Oxygen deficiency in Lake Sihetun; formation of the Lower Cretaceous Liaoning Fossil Lagerstätte (China)

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Abstract: The redox state of Lake Sihetun, represented by the Lower Cretaceous Yixian Formation (western Liaoning, China), is evaluated to understand the formation of this Konservat-Lagerstätte. Lake evolution is subdivided into four phases, of which Phases 2 and 3 exhibit excellent fossil preservation. Exceptional preservation and mass mortality events within Phase 2 were previously attributed to synsedimentary volcanism and oxygen deficiency. However, the volcanic trigger for mass mortality events remains enigmatic and distinction between anoxia and dysoxia has not been put forward so far. To resolve the redox state of the lake during Phase 2, 5394 diameters and decreased framboid-size variabilities correspond to their formation above the sediment–water interface. Pyrite framboid analysis has become a powerful proxy for palaeoredox conditions in modern euxinic, dysoxic, and oxic settings. Small diameters and decreased framboid-size variabilities correlate with bottom-water oxygen depletion ranks among the major causes for mass mortality events and larger-scale biotic crises (e.g. Wignall & Twitchett 1996; Bond et al. 2004; Wignall et al. 2010) and is one of the main factors leading to the formation of Konservat-Lagerstätten, when reducing conditions become established during stagnation, promoting early diagenetic precipitation (Seilacher et al. 1985; Allison 1988). Identification of ancient redox levels can be achieved through various techniques. In addition to geochemical indices such as the degree of pyritization (Jones & Manning 1994), oxygen depletion is best identified through the presence of laminated sediments. However, both lower dysoxic and anoxic conditions generate finely laminated sediments and only the existence of a low-diversity benthic fauna sets them apart (Wignall & Hallam 1991). The distinction between ancient redox levels becomes very challenging when a great extent of sediment alteration is involved, and is the case for the famous Lower Cretaceous palaeolake deposits of western Liaoning, for which a technique that is robust towards such alteration processes is required. Wilkin et al. (1996) have shown that the size distributions of pyrite framboids (spheroidal clusters of equidimensional and equimorphic pyrite crystals; Rickard 1970; Ohfuji & Rickard 2005) correlate with bottom-water redox conditions in modern euxinic, dysoxic, and oxic settings. Small diameters and decreased framboid-size variabilities correspond to their formation above the sediment–water interface. Pyrite framboid analysis has become a powerful proxy for palaeoredox conditions, with case studies performed for the Black Sea (Wilkin et al. 1997), Late Devonian anoxic events (Bond & Wignall 2005), Permo-Triassic boundary sections (Bond & Wignall 2010), Permian–Jurassic pelagic sediments (Wignall et al. 2010), submarine chimneys of the Gulf of Cadiz (Merinero et al. 2009), the Kimmeridge Clay (Wignall & Newton 1998), Upper Permian black shales of the East Greenland Basin (Nielsen & Shen 2004), and end-Permian deep-water sediments of Kashmir (Wignall et al. 2005). All are marine settings with the exception of a Pleistocene to Early Holocene freshwater phase in the Black Sea, which is now permanently anoxic (Ross & Degens 1974; Wilkin et al. 1997).

Here we present a palaeoredox study on Lake Sihetun of the Lower Cretaceous Yixian Formation, which is famous for its outstanding fossil preservation. In particular, feathered dinosaurs (e.g. Xu et al. 1999, 2001) and the putative early flowering plant Archaefructus (Sun et al. 2002) have roused widespread interest. Countless other exceptionally well-preserved vertebrate and invertebrate fossils have been discovered. They represent a time during which the evolution of major clades such as birds and angiosperms took place (Barrett 2000). The evolutionary significance, in combination with the superb preservation, renders the Yixian Formation one of the most important Mesozoic fossil Lagerstätten.

Somewhat surprisingly, palaeoenvironmental studies have long been neglected. Fürsich et al. (2007) and Pan et al. (2012) described Lake Sihetun as a shallow eutrophic lake system controlled by fluctuations of oxygen levels, but those studies were mainly based on fossil assemblages. Sedimentological evidence was put forward by Jiang et al. (2012), who recognized four phases of lake evolution. Hethke et al. (2013) added a high-resolution microfaucy analysis by focusing on two of these phases (2 and 3), which yield most of the excellently preserved fossils mentioned above.

Oxygen deficiency has been suggested to cause recurrent mass mortality events of Phase 2 invertebrate fossils. Fürsich et al. (2007) proposed seasonal dysoxia during summer owing to the consumption of oxygen by respiration processes coupled with winter mixing and reoxygenation. Jiang et al. (2012) and Hethke et al. (2013) refined this model by proposing a mainly stratified water column during Phase 2 with convective mixing seldom reaching the lake floor and leading to short-lived oxygenation events.

Pyrite-framboid pseudomorphs are widespread in the sediments of Phase 2 (Hethke et al. 2013). The depositional environment
proposed for Phase 2 will be developed further in this study through the determination of ancient redox levels using quantitative methods. Further identification of the main factors that controlled iron sulphide formation in Lake Sihetun will lead to a comprehensive lake model.

Geological setting

The Jehol Group of western Liaoning is Early Cretaceous in age and comprises three formations: Yixian, Jiufotang, and Fuxin (Figs 1 and 2; Jiang & Sha 2006). It has been proposed that the Yixian Formation was deposited between 129.7±0.5 and 122.1±0.3 Ma, within an interval of 7 Ma (40Ar/39Ar; Chang et al. 2009). At the time, Liaoning was located at a palaeolatitude of 41.9° (±6.6°) N (Enkin et al. 1992; Zhou et al. 2003; Amiot et al. 2011).

