Palaeoenvironmental and diagenetic reconstruction of a closed-lacustrine carbonate system – the challenging marginal setting of the Miocene Ries Crater Lake (Germany)

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ABSTRACT

Chemostratigraphic studies on lacustrine sedimentary sequences provide essential insights on past cyclic climatic events, on their repetition and prediction through time. Diagenetic overprint of primary features often hinders the use of such studies for palaeoenvironmental reconstruction. Here the potential of integrated geochemical and petrographic methods is evaluated to record freshwater to saline oscillations within the ancient marginal lacustrine carbonates of the Miocene Ries Crater Lake (Germany). This area is critical as it represents the transition from shoreline to proximal domains of a hydrologically-closed system, affected by recurrent emergent events, representing the boundaries of successive sedimentary cycles. Chemostratigraphy targets shifts related to subaerial exposure and/or climatic fluctuations. Methods combine facies changes with δ13C–δ18O chemostratigraphy from matrix carbonates across five closely-spaced, temporally equivalent stratigraphic sections. Isotope composition of ostracod shells, gastropods and cements is provided for comparison. Cathodoluminescence and back-scatter electron microscopy were performed to discriminate primary (syn-)depositional, from secondary diagenetic features. Meteoric diagenesis is expressed by substantial early dissolution and dark-blue luminescent sparry cements carrying negative δ13C and δ18O. Sedimentary cycles are not correlated by isotope chemostratigraphy. Both matrix δ13C and δ18O range from ca. -7.5 to +4.0‰ and show clear positive covariance (R = 0.97) whose nature differs from that of previous basin-oriented studies on the lake: negative values are here unconnected to original freshwater lacustrine conditions but reflect extensive meteoric diagenesis, while positive values likely represent primary saline lake water chemistry. Noisy geochemical curves relate to heterogeneities in (primary) porosity, resulting in selective carbonate diagenesis. This study exemplifies that ancient lacustrine carbonates, despite extensive meteoric weathering, are capable to retain key information for both palaeoenvironmental reconstruction and the understanding of diagenetic processes in relation with those primary conditions. Also, it emphasizes the limitation of chemostratigraphy in fossil
carbonates, and specifically in settings that are sensitive for the preservation of primary environmental signals, such as lake margins prone to meteoric diagenesis.

Keywords: $\delta^{13}$C and $\delta^{18}$O chemostratigraphy, lacustrine carbonates, meteoric diagenesis, Miocene, ostracod shells, palaeoenvironmental reconstruction, sedimentary cycles, subaerial exposure

INTRODUCTION

Carbon and oxygen isotopes are inevitable tools for palaeoenvironmental reconstruction and the study of diagenesis in carbonate rocks (e.g. Dickson & Coleman, 1980; Marshall, 1992; Immenhauser et al., 2003; Brand, 2004; Andrews, 2006; Swart, 2015; Godet et al., 2016). Hence $\delta^{13}$C and $\delta^{18}$O analyses are commonly performed on non-altered modern carbonates for environmental or climatic purposes (e.g. Anderson et al., 1997; Marshall et al., 2007), and on ancient rocks to assess the nature, extent and timing of diagenetic processes (e.g. Mutti & Bernoulli, 2003; van der Kooij et al., 2010; Christ et al., 2012a, b). The geochemical signature associated with the pedogenic alteration of ancient marine carbonates is generally identified based on marine isotopic signatures of modern analogues (Allan and Matthews, 1977, 1982; Beier, 1987, Budd & Land, 1990; Joachimski, 1994; Immenhauser et al., 2002).

In lacustrine deposits, the interpretation of isotopic signatures is not straightforward due to the variable nature of material (i.e. detrital, inorganic, biotically-controlled, or biotically-induced). Owing to their smaller size in comparison to marine bodies and especially in the case of hydrological closure, lacustrine systems are very sensitive to environmental changes. This sensitivity is reflected in high variability of carbon and particularly oxygen isotope composition of the lake water and, consequently, precipitated carbonates (Talbot, 1990; Leng & Marshall, 2004). Geochemical signals in lacustrine carbonates depend, amongst others, on seasonality, climatic and hydrological context, and the origin and mineralogy of carbonates forming (Leng & Marshall, 2004; Gierlowski-Kordesch, 2010). In case of ancient lacustrine carbonates carbon and oxygen isotopes are used for palaeoenvironmental reconstruction mostly from deep-water, basinal homogeneous deposits, and not from marginal lake carbonates, experiencing repetitive episodes of subaerial exposure, diagenetic alteration, and characterized by an incomplete record. These recurring meteoric events alter lacustrine carbonates and affect their isotopic composition, challenging geochemical interpretation and the extraction of primary environmental signals. Unlike marine settings where pedogenic isotopic signatures are well constrained, meteoric diagenesis in continental settings regarding $\delta^{13}$C and $\delta^{18}$O patterns is less understood, partly due to the aforementioned multiple origin of the carbonates. Thus $\delta^{13}$C and $\delta^{18}$O values are, similarly to marine systems, expected to decrease (be negative) beneath exposure surfaces.
(diagenetic signal), but negative δ\textsuperscript{13}C and δ\textsuperscript{18}O values often point to a freshening of saline lake water without necessarily exposure (primary depositional signal) (Talbot, 1990).

Previous work focusing on the Ries Crater Lake (Southern Germany; Fig. 1) included investigations of the geochemical composition of carbonates. The δ\textsuperscript{13}C and δ\textsuperscript{18}O analyses, applied on more basinal deposits, revealed a closed-lake system and a long-term evolution in the lake water chemistry (freshwater versus saline conditions) throughout its infilling (Rothe & Hoefs, 1977; Talbot, 1990; Arp et al., 2013).

The present paper presents and discusses the outcomes of a combined stratigraphic, petrological and geochemical study from a transitional, sublittoral to supratidal setting of the northern margin of the Ries Crater Lake (Figs 1 and 2). This marginal setting is embodied in a present-day outcrop dominated by carbonate algal fabrics. These Miocene-dated eulittoral deposits formed bioherms (Riding, 1979; Arp, 1995) that have allegedly experienced several episodes of subaerial exposure. The aim of this study is three-fold: (i) to test the reliability of chemostratigraphic data in identifying subaerial exposure surfaces; (ii) to identify successive diagenetic phases using petrographic data and component-specific δ\textsuperscript{13}C and δ\textsuperscript{18}O geochemistry; and (iii) to reconstruct palaeoclimatic cycles of the lake using geochemical evidence, to support facies-based interpretations.

