010). The perfectly zoned sphaerosiderites occur in
542 the upper part of soft-sediment deformation structures – “seismites”– identified at both Norra Albert and in
543 the Fleninge No. 266 core (Figs. 3A and C). Soft- sediment deformation structures form in unconsolidated,
544 water-saturated sediments (e.g. Topal and Özkul 2014), and hence are likely to have formed close to the
545 groundwater table. Fracturing and displacement of sphaerosiderite, followed by fracture healing (Fig. 7D),

546 show that local deformation occurred shortly after early diagenesis and could be related to mechanical
547 compaction or soft-sediment deformation structures triggered by seismic events (Lindström et al. 2015).

548

549

550 **Conclusions**

551

552 The late Rhaetian terrestrial succession in northwestern Scania exhibits a variety of siderite
553 micromorphologies, comprising perfectly zoned sphaerosiderite, poorly zoned sphaerosiderite (possibly
554 identical with spherulitic siderite), spheroidal siderite and their rhombohedral and fibrous siderite
555 overgrowths, enclosed in sparry, microspar and micritic concretionary siderite cement. The siderite formed
556 in an apparently similar early diagenetic/pedogenic environment, as indicated by similar trace element
557 variations and meteoric water oxygen isotopic compositions. The characteristic broad range in carbon
558 isotopic compositions indicates that different microbes in the pedogenic environment were involved in
559 degradation of organic matter and supplied C for siderite formation. Here the carbon isotopic composition
560 can be subdivided into sphaerosiderite and spheroidal siderite of low values (-17.3 to -2.4‰ $\delta^{13}\text{C}$) and their
561 rhombohedral or fibrous siderite overgrowths of almost similar values (-13.0 to $+3.1\text{‰}$ $\delta^{13}\text{C}$) sourced from
562 bacterial degradation of organic matter in the Fe-reduction zone. This was followed by concretionary siderite
563 cement of higher isotopic values (-5.8 to $+7.8\text{‰}$ $\delta^{13}\text{C}$) promoted by fermentation activity in the
564 methanogenic zone. Growths of spheroidal siderite may have initiated on organic compounds, for example
565 palynomorphs or stomata; likewise sphaerosiderite growth probably started on other, but specific, types of
566 organic matter, which served as a microbial energy source and controlled the initial crystal growth.

567

568 Perfectly-zoned sphaerosiderite is restricted to the Boserup beds. The perfect multi-layered zonation is
569 related to heterogeneous alteration caused by mineralogical and geochemical variations. The zonation
570 reflects microbial activity, their life conditions, and availability of Fe, Mn, Ca and other cations in the pore
571 water. These conditions are linked to amount of precipitation, water flow and groundwater-level fluctuations.

572 Intervals of continuous water-saturation and flow through the sediments resulted in Fe-rich siderite
573 precipitation in the Fe-reduction zone. Under unsaturated or poorly saturated conditions, for example during
574 episodes of lowered water table, rhodochrosite and Mn-rich siderite formed when the microbial community
575 experienced hostile life conditions and/or the Fe supply was exhausted. The change from the saturated to
576 unsaturated zone caused partial dissolution of poorly and perfectly zoned sphaerosiderite, which explains
577 their continued spherical zonation and rounded shape. The inferred changes in groundwater level suggest
578 deposition under a strongly seasonal climate with episodic drought. During burial the siderite precipitation
579 style changed from bacterially mediated spherical and radiating growth in the Fe-reduction zone to
580 rhombohedral precipitation in the methanogenic zone and still characterized by meteoric water of -5.1‰
581 $\delta^{18}\text{O}$ at a c. 45°N latitudinal position of Scania.

582

583

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585

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593

594

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- 769

770 Figure captions

771

772 **Table 1.**

773 Sphaerosiderite occurrences, their geological background, morphology and geochemistry.

774

775 **Fig. 1.**

776 Stratigraphy of southern Sweden, which is compared with changes in sphaerosiderite occurrence (Troedsson
777 1951 and this study), dominating clay mineralogy (Ahlberg et al. 2003), occurrence of coal and remnants
778 after wildfire activity (Troedsson 1951; Petersen and Lindström 2012) and palynozones (Lund 1977 and this
779 study). Transgressive events are indicated (arrows), including MFS7, which is an important surface for
780 correlation in the region (Nielsen 2003).

