Burning Questions about Preservation:

An Investigation of Cremated Bone Crystallinity at a Bronze Age Cemetery

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Background

Archaeological Context:

Human remains make up a significant portion of the archaeological record and are an important source of information for reconstructing prehistoric lifeways. However, the preservation of human remains recovered from ancient cemeteries can differ based on a range of factors, including mortuary customs (e.g., inhumation vs. cremation) and post-depositional conditions (e.g., conditions of the soil). Assessing the preservation of skeletal material is an essential first step to ensure that later analyses such as isotopic composition or ancient DNA will provide reliable data.

At the Békés 103 cemetery in southeastern Hungary, the predominate burial practice was to cremate the body and bury it in a ceramic urn[3,13]. Ongoing excavations at this Bronze age site (1600-1300 BC) by the Bronze Age Körös Off-Tell Archaeology (BAKOTA) project have recovered 68 burials, of which 59 were cremains. The remaining burials were inhumations (n=5), scattered cremations (n=2), and unknown (n=2). In this project, we studied the chemical composition of cremated bone from samples across the cemetery to evaluate how the crystalline structure of the bone was impacted during the cremation process. The goals are twofold: 1) to evaluate whether burning conditions varied within and between individual burials, and 2) to determine whether calcined bone can provide a reliable source of "in vivo" strontium isotope values for further analysis.

Methodological Background:

The chemical analysis of skeletal material (elemental and isotopic composition) is a commonly used tool in archaeology to help reconstruct what people ate and where they lived. In Hungary, these studies have been able to reconstruct mobility and dietary patterns from periods as early as the Neolithic Age[1,5,6,7,8,9,10,12,15,24]. Much of the previous chemical analysis was conducted on inhumations, because it was thought that burned bones held no usable materials for data collection due to heat induced change in the bone structure that could result in isotope fractionation and diagenesis[2].

Recent work by Snoeck and colleagues indicates that cremated bone may in fact retain "in vivo" chemical signatures (for heavy radiogenic isotopes like ^{87}Sr) due to changes in bone crystallinity during the calcination process[17,18,19,20]. The preservation of the bone minerals is believed to be a result of crystallinity change that makes it more resistant to diagenesis. Crystallinity is a term used often in reference to the organization the lattice structures and composition which make up crystals[4,19,21]. However, the understanding of the crystal structure that makes up burnt bone is still relatively limited. Previous studies have looked at chemical composition of the hydroxyl apatite and isotopic composition of burnt bone[2, 11,14,18,19,20,22,23], but very few have analyzed the change in crystallinity as a means for understanding the preservation of in vivo isotopic values[17,19].

Fourier Transform Infrared Spectroscopy (FTIR) is a technique used to analyze the functional groups present within organic and inorganic matter. Recently, it has been used to analyze the crystal structure of burnt bone. FTIR uses light waves as a means of obtaining crystal structure by calculating the difference in absorption points on the resulting spectra. Crystallinity index, also known as splitting factor, is the measurement in anti-symmetric bonding frequencies that result from FTIR. Using unburnt bone as a model, Weiner and Bar-Yosef created the most commonly used standard of crystallinity index which add together two absorption peaks (603 and 563 cm^{-1}) and divides by the trough between them[4,14,16,17,19,20,25]. In previously conducted research, lower crystallinity indices have been associated with fresh bone with increasing crystallinity trends after heating. Due to the observed higher crystallinity in bone nearing calcination, it is believed that they are more resistant to diagenesis than unburned bone[4,23]. Recently FTIR-ATR (Attenuated Total Reflectance) was used in place of the more common previously used FTIR-KBr (potassium bromide) due to its ability to run small amounts of sample with little to no preparation[17].

Methods

Bone Sampling

A calcined and non-calcined bone fragment was taken from both cranial and post-cranial fragments from 15 burials (i.e., 4 bones per burial). Burials that had examples from all four categories were used in the selection criteria.

