Visualizing and quantifying biomineral preservation in fossil vertebrate dental remains

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In this study, we attempt to illustrate fossil vertebrate dental tissue geochemistry and, by inference, ~~the~~ its extent of diagenetic alteration, ~~state of apatite preservation~~ using quantitative, semi-quantitative and optical tools to evaluate bioapatite preservation. We present visual comparisons of elemental compositions in fish and plesiosaur dental remains ranging in age from Silurian to Cretaceous, based on a combination of micro-scale optical cathodoluminescence (CL) observations (optical images and scanning electron microscope) with *in-situ* minor, trace and rare earth element (REE) compositions (EDS, maps and profiles, REE), as a tool for assessing diagenetic processes and biomineral preservation during fossilization of vertebrate dental apatite. Tissue-selective REE values have been obtained using l~~L~~aser a~~A~~blation~~-~~ i~~I~~nductively c~~C~~oupled p~~P~~lasma~~-~~ m~~M~~ass s~~S~~pectrometry (LA-ICP-MPS), indicating areas of potential REE enrichment, combined with c~~C~~athodoluminescence (CL) analysis. Energy d~~D~~ispersive X-ray s~~S~~pectroscopy (EDS) mapping was also used to identify major elemental components and identify areas of contamination or diagenetic replacement. We conclude that the relative abilities of different dental tissues to resist alteration and proximity to the exposure surface ~~reflect~~ largely determine the REE composition and, accordingly, ~~subsequently~~ the inferred quality of preserved bioapatite.

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Introduction

Assessing the preservation quality of fossil hard tissues such as bone, dentine, enamel or enameloid is fundamental to research that utilizes this material as a source of biogeochemical data. Isotopic and elemental proxies derived from fossil bioapatite rely on unaltered specimens to accurately reflect palaeobiology or the environmental conditions in the past. The chemical composition of fossil bone tissues, including trace elements and stable light isotope ratios, may provide valuable information on the biology of extinct species, such as thermometabolism (e.g. Amiot *et al.* 2007; Bernard *et al.* 2010; Eagle *et al.* 2011; Rey *et al.* 2017; Séon *et al.* 2020; Leuzinger *et al.* 2022), diet (e.g. Heuser *et al.* 2011; Owocki *et al.* 2020; Klock *et al.* 2022), or ecology and environmental occupations (e.g. Daniel Bryant & Froelich 1995; Fricke *et al.* 2008; Amiot *et al.* 2010; Goedert *et al.* 2018, 2020; De Rooij *et al.* 2022; Thibon *et al.* 2022). ~~Our~~ The

Commented [UP2]: Since environmental conditions are often inferred from early-diagenetic signatures in fossils, which is a form of alteration, it might be a bit more accurate to change the wording of this sentence to something like "...rely on specimens which have not experienced significant late-diagenetic alteration to accurately reflect…"

ability to make such inferences depends on the preservation quality of the fossil remains, and at present there exists no definitive methodology for screening out digenetic alteration.

To better understand the effects of diagenesis and to discriminate the primary (or closest-to-primary) geochemical signal from early-diagenetic secondary overprinting, a spatially resolved compositional analysis of the histological sections of fossil bioapatite is required. In this study we combine spectroscopic mapping techniques including cathodoluminescence (CL) and e~~E~~nergy dispersive~~al~~ spectroscopy (EDS) analysis with *in-situ* rare earth element (REE) analysis to visualize compositional changes. We examine plesiosaur teeth and lungfish dental plates from the Lower Cretaceous, as well as Devonian fish scales to compare potential biomineral preservation in enamel, enameloid, and dentinous tissues.

The mineral component of vertebrate hard tissues is composed of biological apatite, commonly present in the form of carbonate hydroxyapatites, which stabilize to fluorapatite [$Ca_5(PO_4)_3F$] during diagenesis as the carbonate component diminishes and is replaced by fluorine (Trotter & Eggins~~,~~ 2006; Keenan *et al.*~~,~~ 2015; Lübke *et al.*~~,~~ 2017). Depending on the conditions and environment of burial, the processes of fossilization may lead to the modification of preserved biominerals through ionic exchange and rearrangements in the primary structure through~~out~~ the incorporation of foreign ions into the crystal lattice. These ~~ions~~ substitutions may include rare earth elements (REEs) for Ca^{2+} in Ca sites (Burton & Wright 1995; Daniel Bryant & Froelich 1995; Trueman & Tuross 2002; Trueman *et al.* 2006; Kocsis, Trueman & Palmer 2010; Heuser *et al.* 2011).

REE composition of fossil vertebrate hard tissues is an established tool for determining the extent of reworking and chemical changes during taphonomy (Trueman, 1999, 2013; Kohn & Cerling, 2002). Rare earth elements are also commonly used in the reconstruction of past environments (Grandjean *et al.* 1987; Kemp & Trueman 2003; Lécuyer, Reynard & Grandjean 2004; Fadel *et al.* 2015; Žigaitė *et al.* 2016; Ivanova *et al.* 2022), principally as a proxy to provenance, taphonomy and diagenesis. The incorporation of REEs and other trace elements into bioapatite predominantly takes place post-mortem (Toyoda & Tokonami~~,~~ 1990) due to ~~the~~ infiltration from either sediment pore water~~,~~ or directly from surrounding water bodies.

