

REE+Y signatures and enamel microstructure constraining early burial diagenesis in Pleistocene *Bison* from northeastern Mexico: Palaeoenvironmental implications

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Abstract: Dental enamel is regarded as a robust archive for geochemical and palaeoecological studies; however, evaluation of diagenetic alteration is essential prior to palaeoenvironmental interpretation. This study assesses the microstructural and geochemical preservation of dental enamel from four fragmentary Pleistocene molariform teeth attributed to *Bison* sp., recovered from Quaternary deposits at Ejido San Lázaro, Villagrán, Tamaulipas, north-eastern Mexico. An analytical approach combining optical microscopy, SEM-EDS and LA-ICP-MS was applied to evaluate enamel integrity, major-element stoichiometry and rare earth element plus yttrium (REE+Y) systematics. Microscopic observations reveal a well-preserved hydroxylapatite microstructure, with densely packed crystallites and no evidence of significant recrystallisation. Major-element compositions (Ca, P and F) display near-stoichiometric Ca/P ratios (~1.67) and low F/P values (<0.1), indicating limited fluorapatite formation and mineralogical alteration. LA-ICP-MS analyses yielded low total REE concentrations ($\Sigma\text{REE}=50\text{--}137$ ppm; $\Sigma\text{REE+Y}$ up to 168 ppm) and flat PAAS-normalised patterns, consistent with restricted post-mortem incorporation of trace elements. Systematic negative Ce anomalies, accompanied by positive La/La* anomalies, indicate early burial under oxidising conditions and interaction with LREE-enriched pore fluids or sediments. Given the regional geological framework, contribution from the surrounding and underlying Cretaceous carbonate and calcareous–argillaceous succession is possible, although Y/Ho ratios are complementary rather than diagnostic evidence for marine influence. The La enrichment is interpreted cautiously as a local early diagenetic signal related to sediment–fluid interaction, pH-dependent REE mobility and sorption/desorption processes, rather than as evidence of a uniquely marine-derived fluid source. Overall, the results indicate a high degree of preservation in the analysed enamel specimens and show that their palaeoenvironmental value depends on recognising limited diagenetic overprinting. By combining microstructural, major-element and REE+Y evidence, this study provides a framework for distinguishing preserved early burial geochemical signals from later alteration, supporting the cautious use of *Bison* enamel specimens as reliable archives for palaeoenvironmental studies in north-eastern Mexico.

Keywords: Pleistocene, Mexico, diagenesis, hydroxylapatite, rare earth elements (REE), SEM-EDS, *Bison*

Introduction

Research on fossil mammals in Mexico has a history spanning more than two centuries. The earliest known published record dates to 12 June 1799, when the *Gaceta de México* reported the discovery of proboscidean remains in the state of Aguascalientes (Maldonado-Koerdell 1948). From the late eighteenth century onwards, both national and foreign naturalists

and explorers began to undertake systematic scientific observations of the country's natural history.

Throughout the nineteenth century, a substantial number of publications described fossil materials; however, in many cases, precise information regarding provenance and stratigraphic context was lacking. By the mid-nineteenth century, notable advances had been achieved in collection methods, descriptive practices and geological cartography of Mexican mineral and fossil resources (Montellano-Ballesteros & Jiménez-Hidalgo 2006).

Later efforts aimed to organise this dispersed information into broader syntheses of the Mexican fossil mammal and

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palaeovertebrate record. In this context, [Maldonado-Koerdell \(1948\)](#) provided an early overview of Quaternary fossil vertebrates in Mexico, whereas [Barrios-Rivera \(1985\)](#) presented a detailed analytical compilation of the national palaeovertebrate record.

The Neogene and Quaternary mammal fossil record – representing the most recent intervals of the Cenozoic – is particularly well represented in Mexico ([Arroyo-Cabrales et al. 2002](#)). Specimen age is a critical factor in geochemical studies, as the degree of diagenetic modification affecting biogenic apatite tends to increase over time ([Shin & Hedges 2012](#)), potentially altering primary geochemical signals. Previous studies have applied stable isotope analyses to infer palaeodietary patterns (e.g., [Pérez-Crespo et al. 2020a](#); [Marín-Leyva et al. 2022](#)), as well as trace element concentrations to investigate mobility and landscape use ([Pérez-Crespo et al. 2020b](#)).

Despite this growing body of work, relatively few studies have explicitly evaluated the extent of diagenetic alteration affecting geochemical datasets. [Pérez-Crespo et al. \(2020b\)](#) addressed this issue in the context of a strontium isotope study of camelids, mammoths and equids, whereas [Pérez-Crespo et al. \(2025\)](#) applied FTIR-ATR spectroscopy in the analysis of a juvenile mammoth. In both cases, the material originated from Pleistocene deposits in San Luis Potosí.

Although dental enamel is generally considered more resistant to diagenetic modification than other skeletal tissues, it is not immune to alteration, and assessment of such transformation is essential for robust palaeoenvironmental interpretation ([Kendall et al. 2018](#)). In addition, environmental factors such as salinity, temperature, altitude and humidity may exert a significant influence on oxygen isotope values ([Waddell & Moore 2008](#); [Iacumin et al. 2022](#)). For these reasons, the incorporation of independent lines of evidence is recommended in order to identify, quantify or exclude diagenetic overprinting.

One such line of evidence is the analysis of rare earth elements (REEs), which, owing to their chemical coherence and systematic distribution patterns, provide a sensitive means of detecting post-mortem processes ([Tostevin et al. 2016](#)). Where REE profiles remain flat and consistent with unaltered apatite, ecological and environmental inferences are considered more reliable. In addition, the evaluation of major elements such as Ca, P and F enables the detection of recrystallisation or chemical substitutions through deviations from stoichiometric proportions ([Domingo et al. 2012](#)).

Recently, [Hernández-Sandoval et al. \(2026\)](#) applied a multi-proxy geochemical approach to fossil mammal enamel from north-western Mexico, integrating trace element data and stable isotope analyses to evaluate palaeoecological patterns and diagenetic effects in Neogene and Quaternary assemblages. Their results highlighted the value of combining microstructural observations with elemental systematics to assess the preservation state of biogenic apatite and to constrain early post-burial geochemical processes.

Building on this framework, the present study focuses on *Bison* dental enamel from northeastern Mexico and aims to evaluate its microstructural and geochemical preservation

while characterising early burial diagenetic conditions through major element composition and REE+Y systematics. The main objective is to assess the extent to which the analysed enamel specimens retain a preserved geochemical signal or have been modified by diagenetic alteration. A secondary aim is to evaluate whether these preservation criteria support the cautious use of the material as a reliable archive for future palaeoenvironmental studies in the region. Accordingly, the study is focused on the depositional and early fossilisation environments recorded by the enamel, rather than on a full reconstruction of the broader regional palaeoenvironment.

Geological and palaeontological framework

Ejido San Lázaro, in the municipality of Villagrán, Tamaulipas, is located in the central-western part of the state, at approximately 24°31' N and 99°36' W ([Fig. 1](#)). The area lies within a transitional zone between the Sierra Madre Oriental and the Northern Gulf Coastal Plain. The regional geology is characterised by a Mesozoic succession deformed during the Laramide orogeny, including Jurassic shales of the La Casita Formation overlain by a Cretaceous sequence dominated by limestones and calcareous–argillaceous units corresponding to the Taraises, Lower Tamaulipas, Upper Tamaulipas, Otates, Cuesta del Cura, Agua Nueva, San Felipe and Méndez formations ([Eguiluz de Antuñano et al. 2000](#); [SGM 2021](#)).

These Mesozoic units form the regional substratum beneath the younger continental deposits and are unconformably overlain by polyimictic conglomerates of Pliocene–Pleistocene age and by Holocene alluvial deposits. At the locality site, the Ejido San Lázaro area is characterised by shallow valleys bounded by elongated, undifferentiated Pleistocene volcanic bodies approximately 20 m high, trending broadly east–west and crossed by seasonal streams ([SGM 2021](#)).

The fossiliferous Quaternary sediments occur within these valley-floor deposits and consist mainly of light-yellow sediment (sand/silt) containing small calcite concretions, approxi-

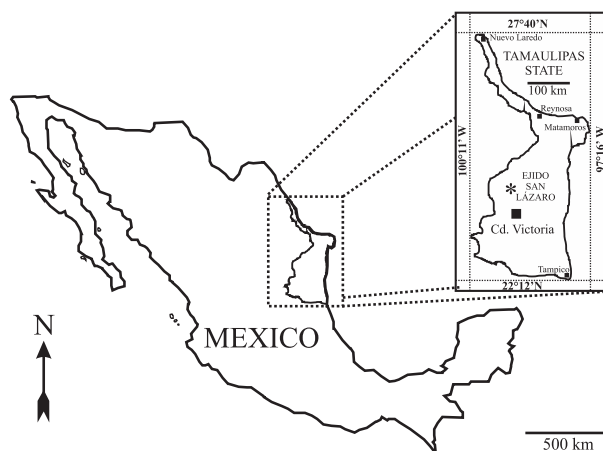


Fig. 1. Location of the study area, Ejido San Lázaro, Municipality of Villagrán (State of Tamaulipas, NE Mexico).

mately 1–2 cm in diameter. The fine-grained composition of these sediments is consistent with deposition under relatively low-energy conditions, as silt- and clay-sized particles are commonly deposited from suspension where flow energy is reduced (Nichols 2009; Boggs 2012). The small calcite concretions may reflect pedogenic or early diagenetic carbonate precipitation, a common process in fine-grained continental deposits affected by pore-water movement and local cementation (Tucker 2001, 2011).

Pleistocene fossil remains recovered from these Quaternary sediments, locally exposed by stream incision, include partial carapaces, skulls and postcranial elements of the tortoise *Gopherus donlatoi* (Reynoso & Montellano-Ballesteros 2004; Carbot et al. 2020), mandibular, cranial and dental remains of *Equus conversidens*, partial carapace and skeletal remains of the glyptodont *Glyptotherium cylindricum*, and isolated molars of *Mammuthus* sp. and *Bison* sp. The four *Bison* teeth analysed in the present study derive from this fossiliferous assemblage. The occurrence of *Bison* sp. is biochronologically significant and supports a Rancholabrean age assignment for the faunal association (Montellano-Ballesteros 2000; Reynoso & Montellano-Ballesteros 2004; Ramírez-Cruz & Montellano-Ballesteros 2014). However, the precise stratigraphic position of the analysed specimens within the Pleistocene cannot be established from the available information.