Preliminary Sampling

Prior to chemical analysis each sample was recorded for fracture pattern, Munsell color, and weight. In conjunction, a photograph and CT scan were taken to record physical structure of the bone fragments before destructive chemical analysis was conducted.

Fourier Transform Infrared Spectroscopy (FTIR)

Chemical composition and crystallinity of the bone samples were analyzed using FTIR-ATR (Attenuated Total Reflectance) in the chemistry department instrument lab at the University of Alabama at Birmingham. The exterior of each sample was mechanically cleaned using a burr attached to a dremel and then homogenized using a mortar and pestle. 100 mg of each sample was weighed for analysis. Each sample was then run on the FTIR-ATR at 24 scans per run.

Data

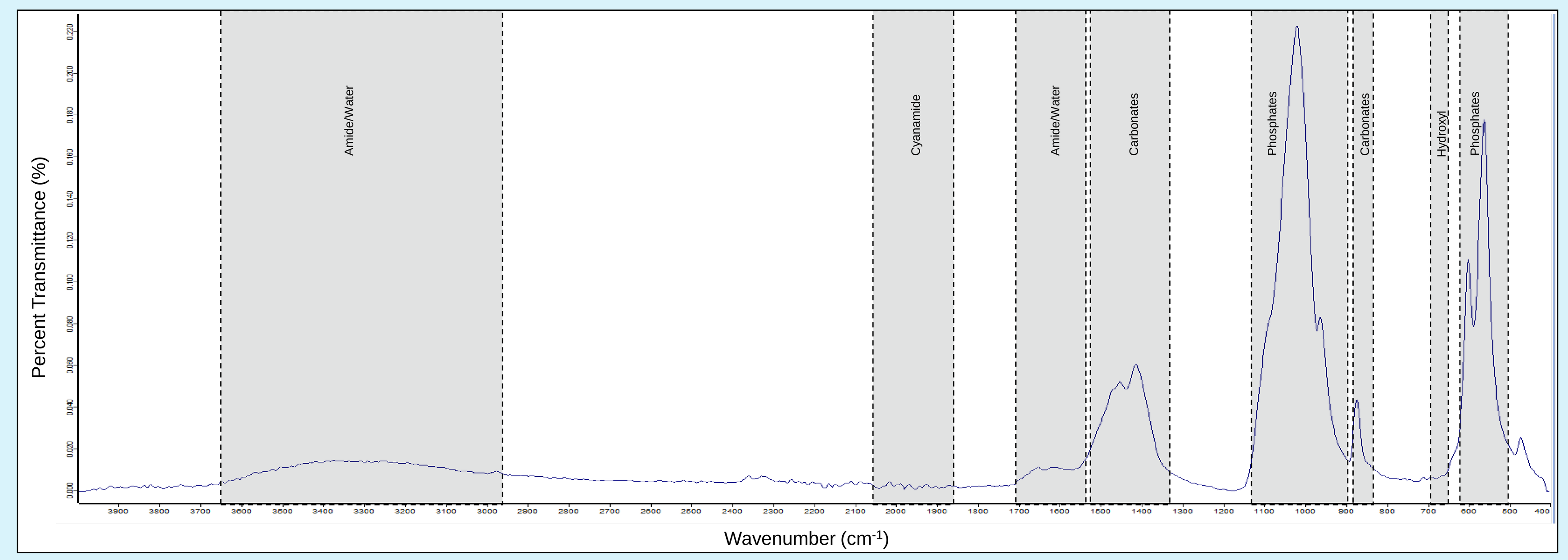

Figure 1: The IR spectra of a burned human bone from the Békés 103 cemetery. The important peaks are noted by the gray boxes and labeled with the appropriate functional groups.

