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Authigenic minerals in fossil bones from the Mesozoic of England: poor correlation with depositional environments

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Abstract

Petrographic microscopy, X-ray diffractometry, and scanning electron microscopy–energy dispersion spectrometry studies of cavity infills of bone samples from English Mesozoic vertebrate deposits (Isle of Wight, Swanage, Lyme Regis, Aust Cliff, Westbury Garden Cliff, Tytherington) allow a better understanding of the distribution of authigenic minerals in bone voids and shed light on the importance of diagenetic processes on bone preservation. Surprisingly few minerals were identified as void fillers in all depositional environments, carbonates, sulphides, oxides, and sulphates being most abundant. Calcite is present in almost all samples. Pyrite is very common in voids as well as incorporated into bone frambolite. In many samples several generations of infills are found, often consisting of layered cements. The co-occurrence of the common minerals indicates anaerobic, slightly alkaline, and often sulphate-reducing environments in the bone voids. Later oxidation is common in iron minerals. Calcite, pyrite, and barite lack unambiguous environmental control, whereas sphalerite is possibly an indicator for marine deposits. Freshwater deposits show no particular mineral combination which would help in separating them from other environments. In some instances, sediment infills and pyrite show geopetal structures.

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1. Introduction

The early diagenesis and mineralisation of bone is a crucial process in the fossilisation of vertebrates, but this diagenesis has not been adequately studied. Existing studies report mainly discrete aspects of bone diagenesis (e.g. Parker and Toots, 1970; Pfretzschner, 2001) or give re-

sults from specific sites without comparing these with other depositional settings (e.g. Barker et al., 1997; Holz and Schultz, 1998; Hubert et al., 1996). Furthermore, most research has been conducted on archaeological bones (e.g. Price et al., 1992) which typically are not fully mineralised and which might never have entered the fossil record because of this and because of burial in an environment with low preservation potential (e.g. upland soil). This results in a major gap regarding our knowledge of the taphonomy and diagenesis of fossil vertebrates remains. Therefore, a comprehensive study of cavity infills of fossil bone sam-

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ples from various English vertebrate deposits was carried out to clarify the interactions between bone francolite, authigenic minerals, and water in the enclosing sediment during diagenesis. Thus, for the first time, a direct comparison between fossil bones from several different depositional environments is possible.

Beside common carbonates, sulphides, and sulphates, the voids were a priori expected to be filled with a large variety of localised minerals, resulting from differences in local depositional environments (e.g. geochemical parameters, ion supply in pore water, presence of bacteria influencing mineral precipitation, and decay of organic parts) during a very early diagenetic stage. Bacteria-triggered precipitations of rare minerals like kutnohorite (Clarke and Barker, 1993) were presumed to be relatively common in fossil bones. Because the bones are preserved as 'apatite', authigenic phosphate was expected in bone voids. Authigenic quartz and chlorite can be major void fillers in fossil bone (Hubert et al., 1996). Gypsum and iron oxides should be frequent as weathering

products. More investigated minerals are listed in Section 3.

Such a variety of minerals might allow an additional clue for taphonomic and depositional settings of vertebrate fossils. On the other hand, the bone cavities could also be filled during later diagenetic stages and therefore would not show a real environmental signature. This study aims to clarify the processes that lead to mineral precipitation in bone and when these processes occur. Samples were obtained from a wide range of environments, including caves, floodplains, lakes, and oceans. To test the influence of late diagenesis operating over long time periods, the sites also cover a broad age range: Triassic, Jurassic, and Cretaceous.

Furthermore, samples collected at Aust Cliff provide the opportunity to examine differences in bone preservation and diagenetic cementation independent from a number of external variables because the samples come from the same stratum. This study also investigates the origin and taphonomy of the non-marine bone material at

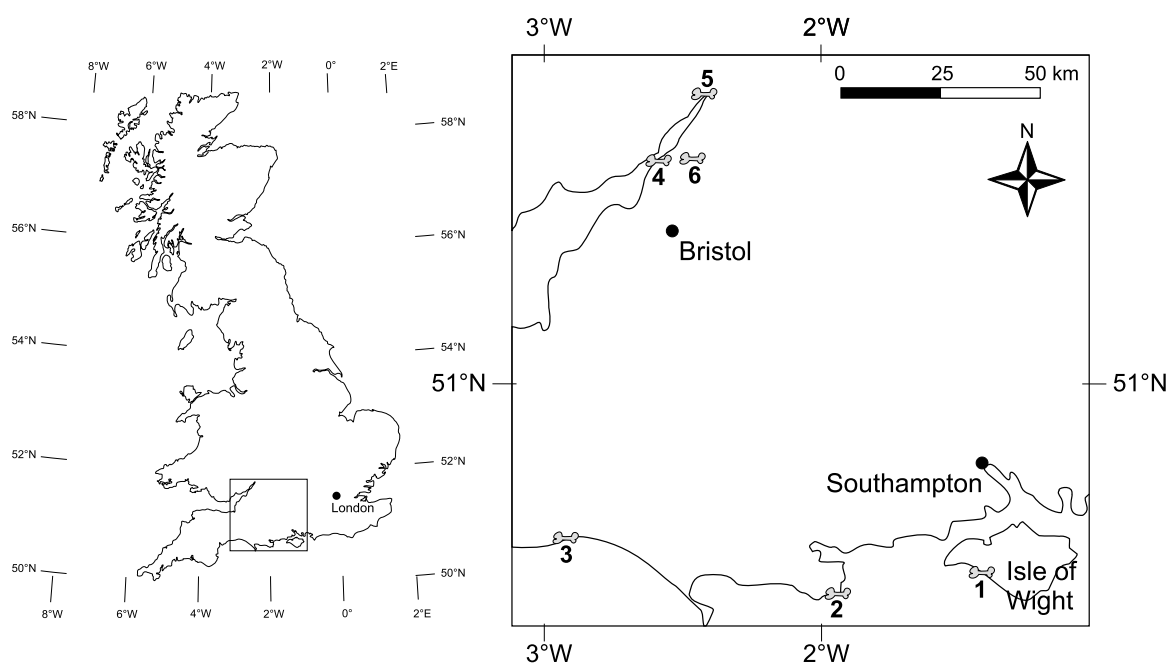


Fig. 1. Map of sampled English vertebrate fossil localities: (1) Isle of Wight; (2) Swanage; (3) Lyme Regis; (4) Aust Cliff; (5) Westbury Garden Cliff; (6) Tytherington.

Aust Cliff. Lastly, the study discusses the suitability of techniques for fossil bone analysis.

2. Area descriptions

A variety of bone samples of different ages and diagenetic histories were collected from a range of well-studied depositional environments. The samples were taken from English vertebrate fossil occurrences including the Wealden on the Isle of Wight (IW), the Lower Cretaceous bone-rich limestone at Swanage (SW), the Liassic shales at Lyme Regis (LR), the Rhaetic bone beds at Aust Cliff (AC) and Westbury Garden Cliff (WB), and the Late Triassic fissure fillings at Tytherington (TY) (Fig. 1). These fossil sites were selected for this study because of the large amount of background research available (e.g. Barker et al., 1997; Benton and Spencer, 1995; Raiswell and Berner, 1985), the variety of depositional environments, and the accessibility of samples. Despite the prominence of some of the sites, this study is concerned with standard types of fossilisation which are common in the fossil record. No special modes of preservation, such as soft tissue preservation, are known from most of the localities.