781

782 **Fig. 2.**

783 Map showing location of the Norra Albert quarry and the wells Albert-1 and Fleninge No. 266. Note that the
784 position of the Norra Albert quarry and the Albert-1 well are identical.

785

786 **Fig. 3.**

787 Sedimentary logs showing typical siderite morphologies for the investigated samples.

788 A. Sedimentary log of the northern wall in the Norra Albert quarry.

789 B. Sedimentary log of the Albert-1 core.

790 C. Constructed sedimentary log of the Fleninge No. 266 well based on the description by Troedsson
791 (1951).

792 Dimensions given in the diagrams are those of sphaerosiderite, spheroidal and rhombohedral siderite, not the
793 dimensions of the concretions.

794

795

796 **Fig. 4. Fieldwork Norra Albert quarry.**

- 797 A. Overview of the northern wall in Norra Albert quarry. The ‘Boserup beds’ are the whitish grey
798 deposits with local siderite concretions; the dark grey deposits of the Bjuv Member are partly
799 covered by scree. The line marks the boundary between the ‘Boserup beds’ and the Bjuv Member.
800 Arrows indicate some of the largest concretions.
- 801 B. Petrified wood enclosed in a siderite concretion.
- 802 C. Undulating siderite concretion following the sedimentary structures.
- 803 D. Close up of A.
- 804 E. Thick siderite concretion with a middle plane following the sedimentary structures, similar to the
805 concretionary development in C, and surrounded by growth that cuts the sedimentary structures.
806 The growth probably started along the most coarse-grained sands and continued both upwards and
807 downwards into the more fine-grained sandstones.
- 808 F. Close up of white box in E. The sedimentary structures seem to end at the concretionary interface,
809 but thin section investigations have shown that sedimentary structures actually continue through the
810 cemented area.

811

812 **Fig. 5.** An early displacive growth of siderite is documented by the high siderite content in concretions
813 compared with sandstones in the Norra Albert quarry. The mineral content is calculated from chemical
814 composition of bulk rock samples.

815

816 **Fig. 6. Poorly zoned sphaerosiderites (spherulites, spherulitic siderite)**

- 817 A. Poorly zoned sphaerosiderite (Si) with a low content of Ca and/or Mn commonly having central
818 dissolution voids (marked by black arrows). Norra Albert quarry, 516816. Back –scatter electron
819 (BSE) image.
- 820 B. Poorly zoned sphaerosiderite (Si) with incipient dissolution in the centre and rims of dissolution void
821 around the central spherical part. The most intensive dissolution accompanies the centre having a
822 small Ca content (compare EDS analyses 1 and 2). Norra Albert quarry, 516807. BSE image.

- 823 C. Poorly zoned sphaerosiderite (Si) with central dissolution void containing possible authigenic quartz
824 (Q) and un-compacted kaolinite (Ka) and surrounded by compacted kaolinite. Fleninge No. 266,
825 151.62 m. BSE image.
- 826 D. Poorly zoned sphaerosiderite (Si) (EDS analysis 3) with a centre possibly made up of iron-
827 oxide/hydroxide (Fe-ox) having a low content of Mn (EDS analysis 4). Norra Albert quarry, 516824.
828 BSE image.