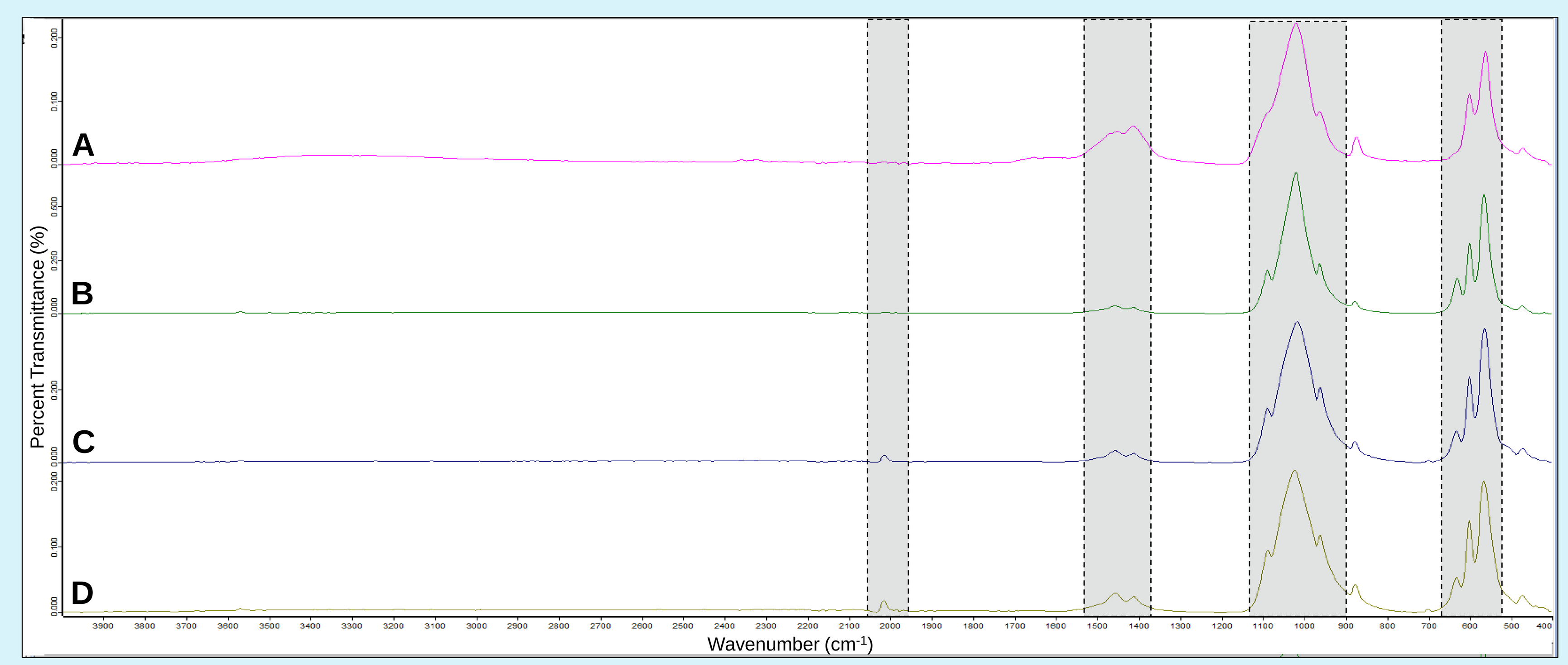

Figure 2: The stacked FTIR shows the differences in the four types of bone as seen by A) Post-Cranial Non-Calcined B)Cranial Non-Calcined C) Cranial Calcined D) Post-Cranial Calcined

