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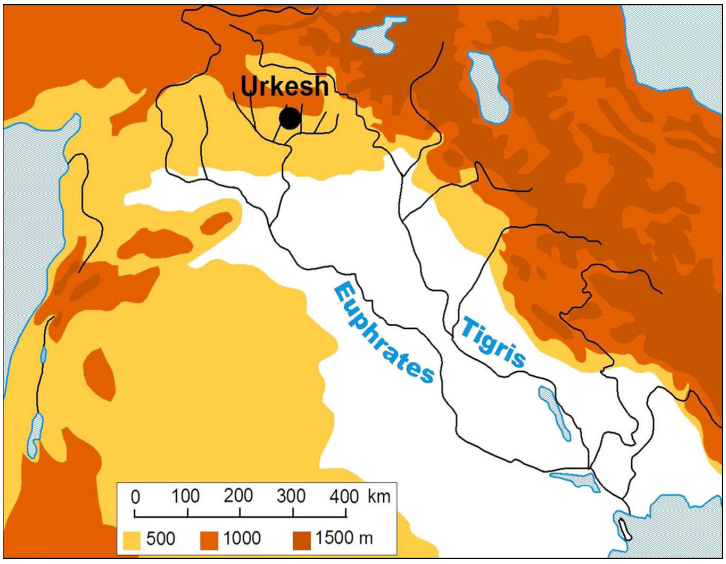

Figure 1. The ancient Hurrian city of Urkesh (Tell Mozan) sits near the foothills of the Taurus Mountains and lies in the Khabur River basin of northeastern Syria.

Using Image Analysis Software to Correlate Sherd Scans in the Field and X-Ray Element Maps in the Laboratory

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Our research involves a novel combination of techniques to investigate the ceramic tradition at ancient Urkesh. Preparing and observing large numbers of samples for traditional ceramic petrography is expensive, time-consuming, and impractical in the field. Our alternative approach uses a flatbed scanner on-site to collect high-resolution images of sectioned sherds. We selected a portion of the scanned sherds for subsequent microanalysis. Element maps of these sherds were made using an electron microprobe (also called an electron probe microanalyzer). Image analysis software correlated the two image sets. The result is a promising way to analyze large numbers of sherds, crucial for understanding chronological and stylistic variations at this particular site and throughout the region.

The Site: Tell Mozan, Syria

Tell Mozan, located in the Khabur triangle of northeastern Syria, is the site of the ancient Hurrian city Urkesh (Figure 1). When the city was founded is unknown, but it was settled by the mid-fourth millennium BC, possibly earlier. The city remained active until 1350 BC when it was abandoned. Our team has excavated the site since 1983. The most important architectural complexes excavated so far include an inner city wall, a royal palace (circa 2250 BC), a deep stone-lined necromantic shaft next to the palace, and a massive temple terrace with a monumental stone stairway. Descriptions of the site and full-text publications are available on the Urkesh website (http://www.urkesh.org).

Each excavation season has yielded between 40,000 and 60,000 pottery sherds and numerous whole vessels (more than 1000 from all seasons). The large body of ceramic data analyzed every season is integrated into the Urkesh Global Record, an HTML-based system for online publication of all observations and data collected during each season. The ceramic data are integrated at the level of the individual shape sherd and its description within its stratigraphic context. Descriptive statistics of the assemblage are generated instantly (Figure 2).

In earlier seasons, the fabric and inclusions of the wares were described in great detail but primarily using macroscopic categories. The ceramic shape catalog has been built up throughout the seasons and spans the city's occupational history. A large and well-categorized reference collection of several thousand sherds allows ceramic analysts to match the paste, shape, and decoration of new sherds against the parameters set for each type. This allows us to maintain full coherence within the system but also avoid the danger of "type creep" (that is, a gradual change in our ware classifications over time when not using a reference collection).