2.1. Isle of Wight

Samples were collected from the southwestern coast of the Isle of Wight (50°38'13"N, 1°25'21"W) between Hanover Point and Barnes High in the Wessex Formation (Wealden Group, Lower Cretaceous). The strata are mainly mudstones, marls, and sandstones, deposited in a coastal floodplain with meanders, lakes, and ponds in a warm to hot climate (Martill and Naish, 2001). The fauna includes fish, crocodiles, turtles, and dinosaurs (Insole et al., 1998). Most bones collected from the beach exposure lacked rock matrix and are unassignable to specific beds. Some samples attached to sandstone matrix evidently are from the Sudmoor Point Sandstone. The majority of bones are considered dinosaurian based on their large size. The most abundant dinosaurs in the Isle of Wight strata are *Iguanodon* and *Hypsilophodon*, and probably they comprise

the majority of the bones collected (Benton and Spencer, 1995). Identification of the type of bone (e.g. tibia) was mostly impossible in the abraded and broken fragments, although some are clearly vertebrae.

2.2. Swanage

This heavily weathered material was collected about 200 m westward of Peveril Point in Swanage (50°36'22"N, 1°56'54"W). All of the section is in the Upper Purbeck Beds (Durlston Formation, Lower Cretaceous). The bones are in the Broken Shell Limestone, a massive shelly bioclastic limestone, which yields mostly fish and turtle remains (House, 1993). However, a well-preserved vertebral centrum of a crocodile or dinosaur was recovered. The Purbeck Beds were deposited in a lagoonal or lacustrine environment similar to the Wessex Formation of the Wealden. Unabraded shells of *Viviparus* in the Broken Shell Limestone indicate a fully freshwater origin for the collected specimens, because the fragile shells would have been broken during transport to the sea.

2.3. Lyme Regis

The bones were collected from the Hettangian Blue Lias Beds (lower Liassic, Lower Jurassic) in cliffs along the coastline from Seven Rock Point (approximately 1 km west of Lyme Regis) and Charmouth (50°42'51"N, 2°57'19"W). The interbedded mudstones and laminated shales with limestones were deposited in a shallow stagnant marine basin (Melville and Freshney, 1982). All bones are from shale, except one fragment of a plesiosaur (?) long bone found in a limestone bolder on the beach. Most samples are broken ichthyosaurian bones: phalanges, long bones, and ribs. Several fragments were identified as plesiosaur ribs because of their size and shape.

2.4. Aust Cliff and Westbury Garden Cliff

As two of the British classic localities of Rhaetic bone beds (Westbury Formation, Penarth Group, Upper Triassic), Aust Cliff (51°36'26"N, 2°37'20"W) and Westbury Garden Cliff

(51°48'38"N, 2°24'27"W) represent marine high energy environments, perhaps intertidal deposits (Antia, 1979). The Aust Cliff stratum is a conglomerate of silty mudstone clasts with a large variety of vertebrate remains (scales, teeth, bones) in a calcite cemented matrix of angular quartz sand. The Westbury Garden Cliff bone bed is a thin sandstone layer, with abundant shell and vertebrate fragments. Authigenic euhedral pyrite is often present as the only cement. For a wider background regarding taphonomy, sedimentology, and genesis of these two bone beds, see Trueman and Benton (1997) and Martill (1999).

The samples from Aust Cliff were collected from one stratum. Unweathered rock samples were found to contain a mixture of complete and broken bones ranging from fresh and shiny to weathered pale-brown skeletal elements. However, most of the bones are abraded and/or fractured and were therefore easily penetrated by mineral-precipitating water. The bone fragments chosen for this study belong to a diverse group of vertebrates, including terrestrial and marine archosaurs. However, the majority of the Aust Cliff samples are fish bones.

2.5. Tytherington

The Mesozoic fissure system within the Carboniferous limestone of Tytherington (51°36'06"N, 2°29'18"W) was essentially formed by carbonate dissolution, producing caves and underground watercourses, which were later filled with terrestrial, herpetofauna-rich sediments under sub-

aqueous or sub-aerial conditions (Whiteside, 1983). The sediment is a carbonate-cemented quartz-rich siltite or arenite, often dolomitised (Whiteside, 1983). Pocket-like structures with several bones were found in some rocks, but layers of dense silt without bones are also present. Silt intraclasts were commonly found near bones. *Thecodontosaurus* long bone and vertebral fragments were used for this study.

3. Methods

To compensate for the variability among bone void infills, approximately 300 nondescript bone samples were cut with a rock saw and examined macroscopically. Typical, unusual, and preferably larger bone pieces were selected for further examination. To compare the cements from a wide variety of samples, 87 large thin sections (50×50 mm and 75×50 mm) were made. Several thin sections also were made from different parts of larger bones in order to identify and investigate any differences in the mineralogy of cavity fillings. In thin sections with more than one bone, only the largest bone was counted for statistical purposes to avoid counting of unwanted regional diagenetic changes. In every thin section, all minerals in the bone voids were determined qualitatively (Table 1). In addition, a semi-quantitative analysis for the abundance (vol%) of pyrite in the thin sections was carried out visually (Table 2). The abundance is estimated in 10% steps.

Images of thin sections were taken with a Ni-

Table 1
Mineral abundances in bone and voids

Locality	Isle of Wight	Swanage	Lyme Regis	Aust Cliff	Westbury Garden	Tytherington	All samples
Number of samples	21	14	22	17	3	10	87
Calcite in voids	20 (95%)	14 (100%)	20 (91%)	17 (100%)	2 (67%)	10 (100%)	83 (95%)
Pyrite in bone	14 (67%)	13 (93%)	18 (82%)	17 (100%)	3 (100%)	5 (50%)	70 (81%)
Pyrite in voids	17 (81%)	10 (71%)	14 (64%)	12 (71%)	3 (100%)	6 (60%)	62 (71%)
Sphalerite in voids	1 (5%)	2 (14%)	12 (55%)	8 (47%)	0 (0%)	0 (0%)	23 (26%)
Barite in voids	11 (52%)	0 (0%)	7 (32%)	1 (6%)	1 (33%)	0 (0%)	20 (23%)
Siderite in voids	9 (43%)	0 (0%)	0 (0%)	0 (0%)	0 (0%)	0 (0%)	9 (10%)
Sediment in voids	13 (62%)	10 (71%)	4 (18%)	17 (100%)	3 (100%)	9 (90%)	56 (64%)

The numbers show the quantity of samples containing the respective mineral. The percent values in brackets are based on the total sample number of each locality.