**GEOGRAPHICAL AND GEOLOGICAL SETTING**

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

METHODS

Study area and fieldwork approach

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

Analytical methods

Laboratory methodology included carbon and oxygen isotope chemostratigraphy and component-specific geochemistry, optical and cathodoluminescence microscopy, scanning electron microscopy and Energy Dispersive X-Ray Spectroscopy (EDX) analyses. Carbon and oxygen isotope values of carbonate matrix have been measured using a high-resolution (one sample every 12.5 cm) chemostratigraphic approach for five stratigraphic sections. Carbonate matrix refers here to composite material: even if fine-grained carbonates were aimed for, the obtained fraction is often heterogeneous, consisting of inorganic carbonates, with a changing admixture of algal–microbial micrite, microcrystalline or microsparitic cements and biogenic skeletal fragments. Additional targeted components were algal–microbial fabrics, ostracod-rich and gastropod-rich carbonates, cement phases and individual ostracod shells. Chosen fabrics were sampled by careful hand microdrilling under binocular microscopy. Ostracod shells were isolated from small pieces of rock samples crushed beforehand, then sieved, and the resulting grains (10² to 10⁵ µm in size) have been cleaned in ultrasonic bath to separate as efficiently as possible allochthonous amalgamated grains from ostracod carapaces. Drilled powder (n = 195) and ostracod shells (n = 29) were analyzed for carbon and oxygen isotope compositions at the German Research Centre for Geosciences GFZ (GeoForschungZentrum), Potsdam, using a Thermo Scientific™ Kiel IV carbonate device coupled to Thermo Scientific™ MAT 253™ Mass Spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). Samples in the range of
0.03 to 0.06 mg were reacted and dissolved with 103% phosphoric acid at 72°C and the isotopic composition was measured from the released and cryogenic purified CO₂. All isotope results are reported in ‰ relative to the V-PDB (Vienna Pee Dee Belemnite) standard in the conventional manner. Replicate analyses of certified reference material NBS 19 provided a reproducibility of 0.06‰ for both δ¹³C and δ¹⁸O.

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

Six thin sections were also examined under the JEOL JSM-6510 Scanning Electron Microscope (SEM; JEOL, Tokyo, Japan)) at the University of Potsdam. The device is equipped with an INCA-based EDS detector (Oxford Instruments, Abingdon, UK) for the chemical characterization of the samples. Two end-member ostracod shells of the same species with distinct preservation pattern and derived from a single sample were also analyzed under the instrument in order to assess their alteration degree.

FACIES AND DEPOSITIONAL ENVIRONMENTS

Facies types

Five main facies types (Fig. 4) have been previously described amongst the marginal lacustrine carbonates of Hainsfarth quarry (Arp, 1995; Arp, 2006). These are the following: (i) conoidal Cladophorites framestone; (ii) nodular Cladophorites bafflestone; (iii) skeletal and non-skeletal grainstone; (iv) stromatolites; and (v) palustrine breccia (Fig. 4). Skeletal and non-skeletal grainstones can be subdivided into gastropodal grainstones, gastropodal–ostracodal grainstones, ostracodal grainstones, ostracodal–peloidal grainstones and peloidal packstones–grainstones. For more details concerning the facies, please refer to the exhaustive characterization provided by Riding (1979) and Arp (1995, 2006). Carbonate algal fabrics (Cladophorites) are the dominant facies forming the Ries deposits in the studied locality (Fig. 3A).

Depositional environments and cyclicity

The overall depositional environment of the Hainsfarth carbonates is attributed to the littoral zone of the Ries Lake (Arp, 1995, 2006). However, the littoral zone can be subdivided into several sub-environments: (i) the infralittoral zone, below lowermost seasonal lake level, where Cladophorites build-ups develop and non-skeletal and skeletal grainstones are deposited; (ii) the supralittoral zone
with palustrine deposits and pedogenic features; and (iii) a playa-lake environment with stromatolites.

Two orders of cyclicity, highlighted by Arp (1995), define the sedimentary pattern and the repetitive record of these depositional environments. The growth pattern of Cladophorites, following seasonal changes (Arp, 1995) reflected as rhythmic laminations, represents the highest frequency cycles. The growth of these algal bioherms is characterized by repetitive lower-frequency sequences mirroring small-scale (freshwater-evaporative?) climatic cycles (Arp, 1995). These cycles generally terminate with the subaerial exposure of the Cladophorites bioherms and their erosion and with the deposition of ostracod and gastropod packstones/grainstones (Fig. 5). Five of such sequences have been identified and described by Arp (1995) along one stratigraphic section (see its spatial position on Figs 3 and 9). This stratigraphic section served as a basis for the lateral, physical tracing of small-scale cycles and their boundaries on either side of the section in the present study. In the studied transect, seven of these repetitive climate-induced (freshwater-evaporative) cycles have been recognized. It is of relevance to mention that only the physical tracing of sedimentary packages and cycle boundaries across the transect enabled the authors to recognize all seven cycles although they have never been identified along one single stratigraphic section. The cycles are well-constrained and are correlated within the five stratigraphic sections. Arp (1995) assessed the Cladophorites growth duration within one sequence to be at least 775 years, assigning a whole duration of several $10^3$ years to ca $10^4$ years for the complete deposition of Hainsfarth carbonates.

**GEOCHEMICAL AND PETROGRAPHIC DATA**

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

**Results**

*Cement stratigraphy, petrography and diagenesis*

Hainsfarth carbonate diagenesis has been previously documented (Riding, 1979; Arp, 1995) and the aim here is not to replicate existing information, but to offer a succinct summary of diagenetic phases, forming the prerequisite for chemostratigraphic interpretation. Previous data are complimented by new CL data, and the volumetric part of each successive diagenetic feature is qualitatively assessed. The latter point serves as a basis for the forthcoming geochemical interpretation, as abundant diagenetic phases may strongly affect primary isotopic signatures. A first important observation is the high porosity amongst Hainsfarth carbonates, albeit strong heterogeneities exist even within thin sections
(Fig. 6). Both primary depositional and secondary porosity (Figs 6 and 7) and several types of pore-filling (cementation and pressure-solution) and pore-enhancing (dissolution and fractures) features are identified within Hainsfarth carbonates (Fig. 7). These features are (from the oldest to the youngest):

(i) lacustrine sedimentation and carbonate microbial precipitation; (ii) thin isopachous dolomicrite precipitation; (iii) early dissolution of aragonite (mainly gastropods) grains; (iv) precipitation of an isopachous, inclusion-rich fibrous calcite; (v) precipitation of ‘dog-tooth’ calcite crystals; (vi) considerable dissolution of carbonate grains; (vii) infilling of some pores by siliciclastic materials; (viii) gravitational pendant and meniscus cement; (ix) main filling of the pores by blocky calcite (two types – A and B); (x) pressure-solution features; and (xi) present-day dissolution and vadose precipitation (Fig. 6).

