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Analysis on Disease Types and Deterioration Mechanisms of Pig Mandibles from Huangshan Site in Nanyang

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Abstract: Natural pig mandibles excavated from the Huangshan Site, Nanyang, feature rich pores and high organic content and undergo serious composite deterioration under burial and post-excavation environments. Targeting bone relic conservation, this study selects fragmented pig mandible samples to identify disease types and microscopic deterioration mechanisms. Field surveys classify diseases into five categories: mechanical degradation, hygrothermal deformation, discoloration, mildew corrosion and salt efflorescence, with obvious coupled deterioration features. Multiple testing methods including ultra-depth-of-field microscopy, SEM, XRF, ion chromatography, XRD, FTIR, nitrogen adsorption and mercury intrusion porosimetry are adopted to characterize micromorphology, elements, anions, mineral phases, pore structure and water content. The results show the samples are dominated by carbonated hydroxyapatite with interconnected pores and an average water content of 39.86%; Cl^- and SO_4^{2-} are major corrosive anions. Bone deterioration follows a two-stage mechanism: preferential collagen degradation accompanied by synchronous dissolution of inorganic minerals. Weakly acidic groundwater and soil components induce latent underground damage, whereas drastic post-excavation humidity-temperature fluctuations and cyclic salt crystallization accelerate visible deterioration. This research reveals the complete deterioration evolution of prehistoric bone relics and offers theoretical and technical support for emergency field treatment and long-term museum preservation of analogous animal bone artifacts.

Keywords: Huangshan Site; pig mandible; bone relics; deterioration mechanism.

1. Introduction

Bone and horn artifacts are core physical materials for zooarchaeology and research on prehistoric subsistence patterns. Unprocessed natural animal bones retain intact primary biological structures with developed pores and high organic matter content, making them more susceptible to erosion from burial and museum environments, faster to weather and damage, and harder to conserve than polished bone tools. As an important prehistoric settlement site in the Central Plains, the Huangshan Site in Nanyang has yielded abundant pig mandible remains, which constitute key materials for exploring Neolithic livestock domestication, ancient human meat consumption patterns, and site resource utilization. Buried long-term in weakly acidic local soil, these pig mandibles suffered groundwater corrosion, salt accumulation and microbial erosion; after excavation, drastic fluctuations in temperature and humidity caused widespread composite damages including pulverization, cracking, deformation, salt efflorescence, mildew and discoloration. The mechanical properties of numerous specimens have severely declined, and their original surface textures and archaeological information face irreversible loss. It is therefore urgent to clarify the development rules and internal deterioration mechanisms of such damages to provide theoretical support for on-site emergency conservation and long-term museum preservation.

Current domestic research on bone cultural relics mostly focuses on processed bone artifacts such as bone hairpins and bone shovels, while systematic analyses of diseases and microscopic deterioration of raw bone remains like pig mandibles remain insufficient, and the chain weathering mechanism driven by the combined effects of burial and post-excavation environments is unclear. Taking fragmented pig mandible specimens unearthed from multiple tombs at the Huangshan Site as research objects, this paper adopts multiple characterization techniques including ultra-depth-of-field microscopy, scanning electron microscopy, X-ray fluorescence, ion chromatography, XRD, FTIR, pore structure measurement and water content testing. It systematically sorts out typical damage types and their coupling characteristics of specimens, reveals the synergistic deterioration law of organic-inorganic two-phase bone from the perspectives of micromorphology, chemical composition and pore structure, distinguishes the differentiated mechanisms of chronic burial damage and post-excavation concentrated deterioration, and establishes a progressive weathering pathway for prehistoric raw bone relics. The findings fill the research gap regarding the deterioration of unprocessed bone remains, and offer scientific references for desalination, consolidation, as well as constant temperature and humidity preservation of animal bone relics excavated in Nanyang and other regions with similar acidic burial conditions.

2. Disease Types and Characteristics of Pig Mandibles from Huangshan Site

2.1. Compositional and Structural Features of Bone Cultural Relics

Bone cultural relics are composites of inorganic hydroxyapatite and organic collagen [1]. Unearthed pig mandibles from the Huangshan Site are natural bone remains, distinct from manually processed bone artifacts such as bone

combs and bone vessels. They feature clear stratification of compact and cancellous bone, developed pores, high organic content and uneven loose texture. The deterioration of these specimens arises from the combined influence of inherent bone component degradation, unique primitive structures, underground burial conditions in Nanyang, and sharp environmental shifts after excavation. Their intact biological structure creates numerous connected pores, making them more susceptible to internal and external erosion, with faster deterioration and more complex damage than processed bone tools.

2.2. Classification of Typical Bone Diseases

Field surveys divide the damage of pig mandibles into five categories: mechanical degradation, hygrothermal deformation, discoloration, mildew corrosion and surface salt contamination. The features and formation mechanisms of each disease are elaborated as follows.

2.2.1. Mechanical Property Degradation

Mechanical attenuation is the fundamental primary damage that causes bone pulverization and collapse, most severe in porous cancellous bone. Collagen fills gaps between hydroxyapatite crystals to maintain bone toughness and integrity. During long-term burial, collagen gradually hydrolyzes and leaches out, while acidic groundwater destroys hydroxyapatite crystals and depletes calcium, breaking the composite two-phase structure. Macroscopically, bones turn brittle with granular fractures and shed powder upon contact, accompanied by pulverization, cracking and delamination. The natural layered structure of pig mandibles leads to uneven deterioration rates between compact and cancellous bone, triggering layer separation. After collagen loss, inherent biological stress lines evolve into crisscross fissures, even penetrating fractures that break mandibles and eliminate mechanical stability.

2.2.2. Hygrothermal Deformation

Hygrothermal deformation is a unique physical damage induced by drastic temperature and humidity fluctuations and alternating dry-wet cycles during burial and after excavation. Pig mandibles have uneven thickness and permeable pores, leading to inconsistent water absorption and loss rates. Underground, porous cancellous bone retains massive water, loosening bone fibers under soil compression and groundwater soaking. Post-excavation cyclic temperature and humidity change repeatedly evaporate pore water. Different bone zones feature disparate expansion and contraction coefficients, resulting in bending, warping and distortion. Cyclic stress continuously widens microcracks, forming a vicious cycle of deformation-cracking-pulverization, which accounts for distorted shapes and dense fissures on specimens.

2.2.3. Discoloration Damage

Discoloration is the most intuitive surface damage caused by chemical erosion and bone component degradation. With richer organic matter and pores, pig mandibles suffer more severe and complex color changes than processed bones, including overall dullness, faded luster, local yellow-brown stains and demineralized whitening. Underground acidic groundwater and soil oxidation damage bone surfaces and oxidize organic substances to lose gloss; infiltrated iron and manganese ions form irregular yellow-brown patches, while demineralization decomposes hydroxyapatite and forms loose off-white surface layers. After excavation, light, oxidation and temperature-humidity shifts accelerate aging and discoloration. Uneven natural pores create fragmented stains, irreversibly destroying biological textures and archaeological information.