The Research Problem

In 2003, we began a more intensive study of technological changes over time in the ceramic wares. Our aim is to assess chronological and stylistic variations in clay choice, tempering materials, and firing techniques. To this end, we decided to supplement our macroscopic analysis with petrographic examination. Traditional ceramic petrography involves finely polishing very thin slices of sherds (exactly 30 microns thick) and using a polarizing microscope to identify the silicate minerals

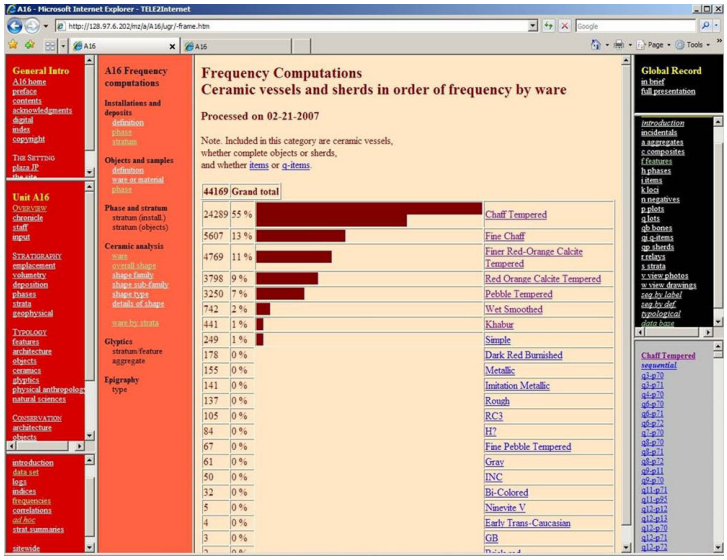

Figure 2. An example screen from the Urkesh Global Record shows how the software generates descriptive statistics of the ceramic assemblage from excavation area A16.

present. Preparing and observing large numbers of samples, though, is expensive and time-consuming. Our team has already recovered nearly a million sherds, so even a "small" sample size is still thousands of sherds. Preparing and examining hundreds of petrographic thin-sections was impractical, as was exporting so many sherds. Additionally, a petrographic microscope and polishing equipment are difficult to transport to the site and maintain. Traditional ceramic petrography also usually ignores the ceramic matrix and any small non-silicate minerals (which are ordinarily all grouped together as "opaques"), omitting potentially valuable information. We needed to develop a different approach.

Approach & Procedures

Our approach combines image analysis with X-ray microanalysis and element mapping. The image analysis process we followed was proposed by Giacomo Chiari (now of the Getty Conservation Institute, Los Angeles), who developed the procedures and software. Standard geologic procedures were followed for the microanalysis and element mapping.

About 500 sherds were selected based on numerous variables in the ceramic corpus. We chose sherds from different contexts (sections of the palace, the temple and ceremonial area, and the residential area), dates (we concentrated on four distinct time periods, or phases, of the habitation period), all major wares (from thin, fine forms to heavily tempered, utilitarian wares), and vessel parts (rims, body fragments, bases).

The sherds were cut on-site using a circular saw (a LEZACO marble cutter with a 110-mm carbide disc) purchased in Syria. The cut surfaces were polished using a sequence of three sandpaper grades (80, 150, and 220 grit) to remove the saw marks. The sherds were then washed carefully so that no residue or debris remained. Their polished surfaces were scanned at a high resolution (2400 dpi; 0.01 mm/pixel) using a flatbed photograph scanner and a computer in the fieldhouse (Figure 3). A key advantage of this method is that we could process most sherds locally, without having to export them. The process was fast and low-cost, and the equipment was easy to transport and maintain.

Image-analysis software (Colormod) was used to identify different areas in the flatbed-scanner images on the basis of the pixels' colors. Clusters of pixels that fall within the same color range are grouped in a scale of grays, and their area coverage is tabulated (Figures 4 and 5). In our case, clusters of chromatically related pixels represent inclusions (mineral and organic) as well as different hues of the firing spectrum. Therefore, we can assess the relative abundances of the different components in the paste, and we can also examine the results of the firing process on the clay body.

To "calibrate" the sherd scans, the mineral inclusions and variations in clay composition were identified using electron microprobe analysis. Sherd samples from the various wares were sent to the University of Minnesota. The sherds were cut, mounted in epoxy plugs, and polished using standard procedures for preparing geologic samples for electron microprobe analysis. We examined the prepared sherds using a JEOL 8900R "SuperProbe" Microanalyzer equipped with five wavelength-dispersive spectrometers (WDS), an energy-dispersive spectrometer (EDS), and secondary-electron (SE) and backscattered-electron (BSE) detectors. We used a combination of electron microscopy and X-ray microanalysis to identify the mineral inclusions and establish the clay chemistry (Figure 6). After the mineral inclusions (both the deliberately added tempers and particles intrinsic to the clay) were identified, we utilized the WDS system to map the concentrations of ten geologically important elements, showing the abundance and distributions of different minerals as well as chemical variations in the clay (Figure 7). The resulting element maps allowed us to visualize the differences among wares (Figure 8). We also used them to identify the inclusions in our flatbed-scanner images, allowing us to extrapolate to the larger set of 500 scanned sherds.