The first cement phase (ii) following sediment deposition (i) is a thin (up to a few tens of microns thick) isopachous rim of dolomicritic surrounding grains (Cladophorites, gastropods; Fig. 6A and B). Shells of gastropod species Hydrobia trochulus are either dissolved and left as mouldic porosity or replaced into fine sparry calcite (iii; Fig. 6 and B), but if dissolved the shape is preserved thanks to the first dolomicritic rim. An isopachous fine to thick rim of fibrous calcite (iv) is commonly the second cement phase observed after the dolomicritic rim, whereas it is not systematically present. In few cases fibrous cement appearing cloudy under transmission light, fills the interparticle pore-space completely. Sometimes, an isopachous rim of bladed to scalenohedral calcite (v) is following the initial microcrystalline dolomite (Fig. 6A). The volumetrically dominant cement phase observed, filling former intergranular and intragranular pore spaces but also moulds of dissolved skeletal grains (mostly gastropods) are blocky, sparry calcite (ix; type A) whose individual crystals may reach up to 500 µm (Fig. 6A, B E and F). This phase post-dates all of the above-mentioned cement rims. The luminescence pattern of the blocky calcite (type A) is principally non-luminescent to dark blue intrinsic, but some zonation can be observed, as well as a dull to bright orange luminescence in some thin sections. This luminescent blocky calcite is referred to type B (ix; Fig. 6B and F). Gravitational cements (viii) in the form of meniscus and pendant cements have been observed in several thin sections (Fig. 6C and D) and are nearly contemporaneous to blocky calcite of type A. Theses phases also have a dark blue luminescence under CL (Fig. 6D). Peloids, algal laminae and indistinct carbonate matrix have a dull to bright orange luminescence, sometimes brown (Fig 6H and J). Dissolution of sub-rounded material, allegedly peloids is frequently observed (vi; Fig. 6G to J). Strandesia risgoviensis ostracods are less commonly dissolved than gastropod shells. When not dissolved, their luminescence pattern under CL is variable, alternating between non-luminescent, brown-orange, dull orange to bright orange. Such variability in luminescence is sometimes observed in a same thin section (Fig. 6I and J). At the erosive surface in section 1 (215 cm above base section) but also in many other intervals, carbonate-poor clastic material accumulated (vii; Fig. 6G and H).

Matrix δ¹³C and δ¹⁸O chemostratigraphy
Both δ\(^{13}\)C and δ\(^{18}\)O values exhibit a wide range of values (Figs 8 and 9). The δ\(^{13}\)C values range from -6.5 to +4.0‰ whereas δ\(^{18}\)O values vary between -7.2 and +3.9‰. Amongst this wide range of values, neither obvious geochemical shifts within individual curves can be distinguished, nor are chemostratigraphic profiles well-correlated between stratigraphic sections (Fig. 8). The δ\(^{13}\)C and δ\(^{18}\)O curves from each of the five stratigraphic sections are clearly distinct from one another. The shape of the δ\(^{13}\)C curves is very similar to that of the δ\(^{18}\)O curves for each individual sections, showing offsets or shifts with nearly identical amplitude (Fig. 8). However, a relationship between stratigraphic and lateral facies change, and carbon and oxygen isotope curves is not evident (Fig. 9).

**Ostracod shell preservation**

As a prerequisite for any geochemical analysis performed on ostracod shells, their preservation degree was assessed. A total of 474 ostracod shells or shell parts (broken, disarticulated, or complete and joined) of the species *Strandesia risgoviensis* (Janz, 1995) were carefully selected out of 23 stratigraphic levels. Two sets with distinct appearance could be isolated (Fig. 10): (i) smooth, pearl-like ostracod shells (169 broken, 64 complete; n = 233); and (ii) rough, mat ostracod shells (155 broken, 86 complete; n = 241). In all but three samples, both types of ostracod shells coexist. Because *Strandesia risgoviensis* (Sieber) (Janz, 1995) is considered the only ostracod species in the Ries Lake, or at least within this marginal setting (Arp, 1995, 2006; Arp et al., 2017), these variations could point to distinct preservation/alteration states of the bioclasts. To assess the degree of alteration of the shells, two specimens (i.e. one pearl-like and one mat) have been compared under SEM and their chemical composition has been determined using EDX analyses (Fig. 10). Most of the complete (i.e. not disarticulated) ostracod shells display an inner cement phase in between their valves (Fig. 10). The latter cement is generally not present or rather dissociated when ostracod shells are broken or disarticulated. The pearl-like ostracod shell appears smooth under high SEM magnification (Fig. 10-B2) and exposes primary structures such as pore canals at the edge of the valves (Fig. 10-B4), while SEM reveals rhombohedral crystals characterizing the mat shell (Fig. 10-C2). The 16 EDX measurements performed on the pearl-like shell reveal that mean MgCO\(_3\) content is less than 2.8% mol (Table 1), which is agreement with an expected low-Mg calcite (< 4% mol MgCO\(_3\)) mineralogy of pristine ostracod shells). Cement phases found inside and outside the valves have MgCO\(_3\) a mean content of 5.9% mol. Regarding the 10 spots analyzed on the rough and mat shell, MgCO\(_3\) content averages 41.6% mol and point to dolomitization. The proportion of magnesium carbonate measured in the material infilling the ostracod valves of the rough shell equals 38.8% mol in average. In comparison to SEM and optical microscopy, CL reveals more subtle distinctions between the two specimens. Some ostracod shells are only present as moulds. Where preserved from dissolution, luminescence patterns of ostracod shells varies between non-luminescent, dull brown-orange, dull orange to bright orange (Fig. 6I-F). When ostracod valves are still articulated, carbonate material filling in the carapace varies between: moderately bright luminescent matrix or peloids, dark blue
luminescent to dull to bright blocky calcite or bright luminescent thick fibrous cement, similar to the
crust [diagenetic feature (iv) mentioned previously]. Both, ostracod mouldic porosity and shells that
luminesce bright orange are predominantly observed in thin sections (i.e. intervals) where overall
porosity is high. Ostracod shells showing either non-luminescence or a dull brown-orange one are
commonly encased in a fine-grained matrix.

Initial alteration cannot be excluded in some of the smooth shells, inasmuch as some
measurements outlie the range for low-Mg calcite (for example, the maximum 10% mol MgCO$_3$).
However, pearl-like shells with a low-Mg calcite, apparently nearly devoid of any – even early –
diagenetic overprint seem well suitable to deliver a geochemical signal that is close to that of
penecontemporaneous lake water, even though early diagenesis does not systematically alter pristine
signatures (e.g. Bennett et al., 2011).