A schematic stratigraphic column (Fig. 2) based on the Villagrán geological map and explanatory information of SGM (2021) has been incorporated to clarify the sedimentological and stratigraphic context of the fossil-bearing area. The analysed *Bison* dental specimens are positioned within the fossiliferous Quaternary deposits exposed at the locality, according to their documented provenance. No absolute age determination is currently available for the analysed teeth or enclosing sediments; therefore, the Rancholabrean assignment is regarded as a biochronological constraint based on the associated fauna, rather than as an independent chronometric age. The column is not a bed-by-bed measured section; consequently, the depositional interpretation is treated as a sedimentological inference based on the available field description, lithological observations and regional geological framework. This limitation is relevant for interpreting diagenetic processes, as the precise duration of post-burial exposure cannot yet be quantified.

Materials and methods

Material

Dental samples were collected in the field and stored in sealed containers to ensure adequate protection during transport. Preliminary taxonomic identification and initial preparation were carried out at the Laboratorio de Paleontología, Instituto de Geología, Ciudad Universitaria, Universidad Nacional Autónoma de México (UNAM). The analysed assemblage consists of four isolated, fragmentary molariform dental

elements attributable to *Bison* sp. In order to minimise the possibility of repeated sampling of equivalent dental material, the specimens were evaluated following a conservative morphometric approach comparable to that of Marín-Leyva et al. (2021). Maximum preserved length, width and height were measured for each fragment using a digital calliper, and the resulting values are reported in Table 1. These measurements correspond to the maximum preserved dimensions of each fragment and do not necessarily represent complete anatomical crown dimensions.

The four analysed specimens differ in preserved dimensions (Table 1). Nevertheless, due to the incomplete preservation of the material and the absence of fully diagnostic anatomical landmarks, they are not interpreted as confirmed representatives of different individuals. As anatomical orientation could not be securely established, these measurements are descriptive rather than strictly anatomical. Species-level identification was not attempted, as the fragments lack the complete diagnostic dental morphology required for robust specific assignment. Accordingly, individual-level attribution remains uncertain, and the geochemical results are discussed at the specimen level. They are not used to infer taxon-wide preservation quality, population-level geochemical homogeneity or intraspecific variability within *Bison*.

Dental mesowear and microwear analyses were not undertaken as the fragmentary preservation of the material and the absence of intact occlusal surfaces precluded reliable standardised assessment, following approaches such as those of Semperebon et al. (2016).

Methods

Thin-section preparation

For preparation, samples were subjected to ultrasonic cleaning using a Cole-Parmer ultrasonic cleaner, model 8893 (Vernon Hills, Illinois), in successive short cycles until complete removal of adhering sedimentary residues was achieved. The dental elements were then air-dried and embedded in epoxy resin in order to prevent fracturing during sectioning. Once the resin had fully cured, the blocks were cut approximately parallel to the occlusal surface in order to obtain comparable sections through the preserved enamel. This orientation maximises comparability among specimens by targeting planes that correspond as closely as possible to equivalent stages of enamel formation.

The resulting sections were mounted on standard petrographic glass slides and ground to thicknesses of approximately 40–50 µm using a Buehler PetroThin system (Lake Bluff, Illinois). Subsequently, the thin sections were progressively polished using silicon carbide abrasives of decreasing grit size (200, 400 and 600), followed by a final ultrasonic bath to remove residual particles. Prepared specimens are housed at the Unidad Multidisciplinaria de Docencia e Investigación, Facultad de Ciencias, Campus Juriquilla (UMDI-FC-J, UNAM), under internal catalogue numbers BT-1 to BT-4 (Fig. 3).

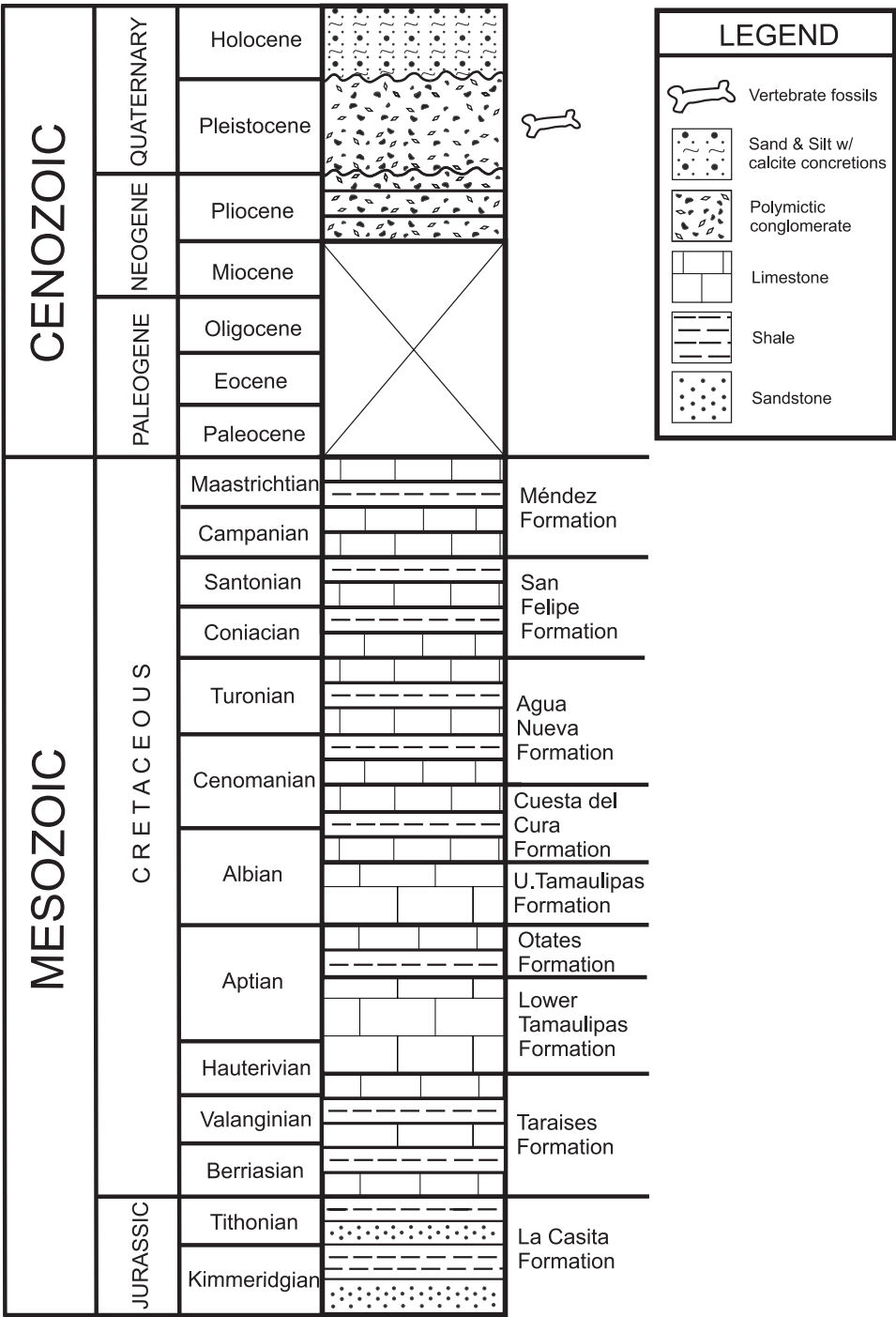


Fig. 2. Regional geological column of the Villagrán area, Tamaulipas, showing the Cenozoic and Mesozoic succession and the approximate position of the fossil-bearing Quaternary deposits analysed in this study. The underlying Cretaceous carbonate and calcareous–argillaceous units are included as part of the geological framework used to interpret early burial sediment–fluid interaction. Lithological patterns are shown in the legend. Relationships among units are schematic and not to scale. Modified from [SGM \(2021\)](#).

Optical microscopy

Thin sections were examined by transmitted-light polarising petrographic microscopy using a Leica DMLSP microscope at the UMDI-FC-J (UNAM), with the aim of identifying micro-structural regions minimally affected by diagenetic processes.

Areas exhibiting the best state of preservation were selected for subsequent geochemical analyses by SEM-EDS and LA-ICP-MS. During preliminary inspection, the dental material displayed features consistent with relatively good preservation, with no macroscopic evidence of significant alteration.

Table 1: Preserved dimensions of the analysed *Bison* sp. dental fragments. Dimensions are expressed in centimetres as maximum preserved length $\times$ maximum preserved width $\times$ maximum preserved thickness, measured prior to sectioning. As anatomical orientation could not be securely established, these values are descriptive rather than strictly anatomical measurements. All specimens correspond to isolated, fragmentary molariform dental elements attributable to *Bison* sp.

Sample	Preserved dimensions before sectioning (cm)	Identification
BT1	$3.0 \times 2.4 \times 2.8$	<i>Bison</i> , sp.
BT2	$3.6 \times 2.7 \times 3.0$	<i>Bison</i> , sp.
BT3	$2.8 \times 2.1 \times 2.6$	<i>Bison</i> , sp.
BT4	$2.6 \times 2.0 \times 2.5$	<i>Bison</i> , sp.

SEM-EDS

Scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDS) analyses were conducted at the Laboratorio de Microscopía (LAMIC), Escuela Nacional de Estudios Superiores, Unidad Morelia, UNAM. These analyses were performed to assess microstructural preservation and to quantify the principal primary constituents of dental enamel. Final concentrations are reported in atomic percentages (Table 2). Observations were carried out using a JEOL JSM IT300 LV scanning electron microscope.

The microscope was operated at an accelerating voltage of 20 kV under low-vacuum conditions (approximately 50 Pa). Signal acquisition employed a combination of backscattered electron (BSE) and secondary electron (SE) detectors in order to optimise microstructural contrast. Chemical analyses were conducted by energy-dispersive X-ray spectroscopy (EDS) using two Oxford X-Max silicon drift detectors (SDDs), each with a 20 mm² active area, coupled to the microscope. Elemental data for Ca, P and F were processed and quantified in

a standardised manner using AZtec software. The EDS system was calibrated and checked using a PELCO® XCS-5 EDS Calibration Standard (Ted Pella Inc., Product No. 659-5), which includes NIST-certified SRM 1155 stainless steel, fused SiO₂, Mn metal, B, glassy C and a Cu aperture/Faraday cage for detector calibration, performance verification and quantitative EDS assessment. Measurement atomic percentage uncertainties ($\sigma_{At\%}$) were assessed from the Wt% Sigma values generated by AZtec during quantification and are indicated in Table 2.

