



Preservation of successive diagenetic stages in Middle Triassic bonebeds: Evidence from in situ trace element and strontium isotope analysis of vertebrate fossils



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ABSTRACT

Bonebeds comprise reworked and time averaged constituents of different phosphatic vertebrate remains and, hence, provide an ideal substrate for the study of long and short term diagenetic processes. To test whether trace elements (U, Sr, REE) and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios can be used for distinguishing between successive diagenetic signals, we performed geochemical analyses on vertebrate remains (bones, teeth, scales and coprolites) from two Triassic bonebeds located near Palzem (Germany). Trace element analysis was done on 170 vertebrate remains by LA-ICP-MS while $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were determined for 39 bioclasts using LA-MC-ICP-MS. Although a low inter- and intra-bioclast REE variability indicates long-term open system behaviour, the observed REE patterns suggest the preservation of different diagenetic stages.

A distinct difference in the geochemical composition exists between dark luminescent SEM-CL domains and greyish ones. Dark domains represent dense, diagenetically more resistant material of low porosities such as enamel and ganoine. These domains display distinctly lower ΣREE contents and a higher inter-clast variability than those of various grey tones. Together with lower, hence more seawater-like $^{87}\text{Sr}/^{86}\text{Sr}$ ratios this argues for a preservation of an earlier diagenetic signal. Notably, most dark domains are characterised by negative Eu anomalies while all grey ones display positive Eu anomalies. With the exception of Eu both domains display almost identical REE patterns with different concentrations indicating that late diagenetic REE uptake is not necessarily accompanied by fractionation processes in vertebrate bioclasts. Negative Eu anomalies are most likely inherited from Eu-depleted surface waters, possibly as a result of Eu-depleted aeolian input. Conversely, positive Eu anomalies were presumably affected by Eu-enriched late diagenetic fluids with a possible high temperature origin causing a fractionation of europium. Our study therefore demonstrates the potential of high-resolution geochemical analysis in bonebed strata to disentangle different stages of diagenesis and to detect least altered areas in vertebrate fossils for recovering pristine palaeoenvironmental signals.

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1. Introduction

The study of rare earth elements (REE) has become especially important in taphonomy and palaeontology since REE occur at very low abundance within living organisms and fresh fossils and are enriched by several orders of magnitude during diagenesis in fossil vertebrate remains (e.g., Trueman and Palmer, 1997; Kohn et al., 1999; Herwartz et al., 2011, 2013a, 2013b; Tütken et al., 2011). Hence, in vivo REE compositions are overprinted in fossil biogenic apatite (Herwartz et al., 2013b) and therefore REE compositions should reflect the geochemical signal of the environment in which they were fossilised (Trueman, 1999).

Traditionally, REE were believed to be incorporated into fossil vertebrate remains exclusively during early diagenesis (<100 ka) (see discussion in e.g., Kocsis et al., 2010; Herwartz et al., 2013b), which ends in bones with the total loss of organic content (mainly collagen) and its replacement by minerals (Pfretzschner, 2004). Thus, REE patterns have frequently been used to study various aspects of the fossilisation environment such as reconstruction of the palaeoenvironment, taphonomy, palaeoceanography, provenance and reworking of vertebrate remains (e.g., Wright et al., 1984, 1987; Elderfield and Pagett, 1986; Denys et al., 1996; Girard and Albarède, 1996; Samoilov et al., 2001; Picard et al., 2002; Kemp and Trueman, 2003; Trueman et al., 2003, 2005, 2006; Lécuyer et al., 2003, 2004; Metzger et al., 2004; Martin et al., 2005; Labs-Hochstein and MacFadden, 2006; Ounis et al., 2008; Anderson et al., 2007; Domingo et al., 2007, 2009a, 2009b, 2011; Cook and

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Trueman, 2009; Grandstaff and Terry, 2009; Kocsis et al., 2009; Iliopoulos et al., 2010; Rogers et al., 2010; Suarez et al., 2010; Patrick, 2013a, 2013b; Zhao et al., 2013).