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

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

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

The $\delta^{13}$C and $\delta^{18}$O values of all analyzed material (matrix, algal-microbial fabrics, ostracod shells,
gastropod shells and sparry cements) are presented in Table 2 and Figs 11 and 12. Sparry cements in
intragranular and intergranular pores and as replacement fabric of gastropod shells show very negative
carbon and oxygen isotope values (mean values around -5 to -6‰ for $\delta^{13}$C, and -6 to -7‰ for $\delta^{18}$O).
All remaining carbonate components (matrix, algal fabrics and ostracods) have (mean) values that are rather positive, ranging from 0 to +2‰ for δ\textsuperscript{13}C and -0.5 to +2‰ for δ\textsuperscript{18}O, although their δ\textsuperscript{13}C and δ\textsuperscript{18}O values vary within a high amplitude range (ca -8‰ to +4‰ for δ\textsuperscript{18}O\textsubscript{matrix} and -7‰ to +4‰ for δ\textsuperscript{13}C\textsubscript{matrix}; ca -3‰ to +4‰ for δ\textsuperscript{18}O\textsubscript{preserved-ostracods} and -2‰ to +3‰ for δ\textsuperscript{13}C\textsubscript{preserved-ostracods}). A second relevant outcome is that despite these clearly distinct groups of geochemical signatures, an obvious covariance (r = 0.97) exists between δ\textsuperscript{13}C and δ\textsuperscript{18}O for all Hainsfarth carbonates analyzed (Fig. 12).

**Interpretation**

*Cement stratigraphy, petrography and diagenesis*

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

Low or negative δ\textsuperscript{13}C and δ\textsuperscript{18}O values in lake carbonates values can be related to: (i) precipitation under freshwater lacustrine conditions (Leng & Marshall, 2004); (ii) subaerial conditions exposure and meteoric alteration, and the incorporation of light \textsuperscript{16}O and \textsuperscript{12}C due to rainwater and soil formation; or (iii) burial diagenesis and precipitation under higher temperatures during burial diagenesis. While negative δ\textsuperscript{13}C and δ\textsuperscript{18}O values are not incompatible with precipitation of the blocky cements (type A) under lacustrine freshwater conditions, it is questionable that they formed under these conditions. Indeed the more positive δ\textsuperscript{18}O (by 6.5‰) of the matrix extracted from the same sample, i.e. stratigraphic interval, strongly suggests distinct environment, with matrix deposited under lacustrine conditions and sparry cements representing secondary diagenetic products. Thus, assuming that the negative values of blocky calcite mirror secondary diagenesis, it is unlikely that they here ensue from elevated temperatures, inasmuch as Arp (1995) mentioned a maximal burial depth of 80 to 100 m for these Miocene deposits. A difference of -6.5‰ implies an increase in temperature by about 25°C or more if it is assumed that matrix isotopic signature has also been altered by burial diagenesis (cf. the orange luminescence under CL). Such high temperatures are incompatible with a burial depth of 100 m and an assumed geothermal gradient of 25 to 50°C/km (Niemann & Read, 1988; Einsele, 2000). Additionally δ\textsuperscript{13}C\textsubscript{cement} is lower by almost 4‰ relative to δ\textsuperscript{13}C\textsubscript{matrix} for the same interval, a disparity that is irreconcilable with a burial geochemical signature, considering that carbon isotope
fractionation with temperature is negligible (Emrich et al., 1970; Romanek, 1992). Therefore burial diagenesis as the main driver for the negative values measured in the cements should be excluded.

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

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

Matrix $\delta^{13}$C and $\delta^{18}$O chemostratigraphy

Carbon and oxygen isotope composition curves between stratigraphic sections are not correlated, and this rules out an immediate palaeoenvironmental reconstruction based on matrix $\delta^{13}$C and $\delta^{18}$O chemostratigraphy (Fig. 9). Moreover, the virtually identical shapes of $\delta^{13}$C and $\delta^{18}$O curves regarding individual stratigraphic sections (Fig. 8) might be related to the diagenetic overprint of the matrix, although it is not yet clear why $\delta^{13}$C and $\delta^{18}$O offsets have nearly equivalent amplitudes. Interestingly, 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 δ^{13}C and δ^{18}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 δ^{13}C and δ^{18}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 δ^{13}C and δ^{18}O signatures (e.g. Bennett et al., 2011). Thus ostracods δ^{13}C and δ^{18}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 δ^{18}O values to the ambient lake water δ^{18}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 δ^{18}O lower by up to -0.9‰ (with respect to lake water δ^{18}O values) (Decrouy et al., 2011). The δ^{13}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 δ^{13}C and δ^{18}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 (Δδ^{18}O_{dol-cal}) at low temperatures, δ^{18}O_{dol} values are
generally enriched regarding $\delta^{18}O_{\text{cal}}$ values by 0-9‰ under the same conditions (Vasconcelos et al., 2005, and references therein). Swart (2015) assesses this enrichment ($\Delta \delta^{18}O_{\text{dol-cal}}$) as between 3‰ and 6‰. Conversely, $\delta^{13}C$ values of dolomite are generally slightly more positive but close to the co-precipitating low-Mg calcite and $\Delta \delta^{13}C_{\text{dol-cal}}$ is generally between 0‰ and 1‰ (Sheppard & Schwarcz, 1970; Swart, 2015). Therefore, the range of measured $\delta^{18}O$ values in the altered shells is expected to be significantly lower (by at least 2 to 3‰) than the range obtained (and to a lesser extent altered shell $\delta^{13}C$ values), perhaps more compatible with the common lower isotopic signature of a meteoric or burial diagenetic fluid. More accurate estimation is not feasible, as the timing of dolomitization, the penecontemporaneous water temperature, the $\delta^{18}O_{\text{water}}$ and the $\delta^{18}O_{\text{calcite}}$ remain unknown. The $\delta^{13}C$ and $\delta^{18}O$ of preserved ostracods values are generally positive, but are likely to represent mixtures of material (original valves and a LMC diagenetic infilling) with distinct geochemical signatures. Three other $Strandesia\ risgoviensis$ ostracods issued from the Nördlingen Ries have been previously analyzed for isotopic composition (Tütken et al., 2006) and yield $\delta^{13}C$ values between +3.5‰ and +3.9‰ and $\delta^{18}O$ values between +1.6‰ and +2.3‰, corresponding to values amongst the highest analyzed in the present study. Unfortunately, Tütken et al. (2006) do not report the stratigraphic interval from which these ostracods are issued, but they interpret them to have lived under saline, evaporative lake conditions.