Results & Interpretations

Combined petrographic and image analyses of representative sherd samples has allowed us to confirm categorizations of fabrics that had been established during the macroscopic analysis of our ceramics. These analyses have also provided a better understanding of the technological patterns behind these categories and have shed light on interesting aspects of the corpus that had been unnoticed or poorly understood:

1. Chronological variations in the composition of calcite-tempered ceramic wares (a broad category which includes mass-produced table and storage wares in a variety of different forms and sizes). Over the four studied

Figure 3. An example of a high-resolution scan (collected at 2400 dpi; reduced to 200 dpi here) collected using a flatbed photograph scanner in the field.

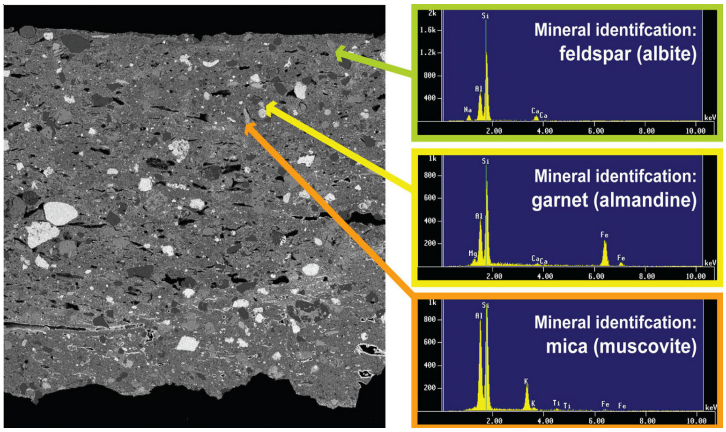

Figure 6. A backscattered-electron (BSE) image of a sherd and the EDS X-ray spectra of three mineral inclusions. This sherd comes from the same Phase-5a Khabur storage jar as shown in Figures 4 and 5. The field of view is 8-mm wide.

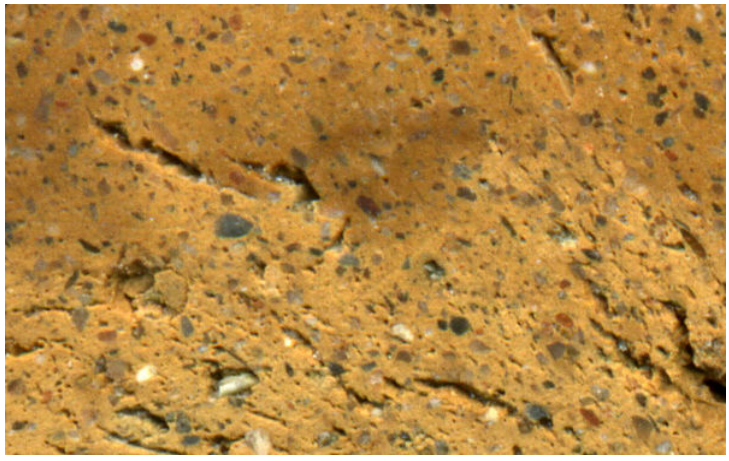

Figure 4. Part of a scanned image of a Khabur storage jar from Phase 5a.