The use of REE in fossil biogenic apatite as a geochemical proxy therefore depends on the assumption that REE are incorporated into the apatite lattice rapidly post-mortem without further late diagenetic exchange (Kocsis et al., 2010). After initial fossilisation, the growth of authigenic apatite into the intra-crystalline porosity originally occupied by collagen, further REE exchange with surrounding pore waters may be prevented or severely reduced (see discussion in e.g., Kohn, 2008; Kocsis et al., 2010).

Recent studies, however, have suggested substantial element exchange between fossil biogenic apatite and late diagenetic fluids over geological timescales (Kocsis et al., 2010; Herwartz et al., 2011, 2013a, 2013b; Tütken et al., 2011; Kowal-Linka et al., 2014). Hence, palaeoenvironmental interpretations based on REE pattern should be done with caution, taking into account possible long-lasting open-system behaviour with regard to the REE and other trace elements. Nevertheless, even in fossil vertebrate material with REE patterns presumably altered after early diagenesis, features such as a Eu anomaly may still reflect an original early diagenetic signal (e.g., Kowal-Linka et al., 2014). In addition, well crystallised, non-porous tissue (enamel, ganoine) has been argued to be less susceptible to late diagenetic alteration in regard to REE uptake (e.g., Domingo et al., 2009; Kocsis et al., 2010) and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (e.g., Budd et al., 2000; Hoppe et al., 2003; Lee-Thorp and Sponheimer, 2003; Becker et al., 2008; Copeland et al., 2010; Kocsis et al., 2013).

In this study we use a comprehensive approach combining multi-trace element analysis, Sr isotopic composition as well as SEM-CL imaging to examine early and late diagenetic processes on a “vertebrate sand” (Reif, 1971) type of bonebed. The analyses have been performed by laser ablation on vertebrate remains of well-known Muschelkalk–Keuper bonebeds from the western part of the Germanic Basin, previously exclusively studied under petrographic or faunal aspects (e.g., Plieninger, 1844; Fraas, 1889; Wagner, 1913; Seilacher, 1943; Reif, 1971, 1982; Hagdorn and Reif, 1988; Dittrich and Schoch, 2004; Löffler and Prinz-Grimm, 2013). The bonebeds of Ladinian age (ca. 239 Ma) (cf. Kozur and Bachmann, 2005) consist of numerous different, very small, densely packed, sand sized vertebrate remains which are believed to be reworked and time averaged (Reif, 1971, 1982; Hagdorn and Reif, 1988; Hagdorn, 1990). The diverse constituents (bones, teeth, scales, coprolites) derive from a range of different environments (Hagdorn and Reif, 1988; Löffler and Prinz-Grimm, 2013) and should therefore exhibit discernible geochemical variations between individual vertebrate remains as well as between separate bonebeds if the early diagenetic signals were preserved. A geochemical study on bonebeds such as these therefore presents an ideal opportunity to study possible long term open system behaviour of vertebrate remains toward trace element (i.e., REE, Sr) uptake.

We performed trace element analysis on 170 vertebrate remains (405 ablation spots) and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were determined for 39 vertebrate remains (77 ablation spots). The in-situ measurements (50 μm spot size) are able to resolve the intra-fossil variability and therefore have a clear advantage over bulk-sampling techniques (e.g., Trueman and Benton, 1997; Trueman et al., 2003). Primary goal was to investigate whether early diagenetic features are still preserved in the various constituents or if they show long-lasting open-system behaviour with regard to the REE and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. In particular we aim to test if diagenetic more resistant parts of vertebrate remains (enameloid) preserve pristine palaeoenvironmental and early diagenetic signals more faithfully, while more porous constituents are more prone to record later stages of diagenesis. Based on the outcome of our study, we propose that in situ measurements of REE patterns, trace elements and radiogenic strontium isotopes via LA-(MC)-ICP-MS of bonebed material are valuable techniques to discern the diagenetic history and to detect least altered areas within fossils.