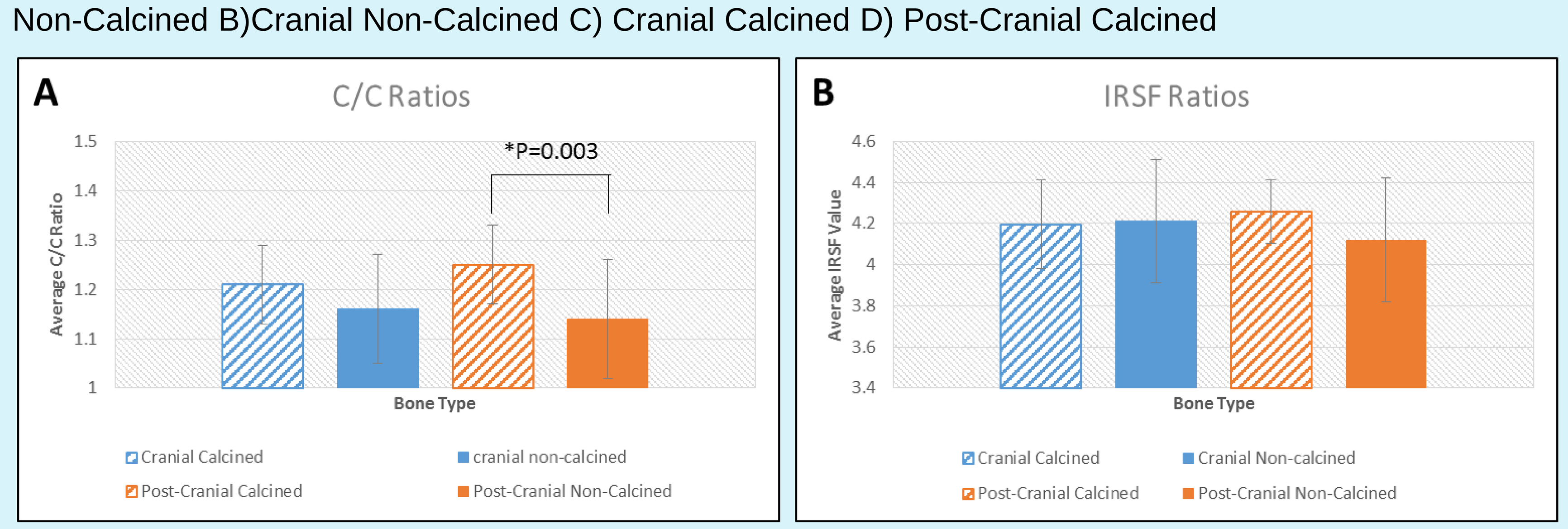

Figure 3: Figure 3A shows the average values of carbon types (C/C). Figure 3B shows the average values for the Infrared splitting factor (IRSF).

FTIR indices used in this study

Name	Significance	Peaks	Reference
C/C	Carbonate A+B to carbonate B ratio	A_{1450}/A_{1415}	Thompson et al. 2009
IRSF	Crystallinity	$A_{605}+A_{565}/A_{590}$	Weiner and Bar-Yosef 1990