Table 2
Abundance of pyrite as void infills

Abundance of pyrite in vol% of void fills	Total number of samples					All localities (in % of all samples with pyrite in voids; <i>n</i> = 62)	In % of total sample number; <i>n</i> = 87
	<i>n</i> = 21 Isle of Wight	<i>n</i> = 14 Swanage	<i>n</i> = 22 Lyme Regis	<i>n</i> = 17 Aust Cliff	<i>n</i> = 3 Westbury Garden		
<10	10	5	6	9		36 (58%)	41%
20	4	4	2	3		13 (21%)	15%
30	2				1	3 (5%)	4%
40	1		2			3 (5%)	4%
50		1	1			2 (3%)	2%
60			2			2 (3%)	2%
70			1			1 (2%)	1%
80					1	1 (2%)	1%
90							
100					1	1 (2%)	1%

kon FX-35A camera attached to a Nikon Optiphot-Pol petrographic microscope. Slides were scanned with a Nikon Coolscan 3 scanner and scale bars and arrows were added in Adobe Photoshop. All thin sections were examined petrographically with reflective and transmitted light microscopy. Bone samples with representative mineral infills were selected for X-ray diffractometry (XRD) analysis. Data collection was performed using a Siemens D5000 powder diffractometer (Bragg–Brentano geometry, Cu K α , 40 kV, 35 mA) from 10° to 65° 2 θ using a step size of 0.02° and variable divergence slits. Samples were ground in an agate mortar and analysed using a rotating standard flat-plate sample holder. Due to the small amount of powder, one sample (SW 3) was analysed using a reflection-free silicon sample holder.

The diffractograms were compared with the PDF-computer database (ICDD) using the computer software EVA (Bruker-AXS). Characteristic diffractograms of minerals which were likely to be found in the samples were selected, compared with each sample, and summarised in Table 3. The tested minerals were chosen from existing observations and descriptions of other authors. The following minerals were searched for but not found in the XRD samples: hydroxyapatite Ca₅(PO₄)₃(OH), chlorapatite Ca₅(PO₄)₃Cl, carbonate hydroxyapatite (dahllite) Ca₁₀(PO₄)₃(CO₃)₃(OH)₂, calcium phosphate carbonate Ca₁₀(PO₄)₆CO₃, siderite FeCO₃, chalcopyrite CuFeS₂, vivianite Fe₃(PO₄)₂·8H₂O, iron sulphide FeS, goethite FeO(OH). Sediment grain analyses are not discussed here.

Major and minor elements were obtained by electron probe microanalyses (EDS). The uncovered thin sections were coated with carbon and analysed with a Stereoscan 250 Mk 3 scanning electron microscope (SEM) with enabled backscatter detection (BSE). The operation conditions for BSE were 15 keV and 1–5 nAmps; with varied dwell times. The results were compared with the microscopic evidence. Additional examinations of mineral habits in etched bone samples were performed.

Table 3
Results of the XRD analysis

mineral	formula	IW 2: C	IW 5: S	SW 3: C+S	SW 13: C+S	LR 4: S	LR 17: C	AC 2: C+S	AC 3: S	TY 1: C+S
calcite	CaCO ₃	+, Mg ^a		++, Mg ^a	++, Mg ^a	++, Mg ^a	++, Mg ^a	++, Mg ^a	++	++
magnesium calcite	(Ca,Mg)(CO ₃) ₂		++							
quartz	SiO ₂			o	o			+	+	++
fluorapatite	Ca ₅ (PO ₄) ₃ F	++	++	++	++	++			++	++
carbonate fluorapatite (francolite)	Ca ₁₀ (PO ₄) ₅ CO ₃ F _{1.5} (OH) _{0.5}						++	++		
witherite	BaCO ₃			?						
oligonite	Fe(Mn,Zn)(CO ₃) ₂		++							
kutnohorite, magnesian	Ca(Mn,Mg)(CO ₃) ₂			o						
marcasite	FeS ₂	?	o			?	+	?	o	?
pyrite	FeS ₂	++	o	+	+	+	++	?	o	
sphalerite	ZnS							o		
iron oxide	Fe ₂ O ₃ (PDF 16-0653)	?		+			o			
iron oxide	Fe ₂ O ₃ (PDF 16-0895)				+			o	?	o
lepidocrocite	FeO(OH)					?				
iron oxide hydroxide	FeOOH									o
gypsum	CaSO ₄ ·2H ₂ O								o	
barite	BaSO ₄						?	o		

Listed are the original sample numbers. Abbreviations: IW, Isle of Wight; SW, Swanage; LR, Lyme Regis; AC, Aust Cliff; TY, Tytherington; C, compacta; S, spongiosa (cancellous bone).

Symbols: ++, phase dominant; +, phase important; o, phase present; ?, phase probably present but due to peak superposition not clearly established.

^a Position of the calcite [104]-peak indicates small amounts of Mg.