In addition, selected thin sections were subjected to brief chemical etching using 10 % v/v HCl for 3–5 s, with the aim of enhancing the visibility of the hexagonal crystal structure of hydroxylapatite (Fig. 4) and providing a preliminary assessment of internal crystallite organisation.

LA-ICP-MS

Trace element analyses were performed by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at the Laboratorio de Estudios Isotópicos (LEI), Instituto de Geociencias, Campus Juriquilla, UNAM. Analyses were conducted using a Resonetics Resolution S-155 laser ablation system (193 nm ArF excimer laser) coupled to a Thermo iCap Qc ICP-MS. The in situ spatial distribution of selected elements was assessed by monitoring the following masses: ⁴⁴Ca, ⁸⁹Y, ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴³Nd, ¹⁴⁷Sm, ¹⁵¹Eu, ¹⁵⁷Gd, ¹⁵⁹Tb, ¹⁶³Dy, ¹⁶⁵Ho, ¹⁶⁶Er, ¹⁶⁹Tm, ¹⁷²Yb and ¹⁷⁵Lu. Elemental concentrations are reported in parts per million (ppm) and are presented in Table 3.

The laser was operated at a fluence of 4 J cm⁻² and a repetition rate of 5 Hz, using a spot diameter of 60 μ m. Ablation pits were approximately 15 μ m deep. For each tooth, five independent measurements were acquired, all conducted on the same thin section in order to approximate a plane parallel

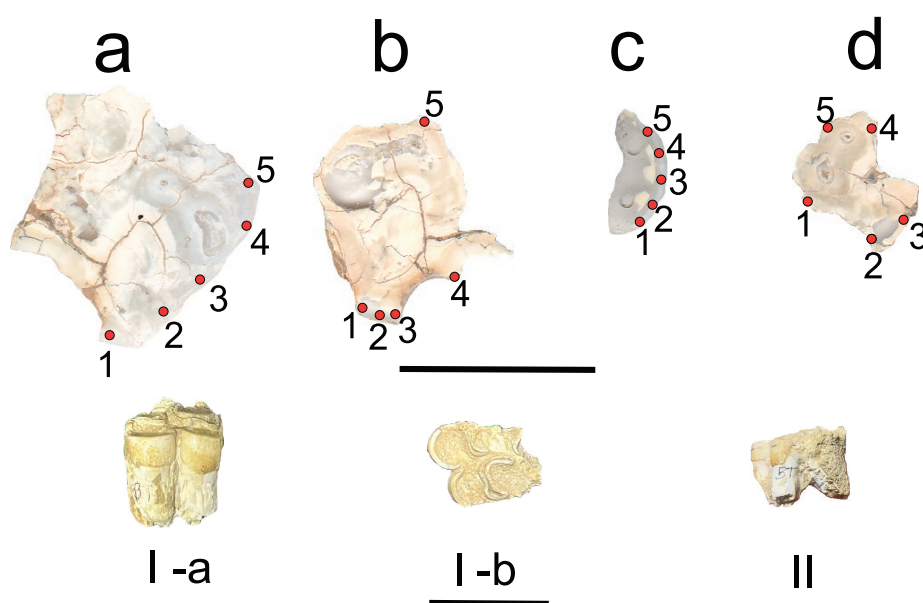


Fig. 3. Analysed *Bison* dental specimens, prepared enamel sections and LA-ICP-MS ablation spots. Panels I-a and I-b show specimen BT-1 prior to sectioning, whereas panel II shows specimen BT-2 prior to sectioning. Panels a–d correspond to the prepared enamel sections of BT-1, BT-2, BT-3 and BT-4, respectively. Numbered red circles indicate the five LA-ICP-MS ablation spots analysed in each specimen. Scale bar=2.5 cm. See text for further details.

to the occlusal surface (Fig. 3). This strategy ensured that the geochemical data were mutually comparable and representative of a single phase of enamel formation, interpreted as broadly coeval at first order (Hernández-Sandoval et al. 2026). Each measurement consisted of approximately 60 individual readings per spot.

Internal normalisation was carried out using ^{44}Ca (e.g., Roberts et al. 2017), while external calibration was achieved using the NIST SRM 612 reference material. Despite substantial compositional differences between NIST SRM 612 and dental enamel, particularly with respect to major elements and matrix structure, the certified homogeneity and analytical stability of this reference material justify its widespread use in multi-element LA-ICP-MS calibration (Jochum et al. 2011). To mitigate and monitor potential matrix effects – defined as systematic variations in signal intensity arising from differences in laser–material interaction or plasma behaviour – a combined strategy was implemented, involving internal Ca normalisation and instrumental verification using Durango Apatite.

Durango Apatite was analysed during the same analytical session as a secondary standard in order to verify instrumental performance and the reliability of the data-reduction protocol. Although Durango Apatite typically contains higher concentrations of rare earth elements (REE) than dental enamel, its comparable crystallographic structure and similar laser ablation response render it suitable for evaluating instrumental behaviour and the coherence of elemental ratios. Analytical equivalence between well-characterised apatites and tooth enamel has been demonstrated previously, supporting the use of apatites as reference materials for biogenic phosphate matrices (Horstwood et al. 2008).

Six repeated analyses of Durango Apatite were used to calculate element-specific mean concentrations, standard deviations, relative standard deviations/coefficient of variation values (RSD/CV %) and internal 2SE values. These results are reported in Supplementary Table S1. Repeated Durango Apatite analyses yielded low external variability, with RSD/CV values of 1.10–2.46 % for Y and REE, and 1.14 % for Ca. All measured mean concentrations for Ca, Y and REE fell within the compiled GeoReM reference ranges for Durango Apatite (Jochum et al. 2005). As GeoReM reports compiled reference ranges rather than a single certified value for this material, agreement with the reference interval is used here as the criterion for secondary-standard accuracy, while deviations from the interval midpoint are reported descriptively in Supplementary Table S1. Data reduction and processing were performed using Iolite v. 3.6 software (Paton et al. 2011). Lower detection limits (LDLs) were calculated individually for each analysis according to Longerich et al. (1996). The maximum LDL obtained for each monitored element across the analytical dataset is reported in Table 3.

In the present study, REE were consistently detected in enamel samples; however, their distribution patterns and relative abundances showed no evidence of cross-contamination or analytical distortion associated with the use of Durango Apatite as a secondary standard.

During analyses, nitrogen gas (N_2) was introduced at an approximate flow rate of 2.5 mL min^{-1} to enhance signal sensitivity for selected elements (Hu et al. 2008). This optimisation contributed to stable instrumental conditions, reflected by ThO^+/Th^+ ratios consistently below 1 % (mean ≈ 0.8 %), thereby minimising potential interferences from oxide or polyatomic species (Sylvester 2008).

Instrumental drift was monitored and corrected using a standard–sample bracketing protocol, effectively reducing signal deviations throughout analytical sessions (Thomas 2013). External standards were analysed at the beginning and end of each session, with each measurement preceded by a 14 s gas blank and followed by a 14 s washout period to prevent cross-contamination. The analytical protocol yielded accuracy and precision values within 5 %, confirming the robustness and reliability of the dataset (Vaggelli & Cossio 2011).

Mathematical and statistical analyses

Mathematical and statistical analyses were carried out using SPSS (IBM, v.26; 2019) and Microsoft Excel (2021).

For LA-ICP-MS data, statistical analyses were conducted at two complementary levels. First, intra-spot signal stability was evaluated from the 60 time-resolved readings acquired during each individual ablation spot. Arithmetic means, standard deviations and coefficients of variation (CV%) were calculated for each element and spot in order to assess short-term signal stability during ablation (Table 3).

Table 2: SEM-EDS major-element composition of the analysed *Bison* enamel specimens, expressed as atomic percentages (at.%) and weight percentages (wt.%). Ca and P are additionally reported as stoichiometric CaO and P_2O_5 equivalents. The $\Sigma\text{CaO}+\text{P}_2\text{O}_5+\text{F}$ values represent a partial compositional sum and show its deviation from 100 wt.%; components other than those reported here are not included in this sum. The near-stoichiometric Ca/P ratios (ca. 1.67) and consistently low F/P ratios indicate limited diagenetic modification of the original apatite composition preserved in the enamel. See text and Fig. 4 for further discussion..

	Unit	BT1	BT2	BT3	BT4
F	at.%	1.13	1.02	1.11	1.21
σ_F	at.%	0.07	0.05	0.06	0.08
F	wt.%	0.97	0.89	0.95	1.03
P	at.%	11.58	11.25	11.69	12.18
σ_P	at.%	0.05	0.04	0.05	0.04
P	wt.%	16.23	15.91	16.29	16.92
Ca	at.%	19.66	19.01	20.04	20.26
σ_{Ca}	at.%	0.08	0.06	0.07	0.08
Ca	wt.%	35.65	34.80	36.14	36.42
CaO	wt.%	49.88	48.69	50.57	50.95
P_2O_5	wt.%	37.18	36.47	37.34	38.77
$\Sigma \text{CaO}+\text{P}_2\text{O}_5+\text{F}$	wt.%	88.04	86.04	88.86	90.76
Deviation from 100 %	wt.%	11.96	13.96	11.14	9.24
Ca/P	atomic ratio	1.698	1.690	1.714	1.663
F/P	atomic ratio	0.098	0.091	0.095	0.099

These parameters were used to assess intra-spot signal stability and to quantify intra-tooth geochemical variability among the five analytical spots. Although the analyses were performed along a plane approximately parallel to the occlusal surface, the replicate spots were retained as individual analytical series rather than treated as fully interchangeable values.

Second, intra-tooth geochemical variability was evaluated by comparing the five independent enamel spots analysed within each tooth. For each tooth and element, spot-mean concentrations were used to calculate arithmetic means, and CV% values across the five analytical spots. These values were used to quantify the relative magnitude of intra-tooth dispersion. The 60 time-resolved readings acquired during each individual ablation event were not treated as independent analytical replicates. Accordingly, intra-tooth geochemical variability was assessed descriptively using the five independent spot-mean concentrations and their corresponding CV% values.