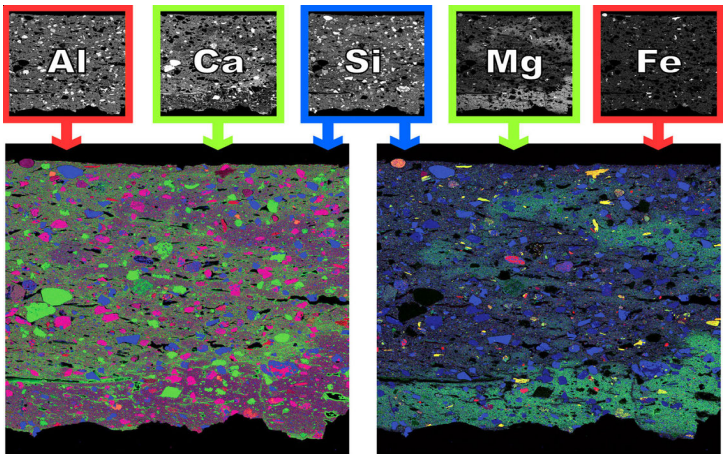

Figure 7. X-ray element maps (shown here overlaying three elements in red-green-blue maps) of the same area as Figure 6. These element maps, collected using the WDS system, show the abundance and spatial distributions of different minerals as well as chemical variations within the clay.

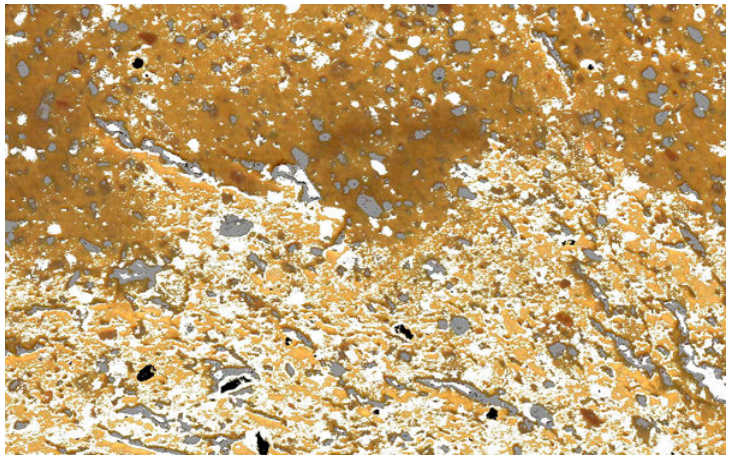

Figure 5. The same image from Figure 4 after partial processing using the Colormod software; clusters of pixels that fall within the same color range are grouped in a scale of grays.

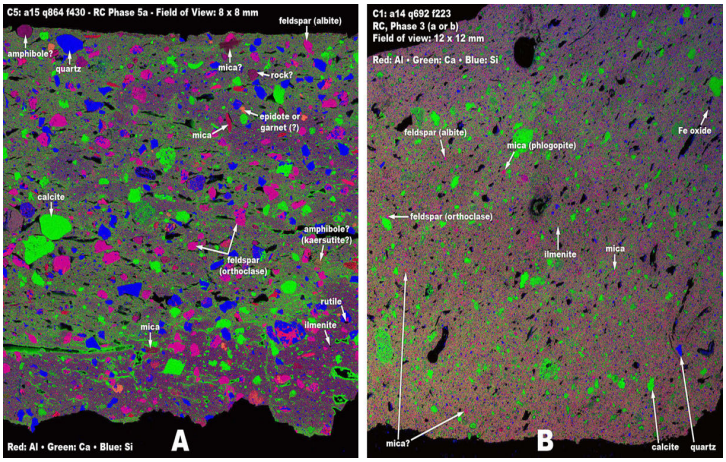

Figure 8. Red-green-blue element maps show the differences between wares. Map A corresponds to the Phase-5a Khabur jar in Figures 6 and 7. Map B shows a Phase-3 ware.

periods, from Phase 3 to Phase 5b, there is an increase in the abundance and sizes of inclusions other than calcite (e.g., quartz, feldspar) and a decrease in the amount of organic temper (Tables 1 and 2). The changes are particularly apparent in the Khabur storage jars of Phase 5a (Figures 4 to 8). Several explanations could account for the shift: special recipes developed for specific types of large vessels that are best made using tempered clays; differing availabilities of raw materials for tempering over time; and/or changes in the potters' technical know-how or preferences (or even a desire to experiment). All these possibilities deserve further exploration.

2. Clearer distinctions among broadly related but distinct wares, such as the fine chaff-tempered (Figure 9) and fine calcite-tempered wares (Figure 10). These two categories coexist for considerable periods of time, although in varying ratios. They are often difficult to distinguish macroscopically. Now we can measure the compositional differences between them and correlate these differences with specific vessel forms and sizes.