829

830 **Fig. 7. Perfectly zoned sphaerosiderites**

- 831 A. Zoned sphaerosiderites replaced by iron-oxides/hydroxides (Fe). Note that the sphaerosiderite at
832 some point has lost contact to their growth substratum, however this has healed later. Norra Albert
833 quarry, 516818. Reflected light image.
- 834 B. Broken perfectly zoned sphaerosiderite with healing rhombohedral siderite that appears the same as
835 the overgrowth on the sphaerosiderite. Later exposure to oxidising water has resulted in replacement
836 by iron-oxides/hydroxides (Fe). Norra Albert quarry, 516818. BSE image.
- 837 C. Microcrystalline anhedral siderite (Si) tightly fills the pore space between the sphaerosiderite and
838 detrital grains. The detrital grains (Q) are dispersed and do not exhibit intergranular contacts, which
839 indicate displacive and/or replacive growth of siderite. Alteration and replacement by iron-
840 oxides/hydroxides (Fe) is probably related to oxidation of siderite along fracture wall probably due
841 to percolation of oxygenated fluids. Norra Albert quarry, 516824D. BSE image.
- 842 D. Zoned sphaerosiderites replaced by iron-oxides/hydroxides (Fe). Altering zones seem to be almost
843 similar for a specific area/concretion. The apparent variation in zonation pattern may be caused by
844 different intersection planes. Norra Albert quarry, 516818. BSE image.
- 845 E. Fine-crystalline morphology of the inner part of the sphaerosiderite, which is ripped out, and coarser
846 crystals as an outer rim. Norra Albert quarry, 516818. Secondary electron (SE) image.
- 847 F. Rhombohedral habit of siderite crystals forming an overgrowth on the sphaerosiderite. Norra Albert
848 quarry, 516818. SE image.

849

850 **Fig. 8. Varieties of zoned sphaerosiderites**

- 851 A. Sphaerosiderite with relatively high content of Mn in the inner core (EDS analysis 1), followed by a
852 rhodochrosite rim (EDS analysis 2) with dissolution voids (white arrows) and an outermost rim of
853 low-Mn siderite . Norra Albert quarry, 516819. BSE image.
- 854 B. Cluster of rhodochrosite rimed sphaerosiderite enclosed in sparry siderite cement. Norra Albert
855 quarry, 516819. SE image.
- 856 C. Concentric and sector zoned sphaerosiderite having a low content of Ca (EDS analysis 3), whereas
857 the alteration rims show siderite with low contents of Si and possible Zn (EDS analysis 4). Norra
858 Albert quarry, 516820. BSE image.
- 859 D. Round siderite core covered by rhombohedral siderite, which is partly dissolved and altered to iron-
860 oxides/hydroxides. Norra Albert quarry, 516825. SE image.

861

862 **Fig. 9. Spheroidal siderite (pseudomorphs after stomata)**

- 863 A. Spheroidal siderite with radiating growth around a spheroidal core and in zones. Norra Albert
864 quarry, 516824C. Transmitted light image, crossed nicols.
- 865 B. Spheroidal siderite with marked spheroidal zones. Norra Albert quarry, 516824C. Reflected light
866 image.
- 867 C. Spheroidal siderite with radiating growth in spheroidal zones. Acid treated sample, Norra Albert
868 quarry, 516824C. SE image.

869

870 **Fig. 10 Chemical composition**

871 Microprobe analyses show that siderite generally has a low content of Mg and Ca, though commonly
872 relatively high content of Mn. The highest Mn contents typically occur in spheroidal siderite, perfectly zoned
873 sphaerosiderite and their overgrowths, whereas the highest Ca contents occur in poorly zoned
874 sphaerosiderite.

875

876

877 **Fig. 11. Isotopic composition**

878 A. IRMS (isotope ratio mass spectrometry) shows a narrow $\delta^{18}\text{O}$ composition and a large span in $\delta^{13}\text{C}$
879 values for bulk rock samples. Also perfectly zoned sphaerosiderite with zones of rhodochrochite
880 groups together with other siderite samples.

881 B. SIMS (secondary ion mass spectrometry) of specific siderite morphologies in thin sections shows
882 that perfectly zoned sphaerosiderite, spheroidal siderite and their siderite overgrowths have similar
883 and lower $\delta^{13}\text{C}$ values than the siderite concretionary cement.

884 SIMS and IRMS analyses show similar $\delta^{18}\text{O}$ values for all siderite micromorphologies and the
885 concretionary cement, which reflect end-Triassic groundwater composition. This fits with the likely
886 meteoric water composition (indicated by the vertical blue lines) according to the Triassic – Jurassic
887 middle latitude position at 45°N of Sweden (Anderson and Arthur 1983; Metcalfe 2011; Blakey 2016).

888

889 **Fig. 12. Overview of siderite precipitation**

890 Diagram showing an overview of the precipitation and growth of the different siderite morphologies in
891 relation to other diagenetic features.

892

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895