2.2.4. Mildew Corrosion

Mildew corrosion is a critical biologically induced damage that accelerates organic loss and structural collapse. Abundant organics and interconnected pores of pig mandibles supply nutrients and habitats for bacteria and mold in soil, which invade bones via pores and fissures to form mildew spots and biofilms. Improper temperature and humidity control after excavation triggers massive microbial reproduction. Microbes secrete hydrolases and organic acids for dual corrosion: hydrolases break collagen chains and destroy bonding systems, while acids dissolve hydroxyapatite and leach calcium. Combined with physical and chemical damage, mildew embrittles and hollows bones and drastically shortens relic preservation life.

2.2.5. Surface Salt Contamination

Salt efflorescence is the most prevalent composite damage dominated by cyclic soluble salt erosion. Underground groundwater carries sodium chloride, sodium sulfate and other salts into bone pores for enrichment. After excavation, periodic temperature and humidity drive repeated salt dissolution and recrystallization, forming white powdery salt efflorescence covering original bone textures. The volume expansion during salt crystallization generates mechanical stress to split pores and widen fissures, aggravating pulverization and peeling. Attached soil impurities and corrosive substances cause secondary contamination, damaging both the appearance and internal structure of bones.

3. Analysis of Microscopic Deterioration Characteristics Based on Multiple Characterization Techniques

3.1. Sample Overview

The pig mandible samples used in the experiment were collected from the Huangshan Site in Nanyang. Most specimens are small fragments with severe pulverization and cracking on the surface. The samples were picked with tweezers from tombs M216, M77, M172, M206, M212 of the site. Each fragment is about 2 cm long and 5 g in weight with high water content, and its color mainly ranges from tawny and brown to olive Table 1.

3.2. Analytical and Testing Methods

(1) Multi-scene ultra-depth-of-field video microscope: Non-destructive microscopic observation of pig mandibles from Huangshan Site, focusing on bone surface morphology, microscopic deterioration features, burial diseases and various traces.

(2) Scanning Electron Microscopy (SEM): Specimens were gold-sputtered by a vacuum coating instrument in advance, then the surface and cross-sectional micromorphology of samples were observed via SEM.

(3) Energy Dispersive Spectroscopy (EDS) and X-ray Fluorescence (XRF) analysis: EDS and XRF spectrometers were adopted to analyze micro-area elemental composition and elemental mapping distribution of samples.

(4) Ion Chromatography (IC): An ion chromatograph was used to detect inorganic anions in bone specimens from Huangshan Site.

Table 1. Sample Information Table

No.	Name	Source No.	Quantity	Remarks
hs1	Pig mandible	20 Huangshan III T0202 M77	1	Fragmentary
hs2	Pig mandible	21 Huangshan IV T0103 M172	1	Fragmentary
hs3	Pig mandible	22 Huangshan IV T0201 M206	1	Fragmentary
hs4	Pig mandible	22 Huangshan III T0101 M212	1	Fragmentary
hs5	Pig mandible	22 Huangshan III T0101 M216	1	Fragmentary

(5) Fourier Transform Micro-infrared Spectroscopy (FTIR) and X-ray Diffraction (XRD): FTIR microscope and X-ray diffractometer were applied to identify the mineral phase composition of specimens.

(6) Porosity analysis: Nitrogen adsorption and high-pressure mercury intrusion porosimetry were carried out to test the porosity and pore size distribution of samples.

(7) Water absorption test: Three pig mandible fragments were vacuum-dried at 80 °C for 9 h to constant weight in a vacuum drying oven, and the initial mass m0 was recorded by an electronic balance. Each group was tested three times to take the average value. Another group of samples was immersed in deionized water for 9 h to reach saturated water absorption, then weighed to calculate the water absorption rate. The calculation formula is as follows:

$$\text{Water absorption rate}=\frac{m1-mo}{mo}\times 100\%$$

m0: mass of dry specimen :m1: mass of water-saturated specimen

3.3. Experimental Instruments and Test Conditions

A series of characterization devices were adopted in this experiment. Bruker TENSOR 27 FTIR, Bruker D8 ADVANCE XRD and Thermo ESCALAB 250Xi XPS were used for functional group & mineral phase identification, crystal structure analysis and surface elemental characterization respectively. ESEM, FE-SEM and Keyence ultra-depth-of-field microscope were combined to observe micromorphology. Bruker M4 Tornado μ-XRF performed non-destructive micro-area elemental analysis, while ion chromatography detected ionic components in sample leachate. Autosorb-6100 nitrogen adsorption analyzer and AutoPore9600 mercury porosimeter characterized pore structure, and a vacuum drying oven was used for constant-temperature dehydration of samples. All instruments were operated under standard matched test parameters for analysis.

4. Results

4.1. Macroscopic morphology

Non-destructive microscopic observation of the Huangshan pig mandible remains was performed using an ultra-depth-of-field video microscope. In Figure 1a, the light-colored layered and banded areas represent the pristine bone matrix dominated by hydroxyapatite and collagen, with relatively dense and intact microstructures. The dark patches correspond to zones of organic degradation, mineral dissolution, and burial contamination, which are the dominant deteriorated regions. Scattered white particles are exogenous quartz and feldspar minerals, indicating external soil contamination during long-term burial.

In Figure 1b, the light bone matrix generally maintains continuity but presents local structural fracture and loosening, corresponding to the early-stage pulverization of bone relics. The diffuse flocculent dark areas are formed by collagen hydrolysis and hydroxyapatite corrosion, while fine dark spots are mainly iron oxides, microbial residues, and carbonized organic matter.

In Figure 1c, abundant foreign mineral particles penetrate the bone matrix, further aggravating structural loosening. The pores generated by complete collagen degradation are filled with humus and soil minerals, forming typical flocculent deteriorated layers. Microcracks extending along the bone bands directly indicate the degradation of mechanical properties.

In Figure 1d, only fractured residual collagen fibers are retained. The white particles consist of inherent hydroxyapatite and exogenous quartz. The passivated crystal edges of hydroxyapatite reveal obvious dissolution. Cubic black iron oxides derived from groundwater infiltration may induce continuous electrochemical corrosion of bone tissue.

4.2. Microscopic Morphology

Scanning electron microscopy (SEM) was employed to characterize the microstructural deterioration of bone specimens. The results show severe pulverization damage within the samples, characterized by extensive penetrating cracks and layered delamination. The inter-particle bonding is severely weakened, forming numerous micron-scale voids and highly porous microstructures. Bone particles are randomly accumulated in clastic and flocculent morphologies, indicating complete degradation of collagen fibers and significant dissolution and collapse of hydroxyapatite crystals.

