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3 1 **Palaeoenvironmental and diagenetic reconstruction of a closed-lacustrine carbonate**
4 2 **system – the challenging marginal setting of the Miocene Ries Crater Lake (Germany)**
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15 11 **Associate Editor – Nathan Sheldon**

16 12 **Short Title – Lacustrine primary and diagenetic geochemical signatures**
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18 14 **ABSTRACT**
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20 16 Chemostratigraphic studies on lacustrine sedimentary sequences provide essential insights on past
21 17 cyclic climatic events, on their repetition and prediction through time. Diagenetic overprint of primary
22 18 features often hinders the use of such studies for palaeoenvironmental reconstruction. Here the
23 19 potential of integrated geochemical and petrographic methods is evaluated to record freshwater to
24 20 saline oscillations within the ancient marginal lacustrine carbonates of the Miocene Ries Crater Lake
25 21 (Germany). This area is critical as it represents the transition from shoreline to proximal domains of a
26 22 hydrologically-closed system, affected by recurrent emergent events, representing the boundaries of
27 23 successive sedimentary cycles. Chemostratigraphy targets shifts related to subaerial exposure and/or
28 24 climatic fluctuations. Methods combine facies changes with $\delta^{13}\text{C}$ – $\delta^{18}\text{O}$ chemostratigraphy from matrix
29 25 carbonates across five closely-spaced, temporally equivalent stratigraphic sections. Isotope
30 26 composition of ostracod shells, gastropods and cements is provided for comparison.
31 27 Cathodoluminescence and back-scatter electron microscopy were performed to discriminate primary
32 28 (syn-)depositional, from secondary diagenetic features. Meteoric diagenesis is expressed by substantial
33 29 early dissolution and dark-blue luminescent sparry cements carrying negative $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$.
34 30 Sedimentary cycles are not correlated by isotope chemostratigraphy. Both matrix $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ range
35 31 from *ca.* -7.5 to +4.0‰ and show clear positive covariance ($R = 0.97$) whose nature differs from that
36 32 of previous basin-oriented studies on the lake: negative values are here unconnected to original
37 33 freshwater lacustrine conditions but reflect extensive meteoric diagenesis, while positive values likely
38 34 represent primary saline lake water chemistry. Noisy geochemical curves relate to heterogeneities in
39 35 (primary) porosity, resulting in selective carbonate diagenesis. This study exemplifies that ancient
40 36 lacustrine carbonates, despite extensive meteoric weathering, are capable to retain key information for
41 37 both palaeoenvironmental reconstruction and the understanding of diagenetic processes in relation
42 38 with those primary conditions. Also, it emphasizes the limitation of chemostratigraphy in fossil
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3 39 carbonates, and specifically in settings that are sensitive for the preservation of primary environmental
4 40 signals, such as lake margins prone to meteoric diagenesis.
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9 42 Keywords: $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ chemostratigraphy, lacustrine carbonates, meteoric diagenesis, Miocene,
10 43 ostracod shells, palaeoenvironmental reconstruction, sedimentary cycles, subaerial exposure
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15 45 INTRODUCTION

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18 47 Carbon and oxygen isotopes are inevitable tools for palaeoenvironmental reconstruction and the study
19 48 of diagenesis in carbonate rocks (e.g. Dickson & Coleman, 1980; Marshall, 1992; Immenhauser et al.,
20 49 2003; Brand, 2004; Andrews, 2006; Swart, 2015; Godet et al., 2016). Hence $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ analyses
21 50 are commonly performed on non-altered modern carbonates for environmental or climatic purposes
22 51 (e.g. Anderson et al., 1997; Marshall et al., 2007), and on ancient rocks to assess the nature, extent and
23 52 timing of diagenetic processes (e.g. Mutti & Bernoulli, 2003; van der Kooij et al., 2010; Christ et al.,
24 53 2012a, b). The geochemical signature associated with the pedogenic alteration of ancient marine
25 54 carbonates is generally identified based on marine isotopic signatures of modern analogues (Allan and
26 55 Matthews, 1977, 1982; Beier, 1987, Budd & Land, 1990; Joachimski, 1994; Immenhauser et al.,
27 56 2002).
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33 57 In lacustrine deposits, the interpretation of isotopic signatures is not straightforward due to the
34 58 variable nature of material (i.e. detrital, inorganic, biotically-controlled, or biotically-induced). Owing
35 59 to their smaller size in comparison to marine bodies and especially in the case of hydrological closure,
36 60 lacustrine systems are very sensitive to environmental changes. This sensitivity is reflected in high
37 61 variability of carbon and particularly oxygen isotope composition of the lake water and, consequently,
38 62 precipitated carbonates (Talbot, 1990; Leng & Marshall, 2004). Geochemical signals in lacustrine
39 63 carbonates depend, amongst others, on seasonality, climatic and hydrological context, and the origin
40 64 and mineralogy of carbonates forming (Leng & Marshall, 2004; Gierlowski-Kordesch, 2010). In case
41 65 of ancient lacustrine carbonates carbon and oxygen isotopes are used for palaeoenvironmental
42 66 reconstruction mostly from deep-water, basinal homogeneous deposits, and not from marginal lake
43 67 carbonates, experiencing repetitive episodes of subaerial exposure, diagenetic alteration, and
44 68 characterized by an incomplete record. These recurring meteoric events alter lacustrine carbonates and
45 69 affect their isotopic composition, challenging geochemical interpretation and the extraction of primary
46 70 environmental signals. Unlike marine settings where pedogenic isotopic signatures are well
47 71 constrained, meteoric diagenesis in continental settings regarding $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ patterns is less
48 72 understood, partly due to the aforementioned multiple origin of the carbonates. Thus $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$
49 73 values are, similarly to marine systems, expected to decrease (be negative) beneath exposure surfaces
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3 74 (diagenetic signal), but negative $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values often point to a freshening of saline lake water
4 75 without necessarily exposure (primary depositional signal) (Talbot, 1990).

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6 76 Previous work focusing on the Ries Crater Lake (Southern Germany; Fig. 1) included
7 77 investigations of the geochemical composition of carbonates. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ analyses, applied on
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9 78 more basinal deposits, revealed a closed-lake system and a long-term evolution in the lake water
10 79 chemistry (freshwater *versus* saline conditions) throughout its infilling (Rothe & Hoefs, 1977; Talbot,
11 80 1990; Arp et al., 2013).

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13 81 The present paper presents and discusses the outcomes of a combined stratigraphic,
14 82 petrological and geochemical study from a transitional, sublittoral to supratidal setting of the northern
15 83 margin of the Ries Crater Lake (Figs 1 and 2). This marginal setting is embodied in a present-day
16 84 outcrop dominated by carbonate algal fabrics. These Miocene-dated eulittoral deposits formed
17 85 bioherms (Riding, 1979; Arp, 1995) that have allegedly experienced several episodes of subaerial
18 86 exposure. The aim of this study is three-fold: (i) to test the reliability of chemostratigraphic data in
19 87 identifying subaerial exposure surfaces; (ii) to identify successive diagenetic phases using
20 88 petrographic data and component-specific $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ geochemistry; and (iii) to reconstruct
21 89 palaeoclimatic cycles of the lake using geochemical evidence, to support facies-based interpretations.
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29 91 **GEOGRAPHICAL AND GEOLOGICAL SETTING**

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32 93 The Ries lacustrine basin, Southern Germany, formed in the depression left by the impact of a
33 94 meteorite *ca* 14 to 15 Ma (Gentner & Wagner, 1969; Staudacher et al., 1982; Abdul Aziz et al., 2008;
34 95 Buchner et al., 2010, 2013; Schwarz & Lippolt, 2014) can be divided into three main geographic
35 96 domains with distinct lithologies: (i) a basinal setting with argillaceous deposits; (ii) marginal lake
36 97 carbonates with algal bioherms, travertine deposits and palustrine limestones; and (iii) a siliciclastic-
37 98 rich transitional fluvio-deltaic setting. A first research drilling campaign that was undertaken across
38 99 basinal deposits (Nördlingen 1973; Figs 1 and 2) shed light on the chemical change in the Ries
39 100 hydrological system, evolving from an initial playa lake to an alkali-saline lake, to eventually
40 101 freshwater conditions. Arp et al. (2013) analyzed material recovered from a second research drilling
41 102 campaign, from a core across the inner slope deposits of the inner ring (Enkingen SUBO 18; Figs 1
42 103 and 2). The latter authors, combining several geochemical and petrographic methods, lithofacies
43 104 markers and palynological proxies, re-interpreted lake water chemistry as evolving through successive
44 105 stages: (i) first, as alkaline freshwater lake to successively; (ii) a soda, (iii) 'marine'-like mode, (iv)
45 106 hypersaline evaporative lake, until eventually returning to (v) freshwater conditions. Such an evolution
46 107 probably represents a change in catchment lithology and ion exchange in the course of the Ries
47 108 lacustrine infilling. Miocene lake sediments were then covered beneath Pleistocene Loess, aeolian
48 109 sands and river gravel deposits, whose ultimate erosion led to the present morphology of the lake and
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3 110 the subsequent exposure of rocks representing the former lake margins in several settings, such as the
4 111 carbonate outcrop of the Hainsfarth quarry.

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7 113 **METHODS**

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10 115 **Study area and fieldwork approach**

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12 117 Five stratigraphic sections (3.5 to 5.5 m thick) were measured along a 330 m wide NNW–SSE transect
13 118 from a former quarry eastwards from Hainsfarth village (Fig. 3). Compared to the average sampling
14 119 resolution of previous studies (*ca* one sample/every 6 m by Rothe & Hoefs, 1977; *ca* one sample/each
15 120 metre Arp et al., 2013) **is and, respectively**, samples were carried out every 12.5 cm (Fig. 3B) in the
16 121 present study to capture potential high-frequency changes in lake chemistry. For this study a total of
17 122 124 samples have been extracted from the outcrop, including 90 cylinder cores (*ca* 5 cm long x 2 cm
18 123 diameter) and 34 slab samples. The average stratigraphic spacing between two successive samples is
19 124 12.5 cm. Care was given to avoid collecting samples from the direct outcrop surface (first 5 to 10 cm),
20 125 because the latter shows features of present-day alteration compromising the preservation of former
21 126 geochemical signatures.

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23 128 **Analytical methods**

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25 130 Laboratory methodology included carbon and oxygen isotope chemostratigraphy and component-
26 131 specific geochemistry, optical and cathodoluminescence microscopy, scanning electron microscopy
27 132 and Energy Dispersive X-Ray Spectroscopy (EDX) analyses. Carbon and oxygen isotope values of
28 133 carbonate matrix have been measured using a high-resolution (one sample every 12.5 cm)
29 134 chemostratigraphic approach for five stratigraphic sections. Carbonate matrix refers here to composite
30 135 material: even if fine-grained carbonates were aimed for, the obtained fraction is often heterogeneous,
31 136 consisting of inorganic carbonates, with a changing admixture of algal–microbial micrite,
32 137 microcrystalline or microsparitic cements and biogenic skeletal fragments. Additional targeted
33 138 components were algal–microbial fabrics, ostracod-rich and gastropod-rich carbonates, cement phases
34 139 and individual ostracod shells. Chosen fabrics were sampled by careful hand microdrilling under
35 140 binocular microscopy. Ostracod shells were isolated from small pieces of rock samples crushed
36 141 beforehand, then sieved, and the resulting grains (10^2 to 10^3 μm in size) have been cleaned in
37 142 ultrasonic bath to separate as efficiently as possible allochthonous amalgamated grains from ostracod
38 143 carapaces. Drilled powder ($n = 195$) and ostracod shells ($n = 29$) were analyzed for carbon and oxygen
39 144 isotope compositions at the German Research Centre for Geosciences GFZ (GeoForschungZentrum),
40 145 Potsdam, using a Thermo Scientific™ Kiel IV carbonate device coupled to Thermo Scientific™ MAT
41 146 253™ Mass Spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). Samples in the range of

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3 147 0.03 to 0.06 mg were reacted and dissolved with 103% phosphoric acid at 72°C and the isotopic
4 148 composition was measured from the released and cryogenic purified CO₂. All isotope results are
5 149 reported in ‰ relative to the V-PDB (Vienna Pee Dee Belemnite) standard in the conventional
6 150 manner. Replicate analyses of certified reference material NBS 19 provided a reproducibility of
7 151 0.06‰ for both δ¹³C and δ¹⁸O.

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10 152 Forty thin sections were prepared for petrographic and microfacies analysis to allow direct
11 153 comparison between geochemical results with correspondent facies. Cathodoluminescence (CL) of 11
12 154 polished thin sections were carried out using a ‘hot cathode’ CL microscope (type HC6-LM) at the
13 155 University of Potsdam. The acceleration voltage of the electron beam is 14 kV and the beam current is
14 156 set to a level of 0.2 mA and an operating vacuum of 10⁻⁵ mbar.

