Analysis of the Peiting Woman Using Portable X-Ray Fluorescence Spectroscopy

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Portable X-ray Fluorescence Spectroscopy was applied to the skeletal remains of 13 bog bodies and their bog burial environments. The objective was to create a better understanding of Northern European bog environmental chemistry and its diagenetic effects on interred bog bodies, determine bog body geographic disparity and/or origin, and identify if post-discovery preservation procedures were applied to the bog body remains. This paper summarizes the findings for one of those 13 bog bodies: the Peiting Woman from Bavaria, Germany. The elements analyzed include Antimony, Cobalt, Copper, Iron, Manganese, Molybdenum, Lead, Strontium, Titanium, Zinc, and Zirconium.

Introduction

X-Ray Fluorescence Spectroscopy (XRFS) is a categorizing term for several forms of spectroscopic techniques that help to determine and quantify the elemental composition of samples by using X-ray excitation. With the advantage of portability through use of a handheld unit, portable XRFS (pXRFS) provides a non-destructive testing method that offers objective, laboratory grade, presumptive analyses on on-site testing samples, such as metal alloys, mineral deposits, soil samples, and bone.[1]

PXRFS can be applied to the analysis of bog body remains in several ways. It can provide information about the diagenetic effects of the bog burial environment on the interred bog body. PXRFS can also help to determine the geographic origin and/or disparity in environmental habitation of bog bodies early and late in life. In addition, pXRFS can allow one to identify whether housing curators and staff applied post-discovery preservation procedures to bog bodies. This research focused on the application of pXRFS to both the skeletal remains and the surrounding burial environment of 13 bog bodies; one of which was the Peiting Woman from Bavaria, Germany. This article summarizes the pXRFS findings for this raised bog body.

Figure 1: Map of Germany highlighting the finding site of the Peiting Woman (see dot).

Background

Peiting Woman

Peiting Woman was discovered in the "Weiten Filz", a raised bog near the small town of Peiting, Bavaria, Germany (47°48'935" N, 10°58'225" E, Fig. 1) on July 23rd, 1957. Her body was found buried in a wooden coffin, dressed in clothing, and with a pair of apparently unused leather boots (Fig. 2). The entire skeleton was present and complete with much of her torso and upper legs still covered by fatty tissue.[2] Shortly after recovery, experts performed an autopsy that involved the removal of numerous internal organs, opening of the skull, and removal of the intact brain. The location of these removed organs is currently unknown. Her age was estimated to be between 20 and 30 years old.[3] This was based on the following cranial suture fusion characteristics: the spheno-occipital synchondrosis showed signs of beginning ossification, demonstrating an age of 15 or older, and the styloid process and the temporal bone, which physiologically occurs after the age of 25, lacked visible ossification. Cause of death is indeterminate for this female bog body.[4]

Analysis of the wood of the coffin by ^{14}C radiocarbon dating was undertaken to estimate the age of the bog body indirectly without having to use tissue samples. ^{14}C dating of the coffin wood revealed an approximate age of 800 years, meaning Peiting Woman presumably died around 1,200 C.E. However, this dating method can only indicate an approximate age; several factors may influence the results obtained, which all involve the tree type used to build the coffin. These factors include tree age, strength, and durability; long-living trees (i.e. oaks or conifers) may overestimate the age of the body.[5] As a result, ^{14}C radiocarbon dating of the skeletal remains resulted in a new approximate time of death within the Middle Ages, between 1,290 and 1,370 C.E. and between 1,380 and 1,440 C.E. with a probability of 95%.[6] Peripheral Quantitative Computer Tomography (pQCT) analysis of

Figure 2: Peiting Woman, a Middle Ages bog body, pictured within her wooden burial coffin.

the skeletal remains revealed a significant loss of cortical Bone Mineral Density (cBMD) of 83.4%. pQCT analysis also applied specifically to the pair of radii present revealed a higher cBMD for the left radius, suggesting left handedness.[7]