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

High positive correlation between $\delta^{13}C$ and $\delta^{18}O$ values of lacustrine carbonates commonly refers to hydrologically-closed systems (Talbot, 1990; Leng & Marshall, 2004). Using observations from modern lakes, Talbot (1990) determined a covariance threshold between $\delta^{13}C$ and $\delta^{18}O$ ($r = ca. 0.75$) under and over which a lacustrine system is open or closed, respectively. The covariance between carbon and oxygen isotope composition of carbonates at Hainsfarth is >0.9 and therefore is in agreement with the previous closed-system interpretation of the Ries Lake (Rothe & Hoefs, 1977; Talbot, 1990; Arp et al., 2013). A geochemical covariance as high as $r = 0.9$ has been measured in carbonates from the research drilling Nördlingen 1973 (Rothe & Hoefs, 1977; Talbot, 1990). Similarly, Arp et al. (2013) reported a covariance of 0.95 from carbonate samples issued from the research drilling Enkingen SUBO 18. Samples from Hainsfarth, however, significantly differ from those of the previous drillings: (i) they correspond to marginal, sublittoral to supratidal carbonates whereas those from previous work refer to deeper-water, more basinal lake deposits; (ii) they are outcrop-based while those from previous research are core-based; and (iii) carbonate facies at Hainsfarth show strong heterogeneity, and lateral and vertical porosity considerably varies. Accordingly, Hainsfarth carbonates probably experienced several episodes of meteoric diagenesis from the Miocene to present-day, due to their particular palaeogeographic position. Meteoric alteration in basinal deposits should be considered of reasonably lesser importance.
The wide range in matrix $\delta^{13}$C and $\delta^{18}$O values (Table 2; Figs 11 and 12) combined with the lack of chemostratigraphic correlation between sections and the noisy behaviour of matrix chemostratigraphic curves (Figs 8 and 9) suggest a mixing (in variable proportions) of carbonate material yielding distinct geochemical signatures, masking any potential primary signal. Carbon and oxygen isotope values in meteoric cement spars are amongst the lowermost values, equivalent to the lowermost values of matrix carbonates (Table 2; Figs 11 and 12). Mouldic porosity of dissolved aragonitic gastropod shells is often filled by early meteoric sparry calcite cement. This cement also fills in a significant volumetric portion of the internal space of the former shells. This explains why $\delta^{13}$C and $\delta^{18}$O values in gastropods are nearly as negative as in meteoric spars (Table 2; Figs 11 and 12). These sparry cements were certainly intermixed with matrix and skeletal components and hence account for negative $\delta^{13}$C and $\delta^{18}$O values. Such an explanation is realistic considering that half of the matrix $\delta^{13}$C values are $>+1.7‰$ and half of the $\delta^{18}$O are $>+0.8‰$ (median values; Table 2; Fig. 11), i.e. they are mostly positive. Meteoric alteration is probably also responsible for the lowest values measured in algal laminated fabrics (some areas featuring trapped gastropod shells), and in ostracod shells and ostracod-rich matrix. However the high positive $\delta^{13}$C and $\delta^{18}$O median values (Table 2; Fig. 11) of algal fabrics and ostracods, as well as the lack of chemostratigraphic correlation, strongly suggest that Hainsfarth primary lacustrine carbonates were mostly positive. The positive character of primary $\delta^{13}$C and $\delta^{18}$O in the present study significantly differs from previous work (Rothe & Hoefs, 1977; Arp et al., 2013) where negative and positive $\delta^{13}$C and $\delta^{18}$O values were interpreted as primary in origin, reflecting relevant changes in lake chemistry.

DISCUSSION

Absence of chemostratigraphic correlation between stratigraphic sections

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

Neither carbon nor oxygen isotope curves of carbonate matrix correlate between the five stratigraphic sections of the Hainsfarth quarry (Fig. 8), despite the short lateral distance separating them (Fig. 3), the high-resolution sampling and the beforehand set stratigraphic boundaries. Noteworthy is that each of the seven recorded cycles ends with the development of nodular to conoidal Cladophorites boundstones and eventually their emersion, mirrored by extensive thicker veneers, the erosion of the algal bioherms, and the presence of oxidized layers or palustrine breccias (Riding, 1979;
While these sequence boundaries coincide with subaerial exposure surfaces based on facies description and cyclicity (Arp, 1995) they lack the saw-tooth shaped shifts in $\delta^{13}C$ and $\delta^{18}O$ values commonly associated with meteoric or freshwater diagenesis beneath emersion surfaces (Allan & Matthews, 1977, 1982). Even assuming a semi-arid climate for the middle Miocene of this area (Böhme et al., 2001; Prieto et al., 2009), minor negative shifts in both $\delta^{13}C$ and $\delta^{18}O$ are expected beneath subaerial exposure surfaces (Christ et al., 2012a).

Even though individual curves cannot be correlated with one another between sections, a striking feature is the covariance of $\delta^{13}C$ and $\delta^{18}O$ curves for each considered stratigraphic section (Fig. 8), suggesting an interdependence between both geochemical isotope systems (C and O).

The clear covariance between matrix $\delta^{13}C$ and $\delta^{18}O$ in Hainsfarth outcrop carbonates is apparently in accordance with geochemical signatures of closed-lake systems and an alternation of freshwater and saline lacustrine conditions (Li & Ku, 1997; Leng & Marshall, 2004) such as formerly mentioned from the Ries Lake (Talbot, 1990; Arp, 2006; Arp et al., 2013). However, the lack of correlation between individual chemostratigraphic profiles (Fig. 8), and also between geochemical curves and sedimentary cycles (Fig. 9), is difficult to reconcile with a primary environmental origin.

Consequently, in case of Ries Crater Lake $\delta^{13}C$ and $\delta^{18}O$ chemostratigraphy fails as an alternative method for the recognition of sedimentary cycles in marginal, sublittoral lacustrine carbonates.