In the Sihetun area, the Yixian Formation is made up of four units (Fig. 2b; Table 1): the Lujiatun Unit, Lower Lava Unit, Jianshangou Unit, and Upper Lava Unit (Jiang & Sha 2007). The lowermost Lujiatun Unit is unconformably overlying the Upper Jurassic–Lower Cretaceous aeolian Tuchengzi Formation (Cheng et al. 1997). Radiometric ages suggest a contemporaneous deposition of the Lujiatun Unit and the Jianshangou Unit (He et al. 2006), but extensive field investigations in the Sihetun area proved that the Lujiatun Unit is underlying the Lower Lava Unit and the Jianshangou Unit in more than ten sections. Furthermore, the Lujiatun Unit might be absent at a few localities, where the Lower Lava Unit and the Jianshangou Unit unconformably overlie the Tuchengzi Formation directly. The Jianshangou Unit is unconformably overlain by the Upper Lava Unit, which also intruded into the lake sediments (Jiang et al. 2011).

Lake Sihetun (Jianshangou Unit) has been proposed to have existed for 1.5 Ma (125.7±2.6 to 124.2±2.5 Ma; 40Ar/39Ar), but there are even shorter estimates for lake duration (0.7 Ma or less) that are based on palaeomagnetic data (Zhu et al. 2007).

The Jianshangou Unit can be subdivided into four beds that correspond to four phases of lake evolution (Table 1; Fig. 3; Jiang et al. 2012). Phase 1 is characterized by fluctuating but gradually rising water levels. During Phase 2, a marginal beach to nearshore facies and a suspension-derived lake-floor facies were deposited, whereas hyperpycnal flows were typical for Phase 3. A fan delta prograded into the lake during Phase 4. Hethke et al. (2013) distinguished six microfacies (Mf 1–6) that occur within the most fossiliferous beds 2 and 3 of the Jianshangou Unit (Table 1): (1) allochthonous, siliciclastic laminae with an average thickness of 26.1 µm; (2) chrysophycean cyst accumulations; (3) tuffaceous silt; (4) lacustrine chemical precipitates; (5) tuff; (6) normal-graded sandy to silty siliciclastic deposits. Pyrite framoids are restricted to Phase 2 and have been reported from Mf 1, associated tuffs as well as tuffaceous sediments (Mf 3 and Mf 5) and, to a lesser degree, from Mf 4.

Material and methods

Data are based on three excavations carried out in the Sihetun area several kilometres apart to identify spatial variations in redox state within the lake: Jianshangou (JSG), Erdaogou (LXBE), and Zhangjiagou (ZJG; Figs 1 and 3). Excavations LXBE and ZJG covered Bed 2 sediments, whereas excavation JSG focused on sediments of Bed 3 with fewer samples retrieved from Bed 2, explaining the smaller amount of framoid-yielding thin sections from JSG.

Traditional optical microscopic methods were used to examine 29 framoid-yielding petrographic thin sections. Quantitative measurements (±0.5 µm) of framoid diameters were taken under transmitted light using the Zeiss AxiosVision Software (Release 4.8.1).
**Table 1.** Units of the Yixian Formation in the Sihetun area, four beds of the Jianshangou Unit from oldest (Bed 1) to youngest (Bed 4), and microfacies present within beds 2 and 3

<table>
<thead>
<tr>
<th>Unit</th>
<th>Description</th>
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<tbody>
<tr>
<td><strong>Units of the Yixian Formation (Jiang et al. 2011)</strong></td>
<td></td>
</tr>
<tr>
<td>Upper Lava</td>
<td>Intermediate–basic lava and intrusive rocks</td>
</tr>
<tr>
<td>Jianshangou</td>
<td>Fine siliciclastic deposits and tuffs, with intercalated calcareous marl</td>
</tr>
<tr>
<td>Lower Lava</td>
<td>Basaltic andesites, olivine basalts, and trachyandesites</td>
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<tr>
<td>Lujiaztun</td>
<td>Volcanic conglomerates, sandstones and lapilli tuffs</td>
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<tr>
<td><strong>Jianshangou Unit (Jiang et al. 2012)</strong></td>
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<tr>
<td>Bed 4</td>
<td>Tuffaceous conglomeratic sandstones and tuffs interbedded with finer siliciclastic deposits</td>
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<tr>
<td>Bed 3</td>
<td>Normal-graded fine sandstones to siltstones</td>
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<tr>
<td>Bed 2</td>
<td>Paper-thin laminae of fine tuffaceous siliciclastic deposits and some evaporites</td>
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<tr>
<td>Bed 1</td>
<td>Comparatively coarse, horizontally or cross-bedded, tuffaceous siliciclastic deposits</td>
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<tr>
<td><strong>Microfacies occurring in beds 2 and 3 (Hethke et al. 2013)</strong></td>
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<tr>
<td>Mf 1</td>
<td>Allochthonous, siliciclastic laminae that are 26 µm thick on average</td>
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<tr>
<td>Mf 2</td>
<td>Chrysophycean cyst accumulations</td>
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<tr>
<td>Mf 3</td>
<td>Tuffaceous silt</td>
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<tr>
<td>Mf 4</td>
<td>Lacustrine calcium carbonate-rich laminae</td>
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<tr>
<td>Mf 5</td>
<td>Tuff</td>
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<tr>
<td>Mf 6</td>
<td>Comparatively coarse, normal-graded siliciclastic deposits</td>
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**Fig. 2.** Stratigraphic columns for (a) the Jehol Group of western Liaoning and (b) the Sihetun area (modified after Jiang et al. 2012). Lines schematically indicate the boundaries between the four units of the Yixian Formation.
Back-scattered electrons (BSE) were detected for compositional imaging using a scanning electron microscope (TESCAN Model Vega\xmu). Compositional changes were revealed by identifying differences in brightness, which are determined by the mean atomic numbers of phases (Reed 2005). Mean atomic numbers relevant for this study from higher to lower are as follows: iron oxides and sulphides > calcite > anorthite and orthoclase > albite > quartz. Therefore, iron oxides and sulphides appear much brighter than quartz. Energy-dispersive X-ray spectroscopy (EDS; program INCA) allowed further qualitative elemental analyses. Conductive coatings for the thin sections were gold or carbon. Statistical analyses were carried out using the PAST software (http://folk.uio.no/ohammer/past/).