Widely distributed interconnected micropores provide preferential channels for water infiltration and pollutant accumulation. Exogenous contaminants such as soil minerals and humus adhere to the pore interiors, further reducing mechanical stability and accelerating continuous deterioration. Four typical microstructural damages are identified: loose granular aggregates with highly developed pores, stress-induced reticular cracking in massive matrices, high-porosity spongy microstructures, and interlayer separation with parallel fissures. These microfeatures collectively demonstrate severe structural failure of the ancient bone remains Figure 2.

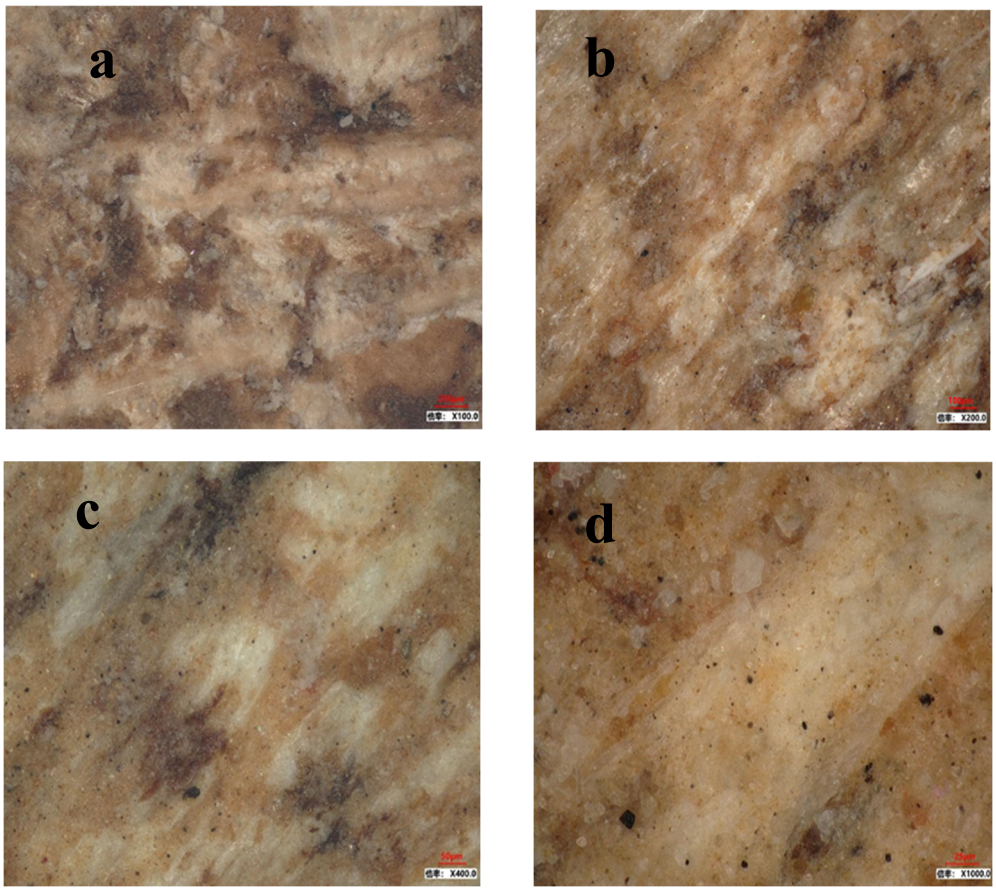


Figure 1. Ultra-depth-of-field microscopic observation

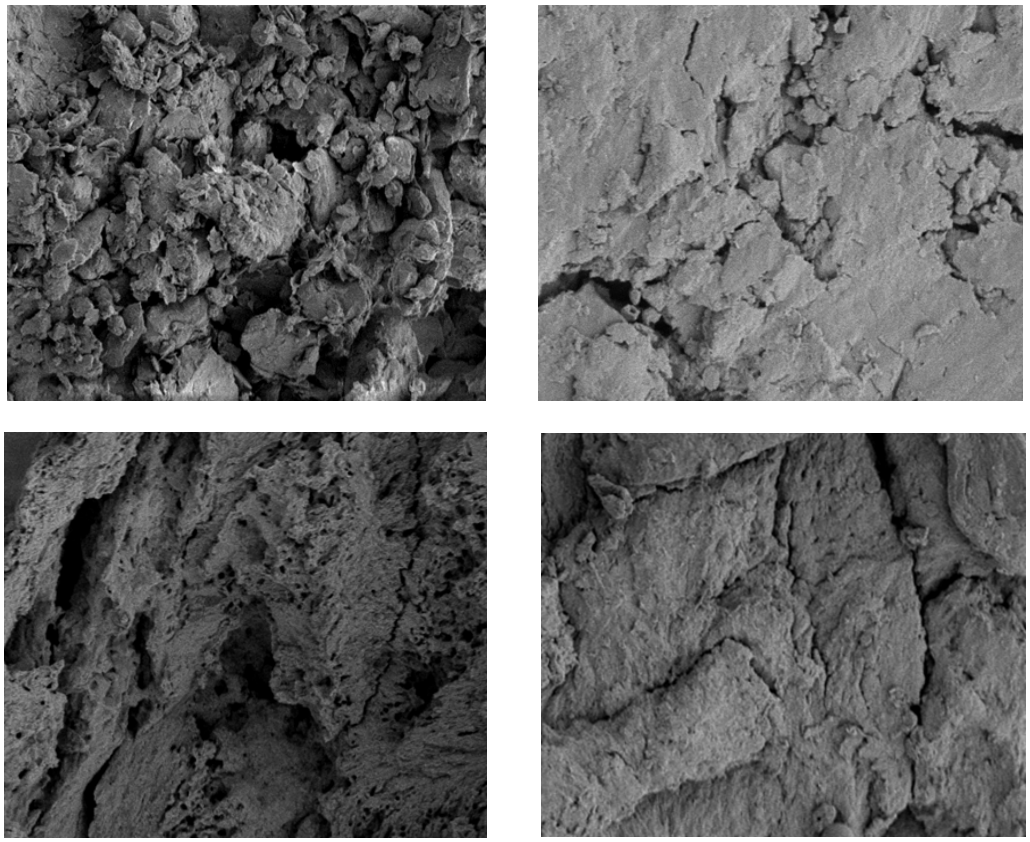


Figure 2. SEM micrographs of specimens

4.3. Elemental Composition

X-ray fluorescence spectroscopy (XRF) was used for non-destructive elemental analysis of bone specimens. The results show that the samples are predominantly composed of Ca and P, consistent with the elemental characteristics of biological hydroxyapatite and confirming the bone origin of the relics. Minor amounts of Al, Si, Fe, and Zn are detected, which are attributed to soil mineral infiltration during burial diagenesis. Figure 3