**Geochemical evidence of Miocene subaerial exposure and meteoric diagenesis**

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

Matrix $\delta^{13}C$ and $\delta^{18}O$ in the study outcrop are as low as -7.3‰ and -7.7‰, respectively, close to those of the blocky cements and replaced gastropod shells (Table 2; Fig. 11). Negative $\delta^{13}C$ and $\delta^{18}O$ values reported from Ries Lake basinal deposits (Rothe & Hoefs, 1977; Pache et al., 2001; Arp et al., 2013) were associated with freshwater lacustrine conditions. Several lines of evidence suggest that the cause for negative $\delta^{13}C$ and $\delta^{18}O$ values in Hainsfarth carbonates is related to primary lacustrine chemistry: (i) the noisy character of the curve and the lack of chemostratigraphic correlation (Figs 8 and 9); (ii) substantial, especially in packstone–grainstone fabrics, volume of calcite spars (type A blocky calcite) feeling pore spaces, gastropod shell moulds and internal spaces, should drag $\delta^{13}C$ and $\delta^{18}O$ signatures towards negative values, when mixed with carbonate matrix. The latter is exemplified by an erosion (exposure?) surface, with matrix carbonates having clearly low $\delta^{13}C$ and $\delta^{18}O$ values below and above the discontinuity surface (Fig. 3). The considered intervals have volumetrically-abundant blocky cements which depletes $\delta^{13}C$ and $\delta^{18}O$ values of the matrix. Meniscus cements and blocky cements from these intervals are interpreted as vadose (Fig. 6), respectively phreatic meteoric phases, and their occurrence in the vicinity of an erosive (exposure?) surface at the interface of which
soil-residue clastic material accumulated (such as quartz, clays and other oxides) are convincing evidence in favour of a meteoric environment (e.g. Sanz et al., 1991; Christ et al., 2012a). Such cement phases and clastic material were also observed amongst many other stratigraphic intervals, suggesting that meteoric features are pervasive within Hainsfarth carbonates (Figs 6 and 7).

**Relationship between facies, porosity and meteoric diagenesis**

According to the previous paragraph, emersion episodes of the margins potentially occurred at a higher frequency than that mirrored by the development of well-defined sedimentary cycles (small-scale climatic cycles; Arp, 1995; Fig. 9). This is evidenced, for example, by the allegedly subaerially exposed surface, subordinately identified within the fourth cycle (Figs 9 and 13). Carbon and oxygen isotope patterns seem to relate to the complex initial morphology of Hainsfarth bioherms, characterized by a high lateral and vertical variability in facies and textures (Figs 8 and 9). These heterogeneities eventually result in strong disparities in porosity and permeability, observable at the scale of thin sections. Porosity varies between 3.9% and 46.3% and permeability between 1.3 mD and 3543.5 mD (Maerz et al., pers. comm) with the most effective pore network commonly belonging to grainstone facies. To simplify, facies types can broadly be grouped into two dominating groups: (i) packstones/grainstones (with variable mixture of fine-grained carbonates, gastropods, ostracods, peloids and cements); and (ii) *Cladophorites* algal-dominated fabrics (microbial micritic boundstone and laminated boundstone facies). While δ$^{13}$C and δ$^{18}$O values measured in grainstones and in algal fabrics range within nearly the same interval, the mean and median δ$^{13}$C and δ$^{18}$O values of packstones/grainstones are clearly distinct from those of the algal fabrics (Fig. 14). Thus median values of grainstone facies are significantly lower than those of algal-dominated facies (Fig. 14). Often grainstones have a higher (effective) porosity and a higher amount of meteoric-related blocky cements, which explains why their mean and median δ$^{13}$C and δ$^{18}$O values are much lower than the mean and median values of algal fabrics. These variations in the lateral and stratigraphic distribution of those two groups of facies certainly account for the geochemical variability (dissimilar isotopic signatures, noisy patterns) observed between stratigraphic sections. Hence, the geochemical expression and the degree of meteoric alteration seem to be controlled by lateral and vertical fluid flow pathways.

**Preservation of primary lacustrine geochemical signature**

Replaced gastropod shells and most of the phreatic pore-filling blocky calcite phases carry the petrographic and geochemical evidence (most negative δ$^{13}$C and δ$^{18}$O values) characteristic for meteoric diagenetic overprint. The remaining carbonate features (matrix, algal laminated fabrics, ostracod-rich matrix and ostracod shells) all represent a mixture of carbonates with distinct carbon and oxygen isotope compositions. Similar to the lowest δ$^{13}$C and δ$^{18}$O values in the matrix, it can be
assumed that the lowest $\delta^{13}$C and $\delta^{18}$O values in algal fabrics, ostracod-rich matrix and altered/preserved ostracod shells are clearly influenced by meteoric diagenesis, due to a variable amount of cements within the mixture (Fig. 11). Evidence for the strong meteoric contribution is given by the large variability of $\delta^{13}$C and $\delta^{18}$O data points for each feature, and above all by the heterogeneous and asymmetrical distribution of $\delta^{13}$C and $\delta^{18}$O mean and median values for all carbonate features (Figs 11 and 12; Table 2). In comparison to $\delta^{13}$C and $\delta^{18}$O mean values, the relatively elevated median values are certainly more representative of signatures resembling primary lacustrine conditions.

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

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

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

Previous studies focusing on the composition of carbonates from two basinal and basinward drilling cores (Rothe & Hoefs, 1977; Arp et al., 2013) reported $\delta^{13}$C values ranging respectively from -11.5‰ to +11.1‰ and $\delta^{18}$O values ranging from -10.4‰ to +6.5‰. This large range of isotopic compositions was interpreted to mirror a geochemical evolution of the lake water from freshwater conditions (negative values) for the oldest deposits, to saline, evaporative conditions (positive values) for some of the youngest ones (Arp et al., 2013), before a return to a freshwater karstic environment during
ultimate lacustrine stage. The geochemical pattern in marginal carbonates, however, cannot be compared to that of the basinal deposits for several reasons: (i) no trend describing an evolution from freshwater towards evaporative conditions or vice versa is shown by the isotopic composition curves; (ii) penecontemporaneous meteoric diagenesis – and not freshwater lake conditions – is clearly responsible for negative \(\delta^{13}C\) and \(\delta^{18}O\) values and well-supported by petrographic observations (mouldic porosity, leaching of grains, blocky cements and replaced gastropod shells); (iii) the Hainsfarth outcrop represents only a small portion of the stratigraphic interval covered by the basinal setting: thus, the time span of \(ca\) 10\(^3\) to 10\(^4\) years involved in the complete deposition of bioherms (Arp, 1995) is rather short and probably represents a younger, ‘snapshot’ moment of the entire lake chemical evolution and the duration of lacustrine conditions assessed to last 0.3 to 2.0 Ma; (Pohl, 1977; Jankowski, 1981). If it is assumed that positive carbon and oxygen isotope composition of Hainsfarth carbonates closely reflects Ries Lake (semi-arid) water conditions at that time, it is in accordance with the former interpretation of these bioherms forming under marine-like to saline lake water conditions (Arp et al., 2013). The latter authors suggest that their ‘claystone member’ (carbonaceous clays, bituminous shales and laminated claystones) is correlated in time with Hainsfarth bioherms and represent a transition towards marine-like, and later saline evaporative conditions of the lake (Fig. 16). This chemical transition was interpreted partly based on the \(\delta^{13}C\) and \(\delta^{18}O\) values of carbonates ranging from -1.2‰ to +3.3‰ and from -0.7‰ to +2.1‰, respectively (Arp et al., 2013). The estimated range of \(\delta^{13}C\) and \(\delta^{18}O\) values in primary carbonates (\(ca\) -1‰ to +4‰ for both geochemical proxies) at Hainsfarth is in agreement with the interval of geochemical values from the corresponding Enkingen SUBO 18 carbonates (Arp et al., 2013; Fig. 16). The slightly higher \(\delta^{18}O\) values (up to +4.0‰) measured amongst Hainsfarth carbonates (this study; Fig. 20) may correspond to the peak evaporative conditions, expected to prevail close to lake margins or rather close to water surface, thus increasing oxygen isotope fractionation due to evaporation. However, Arp (1995) interpreted the (seven) sedimentary cycles at Hainsfarth to mirror short-term (\(ca\) 10\(^3\) years) freshwater to saline evaporative climatic cycles, with a smooth trend from ‘marine-like’ (downsection) to more arid evaporative (upsection) conditions. Based on the outcome of the present geochemical study, these sedimentary sequences are likely to represent small-scale freshwater to saline cycles subordinated on an overall arid evaporative context. While more data would be necessary (but this is beyond the scope of this study), preserved ostracod shells seem to be the most reliable to preserve pristine signatures and express changes at the scale of these short-term climatic fluctuations (Fig. 11).