The reference material is stored at the Paläoumwelt section of the GeoZentrum Nordbayern, University of Erlangen–Nürnberg.

Fig. 3. Lithologs of excavations ZJG, LXBE, and JSG. Framboid-yielding horizons analysed in this study are marked. Beds 2 and 3 of the Jianshangou Unit are separated by a dotted line.
Fig. 4. Phase 2 sediments of allochthonous clay–silt couplets (Mf 1) and intercalated tuff layers (Mf 5). (a) Plane-polarized light. (b–f) BSE images. (a) Framboids appear red (arrowed) to dark under plane-polarized light. (b, c) Original framboïd structures are retained in thin section LXBE L1 and single microcrystallites exhibit reaction rims made up of iron oxide–hydroxides. This thin section was used for a case study (see Fig. 7) that aimed at discriminating between concentrated and matrix framboids. (d) Overview of the profoundly altered sediment of thin section LXBE E and (e) close-up of a concentrated iron sulphide horizon made up of framboids as well as single microcrystals. Smaller framboids (arrowed) have probably been overlooked during size measurements, as concentrated layers often merge to one dark red layer under plane-polarized light. (f) Progressive alteration is expressed by the formation of hollow, lobate (EDS spectrum) or meniscus-like structures (arrowed) that surround framboïd remnants. An almost completely disintegrated structure is traced (13.9 µm).
Fig. 5. Phase 2 sediments of lacustrine carbonate precipitates (Mf 4) and allochthonous clay–silt couplets (Mf 1). (a–e) BSE images. (f) Plane-polarized light. (a, b) Mf 4 clustered pyrites are more readily disintegrated and the octahedral microcrystallites are much larger than Mf 1 framoids. (c–e) Extensive silicification affected many iron sulphide horizons and concealed them. The suggested boundary between ‘iron sulphide sediment’ and detrital sediment is traced in white (e), revealing an original lamina thickness of more than 100 µm. Such layers are proposed to have resulted from the establishment of biofilms at the lake floor or from microenvironments around animals and plants retaining reactive organic matter, corroborated by increasing microcrystal sizes towards the centres of iron sulphide layers (e). (f) Example of quantitative framboid-size measurements. Concentrated as well as matrix framoids are often hard to distinguish and measurements led to distribution overlap (see Fig. 7).
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layers (Fig. 5e). EDS spectra of framboids show predominantly Fe and their sizes characteristically increase towards the centre of such microcrystals may dominate over framboids in iron sulphide layers. The mean diameters of 2.5 µm framboids are often associated with microcrystals, which exhibit maximally well-defined spheroids have also been measured. Most of these are nevertheless spheroidal (Fig. 5a), diameters of 1:10 (Rickard 1970). This ratio is sometimes higher for Mf 4 clustered pyrites. However, as most of these are nevertheless spheroidal (Fig. 5a), diameters of comparatively well-defined spheroids have also been measured.

Framboids occur (1) concentrated in discontinuous iron sulphide layers and (2) scattered throughout the matrix. Concentrated framboids are often associated with microcrystals, which exhibit maximum diameters of 2.5 µm in Mf 1 (Figs 4e and 5c–e). These microcrystals may dominate over framboids in iron sulphide layers and their sizes characteristically increase towards the centre of such layers (Fig. 5e). EDS spectra of framboids show predominantly Fe and O peaks, but element maps (Hethke et al. 2013, fig. 12) confirm that remnant sulphur is preserved within framboids and the single euhedral microcrystals adjacent to them.

There are two processes that obscure pyrite preservation: (I) oxidation and (II) extensive silica replacement (Fig. 5b–e). Fast oxidation rates can be expected because of the high specific surface area of framboids. Original mineralogies are usually better preserved in larger, euhedral pyrite crystals (Merinero et al. 2009). Generally, the alteration process (Fig. 6a) involves the formation of comparatively thin reaction rims made up of iron oxide–hydroxides, the dissolution of interior iron sulphides to a great extent and, in some cases, silicification (spectrum of Fig. 5b). Similar alteration structures have been observed within greigite framboids from methane seep carbonates (Bailey et al. 2010). Lobate alteration rims formed by outgrowth may occur (Figs 4f and 6b). Their interior is hollow and once comprised parts of the original framboid that has readily been dissolved (compare with Bailey et al. 2010, fig. 3p). Virtasalo et al. (2010) described similar alteration rims as radially arranged laths reminiscent of marcasite. Extensive silica replacement resulted in silicified patches (Fig. 5d and e) and led to widespread concealment of iron sulphide layers. Silicification was so severe in Figure 5c that most of the original iron sulphide signature has completely been obscured.