Apatite, with its very high affinity for REEs, frequently contains at least two to three orders of magnitude higher REE concentrations than any other mineral phase present in the fossil bones and teeth (Trueman & Palmer 1997; Kohn, Schoeninger & Barker 1999; Trueman 1999). Concentrations of REEs in fossil apatite from marine basins are higher than any other sedimentary mineral and commonly 5–~~-~~6 orders of magnitude higher than seawater (Kolodny *et al.*~~,~~ 1996). The REE reside in the two calcium sites in the apatite lattice and are normally present in living bone at the ppb level (Shaw & Wasserburg 1985), while fossil bones yield much higher REE levels, usually in the 10^3 ppm range (Kolodny *et al.* 1996).

The REE record is taxon-independent since the REE do not appear to be physiologically vital trace elements and *in vivo* bone concentrations are several orders of magnitude lower than diagenetic concentrations (Trueman 1999).~~-~~ Wright *et al.* (1987) argued that ichthyoliths (disarticulated dermal and dental fish remains), concentrated at the sediment-water interface, exhibit an enrichment in REEs, with no discernible fractionation of REEs occurring during this ~~particular~~ process. However, (Reynard *et al.* 1999) convincingly argued for fractionation between seawater and ichthyoliths. Debate remains (summarized ~~in~~ by Ivanova *et al.* 2022) as to whether REE uptake occurs only during early diagenesis or whether the process occurs continually. Two main mechanisms exist for REE trapping in phosphates – adsorption and substitution (Reynard *et al.* 1999; Trueman & Tuross 2002).

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However, the adsorption process is in equilibrium and desorption of REE^{3+} ions can occur over time, as argued by Li *et al.* (2021). Herwartz *et al.* (2011, 2013a, 2013b) have disputed the view set out by Reynard *et al.* (1999) that adsorption and substitution represent "early" and "late" stages of diagenesis. Further, Chen *et al.* (2015) have shown that in order to capture the composition of contemporary seawater, REE adsorption must occur close to the sediment-water interface, as even shallow burial can result in fractionation during early diagenesis.

Cathodoluminescence (CL) is achieved through the excitation of the sample mineral with a continuous high-energy electron beam to produce photon emission, generally in the visible spectral range (Barbin 2013). CL analysis has been used extensively as a tool to assess preservation quality and diagenetic impact in fossil enamel (e.g. Götze *et al.* 2001; Schoeninger *et al.* 2003; Ségalen *et al.* 2008; Owocki *et al.* 2020; Richard *et al.* 2022). ~~-~~In assessing biomineral preservation in apatitic fossil hard tissues, CL provides a relatively quick ~~tool~~ ~~to~~means of identifying areas of diagenetic replacement (Ségalen *et al*. 2008), without further destruction of the thin section.

Substitution by other elements of Ca sites in the crystal lattice of apatite can be detected through CL, with the elements responsible for the substitution discernible based on the wavelength and hue of the photon emission. For example, s~~S~~ubstitution by Mn^{2+} produces a yellow or orange hue (Gaft *et al.* 1997) of between 565 nm and 585 nm, whereas~~. U~~ unaltered biogenic apatite emits a dull blue luminescence of approximately 400 nm (Schoeninger *et al.* 2003). Hättig *et al.* (2019) have shown that Mn^{2+} incorporation can cause CL emission in enamel from recent sharks, and thus CL alone cannot be relied upon as a diagenetic indicator. Areas of REE substitution were associated with distinct bands with sharp emission lines between 300 nm and 1000 nm (Gaft *et al.* 1997; Blanc *et al.* 2000; Habermann *et al.* 2000; Ségalen *et al*. 2008). Notably, Gaft *et al.* (1997) showed that the luminescence bands are absent where adsorption has occurred and are only present as a result of substitution.

EDS is a widely used scanning electron microscopy (SEM) technique for determining the elemental composition of specimens. EDS has previously been used to study the distribution of elements within dental remains in relation to their structure and functional use(s) (e.g. Enax *et al.* 2012; Dumont *et al.*~~,~~ 2009, ~~; Dumont *et al.*~~ 2011) and to compare the elemental composition present in the teeth of different groups of organisms (Lübke *et al.* 2015).

Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) is an *in-situ* form of mass spectrometry~~scopy with~~ useful for down-hole compositional depth profiling, which provides reliable, quantitative, high-resolution REE and major element compositions with only minor destruction of the thin section (see Trotter and Eggins 2006; Žigaitė *et al.* 2016).

In this study we use cathodoluminescence-microscopy and spectroscopy (micro-CL) combined with ~~energy dispersive spectroscopy (~~EDS~~)~~ and *in-situ* ~~laser ablation inductive coupled plasma mass-spectrometry (~~LA-ICP-MS~~)~~ on fossil bioapatite, using ~~the~~ several types of dental fossils~~,~~ and the same thin and thick sections to be able to ~~combine and~~ cross-verify the results of these three complementary techniques.

Materials & Methods

Samples investigated ~~by~~ in this study include dermal scales from jawless and jawed fishes from the Devonian of Svalbard as well as plesiosaur tooth crowns and fossil lungfish (D~~d~~ipnoi) dental plates from the Cretaceous of southeastern~~SE~~ Australia.