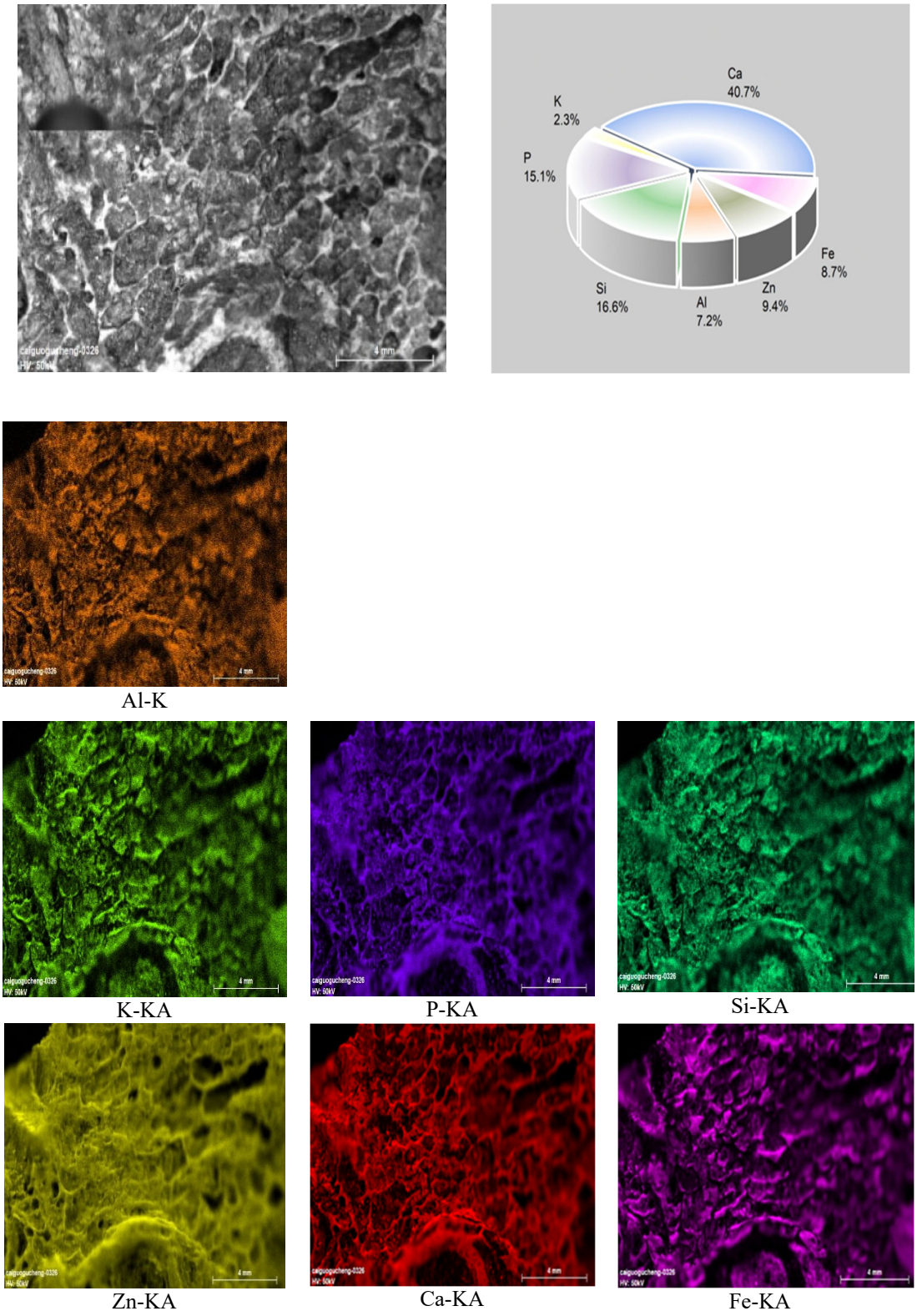


Figure 3. Element content and distribution of specimens

4.4. Anion Content

The anion composition in the weathered bone and horn artifacts from the Huangshan site was analyzed qualitatively and semi-quantitatively using ion chromatography (IC). The typical chromatograms and peak parameters are shown in

Figure 4 and Table2. The results show that three main target anions were detected in the samples, in order of relative content from high to low: sulfate ions (SO_4^{2-}), nitrate ions (NO_3^-), and chloride ions (Cl^-). No other characteristic anions were detected.

Among them, Cl^- is the most abundant anion in the samples, mainly originating from the long-term leaching and infiltration of burial soil and groundwater. The main mineral phase of bone tissue is hydroxyapatite ($Ca_{10}(PO_4)6(OH)_2$), and Cl^- can replace OH^- in the hydroxyapatite lattice through ion exchange, forming chlorapatite or soluble calcium chloride salts. This destroys the structural integrity of the mineral crystals, ultimately leading to bone matrix friability and a significant increase in porosity. At the same time, high concentrations of Cl^- accelerate the hydrolysis and oxidative degradation of bone collagen, making it one of the key factors triggering the friable disease in bone and horn artifacts from the Huangshan site.

The detection of SO_4^{2-} mainly comes from two sources: the first is the dissolution of sulfate minerals in the burial soil, which releases sulfate ions that migrate through groundwater into bone pores and accumulate by adsorption; the second is the degradation products of sulfur-containing amino acids (such as cysteine and methionine) in bone organic matter. SO_4^{2-} can react with Ca^{2+} in bone minerals to form secondary salts like calcium sulfate. When the environmental humidity fluctuates, these secondary salts undergo cycles of dissolution and recrystallization, creating crystallization stress that cracks the bone matrix and causes surface whitening, cracking, and other damages, further accelerating the weathering of bone and horn artifacts.

NO_3^- mainly comes from the biodegradation products of bone organic matter (such as proteins and nucleic acids), transformed through nitrification by microorganisms in the burial environment. It may also be influenced by the leaching of nitrogen-containing organics in the burial soil. This anion has a relatively low content in the samples, and combined with the degradation level of bone collagen, it can indirectly reflect the burial duration and the intensity of microbial activity in the burial environment, providing an important chemical indicator to distinguish the weathering stages of bone and horn artifacts.