15 157 Six thin sections were also examined under the JEOL JSM-6510 Scanning Electron
16 158 Microscope (SEM; JEOL, Tokyo, Japan)) at the University of Potsdam. The device is equipped with
17 159 an INCA-based EDS detector (Oxford Instruments, Abingdon, UK) for the chemical characterization
18 160 of the samples. Two end-member ostracod shells of the same species with distinct preservation pattern
19 161 and derived from a single sample were also analyzed under the instrument in order to assess their
20 162 alteration degree.
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23 164 **FACIES AND DEPOSITIONAL ENVIRONMENTS**

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25 166 **Facies types**

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27 168 Five main facies types (Fig. 4) have been previously described amongst the marginal lacustrine
28 169 carbonates of Hainsfarth quarry (Arp, 1995; Arp, 2006). These are the following: (i) conoidal
29 170 *Cladophorites* framestone; (ii) nodular *Cladophorites* bafflestone; (iii) skeletal and non-skeletal
30 171 grainstone; (iv) stromatolites; and (v) palustrine breccia (Fig. 4). Skeletal and non-skeletal grainstones
31 172 can be subdivided into gastropodal grainstones, gastropodal–ostracodal grainstones, ostracodal
32 173 grainstones, ostracodal–peloidal grainstones and peloidal packstones–grainstones. For more details
33 174 concerning the facies, please refer to the exhaustive characterization provided by Riding (1979) and
34 175 Arp (1995, 2006). Carbonate algal fabrics (*Cladophorites*) are the dominant facies forming the Ries
35 176 deposits in the studied locality (Fig. 3A).
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38 178 **Depositional environments and cyclicity**

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40 180 The overall depositional environment of the Hainsfarth carbonates is attributed to the littoral zone of
41 181 the Ries Lake (Arp, 1995, 2006). However, the littoral zone can be subdivided into several sub-
42 182 environments: (i) the infralittoral zone, below lowermost seasonal lake level, where *Cladophorites*
43 183 build-ups develop and non-skeletal and skeletal grainstones are deposited; (ii) the supralittoral zone
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3 184 with palustrine deposits and pedogenic features; and (iii) a playa-lake environment with stromatolites.
4 185 Two orders of cyclicity, highlighted by Arp (1995), define the sedimentary pattern and the repetitive
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6 186 record of these depositional environments. The growth pattern of *Cladophorites*, following seasonal
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8 187 changes (Arp, 1995) reflected as rhythmic laminations, represents the highest frequency cycles. The
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10 188 growth of these algal bioherms is characterized by repetitive lower-frequency sequences mirroring
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12 189 small-scale (freshwater-evaporative?) climatic cycles (Arp, 1995). These cycles generally terminate
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14 190 with the subaerial exposure of the *Cladophorites* bioherms and their erosion and with the deposition of
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16 191 ostracod and gastropod packstones/grainstones (Fig. 5). Five of such sequences have been identified
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18 192 and described by Arp (1995) along one stratigraphic section (see its spatial position on Figs 3 and 9).
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20 193 This stratigraphic section served as a basis for the lateral, physical tracing of small-scale cycles and
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22 194 their boundaries on either side of the section in the present study. In the studied transect, seven of
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24 195 these repetitive climate-induced (freshwater-evaporative) cycles have been recognized. It is of
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26 196 relevance to mention that only the physical tracing of sedimentary packages and cycle boundaries
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28 197 across the transect enabled the authors to recognize all seven cycles although they have never been
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30 198 identified along one single stratigraphic section. The cycles are well-constrained and are correlated
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32 199 within the five stratigraphic sections. Arp (1995) assessed the *Cladophorites* growth duration within
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34 200 one sequence to be at least 775 years, assigning a whole duration of several 10^3 years to *ca* 10^4 years
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36 201 for the complete deposition of Hainsfarth carbonates.
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39 203 **GEOCHEMICAL AND PETROGRAPHIC DATA**

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41 205 The purpose of stable isotope chemostratigraphy was two-fold: (i) to provide an alternative (to facies
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43 206 analysis) for the identification of the sequence boundaries, i.e. geochemical shifts related to subaerial
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45 207 exposure of the lacustrine carbonate; and (ii) to evaluate a climatic control over cyclicity. The
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47 208 petrographic determination of successive diagenetic phases combined with their $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$
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49 209 signatures form the fundamental basis for the understanding and interpretation of any
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51 210 chemostratigraphic curves.
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54 212 **Results**

55 213 *Cement stratigraphy, petrography and diagenesis*

56 214 Hainsfarth carbonate diagenesis has been previously documented (Riding, 1979; Arp, 1995) and the
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58 215 aim here is not to replicate existing information, but to offer a succinct summary of diagenetic phases,
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60 216 forming the prerequisite for chemostratigraphic interpretation. Previous data are complimented by new
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218 217 CL data, and the volumetric part of each successive diagenetic feature is qualitatively assessed. The
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220 218 latter point serves as a basis for the forthcoming geochemical interpretation, as abundant diagenetic
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220 219 phases may strongly affect primary isotopic signatures. A first important observation is the high
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221 220 porosity amongst Hainsfarth carbonates, albeit strong heterogeneities exist even within thin sections

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3 221 (Fig. 6). Both primary depositional and secondary porosity (Figs 6 and 7) and several types of pore-
4 222 filling (cementation and pressure-solution) and pore-enhancing (dissolution and fractures) features are
5 223 identified within Hainsfarth carbonates (Fig. 7). These features are (from the oldest to the youngest):
6 224 (i) lacustrine sedimentation and carbonate microbial precipitation; (ii) thin isopachous dolomicrite
7 225 precipitation; (iii) early dissolution of aragonite (mainly gastropods) grains; (iv) precipitation of an
8 226 isopachous, inclusion-rich fibrous calcite; (v) precipitation of 'dog-tooth' calcite crystals; (vi)
9 227 considerable dissolution of carbonate grains; (vii) infilling of some pores by siliciclastic materials;
10 228 (viii) gravitational pendant and meniscus cement; (ix) main filling of the pores by blocky calcite (two
11 229 types – A and B); (x) pressure-solution features; and (xi) present-day dissolution and vadose
12 230 precipitation (Fig. 6).

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18 231 The first cement phase (ii) following sediment deposition (i) is a thin (up to a few tens of
19 232 microns thick) isopachous rim of dolomicritic surrounding grains (*Cladophorites*, gastropods; Fig. 6A
20 233 and B). Shells of gastropod species *Hydrobia trochulus* are either dissolved and left as mouldic
21 234 porosity or replaced into fine sparry calcite (iii; Fig. 6 and B), but if dissolved the shape is preserved
22 235 thanks to the first dolomicritic rim. An isopachous fine to thick rim of fibrous calcite (iv) is commonly
23 236 the second cement phase observed after the dolomicritic rim, whereas it is not systematically present.
24 237 In few cases fibrous cement appearing cloudy under transmission light, fills the interparticle pore-
25 238 space completely. Sometimes, an isopachous rim of bladed to scalenohedral calcite (v) is following the
26 239 initial microcrystalline dolomite (Fig. 6A). The volumetrically dominant cement phase observed,
27 240 filling former intergranular and intragranular pore spaces but also moulds of dissolved skeletal grains
28 241 (mostly gastropods) are blocky, sparry calcite (ix; type A) whose individual crystals may reach up to
29 242 500 μm (Fig. 6A, B E and F). This phase post-dates all of the above-mentioned cement rims. The
30 243 luminescence pattern of the blocky calcite (type A) is principally non-luminescent to dark blue
31 244 intrinsic, but some zonation can be observed, as well as a dull to bright orange luminescence in some
32 245 thin sections. This luminescent blocky calcite is referred to type B (ix; Fig. 6B and F). Gravitational
33 246 cements (viii) in the form of meniscus and pendant cements have been observed in several thin
34 247 sections (Fig. 6C and D) and are nearly contemporaneous to blocky calcite of type A. These phases
35 248 also have a dark blue luminescence under CL (Fig. 6D). Peloids, algal laminae and indistinct
36 249 carbonate matrix have a dull to bright orange luminescence, sometimes brown (Fig 6H and J).
37 250 Dissolution of sub-rounded material, allegedly peloids is frequently observed (vi; Fig. 6G to J).
38 251 *Strandesia risgoviensis* ostracods are less commonly dissolved than gastropod shells. When not
39 252 dissolved, their luminescence pattern under CL is variable, alternating between non-luminescent,
40 253 brown-orange, dull orange to bright orange. Such variability in luminescence is sometimes observed in
41 254 a same thin section (Fig. 6I and J). At the erosive surface in section 1 (215 cm above base section) but
42 255 also in many other intervals, carbonate-poor clastic material accumulated (vii; Fig. 6G and H).

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48 257 *Matrix $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ chemostratigraphy*
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3 258 Both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values exhibit a wide range of values (Figs 8 and 9). The $\delta^{13}\text{C}$ values range from
4 259 -6.5 to $+4.0\text{‰}$ whereas $\delta^{18}\text{O}$ values vary between -7.2 and $+3.9\text{‰}$. Amongst this wide range of values,
5 260 neither obvious geochemical shifts within individual curves can be distinguished, nor are
6 261 chemostratigraphic profiles well-correlated between stratigraphic sections (Fig. 8). The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$
7 262 curves from each of the five stratigraphic sections are clearly distinct from one another. The shape of
8 263 the $\delta^{13}\text{C}$ curves is very similar to that of the $\delta^{18}\text{O}$ curves for each individual sections, showing offsets
9 264 or shifts with nearly identical amplitude (Fig. 8). However, a relationship between stratigraphic and
10 265 lateral facies change, and carbon and oxygen isotope curves is not evident (Fig. 9). ,
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17 267 *Ostracod shell preservation*

18 268 As a prerequisite for any geochemical analysis performed on ostracod shells, their preservation degree
19 269 was assessed. A total of 474 ostracod shells or shell parts (broken, disarticulated, or complete and
20 270 joined) of the species *Strandesia risgoviensis* (Janz, 1995) were carefully selected out of 23
21 271 stratigraphic levels. Two sets with distinct appearance could be isolated (Fig. 10): (i) smooth, pearl-
22 272 like ostracod shells (169 broken, 64 complete; $n = 233$); and (ii) rough, mat ostracod shells (155
23 273 broken, 86 complete; $n = 241$). In all but three samples, both types of ostracod shells coexist. Because
24 274 *Strandesia risgoviensis* (Sieber) (Janz, 1995) is considered the only ostracod species in the Ries Lake,
25 275 or at least within this marginal setting (Arp, 1995, 2006; Arp et al., 2017), these variations could point
26 276 to distinct preservation/alteration states of the bioclasts. To assess the degree of alteration of the shells,
27 277 two specimens (i.e. one pearl-like and one mat) have been compared under SEM and their chemical
28 278 composition has been determined using EDX analyses (Fig. 10). Most of the complete (i.e. not
29 279 disarticulated) ostracod shells display an inner cement phase in between their valves (Fig. 10). The
30 280 latter cement is generally not present or rather dissociated when ostracod shells are broken or
31 281 disarticulated. The pearl-like ostracod shell appears smooth under high SEM magnification (Fig. 10-
32 282 B2) and exposes primary structures such as pore canals at the edge of the valves (Fig. 10-B4), while
33 283 SEM reveals rhombohedral crystals characterizing the mat shell (Fig. 10-C2). The 16 EDX
34 284 measurements performed on the pearl-like shell reveal that mean MgCO_3 content is less than 2.8%
35 285 mol (Table 1), which is agreement with an expected low-Mg calcite ($< 4\%$ mol MgCO_3) mineralogy of
36 286 pristine ostracod shells). Cement phases found inside and outside the valves have MgCO_3 a mean
37 287 content of 5.9% mol. Regarding the 10 spots analyzed on the rough and mat shell, MgCO_3 content
38 288 averages 41.6% mol and point to dolomitization. The proportion of magnesium carbonate measured in
39 289 the material infilling the ostracod valves of the rough shell equals 38.8% mol in average. In
40 290 comparison to SEM and optical microscopy, CL reveals more subtle distinctions between the two
41 291 specimens. Some ostracod shells are only present as moulds. Where preserved from dissolution,
42 292 luminescence patterns of ostracod shells varies between non-luminescent, dull brown-orange, dull
43 293 orange to bright orange (Fig. 6I-F). When ostracod valves are still articulated, carbonate material
44 294 filling in the carapace varies between: moderately bright luminescent matrix or peloids, dark blue
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3 295 luminescent to dull to bright blocky calcite or bright luminescent thick fibrous cement, similar to the
4 296 crust [diagenetic feature (iv) mentioned previously]. Both, ostracod mouldic porosity and shells that
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6 297 luminesce bright orange are predominantly observed in thin sections (i.e. intervals) where overall
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8 298 porosity is high. Ostracod shells showing either non-luminescence or a dull brown-orange one are
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10 299 commonly encased in a fine-grained matrix.

11 300 Initial alteration cannot be excluded in some of the smooth shells, inasmuch as some
12 301 measurements outlie the range for low-Mg calcite (for example, the maximum 10% mol MgCO_3).
13 302 However, pearl-like shells with a low-Mg calcite, apparently nearly devoid of any – even early –
14 303 diagenetic overprint seem well suitable to deliver a geochemical signal that is close to that of
15 304 penecontemporaneous lake water, even though early diagenesis does not systematically alter pristine
16 305 signatures (e.g. Bennett et al., 2011).