Spectroscopic analysis of the tissue's elemental content revealed that the coffin wood was well-preserved. Microbiological testing demonstrated only slight wood decay, considering such an extended period of submersion. The acidic and anaerobic conditions of the bog provided special preservative conditions for the wooden coffin. Additional analysis also revealed that the boards (i.e. sides, bottom and lid) were made of spruce (Picea abies), and the dowels used for fastening the boards were made of ash (Fraxinus excelsior). There were too few growth rings present to determine a dendrochronological age of the coffin reliably.[8]

Our examination of the skeletal remains additionally determined this individual to be a probable Caucasian female. Based on her erupted third molars and the limited visibility of her long bone epiphyseal-diaphyseal union sites, we could only narrow her age to greater than 20. Her stature range is 4 ft 7 in to 5 ft 9 in (1.43 m – 1.80 m) based on maximum lengths of visible long bones. We believe that entombment within the wooden coffin prevented the effect of bog compression and warping of the skeletal remains.

Preservative treatment applied to the remains involved metal coiling used to keep the forearms and hands in anatomical position (Fig. 3). The sites of application include the proximal and distal ends of both radii and ulnae, as well as throughout the carpal bones and phalanges of both hands. Peiting Woman is currently stored at the Archaeological Staatssammlung in Munich, Germany.

Procedures

During the summers of 2009 to 2011, elemental readings were collected using an Innov-X Alpha Series analyzer. The Peiting Woman was investigated in 2010. The body was scanned three times at various pre-determined anatomical areas to enable the most accurate average concentrations for elements of interest as measured in parts per million (ppm). These averages were used to create a concentration range for each element of interest. Each scan lasted 30 seconds.

Since we were unable to visit the discovery site of the Peiting Woman during our investigations, we used geochemical soil data standards collected by the German

Figure 3: Metal coiling used to keep the forearms and hands in anatomical position (see arrows).

Federal Institute for Geosciences and Natural Resources instead.[9] These soil standards were taken at 5 km increments (5 km, 10 km, 15 km) relative to the estimated discovery site to assure the correct soil elemental concentrations of the actual finding site were being compared to the bog body found at that location. After assembling all recorded measurements for the bog body and her discovery site, we compared the elemental composition of the teeth and bones to the elemental concentrations of the excavation environment, using pXRFS and the process of fluorescence.[10]

For this research, we compared bone, soil, and tooth Strontium (Sr) concentrations to determine if this individual migrated between infancy and death, and her possible birthplace. During childhood when permanent teeth become set in an individual's maxilla and mandible, Sr levels accumulated during that period of tooth development become fixed within the dental enamel and remain unchanged throughout life.[11] Alternatively, the Sr content of the individual's bone constantly changes throughout life because bone regenerates its chemical constituents continuously.[12] By comparing the Sr concentrations in bones and teeth to those in specific geographic regions, one can determine whether an individual migrated between infancy and death, and sometimes can even identify the location of his/her birthplace.[13]

To assess potential bog diagenetic effects, we also measured Copper (Cu), Iron (Fe), Manganese (Mn), Molybdenum (Mo), Lead (Pb), Zinc (Zn), and Zirconium (Zr). These concentrations were also used to assess the application of post-discovery preservation procedures. In addition, to further support or reject evidence of the application of preservatives, we evaluated the elemental concentrations of Cobalt (Co), Antimony (Sb), and Titanium (Ti).[14]

Hypotheses

We hypothesized that the Sr concentrations of the bone and teeth measurements for the Peiting Woman and the corresponding discovery site soil samples would be similar. This hypothesis would support the conclusion that this bog body was native to her discovery site. In addition, we hypothesized that the chemical composition of the raised bogs would alter the elemental concentrations of the bog body. Further, the elements analyzed would show incorporation into her bone and teeth with elevated elemental concentrations much higher than those of normal bone and teeth. Unlike the other elements analyzed, however, we hypothesized that Sr should withstand the diagenetic effects of the raised bog and maintain its bodily elemental concentrations accumulated during life. Lastly, we believed that pXRFS would verify that the remains

of the Peiting Woman underwent additional elemental incorporation due to post-discovery preservative procedures conducted by curators and staff at her housing museum.