**Size measurements**

 Principally, there are differences in framboid formation between anoxic, dysoxic and oxic bottom waters that result in distinct size distributions (Muramoto et al. 1991; Wilkin et al. 1996). The analysis of framboid diameters involves descriptive statistics summarized in Figures 7–10. Measurement bias may come from overlooking smaller framboids within concentrated layers that are generally harder to discern under transmitted light (arrowed in Fig. 4e), possibly shifting the spectrum towards larger sizes. Such shifts are compensated for, as framboid diameters tend to be underestimated, because spheres are usually not exactly cut in half. Generally, framboids embedded within Mf 1 and associated tuffs exhibit smaller average diameters than clustered pyrites that are associated with carbonate precipitates (Mf 4).

Concentrated framboids are often hard to separate from matrix framboids in bulk measurements (e.g. Fig. 5f, upper left region). To check for discrepancies between diameters of the two statistical populations, framboids concentrated in a layer as well as matrix framboids in its vicinity have been measured independently (Fig. 7). Framboid diameters from the concentrated layer in Figure 7a are distributed around a mean diameter of 10.5 µm and are thus distinctly larger than those that are scattered in the matrix (ø 6.9 µm on average; p(same mean) = 4.7 x 10^{-27}; t test). Concentrated framboids tend to be normally distributed, whereas scattered framboids exhibit positively skewed distributions. Quantitative measurements often reveal polymodal distributions (Fig. 8) that are evidence of overlap of these two statistical populations.

Average diameters and standard deviations (Fig. 9) are smallest in horizons ZIG E and ZIG D (ø 5.5 µm; SD = 2.0 µm) and largest in horizons LXBE K1 and LXBE J (ø 25.7 µm; SD = 6.7 µm), which are characterized by carbonate precipitates (Mf 4 clustered pyrites). The relationship between mean diameter and standard deviation (Fig. 10) reveals that there are distinct differences between the three excavations. Framboid diameters of LXBE are generally larger and more dispersed, owing to a larger number of thin sections yielding only concentrated framboids within this particular excavation. ZIG framboids are smaller and their sizes are less dispersed. JSG framboids plot at an intermediate position.

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**Results**

**Observations**

Pseudomorphs of iron sulphide framboids are especially common in the clay–silt couplets of Mf 1 (Fig. 4), the dominant microfacies of Bed 2, and in associated tuffs and tuffaceous sediments. Pyrites of calcium carbonate-rich laminae (Mf 4; Fig. 5a and b) form aggregates that are only crudely spherical and termed clustered pyrite (Canfield & Raiswell 1991). They are larger (<50 µm) and made up of octahedral microcrystallites of variable sizes (<12 µm). Framboids are defined by an arbitrary maximum ratio of microcrystallite size to spheroid diameter of 1:10 (Rickard 1970). This ratio is sometimes higher for Mf 4 clustered pyrites. However, as most of these are nevertheless spheroidal (Fig. 5a), diameters of comparatively well-defined spheroids have also been measured.

Framboids occur (1) concentrated in discontinuous iron sulphide layers and (2) scattered throughout the matrix. Concentrated framboids are often associated with microcrystals, which exhibit maximum diameters of 2.5 µm in Mf 1 (Figs 4e and 5c–e). These microcrystals may dominate over framboids in iron sulphide layers and their sizes characteristically increase towards the centre of such layers (Fig. 5e). EDS spectra of framboids show predominantly Fe and O peaks, but element maps (Hethke et al. 2013, fig. 12) confirm that remnant sulphur is preserved within framboids and the single euhedral microcrystals adjacent to them.
Discussion

Pyrite framboid formation and control parameters

The sediments of Lake Sihetun yield concentrated framboids, which are often associated with iron sulphide microcrystals, as well as matrix framboids of different size distributions. All have been altered to iron oxide–hydroxides. Iron sulphides are usually referred to as early diagenetic products that form in shallow sediment depths under oxic bottom waters through the reaction of detrital iron minerals with \( \text{H}_2\text{S} \), but syngenetic iron sulphides precipitating directly from a euxinic water column have also been reported (e.g. Degens et al. 1972; Muramoto et al. 1991). Stable iron minerals under reducing conditions are pyrite, siderite and magnetite, depending on carbonate and sulphur concentrations. Higher concentrations of dissolved sulphur and lower dissolved carbonate concentrations extend the stability field of pyrite (Krauskopf & Bird 1995).

Experimental synthesis of pyrite framboids can be achieved at high supersaturation and rapid nucleation rates. Suitable environments are realized by the addition of sulphur and oxygen, or by increasing temperature (Butler & Rickard 2000; Ohfuji & Rickard 2005). Some workers have argued for the formation of metastable pyrite precursors that precede pyrite framboid formation (Farrand 1970; Sweeney & Kaplan 1973; Wilkin & Barnes 1996). Those precursor iron monosulphides may rapidly convert to pyrite or be transformed to ferrimagnetic greigite (\( \text{Fe}_3\text{S}_4 \)). In turn, other workers have put forward experimental evidence that framboid formation may be independent of greigite precursors (Butler & Rickard 1970).