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21 307 *Ostracod shell $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$*

22 308 Shell material (n = 29) of the single ostracod species *Strandesia risgoviensis*, collected from 19
23 309 drilling cores (i.e. stratigraphic levels), was used for carbon and oxygen isotope geochemistry. Each
24 310 analyzed sample consists of several shells representing mixture of carapaces and disarticulated valves.
25 311 The aim was to compare $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in ostracod shells with those in carbonate matrix in
26 312 stratigraphic intervals where both were analyzed, and to test the reliability of both proxies for the
27 313 identification of climatic changes. Amongst the samples, ten allow the measurement of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$
28 314 values in both types of shells (pearl-like and mat specimens), four in pearl-like preserved shells only
29 315 and five in mat altered shells solely. The authors concede that all types of analyzed shells represent a
30 316 mixture of carbonate materials of difference nature (preserved and/or altered shell with various
31 317 diagenetic infilling), inasmuch as shells were not isolated from allochthonous carbonate material,
32 318 especially when being complete (not disarticulated). However, a quantitative investigation of shell
33 319 isotope geochemistry is beyond the scope of this study and the isotope composition analysis of shells
34 320 is only achieved here to provide a qualitative comparison with matrix $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values and to
35 321 determine the diagenetic history of these marginal carbonates. The $\delta^{13}\text{C}$ values in preserved ostracods
36 322 range from -1.7‰ to +3.1‰ (Table 2 and Fig. 11), while $\delta^{18}\text{O}$ values vary between -3.3‰ and +4.0‰.
37 323 In altered dolomitic or dolomite-rich shells, $\delta^{13}\text{C}$ values vary between -4.1‰ and +3.8‰ and $\delta^{18}\text{O}$
38 324 values from -6.2‰ to +4.3‰. Mixed sets of preserved and altered ostracods yield $\delta^{13}\text{C}$ values varying
39 325 between -4.1‰ and +3.2‰ and $\delta^{18}\text{O}$ values ranging from -5.9‰ to +3.2‰.

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44 327 *Multi-component and facies-specific $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ and petrography*

45 328 The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of all analyzed material (matrix, algal-microbial fabrics, ostracod shells,
46 329 gastropod shells and sparry cements) are presented in Table 2 and Figs 11 and 12. Sparry cements in
47 330 intragranular and intergranular pores and as replacement fabric of gastropod shells show very negative
48 331 carbon and oxygen isotope values (mean values around -5 to -6‰ for $\delta^{13}\text{C}$, and -6 to -7‰ for $\delta^{18}\text{O}$).

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3 332 All remaining carbonate components (matrix, algal fabrics and ostracods) have (mean) values that are
4 333 rather positive, ranging from 0 to +2‰ for $\delta^{13}\text{C}$ and -0.5 to +2‰ for $\delta^{18}\text{O}$, although their $\delta^{13}\text{C}$ and
5 334 $\delta^{18}\text{O}$ values vary within a high amplitude range (ca -8‰ to +4‰ for $\delta^{18}\text{O}_{\text{matrix}}$ and -7‰ to +4‰ for
6 335 $\delta^{13}\text{C}_{\text{matrix}}$; ca
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8 336 -3‰ to +4‰ for $\delta^{18}\text{O}_{\text{preserved-ostracods}}$ and -2‰ to +3‰ for $\delta^{13}\text{C}_{\text{preserved-ostracods}}$). A second relevant outcome
9 337 is that despite these clearly distinct groups of geochemical signatures, an obvious covariance ($r = 0.97$)
10 338 exists between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ for all Hainsfarth carbonates analyzed (Fig. 12).
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15 340 Interpretation

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17 342 *Cement stratigraphy, petrography and diagenesis*

18 343 Petrographic investigation suggests that most of the diagenetic features affecting Hainsfarth carbonates
19 344 occurred during an early stage, within the eogenetic lacustrine and meteoric environments. The first
20 345 rim of isopachous microdolomite rhombs formed in a phreatic environment but whether its nature is
21 346 related to the original lake water or meteoric diagenetic fluids remains unclear (Riding, 1979). The
22 347 isopachous rim of cloudy, inclusion-rich fibrous calcite likely precipitated in a lacustrine phreatic
23 348 environment with a high-Mg mineralogy, similar to those forming in marine environments (Lohmann
24 349 & Meyers, 1977; Gray & Adams, 1995; Wilson & Dickson, 1996; Richter et al., 2011; Christ et al.,
25 350 2012a).

26 351 Low or negative $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in lake carbonates values can be related to: (i)
27 352 precipitation under freshwater lacustrine conditions (Leng & Marshall, 2004); (ii) subaerial conditions
28 353 exposure and meteoric alteration, and the incorporation of light ^{16}O and ^{12}C due to rainwater and soil
29 354 formation; or (iii) burial diagenesis and precipitation under higher temperatures during burial
30 355 diagenesis. While negative $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are not incompatible with precipitation of the blocky
31 356 cements (type A) under lacustrine freshwater conditions, it is questionable that they formed under
32 357 these conditions. Indeed the more positive $\delta^{18}\text{O}$ (by 6.5‰) of the matrix extracted from the same
33 358 sample, i.e. stratigraphic interval, strongly suggests distinct environment, with matrix deposited under
34 359 lacustrine conditions and sparry cements representing secondary diagenetic products. Thus, assuming
35 360 that the negative values of blocky calcite mirror secondary diagenesis, it is unlikely that they here
36 361 ensue from elevated temperatures, inasmuch as Arp (1995) mentioned a maximal burial depth of 80 to
37 362 100 m for these Miocene deposits. A difference of -6.5‰ implies an increase in temperature by about
38 363 25°C or more if it is assumed that matrix isotopic signature has also been altered by burial diagenesis
39 364 (cf. the orange luminescence under CL). Such high temperatures are incompatible with a burial depth
40 365 of 100 m and an assumed geothermal gradient of 25 to 50°C/km (Niemann & Read, 1988; Einsele,
41 366 2000). Additionally $\delta^{13}\text{C}_{\text{cement}}$ is lower by almost 4‰ relative to $\delta^{13}\text{C}_{\text{matrix}}$ for the same interval, a
42 367 disparity that is irreconcilable with a burial geochemical signature, considering that carbon isotope
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3 368 fractionation with temperature is negligible (Emrich et al., 1970; Romanek, 1992). Therefore burial
4 369 diagenesis as the main driver for the negative values measured in the cements should be excluded.

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6 370 The intrinsic luminescence or non-luminescence of cements seen under CL generally implies
7 371 precipitation in an oxidizing environment (Barnaby & Rimstidt, 1989; Richter et al., 2003), either
8 372 from marine, lacustrine or meteoric waters. Because this study ruled out lacustrine conditions for the
9 373 precipitation of the spars, negative $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in cements here rather ensue from meteoric
10 374 diagenesis (Allan & Matthews, 1977, 1982). Additionally, the blue luminescence pattern of most of
11 375 the blocky spars is nearly identical to that of the meniscus and pendant cements, which are
12 376 unequivocal evidence for vadose conditions (Flügel, 2004). According to Riding (1979) meteoric
13 377 conditions affecting Hainsfarth carbonates contributed only sparsely to the precipitation of cements;
14 378 this statement is definitely true regarding *Cladophorites* build-ups that are much less porous than
15 379 grainstones and remains mostly devoid of large calcite spars. However, blocky calcite accounts for a
16 380 large volume of carbonate material within packstone/grainstone intervals and, based on their
17 381 luminescence pattern under CL and their very negative carbon and oxygen isotope composition values
18 382 (both down to *ca* -7‰), they are best interpreted as representing significant freshwater cementation
19 383 under meteoric phreatic conditions during Miocene lacustrine lowstands. Further evidence of
20 384 penecontemporaneous subaerial exposure is also supported by the brecciated palustrine deposits, the
21 385 clastic-rich infilling of grainstone pores and at erosion surfaces, erosion of the build-ups, and the
22 386 laminated sinter veneering algal cones and nodules (Riding, 1979; Arp, 1995). Although blocky calcite
23 387 is undeniable evidence for Miocene meteoric phreatic diagenesis, meteoric vadose alteration certainly
24 388 also occurred, both in the course of the Miocene during lacustrine lowstands and at present-day
25 389 following exhumation. Regarding the elevated porosity of Hainsfarth carbonates, vadose diagenesis is
26 390 expected to be still an ongoing process.

27 391 Burial diagenesis has definitely affected Hainsfarth carbonates, as witnessed by the orange
28 392 luminescence under CL of some blocky cements (type B) and matrix that suggests precipitation in a
29 393 reducing environment (Barnaby & Rimstidt, 1989; Richter et al., 2003; Christ et al., 2012a). It is
30 394 however assumed that burial diagenesis was insignificant compared to meteoric alteration, and thus
31 395 limited to a very shallow domain (maximum 80 to 100 m) that barely influenced geochemical
32 396 signatures of the carbonates.

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38 398 *Matrix $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ chemostratigraphy*

39 399 Carbon and oxygen isotope composition curves between stratigraphic sections are not correlated, and
40 400 this rules out an immediate palaeoenvironmental reconstruction based on matrix $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$
41 401 chemostratigraphy (Fig. 9). Moreover, the virtually identical shapes of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ curves regarding
42 402 individual stratigraphic sections (Fig. 8) might be related to the diagenetic overprint of the matrix,
43 403 although it is not yet clear why $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ offsets have nearly equivalent amplitudes. Interestingly,
44 404 previous studies (Rothe & Hoefs, 1977; Arp et al., 2013) documented trends related to long-term

changes in the chemistry of the Ries lake water, based on $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ chemostratigraphy but at a significantly reduced stratigraphic resolution (one sample per metre or more). While spanning the nearly complete depositional succession of the lake, these studies targeted basinward or basinal lacustrine carbonates that were not directly (physically) affected by lake level changes. Based on the outcome of the present study, it appears that the chemostratigraphic approach fails to record environmental changes in ancient marginal lake deposits, most likely because of repetitive emergence and submergence affecting primary signatures of the carbonates.

Ostracod shell $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ geochemistry

Pleistocene–Holocene ostracod shells are often unaltered, and thus suitable for geochemical analyses because they generally preserve the original signal of lake or seawater (e.g. Heaton et al., 1995; Holmes, 1996; Leng et al., 1999; Mischke et al., 2002; Anadon et al., 2006; Kwiecien et al., 2009; Gouramanis et al., 2010; Stansell et al., 2013; Mayr et al., 2015; Li et al., 2016). Despite their (stable) low-Mg calcite mineralogy, ancient specimens commonly undergo diagenesis (shell compaction, dissolution, recrystallization, etc.) at various degrees, and therefore are less likely to preserve the geochemical information of the water from which their carapaces formed. Several studies investigated diagenetic effects on ostracods (Depeche, 1982; Danielopol et al., 1986; Kontrovitz et al., 1992; Dwyer et al., 2002) but only few documented the effect of diagenesis on ostracod shell structures and on their $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ signatures (e.g. Bennett et al., 2011). Thus ostracods $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ have been only sparsely used for pre-Pleistocene lake reconstruction (Pliocene – Anadón et al., 2008; Miocene – Janz & Vennemann, 2005; Mazzini et al., 2013; Cretaceous – Chamberlain et al., 2013; Carboniferous – Bennett et al., 2011). Beside diagenetic alteration, another aspect that limits the direct linkage of ancient ostracod shell $\delta^{18}\text{O}$ values to the ambient lake water $\delta^{18}\text{O}$ values are vital effects, reflecting the non-equilibrium fractionation of oxygen isotopes during shell calcification (von Grafenstein et al., 1999; Decrouy et al., 2011; Börner et al., 2013). In the case of ostracods, the shift from isotopic equilibrium with the host water is generally constant for a same species (Xia et al., 1997, von Grafenstein et al., 1999; Keatings et al., 2002; Börner et al., 2013, and references therein). Oxygen isotope offsets from most of the species are generally positive (by up to +3.3‰) regarding ambient lake water but few species have $\delta^{18}\text{O}$ lower by up to -0.9‰ (with respect to lake water $\delta^{18}\text{O}$ values) (Decrouy et al., 2011). The $\delta^{13}\text{C}$ values of various ostracod genera were mentioned to mirror near isotopic equilibrium with lake water (Keatings et al., 2002; Decrouy et al., 2011). For extinct species such as *Strandesia risgoviensis*, vital offset will probably stay unresolved.