3. Insights into the manufacturing, finishing, and firing processes. Varying concentrations of the inclusions in different parts of the vessel (rim versus base) can be related to the potter's building technique during successive stages of throwing. Cracks and firing cores (with a characteristic "sandwich effect," Figure 11) are evidence for varying success in the firing kiln. Electron microscopy and X-ray microanalysis can be fruitfully extended to the examination of slips, paints, and other surface decorations (Figure 12).

Table 1. Modal analysis based on a sherd scan from a Phase-5a Khabur storage jar (the same ware shown in Figure 8A and Figures 4 to 7).

Mineral	Mean % Area	Sigma	Pixel Color Value Range		
			R	G	B
feldspar	7.30	0.03	145-186	132-183	107-155
calcite	5.04	0.03	190-255	162-254	116-221
quartz	2.53	0.02	068-113	061-099	034-074
mica	2.28	0.02	118-130	078-109	049-073
pore	0.46	0.01	053-094	041-072	012-047
Total	17.62				

Table 2. Modal analysis based on a sherd scan from a Phase-3 ware (the same ware shown in Figure 8B).

Mineral	Mean % Area	Sigma	Pixel Color Value Range		
			R	G	B
calcite	7.07	0.02	180-231	165-218	122-186
feldspar	1.01	0.01	160-183	149-176	127-152
quartz	0.58	0.01	067-096	056-085	028-063
pore	0.37	0.01	019-077	016-057	000-030
Total	9.04				

4. Understanding the fourth-millennium Late Chalcolithic wares. During recent seasons, we have started finding stratified mid-fourth millennium deposits of sherds (Figure 11) and cylinder seal impressions connected with the temple terrace. Our macroscopic ware descriptions from this period are now being integrated with the results of the image analysis and correlated with the microanalysis and element maps. This is allowing us to build an important database for research into the Late Chalcolithic pottery tradition at the site and throughout the region.

Acknowledgements

The excavations are carried out under a permit from, and with the collaboration of the Directorate General of Antiquities and Museums, Ministry of Culture, Syrian Arab Republic. The expedition is under the aegis of the International Institute for Mesopotamian Area Studies. The electron imaging and X-ray microanalyses were carried out by one of the authors (Frahm) at the Electron Microprobe Laboratory, University of Minnesota

Figure 9. An example of a fine chaff-tempered sherd.

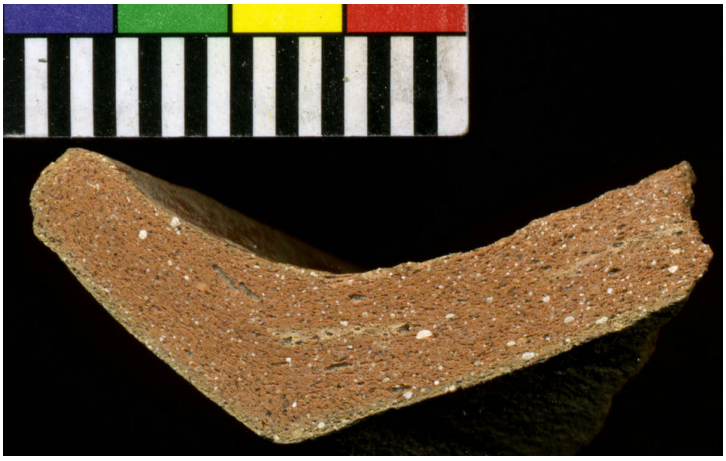

Figure 10. An example of a fine calcite-tempered sherd.