Covariance in \(\delta^{13}C\) and \(\delta^{18}O\): insights to lake chemistry, freshwater diagenesis and climate

The outcome of the previous paragraphs suggests that the linear trend between \(\delta^{13}C\) and \(\delta^{18}O\) in Hainsfarth carbonates reflects (at least) two diametrically distinct processes: (i) primary carbonate sedimentation in a closed-lake system; and (ii) their overprint by meteoric diagenesis. Therefore the
authors suggest that the geochemical covariance may be bimodal: (a) densely-packed, higher $\delta^{13}C$ and $\delta^{18}O$ values closely reflect the original (globally evaporative) signature of the lake water; while (b) scattered negative $\delta^{13}C$ and $\delta^{18}O$ values mirror the freshwater diagenetic overprint of early products and the precipitation of meteoric spars. A clear threshold of values and data points where both processes are clearly isolated from one another is not identified, because most of the values certainly represent a mixture of lacustrine and meteoric signatures, pondered upward or downward by either of the volumetrically dominant sources. In marine environments, the $\delta^{13}C$ and $\delta^{18}O$ signatures of carbonates related to meteoric diagenesis are generally distinct (i.e. more negative) from primary depositional carbonates (Allan & Matthews, 1977, 1982; Goldstein, 1991; Christ et al., 2012a; Swart, 2015), while it may not necessarily be the case in lacustrine settings. The questions: (i) how such a positive linear trend is obtainable from carbonates whose origin is clearly distinct (primary lacustrine versus diagenetic); and (ii) how to explain the linear covariance between $\delta^{13}C$ and $\delta^{18}O$ despite meteoric diagenesis, are not straightforward ones but should be discussed.

In marine coastal settings, $\delta^{13}C$ and $\delta^{18}O$ values in carbonates are often lower than normal marine values under considerable meteoric influence in the vadose and phreatic freshwater environments (Allan & Matthews, 1982). However, carbon and oxygen isotope compositions are rarely covariant in these two diagenetic environments (Allan & Matthews, 1982; Swart, 2015), and can even show antagonistic shifts (for example, positive $\delta^{18}O$ due to evaporation, negative $\delta^{13}C$ due to soil-zone CO$_2$). Although $\delta^{13}C$ and $\delta^{18}O$ values in carbonates tend to be more negative in coastal vadose and phreatic meteoric environments, $\delta^{13}C$ values increase with increasing distance from the soil-zone as a result of dissolution of the carbonates in the vadose environment progressively enriching waters in $^{13}C$, while $\delta^{18}O$ values remain rather stable within the altered environment (Allan & Matthews, 1982; Lohmann, 1988). The only reported domain where $\delta^{13}C$ and $\delta^{18}O$ values show a covariance is the mixing-zone (transition domain between fresh and marine waters) with both $\delta^{13}C$ and $\delta^{18}O$ increasing towards the marine environment (Allan & Matthews, 1982; Swart, 2015), although this trend is not described as linear but hyperbolic (Lohmann, 1988). Additionally, while it is conceivable that a mixing-zone exists in the coastal area of a hypersaline lake, there is no evidence that lacustrine carbonates in Hainsfarth have (only) been altered in this environment. As successive exposure surfaces are stratigraphically close to one another, it is plausible that the same carbonates were repetitively altered by meteoric fluids during recurring emergence, achieving homogenization of $\delta^{13}C$ and $\delta^{18}O$ values. The identification under CL of two successive stages of precipitation of sparry calcite (Fig. 6B and F) indeed suggests repetitive meteoric-driven cementation (the blue intrinsic 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 ($\delta^{13}C$ and $\delta^{18}O$) methods (Benito et al., 2001; Alonso-Zarza et al., 2003). High variability...
in δ¹³C and δ¹⁸O values, especially amongst negative ones, points to variable ratios of altered and preserved carbonates.

The maximal amplitude (in ‰) of the negative shifts ensuing from meteoric diagenesis can, in the best case, only be assessed. Several studies reported freshwater alteration in marine carbonate environments to be a fast process, achieving to considerably or completely alter primary features in 10⁰ to 10³ years (Halley & Harris, 1979; Budd & Land, 1990; Dravis, 1996). Even if climate was semi-arid during Ries Lake development (Böhme et al., 2001, 2007; Prieto et al., 2009), meteoric or freshwater diagenesis should have transformed primary carbonates of the Hainsfarth bioherms relatively rapidly or sequentially. At this mid-latitude setting and assuming a certain degree of continentality (Orszag-Sperber et al, 1993; https://deeptimemaps.com), a δ¹⁸O depletion by 7 to 12‰ relative to primary signatures due to meteoric fluids is reasonable (Hays & Grossman, 1991). Younger marginal lacustrine carbonates (bioherms from the Staudigberg member; Arp, 2006; Arp et al., 2013) developing when lake conditions were more saline (more arid?) are characterized by equivalent, mostly positive δ¹³C and δ¹⁸O values and meteoric cements have δ¹³C and δ¹⁸O reported as low, if not lower, than diagenetic calcite in Hainsfarth bioherms (down to -9.3‰ and -6.4‰, respectively; Pache et al., 2001)

CONCLUSIONS

This study presents the first outcrop-based δ¹³C and δ¹⁸O chemostratigraphic and component-specific geochemical and petrographic investigation of carbonate deposits from the closed-lake-system of the Miocene Ries Crater Lake in Hainsfarth quarry, Southern Germany. The aim was to identify ancient subaerial exposure events in a marginal lacustrine setting through stable isotope geochemistry, and above all to assess the applicability of chemostratigraphic approach for the identification of sedimentary cycles previously recognized based on vertical and lateral facies change.