A significant observation is that ostracod shells showing different degrees of alteration display a similar range of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values, with the minimal values significantly higher for non-altered shells (Fig. 11). This apparent similarity has to be put into perspective, as altered shells are mostly made of dolomite (along with a minimal amount of calcite). With an almost systematic fractionation factor at equilibrium between dolomite and calcite ($\Delta\delta^{18}\text{O}_{\text{dol-cal}}$) at low temperatures, $\delta^{18}\text{O}_{\text{dol}}$ values are

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3 442 generally enriched regarding $\delta^{18}\text{O}_{\text{cal}}$ values by 0-9‰ under the same conditions (Vasconcelos et al.,
4 443 2005, and references therein). Swart (2015) assesses this enrichment ($\Delta\delta^{18}\text{O}_{\text{dol-cal}}$) as between 3‰ and
5 444 6‰. Conversely, $\delta^{13}\text{C}$ values of dolomite are generally slightly more positive but close to the co-
6 445 precipitating low-Mg calcite and $\Delta\delta^{13}\text{C}_{\text{dol-cal}}$ is generally between 0‰ and 1‰ (Sheppard & Schwarcz,
7 446 1970; Swart, 2015). Therefore, the range of measured $\delta^{18}\text{O}$ values in the altered shells is expected to
8 447 be significantly lower (by at least 2 to 3‰) than the range obtained (and to a lesser extent altered shell
9 448 $\delta^{13}\text{C}$ values), perhaps more compatible with the common lower isotopic signature of a meteoric or
10 449 burial diagenetic fluid. More accurate estimation is not feasible, as the timing of dolomitization, the
11 450 penecontemporaneous water temperature, the $\delta^{18}\text{O}_{\text{water}}$ and the $\delta^{18}\text{O}_{\text{calcite}}$ remain unknown. The $\delta^{13}\text{C}$
12 451 and $\delta^{18}\text{O}$ of preserved ostracods values are generally positive, but are likely to represent mixtures of
13 452 material (original valves and a LMC diagenetic infilling) with distinct geochemical signatures. Three
14 453 other *Strandesia risgoviensis* ostracods issued from the Nördlingen Ries have been previously
15 454 analyzed for isotopic composition (Tütken et al., 2006) and yield $\delta^{13}\text{C}$ values between +3.5‰ and
16 455 +3.9‰ and $\delta^{18}\text{O}$ values between +1.6‰ and +2.3‰, corresponding to values amongst the highest
17 456 analyzed in the present study. Unfortunately, Tütken et al. (2006) do not report the stratigraphic
18 457 interval from which these ostracods are issued, but they interpret them to have lived under saline,
19 458 evaporative lake conditions.

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460 *Multi-component and facies-specific $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ and petrography*

461 High positive correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of lacustrine carbonates commonly refers to
462 hydrologically-closed systems (Talbot, 1990; Leng & Marshall, 2004). Using observations from
463 modern lakes, Talbot (1990) determined a covariance threshold between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ ($r = ca\ 0.75$)
464 under and over which a lacustrine system is open or closed, respectively. The covariance between
465 carbon and oxygen isotope composition of carbonates at Hainsfarth is >0.9 and therefore is in
466 agreement with the previous closed-system interpretation of the Ries Lake (Rothe & Hoefs, 1977;
467 Talbot, 1990; Arp et al., 2013). A geochemical covariance as high as $r = 0.9$ has been measured in
468 carbonates from the research drilling Nördlingen 1973 (Rothe & Hoefs, 1977; Talbot, 1990).
469 Similarly, Arp et al. (2013) reported a covariance of 0.95 from carbonate samples issued from the
470 research drilling Enkingen SUBO 18. Samples from Hainsfarth, however, significantly differ from
471 those of the previous drillings: (i) they correspond to marginal, sublittoral to supratidal carbonates
472 whereas those from previous work refer to deeper-water, more basinal lake deposits; (ii) they are
473 outcrop-based while those from previous research are core-based; and (iii) carbonate facies at
474 Hainsfarth show strong heterogeneity, and lateral and vertical porosity considerably varies.
475 Accordingly, Hainsfarth carbonates probably experienced several episodes of meteoric diagenesis
476 from the Miocene to present-day, due to their particular palaeogeographic position. Meteoric alteration
477 in basinal deposits should be considered of reasonably lesser importance.

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3 478 The wide range in matrix $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values (Table 2; Figs 11 and 12) combined with the
4 479 lack of chemostratigraphic correlation between sections and the noisy behaviour of matrix
5 480 chemostratigraphic curves (Figs 8 and 9) suggest a mixing (in variable proportions) of carbonate
6 481 material yielding distinct geochemical signatures, masking any potential primary signal. Carbon and
7 482 oxygen isotope values in meteoric cement spars are amongst the lowermost values, equivalent to the
8 483 lowermost values of matrix carbonates (Table 2; Figs 11 and 142). Mouldic porosity of dissolved
9 484 aragonitic gastropod shells is often filled by early meteoric sparry calcite cement. This cement also
10 485 fills in a significant volumetric portion of the internal space of the former shells. This explains why
11 486 $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in gastropods are nearly as negative as in meteoric spars (Table 2; Figs 11 and
12 487 12). These sparry cements were certainly intermixed with matrix and skeletal components and hence
13 488 account for negative $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values. Such an explanation is realistic considering that half of the
14 489 matrix $\delta^{13}\text{C}$ values are $>+1.7\text{‰}$ and half of the $\delta^{18}\text{O}$ are $>+0.8\text{‰}$ (median values; Table 2; Fig. 11), i.e.
15 490 they are mostly positive. Meteoric alteration is probably also responsible for the lowest values
16 491 measured in algal laminated fabrics (some areas featuring trapped gastropod shells), and in ostracod
17 492 shells and ostracod-rich matrix. However the high positive $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ median values (Table 2; Fig.
18 493 11) of algal fabrics and ostracods, as well as the lack of chemostratigraphic correlation, strongly
19 494 suggest that Hainsfarth *primary* lacustrine carbonates were mostly positive. The positive character of
20 495 primary $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in the present study significantly differs from previous work (Rothe & Hoefs,
21 496 1977; Arp et al., 2013) where negative and positive $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values were interpreted as primary
22 497 in origin, reflecting relevant changes in lake chemistry.
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499 DISCUSSION

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501 Absence of chemostratigraphic correlation between stratigraphic sections

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503 Chemostratigraphic analyses are commonly undertaken on recent core-based Quaternary lake
504 carbonates in order to document climatic changes on seasonal to multi-millennial time scales (Junge &
505 Bottger, 1994; Stevens et al., 2006; Mangili et al., 2007, 2010; Wittkop et al., 2014; Oehlerich et al.,
506 2015). While $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ chemostratigraphy is widely used to characterize Pleistocene–Holocene
507 glacial and interglacial periods, it has been only rarely applied for the palaeoenvironmental
508 reconstruction of ancient lacustrine successions (e.g. Melezhik et al., 2005; Montgomery et al., 2014).

509 Neither carbon nor oxygen isotope curves of carbonate matrix correlate between the five
510 stratigraphic sections of the Hainsfarth quarry (Fig. 8), despite the short lateral distance separating
511 them (Fig. 3), the high-resolution sampling and the beforehand set stratigraphic boundaries.
512 Noteworthy is that each of the seven recorded cycles ends with the development of nodular to conoidal
513 *Cladophorites* boundstones and eventually their emersion, mirrored by extensive thicker veneers, the
514 erosion of the algal bioherms, and the presence of oxidized layers or palustrine breccias (Riding, 1979;

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3 515 Arp, 1995; Fig. 5). While these sequence boundaries coincide with subaerial exposure surfaces based
4 516 on facies description and cyclicity (Arp, 1995) they lack the saw-tooth shaped shifts in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$
5 517 values commonly associated with meteoric or freshwater diagenesis beneath emersion surfaces (Allan
6 518 & Matthews, 1977, 1982). Even assuming a semi-arid climate for the middle Miocene of this area
7 519 (Böhme et al., 2001; Prieto et al., 2009), minor negative shifts in both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ are expected
8 520 beneath subaerial exposure surfaces (Christ et al., 2012a). Even though individual curves cannot be
9 521 correlated with one another between sections, a striking feature is the covariance of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$
10 522 curves for each considered stratigraphic section (Fig. 8), suggesting an interdependence between both
11 523 geochemical isotope systems (C and O).

12 524 The clear covariance between matrix $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in Hainsfarth outcrop carbonates is
13 525 apparently in accordance with geochemical signatures of closed-lake systems and an alternation of
14 526 freshwater and saline lacustrine conditions (Li & Ku, 1997; Leng & Marshall, 2004) such as formerly
15 527 mentioned from the Ries Lake (Talbot, 1990; Arp, 2006; Arp et al., 2013). However, the lack of
16 528 correlation between individual chemostratigraphic profiles (Fig. 8), and also between geochemical
17 529 curves and sedimentary cycles (Fig. 9), is difficult to reconcile with a primary environmental origin.
18 530 Consequently, in case of Ries Crater Lake $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ chemostratigraphy fails as an alternative
19 531 method for the recognition of sedimentary cycles in marginal, sublittoral lacustrine carbonates.
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21 533 **Geochemical evidence of Miocene subaerial exposure and meteoric diagenesis**

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23 535 The question remains as to whether geochemical and petrographic data retain evidence for subaerial
24 536 exposure and meteoric diagenesis, despite not being expressed by the emersion-related isotope $\delta^{13}\text{C}$
25 537 and $\delta^{18}\text{O}$ shifts beneath surfaces (Allan & Matthews, 1982; Christ et al., 2012a).

26 538 Matrix $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in the study outcrop are as low as -7.3‰ and -7.7‰, respectively, close
27 539 to those of the blocky cements and replaced gastropod shells (Table 2; Fig. 11). Negative $\delta^{13}\text{C}$ and
28 540 $\delta^{18}\text{O}$ values reported from Ries Lake basinal deposits (Rothe & Hoefs, 1977; Pache et al., 2001; Arp et
29 541 al., 2013) were associated with freshwater lacustrine conditions. Several lines of evidence suggest that
30 542 the cause for negative $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in Hainsfarth carbonates is related to primary lacustrine
31 543 chemistry: (i) the noisy character of the curve and the lack of chemostratigraphic correlation (Figs 8
32 544 and 9); (ii) substantial, especially in packstone–grainstone fabrics, volume of calcite spars (type A
33 545 blocky calcite) **feeling** pore spaces, gastropod shell moulds and internal spaces, should drag $\delta^{13}\text{C}$ and
34 546 $\delta^{18}\text{O}$ signatures towards negative values, when mixed with carbonate matrix. The latter is exemplified
35 547 by an erosion (exposure?) surface, with matrix carbonates having clearly low $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values
36 548 below and above the discontinuity surface (Fig. 3). The considered intervals have volumetrically-
37 549 abundant blocky cements which depletes $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the matrix. Meniscus cements and
38 550 blocky cements from these intervals are interpreted as vadose (Fig. 6), respectively phreatic meteoric
39 551 phases, and their occurrence in the vicinity of an erosive (exposure?) surface at the interface of which

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3 552 soil-residue clastic material accumulated (such as quartz, clays and other oxides) are convincing
4 553 evidence in favour of a meteoric environment (e.g. Sanz et al., 1991; Christ et al., 2012a). Such
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6 554 cement phases and clastic material were also observed amongst many other stratigraphic intervals,
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8 555 suggesting that meteoric features are pervasive within Hainsfarth carbonates (Figs 6 and 7).
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11 **Relationship between facies, porosity and meteoric diagenesis**

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13 559 According to the previous paragraph, emersion episodes of the margins potentially occurred at a
14 560 higher frequency than that mirrored by the development of well-defined sedimentary cycles (small-
15 561 scale climatic cycles; Arp, 1995; Fig. 9). This is evidenced, for example, by the allegedly subaerially
16 562 exposed surface, subordinately identified within the fourth cycle (Figs 9 and 13). Carbon and oxygen
17 563 isotope patterns seem to relate to the complex initial morphology of Hainsfarth bioherms,
18 564 characterized by a high lateral and vertical variability in facies and textures (Figs 8 and 9). These
19 565 heterogeneities eventually result in strong disparities in porosity and permeability, observable at the
20 566 scale of thin sections. Porosity varies between 3.9% and 46.3% and permeability between 1.3 mD and
21 567 3543.5 mD (Maerz et al., pers. comm) with the most effective pore network commonly belonging to
22 568 grainstone facies. To simplify, facies types can broadly be grouped into two dominating groups: (i)
23 569 packstones/grainstones (with variable mixture of fine-grained carbonates, gastropods, ostracods,
24 570 peloids and cements); and (ii) *Cladophorites* algal-dominated fabrics (microbial micritic boundstone
25 571 and laminated boundstone facies). While $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values measured in grainstones and in algal
26 572 fabrics range within nearly the same interval, the mean and median $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of
27 573 packstones/grainstones are clearly distinct from those of the algal fabrics (Fig. 14). Thus median
28 574 values of grainstone facies are significantly lower than those of algal-dominated facies (Fig. 14). Often
29 575 grainstones have a higher (effective) porosity and a higher amount of meteoric-related blocky cements,
30 576 which explains why their mean and median $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are much lower than the mean and
31 577 median values of algal fabrics. These variations in the lateral and stratigraphic distribution of those
32 578 two groups of facies certainly account for the geochemical variability (dissimilar isotopic signatures,
33 579 noisy patterns) observed between stratigraphic sections. Hence, the geochemical expression and the
34 580 degree of meteoric alteration seem to be controlled by lateral and vertical fluid flow pathways.
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582 **Preservation of primary lacustrine geochemical signature**

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584 Replaced gastropod shells and most of the phreatic pore-filling blocky calcite phases carry the
585 petrographic and geochemical evidence (most negative $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values) characteristic for
586 meteoric diagenetic overprint. The remaining carbonate features (matrix, algal laminated fabrics,
587 ostracod-rich matrix and ostracod shells) all represent a mixture of carbonates with distinct carbon and
588 oxygen isotope compositions. Similar to the lowest $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in the matrix, it can be

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3 589 assumed that the lowest $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in algal fabrics, ostracod-rich matrix and
4 590 altered/preserved ostracod shells are clearly influenced by meteoric diagenesis, due to a variable
5 591 amount of cements within the mixture (Fig. 11). Evidence for the strong meteoric contribution is given
6 592 by the large variability of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ data points for each feature, and above all by the
7 593 heterogeneous and asymmetrical distribution of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ mean and median values for all
8 594 carbonate features (Figs 11 and 12; Table 2). In comparison to $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ mean values, the
9 595 relatively elevated median values are certainly more representative of signatures resembling primary
10 596 lacustrine conditions.