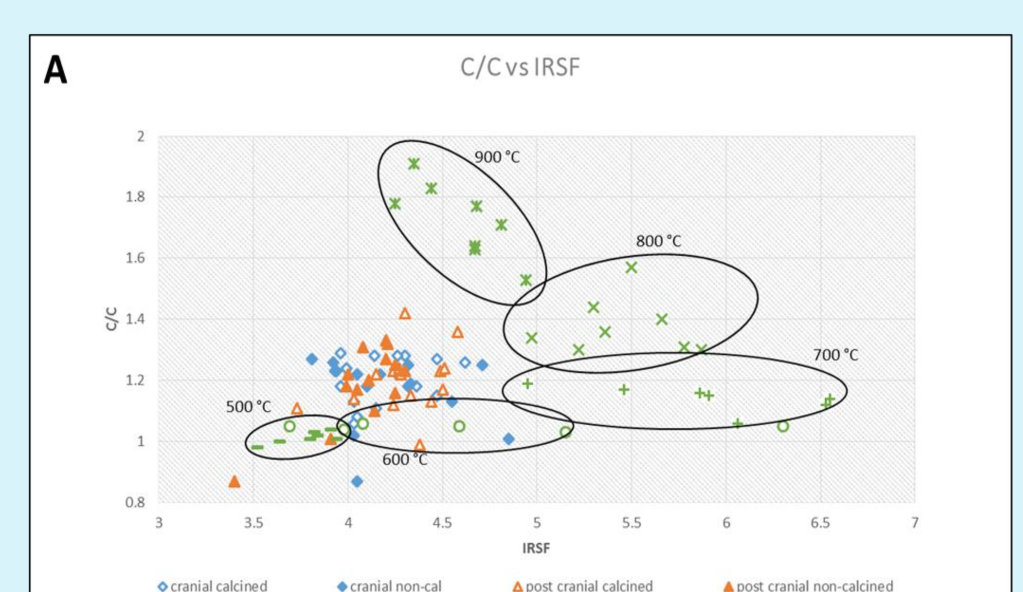

Figure 4: A) A scatter plot comparison of the values of carbon types (C/C) vs the Crystallinity (IRSF). The green markers show reference to experimental burning temperature data collected from animal bones (cow tibia) in Snoeck et al. 2014. Each symbol denotes a different temperature of burning which is given a general C/C vs IRSF range by the circle and label.

Results and Discussion

- The FTIR peak distribution of burned human bones is seen in Figure 1. The peaks highlighted show spectra regions that can be used to make inferences about chemical and structural changes in bone due to burning.
- The comparison of the spectra can be seen in Figure 2 by the stacked IR spectra. The three highlighted areas show differences in the cyanamide, carbonates, and phosphate groups indicating that there are only minor differences between the bone types measured in this study.
  - The first box notes the cyanamide peak (NH_2CN) which has a higher presence in calcined bones however, it is not a significant presence.
  - The second box notes the ratio between the carbonate A and B groups (C/C). As seen in the spectra, a deeper trough can be noted by the calcined bones than the non-calcined bones, this results in a higher C/C ratio (which is correlated with burning at higher temperatures)[17].
  - The last two boxes highlight the phosphate groups; the calcined bones show a larger presence of multiple peaks compared to the non-calcined bones. These peaks can indicate the ways in which the bones may have been burned (fuel vs unfueled), how hot and long they were burned, and crystallinity changes[17].
- The measurement of the C/C ratio as seen in Figure 3A shows that calcined bones of both the crania and post-crania were higher than non-calcined samples, indicating higher burning temperatures. This differences was statistically significant between calcined and non-calcined post-cranial bones according to a student's T-test.
- The measurement of IRSF (Crystallinity Index) is shown in Figure 3B. Similar to 3A, calcined post-cranial bones show the highest values; however, unlike the C/C ratio it is not statistically significant according to a student's T-test.
- Figure 4A, shows a bivariate plot of C/C vs IRSF relative to previously published data of experimentally burned animal bone from Snoeck et al. 2014. The C/C data indicates that a majority of the bones were burned at temperatures around 700°C. The two samples that had the lowest C/C values were non-calcined samples. The C/C data were not statistically correlated with IRSF values according to a best fit line correlation.
- While our data does not match very well with the experimentally burned animal data, they are similar to the archaeological samples presented in Snoeck et al. 2014. Other authors have noted the beginning of a change in crystal structure around 700°C similar to where we have noted a significant change in C/C ratios, a primary component of the lattice structure[14,22,23].

Conclusions & Future Research

- FTIR results from this study show that a majority of the bones selected for analysis (calcined and non-calcined) were cremated at relatively high temperatures, between 600 and 800°C. While major chemical and structural changes between our four bone categories were not observed; calcined post-cranial bones had the highest values for both FTIR indices. This may indicate that calcined post-cranial bones make the best candidates for future chemical analyses as compared to calcined crania and non-calcined postcranial bone .
- To evaluate whether temperature and crystallinity make cremated bone more resistant to diagenesis, future research will analyze the trace element composition between calcined and non-calcined post-cranial bones. The goal of this work will be to determine whether elements commonly associated with diagenetic contamination (such as rare earth elements and uranium) are absent or reduced in the samples with higher C/C and IRSF values.

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