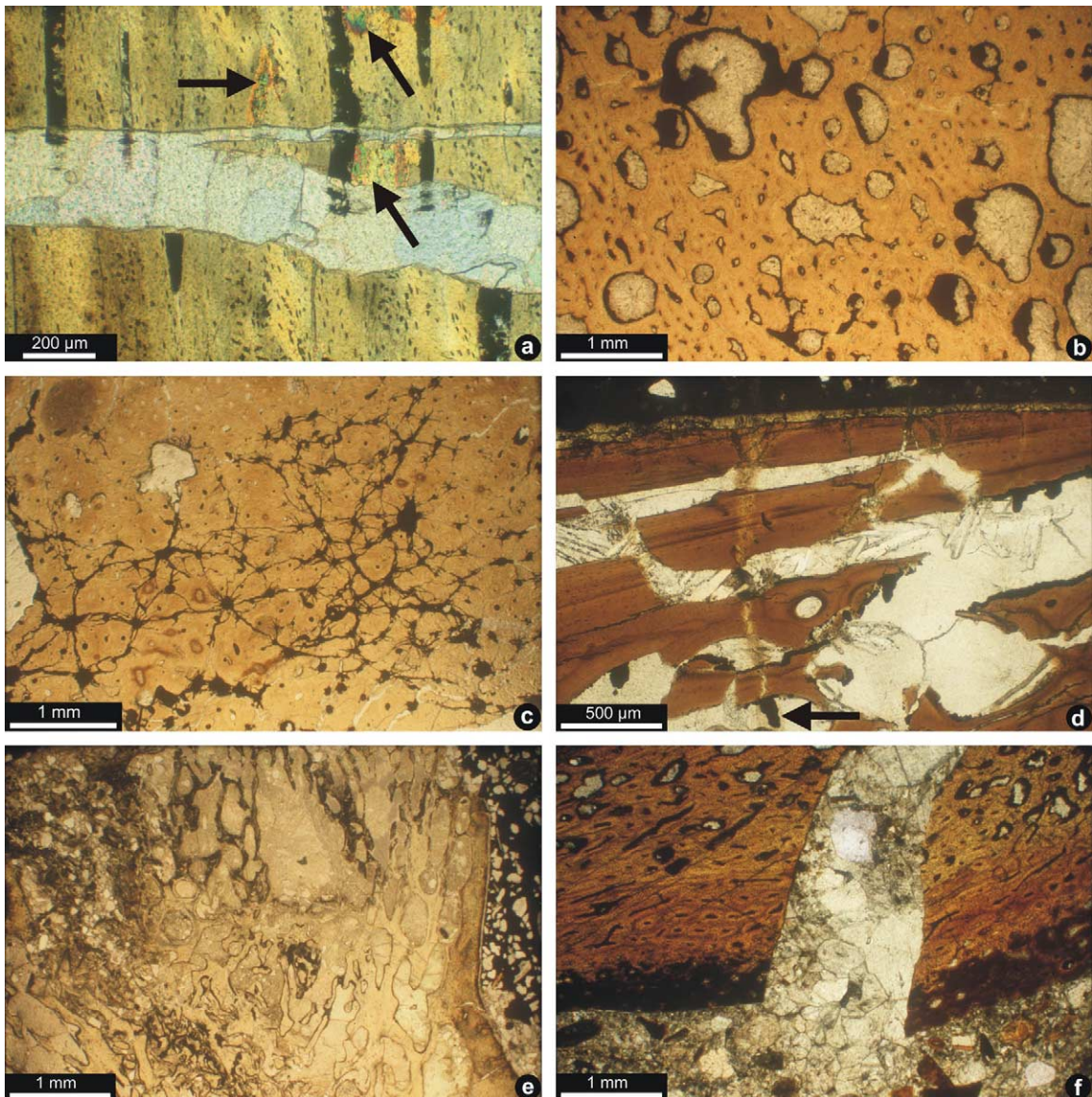


Fig. 2. (a) Plesiosaur (?) longbone fragment. The continuation of pyrite from void infills into the sparite-filled crack suggests an almost simultaneous formation. The bone mineral is partly recrystallised (arrows). Crossed Nicols (XN), $1/4 \lambda$ plate. (b) Isle of Wight bone fragment showing geopetal pyrite infill. The pyrite accumulated on the bottom of the voids (left side), and a final calcite cement filled the voids. Plain Polarised Light (PPL). (c) Pyrite filling in vascular canals of an Isle of Wight sample, showing the formerly interconnecting pathways between the bone voids and cracks probably caused by crystallisation pressure. The white parts are resin. PPL. (d) Isle of Wight bone fragment showing stalactitic pyrite. The initial growing direction of all stalactites has been identical, the variant stalactite on the bone fragment in the lower centre (arrow) was broken off during a later diagenetic stage. PPL. (e) Heavily pyritised bone fragment from Westbury Garden Cliff. Most voids are filled with blocky sparite. Pyrite-cemented quartz grains are visible in the sediment beyond the bone surface to the right. PPL. (f) Aust Cliff bone with a sparite-filled crack. The iron minerals in the bone are pyrite on the right (opaque) and hematite (brown colour) on the left side of the crack. PPL (for colour see online version).

4. Results and analyses

4.1. Apatite – $\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{Cl}, \text{OH})$ and Phosphates – $[\text{PO}_4^{3-}]$

The XRD results (Table 3) indicate two clearly different fossil bone minerals, the more common fluorapatite $\text{Ca}_5(\text{PO}_4)_3\text{F}$ in seven samples and carbonate-fluorapatite (francolite) $\text{Ca}_{10}(\text{PO}_4)_5\text{CO}_3\text{F}_{1.5}(\text{OH})_{0.5}$ in two samples (AC 2 and LR 17). Recrystallisation in specific areas of bone is frequently visible under polarised light (Fig. 2a). This recrystallisation is common in cortical bone from all sites and is often restricted to permeable parts like voids (osteons and lacunae) or cracks. Small amounts of bone francolite were found to have been replaced by pyrite. However, replacement of phosphate by calcium carbonate in dissolved bone as described by Holz and Schultz (1998) was not observed. No evidence of diagenetic phosphate infill of voids has been observed in any of the samples studied.

4.2. Calcite – CaCO_3 and Mg–Calcite – $(\text{Ca}, \text{Mg})(\text{CO}_3)_2$

Calcite was found in every XRD sample and in 95% of all samples. Blocky sparite, drusy mosaic, bladed, and fibrous crystals exist in the bone voids in a range of sizes. Both, non-ferroan and ferroan calcite are present.

The position of the calcite [104] peak indicates a small amount of Ca^{2+} substitution by Mg^{2+} in most of the XRD samples. The position of this peak in sample IW-5 at $29.7^\circ 2\theta$ for example indicates magnesium-rich calcite which may contain around 10 mol% MgCO_3 (see Goldsmith et al., 1961). Small amounts of Mg are often integrated into the calcite lattice.

4.3. Pyrite and marcasite – FeS_2

FeS_2 was found in every XRD sample as marcasite or pyrite. Due to the overlap of peaks, it was not possible to prove the presence of these minerals in samples TY 1 and AC 2. Reflective light microscopy showed that most FeS_2 is present as pyrite rather than marcasite, making



Fig. 3. Polished section of a cancellous bone from Lyme Regis with three generations of void infills. The outer part is filled with a coarse sparite, followed by a band of pyrite (pale zone) and finally an infill of blocky calcite (light grey in centre, for colour see online version).

pyrite the second most common mineral after calcite. It is common in voids of all sizes (Fig. 2a–e) as well as in the sediment as integral cement or isolated grains. Euhedral and subhedral crystals of pyrite were found to encrust voids, cracks, and entire bone surfaces, but framboidal pyrite was found most commonly. Occurrences of ‘globular’ pyrite, as described by Pfretzschner (2001), were also found within bone ‘apatite’. Pyrite and calcite cements were frequently found in close association. For example, a bone fragment collected at Lyme Regis exhibits a band of pyrite enclosed between two different blocky sparite generations (Fig. 3). A sample from Aust Cliff, however, only has the voids in the central area of the cortex infilled with pyrite. In several Isle of Wight samples, at least three generations of infills were found: (1) an initial pyrite coating, (2) calcite precipitation, and (3) mixture between pyrite and calcite filling in the remaining pore space.

In Tytherington bones, Fe minerals are very rare, although the surface of bone samples frequently exhibited a thin, brownish, iron-rich cover. Any pyrite found within bone samples was present as infills in osteons and lacunae and isolated framboidal grains in poikilotopic calcite, while hematite was found more commonly in voids.

The amount of pyrite found in bone and in voids can be quite variable even at one location (Table 1). In material collected from Aust Cliff, for instance, pyrite commonly appears in the bone francolite, but rarely occurs in the voids. Only in one Westbury Garden sample does pyrite occupy all the pore space (Table 2). Overall, in 79% of samples which were found to contain pyrite, the mineral infilled less than 20% of the available void space. Samples with smaller void spaces were completely infilled with pyrite, whereas larger voids were only partially filled and often exhibit a pyrite fringe.

4.4. Hematite Fe_2O_3 and iron hydroxides $FeO(OH)$; $FeOOH$

Several iron oxides and hydroxides were identified in the XRD samples (Table 3) except for sample IW 5 which contained none. One Aust Cliff sample shows the same amount of iron minerals in a bone fragment divided by a crack, on one side still preserved as pyrite, but on the other side oxidised to hematite (Fig. 2f).

4.5. Sphalerite – ZnS

Microscopic investigation revealed sphalerite in 26% of the samples. ZnS is mostly found as euhedral crystals embedded in sediment or calcite. A small ichthyosaurian carpal collected from Lyme Regis was found to be completely infilled by sphalerite, while other bones from Lyme Regis have sphalerite present in voids, brecciated bone, and cracks (Figs. 4b and 5a). In Aust Cliff samples, sphalerite was frequently found in sediment surrounding bone samples and as isolated grains in the voids.

Among the XRD samples, ZnS was only found in AC 2. The δ -spacings of sphalerite are nearly

coincident with those of iron sulphide (FeS) or pyrite (FeS_2), which makes identification more difficult. In the case of AC 2, the relative intensity of the δ -spacings were used to identify sphalerite.