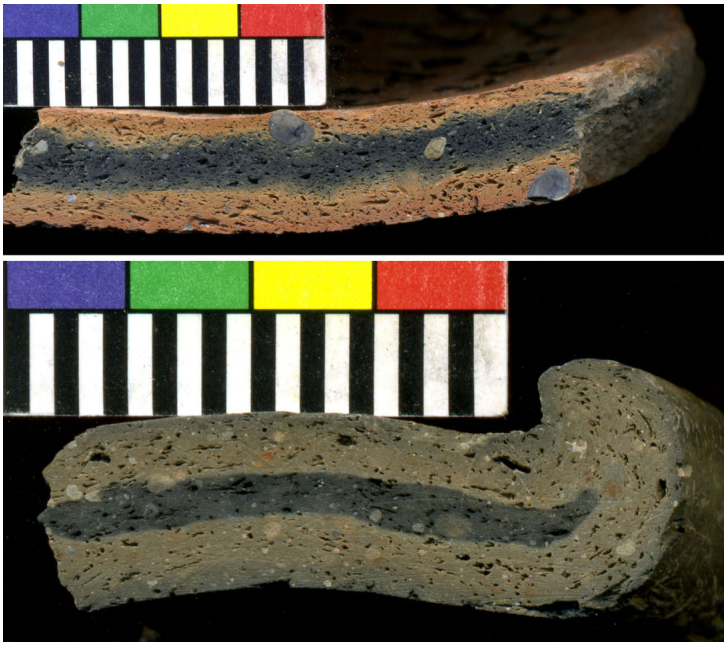

Figure 11. Two examples of fourth-millennium Late Chalcolithic wares that exhibit firing cores.

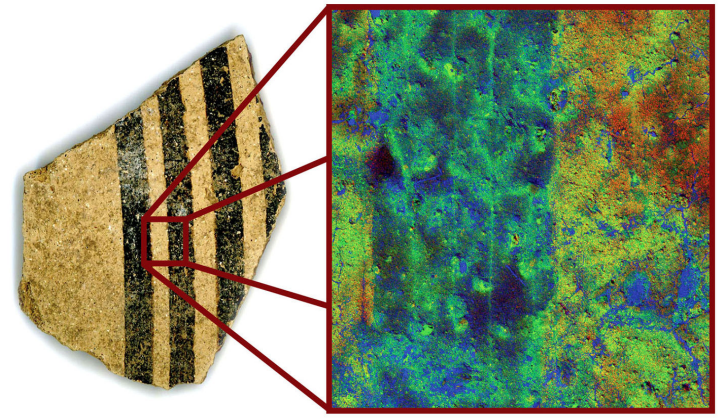

Figure 12. A red-green-blue combination element map shows the compositional differences between the slip and paint on this sherd from a Khabur storage jar. This image also reveals a series of parallel incised lines not apparent to the naked eye.

(probelab.geo.umn.edu). Travis Tenner assisted in preparing sherd specimens for microprobe analysis. Image analyses were done using Colormod Software by Dr. Giacomo Chiari of the Getty Conservation Institute. Dr. Michael Rauch of the Carnegie Institution assisted with processing and analyzing sherds during the 2006 and 2007 field seasons. This report benefited from comments from Giorgio Buccellati and Penny Frahm.

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SAS R. E. Taylor Poster Award Winner

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Miriam Hinman

Isotopes, Collagen, and Degradation: New Evidence from Pyrolysis GC-MS and Solid State ^{13}C NMR

Miriam Hinman
Harvard University

Collagen is the most abundant protein found in calcified tissues and is used as a substrate in important applications such as radiocarbon dating and stable isotope reconstruction of diet and environment. In an archaeological context, collagen degrades, but the type and rate of degradation mechanisms on the molecular level are poorly understood. This study uses stable isotope mass spectrometry, amino acid analysis, protein sequencing, infrared spectroscopy, pyrolysis GC-MS, and solid state ^{13}C NMR to analyze the structure and alteration of the collagen molecule in different states of preservation. Major chemical transformations occur in samples with C/N_m greater than 3.1 (atomic C/N_a greater than 3.6). These data suggest that collagen degradation involves bacterially driven denaturation and deamination of R group nitrogen, followed by hydrolysis, deamination of peptide nitrogen, and formation of Maillard-type condensation products. The hydrolyzed peptide fragments, condensation products, and bacterial biomarkers are preserved in close association with each other by clay. These molecular changes have implications for use of collagen in diet studies and other archaeological applications.

Introduction

Collagen extracted from bones collected at archaeological sites provides dietary information about ancient humans, because the carbon and nitrogen isotopic composition of bone collagen reflects an animal's trophic level, marine versus terrestrial diet, and relative contributions of C3 and C4 plants (Neuberger and Richards, 1964; DeNiro and Epstein, 1981; Schoeninger and DeNiro, 1984). However, performing isotopic analysis on ancient collagen is problematic due to degradation.