Results

Geographic Origin and Migration Studies Using Strontium

The Sr level measurements for the bone, tooth, and geochemical soil data standards could not be used reliably to determine the geographic origin and migration history of the Peiting Woman. Within the submerged, acidic environment of a raised bog, both bone and tooth material is subjected to both Sr leaching and incorporation. Sr has the same charge and a similar atomic radius to Calcium (Ca) in the form of Sr2+ and Ca2+; thus, sphagnan and humic acid will specifically select for Sr, as they do for Ca.[15] In addition, the increased solubility of hydroxyapatite under environmental conditions with a pH lower than 6.0 greatly facilitates Sr leaching.[16] Finally, Sr incorporation can occur by free Sr ions penetrating the porous composition of the bog body bone and teeth through precipitation and ionic exchange from the surrounding soil. Consequently, the Sr concentration readings taken from raised bog body bone and teeth do not provide accurate reference values for determining the geographic origin and migration of bog bodies.[17]

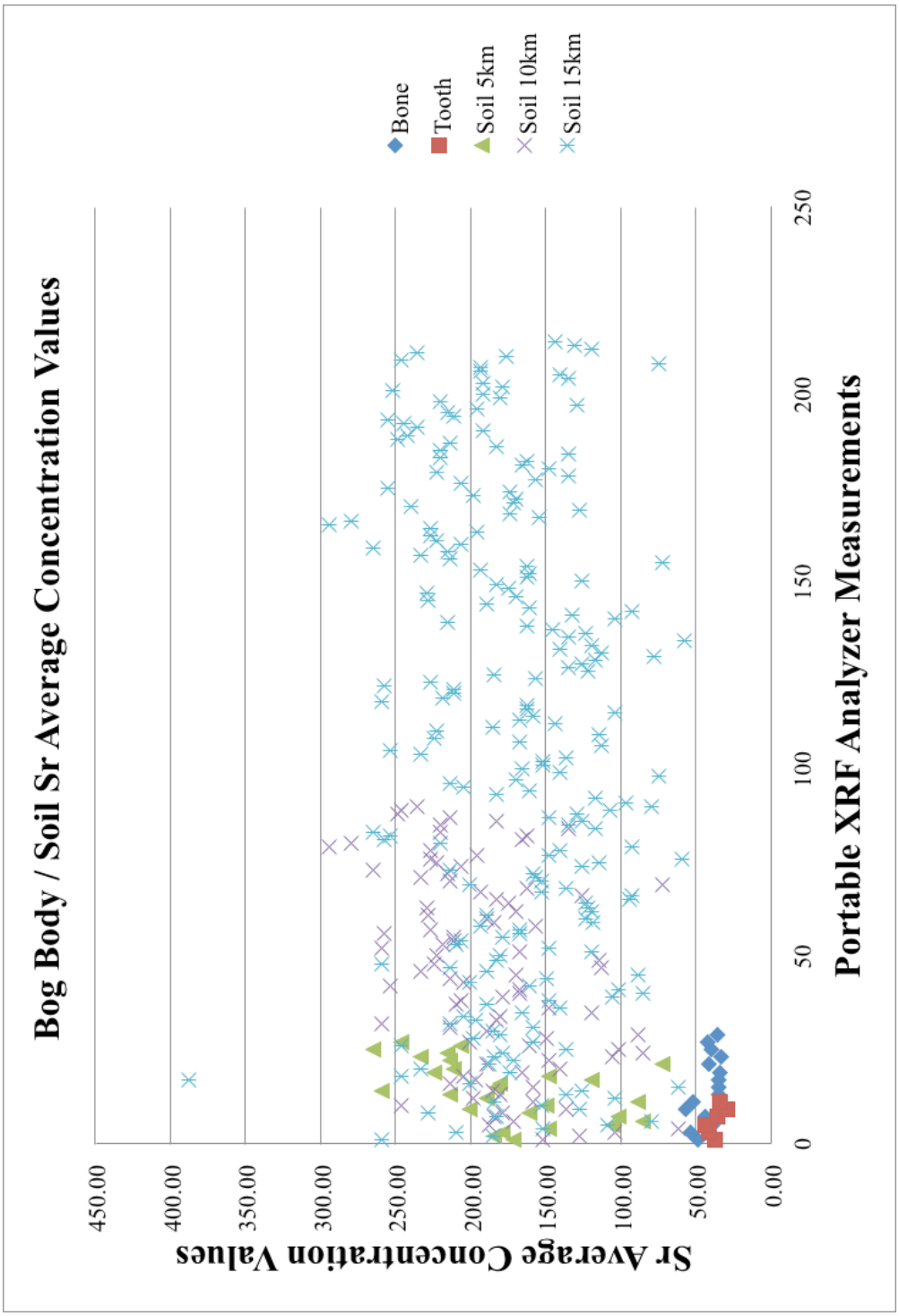
Bone measurements and soil standards were compared to support or refute that bog diagenesis affected the remains of the Peiting Woman (Table 1). Inspection of the data displayed in the corresponding graph and boxplot reveals that the bone and tooth Sr levels do not fall within the soil Sr range (Graph 1, Fig. 4). As a result, one can analyze the data statistically, using the one-way ANOVA and pair-wise comparisons, to demonstrate the extent of significant difference between the body and soil Sr levels. The resulting F-value ($F = 74.05$) is significant for the one-way ANOVA analysis (Fig. 4). To determine which groups demonstrated significant difference, pair-wise comparisons revealed significant differences in both bone and tooth Sr levels from those of the soil ($p < 0.0001$), while bone and tooth levels did not differ significantly from each other ($p = 0.9778$).