The distribution of rare earth elements plus yttrium (REE+Y) in different geochemical reservoirs follows well-defined and systematic patterns (Tostevin 2021). Accordingly, a normalisation procedure was applied to minimise the influence of natural variations in absolute abundances and to enhance the detection of subtle differences in geochemical behaviour. In studies of sedimentary rocks and fossils, such normalisation is conventionally performed relative to the Post-Archean Australian Shale (PAAS; McLennan 1989), which is widely used as a reference standard (e.g., Nothdurft et al. 2004; Madhavaraju & Lee 2009). Elemental anomalies were calculated from the PAAS-normalised values. Cerium anomalies were evaluated using the method of Bau & Dulski (1996), and were also calculated according to Lawrence et al. (2006) for comparative purposes. Prior to calculating Ce anomalies, Pr/Pr* was evaluated because natural Pr anomalies are not expected to occur, and apparent Pr anomalies may instead reflect anomalous behaviour of neighbouring REE:

$$Pr/Pr^* = Pr_{SN} / (0.5Ce_{SN} + 0.5Nd_{SN}) \quad (1)$$

Cerium anomalies were then calculated using the following expression:

$$Ce/Ce^* = Ce_{SN} / (0.5La_{SN} + 0.5Pr_{SN}) \quad (2)$$

following Bau & Dulski (1996). In addition, Ce/Ce* was calculated using the formulation proposed by Lawrence et al. (2006):

$$Ce/Ce^* = Ce_{SN} / (Pr_{SN} \times (Pr_{SN}/Nd_{SN})) \quad (3)$$

The use of both formulations allowed comparison between the conventional interpolation-based estimate and an alternative calculation that accounts for the behaviour of adjacent REE in normalised patterns. These calculations were used to evaluate deviations from expected REE+Y distributions and to support the interpretation of geochemical signatures in fossil bioapatite. The complete analytical datasets, including raw concentrations and PAAS-normalised REE+Y values, are provided in Table 3.

Results

Scanning electron microscopy (SEM) of untreated fracture surfaces provided only limited visualisation of crystal morphology, without clear differentiation of transverse, longitudinal or oblique crystallite orientations (Fig. 4a). However, following brief chemical etching with 10 % v/v HCl, a well-preserved microstructure became evident (Fig. 4b,c). The enamel is characterised by an intact and coherent arrangement of hydroxylapatite crystallites, indicating a high degree of microstructural preservation. It is important to note that all subsequent analyses conducted on thin sections (SEM-EDS and LA-ICP-MS) were performed exclusively on unetched specimens or prior to etching, thereby ensuring that this treatment did not influence the geochemical results.

Quantitative energy-dispersive X-ray spectroscopy (EDS) analyses indicate that calcium (Ca) contents in the analysed *Bison* teeth range from 19.01 to 20.26 at.%, corresponding to 34.80 to 36.42 wt.%, whereas phosphorus (P) values vary between 11.25 and 12.18 at.% (15.91–16.92 wt.%). Fluorine (F) concentrations are relatively uniform, ranging from 1.02 to 1.21 at.% (0.89–1.03 wt.%; Table 2). When expressed as stoichiometric oxide equivalents, CaO ranges from 48.69 to 50.96 wt.% and P₂O₅ from 36.47 to 38.77 wt.%. The calculated CaO+P₂O₅+F sums range from 86.04 to 90.76 wt.%, corresponding to deviations of 9.24–13.96 wt.% from 100 %. Ca/P ratios range between 1.663 and 1.714, whereas F/P ratios yield values from 0.091 to 0.099. These proportions are consistent with a composition dominated by biogenic apatite and show no evidence of anomalous enrichment or significant chemical modification at the microstructural scale.

Overall, these results demonstrate that the analysed *Bison* dental enamel specimens (BT1–BT4) retain a homogeneous and internally consistent elemental composition. This supports the suitability of the material for higher-resolution geochemical analyses and for subsequent trace-element-based interpretations.

LA-ICP-MS analyses of *Bison* enamel yielded calcium (Ca) concentrations between 37.9 and 38.8 wt.%. Ca concentrations were initially calculated in ppm during data reduction and subsequently converted to wt.%. These values display limited variation among specimens and are reported in Table 3 for analytical completeness, as ⁴⁴Ca was used for internal normalisation during LA-ICP-MS data reduction. They are not used for quantitative interpretation of major-element composition.

Total rare earth element concentrations (ΣREE) range from 50 to 137 ppm, while yttrium (Y) concentrations vary between 13 and 32 ppm (Table 3). The consistent detection of REE and Y in all samples indicates their systematic occurrence in the analysed enamel, without evidence for anomalous enrichment or substantial signal loss.

Elemental concentrations remained stable throughout individual ablation time series at each analytical point, as indicated by the intra-spot coefficients of variation calculated from the 60 time-resolved readings acquired for each element

Table 3: Calcium and rare earth element plus yttrium (REE+Y) mean concentrations for all subsample sets from BT1 to BT4, as determined by LA-ICP-MS. Ca values are reported as percentages, whereas Y and REE concentrations are reported in ppm. The maximum lower detection limit (LDL) obtained for each monitored element across the analytical dataset, calculated according to Longerich et al. (1996), is also reported in ppm. Ca is retained for analytical completeness, as ⁴⁴Ca was used for internal normalisation during LA-ICP-MS data reduction; these values are not used for quantitative interpretation of major-element composition or enamel stoichiometry. For each subsample, the concentration row reports Ca-normalised LA-ICP-MS values, whereas the row labelled “_{SN}” reports the corresponding PAAS shale-normalised values, which are dimensionless. Standard deviation (SD) and coefficient of variation (CV) values are also reported for each subsample set. Calculated La/La* and Ce/Ce* anomalies following (1) Bau & Dulski (1996) and (2) Lawrence et al. (2006) are shown, together with Y/Ho ratios, total rare earth element concentrations (ΣREE) and total rare earth elements including yttrium (ΣREE+Y). Direct numerical comparison between Ca concentrations reported here in ppm and SEM-EDS Ca values reported in atomic percent in Table 2 is not intended, owing to differences in quantification approach, analytical volume and reporting units. See text and Figures 5–7 for further details.

	Ca	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu	ΣREE	ΣREE + Y	Y/Ho	Pr/Pr*	Ce/Ce*	Ce/Ce*
PAAS		38.20	79.60	8.83	33.90	5.55	1.08	0.029	0.281	0.014	0.301	6.860	0.119	0.196	0.285	0.41	0.028	0.342	0.43			
Maximum LDL (ppm)	143.96	1.122	0.189	0.141	1.627	0.179	0.029	0.281	0.014	0.301	6.860	0.119	0.196	0.285	0.41	0.028	0.342	0.43				
BT1-1	38.50 %	24.79	25.86	6.36	27.55	5.33	0.98	4.92	0.76	4.47	24.02	0.93	2.72	0.43	2.23	0.33	107.67	131.69	25.70			
SD	11.02 %	1.5	2.0	0.4	1.7	0.4	0.1	0.6	0.1	0.3	1.2	0.1	0.2	0.0	0.2	0.0						
CV	0.03	0.06	0.08	0.06	0.06	0.08	0.08	0.13	0.13	0.08	0.05	0.07	0.06	0.06	0.07	0.06						
SN		0.65	0.32	0.72	0.81	0.96	0.90	1.06	0.98	0.95	0.89	0.94	0.96	1.06	0.79	0.77				1.27	0.47	0.51
BT1-2	37.92 %	13.31	17.14	5.50	23.09	4.20	0.80	3.99	0.56	3.70	20.30	0.76	2.09	0.32	1.77	0.27	77.52	97.82	26.65			
SD	16.91 %	1.00	1.17	0.33	1.25	0.23	0.05	0.24	0.03	0.48	1.11	0.10	0.14	0.03	0.10	0.02						
CV	0.04	0.08	0.07	0.06	0.05	0.05	0.06	0.06	0.05	0.13	0.05	0.13	0.07	0.08	0.06	0.06						
SN		0.35	0.22	0.62	0.68	0.76	0.74	0.86	0.72	0.79	0.75	0.77	0.73	0.79	0.63	0.63				1.39	0.44	0.38
BT1-3	38.74 %	18.28	20.15	4.10	21.64	3.78	0.71	3.23	0.56	3.30	19.08	0.62	1.94	0.31	1.98	0.27	80.88	99.96	30.86			
SD	16.97 %	1.46	1.17	0.30	1.46	0.29	0.05	0.25	0.04	0.20	1.18	0.03	0.25	0.04	0.12	0.02						
CV	0.04	0.08	0.06	0.07	0.07	0.08	0.06	0.08	0.08	0.06	0.06	0.05	0.13	0.13	0.06	0.08						
SN		0.48	0.25	0.46	0.64	0.68	0.66	0.69	0.73	0.70	0.71	0.62	0.68	0.76	0.70	0.62				1.04	0.54	0.75
BT1-4	38.26 %	25.30	31.36	5.24	22.95	4.30	0.80	3.78	0.56	3.87	20.10	0.72	2.11	0.30	1.70	0.26	103.23	123.33	27.74			
SD	12.41 %	1.91	2.28	0.37	1.47	0.32	0.04	0.52	0.04	0.25	1.55	0.05	0.14	0.02	0.11	0.04						
CV	0.03	0.08	0.07	0.07	0.06	0.07	0.05	0.14	0.07	0.06	0.08	0.07	0.07	0.05	0.06	0.14						
SN		0.66	0.39	0.59	0.68	0.77	0.74	0.81	0.72	0.83	0.74	0.73	0.74	0.75	0.60	0.59				1.11	0.63	0.76
BT1-5	38.69 %	31.25	38.30	6.61	28.51	5.42	0.98	4.74	0.70	4.91	25.12	0.91	2.60	0.36	2.09	0.32	127.70	152.83	27.68			
SD	16.01 %	1.71	2.79	0.44	2.07	0.32	0.06	0.24	0.09	0.65	1.27	0.05	0.21	0.02	0.14	0.02						
CV	0.04	0.05	0.07	0.07	0.07	0.06	0.06	0.05	0.13	0.13	0.05	0.06	0.08	0.06	0.07	0.07						
SN		0.82	0.48	0.75	0.84	0.98	0.91	1.02	0.90	1.05	0.93	0.92	0.91	0.89	0.74	0.75				1.13	0.61	0.72
BT2-1	38.05 %	18.57	13.98	3.51	13.48	3.04	0.40	3.58	0.72	5.24	32.11	1.33	4.11	0.60	3.94	0.57	73.05	105.16	24.16			
SD	10.00 %	0.63	0.51	0.18	0.65	0.16	0.03	0.28	0.05	0.14	0.69	0.03	0.10	0.01	0.10	0.02						
CV	0.03	0.05	0.04	0.05	0.04	0.05	0.05	0.13	0.13	0.05	0.04	0.04	0.05	0.05	0.05	0.06						
SN		0.49	0.18	0.40	0.40	0.55	0.37	0.77	0.93	1.12	1.19	1.34	1.44	1.47	1.40	1.31				1.39	0.40	0.44
BT2-2	38.76 %	13.84	13.32	3.77	15.09	3.12	0.54	2.09	0.39	3.00	18.41	0.62	1.96	0.30	1.91	0.29	60.23	78.64	29.91			
SD	17.69 %	0.53	0.38	0.13	0.71	0.10	0.02	0.11	0.02	0.38	0.98	0.09	0.22	0.01	0.10	0.01						
CV	0.05	0.05	0.05	0.04	0.05	0.04	0.04	0.04	0.04	0.14	0.05	0.14	0.05	0.04	0.05	0.06						
SN		0.36	0.17	0.43	0.45	0.56	0.50	0.45	0.50	0.64	0.68	0.62	0.69	0.74	0.68	0.67				1.40	0.42	0.41
BT2-3	38.71 %	11.21	7.81	3.12	14.89	2.32	0.44	2.56	0.43	2.66	19.66	0.65	1.63	0.28	1.97	0.24	50.22	69.88	30.24			
SD	16.98 %	0.50	0.35	0.11	0.61	0.09	0.02	0.13	0.02	0.12	0.79	0.03	0.07	0.04	0.08	0.04						
CV	0.04	0.05	0.05	0.04	0.04	0.04	0.05	0.05	0.05	0.04	0.04	0.04	0.04	0.04	0.04	0.15						
SN		0.29	0.10	0.35	0.44	0.42	0.41	0.55	0.55	0.57	0.73	0.66	0.57	0.70	0.70	0.56				1.32	0.30	0.34
BT2-4	38.33 %	19.71	14.12	3.71	13.86	2.71	0.56	2.41	0.38	2.93	14.39	0.54	1.73	0.22	1.89	0.24	65.01	79.40	26.82			
SD	18.27 %	0.94	0.59	0.16	0.64	0.11	0.03	0.33	0.02	0.43	0.66	0.02	0.08	0.01	0.09	0.03						
CV	0.05	0.05	0.04	0.04	0.05	0.04	0.05	0.14	0.04	0.15	0.05	0.05	0.05	0.05	0.05	0.13						
SN		0.52	0.18	0.42	0.41	0.49	0.52	0.52	0.50	0.63	0.53	0.54	0.61	0.54	0.67	0.56				1.43	0.38	0.41