Fig. 7. Framboid diameters have been measured within a concentrated layer (a) and from the matrix in the immediate proximity of the concentrated layer (b), no more than 300 \( \mu\text{m} \) above and below. (c) Box plot of concentrated and matrix framboid diameters. A normal distribution (continuous curve, parametric estimation) is fitted to the concentrated diameters (Shapiro–Wilk \( W = 0.98 \)). Both exhibit the same standard deviation, but average diameters differ by several micrometres. The mean diameter of 10.5 \( \mu\text{m} \) for concentrated framboids is comparable with the average framboid size of the Pleistocene-early Holocene freshwater phase of the Black Sea. The box for the matrix framboids slightly overlaps the dashed line that indicates average euxinic diameters of modern Black Sea pyrite framboids, but a standard deviation of 3.0 points to lower dysoxic bottom waters. Both distributions were derived from framboid populations that originated from early diagenetic growth, but whereas matrix framboids formed in an open system under lower dysoxic bottom waters, concentrated framboids, at least partly, stem from growth in a confined microenvironment.

Fig. 8. Composite framboid-size distribution of four horizons from the same thin section. Framboids occurring within a thin section have been measured quantitatively, because concentrated as well as matrix framboids are often hard to discriminate (e.g. Fig. 5f); consequently, distributions are superimposed. The resultant positively skewed distribution is bimodal and arrows point to the two main framboid populations, delineating concentrated (2) and matrix framboid (1) signatures.
Variables leading to single microcrystal growth instead of frambooidal textures, which is the case for a number of concentrated iron sulphide layers in Lake Sihetun (Fig. 5c–e), include slower nucleation rates and lower oxidation-reduction potential (Eh) (Butler & Rickard 2000), conditions that were realized in pore spaces of postglacial lacustrine clays of the northern Baltic Sea that were not enriched in reactive organic matter (Virtasalo et al. 2010). Butler & Rickard (2000) argued that texture is a function of Eh. At a pH of 6 and under the exclusion of oxygen, frambooidal pyrite forms at Eh > −250 mV, whereas small octahedra are predominant at lower Eh values of −400 mV. It should be noted that reaction temperatures were set between 60 and 140 °C. Under these conditions, greigite intermediates, molecular oxygen, or biological forcing are not involved.

According to Wilkin & Barnes (1996), the fastest rates of experimental frambooid formation are achieved when air is periodically bubbled into the reaction vessel. Therefore, there are steps in frambooid formation that involve weakly oxidizing conditions under non-excessive amounts of H2S. Maximum simultaneous production rates of the reactants required (dissolved sulphide, ferrous iron, and an oxidant) are found directly subjacent to redox interfaces (Wilkin et al. 1996; Wignall & Newton 1998).
The role bacteria play in iron sulphide precipitation is being debated. Although it has been proven that framboindal sulphides may form in vitro from suspension in the absence of bacteria (Farrand 1970; Butler & Rickard 2000), we are dealing with a natural environment, where bacteria are likely to be an important factor. Iron sulphides may result from anaerobic biologically mediated processes of sulphate-reducing bacteria, which raise the $\text{H}_2\text{S}$ concentration. There are also arguments that framboinds are pseudomorphic after pre-existing organic spherules such as organic coacervates or gaseous vacuoles (e.g. Rickard 1970). Other workers have pointed out that diagenetically altered framboinds only mimic the morphology of synthetic archaeobacterial consortia, implying acellular framboinds (Bailey et al. 2010); similar diagenetically altered framboinds have also been observed within the sediments of Lake Sihetun (Figs 4f and 6b). Another possibility for bacterial involvement would be the formation of intracellular iron sulphides reported from magnetotactic bacteria living in freshwater (Fassbinder et al. 1990). However, the single microcrystals which are inferred from the presence of chrysophycean cysts and a trophic to mesotrophic intervals occurred during Phase 2 as well, nutrient concentrations must have been high within the eutrophic bottom waters, more reactive organic compounds must have been readily destroyed and only resistant organic compounds should have remained for sulphate reduction (Berner 1984). Therefore, nutrient concentrations must have been high within the eutrophic Lake Sihetun to compensate for the low sedimentation rate by generating a high amount of organic matter. Nevertheless, rare oligotrophic to mesotrophic intervals occurred during Phase 2 as well, which are inferred from the presence of chrysophycean cysts and a general absence of iron sulphides within the corresponding sediments (Hethke et al. 2013).

When mixing of the water column is limited and organic matter supply is high, the redox interface rises above the bottom sediments. In the Black Sea, anoxic, sulphidic waters are present at 100 m depth and greigite concentrations in the water column are highest at a depth of 125 m (1988 R.V. Knorr cruise). Maximum concentrations of total dissolved iron were found at 180 m depth, decreasing below that depth. The depth interval immediately below the redox interface in the Black Sea is a zone of net consumption of dissolved sulphide by oxidation and precipitation (Muramoto et al. 1991). Furthermore, the average $\delta^{34}\text{S}$ composition of dissolved sulphide from the uppermost 70–100 m of the sulphide zone of the Black Sea is similar to that of particulate sulphur fluxes and of sediment sulphides, corroborating their place of origin from immediately below the oxic–anoxic interface within the water column (Fry et al. 1991; Muramoto et al. 1991). Shifts to positive isotopic values as observed within the lacustrine beds of the Black Sea (2500 to >7000 years BC; Ross & Degens 1974) indicate freshwater conditions and even closed-system growth (Calvert et al. 1996).
OXYGEN EFFICIENCY IN LAKE SIHETUN

Framboid size distributions

Intense diagenetic alteration and weathering within the sediments of Lake Sihetun led to the formation of characteristic reaction rims made up of iron oxide–hydroxides around numerous microcrystals (Figs 4c, 5b and 6a), as well as to alteration rinds (Figs 4f and 6b). Provided that primary iron sulphide textures are preserved (Fig. 6a), framboid size distributions can be used to discriminate between oxic, dysoxic, and anoxic conditions within the bottom waters. Wilkin et al. (1996) surveyed framboids in modern (1) anoxic–sulphidic (euxinic), (2) dysoxic, and (3) oxic environments.