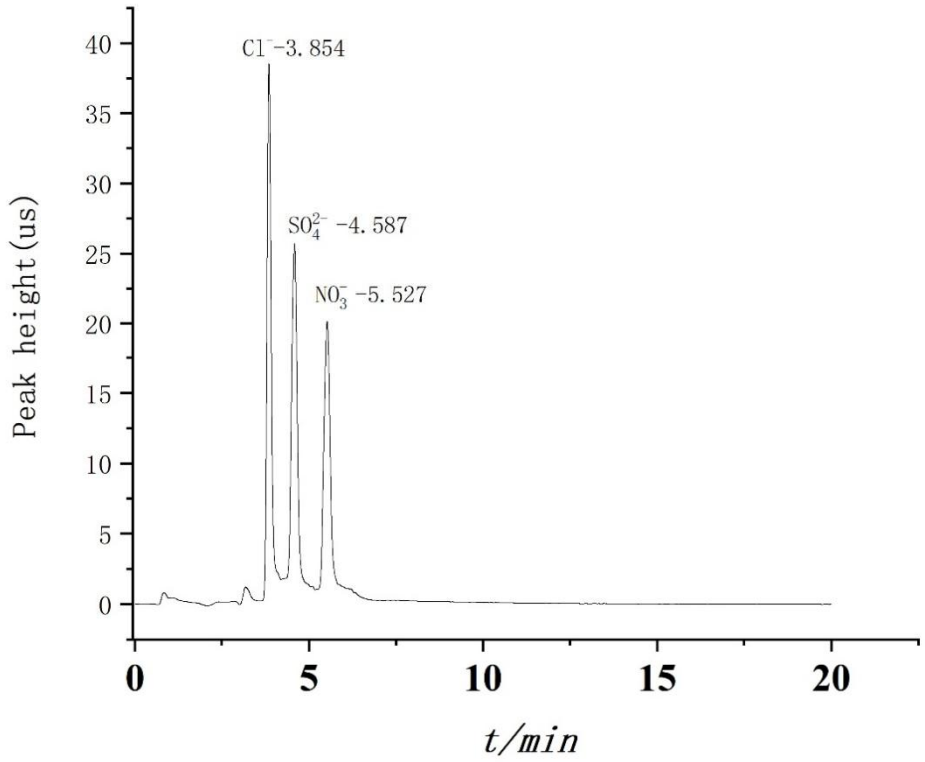


Figure 4. Ion chromatography test results

Table 2. Analysis of anion contents

No.	Time (min)	Peak Name	Peak Type	Peak Area / S·min	Peak Height / S	Concentration (mg/L)
1	3.85	Cl	M	5.533	38.161	24.2738
2	4.59	SO4	M	5.107	24.991	30.0779
3	5.53	NO3	BMB	3.829	18.941	27.2693
TOTAL				14.47	82.09	81.62

4.5. Phase Composition

X-ray diffraction (XRD) results reveal that the dominant inorganic phase in samples hs1 and hs2 is hydroxyapatite. The characteristic diffraction peaks (2θ ≈ 25.83°, 31.82°, 39.97°, 46.69°, 49.53°) show excellent agreement with standard

reference patterns, and no obvious impurity peaks are detected. This indicates that the primary mineral phase of the specimens has not undergone substantial transformation. Figure 5

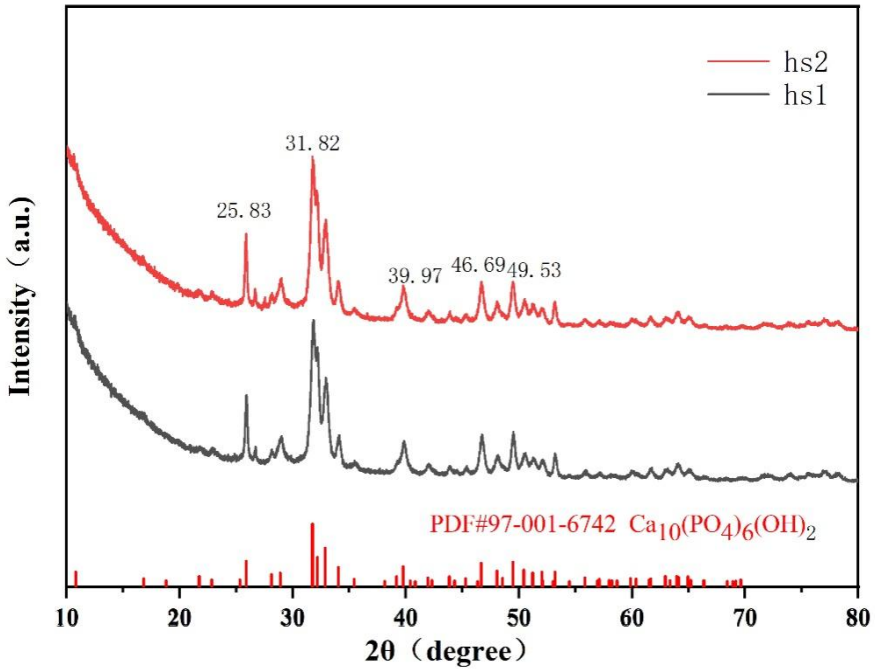


Figure 5. XRD data of specimens

4.6. Fourier-transform Infrared Spectroscopy

Fourier-transform infrared (FT-IR) spectroscopic analysis reveals distinct characteristic absorption peaks for the bone specimens, as illustrated in the corresponding figure. The strong broad band near 3564.15 cm^{-1} is assigned to the –OH stretching vibration of water molecules adsorbed within micropores and microcracks, indicating high internal moisture content that may further induce pulverization deterioration. The Amide I band is detected at 1656.63 cm^{-1}, corresponding to the stretching vibration of peptide C=O groups. The Amide II band appears at 1485.08 cm^{-1} with a slight peak shift, which is likely associated with collagen degradation and interference from mineral phases. This band originates from coupled vibrations of N-H bending and C-N stretching, demonstrating that partial collagen fractions serving as bonding matrices remain in the samples.

Meanwhile, the intense absorption band at 1171.54 cm^{-1} corresponds to the asymmetric stretching vibration of PO_4^{3-}in hydroxyapatite. The absorption peaks at 635.56 cm^{-1} and 514.91 cm^{-1} are attributed to the out-of-plane bending vibration of lattice hydroxyl groups and the bending vibration of PO_4^{3-} in hydroxyapatite, respectively. These features confirm that the inorganic hydroxyapatite phase remains relatively intact and stable within the specimens Figure 6.