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Figure 1

The Devonian fish scales were obtained from the palaeontological collections of the Paris National Natural History Museum (Museum N~~n~~ational d'Histoire ~~n~~Naturelle), France. Original sampling of this material was from the Andrée Land Group of Spitsbergen Island, Svalbard archipelago, Norway. The s~~S~~cales analysed ~~comprise~~ derive from two taxa, the thelodont *Talivalia svalbardae* and an undescribed putative chondrichthyan, both of which come from the Grey Hoek Formation in the upper part of the Andrée Land Group succession. The thelodont has~~ve~~ been described by Žigaitė *et al.* ~~in (~~2013), and the putative chondrichthyan is currently being described~~by Žigaitė *et al.* recently (in prep)~~.

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The Early Cretaceous plesiosaur and lungfish fossils were sampled from the palaeontological collection of the Melbourne Museum (Museums Victoria) (NMV), Melbourne, Australia. One plesiosaur tooth and one lungfish toothplate (see Fig. 1) were selected from the lower Albian~~, the~~ Eumeralla Formation and uppermost Barremian to lowermost Aptian~~, the~~ Wonthaggi Formation of southeastern Australia (Wagstaff *et al.*~~,~~ 2020). Previous taxonomic evaluations of these plesiosaur teeth suggested leptocledian affinity (Kear~~,~~ 2006; Kear & Hamilton-Bruce~~,~~ 2011; Poropat *et al.*~~,~~ 2018, 2023; Kear *et al.*~~,~~ 2018); the lungfish toothplates cannot be confidently identified beyond Ceratodontiformes indet. (see Poropat *et al.* [2018] for discussion).

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All specimen sections are held in The Museum of Evolution Palaeontological Collections (PMU), Uppsala University, Sweden.

Geological S~~s~~ettings

Svalbard M~~m~~aterial

The thelodont and chondrichthyan scales used in this study come from the Andrée Land~~,~~ territory in the northern part of Spitsbergen Island, Svalbard archipelago. Stratigraphically the material originates from the Lower Devonian Old Red Sandstone succession referred to as the Andrée Land Group (Blomeier *et al.*~~,~~ 2003) and represents deposition in a continental rift basin along the northern margin of the Old Red Sandstone (ORS) landmass. The succession is essentially confined to a major graben with a unique depositional history, involving a shift from coarse clastic red-beds, mainly of alluvial fan and fluvial origin, to a series of more greyish fluvial and possibly deltaic sediments ~~illustrating~~ recording a~~the~~ transition from the southern arid zone to the equatorial tropics. The nature of the basin and, more specifically, ~~the~~ its palaeoenvironmental conditions are as yet poorly understood, although it plays an important role as a regional niche and separate biogeographical province in the Early Devonian.

Vertebrate microfossils are quite common in the Andrée Land deposits, and include isolated micromeric elements of the dermal exoskeleton (dentine scales) of acanthodians, chondrichthyans, and thelodonts (Ørvig 1967; Blom & Goujet 2002; Žigaitė *et al.* 2013). The Formation extends from the Lower to Middle Devonian (Blomeier *et al.* 2003). It is subdivided into three litholog~~graph~~ical units: the Verdalen, Skamdalen and Tavlefjellet members (Blomeier *et al.* 2003; Volohonsky *et al.* 2008). The t~~T~~helodont scales come both from the Tavlefjellet and Skamdalen, while the undescribed chondrichthyan comes only from the Skamdalen, specifically from the Gråkammen locality (Žigaitė *et al.* 2013).

Australian M~~m~~aterial

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The Wonthaggi and Eumeralla formations consist of fluvial sandstone and mudstone deposits which formed part of a wider floodplain arising from the rifting of mainland Australia, Tasmania and Antarctica (Mutter *et al.* 1985). Both formations have previously yielded a diverse array of vertebrate body and ichnofossils (Martin *et al.* 2012; Poropat *et al.* 2018; Romilio & Godfrey, 2022).

The informally designated ´Wonthaggi Formation` is a unit of the Strzelecki Group correlated asassigned to the latest Barremian to earliest Aptian on the basis of palynology (Wagstaff *et al.* 2020). The Eumeralla Formation from the Otway Group is early Albian in age (Wagstaff *et al.* 2020). The Wonthaggi Formation` records evidence of possible freezing in the winter (Wagstaff and & Mason 1989) in contrast with more temperate conditions present in the Eumeralla Formation. Both units are associated with high palaeolatitudes, the position of Australia during the Lower Cretaceous being approximately 60-–80º S (Embleton & McElhinny 1982). An assessment of the floral communities of the Eumeralla Formation by Tosolini *et al.* (2018) concluded that itsa warmer climate may have included been involved strong seasonal variations.

Sample Preparation

Sectioning and preparation of dental fossils used examined in this study wereas carried out at the Department of Organismal Biology at Uppsala University, Sweden and at the NordSIM facility, Department of Mineralogy, Swedish Museum of Natural History, Stockholm, Sweden. Sections were taken along the vertical axial plane of each tooth fragment, through both the enamel and the dentine. The sample sections were selected on the basis of enamel thickness to provide a reasonable amount of working material. Thin sections (30 µm) were polished and carbon-coated before CL-spectroscopy analysis ~~at~~ by the Biomineralizations and Palaeoenvironment group at~~,~~ the University of Pierre and Marie Curie, Paris~~, 6,~~ France. The same sections of plesiosaur teeth and the dental plates of lungfish were subsequently analysed through SEM analysis.