These findings, however, may not refute bog diagenesis occurring within the raised bog environment. One could hypothesize that the ranges do not correlate when comparing teeth and bone to soil for Peiting Woman because of her unique burial circumstances. Her wooden burial coffin may have impeded equilibrium of Sr concentration between her skeletal remains and the surrounding raised bog environment. This does not, however, imply that the bone and teeth were unaffected by the surrounding environment. This ancient wooden coffin was not impermeable. Skin and tissue deteriorated considerably from her upper body, mainly the arms and head. These bones had turned a brownish/blackish color, similar to other bog bodies put in direct contact with the water of the raised bog. Acidic bog water may have still seeped into the coffin to some degree, causing leaching of Sr from the bones and teeth and/or free Sr ion exchange. Since the bone and teeth

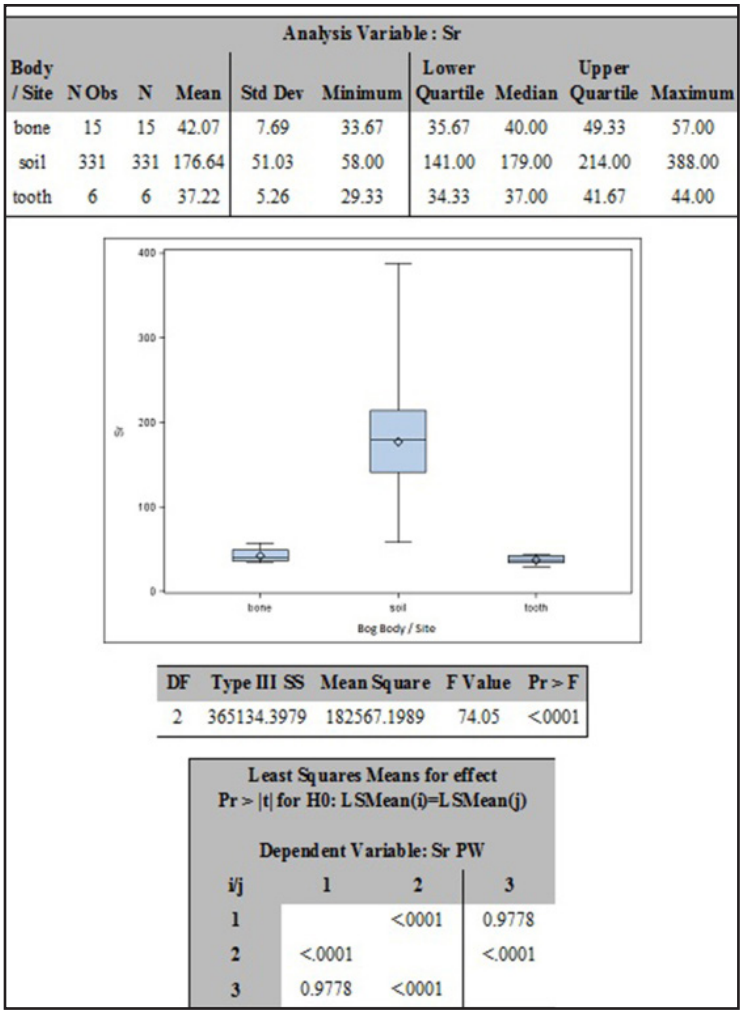
Bog Body and Range/Site Type	**Sr ECR* (ppm)**
Bone Range	22.00 – 57.00
Tooth Range	29.33 – 44.00
Soil 5km Range	73.00 – 265.00
Soil 10km Range	62.00 – 295.00
Soil 15km Range	62.00 – 295.00

*ECR = Elemental Concentration Range

Table 1: Body / Soil Sr Concentration Ranges



Graph 1: Body / Soil Sr Average Concentration Values



Analysis Variable : Sr

Body / Site	N Obs	N	Mean	Std Dev	Minimum	Lower Quartile	Median	Upper Quartile	Maximum
bone	15	15	42.07	7.69	33.67	35.67	40.00	49.33	57.00
soil	331	331	176.64	51.03	58.00	141.00	179.00	214.00	388.00
tooth	6	6	37.22	5.26	29.33	34.33	37.00	41.67	44.00

DF	Type III SS	Mean Square	F Value	Pr > F