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15 597 Despite the dissimilar amplitude in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values between matrix (wide distribution of
16 598 data points), algal fabrics (relatively wide distribution), preserved ostracods (moderate distribution)
17 599 and nearly cement-free preserved ostracods (narrow distribution), both their $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ median
18 600 values are strikingly very close to one another (Table 2; Fig. 11). Solely ostracod-rich matrix shows
19 601 $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ median values that are distinctively higher, certainly positively skewed by uncorrected
20 602 dolomite geochemical signatures, the latter certainly affecting isotopic composition of *Cladophorites*
21 603 fabrics and skeletal and non-skeletal packstone to grainstones as well.

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26 604 While the geochemical data fail to faithfully link the isotopic composition of the carbonates to
27 605 that of primary Ries lake water due to meteoric diagenetic overprint, the overall chemistry of the water
28 606 can be qualitatively assessed. Considering maximum $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of +4‰ and median values
29 607 of *ca* +1 to +2‰, and assuming a symmetrical distribution (i.e. median \sim mean) of the original
30 608 geochemical signatures for the carbonate matrix, algal fabrics and ostracod material, then minimum
31 609 values for primary lacustrine carbonates are assessed as low as -1 to 0‰. (Fig. 15). The authors
32 610 concede that these values represent nothing but an approximation, since it is unknown whether or not
33 611 the maximum of +4‰ corresponds to diagenetically unaltered $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values. Nevertheless the
34 612 range of -1/0‰ to +3/+4‰ is reasonable considering the ranges of $\delta^{13}\text{C}$ (+0.3 to +3.1‰) and $\delta^{18}\text{O}$ (-
35 613 0.7 to +4.0‰) obtained from the (cement-free) preserved ostracods despite unknown vital effects (Fig.
36 614 15). The assumption of mostly positive $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ signatures for primary lacustrine carbonates in
37 615 Hainsfarth suggests that evaporative saline conditions were prevailing over freshwater ones during the
38 616 development of the bioherms (see also Leng & Marshall, 2004).

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618 **Marine-like to saline lacustrine conditions during the development of Hainsfarth bioherms**

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620 Previous studies focusing on the composition of carbonates from two basinal and basinward drilling
621 cores (Rothe & Hoefs, 1977; Arp et al., 2013) reported $\delta^{13}\text{C}$ values ranging respectively from -11.5‰
622 to +11.1‰ and $\delta^{18}\text{O}$ values ranging from -10.4‰ to +6.5‰. This large range of isotopic compositions
623 was interpreted to mirror a geochemical evolution of the lake water from freshwater conditions
624 (negative values) for the oldest deposits, to saline, evaporative conditions (positive values) for some of
625 the youngest ones (Arp et al., 2013), before a return to a freshwater karstic environment during

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3 626 ultimate lacustrine stage. The geochemical pattern in marginal carbonates, however, cannot be
4 627 compared to that of the basinal deposits for several reasons: (i) no trend describing an evolution from
5 628 freshwater towards evaporative conditions or vice versa is shown by the isotopic composition curves;
6 629 (ii) penecontemporaneous meteoric diagenesis – and not freshwater lake conditions – is clearly
7 630 responsible for negative $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values and well-supported by petrographic observations
8 631 (mouldic porosity, leaching of grains, blocky cements and replaced gastropod shells); (iii) the
9 632 Hainsfarth outcrop represents only a small portion of the stratigraphic interval covered by the basinal
10 633 setting: thus, the time span of *ca* 10^3 to 10^4 years involved in the complete deposition of bioherms
11 634 (Arp, 1995) is rather short and probably represents a younger, ‘snapshot’ moment of the entire lake
12 635 chemical evolution and the duration of lacustrine conditions assessed to last 0.3 to 2.0 Ma; (Pohl,
13 636 1977; Jankowski, 1981). If it is assumed that positive carbon and oxygen isotope composition of
14 637 Hainsfarth carbonates closely reflects Ries Lake (semi-)arid water conditions at that time, it is in
15 638 accordance with the former interpretation of these bioherms forming under marine-like to saline lake
16 639 water conditions (Arp et al., 2013). The latter authors suggest that their ‘claystone member’
17 640 (carbonaceous clays, bituminous shales and laminated claystones) is correlated in time with Hainsfarth
18 641 bioherms and represent a transition towards marine-like, and later saline evaporative conditions of the
19 642 lake (Fig. 16). This chemical transition was interpreted partly based on the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of
20 643 carbonates ranging from -1.2‰ to +3.3‰ and from -0.7‰ to +2.1‰, respectively (Arp et al., 2013).
21 644 The estimated range of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in primary carbonates (*ca* -1‰ to +4‰ for both
22 645 geochemical proxies) at Hainsfarth is in agreement with the interval of geochemical values from the
23 646 corresponding Enkingen SUBO 18 carbonates (Arp et al., 2013; Fig. 16). The slightly higher $\delta^{18}\text{O}$
24 647 values (up to +4.0‰) measured amongst Hainsfarth carbonates (this study; Fig. 20) may correspond to
25 648 the peak evaporative conditions, expected to prevail close to lake margins *or rather* close to water
26 649 surface, thus increasing oxygen isotope fractionation due to evaporation. However, Arp (1995)
27 650 interpreted the (seven) sedimentary cycles at Hainsfarth to mirror short-term (*ca* 10^3 years) freshwater
28 651 to saline evaporative climatic cycles, with a smooth trend from ‘marine-like’ (downsection) to more
29 652 arid evaporative (upsection) conditions. Based on the outcome of the present geochemical study, these
30 653 sedimentary sequences are likely to represent small-scale freshwater to saline cycles subordinated on
31 654 an overall arid evaporative context. While more data would be necessary (but this is beyond the scope
32 655 of this study), preserved ostracod shells seem to be the most reliable to preserve pristine signatures and
33 656 express changes at the scale of these short-term climatic fluctuations (Fig. 11).

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51 658 **Covariance in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$: insights to lake chemistry, freshwater diagenesis and climate**

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53 660 The outcome of the previous paragraphs suggests that the linear trend between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in
54 661 Hainsfarth carbonates reflects (at least) two diametrically distinct processes: (i) primary carbonate
55 662 sedimentation in a closed-lake system; and (ii) their overprint by meteoric diagenesis. Therefore the

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3 663 authors suggest that the geochemical covariance may be bimodal: (a) densely-packed, higher $\delta^{13}\text{C}$ and
4 664 $\delta^{18}\text{O}$ values closely reflect the original (globally evaporative) signature of the lake water; while (b)
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6 665 scattered negative $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values mirror the freshwater diagenetic overprint of early products
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8 666 and the precipitation of meteoric spars. A clear threshold of values and data points where both
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10 667 processes are clearly isolated from one another is not identified, because most of the values certainly
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12 668 represent a mixture of lacustrine and meteoric signatures, pondered upward or downward by either of
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14 669 the volumetrically dominant sources. In marine environments, the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ signatures of
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16 670 carbonates related to meteoric diagenesis are generally distinct (i.e. more negative) from primary
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18 671 depositional carbonates (Allan & Matthews, 1977, 1982; Goldstein, 1991; Christ et al., 2012a; Swart,
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20 672 2015), while it may not necessarily be the case in lacustrine settings. The questions: (i) how such a
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22 673 positive linear trend is obtainable from carbonates whose origin is clearly distinct (primary lacustrine
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24 674 *versus* diagenetic); and (ii) how to explain the linear covariance between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ despite
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26 675 meteoric diagenesis, are not straightforward ones but should be discussed.

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28 676 In marine coastal settings, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in carbonates are often lower than normal
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30 677 marine values under considerable meteoric influence in the vadose and phreatic freshwater
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32 678 environments (Allan & Matthews, 1982). However, carbon and oxygen isotope compositions are
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34 679 rarely covariant in these two diagenetic environments (Allan & Matthews, 1982; Swart, 2015), and
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36 680 can even show antagonistic shifts (for example, positive $\delta^{18}\text{O}$ due to evaporation, negative $\delta^{13}\text{C}$ due to
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38 681 soil-zone CO_2). Although $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in carbonates tend to be more negative in coastal
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40 682 vadose and phreatic meteoric environments, $\delta^{13}\text{C}$ values increase with increasing distance from the
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42 683 soil-zone as a result of dissolution of the carbonates in the vadose environment progressively enriching
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44 684 waters in ^{13}C , while $\delta^{18}\text{O}$ values remain rather stable within the altered environment (Allan &
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46 685 Matthews, 1982; Lohmann, 1988). The only reported domain where $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values show a
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48 686 covariance is the mixing-zone (transition domain between fresh and marine waters) with both $\delta^{13}\text{C}$ and
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50 687 $\delta^{18}\text{O}$ increasing towards the marine environment (Allan & Matthews, 1982; Swart, 2015), although
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52 688 this trend is not described as linear but hyperbolic (Lohmann, 1988). Additionally, while it is
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54 689 conceivable that a mixing-zone exists in the coastal area of a hypersaline lake, there is no evidence
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56 690 that lacustrine carbonates in Hainsfarth have (only) been altered in this environment. As successive
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58 691 exposure surfaces are stratigraphically close to one another, it is plausible that the same carbonates
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60 692 were repetitively altered by meteoric fluids during recurring emergence, achieving homogenization of
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694 $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values. The identification under CL of two successive stages of precipitation of sparry
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696 calcite (Fig. 6B and F) indeed suggests repetitive meteoric-driven cementation (the blue intrinsic
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698 luminescence) related to groundwater vertical movement, potentially interrupted by (shallow) burial
diagenesis (the zoned or bright orange luminescence). Similar successive phases of meteoric
diagenesis have been observed in ancient lacustrine settings through petrographic (CL) and
geochemical ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) methods (Benito et al., 2001; Alonso-Zarza et al., 2003). High variability

699 in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values, especially amongst negative ones, points to variable ratios of altered and
700 preserved carbonates.

701 The maximal amplitude (in ‰) of the negative shifts ensuing from meteoric diagenesis can, in
702 the best case, only be assessed. Several studies reported freshwater alteration in marine carbonate
703 environments to be a fast process, achieving to considerably or completely alter primary features in
704 10^0 to 10^3 years (Halley & Harris, 1979; Budd & Land, 1990; Dravis, 1996). Even if climate was
705 semi-arid during Ries Lake development (Böhme et al., 2001, 2007; Prieto et al., 2009), meteoric or
706 freshwater diagenesis should have transformed primary carbonates of the Hainsfarth bioherms
707 relatively rapidly or sequentially. At this mid-latitude setting and assuming a certain degree of
708 continentality (Orszag-Sperber et al, 1993; <https://deeptimemaps.com>), a $\delta^{18}\text{O}$ depletion by 7 to 12‰
709 relative to primary signatures due to meteoric fluids is reasonable (Hays & Grossman, 1991). Younger
710 marginal lacustrine carbonates (bioherms from the Staudigberg member; Arp, 2006; Arp et al., 2013)
711 developing when lake conditions were more saline (more arid?) are characterized by equivalent,
712 mostly positive $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values and meteoric cements have $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ reported as low, if not
713 lower, than diagenetic calcite in Hainsfarth bioherms (down to -9.3‰ and -6.4‰, respectively; Pache
714 et al., 2001)

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717 CONCLUSIONS

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719 This study presents the first outcrop-based $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ chemostratigraphic and component-specific
720 geochemical and petrographic investigation of carbonate deposits from the closed-lake-system of the
721 Miocene Ries Crater Lake in Hainsfarth quarry, Southern Germany. The aim was to identify ancient
722 subaerial exposure events in a marginal lacustrine setting through stable isotope geochemistry, and
723 above all to assess the applicability of chemostratigraphic approach for the identification of
724 sedimentary cycles previously recognized based on vertical and lateral facies change.