4.6. Barite $BaSO_4$ and Witherite $BaCO_3$

With XRD, barite was found in AC 2 and may also be present in LR 17, although the presence of small amounts of barite are difficult to determine due to overlapping δ -spacings of major phases. Subhedral clusters of prismatic crystals were commonly found in thin sections. Other growth types observed were isolated blades, fascicular, and euhedral crystals. A few samples were observed to have entire pore spaces infilled with barite, either in sparry (Fig. 4b) or fascicular form (Fig. 4d). Samples from Lyme Regis exhibited isolated barite grains scattered in the voids.

XRD analysis of a Swanage sample indicated minor amounts of witherite $BaCO_3$.

4.7. Quartz and other minerals in sediments

In XRD results, no quartz was found in the samples from Lyme Regis and the Isle of Wight. Quartz was one of the major phases in sample TY 1, important in AC 2 and AC 3 and present in SW 3 and SW 13.

Nevertheless, there is no authigenic quartz in any of the examined bones. The quartz found in the samples (mainly Tytherington, Aust Cliff, and Swanage) results from sediments infilling voids (Fig. 4e). The sediment grains range in size from mud to sand and were found to be concentrated in the outermost voids of samples collected from Swanage and Aust Cliff. Isolated grains of glauconite were identified in two larger cancellous bone fragments from Aust Cliff. In Lyme Regis bones, sediment was found in the cracks, commonly those near the sediment/bone boundary, but not in the voids.

4.8. Siderite $FeCO_3$ and Oligonite $Fe(Mn,Zn)(CO_3)_2$

Siderite is relatively abundant as isopachous

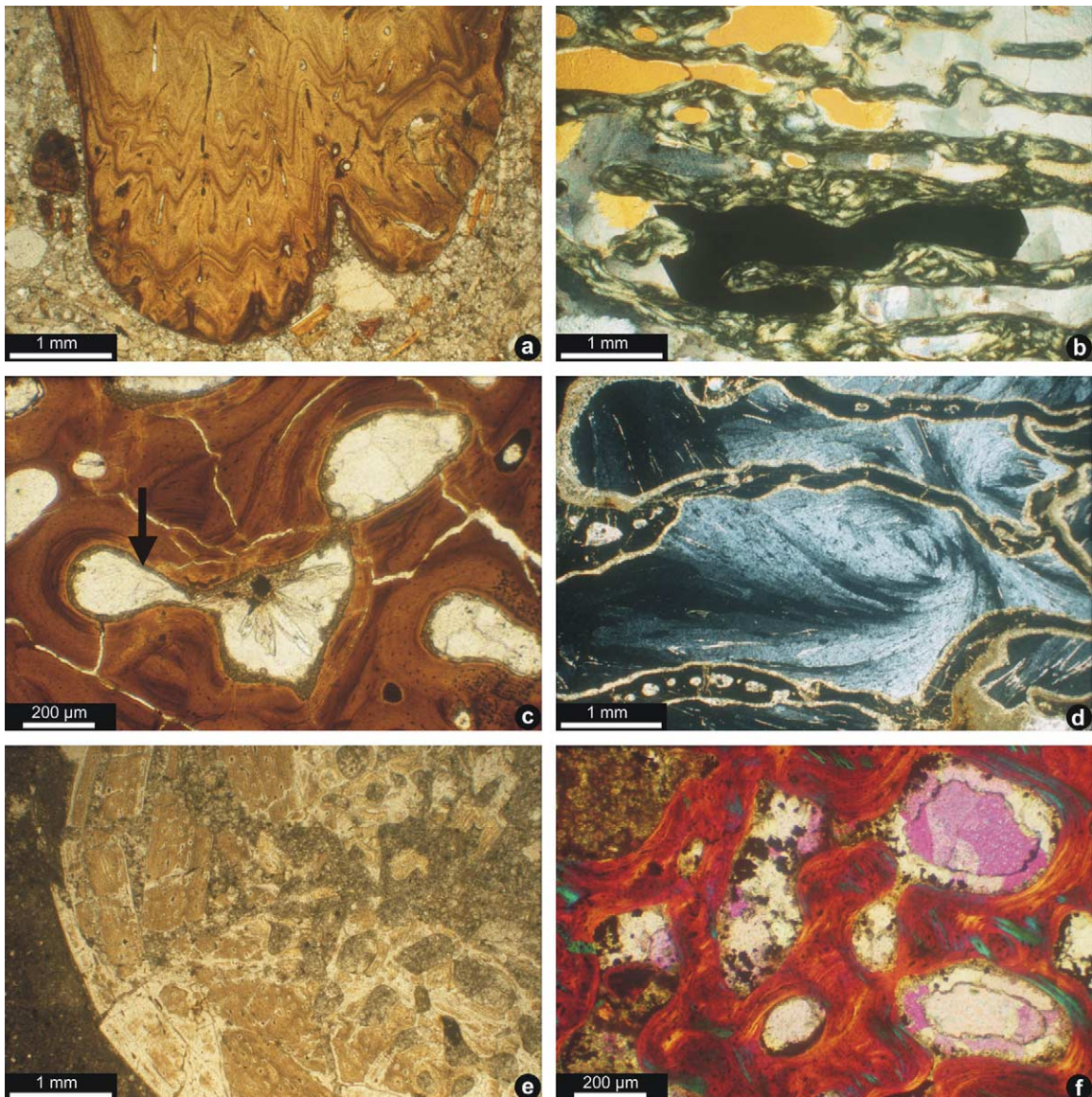


Fig. 4. (a) Different bone colours caused by iron oxides in an Aust Cliff bone fragment. These layers are growth marks which were enhanced during the recrystallisation of the bone francolite. PPL. (b) *Plesiosaurus dolichodeirus* vertebra, Lyme Regis. Cancellous bone with isotropic sphaerulite (black) in the lower centre of image. The voids in the upper left area are completely infilled with barite (light grey). All other voids are filled with coarse sparite. XN. (c) Void infills in an Isle of Wight bone. The first small isopachous fringe consists of siderite (arrow). A framboidal pyrite crystal served as nucleus for the crystallisation of bladed barite and the remaining pore space is filled in by blocky sparite. PPL. (d) Arch-shaped fascicular barite in an Isle of Wight sample. XN. (e) *Thecodontosaurus* long bone section from Tytherington. The bone is heavily cracked and the voids are sediment filled (calcite-bound arenite). PPL. (f) Bone fragment from Swanage. The voids are filled in by isolated framboidal pyrite clusters, followed by different generations of spar with changing iron content in the calcite. The void in the upper left corner is infilled with carbonate-cemented silty sediment. XN, sensitive tint plate (for colour see online version).