(1) Euxinic framboids are small and less variable in size, being subjected to shorter growth times, because nucleation occurs syn-genetically within the anoxic water column. As the zone of framboi formation is limited (immediately subjacent to the redox interface and above the sulphidic zone), syngenetic framboid growth is restricted in size. Because settling velocity varies with the square of the particle radius, standard deviations are small, corresponding to narrow size distributions (Stokes' law; Muramoto et al. 1991; Wilkin et al. 1996). Overall syngenetic diameters are smaller than those produced by diagenetic growth (Wignall et al. 2005). Importantly, syngenetic framboids of the Black Sea were not observed in larger clusters, but as single occurrences (Muramoto et al. 1991; Wilkin et al. 1996).

(2, 3) Framboids forming within sediment pore waters that underlie dysoxic and oxic water columns have more time for nucleation and growth, and consequently have larger diameters. Lower dysoxic conditions are indicated by framboids having a similar small size to euxinic ones, but occasional larger diameters occur. Higher oxygen saturation is revealed by larger framboids exhibiting a broader size distribution (upper dysaerobic; Wignall & Newton 1998).

These findings have been tested (Wignall & Newton 1998), and a close correlation between framboid diameter and the degree of oxygen deficiency determined by other palaeoecological proxies has been discovered. A unique opportunity to test this relationship is provided by Holocene deep-water sediments of the Black Sea (Wilkin et al. 1997), which are subdivided into three units (Ross & Degens 1974): Pleistocene–early Holocene lacustrine, organic carbon-poor layers (Unit 3), a sapropel (Unit 2), and the most recent carbonate-rich sediments (Unit 1). The development of water-column anoxia in the Black Sea, which coincided with the beginning of Unit 2, resulted in a drop in mean framboid diameters from 10 µm to 5 µm (Wilkin et al. 1997). Hence, a mean of 10.5 µm for the concentrated framboids of ancient Lake Sihetun (Fig. 7) implies growth within anoxic sediment pore waters, similar to Unit 3 of the Black Sea. Co-occurring matrix framboids, however, carry a lower dysoxic signal.

Mf 1 framboids. Crystal size distributions can be related to crystal growth mechanisms (Kile et al. 2000). Log-normal distributions of Mf 1 framboids (Fig. 9) indicate initial growth by surface control and subsequent supply-controlled growth suggestive of open-system growth (Kile et al. 2000; Merinero et al. 2009).

Diameter means of euxinic Black Sea and Framvaren framboids range between 4.3 and 6.1 µm with standard deviations of 1.4–2.0 µm (Wilkin et al. 1996). According to these criteria, euxinic conditions were established in Lake Sihetun during the deposition of horizons ZJG E and ZJG D, which yield mean diameters of 5.4 and 5.6 µm, respectively. Two other thin sections (LXBE...
N1 and LXBE G1) might yield an episodically anoxic signal, considering the distribution overlap between concentrated and matrix framboids (Figs 9 and 10). The existing discrepancy between euxinic framboids of the Black Sea and those of Lake Sihetun results from parameters that affect the settling rate; for example, density differences, thermal motions, turbulence, and particle–particle interactions (Wilkin et al. 1996). Euxinic framboids of the Black Sea, for example, frequently adhere to biogenic particles (Muramoto et al. 1991).

A similar case is the size discrepancy between euxinic framboid diameters of the modern Black Sea and those of the Kimmeridge Clay (5.0 and 3.0µm, respectively; Wilkin et al. 1996; Wignall & Newton 1998). This discrepancy was suggested to result from more rapid settling rates of Kimmeridge Clay framboids compared with those of the Black Sea, where framboids form directly subjacent to the redox interface for several months until they reach a critical size and begin to settle. The Kimmeridge Clay sea exhibited a less pronounced density contrast, because it was thermally stratified in contrast to the salinity-stratified Black Sea (Wignall & Newton 1998).

Dysoxic distributions, in turn, are characterized by the addition of large diameters to the spectrum (Wignall & Newton 1998). Standard deviations of most Mf 1 framboids range around 3.1µm (Fig. 9), which is similar to those of framboids recovered from the dysoxic Peru margin (Wilkin et al. 1996). However, Figures 7 and 8 demonstrate that there is a considerable distribution overlap between concentrated and matrix framboids that raises standard deviations significantly. It can therefore be assumed that some distributions contain an anoxic signal, especially those of excavation ZJG.

Mf 4 clustered pyrites. Secondary pyrite overgrowth resulted in higher mean diameters and standard deviations of Mf 4 clustered pyrites (LXBE K1 and J; Fig. 5a and b). This effect is more pronounced the longer pyrite is subjected to solutes such as Fe²⁺ or HS⁻. Bioturbation promotes transportation of these by sediment remixing. Wilkin et al. 1996 and Hethke et al. (2013) noted the presence of meiofaunal bioturbation in Mf 4. Furthermore, Mf 4 standard deviations are similar to those of oxic environments of salt marshes (Wilkin et al. 1996), but the mean diameters of the Lake Sihetun clustered pyrites are significantly larger (Fig. 9).