Table 3 (continued):

	Ca	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu	SREE	SREE + Y	Y/Ho	Pr/Pr*	Ce/Ce*	Ce/Ce*
BT2-5	38.44 %	29.64	16.62	3.51	15.37	3.05	0.54	2.35	0.35	2.55	15.61	0.64	2.07	0.29	1.98	0.26	79.23	94.83	24.56			
SD	17.60 %	1.31	0.73	0.14	0.75	0.15	0.03	0.10	0.04	0.11	0.78	0.09	0.11	0.01	0.08	0.01						
CV	0.05	0.04	0.04	0.04	0.05	0.05	0.05	0.04	0.13	0.04	0.05	0.14	0.05	0.04	0.04	0.05						
SN	0.78	0.21	0.40	0.40	0.45	0.55	0.50	0.50	0.46	0.55	0.58	0.64	0.73	0.71	0.70	0.60				1.20	0.36	0.60
BT3-1	38.19 %	23.12	18.43	4.06	17.05	3.11	0.61	2.49	0.42	2.59	17.12	0.68	2.14	0.24	2.03	0.24	77.21	94.33	25.18			
SD	13.25 %	0.96	1.28	0.18	2.36	0.23	0.04	0.32	0.02	0.18	0.45	0.04	0.08	0.01	0.13	0.03						
CV	0.03	0.04	0.07	0.04	0.14	0.07	0.07	0.13	0.04	0.07	0.03	0.05	0.04	0.05	0.06	0.14						
SN	0.61	0.23	0.46	0.46	0.50	0.56	0.56	0.53	0.54	0.55	0.63	0.69	0.75	0.59	0.72	0.55				1.25	0.43	0.55
BT3-2	38.76 %	17.95	14.06	3.14	12.08	2.45	0.39	1.94	0.24	2.19	13.94	0.54	2.01	0.18	1.56	0.18	58.91	72.85	25.81			
SD	16.64 %	0.91	0.90	0.19	0.87	0.10	0.05	0.10	0.03	0.12	0.71	0.04	0.11	0.01	0.11	0.01						
CV	0.04	0.05	0.06	0.06	0.07	0.04	0.14	0.05	0.13	0.05	0.05	0.07	0.05	0.06	0.07	0.06						
SN	0.47	0.18	0.36	0.36	0.36	0.44	0.36	0.42	0.31	0.47	0.52	0.54	0.71	0.44	0.55	0.42				1.33	0.43	0.50
BT3-3	38.12 %	19.42	16.38	3.29	12.47	2.38	0.41	2.12	0.27	2.33	14.34	0.62	2.15	0.23	1.71	0.23	64.01	78.35	23.13			
SD	20.81 %	1.33	1.09	0.13	0.43	0.12	0.02	0.36	0.01	0.10	0.59	0.10	0.12	0.03	0.08	0.01						
CV	0.05	0.07	0.07	0.04	0.03	0.05	0.05	0.17	0.03	0.04	0.04	0.16	0.05	0.13	0.05	0.04						
SN	0.51	0.21	0.37	0.37	0.37	0.43	0.38	0.45	0.35	0.50	0.53	0.63	0.75	0.57	0.61	0.53				1.30	0.47	0.55
BT3-4	38.65 %	12.46	8.13	3.35	14.52	2.28	0.39	2.38	0.41	2.42	17.15	0.53	1.46	0.24	1.93	0.26	50.76	67.91	32.36			
SD	20.48 %	0.58	0.45	0.13	0.45	0.17	0.02	0.13	0.05	0.32	0.89	0.04	0.08	0.01	0.10	0.01						
CV	0.05	0.05	0.06	0.04	0.03	0.07	0.04	0.06	0.12	0.13	0.05	0.07	0.06	0.06	0.05	0.06						
SN	0.33	0.10	0.38	0.43	0.43	0.41	0.36	0.51	0.53	0.52	0.64	0.53	0.51	0.59	0.68	0.60				1.43	0.29	0.30
BT3-5	38.00 %	20.27	16.98	3.39	12.75	2.61	0.46	2.37	0.46	2.34	16.46	0.65	2.17	0.25	1.75	0.30	66.75	83.21	25.32			
SD	9.94 %	0.86	0.96	0.12	0.72	0.16	0.03	0.31	0.02	0.17	1.03	0.02	0.37	0.02	0.12	0.04						
CV	0.03	0.04	0.06	0.03	0.06	0.06	0.07	0.13	0.03	0.07	0.06	0.03	0.17	0.07	0.07	0.12						
SN	0.53	0.21	0.38	0.38	0.38	0.47	0.43	0.51	0.59	0.50	0.61	0.66	0.76	0.62	0.62	0.69				1.30	0.47	0.54
BT4-1	38.56 %	33.42	40.01	6.96	30.12	7.01	1.06	5.14	0.94	5.17	30.95	1.12	3.01	0.45	2.38	0.49	137.28	168.23	27.63			
SD	20.75 %	2.65	2.92	0.33	1.98	1.03	0.05	0.74	0.06	0.36	2.33	0.04	0.16	0.02	0.14	0.06						
CV	0.05	0.08	0.07	0.05	0.07	0.15	0.04	0.14	0.06	0.07	0.08	0.03	0.05	0.05	0.06	0.13						
SN	0.87	0.50	0.79	0.89	0.89	1.26	0.98	1.10	1.21	1.10	1.15	1.13	1.06	1.11	0.84	1.13				1.13	0.60	0.72
BT4-2	38.40 %	29.06	36.48	6.68	29.14	5.78	1.01	4.98	0.88	4.89	26.53	0.94	2.47	0.39	2.16	0.35	125.21	151.74	28.22			
SD	19.65 %	2.14	4.94	0.28	1.28	0.29	0.05	0.25	0.13	0.35	1.67	0.04	0.12	0.02	0.07	0.03						
CV	0.05	0.07	0.14	0.04	0.04	0.05	0.05	0.05	0.15	0.07	0.06	0.04	0.05	0.06	0.03	0.08						
SN	0.76	0.46	0.76	0.76	0.86	1.04	0.94	1.07	1.14	1.04	0.98	0.95	0.87	0.96	0.77	0.81				1.15	0.60	0.69
BT4-3	37.90 %	26.42	35.19	5.97	28.13	4.04	0.78	4.76	0.85	4.77	31.13	0.85	2.16	0.33	2.01	0.28	116.54	147.67	36.62			
SD	24.15 %	1.54	1.30	0.43	1.24	0.28	0.05	0.71	0.04	0.38	1.62	0.13	0.12	0.02	0.08	0.04						
CV	0.06	0.06	0.04	0.07	0.04	0.07	0.07	0.15	0.05	0.08	0.05	0.16	0.06	0.05	0.04	0.13						
SN	0.69	0.44	0.68	0.68	0.83	0.73	0.72	1.02	1.10	1.02	1.15	0.86	0.76	0.81	0.71	0.65				1.06	0.65	0.80
BT4-4	38.61 %	30.79	32.16	6.07	28.54	4.72	0.85	4.87	0.91	4.90	32.04	0.76	1.99	0.39	1.77	0.23	118.95	150.99	42.16			
SD	17.27 %	2.32	1.81	0.43	0.87	0.21	0.04	0.17	0.14	0.70	2.05	0.03	0.11	0.02	0.12	0.01						
CV	0.04	0.08	0.06	0.07	0.03	0.04	0.05	0.04	0.16	0.14	0.06	0.04	0.05	0.06	0.07	0.04						
SN	0.81	0.40	0.69	0.84	0.85	1.05	0.79	1.05	1.18	1.05	1.19	0.77	0.70	0.96	0.63	0.53				1.10	0.54	0.72
BT4-5	38.75 %	25.14	16.36	4.32	16.01	2.96	0.54	2.32	0.39	2.23	24.54	0.49	2.01	0.19	1.94	0.18	75.08	99.62	50.08			
SD	16.42 %	0.81	1.08	0.27	0.64	0.12	0.04	0.36	0.03	0.15	1.34	0.02	0.27	0.01	0.13	0.02						
CV	0.04	0.03	0.07	0.06	0.04	0.04	0.07	0.16	0.08	0.07	0.05	0.05	0.13	0.05	0.07	0.14						
SN	0.66	0.21	0.49	0.49	0.47	0.53	0.50	0.50	0.50	0.48	0.91	0.49	0.71	0.47	0.69	0.42				1.44	0.36	0.41

and spot (Table 3; Supplementary Table S2). Most intra-spot CV values were below 14 %, with isolated higher values reaching approximately 15–17 %, mainly among middle and heavy REE (Supplementary Table S2). These isolated cases do not define a systematic instability pattern and are therefore interpreted as minor short-scale signal variability during individual ablations. Overall, the intra-spot CV results support short-term signal stability and the robustness of the LA-ICP-MS analytical protocol.