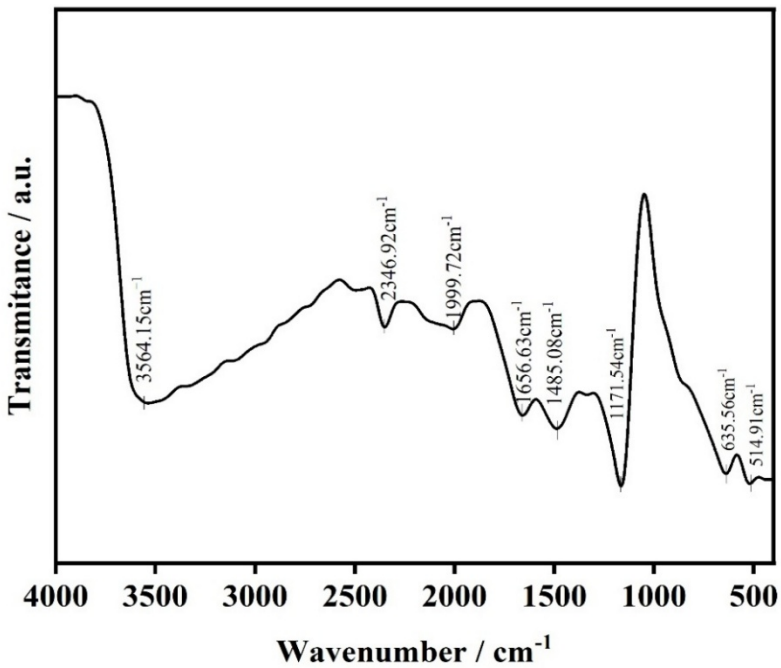


Figure 6. FTIR spectra of specimens

4.7. BET Surface Area:

Pore structural characteristics and evolutionary trends of samples HS1–HS4 can be systematically revealed by combining BET specific surface area, micropore parameters, pore size distribution curves and nitrogen adsorption–desorption isotherms. The nitrogen adsorption–desorption isotherms exhibit typical Type IV features, with obvious hysteresis loops observed at medium-high relative pressure. The hysteresis loops are close to Type H3, indicating that the samples are dominated by slit-shaped mesopores formed by particle accumulation with favourable pore connectivity.

Differential pore volume distribution curves show that the main mesopore peak of the samples lies between 10–20 nm, which is highly consistent with the average adsorption pore size ranging from 12.44 nm to 15.04 nm. Meanwhile, only weak minor peaks appear below 5 nm, suggesting an extremely low contribution of micropores. This observation agrees with the low values of micropore surface area (3.52–4.50 m^2/g) and micropore volume (0.0014–0.0019 cm^3/g) Figure 7.

From HS1 to HS4, the BET specific surface area continuously decreases from 84.69 m^2/g to 66.17 m^2/g, and the average adsorption pore size gradually reduces from 15.04 nm to 12.44 nm, showing a synchronous downward trend. In contrast, no obvious monotonic variation is found in micropore parameters. This demonstrates that the reduction in pore size is not caused by increased micropore content, but by uniform shrinkage of the overall mesopore size. Such evolution reflects gradual densification of particle accumulation and continuous reduction of pore dimensions in the samples Figure 8.

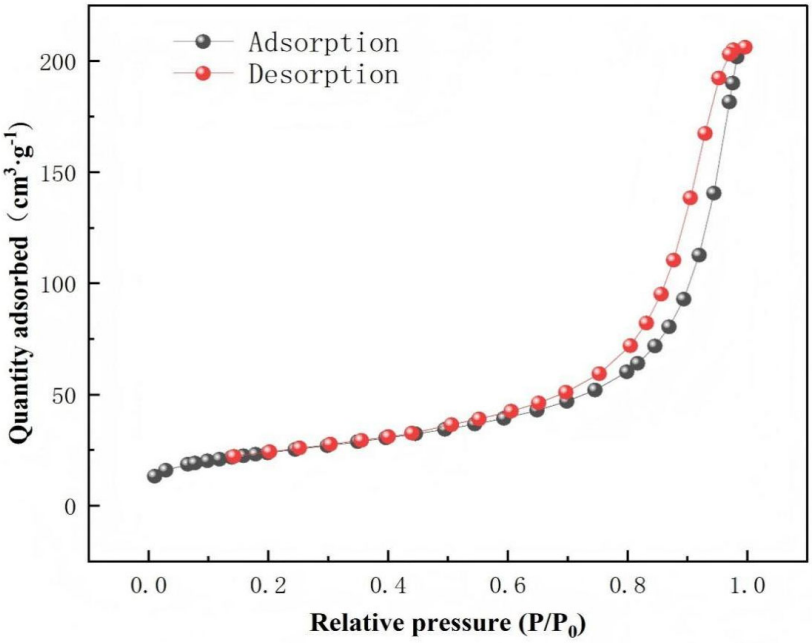


Figure 7. Adsorption–desorption isotherms of specimens

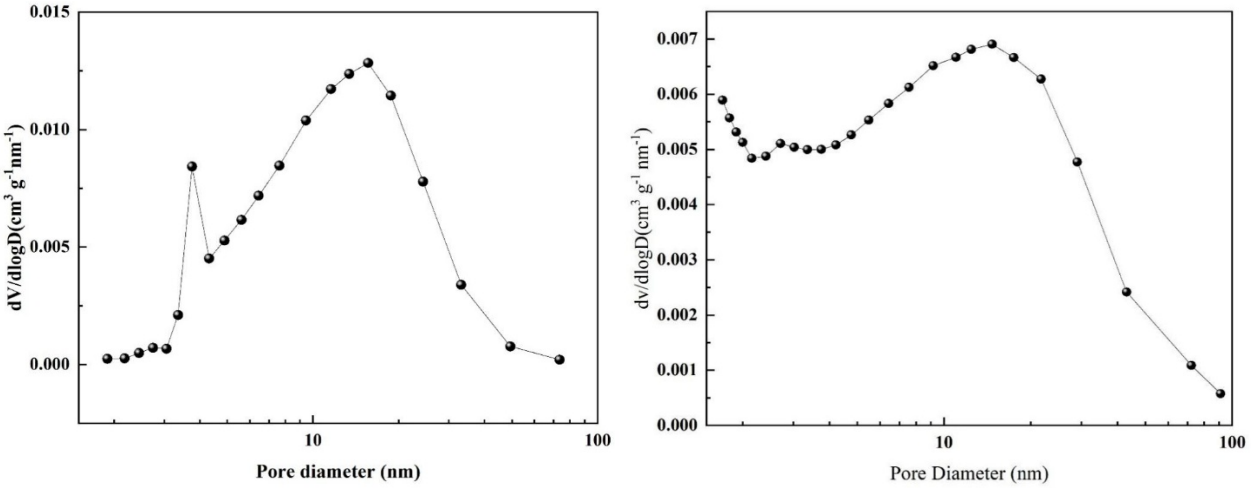


Figure 8. Pore size distribution of specimens

Table 3. Pore structure parameters of HS specimens

Thermophysical properties	HS1	HS2	HS3	HS4
BET Surface Area:	84.6859 m²/g	72.6630 m²/g	69.4216 m²/g	66.1722 m²/g
Micropore Area	3.9451 m²/g	3.8589 m²/g	4.4969 m²/g	3.5248 m²/g
micropore volume:	0.001524 cm³/g	0.001557 cm³/g	0.001884 cm³/g	0.001428 cm³/g
Adsorption average pore diameter	15.0382 nm	14.9232 nm	14.6294 nm	12.4365 nm

4.8. Mercury intrusion porosimetry

Mercury intrusion porosimetry (MIP) was adopted to characterize the pore structure of samples. The results are as follows: the total pore volume is 0.2915 mL/g, the total specific pore surface area is 6.231 m²/g, and the average pore diameter (4V/A) is 187.12 nm. The volume median pore diameter is 27.88 μm and the area median pore diameter is 32.39 nm. According to the definition proposed by the International Union of Pure and Applied Chemistry (IUPAC), pores with diameters below 2 nm are classified as micropores, those ranging from 2 nm to 50 nm as mesopores, and those larger than 50 nm as macropores [2]. The pore size distribution exhibits a typical bimodal feature: macropores dominate pore volume, while mesopores contribute most of the specific surface area.