The negatively skewed framboid size distribution of LXBE K1 is indicative of an eventual formation of a closed system. As saturation was being reduced, small pyrite crystals and clusters became unstable, whereas larger clusters grew at their expense owing to their large surface free energy (Ostwald ripening; Kile et al. 2000; Merinero et al. 2009). However, Merinero et al. (2009) mentioned low values of size variance for closed-system conditions, which is not true of Mf 4 distributions. This might be a measurement artefact owing to the general disintegration of most Mf 4 clustered pyrites or a result of a combined open-system–closed-system growth. Nevertheless, the general evidence strongly implies early diagenetic, intergranular formation of Mf 4 pyrites and an oxic water column.

Methane-derived carbonates? Methanogenic fermentation of buried organic matter leads to methane accumulation within organic-rich sediments. In view of the continuing synsedimentary volcanism within Lake Sihetun, thermogenic methane may also be considered. Seepage of methane-rich fluids causes carbonate precipitation, taking place inside the anoxic sediment in case of oxic bottom waters (Peckmann et al. 2001). Such methane-derived carbonates are induced by anaerobic methane oxidation that is coupled to bacterial sulphate reduction. Increased alkalinity causes carbonate formation. Carbonates (MF4) are layered within the sediments of Lake Sihetun. In the Black Sea, flat crusts develop under oxic bottom waters instead

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**Fig. 12.** Phase 2, meromictic setting. Meromictic conditions in a chemically stratified Lake Sihetun with syngenetic iron sulphide framboids precipitating immediately below the redox interface, which had moved into the water column. The three main controls on pyrite formation are numbered: (1) organic matter; (2) sulphate; (3) detrital iron minerals. Two possible causes of meromixis are proposed for Lake Sihetun: (1) meromixis probably arose as a result of extensive decomposition of organic matter in combination with a moderately deep to deep Lake Sihetun in relation to its surface area, where mixing was limited to the upper water column. Climates were dry; (2) as the lake was volcanically influenced, it might have been subjected to hydrothermal events, which corresponded to wetter climates when local rainwater became activated with CO₂ and H₂S. The chemical stratification must have been delicate, as it was almost offset by increasing temperatures with depth, and catastrophic outgassing of CO₂ might have led to mass mortality events during times of reduced rainfall.
of chimney-like structures, which are found within the anoxic zone. Iron sulphides accompany these microbial carbonates. The diameters of single framboids reported from Black Sea methane seeps are 20–30 µm (Peckmann et al. 2001), similar to those of Mf 4 clustered pyrites. Therefore, in addition to the seasonal interpretation of Mf 4 deposits put forward by Hethke et al. (2013), there might be a second cause involving the formation of methane-derived carbonates (MF4) induced by methane oxidation (Fig. 11).

Environmental inferences

There are three major environmental settings leading to pyrite formation that intermittently dominated Lake Sihetun during Phase 2. They are oxic, dysoxic, and anoxic bottom waters. Generally, palaeoecological evidence points towards anoxic to lower dysoxic bottom waters in Lake Sihetun, expressed by a general lack of bioturbation that left the laminated sediments undisturbed as well as by very low faunal diversities with abundant mono- to paucispecific assemblages of opportunistic taxa (Wignall & Hallam 1991; Fürsich et al. 2007).

Setting 1: euxinic (Fig. 12). This setting implies oxygen-free and H₂S-bearing bottom waters in a permanently stratified water column. Evidence for such conditions has been found within four horizons of excavations ZIG and LXBE (Fig. 10). There are several causes for the establishment of such meromictic conditions in Lake Sihetun, as follows.

(1) Stagnation owing to minimal circulation might have arisen as Lake Sihetun was comparatively deep in contrast to its surface area. It may have led to an occurrence of H₂S above the sediment–water interface, so that iron sulphides could precipitate from the water column, usually through high rates of organic matter sedimentation as a result of eutrophic conditions. 'Fresh' and more reactive organic compounds were retained and accumulated, which would have otherwise been rapidly destroyed. Bacterial sulphate reduction was extensive in both bottom waters and sediments, and pyrite formation was possible even during sedimentation (Berner 1984). Detrital iron minerals were present in ample amounts during Phase 2, as most of the sediments are tuffaceous. Matrix framboids (Fig. 7) are proposed to be syngenetic in such a setting. Concentrated frambooids and associated single euhedral microcrystals occurring adjacent to matrix framboids formed diagenetically within the sediment at a different time, possibly even underneath oxic to dysoxic bottom waters (e.g. Fig. 5e).

(2) As Lake Sihetun was volcanically influenced, hydrothermal spring activity might have occurred (Fig. 12) and lead to high concentrations of dissolved gases, specifically CO₂, CH₄, and H₂S. Hydrothermal events correspond to wetter climates, as rainwater infiltration may have led to an occurrence of H₂S above the sediment–water interface and in the top sediment layers, and only more resistant compounds were able to survive for sulphate reduction. However, the presence of biofilms at the bottom of Lake Sihetun may have provided favourable conditions for framboid formation. Concentrated framboid layers dominated by frambooidal textures and similar to those shown in Figure 4b and c are stratiform and the grain fabric is loose, meeting the criteria described by Schieber (2002) for the presence of an organic slime matrix, which is a favourable culture medium for sulphate-reducing bacteria. Pyrite concretions with framboid-dominated textures in Holocene lacustrine clays of the northern Baltic Sea, for example, formed within burrows by the decomposition of mucous coatings on the burrow walls (Virtasalo et al. 2010).

Several contradictory explanations are possible for the comparatively thick irregular layers dominated by euhedral microcrystals (Fig. 5c–e).