2. Geological setting

The bonebed material examined in this study is derived from the active Reinhold Hippert GmbH quarry (49.56°N, 6.39°E) near Palzem, Germany (Fig. 1 A). The Hippert quarry is located approximately 250 m north of Schloss Thorn by the river Moselle, southeast of the municipality Palzem in the Trier–Saarburg district. Geologically the exposed rocks of the quarry belong to the Trier–Luxembourg Basin (TLB) and are of Triassic age. The two bonebeds studied here formed during and shortly after the Muschelkalk–Keuper transition.

The Trier–Luxembourg Embayment is considered a sub-basin of the Germanic Basin in the Lower and Middle Triassic and is often referred to as the southwest part of the Germanic Basin (e.g., Vecsei, 1998; Vecsei and Düringer, 2003; Vecsei et al., 2003; Bourquin et al., 2006), but also a sub-basin of the Paris Basin in the late Triassic (Schintgen and Förster, 2013). It is primarily filled with sediments of Mesozoic age (Fig. 1 A). In the Triassic the sedimentation area of the TLB progressively expanded to the west at the expense of the Ardennes (Schröder, 1951; Wagner et al., 2012; Schintgen and Förster, 2013). In the Upper Muschelkalk the Eifel Depression was a relatively wide shallow seaway and the central part of the TLB was a facially independent, at times isolated, shallow marine to lagoonal basin (LGB, 2005). The carbonates of the “Trochitenschichten” (mo1) and “Ceratitenschichten” (mo2) are almost exclusively dolostones (Dittrich, 1989; LGB, 2005; Wagner et al., 2012). In the upper units of the Upper Muschelkalk (“Ceratitenschichten”) a high energy facies with ooids, bioclasts and cross-bedding is confined to the area of the Ridge of Mettlach–Sierck (LGB, 2005). Within the basin centre an argillaceous marl–dolostone alternating sequence was deposited in a shallow marine lagoon (LGB, 2005; Wagner et al., 2012). In the uppermost Upper Muschelkalk cross-bedded sandy dolostones or dolomitic sandstones (“Sandige Ceratitenschichten”) prograded from the basin margin reaching a wide distribution (Dittrich, 1989; Vecsei and Düringer, 2003).

A regional regression terminated the Muschelkalk carbonate sedimentation initiating the Keuper sedimentation (Ziegler, 1982) represented by nearshore sabkha deposits with extreme evaporation conditions and periodic flooding events forming minerals such as dolomite, gypsum and magnesite (Wagner, 1989).

The Upper Muschelkalk dolostones that are being mined in the Hippert quarry belong to the Thron-Subformation of the “Obere Ceratitenschichten” (mo2C2). The Thron-Subformation also known as “Hartsteinlager 4” (Wagner, 1984) consists of wavy bedded dolostones and reaches a thickness of almost 30 m within this quarry (Wagner et al., 2012). These dolostones were strongly influenced by the Ridge of Mettlach–Sierck and interpreted as being deposited in a shallow marine, high-energy area (LGB, 2005; Wagner et al., 2012). A series of up to three thin bonebed layers can be currently found on top of the Upper Muschelkalk dolostones, the so called “Grenzbonebed”. A clear distinction between the individual layers of the Grenzbonebed is difficult as, firstly, they are almost exclusively exposed as a ca. 900 m² surface in the northern part of the quarry and secondly, the individual layers continuously intersect with each other. Additionally, this trichotomy is not constantly represented in the outcrop making it impossible to differ between the layers.

The Grenzbonebed is the base of the Basisschichten (ku1B) of the Lettenkeuper and is overlain by approximately 40 cm thick dark greyish dolomitic claystones (Fig. 1 B). They are followed by a quartz siltstone with variable carbonate content expressing fine planar lamination, the “Untere Lettenkohlsandstein” (cf., Gittinger, 1968; Dittrich, 1989; Wagner et al., 2012), overlain by dark greyish, greenish and beige-coloured mudstones. Additionally, a distinct dolostone horizon is interbedded in this marl, mudstone and siltstone alternate bedding of the Basisschichten.

Up to three thin bonebed layers termed the “Basisschichten bonebed” are found at or near the top of this dolostone bed (Fig. 1 B), although the uppermost bonebed layer termed K3 could not yet be

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