- 725 • The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ chemostratigraphic study fails to identify shifts associated to subaerial
726 exposure surfaces and to the recognition of sedimentary cycles.
- 727 • Emergent episodes, mentioned in previous studies for Hainsfarth carbonates, are identified on the
728 **base** of petrographic properties of meteoric vadose and phreatic cements, and the frequent
729 enrichment of siliciclastic material.
- 730 • Sparry calcite carrying very negative $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ signatures point to precipitation in a
731 meteoric–phreatic environment.
- 732 • The abundance of meteoric cements in Hainsfarth carbonates (and not only within the immediate
733 interval beneath sedimentary cycle tops) can be related to the high porosity in the rocks. The
734 omnipresence of these cements is interpreted in terms of repetitive emergent episodes and

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3 735 freshwater diagenesis pervasively affecting subsurface deposits. Only *Cladophorites* build-ups
4 736 are less altered by meteoric diagenesis due to their initial fine-grained lithology.
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6 737 • Clear positive covariance between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ is observed for Hainsfarth, similar to previous
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8 738 basal studies of the Ries Lake that interpreted this covariance to reflect changes in lake water
9 739 chemistry from freshwater (negative $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) to saline conditions (positive $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$).
10 740 However, the nature of the covariance between carbon and oxygen isotope compositions for the
11 741 carbonates of Hainsfarth differs from that of previous studies. Negative $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ do not
12 742 characterize primary carbonates formed in a lacustrine freshwater environment but reflect
13 743 extensive meteoric diagenesis, while the positive $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ closely seemingly witness marine
14 744 to saline evaporative conditions of the lake water at the time of deposition. Burial diagenesis is
15 745 considered to be a marginal and shallow process in the history of Hainsfarth carbonates with
16 746 weak influence on their geochemical signature.
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18 747 • *Cladophorites* fabrics that are largely unaffected by meteoric alteration, and indeed carry the most
19 748 positive $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values, have reduced porosities. Preserved ostracod shells also carry
20 749 amongst the least negative $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ signatures which probably reflect the saline chemical
21 750 conditions of lake water.
22
23 751 • Such evaporative conditions are in agreement with previous work mentioning similar
24 752 circumstances for time-equivalent basinward deposits.
25
26 753 • This study emphasizes that caution is required before interpreting $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in ancient
27 754 carbonate sedimentary cycles, because stable isotopes represent circumstantial tools that usually
28 755 need to be supported by additional geochemical and petrographic methods. A combination of
29 756 approaches and evidence is mandatory in (marginal) lacustrine systems where the geochemical
30 757 nature of coexisting carbonates is complex and often strongly variable.
31
32 758 • The present study is of significance for those investigating palaeolacustrine systems: it shows that
33 759 ancient marginal lacustrine carbonates, while challenged by extensive meteoric weathering, are
34 760 capable of providing key information for palaeoenvironmental reconstruction and the
35 761 understanding of fluid flow patterns, porosity evolution and diagenetic processes in relation to
36 762 those primary conditions.
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764 **ACKNOWLEDGEMENTS**

765 Birgit Plessen (GFZ, Potsdam) is acknowledged for a precious assistance in the laboratory. We are
766 also grateful to Christine Fischer for the preparation of thin sections, and to Christina Günter and Uwe
767 Altenberger for their help with the SEM.
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770 REFERENCES

771

772 **Abdul Aziz, H., Böhme, M., Rocholl, A., Zwing, A., Prieto, J., Wijbrans, J.R., Heissig, K. and**
773 **Bachtadse, V.** (2008) Integrated stratigraphy and $40\text{Ar}/39\text{Ar}$ chronology of the Early to Middle
774 Miocene Upper Freshwater Molasse in eastern Bavaria (Germany). *Int. J. Earth Sci.*, **97**, 115-134.

775 **Allan, J.R. and Matthews, R.K.** (1977) Carbon and oxygen isotopes as diagenetic and stratigraphic
776 tools: Surface and subsurface data, Barbados, West Indies. *Geology*, **5**, 16-20.

777 **Allan, J.R. and Matthews, R.K.** (1982) Isotope signatures associated with early meteoric diagenesis.
778 *Sedimentology*, **29**, 797-817.

779 **Alonso-Zarza, A.M.** (2003) Palaeoenvironmental significance of palustrine carbonates and calcretes
780 in the geological record. *Earth-Sci. Rev.*, **60**, 261-298.

781 **Anadón, P., Utrilla, R., Vázquez, A., Martín-Rubio, M., Rodríguez-Lázaro, J. and Robles, F.** (2008)
782 Palaeoenvironmental evolution of the Pliocene Villarroya Lake, northern Spain, from stable isotopes
783 and trace-element geochemistry of ostracods and molluscs. *J. Paleolimnol.*, **39**, 399-419.

784 **Anadon, P., Moscariello, A., Rodriguez-Lazaro, J. and Filippi, M.L.** (2006) Holocene environmental
785 changes of lake Geneva (Lac Lemán) from stable isotopes ($\delta\text{C-13}$, $\delta\text{O-18}$) and trace element
786 records of ostracod and gastropod carbonates. *J. Paleolimnol.*, **35**, 593-616.

787 **Anderson, W.T., Mullins, H.T. and Ito, E.** (1997) Stable isotope record from Seneca Lake, New York:
788 Evidence for a cold paleoclimate following the Younger Dryas. *Geology*, **25**, 165-138.

789 **Andrews, J.E.** (2006) Paleoclimatic records from stable isotopes in riverine tufas: Synthesis and
790 review. *Earth-Sci. Rev.*, **75**, 85-104.

791 **Arp, G.** (1995) Lacustrine bioherms, spring mounds, and marginal carbonates of the Ries-impact-
792 crater (Miocene, Southern Germany). *Facies*, **33**, 35-89.

793 **Arp, G.** (2006) Sediments of the Ries Crater Lake (Miocene, Southern Germany). In: *Sediment 2006:*
794 *21th Meeting of Sedimentologists / 4th Meeting of SEPM Central European Section*, pp. 213-235.

795 **Arp, G., Blumenberg, M., Hansen, B.T., Jung, D., Kolepka, C., Lenz, O., Nolte, N., Poschlod, K.,**
796 **Reimer, A. and Thiel, V.** (2013) Chemical and ecological evolution of the Miocene Ries impact crater
797 lake, Germany: A reinterpretation based on the Enkingen (SUBO 18) drill core. *Geol. Soc. Am. Bull.*,
798 **125**, 1125-1145.

799 **Arp, G., Hansen, B.T., Pack, A., Reimer, A., Schmidt, B.C., Simon, K., Jung, D.** (2017) The soda lake—
800 mesosaline halite lake transition in the Ries impact crater basin (drilling Löpsingen 2012, Miocene,
801 southern Germany). *Facies*, **63**. DOI 10.1007/s10347-016-0483-7.

802 **Barnaby, R.J. and Rimstidt, J.D.** (1989) Redox conditions of calcite cementation interpreted from Mn
803 and Fe contents of authigenic calcites. *Geol. Soc. Am. Bull.*, **101**, 795-804.

804 **Beier, J.A.** (1987) Petrographic and geochemical analysis of caliche profiles in a Bahamian Pleistocene
805 dune. *Sedimentology*, **34**, 991-998.

806 **Benito, M.I., Lohmann, K.C. and Mas, R.** (2001) Discrimination of multiple episodes of meteoric
807 diagenesis in a Kimmeridgian reefal complex, North Iberian Range, Spain. *J. Sed. Res.*, **71**, 380-393.

808 **Bennett, C.E., Williams, M., Leng, M.J., Siveter, D.J., Davies, S.J., Sloane, H.J. and Wilkinson, I.P.**
809 (2011) Diagenesis of fossil ostracods: Implications for stable isotope based palaeoenvironmental
810 reconstruction. *Palaeogeogr., Palaeoclimatol., Palaeoecol.*, **305**, 150-161.

811 **Böhme, M., Bruch, A.A. and Selmeier, A.** (2007) The reconstruction of Early and Middle Miocene
812 climate and vegetation in Southern Germany as determined from the fossil wood flora. *Palaeogeogr.,*
813 *Palaeoclimatol., Palaeoecol.*, **253**, 91-114.

814 **Böhme, M., Gregor, H.-J. and Heissig, K.** (2001) The Ries- and Steinheim meteorite impacts and their
815 effect on environmental conditions in time and space. In: *Geological and Biological Effects of Impact*
816 *Events* (Ed E. Buffetaut, Koebel, C. (Eds.)), pp. 215-235. Springer, Berlin.

817 **Börner, N., De Baere, B., Yang, Q., Jochum, K.P., Frenzel, P., Andreae, M.O. and Schwab, A.** (2013)
818 Ostracod shell chemistry as proxy for palaeoenvironmental change. *Quatern.Int.*, **313–314**, 17-37.

819 **Brand, U.** (2004) Carbon, oxygen and strontium isotopes in Paleozoic carbonate components: an
820 evaluation of original seawater-chemistry proxies. *Chem. Geol.*, **204**, 23-44.

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3 821 **Buchner, E., Schwarz, W.H., Schmieder, M. and Trieloff, M.** (2010) Establishing a 14.6 ± 0.2 Ma age
4 822 for the Nördlinger Ries impact (Germany)—A prime example for concordant isotopic ages from
5 823 various dating materials. *Meteoritics & Planetary Science*, **45**, 662-674.
- 6 824 **Buchner, E., Schmieder, M., Schwarz, W.H. and Trieloff, M.** (2013) The age of the Nördlinger Ries
7 825 impact crater (Germany) - an overview and brief discussion of the new isotopic ages for the Ries
8 826 impact. *Zeitschrift der Deutschen Gesellschaft für Geowissenschaften*, **164**, 433-445.
- 9 827 **Budd, D.A. and Land, L.S.** (1990) Geochemical imprint of meteoric diagenesis in Holocene ooid sands,
10 828 Schoner Cays, Bahamas: Correlation of calcite cement geochemistry with extant groundwaters. *J.*
11 829 *Sed. Petrol.*, **60**, 361-378.
- 12 830 **Chamberlain, C.P., Wan, X.Q., Graham, S.A., Carroll, A.R., Doebbert, A.C., Sageman, B.B., Blisniuk,**
13 831 **P., Kent-Corson, M.L., Wang, Z. and Wang, C.S.** (2013) Stable isotopic evidence for climate and basin
14 832 evolution of the Late Cretaceous Songliao basin, China. *Palaeogeogr., Palaeoclimatol., Palaeoecol.*,
15 833 **385**, 106-124.
- 16 834 **Christ, N., Immenhauser, A., Amour, F., Mutti, M., Preston, R., Whitaker, F.F., Peterhänsel, A.,**
17 835 **Egenhoff, S.O., Dunn, P.A. and Agar, S.M.** (2012a) Triassic Latemar cycle tops - Subaerial exposure of
18 836 platform carbonates under tropical arid climate. *Sed. Geol.*, **265-266**, 1-29.
- 19 837 **Christ, N., Immenhauser, A., Amour, F., Mutti, M., Tomás, S., Agar, S.M., Always, R. and Kabiri, L.**
20 838 (2012b) Characterization and interpretation of discontinuity surfaces in a Jurassic ramp setting (High
21 839 Atlas, Morocco). *Sedimentology*, **59**, 249-290.
- 22 840 **Danielopol, D.L., Casale, L.M. and Olteanu, R.** (1986) On the preservation of carapaces of some
23 841 limnic ostracods: An exercise in actuopalaeontology. *Hydrobiologia*, **143**, 143-157.
- 24 842 **Decrouy, L., Vennemann, T.W. and Ariztegui, D.** (2011) Controls on ostracod valve geochemistry:
25 843 Part 2. Carbon and oxygen isotope compositions. *Geochim. Cosmochim. Acta*, **75**, 7380-7399.
- 26 844 **Depeche, F.** (1982) Ultrastructure of the wall of two living ostracods, *Herpetocypris chevreuxi* (Sars)
27 845 and *Pontocythere elongate* (Brady), in comparison with fossil ostracods from the Middle Jurassic of
28 846 Normandy. In: *Fossil and Recent ostracods* (Ed E.R.L.M.S.e. R. H. Bate), pp. 61-75. Ellis Horwood Ltd.,
29 847 London, London.
- 30 848 **Dickson, J.A.D. and Coleman, M.L.** (1982) Changes in carbon and oxygen isotope composition during
31 849 limestone diagenesis. *Sedimentology*, **27**, 107-118.
- 32 850 **Dravis, J.** (1996) Rapidity of freshwater calcite cementation - implications for carbonate diagenesis
33 851 and sequence stratigraphy. *Sed. Geol.*, **107**, 1-10.
- 34 852 **Dwyer, G.S., Cronin, T.M. and Baker, P.A.** (2002) Trace elements in marine ostracodes. In: *American*
35 853 *Geophysical Union monograph 131. The ostracoda: applications in quaternary research* (Ed J.A.H.A.R.
36 854 Chivas). American Geophysical Union, Washington, DC.
- 37 855 **Ehrenberg, S.N., Svänå, T.A. and Swart, P.K.** (2008) Uranium depletion across the Permian–Triassic
38 856 boundary in Middle East carbonates: Signature of oceanic anoxia. *AAPG Bulletin*, **92**, 691-707.
- 39 857 **Einsele, G.** (2000) *Sedimentary Basins*. Springer-Verlag Berlin Heidelberg, 792 pp.
- 40 858 **Emrich, K., Ehhalt, D.H. and Vogel, J.C.** (1970) Carbon isotope fractionation during the precipitation
41 859 of calcium carbonate. *Earth Planet. Sci. Lett.*, **8**, 363-371.
- 42 860 **Flügel, E.** (2004) *Microfacies of Carbonate Rocks*. Springer-Verlag Berlin, 976 pp.
- 43 861 **Gentner, W. and Wagner, G.A.** (1969) Alterbestimmung an Riesgläsern und Moldaviten. *Geol.*
44 862 *Bavarica*, **61**, 296-303.
- 45 863 **Gierlowski-Kordesch, E.H.** (2010) Lacustrine Carbonates. *Dev. Sedimentol.*, **61**, 1-101.
- 46 864 **Godet, A., Durlet, C., Spangenberg, J.E. and Fölmml, K.B.** (2016) Estimating the impact of early
47 865 diagenesis on isotope records in shallow-marine carbonates: A case study from the Urgonian
48 866 Platform in western Swiss Jura. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, **454**, 125-138.
- 49 867 **Goldstein, R.H.** (1991) Stable isotope signatures associated with paleosols, Pennsylvanian Holder
50 868 Formation, New Mexico. *Sedimentology*, **38**, 67-77.
- 51 869 **Gouramanis, C., Wilkins, D. and De Deckker, P.** (2010) 6000 years of environmental changes
52 870 recorded in Blue Lake, South Australia, based on ostracod ecology and valve chemistry. *Palaeogeogr.*
53 871 *Palaeoclimatol. Palaeoecol.*, **297**, 223-237.
- 54
55
56
57
58
59
60