Energy Dispersive X-ray Spectroscopy (EDS)

The chemical composition of the biomineral was investigated using e~~E~~nergy-d~~D~~ispersive X-r~~R~~ay s~~S~~pectroscopy (EDS) at the Max Plank Institute for Iron Research, Duesseldorf, Germany, in accordance with the methods outlined ~~in~~ by Dumont *et al.* (2014). EDS elemental map sections and profiles have been generated for the plesiosaur teeth and the tooth plates of lungfish. SEM imaging was conducted using a Jeol JSM-6500F scanning electron microscope operating at 15 kV with a tungsten filament instrument. The microscope was equipped with an EDAX-TSL EBSD system. The chemical compositions used in mapping were determined using EDAX energy-dispersive X-ray spectrometers (EDS) attached to the electron microscope. The microanalyses were conducted using the EDAX library standard-less procedure with a 20 s~~econd~~ dwell time.

Laser Ablation~~-~~-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS)

All specimens subject to LA-ICP-MS underwent gold spattering and polishing prior to analysis. The elemental compositions were obtained by ~~laser ablation inductively coupled plasma mass spectrometry (~~LA-ICP-MS~~)~~ at the Imaging and Analysis Centre of the Science Facilities Department, Natural History Museum, London (UK). LA-ICP-MS is a widely used technique to determine *in-situ* mineral elemental compositions, and offers the necessary high spatial resolution required to analyse REE the *in-situ*~~and~~ trace element compositions of separate tissues of micron-sized scales ~~*in-situ* at a separate tissue level~~. Analyses were performed using a New Wave Research UP213AI 213 nm aperture imaged laser ablation accessory coupled to a Thermo Elemental PQ3 ICP-MS with an enhanced sensitivity S-option interface. Data were acquired for 120 s~~econds~~ at each analysis site on the plesiosaur and lungfish specimens, taking individual points in histologically different regions (dentine or enamel). Background signals were collected for the first ~~ca~~ ~ 60 s, then ~~and~~ the laser was fired at the sample to collect sample signals for the remaining acquisition time. Data were collected using the time resolved method and were processed offline using LAMTRACE software (Simon Jackson, Macquarie University, Sydney).

Elemental concentrations were calculated using the National Institute of Standards and Technology (NIST) standard reference material 612 for calibration and calcium was used for internal standardization. The limit of detection was taken as 1σ of the mean background count, and the data filtered at twice this limit (2σ). Calculated precision was better than 3% RSD (at 1σ error) when using ^{43}Ca as an internal standard. The concentrations of REEs were measured in parts per million and normalized to Post-Archaean Australian Shale (PAAS) concentration values (McLennan 1989). The obtained *in-situ* REE compositions are explored below using basic geochemical calculations and quantifications for sedimentary rocks (Reynard *et al*.~~, Lécuyer and Grandjean~~ 1999; Johannesson *et al.* 2006; Žigaitė *et al.* 2016 and citations therein). Elemental

Commented [UP15]: These suggestions will make this easier to understand

Commented [UP16]: Although I know what this means, some readers may not, so a tilda symbol may be more universally understood compositions were measured in parts per million (ppm), and the Al_2O_3, SiO_2, TiO_2, MgO, CaO, MnO and FeO oxides, in weight percentages (wt%) (see Supplementary Tables 1–-7).

Optical Ccathodoluminescence

Optical CL examination of the samples was performed at the Imaging and Analysis Center (NHMUK) using an OPEA Catodym luminoscope operating at 15 kV and 300 -µA. Transmitted light and CL images of the samples were taken using a Nikon D70 digital camera. CL images were subsequently processed in Adobe Photoshop by raising brightness 150%. This was done to enhance the visibility of histological features as well as cracks, in order to visualize any changes in the distribution of secondary elements associated with these features. The luminescence colours and their corresponding wavelengths were then compared to the peak shifts for REE emission spectra (Ségalen *et al.*, 2008).

Results

Optical Cathodoluminescence

Figure 2

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The optical CL images of the specimens from the Eumeralla Formation show a red-orange luminescence present in the biomineralized tissue of all of our the samples, most likely attributable to REE substitution in the Ca^+ sites of the preserved apatite. Luminescence of this hue is associated with replacement by Eu^{3+} and Sm^{2+} ions (Blanc *et al.* 2000, Ségalen *et al.* 2008). In the lungfish plate, distinct areas of light blue or violet luminescence can be seen in the matrix infill around the denteon~~s~~ (Fig. 2C). Light blue/violet luminescence is not exclusive to bioapatite, ~~and~~ as it also can be generated by a~~occurs~~ number of silicate minerals (Götze~~,~~ 2012). The EDS maps of this specimen (see S~~s~~upplementary Figures~~data~~) show enrichment of silicon and aluminium within this infill. These elements are not ~~signature of~~present in the~~an~~ original bioapatite, suggesting this luminescence is representative of secondary mineral infilling rather than the preserved dentine.