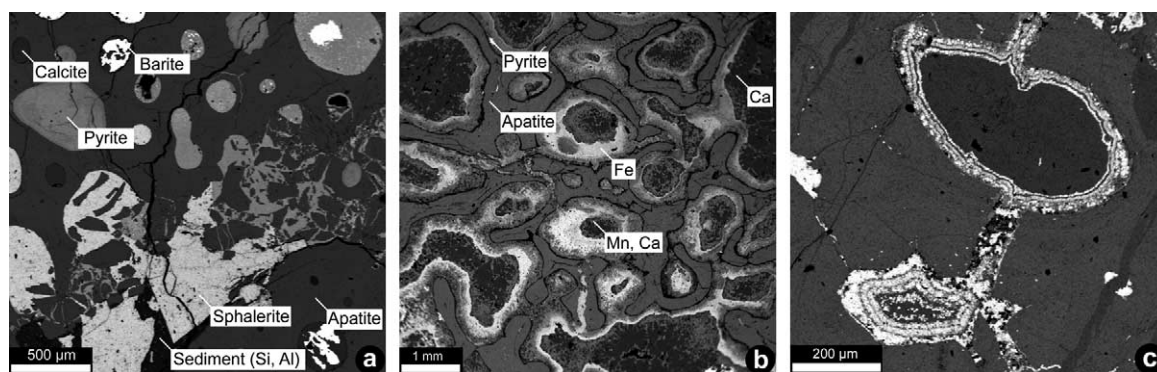


Fig. 5. (a) BSE-image of a Lyme Regis thin section showing four authigenic minerals in voids and brecciated bone. Note the sediment outlining euhedral sphalerite. (b) BSE-image of an Isle of Wight thin section showing close interactions between precipitated minerals. The minerals siderite (Fe), calcite (Ca), and kutnohorite (Mn, Ca) feature a gradual transition. Note that the kutnohorite is a later infill, predated by siderite. (c) BSE-image of an Isle of Wight thin section showing voids with several alternating layers of calcite (dark grey) and pyrite (white).

cement in Isle of Wight material. Siderite is not identifiable in any of the samples from any other site studied. Oligonite, which is a siderite (FeCO_3) in which the Fe^{2+} is partly substituted by Mn^{2+} and/or Zn^{2+} , was found with XRD to be a major phase in sample IW 5. EDS analysis of this sample identified only Fe ions. However, the characteristic peak positions in the X-ray diffractogram clearly show that the mineral is not pure siderite.

4.9. Gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

One sample from Aust Cliff (AC 3) was found to contain $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in the XRD, identified by its characteristic [020] peak at $11.7^\circ 2\theta$. Microscopic investigation of the sample did not detect any gypsum.

4.10. Kutnohorite $\text{Ca}(\text{Mn}, \text{Mg})(\text{CO}_3)_2$

A magnesium-rich kutnohorite was identified with XRD in sample SW 3, and microscopic investigation revealed in several thin sections from the Isle of Wight kutnohorite as an isopachous rim and as a non-layered inner-void infill precipitated on siderite and pyrite-rich sediment infill.

5. Discussion and conclusions

5.1. General features of fossil bone

Different sections of the same bones were studied on a plesiosaur rib from Lyme Regis (approximately 20 cm in length) and a sauropod (?) bone fragment from the Isle of Wight (approximately 15 cm in length). In both samples, uniformity in the mineralogy of cavity infills has been observed. Unfortunately, verification of the hypothesis that longer bones are generally characterised by homogeneous mineral infills was handicapped by the limited sample size.

Cements such as calcite, siderite, and kutnohorite commonly show a layered appearance (Fig. 4f), indicating microbial participation during their formation (Clarke and Barker, 1993; Flügel, 1982; Mortimer et al., 1997; Sagemann et al., 1999). Framboidal pyrite formation is also enhanced by biologically mediated reactions (Canfield and Raiswell, 1991).

5.2. Geopetal structures

In addition to common geopetal pyrite-rich sediment infills, pure pyrite also shows evidence of gravitational orientation (Fig. 2b). The occur-

rence of pyrite in distinct regions of bone voids is an indication of geopetal structures. The precipitation of pyrite can be initiated by bacteria which concentrate in low positions in the voids due to gravity. This type of geopetal pyrite infills was not reported by Hudson (1982), who described the geopetal infilling of ammonite chambers with pyritic sediment and pyrite stalactite. In this study, pyritic sediment similar to that found in ammonite chambers (Hudson, 1982) was found in bone samples from all sites, whereas the generally rare stalactitic pyrite was only found in one sample from the Isle of Wight (Fig. 2d).

5.3. Cracking and brecciation

The sediment/bone interface seems to be easily permeated by pore water. This might result from compaction-caused forces: sediment and bone have different deformation characteristics and therefore the interplay of compression and tension often causes a small gap on the bone surface. In most of the samples used in this study, this cavity is filled with a small fringe of calcite cement and the outermost region of any broken bone is sometimes heavily pyritised which is not necessarily

due to the initial decay of soft tissue (Pfretzschner, 2000). Pyrite is only enriched in the outermost parts of the bone, indicating that this pyritisation happened later in the diagenetic process. The necessary supply of ion-carrying pore waters was made possible by the gap between bone and sediment.

Almost every bone shows cracks (Fig. 2a). In many of the cancellous bone samples, crushed and brecciated areas are visible (Fig. 5a). These zones were interpreted by Hubert et al. (1996) as evidence of trampling by large animals before the bones were buried. This explanation seems very implausible because such zones of crushing are also commonly found in bones from fully marine sediments, like the Lyme Regis shales, and they often exhibit a different mineral infill. Hence, a diagenetic origin due to overburden pressure must be assumed for these structures. Pyrite is concentrated in the crushed part of one Lyme Regis sample which implies that precipitation took place soon after the crushing occurred.

Small-scale cracks are much more likely to be found in certain areas of bone tissue. Dense bone parts are more affected by the cracking than cancellous areas. The structure of the cancellous bone

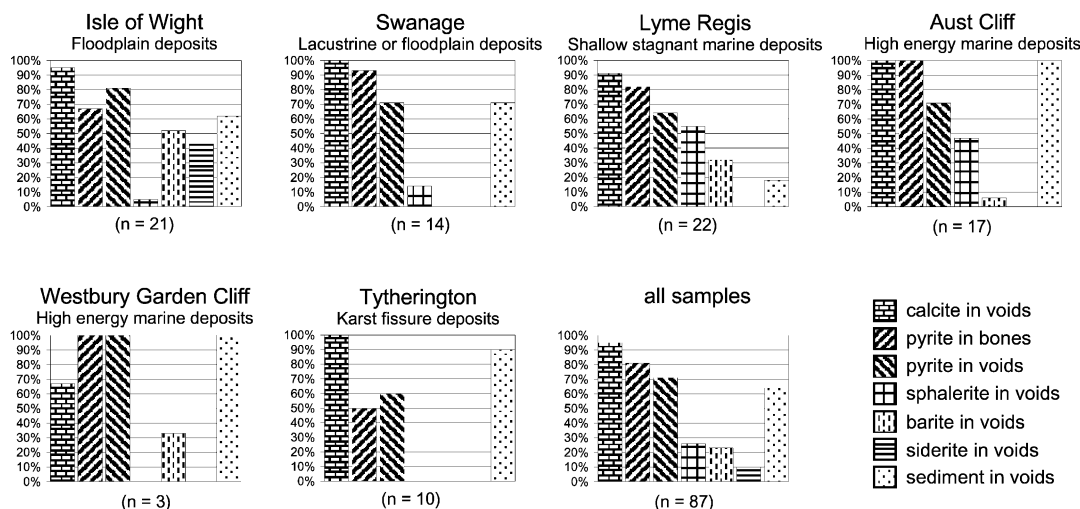


Fig. 6. Mineral occurrences in bone and voids. The graphs are created from data in Table 1. The values are based on the total number of samples from each locality. Note the limited significance of some data due to the low number of samples from some localities (e.g. Westbury Garden Cliff with 3 samples).