- The δ¹³C and δ¹⁸O chemostratigraphic study fails to identify shifts associated to subaerial exposure surfaces and to the recognition of sedimentary cycles.
- Emergent episodes, mentioned in previous studies for Hainsfarth carbonates, are identified on the base of petrographic properties of meteoric vadose and phreatic cements, and the frequent enrichment of siliciclastic material.
- Sparry calcite carrying very negative δ¹³C and δ¹⁸O signatures point to precipitation in a meteoric–phreatic environment.
- The abundance of meteoric cements in Hainsfarth carbonates (and not only within the immediate interval beneath sedimentary cycle tops) can be related to the high porosity in the rocks. The omnipresence of these cements is interpreted in terms of repetitive emergent episodes and
freshwater diagenesis pervasively affecting subsurface deposits. Only Cladophorites build-ups are less altered by meteoric diagenesis due to their initial fine-grained lithology.

- Clear positive covariance between δ^{13}C and δ^{18}O is observed for Hainsfarth, similar to previous basinal studies of the Ries Lake that interpreted this covariance to reflect changes in lake water chemistry from freshwater (negative δ^{13}C and δ^{18}O) to saline conditions (positive δ^{13}C and δ^{18}O). However, the nature of the covariance between carbon and oxygen isotope compositions for the carbonates of Hainsfarth differs from that of previous studies. Negative δ^{13}C and δ^{18}O do not characterize primary carbonates formed in a lacustrine freshwater environment but reflect extensive meteoric diagenesis, while the positive δ^{13}C and δ^{18}O closely seemingly witness marine to saline evaporative conditions of the lake water at the time of deposition. Burial diagenesis is considered to be a marginal and shallow process in the history of Hainsfarth carbonates with weak influence on their geochemical signature.

- Cladophorites fabrics that are largely unaffected by meteoric alteration, and indeed carry the most positive δ^{13}C and δ^{18}O values, have reduced porosities. Preserved ostracod shells also carry amongst the least negative δ^{13}C and δ^{18}O signatures which probably reflect the saline chemical conditions of lake water.

- Such evaporative conditions are in agreement with previous work mentioning similar circumstances for time-equivalent basinward deposits.

- This study emphasizes that caution is required before interpreting δ^{13}C and δ^{18}O in ancient carbonate sedimentary cycles, because stable isotopes represent circumstantial tools that usually need to be supported by additional geochemical and petrographic methods. A combination of approaches and evidence is mandatory in (marginal) lacustrine systems where the geochemical nature of coexisting carbonates is complex and often strongly variable.

- The present study is of significance for those investigating palaeolacustrine systems: it shows that ancient marginal lacustrine carbonates, while challenged by extensive meteoric weathering, are capable of providing key information for palaeoenvironmental reconstruction and the understanding of fluid flow patterns, porosity evolution and diagenetic processes in relation to those primary conditions.

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REFERENCES


FIGURE CAPTIONS

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

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

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

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

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

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

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

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

Fig. 9. Stratigraphic profiles 1 to 5 with their respective facies distribution and oxygen isotope chemostratigraphic curve. Note the difficulty to correlate individual curves together, while (freshwater to saline) climatic cycles (C1 to C7) are well-constrained by sedimentological continuity of cycle
boundaries. For clarity, the δ\textsuperscript{13}C curves are not shown because they show a nearly identical trend to δ\textsuperscript{18}O curves. For key to symbols, see Fig. 8.

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

Fig. 11. Diagram representing and comparing the range of δ\textsuperscript{18}O and δ\textsuperscript{13}C values (respectively in the upper and lower part) of matrix carbonates and other carbonate material (shells and cements). Mean and median values are provided. (*) Seven ostracod shell samples (mostly) free from diagenetic cement or allochthonous material are included within the 14 samples of ‘preserved ostracod shells’.

Fig. 12. Scatter plot representing the δ\textsuperscript{13}C versus δ\textsuperscript{18}O values of all the Hainsfarth carbonates. Note the clear covariance between δ\textsuperscript{13}C and δ\textsuperscript{18}O values.

Fig. 13. Transversal section of a cylinder core showing an erosive surface (dashed line) between a gastropod-dominated grainstone (beneath) to a peloidal-dominated grainstone (above). The erosion surface potentially depicts a short-term subaerial exposure surface (SES). Very negative δ\textsuperscript{18}O and δ\textsuperscript{13}C values characterize the matrix sampled above and below this discontinuity. (B) Close-up view of the erosive surface. Note the enrichment in siliciclastics at the surface (brown-black material). (C) and (D) Close-up of gastropod shell vestige below the surface. Note the erosion of the shell. (C) Both the shell and inner-shell space are filled with blocky calcite with a certain amount of secondary porosity remaining unfilled. (D) The same microphotograph under CL: ‘1’ microdolomitic crust; ‘2a/2b’ several phases of dark blue luminescent blocky calcite intercalated by a thin bright orange phase of the same fabric ‘3’; ‘cl’ siliciclastics. (E) EDS spectrum reveals siliciclastics; (F) EDS spectrum of quartz mineral.

Fig. 14. Diagram representing and comparing the range of δ\textsuperscript{18}O and δ\textsuperscript{13}C values of grainstone and algal–microbial dominated fabrics. While the range of δ\textsuperscript{18}O and δ\textsuperscript{13}C values characterizing the two groups of facies is similar, their respective mean and median values differ significantly.

Fig. 15. Diagram representing and comparing the range of δ\textsuperscript{18}O values of all Hainsfarth carbonates, and their significance with respect to assessed primary lacustrine versus meteoric diagenetic δ\textsuperscript{18}O signatures

Fig. 16. Scatter plot comparing the δ\textsuperscript{18}O and δ\textsuperscript{13}C values of all Hainsfarth outcrop carbonates (green circles) with values of time-equivalent, slightly more ‘basinal’ carbonates (red data points from Arp et al., 2013). The blue area designates the range of δ\textsuperscript{18}O and δ\textsuperscript{13}C values interpreted as primary lacustrine while the green data points (negative δ\textsuperscript{18}O and δ\textsuperscript{13}C values) outside the area are interpreted to reflect the meteoric diagenetic overprint of those original values.