In the Devonian fish from Svalbard, a yellow-orange luminescence is observed. Substitution by Dy^{3+}, Sm^{3+}, and Eu^{3+} ions is associated with these hues (Blanc *et al.* 2000, Ségalen *et al.* 2008). Notably, the interior pulp cavity in the thelodont scale from Tavlefjellet (Fig. 2G) appears to luminesce a bright yellow, although this it must be noted that this luminescence is filtered through the external enameloid. Yellow luminescence can also arise from Mn^{2+} substitution, which may also contribute to this effect. However, the overall concentration of MnO is lower in the Gråkammen scales in comparison to the Tavlefjellet scale, as measured by *in-situ* LA-ICP-MS (see below).

As optical cathodoluminescence imaging is limited to the visible spectrum of light, luminescence in wavelengths outside the visible range is not detected. Thus, despite the abundance of Gd in the specimens being comparable to, or exceeding, that of Sm and Eu (Fig. 3, D), the influence of this element on the CL images is not observed, as the emission peak of the Gd^{3+} ion in apatite has a wavelength in the ultraviolet range (Blanc *et al.* 2000).

Trace E~~e~~lement ~~a~~Analysis

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The EDS maps (Supplementary Figures) show that secondary elements are concentrated in areas accessible by pore fluids,~~;~~ most significantly in the dentine and internal pores and voids but also at the enamel-matrix interface and in cracks. Differences in secondary mineralization between the two formations appear to be minor and are best explained by the histology of the samples.

The plesiosaur teeth from the Eumeralla Formation exhibit a limited secondary element presence, with high calcium and phosphorous concentrations in both the dentine and enamel. Samples 1122A and 1122B both feature homogenous distribution of Ca and P across the enamel layers (Supplementary~~.~~ Figures). Secondary minerals are largely concentrated in and around cracks. No surficial inclusions are present in these samples.

The Eumeralla Formation lungfish dental plates overall show more widespread secondary mineralization than the plesiosaur teeth, but with strong histological differentiation in the distribution of these minerals. For example, the enamel does not appear to have undergone significant secondary mineralization, both according to the REE concentrations~~,~~ and the micro-CL and EDS imaging. Sample 1122C exhibits a slight reduction in calcium and phosphorous in areas of cracked enamel and in the vicinity of the enamel-dentine junction. Both specimens 1122C and 1122D exhibit surficial inclusions of Si-, Al-, and Na-~~-~~rich~~based~~ secondary precipitate minerals. By comparison, the dentine of each of these samples contains a greater number of minerals present in relatively high concentration. For instance, t~~T~~he dentine of sample 1122D has been infiltrated by iron-, aluminium-, and silicon-~~-~~rich~~based~~ minerals which have crystalized within cavities in the dentine. Outside of these cavities calcium and phosphorous remain abundant, with similar concentrations observed in both enamel and dentine.

REE Analysis

REE concentrations are highest in the dentine and lowest in the inner enamel of the plesiosaur teeth. The ~~EDJ (~~enamel-dentine junction (EDJ) generally has a~~n~~ REE content lower than the dentine but higher than the lower enamel. More REEs are present in the outer part of the enamel than in the inner part. This suggests that the samples experienced approximately the same degree of post-mortem ~~crystallization~~diagenetic alteration, independent of age and burial environments. Contrastingly, in the Svalbard fish scales REE concentrations are substantially higher in the pulp cavity than the outer enameloid layers, with ~~europium (~~Eu~~)~~ anomalies present in all samples and tissue types.

Figure 3

Cerium (Ce) and Lanthanum (La) anomalies can be calculated based on the LA-ICP-MS data and represent an important paleoenvironmental indicator, as these anomalies are linked to the oxic state of pore waters (e.g. Reynard *et al.* 1999; Kemp & Trueman 2003; Patrick *et al.* 2004). Negative Ce anomalies are associated with oxic conditions, whilst positive anomalies - or the absence of an anomaly - may indicate anoxia. The shale-normalized cerium $(Ce/Ce^*)_{sn}$ -and praseodymium- $(Pr/Pr^*)_{sn}$ -anomalies were~~was~~ calculated using the following respective formulae: $Ce/Ce^* = 2Ce_{sn}/(La_{sn} + Nd_{sn})$ and $Pr/Pr^* = 2Pr_{sn}/(Ce_{sn} + Sm_{sn})$ (Barrat *et al.* 2023) (~~f~~Figure 4).

Figure 4

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Commented [UP21]: This sentence sounds like it belongs in the Discussion rather than the Results, as it is an interpretation of your results

Commented [UP22]: You've already used the abbreviation Eu above, and it's common to simply say 'Eu' without having to define it. Also, it would be nice to clarify in this sentence whether you see positive, negative, or both positive and negative Eu anomalies

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Discussion

Most of the enamel present in the samples studied appears to represent the original biomineralized material. The outermost enamel at the surface of the teeth and dental plates has a higher secondary element content than the inner enamel. The exposure of the outer surface of the hard tissues to the environment may account for this to some extent; it is the area with the most contact with the matrix fluids that are the source of many of the secondary elements. The presence of elevated REE concentrations i~~o~~n the outermost enamel relative to the inner enamel is consistent with the observations of Williams *et al.* (1997) and Ségalen *et al.* (2008) that REE integration occurs primarily at the interface between the preserved tissue and the sediment. The density and poor permeability of the outer enamel may shield the inner matrix from significant pore fluid infiltration.