- 1
2
3 872 **Gray, A.F. and Adams, A.E.** (1995) Sheet voids and radial fibrous calcite cement fills from Upper
4 873 Jurassic beachrock, Calcaires Blancs de Provence, southeast France. *Carbonates Evaporites*, **10**.
5 874 **Halley, R.B. and Harris, P.M.** (1979) Fresh-water cementation of a 1,000-year-old oolite. *J. Sed. Res.*,
6 875 **49**, 969-987.
7 876 **Hays, P.D. and Grossman, E.L.** (1991) Oxygen isotopes in meteoric calcite cements as indicators of
8 877 continental paleoclimate. *Geology*, **19**, 441-444.
9 878 **Heaton, T.H.E., Holmes, J.A. and Bridgwater, N.D.** (1995) Carbon and oxygen isotope variations
10 879 among lacustrine ostracods: Implications for palaeoclimatic studies. *Holocene*, **5**, 428-434.
11 880 **Holmes, J.A.** (1996) Trace-element and stable-isotope geochemistry of non-marine ostracod shells in
12 881 Quaternary palaeoenvironmental reconstruction. *J. Paleolimnol.*, **15**, 223-235.
13 882 **Immenhauser, A., Della Porta, G., Kenter, J.A.M. and Bahamonde, J.R.** (2003) An alternative model
14 883 for positive shifts in shallow-marine carbonate $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$. *Sedimentology*, **50**, 953-959.
15 884 **Immenhauser, A., Kenter, J.A.M., Ganssen, G., Bahamonde, J.R., Van Vliet, A. and Saher, M.H.**
16 885 (2002) Origin and significance of isotope shifts in Pennsylvanian carbonates (Asturias, NW Spain) *J.*
17 886 *Sed. Res.*, **72**, 82-94.
18 887 **Jankowski, B.** (1981) Die Geschichte der Sedimentation im Nördlinger Ries und Randecker Maar.
19 888 *Bochumer geol. geotechn. Abh.*, 1-315.
20 889 **Janz, H.** (1995) Neubeschreibung von *Strandesia risgoviensis* nov. comb. (Sieber 1905) (Crustacea,
21 890 Ostracoda) aus dem Nördlinger Ries (Miozän, Süddeutschland). *Stuttgarter Beitr Naturk B*, **233**, 1-17.
22 891 **Janz, H. and Vennemann, T.W.** (2005) Isotopic composition (O, C, Sr, and Nd) and trace element
23 892 ratios (Sr/Ca, Mg/Ca) of Miocene marine and brackish ostracods from North Alpine Foreland deposits
24 893 (Germany and Austria) as indicators for palaeoclimate. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*,
25 894 **225**, 216-247.
26 895 **Joachimski, M.M.** (1994) Subaerial exposure and deposition of shallowing upward sequences:
27 896 evidence from stable isotopes of Purbeckian peritidal carbonates (basal Cretaceous), Swiss and
28 897 French Jura Mountains. *Sedimentology*, **41**, 805-824.
29 898 **Junge, F.W. and Bottger, T.** (1994) Isotope geochemical studies on carbonates of Quaternary glacio-
30 899 lacustrine lake-sediments as indicators of paleoenvironment. *Isotopenpraxis*, **30**, 9-21.
31 900 **Keatings, K.W., Heaton, T.H.E. and Holmes, J.A.** (2002) Carbon and oxygen isotope fractionation in
32 901 non-marine ostracods: results from a 'natural culture' environment. *Geochim. Cosmochim. Acta*, **66**,
33 902 1701-1711.
34 903 **Kontrovitz, M., Ainsworth, N.R., Burnett, R.D. and Slack, J.M., 1992** (1992) Induced color in
35 904 ostracode shells: an experimental study. *The University of Kansas Paleontological Contributions, New*
36 905 *Series*, **2**, 1-10.
37 906 **van der Kooij, B., Immenhauser, A., Steuber, T., Bahamonde, J.R. and Merino Tomé, O.** (2010)
38 907 Precipitation mechanisms of volumetrically important early marine carbonate cement volumes in
39 908 deep slope settings. *Sedimentology*, **57**, 1491-1525.
40 909 **Kwiecien, O., Arz, H.W., Lamy, F., Plessen, B., Bahr, A. and Haug, G.H.** (2009) North Atlantic control
41 910 on precipitation pattern in the eastern Mediterranean/Black Sea region during the last glacial.
42 911 *Quatern. Res.*, **71**, 375-384.
43 912 **Leng, M.J. and Marshall, J.D.** (2004) Palaeoclimate interpretation of stable isotope data from lake
44 913 sediment archives. *Quatern. Sci. Rev.*, **23**, 811-831.
45 914 **Leng, M.J., Roberts, N., Reed, J.M. and Sloane, H.J.** (1999) Late Quaternary palaeohydrology of the
46 915 Konya Basin, Turkey, based on isotope studies of modern hydrology and lacustrine carbonates. *J.*
47 916 *Paleolimnol.*, **22**, 187-204.
48 917 **Li, H.C. and Ku, T.L.** (1997) $\delta^{13}\text{C}$ - $\delta^{18}\text{C}$ covariance as a paleohydrological indicator for closed-basin
49 918 lakes. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, **133**, 69-80.
50 919 **Li, X.Z., Zhou, X., Liu, W.G., Wang, Z., He, Y.X. and Xu, L.M.** (2016) Carbon and oxygen isotopic
51 920 records from Lake Tuosu over the last 120 years in the Qaidam Basin, Northwestern China: The
52 921 implications for paleoenvironmental reconstruction. *Global Planet. Change*, **141**, 54-62.
53 922 **Lohmann, K.C.** (1988) Geochemical Patterns of Meteoric Diagenetic Systems and Their Application to
54 923 Studies of Paleokarst. In: *Paleokarst* (Eds N.P. James and P.W. Choquette), pp. 58-80. Springer, Berlin.

- 1
2
3 924 **Lohmann, K.C. and Meyers, W.J.** (1977) Microdolomite inclusions in cloudy prismatic calcites: a
4 925 proposed criterion for former high-magnesium calcites. *J. Sed. Res.*, **47**, 1078-1088.
- 5 926 **Mangili, C., Brauer, A., Plessen, B., Dulski, P., Moscariello, A. and Naumann, R.** (2010) Effects of
6 927 detrital carbonate on stable oxygen and carbon isotope data from varved sediments of the
7 928 interglacial Pianico palaeolake (Southern Alps, Italy). *J. Quatern. Sci.*, **25**, 135-145.
- 8 929 **Mangili, C., Brauer, A., Plessen, B. and Moscariello, A.** (2007) Centennial-scale oscillations in oxygen
9 930 and carbon isotopes of endogenic calcite from a 15,500 varve year record of the Piànico interglacial.
10 931 *Quatern. Sci. Rev.*, **26**, 1725-1735.
- 11 932 **Marshall, J.D.** (1992) Climatic and oceanographic isotopic signals from the carbonate rock record and
12 933 their preservation. *Geol. Mag.*, **129**, 143-160.
- 13 934 **Marshall, J. D., Lang, B., Crowley, S. F., Weedon, G. P., van Calsteren, P., Fisher, E. H., Holme, R.,**
14 935 **Holmes, J. A., Jones, R. T., Bedford, A., Brooks, S. J., Bloemendal, J., Kiriakoulakis, K. and Ball, J. D.**
15 936 (2007) Terrestrial impact of abrupt changes in the North Atlantic thermohaline circulation: Early
16 937 Holocene, UK. *Geology*, **35**, 639-642.
- 17 938 **Mayr, C., Laprida, C., Lucke, A., Martin, R. S., Massafiero, J., Ramon-Mercau, J. and Wissel, H.**
18 939 (2015) Oxygen isotope ratios of chironomids, aquatic macrophytes and ostracods for lake-water
19 940 isotopic reconstructions - Results of a calibration study in Patagonia. *J. Hydrol.*, **529**, 600-607.
- 20 941 **Mazzini, I., Hudackova, N., Joniak, P., Kovacova, M., Mikes, T., Mulch, A., Rojay, F.B., Lucifora, S.,**
21 942 **Esu, D. and Soulie-Marsche, I.** (2013) Palaeoenvironmental and chronological constraints on the
22 943 Tuglu Formation (Cankiri Basin, Central Anatolia, Turkey). *Turk. J. Earth Sci.*, **22**, 747-777.
- 23 944 **Melezhik, V.A., Fallick, A.E. and Kuznetsov, A.B.** (2005) Palaeoproterozoic, rift-related, ¹³C-rich,
24 945 lacustrine carbonates, NW Russia. Part II: Global isotope signal recorded in the lacustrine
25 946 dolostones. *Trans. Roy. Soc. Edinb. Earth Sci.*, **95**, 423-444.
- 26 947 **Mischke, S., Fuchs, D., Riedel, F. and Schudack, M.E.** (2002) Mid to Late Holocene
27 948 palaeoenvironment of Lake Eastern Juyanze (north-western China) based on ostracods and stable
28 949 isotopes. *Geobios*, **35**, 99-110.
- 29 950 **Montgomery, E., Al-Suwaidi, A.H., Suarez, M.B., Kirkland, J.I. and Suarez, C.A.** (2014) Exploring the
30 951 Stable Isotope Record of Lake Carpenter: A Lacustrine Sequence in the Aptian-Albian Cretaceous
31 952 Cedar Mountain Formation, Utah, USA. Abstract PP13A-1398 presented at 2014 Fall Meeting, AGU,
32 953 San Francisco, Calif., 15-19 Dec.
- 33 954 **Mutti, M. and Bernoulli, D.** (2003) Early marine lithification and hardground development on a
34 955 Miocene ramp (Maiella, Italy): key surfaces to track changes in trophic resources in nontropical
35 956 carbonate settings, *J. Sed. Res.*, **73**, 296-308.
- 36 957 **Niemann, J.C. and Read, J.F.** (1988) Regional cementation from unconformity-recharged aquifer and
37 958 burial fluids, Mississippian Newman Limestone, Kentucky. In: *Carbonate Sedimentology and*
38 959 *Petrology* (Eds P.A. Scholle, N.P. James and J.F. Read), pp. 334. American Geophysical Union,
39 960 Washington D.C.
- 40 961 **Oehlerich, M., Mayr, C., Gussone, N., Hahn, A., Hölzl, S., Lücke, A., Ohlendorf, C., Rummel, S.,**
41 962 **Teichert, B.M.A. and Zolitschka, B.** (2015) Lateglacial and Holocene climatic changes in south-eastern
42 963 Patagonia inferred from carbonate isotope records of Laguna Potrok Aike (Argentina). *Quatern. Sci.*
43 964 *Rev.*, **114**, 189-202.
- 44 965 **Orszag-Sperber, F., Butterlin, J., Clermonte, J., Colchen, M., Guiraud, R., A., P. and Ricou, L.E.** (1993)
45 966 Tortonian (11.5-6). In: *Atlas Tethys Palaeoenvironmental Maps. Explanatory Notes.* (Ed J. Dercourt,
46 967 Ricou, L. E. and Vrielynck, B. (eds)), pp. 243-258. Gauthier-Villars, Paris.
- 47 968 **Pache, M., Reitner, J. and Arp, G.** (2001) Geochemical evidence for the formation of a large miocene
48 969 "travertine" mound at a sublacustrine spring in a soda lake (Wallerstein castle rock, nördlinger ries,
49 970 Germany). *Facies*, **45**, 211-230.
- 50 971 **Pohl, J., Stoeffler, D., Gall, H. and Ernstson, K.** (1977) The Ries impact crater. In: *Impact and*
51 972 *explosion cratering: Planetary and terrestrial implications; Proceedings of the Symposium on*
52 973 *Planetary Cratering Mechanics, Flagstaff, Ariz. , September 13-17, 1976*, pp. 343-404. Pergamon
53 974 Press, Inc., New York.
- 54
55
56
57
58
59
60