The bulk density of the sample is 1.5992 g/mL and the apparent (skeletal) density is 2.7260 g/mL, yielding a calculated porosity of 17.47%. The permeability reaches 2356.21 mD, the threshold pressure is 0.95 psia, and the pore tortuosity is 2.9218. The mercury intrusion-extrusion curves are shown in the corresponding figure. The low mercury extrusion efficiency indicates that well-connected macropore networks have formed inside the samples, accompanied by moderate pore tortuosity and structural complexity Figure 9.

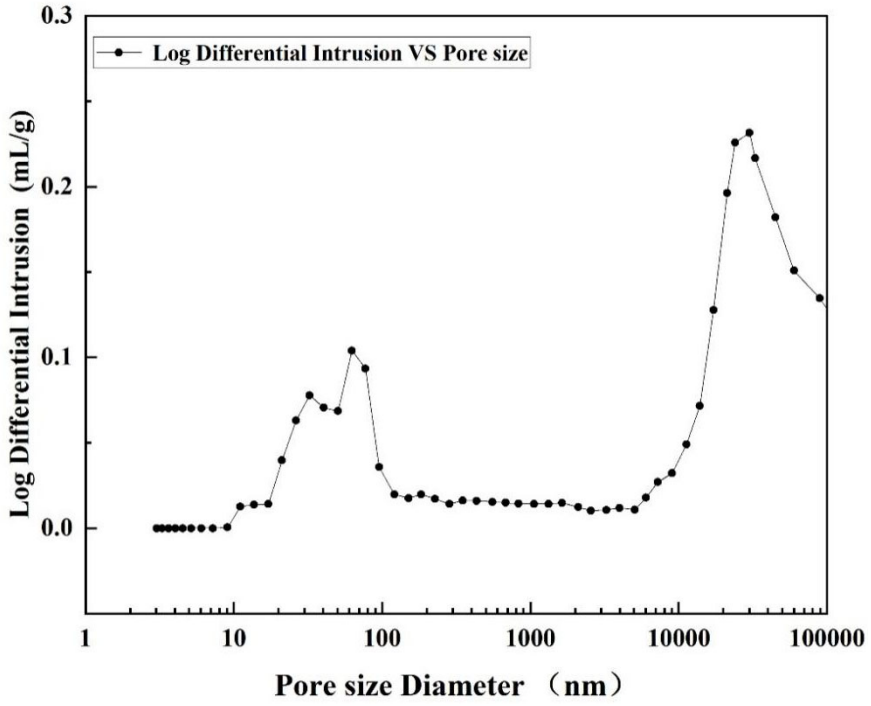


Figure 9. (MIP)Pore size distribution of specimens

Mass variations of specimens before and after water immersion are summarized in the table. The mass of all bone specimens increases remarkably after saturated water absorption. Bone tissue possesses inherently loose microstructures containing abundant micropores and hydrophilic groups, which readily capture external water and lead to distinct moisture-induced mass gain.

The water absorption rate varies among groups. Specimen Hs1 exhibits the lowest water absorption rate of 21.14%, while the other samples display generally higher values. This reveals individual differences in pore structure and compactness among bone specimens. Overall, bone materials feature strong water uptake capacity. Under long-term humid conditions, water absorption may trigger swelling and structural deterioration. These findings also provide fundamental data support for subsequent consolidation and modification treatments Table4.

Table 4. Mass variation of specimens before and after water immersion

Condition / Sample mass (g)	Hs1	Hs2	Hs3	Hs4	Hs5
Dry state	1.9708	2.5700	1.4275	0.9941	0.8136
Water-saturated state	2.3875	3.4093	2.1934	1.3989	1.3224
Water-absorption rate	21.14%	32.6%	53.6%	40.17%	51.08%
Average water absorption rate: 39.86%					

4.9. Theoretical Basis of Deterioration Mechanism

Bone relics possess an organic–inorganic composite structure, predominantly composed of tightly interlocked organic collagen phases and inorganic hydroxyapatite phases. Multiple environmental stresses during burial and post-excavation trigger synergistic degradation of the two phases, which constitutes the fundamental cause of typical damages including pulverization, cracking, peeling and fragmentation observed on pig mandibles from the Huangshan Site. The overall deterioration of bone relics is essentially a progressive evolution of coupled physical and chemical damage to organic and inorganic phases driven by multifaceted environmental factors, following a clear sequential and progressive mechanism.

Hydrolytic degradation of collagen acts as the initial and critical step of bone deterioration. As the primary binder maintaining interconnection between hydroxyapatite crystals and supporting the overall bone framework, hydrolytic fracture and continuous loss of collagen fibres deprive the tightly bound inorganic mineral crystals of cohesive restriction and ductile support. This directly leads to a remarkable increase in internal porosity and structural permeability, accompanied by substantial deterioration in mechanical strength and toughness of the relics, creating preconditions for the invasion of external corrosive agents and subsequent damage development.

Following the destabilization of the organic phase, the residual inorganic hydroxyapatite framework undergoes continuous mineral structural modifications such as grain coarsening and crystallinity variation under combined environmental effects, including long-term groundwater dissolution, erosion by acidic–alkaline soil media, and periodic temperature-humidity fluctuations. These changes steadily weaken interparticle bonding and induce gradual disintegration of the original compact bone structure. In summary, the progressive synergistic damage mechanism, whereby the organic phase degrades and destabilizes first followed by structural deterioration of the inorganic phase, ultimately results in irreversible degradation phenomena of the Huangshan pig mandibles, such as surface pulverization, pervasive powdering and structural fragmentation.