In the Wonthaggi plesiosaur teeth, secondary minerals are more prevalent. In sample 1223A the pulp cavity has undergone extensive infilling, with Al, Si, Fe and Zn present in higher concentrations than the surrounding dentine. The enamel of this sample is less secondarily mineralized, though infilling of cracks by Si- and Al-rich ~~based~~ minerals is observed. Sample 1223B also exhibits some secondary mineralization. Whilst there is no infilling of the pulp cavity, the dentine is marked in places by areas ~~of~~ exhibiting increased F and C; while Al, Si, and C fillings in the cracks of the inner part of the tooth surficial inclusions are observed, along with infiltrations of Fe at the outermost extent of the dentine. The lungfish plates display high levels of Ca and P, more so than is seen in the dentine of other samples. Secondary mineralization is also present in the lungfish teeth, with extensive infilling of pore spaces and dentine tubules by Si, Al, and Fe. Although infilling is widespread, particularly in sample 1123D (Suppl. Figure

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Commented [PU29]: This is difficult to understand as written. Perhaps rephrase alike "secondary inclusions containing Al, Si, and C are observed along the internal pulp cavity surface of this tooth, and Fe is also observed to infiltrate the external-most portion of the dentine."

11), no large areas of recrystallisation alike those~~as seen~~ in the Eumeralla Formation specimens are seen.

In both sets of samples Si, Al and Fe are the most abundant elements present in cracks. The probable source of these elements is the matrix in which the specimens were deposited; the formations in which the specimens were found consist of sandstones and mudstones from which high quantities of quartz and clay minerals are to be expected. Fluorine (F) is generally elevated in fossil hard tissues relative to contemporary remains, as *in vivo* incorporation of F into bioapatite~~s~~ is comparatively low yet~~, while~~ fluoride ions readily replace OH^- during diagenesis (Ghadimi *et al.* 2013; Keenan *et al.* 2015). An exception would be enameloid, which has close chemical composition to geological fluorapatite (Sasagawa *et al.* 2009; Enax e*t al.* 2012). In ~~our~~ these samples, F is present in the matrix and has accumulated~~ds~~ in areas close to psurficial cracks, but it is also present within the fossil tissue. The distribution of F within all the analysed tissues is largely homogenous, with no clear distinction between dentine and enamel visible ~~from~~ within the EDS maps (see Supplementary ~~data~~Figures).

Secondary elements are marginally more ~~prevalent~~ abundant in the lungfish plates than in the plesiosaur teeth. ~~-~~Lungfish do not shed their dental plates (Kemp 2002), and they are thus only deposited with the death of the animal. The outer surface of the plate is susceptible to mechanical wear, which may expose the eroded dentine to secondary elements. Wearing may be exacerbated by environmental stresses such as food availability and o~~O~~xygen concentration (Kemp 2005). It should also be noted that some lungfish taxa replace eroded enamel with hydroxyapatite-~~-~~enriched petrodentine which is continuously produced (Kemp 2001; Smith & Krupina 2001~~; Kemp 2001~~). By contrast, plesiosaurs are known to have ~~undergone~~ experienced continuous tooth shedding and replacement (Kear *et al.* 2017). Polyphyodonty (tooth shedding)

Commented [PU30]: Perhaps "the most abundant elements, being primarily present in secondary phases infilling cracks."

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Commented [PU31]: Perhaps "adjacent to" rather than "close to"?

Commented [PU32]: Do you mean "such as changes in diet driven by limited food availability and variations in ambient oxygen concentrations"? In other words, it would be clearer to specify what about food availability and oxygen concentrations can cause greater wearing

Commented [PU33]: Switching them into alphabetical order since the year is the same is a trait found in the majority of vertebrate groups and is not indicative of an animal's metabolism. Kear (2006) noted that the plesiosaur teeth used in this study also exhibited wear to some degree, though not to the extent that inclusions in worn enamel present a significant route for secondary mineral infiltration into the dentine (compared to compaction-induced cracks or natural pores~~holes~~).

As with the secondary elements, luminescence is strongly associated with cracks and the outer surfaces of the samples, reflecting the vulnerability of these areas to infiltration by pore waters during diagenesis. The enamel present in the plesiosaur teeth superficially appears to luminesce more strongly than the dentine, contrary to expectations based on the LA-ICP-MS results. We suggest this may result from the transparency of the enamel, allowing for more photon transmission than in ~~relatively~~ comparatively more opaque dentine, rather than a signal of potentially greater diagenetic ~~infiltrations~~alteration. The wavelength of the luminescence, inferred from the hue, is of greater importance to this study than the intensity, as it is indicative of whether REE replacement has occurred. It is also suggestive of which elements may be responsible for said replacement, though this information is substantially less quantitative in comparison to those derived from methods such as LA-ICP-MS.

The compositional profiles obtained in the context of fossil tissue histology determine~~s~~ potential systematic trends in their relative permeability and susceptibility to diagenesis. Enamel and enameloid are more resistant to elemental and mineral replacement and alteration than dentine as they are of a lower porosity and more extensively mineralised, with < 2% organic content (Hoppe *et al.* 2003) in comparison to approximately 70% in dentine. Dentine is less mineralised *in vivo* than enamel and is co~~n~~mposed of micro-sized tubules which increase its porosity and permeability. In lungfish dental plates the dentine is also vascularized (Kemp &

Commented [PU34]: This sounds like it needs a citation at the end of this sentence

Commented [PU35]: This sentence is a bit confusing and unclear. Consider rephrasing to make it clearer

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Barry~~,~~ 2006), with voids left by blood vessels providing ~~an~~ effective entry ~~-~~points for groundwater during ~~taphonomy and~~ early diagenesis. These factors increase the potential for infiltration of the dentine by secondary elements, in turn increasing the likelihood of mineral alteration and replacement.