The relative magnitude of intra-tooth variability among the five independent enamel spots was assessed using coefficients of variation calculated across the five spot-mean concentrations for each element. Most CV values were below 10 %, with only a limited number of isolated cases reaching approximately 14 %, indicating low to moderate intra-tooth dispersion among replicate enamel spots. The observed dispersion reflects measurable small-scale geochemical variability within the sampled enamel plane, rather than instability of the analytical protocol. Accordingly, the five measurements acquired per tooth were retained as individual analytical series, allowing direct evaluation of intra-tooth geochemical coherence and variability without treating the replicate analyses as fully interchangeable values.

Discussion

Preservation and diagenetic alteration of dental enamel

Prior to undertaking any palaeoenvironmental interpretation based on dental enamel geochemistry, it is essential to rigorously evaluate the potential extent of diagenetic alteration affecting the fossil material (Kohn et al. 1999; Flügel 2010). Dental enamel is widely regarded as one of the most diagenetically resistant tissues in the vertebrate skeleton, although post-depositional processes may modify its chemical composition under specific burial conditions (Lüdecke et al. 2022). In the present study, the primary emphasis is placed on the integrated assessment of microstructural and geochemical preservation of enamel as a foundation for interpreting the recorded elemental signals, rather than on the development of a full regional palaeoenvironmental reconstruction.

Microstructure

Following preparation of the analysed *Bison* enamel sections, no obvious alteration of the hydroxylapatite crystal microstructure was detected either in thin section or by direct SEM observation, indicating a high degree of microstructural preservation (Fig. 4a–c). Visualisation of individual crystallites required brief chemical etching with 10 % v/v HCl, after which a dense and coherent crystal microstructure was observed, exposing transverse, oblique and longitudinal planes (Fig. 4b–c). This crystallographic arrangement is comparable to that reported for well-preserved enamel by multiple authors (Dauphin & Williams 2007; Eberle et al. 2020; Pessoa-Lima et

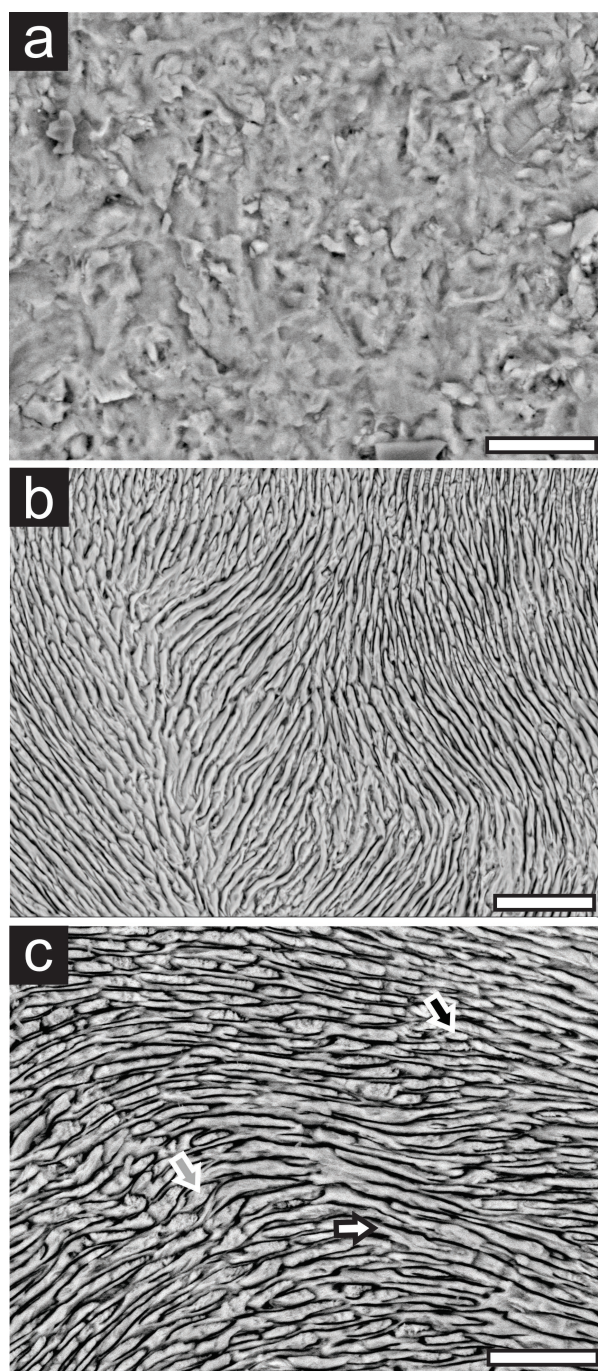


Fig. 4. SEM micrographs of dental enamel from *Bison* sp. samples. (a) Sample BT1 prior to chemical etching. Scale bar=20 µm. (b) Sample BT2 after etching, showing apatite crystallites. Scale bar=500 µm. (c) Sample BT4, illustrating crystallites exposed in different orientations, including longitudinal (white arrow), transverse (black arrow) and oblique planes (grey arrow). Scale bar=20 µm. See text for further details.

al. 2022) and is associated with enhanced mechanical resistance of enamel to fracture (Shen et al. 2024).

The integrity of the observed microstructure supports the suitability of the samples for high-resolution geochemical

analyses and constitutes a key line of evidence for primary enamel preservation, which is central to the interpretation of the elemental signals discussed in this study.

Major elements and substitutions in hydroxylapatite (Ca, P, F)

Elemental proportions of Ca, P and F obtained by SEM-EDS indicate substantial retention of original hydroxylapatite mineralogy in *Bison* dental enamel. In all analysed samples, Ca/P ratios remain very close to the theoretical stoichiometric value for hydroxylapatite (~1.67), with only a single sample exhibiting a slightly higher value (~1.71; Table 2). This limited variation falls within the expected range for well-preserved biogenic enamel (Hatim et al. 2009). The partial $\text{CaO}+\text{P}_2\text{O}_5+\text{F}$ totals reported in Table 2 depart from 100 wt.%. Nevertheless, the Ca/P ratios remain close to the theoretical stoichiometric value for hydroxylapatite, indicating preservation of the relative Ca–P proportions within the apatite phase. Minor constituents, structural substitutions and hydroxyl groups may contribute to the remaining compositional difference. Biological dental enamel consists of a substituted, carbonated apatite rather than pure stoichiometric hydroxylapatite. Carbonate contents of approximately 3.5–5 wt.% have been reported for dental enamel (Finke et al. 2001; Kono et al. 2022), and carbonate substitution may therefore account for part of the departure from an idealised $\text{CaO}-\text{P}_2\text{O}_5$ composition. Carbon was detected during the SEM-EDS analyses but was not included quantitatively in Table 2 or converted to CO_2 , as the EDS data alone do not allow the carbon signal to be unequivocally assigned to structural carbonate. Accordingly, the difference between the partial compositional sum and 100 wt.% is not interpreted quantitatively as carbonate content.

In addition, SEM-EDS Ca/P ratios (Table 2) and the LA-ICP-MS internal normalisation based on ^{44}Ca (Table 3) are mutually consistent with the interpretation of a well-preserved apatite phase. Direct numerical comparison between SEM-EDS and LA-ICP-MS is not intended, owing to differences in reporting units, analytical volume and quantification procedures. Instead, the internal coherence of the major-element stoichiometry and the trace-element analytical protocol supports the reliability of the elemental dataset and suggests limited diagenetic modification of the enamel mineral phase.

Consistently, F/P ratios are below 0.1 in all samples, indicating limited substitution of hydroxyl groups by fluorine within the crystal lattice (Table 2). This pattern suggests minimal diagenetic fluorapatite formation and is consistent with previous observations in well-preserved fossil enamel (Yoshimura et al. 2021), as well as with studies indicating that fluorine content in fossil mammals does not necessarily correlate with fossilisation time (Białas et al. 2021). Taken together, the near-stoichiometric Ca/P ratios, low F/P ratios and preserved enamel microstructure indicate limited diagenetic modification of the original apatite composition.

Rare earth elements and yttrium (REE+Y) as geochemical indicators of preservation and burial conditions

Rare earth element concentrations in *Bison* dental enamel are low to moderate, with ΣREE values ranging from 50 to 137 ppm when yttrium is excluded. When Y is included, total $\Sigma\text{REE}+\text{Y}$ concentrations reach a maximum of 168 ppm (Table 3). These values remain well below those reported for enamel affected by pronounced diagenetic alteration, where concentrations may greatly exceed several hundred ppm (Martin et al. 2005). This range therefore provides an additional indication of limited post-mortem incorporation of REE+Y into the hydroxylapatite lattice (Ivanova et al. 2022). Y/Ho ratios were also evaluated as a complementary indicator of REE+Y fractionation. Values close to ~26–28 are generally regarded as chondritic (Pack et al. 2007), whereas higher ratios indicate increasing superchondritic fractionation. Most values in the present dataset fall within a chondritic to slightly superchondritic interval, mainly between 23.13 and 32.36. Only three subsamples, all from BT4, show more pronounced fractionation: BT4-3=36.62, BT4-4=42.16 and BT4-5=50.08. This pattern indicates that stronger Y–Ho fractionation is not pervasive across the dataset, and is instead restricted to a localised signal within one specimen. Accordingly, Y/Ho ratios are treated here as complementary evidence for limited intra-sample geochemical heterogeneity; their broader significance in relation to the local sedimentary context is considered below.