(1) Masses of euhedral microcrystals similar to those observed in Lake Sihetun are known from Holocene lacustrine clays of the Baltic Sea, where they crystallized in organic-poor pore spaces (Virtasalo et al. 2010, 2013). Pore spaces in the sediments of Lake Sihetun may have resulted from gases forming during the decomposition of biofilms, as observed in the Solnhofen Plattenkalk (Link & Fürsich 2001).

(2) There might be a purely chemical explanation for the dominance of microcrystals, as texture is also a function of Eh and euhedral microcrystals are formed at an Eh lower than that for framboid formation (Butler & Rickard 2000). Mixed textures of framboids and euhedra, as present in Lake Sihetun (Fig. 5c), have also been observed by Butler & Rickard (2000).

(3) Furthermore, the establishment of microenvironments around and within plant and animal remains might have preserved reactive organic compounds and led to iron sulphide replacement (Briggs et al. 1996) that can be observed in many fossils of Bed 2 (Leng & Yang 2003). Microcrystals similar to those of the iron sulphide layers observed in Bed 2 have been reported from pyritized insect fossils of the Middle Jurassic of Daohugou, Inner Mongolia (Wang et al. 2009).

With the onset of Phase 3, conditions in Lake Sihetun became more strongly oxidizing at the sediment–water interface. This was accompanied by a cessation of extensive iron sulphide formation. Coarser sediments, as deposited during Phase 3, are usually much better oxidized than clay-sized particles (Baas Becking et al. 1960).

Lake analogue for setting 1

Volcanic and meromictic Lake Kivu (DR Congo and Rwanda) may be viewed as a lake analogue to Lake Sihetun in some respects. It is permanently stratified and anoxic below depths of 50–80 m. Evidence for lacustrine, syngenetic pyrite framboids has been reported by Degens et al. (1972), who found pyrite frambooids (5–10 µm in diameter) suspended within the H₂S zone of the lake. Hydrothermal events lead to a temperature and salinity stratification of chimney-like structures, which are found within the anoxic zone. Iron sulphides accompany these microbial carbonates. The diameters of single framboids reported from Black Sea methane seeps are 20–30 µm (Peckmann et al. 2001), similar to those of Mf 4 clustered pyrites. Therefore, in addition to the seasonal interpretation of Mf 4 deposits put forward by Hethke et al. (2013), there might be a second cause involving the formation of methane-derived carbonates (MF4) induced by methane oxidation (Fig. 11).

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in Lake Kivu. According to Degens et al. (1972), the water discharge through hydrothermal springs is so high that the lake would fill up in only 100 years. Hydrothermal solutions originate from rainwater that becomes activated with CO₂ and H₂S. Accordingly, concentrations of CO₂ and CH₄ increase with lake depth (Tassi et al. 2009). Sedimentary properties of Lake Sihetun deposits are very similar to those of Lake Kivu, except that the H₂S zone in Lake Kivu is marked by sphalerite (ZnS), which has not been found in Lake Sihetun. This is related to zinc availability within the adjacent rock formations the hydrothermal solution is passing through.

To sustain meromictic conditions, prolonged hydrothermal input is needed. Haberyan & Hecky (1987) noted that Lake Kivu’s modern chemical stratification is almost offset by increasing temperatures with depth. The surface waters have to be constantly diluted to prevent lake overturn. Overturn would increase deep water pH through the release of CO₂, allowing for carbonate to precipitate. Therefore, carbonate precipitation occurs during strongly reduced inflow (Haberyan & Hecky 1987). Evidently, pyrite must be scarce during severely high CO₂ concentrations leading to low pH levels. Nevertheless, somewhat surprisingly, pyrite frambooids have been reported from Lake Kivu (Degens et al. 1972).

One of the most striking similarities to Lake Sihetun is that Lake Kivu has been affected by mass mortality events triggered by extreme hydrothermal events that account for the mortality of plankton as well as the elimination of higher trophic levels, explaining the modern low fish diversity (Haberyan & Hecky 1987). Lake-overturn events could potentially devastate terrestrial animals in low-lying areas. It is possible that similar catastrophic overturn was responsible for mass mortality events in Lake Sihetun and its surroundings.

Conclusions

Phase 2 of Lake Sihetun, which is known for its excellently preserved vertebrate and invertebrate fossils, is characterized by predominantly dysoxic bottom waters, but intermittent euxinic spells occurred. Rarely, oxic bottom waters existed, mainly during the deposition of calcium carbonate-rich sediments, which were possibly methane derived. Marked spatial variations in redox state across the lake floor are probably related to changing water depths. Phase 3 is characterized by a fully oxygenated lake and iron sulphides have not been observed within this lake interval.

Stagnation during Phase 2 episodically led to the establishment of meromictic conditions and reducing bottom waters provided environments suitable for syngenetic frambooid formation taking place immediately below the redox interface in the water column. Frambooids sank to the lake floor and became scattered throughout the matrix. Such euxinic conditions have been triggered by minimal circulation, eutrophy, and, because Lake Sihetun was volcanically influenced, possibly also by hydrothermal events, which may have led to high concentrations of dissolved gases. Recurrent sudden outgassing events are proposed as a cause for vertebrate and invertebrate mass mortality events within the lake.

Frambooids occurring in concentrated layers are often associated with iron sulphide microcrystals. A dominance of microcrystal textures within such layers reveals formation in organic-poor pore spaces or a decrease in Eh. Concentrated frambooid layers represent the formation of early diageneric restricted microenvironments around mucous biofilms at the lake floor or around other organic remains. Highly reactive organic matter was preserved and eventually oxidized, leading to suitable geochemical conditions for iron sulphide formation and ultimately excellent fossil preservation.

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