- 1
2
3 975 **Prieto, J., Böhme, M., Maurer, H., Heissig, K. and Abdul Aziz, H.** (2009) Biostratigraphy and
4 976 sedimentology of the Fluviale Untere Serie (Early and Middle Miocene) in the central part of the
5 977 North Alpine Foreland Basin: implications for palaeoenvironment and climate. *Intern. J. Earth Sci.*, **98**,
6 978 1767-1791.
- 7 979 **Richter, D.K., Götte, T., Götze, J. and Neuser, R.D.** (2003) Progress in application of
8 980 cathodoluminescence (CL) in sedimentary petrology. *Mineralogy and Petrology*, **79**, 127-166.
- 9 981 **Richter, D.K., Neuser, R.D., Schreuer, J., Gies, H. and Immenhauser, A.** (2011) Radial-fibrous
10 982 calcites: A new look at an old problem. *Sed. Geol.*, **239**, 23-36.
- 11 983 **Riding, R.** (1979) Origin and diagenesis of lacustrine algal bioherms at the margin of the Ries crater,
12 984 Upper Miocene, southern Germany. *Sedimentology*, **26**, 645-680.
- 13 985 **Romanek, C.S., Grossman, E.L. and Morse, J.W.** (1992) Carbon isotopic fractionation in synthetic
14 986 aragonite and calcite: Effects of temperature and precipitation rate. *Geochim. Cosmochim. Acta*, **56**,
15 987 419-430.
- 16 988 **Rothe, P. and Hoefs, J.** (1977) Isotopen-geochemische Untersuchungen an Karbonaten der Ries-See-
17 989 Sedimente der Forschungsbohrung Nördlingen 1973. *Geol. Bavar.*, 59-66.
- 18 990 **Sanz, M.E., Calvo, J.P., García del Cura, M.A., Ordóñez, S.** (1991) Origin and diagenesis of calcretes in
19 991 Upper Miocene limestones, Southern Madrid Basin, Spain. *Rev. Soc. Geol. Esp.*, **4**, 127-142.
- 20 992 **Schwarz, W.H. and Lippolt, H.J.** (2014) ⁴⁰Ar-³⁹Ar step-heating of impact glasses from the Nördlinger
21 993 Ries impact crater—Implications on excess argon in impact melts and tektites. *Meteoritics &*
22 994 *Planetary Sci.*, **49**, 1023-1036.
- 23 995 **Sheppard, S.M.F. and Schwarcz, H.P.** (1970) Fractionation of carbon and oxygen isotopes and
24 996 magnesium between coexisting metamorphic calcite and dolomite. *Contrib. Mineral. Petrol.*, **26**, 161-
25 997 198.
- 26 998 **Stansell, N. D., Steinman, B. A., Abbott, M. B., Rubinov, M., Roman-Lacayo, M.** (2013) Lacustrine
27 999 stable isotope record of precipitation changes in Nicaragua during the Little Ice Age and Medieval
30 1000 Climate Anomaly. *Geology*, **41**, 151-154.
- 31 1001 **Staudacher, T., Jessberger, E.K., Dominik, B., Kirsten, T. and Schaeffer, O.A.** (1982) Ar-40-Ar-39 ages
32 1002 of rocks and glasses from the Noerdlinger Ries crater and the temperature history of impact breccias.
33 1003 *J. Geophys.*, **51**, 1-11.
- 34 1004 **Stevens, L.R., Stone, J.R., Campbell, J. and Fritz, S.C.** (2006) A 2200-yr record of hydrologic variability
35 1005 from Foy Lake, Montana, USA, inferred from diatom and geochemical data. *Quatern. Res.*, **65**, 264-
36 1006 274.
- 37 1007 **Swart, P.K.** (2015) The geochemistry of carbonate diagenesis: The past, present and future.
38 1008 *Sedimentology*, **62**, 1233-1304.
- 39 1009 **Talbot, M.R.** (1990) A review of the palaeohydrological interpretation of carbon and oxygen isotopic
40 1010 ratios in primary lacustrine carbonates. *Chem. Geol.*, **80**, 261-279.
- 41 1011 **Tütken, T., Vennemann, T.W., Janz, H. and Heimann, E.P.J.** (2006) Palaeoenvironment and
42 1012 palaeoclimate of the Middle Miocene lake in the Steinheim basin, SW Germany: A reconstruction
43 1013 from C, O, and Sr isotopes of fossil remains. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, **241**, 457-491.
- 44 1014 **Vasconcelos, C., McKenzie, J.A., Warthmann, R. and Bernasconi, S.M.** (2005) Calibration of the delta
45 1015 O-18 paleothermometer for dolomite precipitated in microbial cultures and natural environments.
46 1016 *Geology*, **33**, 317-320.
- 47 1017 **von Grafenstein, U., Erlenkeuser, H. and Trimborn, P.** (1999) Oxygen and carbon isotopes in
48 1018 modern fresh-water ostracod valves: assessing vital offsets and autecological effects of interest for
49 1019 palaeoclimate studies. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, **148**, 133-152.
- 50 1020 **Wilson, P.A. and Dickson, J.A.D.** (1996) Radial calcite: Alteration product of and petrographic
51 1021 proxy for magnesian calcite marine cement. *Geology*, **24**, 945-948.
- 52 1022 **Wittkop, C., Teranes, J., Lubenow, B. and Dean, W.E.** (2014) Carbon- and oxygen-stable isotopic
53 1023 signatures of methanogenesis, temperature, and water column stratification in Holocene siderite
54 1024 varves. *Chem. Geol.*, **389**, 153-166.
- 55 1025 **Xia, J., Ito, E. and Engstrom, D.R.** (1997) Geochemistry of ostracode calcite: Part 1. An experimental
56 1026 determination of oxygen isotope fractionation. *Geochim. Cosmochim. Acta*, **61**, 377-382.

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1028 **FIGURE CAPTIONS**

1029 Fig. 1. Location of the study area and the precedent studies and drilling campaigns undertaken within
1030 the palaeo Ries basin. Modified after Arp et al., 2013.

1031 Fig. 2. Simplified north–south cross-section of the Ries Lake with position of the two precedent
1032 drilling campaigns (yellow and blue) and the location of the present outcrop study (red circle and star).
1033 Modified after Arp et al., 2013.

1034 Fig. 3. The Hainsfarth study outcrop. (A) Well-preserved outcropping algal–microbial (*Cladophorites*)
1035 buildups. Total height of the outcrop is *ca* 6 to 7 m. (B) High-resolution sampling strategy for
1036 petrographic and chemical analyses, here on section 1. (C) Aerial Google Earth view of the outcrop
1037 and the relative location of the five investigated stratigraphic sections; Position of the stratigraphic
1038 section investigated by Arp et al., (1995) is shown by the blue arrow.

1039 Fig. 4. Overview of the main microfacies present within Hainsfarth lacustrine carbonates. (A)
1040 Ostracodal–peloidal packstone from the bioclastic–peloidal packstone to grainstone facies; (B)
1041 Nodular *Cladophorites* boundstone. Algal–microbial micrite growing onto peloidal grainstone facies.
1042 (C) Conoidal *Cladophorites* framestone. Transversal section of densely packed filaments or tubes of
1043 *Cladophorites* algae. (D) Palustrine facies composed of reworked clasts of *Cladophorites* boundstone,
1044 grainstone facies and siliciclastics. Note that a stromatolite facies can also be observed, sometimes
1045 terminating cycles C5 to C7 (see section 3 and 5 in Fig. 9). For an exhaustive description of the facies
1046 present at Hainsfarth, the reader is directed to the previous publications of Riding (1979) and Arp
1047 (1995, 2006).

1048 Fig. 5. Ideal freshwater to saline ‘bioherms’ cycle of the Hainsfarth outcrop and the expected
1049 occurrence of different facies types.

1050 Fig. 6. Diagenetic phases observed under transmitted light and equivalent cathodoluminescence
1051 microscopy (CL); scale is 1 mm. (A) Highly cemented bioclastic grainstone facies by secondary
1052 blocky calcite. (B) Same photograph under CL: ‘1’ dull-orange luminescent isopachous microdolomite
1053 phase; ‘2a/2b’ dark blue luminescent blocky calcite separated by a ‘3’ thin bright luminescent phase of
1054 the same blocky calcite. (C) Meteoric vadose pendant and meniscus cements in a bioclastic–peloidal
1055 grainstone. (D) Same photograph under CL showing the dark blue luminescence of the gravitational
1056 cements followed by a dull orange-red (microdolomite?) phase. (E) Blocky calcite and siliciclastics
1057 (black material) partly filling a secondary pore space. (F) Same photograph under CL. Several phases
1058 of dark blue luminescent calcite are also recognized here ‘2’ separated by a thin bright luminescent
1059 phase ‘3’. Note the red-brown characteristic luminescence of the clastics ‘cl’ punctuated by yellow,
1060 blue and green luminescent minerals, such as quartz and clays. (G) Siliciclastics filling the porosity of
1061 a peloidal packstone to grainstone. Note the roundness of the edges between siliciclastics and open
1062 pore spaces, suggesting post-depositional dissolution of ?peloids. (H) Same photograph under CL with
1063 brown luminescent clastics and dissolved ?peloids (d). (I) Ostracod–peloidal packstone showing
1064 several assembled and disarticulated shells of the ostracod species *Strandesia risgoviensis*. (J) Note the
1065 varying luminescence of different shells (‘a’ to ‘d’) certainly accounting for varying alteration degrees.

1066 Fig. 7. Paragenetic sequence of diagenetic processes in the Hainsfarth marginal lacustrine carbonates.
1067 Note the discrete burial diagenesis and the absence of deep burial alteration.

1068 Fig. 8. Carbon (black curve) and oxygen (grey curve) isotope chemostratigraphy along the five
1069 investigated stratigraphic sections 1 to 5.

1070 Fig. 9. Stratigraphic profiles 1 to 5 with their respective facies distribution and oxygen isotope
1071 chemostratigraphic curve. Note the difficulty to correlate individual curves together, while (freshwater
1072 to saline) climatic cycles (C1 to C7) are well-constrained by sedimentological continuity of cycle

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3 1073 boundaries. For clarity, the $\delta^{13}\text{C}$ curves are not shown because they show a nearly identical trend to
4 1074 $\delta^{18}\text{O}$ curves. For key to symbols, see Fig. 8.

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6 1075 Fig. 10. (A) Two aspects or degrees of preservation of the same ostracod species *Strandesia*
7 1076 *risgoviensis*: (B) preserved, pearl-like, smooth specimen; (C) altered mat, rough specimen. (B) and (C)
8 1077 Comparison under SEM between preserved ostracod shell (B1 to B4) and altered shell (C1 to C4).
9 1078 (B2) Close-up view of an area of the smooth shell [white rectangle in (B1)] showing smooth
10 1079 microstructure. (B4) Close-up view of a lateral area between the two carapaces of the smooth shell
11 1080 [white rectangle in (B3)] again showing the well-preserved pore canals and a diagenetic infill of the
12 1081 inner shell. (C2) Close-up view of an area of the mat shell [white rectangle in (C1)] showing
13 1082 replacement with secondary microdolomitic rhombs. (C4) The inner part of the mat shell [close-up
14 1083 view of a lateral area, shown in (C3)] is also filled with dolomite rhombs.

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16 1084 Fig. 11. Diagram representing and comparing the range of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values (respectively in the
17 1085 upper and lower part) of matrix carbonates and other carbonate material (shells and cements). Mean
18 1086 and median values are provided. (*) Seven ostracod shell samples (mostly) free from diagenetic
19 1087 cement or allochthonous material are included within the 14 samples of 'preserved ostracod shells'.

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21 1088 Fig. 12. Scatter plot representing the $\delta^{13}\text{C}$ versus $\delta^{18}\text{O}$ values of all the Hainsfarth carbonates. Note the
22 1089 clear covariance between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values.

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24 1090 Fig. 13. Transversal section of a cylinder core showing an erosive surface (dashed line) between a
25 1091 gastropod-dominated grainstone (beneath) to a peloidal-dominated grainstone (above). The erosion
26 1092 surface potentially depicts a short-term subaerial exposure surface (SES). Very negative $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$
27 1093 values characterize the matrix sampled above and below this discontinuity. (B) Close-up view of the
28 1094 erosive surface. Note the enrichment in siliciclastics at the surface (brown-black material). (C) and (D)
29 1095 Close-up of gastropod shell vestige below the surface. Note the erosion of the shell. (C) Both the shell
30 1096 and inner-shell space are filled with blocky calcite with a certain amount of secondary porosity
31 1097 remaining unfilled. (D) The same microphotograph under CL: '1' microdolomitic crust; '2a/2b'
32 1098 several phases of dark blue luminescent blocky calcite intercalated by a thin bright orange phase of the
33 1099 same fabric '3'; 'c' siliciclastics. (E) EDS spectrum reveals siliciclastics; (F) EDS spectrum of quartz
34 1100 mineral.

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37 1101 Fig. 14. Diagram representing and comparing the range of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of grainstone and
38 1102 algal-microbial dominated fabrics. While the range of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values characterizing the two
39 1103 groups of facies is similar, their respective mean and median values differ significantly.

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41 1104 Fig. 15. Diagram representing and comparing the range of $\delta^{18}\text{O}$ values of all Hainsfarth carbonates,
42 1105 and their significance with respect to assessed primary lacustrine versus meteoric diagenetic $\delta^{18}\text{O}$
43 1106 signatures

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45 1107 Fig. 16. Scatter plot comparing the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of all Hainsfarth outcrop carbonates (green
46 1108 circles) with values of time-equivalent, slightly more 'basinal' carbonates (red data points from Arp et
47 1109 al., 2013). The blue area designates the range of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values interpreted as primary lacustrine
48 1110 while the green data points (negative $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values) outside the area are interpreted to reflect
49 1111 the meteoric diagenetic overprint of those original values.

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51 1112

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53 1113

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