After normalisation of individual concentrations to the PAAS standard (McLennan 1989), the resulting patterns display a relatively flat distribution with little dispersion among samples (Fig. 5a–d). Such behaviour is characteristic of fossil enamel that has experienced minimal diagenetic overprinting (Trueman & Tuross 2002; Ivanova et al. 2022) and supports the interpretation of a relatively well-preserved enamel geochemical composition. These data are therefore appropriate for evaluating both the degree of preservation and, in a secondary sense, certain aspects of the early burial geochemical environment.

The five subsamples within each tooth show measurable spot-scale variability in absolute concentrations. This variability is interpreted as small-scale intra-enamel geochemical heterogeneity rather than analytical instability. The multi-spot LA-ICP-MS approach therefore provides a direct assessment of intra-tooth variability, instead of treating the five measurements as fully interchangeable replicates. This interpretation is consistent with the purpose of high-resolution trace-element analysis, which is to document both coherent geochemical patterns and localised heterogeneity within the sampled enamel plane.

Within these PAAS-normalised patterns, a consistent negative Ce anomaly accompanied by a positive La anomaly is recognised (Figs. 6a–d; 7a–d). Although these anomalies are not large in magnitude, their systematic and reproducible expression across samples suggests that they do not reflect analytical noise or instrumental artefacts. The negative Ce

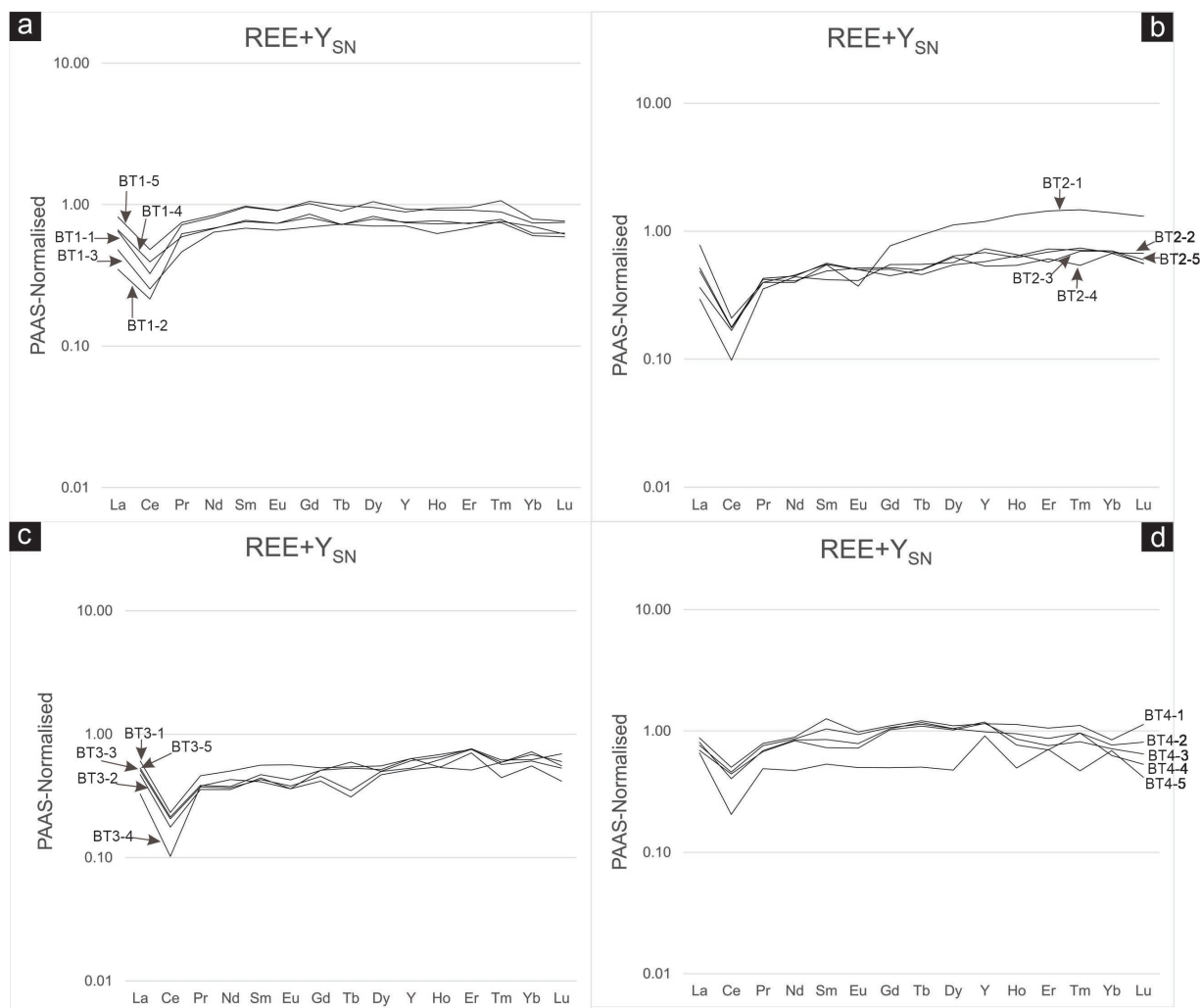


Fig. 5. PAAS-normalised REE+Y patterns for samples BT1 to BT4 (a–d). A consistent positive La anomaly and negative Ce anomaly are observed in all subsamples within each individual specimen. See text for further details.

anomaly is compatible with REE incorporation under oxidising conditions, likely recorded in interstitial pore fluids during early stages of burial. As such, this signal provides information on the geochemical context of fossilisation rather than on broader regional palaeoenvironmental conditions (Trueman & Tuross 2002; Domingo et al. 2012; Ivanova et al. 2017, 2022).

Ce and La anomalies were evaluated using the formulations of Bau & Dulski (1996) and Lawrence et al. (2006), without applying discrimination fields developed for non-biogenic sedimentary systems. In both calculation schemes, all subsamples from BT1 to BT4 display the coupled occurrence of a positive La anomaly and a negative Ce anomaly (Figs. 6a–d; 7a–d). This consistency indicates that the observed anomaly pattern is not an artefact of a single calculation method.

The interpretation of these anomalies is framed within the context of REE uptake and diagenetic behaviour in vertebrate fossil apatite. Previous studies have shown that REE incorporation into fossil bone and enamel commonly occurs during early diagenesis through interaction with pore waters, and that REE patterns in vertebrate bioapatite may record local burial

conditions rather than primary biological compositions (Trueman & Tuross 2002; Ivanova et al. 2017, 2022). Within this framework, the systematic association of negative Ce anomalies and positive La anomalies in the analysed *Bison* enamel is interpreted as a reproducible early diagenetic signal, compatible with oxidising conditions during fluid–enamel interaction.

BT1-3 (arrow, Figs. 6a and 7a) shows the same overall anomaly pattern observed in the remaining subsamples, including a negative Ce anomaly, although Ce depletion is less pronounced than in the remaining BT1 subsamples. Consequently, BT1-3 plots closer to the Ce/Ce=1 reference boundary. Its marginal position is interpreted as minor intra-sample variability in the magnitude of the Ce anomaly, rather than as evidence for a separate geochemical regime affecting that portion of enamel.

The positive La anomaly is interpreted as evidence of interaction between enamel and LREE-enriched fluids or sediments during early burial. Given the regional geological framework of Villagrán, Tamaulipas, a possible contribution

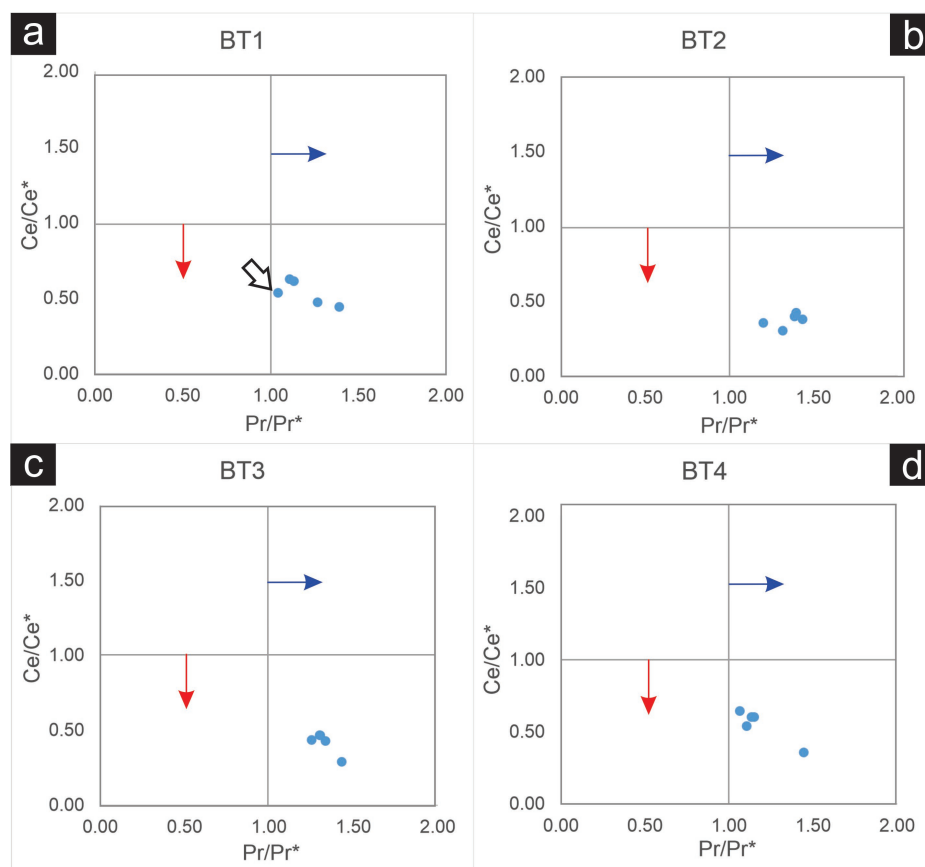


Fig. 6. Anomaly-discrimination plots of La/La^* versus Ce/Ce^* for samples BT1 to BT4 (a–d), calculated using the formulation of Bau & Dulski (1996). Reference lines at $\text{La}/\text{La}^* = 1$ and $\text{Ce}/\text{Ce}^* = 1$ are shown to distinguish positive and negative deviations from unity. The red arrow indicates the field corresponding to positive La anomalies, whereas the blue arrow indicates the field corresponding to negative Ce anomalies. Nearly all data points show coupled positive La anomalies and negative Ce anomalies. Subsample BT1-3 (Fig. 6a, white arrow) exhibits a weaker negative Ce anomaly relative to the remaining BT1 subsamples and consequently plots close to the $\text{Pr}/\text{Pr}^* = 1$ reference boundary. Its position is interpreted as showing minor intra-sample variability in the magnitude of Ce depletion. See text for further information.

from the surrounding and underlying Cretaceous carbonate and calcareous–argillaceous succession should be considered. These units include marine-derived formations exposed or subcropping in the area, and may have influenced the geochemical composition of sediments and pore waters during early fossilisation (Eguiluz de Antuñano et al. 2000; SGM 2021). This interpretation is treated cautiously. Y/Ho ratios do not provide strong independent evidence for a pervasive marine-influenced signal, as most values remain chondritic to slightly superchondritic whereas the highest values are restricted to only three subsamples from BT4. These ratios are therefore considered complementary, not diagnostic, evidence.