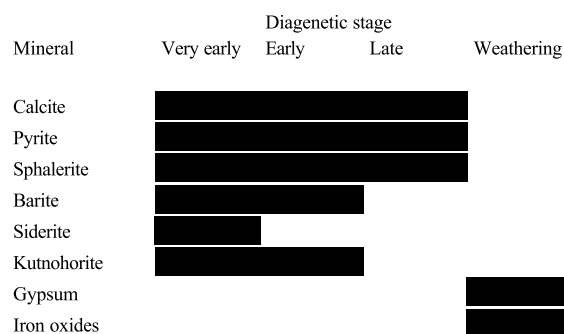


Fig. 7. Simplified paragenetic diagram for all localities. Listed are the most important mineral infills in all bone voids. Differences between the localities are relatively insignificant and are characterised mainly by the absence of some minerals (see Fig. 6).

is probably more flexible under initial burial pressure than compact bone, but tends to completely collapse and brecciate under high compaction pressure.

5.4. Mineral occurrences

Precipitation and mineral replacement are two of the complex diagenetic physicochemical processes which occur during infilling of openings in bone (Downing and Park, 1998; Pate et al., 1989; Piepenbrink, 1989; Williams and Marlow, 1987). This study revealed that relatively few minerals are responsible for the infill of bone voids during diagenesis. The most common infill minerals are carbonates (CaCO_3 , FeCO_3 , BaCO_3), sulphides (FeS , ZnS), oxides (FeO , Fe_2O_3), and sulphates (BaSO_4 , CaSO_4). The summarised paragenesis of the most important mineral infills from all localities can be seen in Fig. 7.

Calcite is present in almost all samples, indicating its importance as a void infiller. The various carbonate cements observed in the material are beyond the scope of this paper and are therefore discussed in detail elsewhere (Wings, in preparation). The most prevalent infill observed was sparite, which appears to have been precipitated during the later stages of diagenesis, as suggested by Flügel (1982).

Pyrite is very abundant in the voids as well as in bone 'apatite'. The reasons for the pyrite abun-

dance in fossil bone were discussed in detail by Pfretzschner (2000, 2001), whereas the mechanisms of pyrite formation were summarised by Canfield and Raiswell (1991). The pyrite content in the bone can vary very much in different bones next to each other in the sediment or even in the same bone (Fig. 2e), implying different permeability pathways or a complex arrangement of micro-environments.

The described diagenetic order in several Isle of Wight samples is different from the very late precipitation of pyrite described by Pfretzschner (2001). Samples used in this study demonstrate that both calcite and pyrite co-precipitated intermittently as a result of varying pore water chemistry. An example of this pattern of mineralisation can be seen in a crack infill of a Lyme Regis plesiosaur bone (Fig. 2a). The integrated pyrite in the sparite is a strong indicator for simultaneous formation of both. Pyrite is also common as crack infill in Isle of Wight material, here suggesting a later diagenetic origin.

The higher pyrite content inside the voids of Swanage material suggests that the decay of the organic tissue was incomplete when the infill began – otherwise the same amount of pyrite would be found in the surrounding sediment. However, the total amount of iron in body tissue is very low (about 4 g in an adult human; Schmidt-Nielsen, 1997), making organic tissue a poor source of Fe for pyrite formation. The most important source of reactive iron are sedimentary iron minerals (Canfield, 1989; Canfield and Raiswell, 1991; Canfield et al., 1992). Yet, early pyrite formation is also controlled by the availability of sulphide (Canfield et al., 1992; Raiswell and Berner, 1985) and by the Eh/pH conditions caused by decay of organic matter (Canfield and Raiswell, 1991; Krumbein and Garrels, 1952; Pfretzschner, 1998).

Interestingly, in Tertiary bones studied by Parker (1966) and Parker and Toots (1970), no pyrite or any other mineral containing sulphur was detected. This may be a result of late diagenetic oxidisation, as iron oxides were found (Parker, 1966; Parker and Toots, 1970). Limonite, hematite, and other iron oxides (Table 3) in the samples are mainly weathering products of pyrite (Barker et al., 1997).

The bands of darker coloured iron oxides in bone francolite (Fig. 4a) may have been caused by varying primary ion contents in the bone tissue, but more plausible is an early diagenetic penetration of iron-rich water into the collagen material along the borders of the recrystallised colophonane/francolite areas (Pfretzschner, 2000). Therefore, the denser arrangement of francolite crystals along growth marks caused a slower speed of the recrystallisation, and permitted the storage of colouring ions due to a longer reaction time. This distinctive layering, likely preserved during recrystallisation of bone as 'globular' pyrite (Pfretzschner, 2001), is also visible inside the bone material. Some smaller cracks in other samples were observed to be surrounded by FeO of a later diagenetic origin, indicating that iron minerals were transported into the cracks and penetrated the outer bone francolite.

The simultaneous precipitation of calcite and hematite (Holz and Schultz, 1998) is only possible under oxidising conditions (Krumbein and Garrels, 1952) and was not observed in this study. Far more common in the fossil record is the nearly concurrent precipitation of pyrite and calcite (Krumbein and Garrels, 1952), and the later oxidisation of pyrite to hematite. The concurrent appearance of calcite and pyrite means that ions of both minerals were present in the pore fluids and precipitated interchangeably (Fig. 2a).

The isolated sphalerite grains in Aust Cliff samples could also have been deposited and are not necessarily authigenic. However, most sphalerite was found to completely infill the voids, indicating precipitation in situ. The presence of sphalerite in cracks demonstrates that the mineralisation postdated the main compaction phase, as reported by Martill (1987). Overall, sphalerite is more common than barite which was found in 23% of all samples. Barite in the Isle of Wight material predates most of the calcite cementation (Figs. 2d and 4c) and therefore cannot be considered a late-phase mineral infill as reported by Martill (2001). The witherite founding in one sample may have been formed by pseudomorph alteration of barite, which was not present in the sample. Siderite always appears as a very early phase,

often forming the first isopachous cement in the voids.

The sediment grains in the outermost bone voids may imply an early infill of broken bone with embedding sediment and silicates. The distribution of quartz grains in Tytherington samples is more uniform throughout the bone voids, perhaps indicating a longer transport and stronger disintegration of bone before sedimentation. The consistent grain distribution may also be a result of stronger groundwater currents at Tytherington. Sediment infilling of the tiny surface cracks in Lyme Regis bones may have occurred early in the diagenesis when the sediment was still mobile enough to penetrate these spaces. The mineral infills, on the other hand, are the same in cracks and voids, and likely filled in the cavities later in the diagenesis.

The complete absence of authigenic quartz in the bones indicates that soluble silica was not a major component in the groundwater. This is consistent with the observation that the sediments at the examined localities offer no exceptionally rich source for soluble silica, like silicic ash, which is perhaps the most common source of silica cements in bones (personal observations in the Morrison Formation and the White River Group, USA, and in the Cañadón Calcareo Formation, Chubut province, Argentina).

Gypsum can be a sign of sample weathering (Barker et al., 1997). The Aust Cliff material used in this study was very fresh and without any sign of recent weathering, which may suggest that any gypsum precipitation took place during a period of exposure prior to final burial of the bone. On the other hand, as gypsum is not very resistant against weathering and erosion, the infill precipitated probably quite recently.