5. Analysis of Damage Causes

Bone, horn and tooth relics are collectively categorized as keratinous bone cultural relics, which consist of approximately 70% organic components and 30% inorganic substances. The organic fraction is dominated by proteins and lipids, while the inorganic part mainly contains phosphate, carbonate and fluoride minerals [1]. Lipids serve as binders that tightly connect organic and inorganic phases via physical filling and chemical bonding, and buffer interfacial stress arising from their divergent physicochemical properties to maintain the structural integrity and stability of relics. Calcium phosphate is the primary phosphate in bone relics, and its unique reticular crystal structure endows bone materials with compressive, flexural and crack resistance.

5.1. Groundwater

Buried in ancient tombs and sites, keratinous bone relics are highly susceptible to deterioration driven by groundwater, which acts as a dominant deterioration factor for specimens from the Huangshan Site. Long-term underground humid burial conditions are verified by the high water content, extensively interconnected pores and characteristic absorption peaks of water molecules detected by Fourier-transform infrared spectroscopy.

Carbon dioxide dissolved in groundwater forms a weak acid system that continuously corrodes carbonated hydroxyapatite in bone matrices. X-ray diffraction and microscopic observations reveal that calcium and phosphorus readily migrate and leach out via pore water under acidic conditions, generating secondary minerals such as calcium pyrophosphate and potassium calcium hydrogen phosphate. Mineral crystals suffer corrosion and edge passivation, destroying the inorganic mineral framework and drastically reducing structural compactness and mechanical performance.

XRF detects exogenous elements including Al, Fe, Zn, K and Si, while ion chromatography identifies three anions (Cl^-, SO_4^{2-}, NO_3^-), proving groundwater transports ions, iron-manganese oxides, quartz and feldspar into internal pores. On one hand, anions disrupt hydroxyapatite lattices through ion exchange and chemical reactions: SO_4^{2-}, NO_3^- and Cl^- react with Ca^{2+} to form soluble salts, accelerating calcium loss and triggering pulverization and cracking. On the other hand, soil mineral particles infiltrate pores and replace degraded organic matter, aggravating matrix loosening and mineral embrittlement.

Weak acid formed by dissolved acidic oxides gradually dissolves carbonated hydroxyapatite, converting solid calcium ions into soluble calcium bicarbonate that leaches away with pore water and collapses the inorganic supporting skeleton [3]. Subsurface pore water temporarily balances interfacial stress between organic and inorganic phases to stabilize bone structures, yet rapid water loss after excavation creates uneven shrinkage stress that expands microcracks and causes surface pulverization, consistent with ultra-depth-of-field and SEM observations [4]. Meanwhile, groundwater-derived weak acid accelerates lipid oxidation; combined with microbial decomposition, the lipid buffer between organic and inorganic phases fails, leading to severe pulverization and cracking [5].

5.2. Temperature Variation

Diurnal and seasonal temperature fluctuations in burial and storage environments induce multi-scale deterioration of bone relics. Organic collagen and inorganic hydroxyapatite feature distinct thermal expansion and contraction rates, generating alternating internal stress at phase interfaces under cyclic temperature changes. Cumulative stress exceeding the fracture strength of bone materials initiates microcracks, further developing into splitting, delamination and pulverization, matching the reticular cracks and interlayer separation observed under SEM [6].

Temperature fluctuations drive repeated dissolution-recrystallization cycles of soluble salts inside pores and accelerate matrix damage. Abundant corrosive Cl^- and SO_4^{2-} dissolve at high temperature and migrate through interconnected pores via capillary action, then recrystallize at low temperature. Volume expansion during salt crystallization produces strong mechanical stress that widens and connects microcracks, expanding damaged areas and intensifying weathering [7].

Temperature also regulates microbial metabolic activity as a critical factor for biological corrosion. It modulates

microbial enzyme activity, membrane fluidity and metabolic pathways to control reproduction and corrosive capacity. Bacteria and fungi proliferate massively at 20–30 °C with sufficient soil nutrients [6]. Microbes secrete organic acids such as lactic acid and acetic acid to dissolve hydroxyapatite into soluble calcium salts, and proteases to degrade cementitious collagen. Detected NO_3^-, microbial residues in micrographs and shifted collagen characteristic peaks in FTIR spectra collectively verify severe microbial erosion, which raises porosity, loosens bone structures and weakens mechanical properties.

5.3. Soil Composition

Soil components and acidity are fundamental factors governing bone preservation and weathering. Soil pH around pig mandibles at the Huangshan Site ranges from 3.0 to 6.5 (mostly 6.5, partial areas as low as 5.5), showing typical weak acidity that accelerates bone deterioration through chemical corrosion, mineral replacement and biological induction. Highly acid-sensitive hydroxyapatite lattices are disrupted by free hydrogen ions, which replace lattice calcium to form unstable intermediate calcium hydrogen phosphate [8]. Continuous acid leaching elutes calcium and phosphorus, transforming dense bone matrices into porous structures, consistent with high porosity and well-connected pore characteristics from BET and mercury intrusion tests.

Weak soil acidification brings superimposed adverse effects. Microbially secreted organic acids synergistically corrode hydroxyapatite and drastically reduce mechanical strength. Silica and carbonate soil minerals infiltrate pores with groundwater and occupy voids left by degraded collagen, forming exogenous secondary mineral phases confirmed by XRD and microscopic mineral particle observations. Such mineralization increases bone brittleness, resulting in irreversible mechanical fracture during excavation, transportation and storage.

Furthermore, humus and organic substances in soil penetrate pore systems along with groundwater. Exogenous organics alter original pore parameters and disrupt internal water-gas exchange, while providing nutrients for microbial reproduction. This amplifies biological acid corrosion and collagen degradation, forming a vicious cycle: acid corrosion → structural loosening → microbial enrichment → aggravated deterioration.

6. Conclusion

In this study, pig mandible specimens excavated from the Huangshan Site in Nanyang were selected as research objects. The five main types of typical deterioration and the coupled deterioration law of multiple damages were systematically identified. Combined with multi-dimensional characterizations including microscopic observation, elemental analysis, phase identification, pore structure testing and water absorption measurement, the complete deterioration mechanism of such natural bone relics was clarified. The inherent high-porosity and organic-rich primary microstructure of pig mandibles serves as the internal basis for deterioration development. Long-term actions of weakly acidic buried soil, groundwater, soluble salts and microorganisms lead to collagen degradation and hydroxyapatite dissolution within bones, generating latent chronic damage. After excavation, sharp fluctuations in temperature and relative humidity induce repeated salt crystallization and uneven dehydration shrinkage of bone tissues, triggering the concentrated occurrence of cracks, pulverization, deformation, salt efflorescence and other damages. This study confirms that chloride and sulfate ions are critical corrosive ions accelerating bone pulverization, and the synergistic deterioration of organic–inorganic phases represents the core pathway for bone structural destabilization. The research results provide scientific references for desalination, in-situ consolidation and constant temperature–humidity museum preservation of prehistoric animal bone relics buried in acidic soil environments of the Central Plains of China.

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