Alternative mechanisms may also have contributed to the observed La enrichment. REE fractionation in natural waters and sediments can be strongly influenced by pH, colloids, salinity and surface–solution reactions, including preferential removal, release or redistribution of LREE during water–particle interaction (Sholkovitz 1995). In addition, vadose-zone processes may promote local fluctuations in pH, redox conditions, water residence time and mineral–fluid interaction,

thereby favouring selective mobilisation, sorption or desorption of LREE during early post-burial alteration (Huang et al. 2021). Sorption and scavenging onto mineral surfaces may further modify REE patterns, particularly through interactions with Fe–Mn oxyhydroxides and other reactive substrates (Byrne & Kim 1990; Ohta & Kawabe 2000, 2001). In fossil bioapatite, REE compositions commonly reflect interaction with local pore waters, sedimentary particles and mineral surfaces during diagenesis, rather than primary biological uptake alone (Trueman & Tuross 2002; Trueman et al. 2006, 2011; Ivanova et al. 2017, 2022). Recent work on bioapatite also shows that REE+Y uptake may begin rapidly after deposition and that local depositional facies can exert a primary control on Ce/Ce^* , Y/Ho and other REE+Y ratios, allowing bioapatite to record early diagenetic pore-water conditions rather than pristine environmental signatures (Lumiste et al. 2023). Comparable behaviour has been reported in continental fossil systems, where La and REE patterns have been related to local sedimentary and early diagenetic controls rather than direct palaeoenvironmental signals (Schroeter et al. 2022).

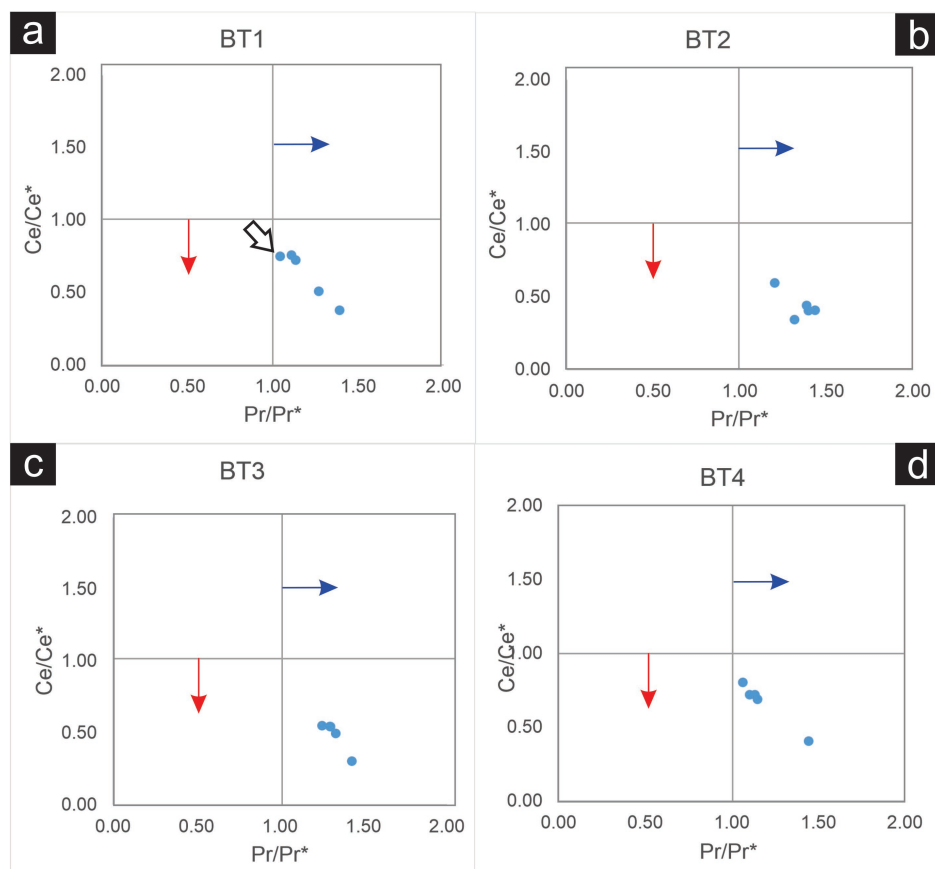


Fig. 7. Anomaly-discrimination plots of La/La^* versus Ce/Ce^* for samples BT1 to BT4 (a–d), calculated according to Lawrence et al. (2006). Reference lines at $\text{La}/\text{La}^*=1$ and $\text{Ce}/\text{Ce}^*=1$ are shown to distinguish positive and negative deviations from unity. The red arrow indicates the field corresponding to positive La anomalies, whereas the blue arrow indicates the field corresponding to negative Ce anomalies. As in Fig. 6, most data points show coupled positive La anomalies and negative Ce anomalies. Subsample BT1-3 (white arrow) exhibits a weaker negative Ce anomaly relative to the remaining BT1 subsamples. See text for further details.

Accordingly, the positive La anomaly is best interpreted as a local early diagenetic signal influenced by sediment–fluid interaction, pH-dependent LREE mobility and sorption/desorption processes, with possible contribution from the Cretaceous carbonate and calcareous–argillaceous substrate. It is therefore not treated as evidence for a uniquely marine-derived fluid source.

The La/La^* , Ce/Ce^* and Pr/Pr^* relationships therefore support a reproducible REE+Y signal in the analysed enamel, characterised by negative Ce and positive La anomalies. This signal is best understood as recording early post-burial geochemical conditions, rather than a direct or complete regional palaeoenvironmental signal.

The palaeoenvironmental implications of these results should be interpreted within the depositional and early fossilisation context of the fossil-bearing deposits. The REE+Y patterns, Ce and La anomalies, and Y/Ho behaviour primarily record early burial conditions, including pore-water composition, sediment–fluid interaction and local redox processes during fossilisation. They do not, by themselves, provide a complete regional palaeoenvironmental reconstruction. Their main relevance lies in documenting whether the enamel preserves

a coherent geochemical signal that can be distinguished from later diagenetic overprinting. In this sense, the present study provides a preservation and early diagenetic baseline for future palaeoenvironmental work. Stable isotope analyses, including $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, were not included in the present study, as the scope was restricted to evaluating enamel preservation and early burial diagenesis through microstructural, major-element and REE+Y evidence. This approach was intended to establish whether the analysed enamel retains a reliable geochemical signal before applying palaeoecological proxies that require additional sampling and interpretative assumptions. The preservation criteria documented here therefore provide a basis for selecting suitable specimens for subsequent $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ analyses aimed at palaeoecological and palaeoclimatic interpretation.

Conclusions

The integrated evaluation of enamel microstructure, major-element composition and REE+Y systematics indicates a high degree of preservation in the four analysed *Bison* dental

specimens, supporting their suitability for high-resolution geochemical assessment of early burial conditions.

Optical microscopy and SEM observations reveal a well-preserved hydroxylapatite crystal organisation, with no evidence for significant recrystallisation. Together with Ca/P ratios close to the stoichiometric value of hydroxylapatite (~1.67) and consistently low F/P ratios (< 0.1), these data indicate limited mineralogical alteration and restricted fluorapatite formation in the analysed enamel.

The relatively low REE+ Y concentrations and predominantly flat PAAS-normalised patterns suggest limited post-mortem incorporation of trace elements. The observed geochemical coherence is therefore interpreted at the level of the analysed specimens and replicate enamel measurements, not as evidence for genus-level, species-level or population-level homogeneity within *Bison*.

The negative Ce anomalies provide evidence for oxidising conditions during early burial, whereas the positive La anomalies are interpreted as local early diagenetic signals related to interaction with LREE-enriched pore fluids or sediments. This La enrichment is not treated as evidence for a uniquely marine-derived fluid source; instead, it may reflect sediment–fluid interaction, pH-dependent LREE mobility, sorption/desorption processes, vadose-zone effects and possible influence from the carbonate–calcareous–argillaceous substrate in the study area.

The fragmentary nature of the material, the absence of species-level identification and the lack of secure anatomical positioning constrain the taxonomic and population-level scope of the interpretations. Consequently, the results establish a specimen-level framework for assessing preservation and early burial geochemical conditions in *Bison* enamel from this locality.

The preservation documented in the analysed enamel specimens provides a necessary baseline for future palaeoenvironmental studies. The present results primarily inform depositional and early fossilisation conditions, rather than constituting a complete regional palaeoenvironmental reconstruction. Subsequent stable isotope analyses, including $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, may build on this preservation framework to obtain higher-resolution palaeoecological and palaeoclimatic information from the Pleistocene record of north-eastern Mexico.

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Electronic supplementary material is available online:

Supplementary Table S1 at https://geologicacarthica.com/data/files/supplements/GC-77-6-Reyes-Munoz_TableS1.xlsx
 Supplementary Table S2 at https://geologicacarthica.com/data/files/supplements/GC-77-6-Reyes-Munoz_TableS2.xlsx