Commented [PU36]: This was a bit redundant as written. It can just say “during early diagenesis”

The strong yellow luminescence in the pulp cavity of the Tavlefjellet thelodont scale (Fig. 2G) suggests stronger infiltration of the cavity by REEs relative to the dentine and enameloid. This is supported by our LA-ICP-MS analysis showing REE concentrations in the pulp cavity~~, in particular Eu,~~ up to an order of magnitude higher than in other tissues, especially for Eu. Pulp is extensively vascularised and has a greater organic component than dentine, and so it is more susceptible to fluid infiltration. Greater REE enrichment of the pulp cavity tissue in comparison to the other tissues further supports the porosity of hard tissues being a significant factor in diagenetic REE uptake.

The observed REE profiles of the fossils are indicative of limited diagenetic alteration. In the plesiosaur teeth, the degree of preservation in the inner enamel is such that the observed isotope signals ~~produced~~ can be interpreted as primary. In these fossil specimens, REE content varies based on histology and does so in a way that largely mimics the distribution of secondary elements seen in the EDS maps. The dentine of the samples is, with some exceptions, more strongly enriched than the enamel. However, the enamel exhibits greater variability ~~of~~ in enrichment within the same tissue; while it is generally the case that the outer enamel is more strongly enriched than the inner, both areas possess regions either more strongly or weakly enriched than would be predicted based on histology. Even within the same tooth this is the case, as seen in the Wonthaggi plesiosaur tooth. ~~Here~~ In that specimen, the inner enamel is split between areas of high REE concentration exceeding that of the enamel (approaching 10^3 ppm

Commented [PU37]: This would be a clearer way of saying this

Commented [PU38]: You mean elemental rather than isotope, I think, correct? Yes it’s isotopes of REEs you’re looking at, but using this term makes the reader think of stable isotope analysis, which is not what you are doing

Commented [PU39]: Specifically you mean “enriched in trace elements”, correct? It could be useful to be more specific like this

Commented [PU40]: It would be great to cite the relevant figure(s) at the end of this sentence to remind the reader of what this variation looks like (log))~~,~~ and exceptionally low concentration, between 10^{-1} ppm (log) for LREEs and 1 ppm (log) for HREEs.

All the Australian Cretaceous samples exhibit a slightly “bell shaped” shale-normalized REE profile, with MREEs being more abundant than LREEs and HREEs, though this is most pronounced in the plesiosaur samples. The abundance of MREEs, and in particular Eu, is reflected in the ~~C~~dathodoluminescence images. Strong MREE enrichment is associated with the overprinting of early diagenetic signals by later recrystallization and fractionation (Lécuyer *et al.* 2004). This pattern supports the interpretation of the specimens as being well preserved, displaying minor REE adsorption from early diagenesis rather than the fractionated incorporation of a significant amount of REEs associated with later overprinting (Fadel *et al.* 2015; Žigaitė *et al.* 2015).

Cerium state varies greatly between tissue types in the examined fossils. In the Wonthaggi plesiosaur tooth, the Ce anomaly ~~of~~ throughout its dentine appears to be influenced by a negative La anomaly, while the enamel is influenced by a positive La anomaly. The enamel of both plesiosaur teeth exhibits an overall positive Ce anomaly. The lungfish plate broadly displays no Ce anomaly. Positive La anomalies have been linked to riverine conditions (Kulaksız & Bau 2011). The HREE concentrations in our samples are lower than would be expected from ocean waters (Patrick *et al.* 2004). In the Svalbard fish ~~material~~samples, REE enrichment is more varied. The t~~T~~helodont scales display~~ a~~ considerably~~e~~ positive Eu anomalies~~y~~, which may be attributed to reworking during diagenesis (see Žigaitė *et al.* 2016).

Conclusions

Commented [PU41]: The use of (log) here is odd and unclear. It would be much simpler to just change each of these to their numbers: “(approaching 1,000 ppm) and exceptionally low concentration, between 0.1 ppm for LREEs and 1 ppm for HREEs.”

Commented [PU42]: Maybe “especially apparent” rather than “reflected”?

Commented [PU43]: This isn’t necessarily always true, as natural waters in some environments are inherently MREE enriched, which can impart such fractionation patterns to bone during early diagenesis. Thus, it seems important to add a qualifying word like “often”, “sometimes”, or “occasionally” before “associated” in this sentence

Commented [PU44]: It’s also important to note the magnitude of REE enrichment, which would be expected to increase or be high as a result of late-diagenetic overprinting. I therefore suggest adding a phrase to this sentence alike “incorporation of a significant amount of REEs…”

Commented [PU45]: The implications of the trends noted in this paragraph are not particularly clear. Can you please clarify the importance and/or meanings of the patterns noted throughout this paragraph?

Commented [PU46]: Again, it would be nice to recite the relevant figure at the end of this sentence, to remind the reader of what data is being interpreted for these conclusions

Commented [PU47]: Perhaps change to “generally”

Commented [PU48]: They may also arise by other means too, such as fractionation during early-diagenetic uptake (see your citation Herwartz et al. 2013 and Ullmann et al. 2021 for two examples). This additional possible cause should be acknowledged here, perhaps by adding another sentence right after this one.