It is interesting that kutnohorite appears not only as an isopachous rim, as reported by Clarke and Barker (1993) and Barker et al. (1997), but also as a non-layered inner-void infill precipitated on siderite and pyrite-rich sediment infill. This permits speculation about the biological origin of the kutnohorite, as suggested by Clarke and Barker (1993). A bacteria film in a later stage of void infill seems implausible because all nutrients

set free by the organic decay would likely have already been consumed.

5.5. *Geochemical conditions*

The co-occurrence of calcite, pyrite, barite, and siderite indicates a mineral stability field in the region of pH7 to pH8, representing slightly alkaline conditions (Krumbein and Garrels, 1952). The redox potential of the burial environment appears to have been slightly variable. While siderite precipitates at $Eh = -0.1$, calcite and pyrite precipitation is most common at $Eh = -0.3$ (Krumbein and Garrels, 1952). All minerals presumably precipitated under anoxic conditions. Some minerals, especially the sulphides, underwent later oxidation, most commonly from pyrite to hematite. Unfortunately, the presence of sphalerite and barite does not allow a tight constraining of the geochemical conditions during their formation. Both are common minerals with a wide distribution (Klein and Hurlbut, 1993).

The question why so few minerals are responsible for bone void infills in different environments is perhaps answered by the chemical composition of the pore waters. The constituent ions of all minerals are common in groundwater as well as marine water. As expected by the ion composition of water, the most common ions (CO_3^{2-} , SO_4^{2-} , Ca^{2+} , Fe^{3+}) formed the most abundant minerals (carbonates, sulphides, and sulphates) in the anaerobic, alkaline, and often sulphate-reducing environments of the bone voids. The actual composition of water may easily vary on a seasonal basis (Hedges and Millard, 1995), causing the precipitation of different mineral generations (e.g. Fig. 5c) in a reasonably short time. However, the complete absence of some mineral groups, like all Cu^{2+} -compounds and authigenic phosphate, is rather remarkable. Especially phosphatisation of the bone voids should be expected in phosphate-rich deposits with abundant organic matter available and an oxygen-depleted environment (Prévot and Lucas, 1997).

5.6. *Occurrence of phosphate*

The presence of fluorapatite and francolite

shows a diagenetic change from original, unaltered bone mineral, consisting of microcrystalline, non-stoichiometric carbonate hydroxyapatite $Ca_5(PO_4)_3(OH)$ (Francillon-Vieillot et al., 1990; Hubert et al., 1996) to francolite. Phosphatic minerals have very rarely been interpreted authigenic in bone (Macquaker, 1994) and these interpretations are argumentative. Martill (1999) found no authigenic phosphate in bone samples from the same locality described by Macquaker (1994).

The absence of diagenetic phosphate infill of voids is noteworthy. Phosphatic coprolites comprise 20% of Aust Cliff sediments, indicating an ample supply of phosphate. Phosphorites form under the same Eh/pH conditions as calcite and pyrite (Krumbein and Garrels, 1952). These two minerals are most common as bone void infills. However, the greatest difference between experimental phosphatisation and the diagenetic conditions obtained for the bone samples is in the pH value. Authigenic phosphate forms during anoxic and acidic conditions (Kear et al., 1993) whereas the void-filling minerals point to alkaline settings. Perhaps some kind of chemical rejection at the bone surface prevented phosphate ions from precipitating in bone cavities. Special organic substances which protected, for instance, aragonitic nacre of ammonites from solution (Keupp, 2000) could also have prohibited the phosphate precipitation in bone voids. Yet, any speculation on that subject is idle without future experimental research.

5.7. *Comparison to voids in carbonate fossils*

Compared with chambered or segmented fossils with a primary carbonate mineralogy (e.g. cephalopod shells) the bone void infills show no great differences in mineralogy. Calcite and pyrite are the most abundant minerals in both fossil types. The presence of siderite, barite, and sphalerite is also common in ammonites (Keupp, 2000). Phosphatisation of organic tissue and the replacement of the shell with phosphate is common with ammonites (Keupp, 2000; Weitschat, 1986), in contrast to fossil bone. In summary, the organic hard part mineralogy (aragonite and calcite in

shells; ‘apatite’ in bones), which do provide the porosity for authigenic mineral precipitation, is apparently irrelevant not only to pyrite formation (Hudson, 1982), but also to most other authigenic minerals with the exception of phosphate.

5.8. Relationship between minerals and depositional environment

The main minerals found in all bone samples lack apparent control by their environment of formation. Especially the distribution of calcite and pyrite does not follow a clear pattern. Nevertheless, a few differences in mineral distribution are obvious and permit limited insights (Fig. 6). Siderite is only present in Isle of Wight material, perhaps indicating a special microbial influence in these bones (Mortimer et al., 1997). The karst site Tytherington is lacking sphalerite and barite, possibly an indication for a restricted supply of the specific ions Zn^{2+} and Ba^{2+} . Tytherington bone also shows less pyrite in bone and pores, resulting from the more aerated karst environment. Sphalerite is abundant in two of the three marine deposits. In addition, the absence of sphalerite in the marine Westbury Garden Cliff material could be caused by the insufficient sample size. Therefore, sphalerite is a possible indicator for marine deposits. In contrast, barite is present in marine and freshwater deposits, but not consistently, thus lacking any environmental signal. The freshwater deposits of the Isle of Wight and Swanage show no unambiguous mineral combination which could help separate them from other environments. Sedimentary grains are common in all sites except Lyme Regis. This is probably due to differences in depositional energy levels in the aquatic environment. Abrasion opens up many new pathways for sediment grains into the bone, whereas even fine-grained sediments like the Lyme Regis mudstones cannot penetrate bones without sufficient connections to the bone cavities.

The greater variation in the mineralogy of Isle of Wight and Lyme Regis bone voids compared with the other sites can be explained by the greater diversity of sediment types at these two local-

ities. No significant mineralogical variations were found among samples from Aust Cliff. Consequently, any distinction between bones of marine and non-marine animals was not possible on this basis.

5.9. Synopsis

In summary, authigenic minerals in the examined bone voids show only little relationship to sedimentary settings. No unique mineral association was found in specific sediments or rocks. The differences in minerals in fossil bone voids represent only very weak signals of the depositional environment. Geopetal structures in bone voids provide useful information about taphonomic and diagenetic processes, because they reveal transport and reburial.

5.10. Suitability of techniques for fossil bone analysis

Petrographic microscopy of thin sections is the easiest and fastest method for identification of minerals in voids. On one hand, bone thin sections are often not ground down to exactly 30 μm because histologic features of fossil bones are poorly visible at this standard thickness of petrographic thin sections. On the other hand, mineral optics demands this thickness for thin section studies. Hence, petrographic microscopy data of bones may be inaccurate and should be interpreted with care. For a general survey of mineral contents, EDS/BSE are the best options and can also help in providing details of crystal growth (Fig. 5b,c). EDS is not very sensitive to small amounts of foreign ions in the crystal lattice, as concentrations $< 2\text{--}5\%$ are hardly detectable. WDS (microprobe) is more sensitive but rather labour-intensive. A good alternative to WDS can be XRD which is often accurate in detection of small amounts of minerals. Adversely, a peak overlap of certain minerals does often occur and prohibits unambiguous detection. Therefore, a combination of methods, EDS/BSE with SEM, petrographic microscopy, and XRD gives very good results.

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