Ullmann PV, Macauley K, Ash RD, Shoup B, Scannella JB. 2021. Taphonomic and diagenetic pathways to protein preservation, part I: the case of *Tyrannosaurus rex* specimen MOR 1125. *Biology* 10: 1193.

Commented [PU49]: Should be plural because you’re discussing the patterns in multiple fossils

Commented [PU50]: Can this be explained here rather than simply cited to Zigaite et al. 2016? It feels like it needs more explanation, even if by just adding one more sentence to the end of the paragraph which talks about how the Eu anomalies are thought to arise from reworking

The REE distribution patterns in the fossil samples studied herein are indicative of generally minimal diagenetic overprinting~~ in the samples overall~~, with histological variations that overlap with the secondary element distributions seen ~~from~~ in ~~the~~ EDS maps.

Our ~~analysis~~ data therefore supports the ~~view~~ conclusion that the primary chemical composition of the fossil bioapatite is largely ~~well~~ preserved in the studied specimens. In particular, the inner enamel of our samples likely consists of mostly unaltered, original tissues and is a prime candidate for future study. We ~~a~~were also able to ~~show~~ identify the extent to which secondary elements had infiltrated these samples through diagenetic processes, including ~~and identify~~ their spatial distributions. We conclude that histology is a better indicator of the extent of both preserved biominerals and secondary replacement than either diagenetic or non-histology-related biological factors.

The distribution of REEs in our samples in line with the interpretation of a freshwater system being present, in agreement with previous paleoenvironmental assessments. Our results unfortunately provide no further insights into the climate of southeastern~~SE~~ Australia in the ~~Lower~~ Early Cretaceous, though the cool environment identified by other studies (Rich *et al.* 2002) may have been a factor in the high level of biomineral ~~chemical~~ preservation seen in our samples (Tütken *et al.* 2008). The elevated quantities of MREEs in the p~~P~~lesiosaur samples may be reflective of the marine conditions inhabited by the animals ~~in~~ during life (Žigaitė *et al.* 2016). Given the fluvial interpretation of the Eumeralla F~~f~~ormation (Kear 2006; Kear *et al.* 2006; ~~Kear 2006;~~ Benson *et al.* 2013), this further supports the idea of euryhaline behaviour in plesiosaurs (Benson *et al.* 2013; Bunker *et al.* 2022, and citations therein).

Mapping of REE and trace element distributions through electrospectroscopic techniques provides the benefit of visualising geochemical composition. In so doing, it allows for areas of

Commented [PU51]: I would recommend combining these paragraphs, especially because the first one at the moment consists of just a single sentence, which is generally considered too short to constitute a paragraph

Commented [PU52]: Collectively, the minor edits I suggest in this sentence would make it easier to read and more technically accurate

Commented [PU53]: Can you clarify "future studies of ___" at the end of the sentence? This would be especially useful for readers who are less familiar with the variety of utilities of trace elements and stable isotopes in vertebrate fossils

Commented [PU54]: I think you mean something more like "preservation quality" here, correct?

Commented [PU55]: This phrasing is confusing. Perhaps rephrase alike this: "….samples appears reflective of early-diagenetic uptake having occurred from freshwater surface and/or pore fluids,"

Commented [PU56]: Since your meaning is more temporal than stratigraphic here, Early would be more appropriate than Lower

Commented [PU57]: The single author citation should come first here

Commented [PU58]: Is this really a word? I haven't heard this adjective used before to describe the methods used in this study significant diagenetic alteration to be identified, providing insight into the specific mechanism(s) of diagenetic change. Conversely, ~~it~~ these mapping techniques highlight~~s~~ areas in which primary biomineral composition is likely to be preserved, and thus they provide~~serves as a~~ useful tools to guide ~~other~~ paleobiological, paleoecological, and paleoenvironmental analys~~e~~is. In particular, mapping is likely to benefit the design and spatial targeting while conducting *in-situ* microanalyses. Consequently, the application of mapping from multiple sources increases confidence in biogeochemistry-based reconstructions of past organisms and environments.

Commented [PU59]: And, at least potentially, into the temporal sequence of those diagenetic alterations (in some cases anyway)

Commented [PU60]: Since the sentence is noting a positive second use of the techniques, it might sound better to use a positive transition word here, such as "Additionally,"

Commented [PU61]: This is the direction you meant, yes? Again, it would be useful to add these descriptors to increase clarity

Acknowledgements

The ~~A~~authors would like to express gratitude to the late Teressa Jeffries (NHMUK) for her invaluable assistance with conducting the LA-ICP-MS analyses, as well as Kerstin Lindén (NordSIM facility, Stockholm) for sample preparation. We are grateful to Thomas Rich and Tim Ziegler (Museums Victoria) and Patricia Vickers Rich (Monash University) for generous provision of the Australian samples, and likewise to Daniel Goujet and Gaël Clément (MNHN) for the Svalbard fossil material. We would like to thank Aleksander Kostka for his advice and assistance with EDS~~X~~ experimentation.

We are particularly grateful to Sophie Sanchez (Uppsala University), as well as Mary Kate Branigan (Uppsala University) and Ethan Killian for helpful discussions.

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