2	365134.3979	182567.1989	74.05	<0001

Least Squares Means for effect
Pr > |t| for H0: LSMean(i)=LSMean(j)

Dependent Variable: Sr PW

i/j	1	2	3
1		<.0001	0.9778
2	<.0001		<.0001
3	0.9778	<.0001	

Figure 4: Boxplots, one-way ANOVA, and pair-wise comparisons for bone, soil, and tooth Sr data.

levels did not mimic that of the surrounding bog soil, the wooden coffin may have impeded ionic exchange so all that could affect the bone was Sr leaching. The similar ranges of Sr for both the teeth and bone of Peiting Woman may affirm leaching and/or incorporation, but it may also support that Peiting Woman was not native to her burial site. She may have grown up and even died elsewhere, accumulating similar Sr concentrations in her bone and teeth from that environment, and then been buried in the peat bogs of Peiting. Measuring the bones covered entirely by adhering skin, fat, and muscle found either in the abdomen or lower legs may help to support whether the bones exposed in the coffin were contaminated or not. Unfortunately for these investigations, such examination was not permitted.[18]

Raised Bog Body Elemental Composition

Repeated measures ANOVA with bone locations was added as a random effect to compute 95% confidence intervals (CIs) for the overall mean element values to determine statistically if bog diagenesis affected the other elements of interest. These intervals were then compared to normal human bone elemental

ranges for each element of interest to test whether significant difference occurred among them (Table 2).

Similar to the diagenetic effects on the bone and teeth Sr levels, diagenesis in this bog environment also affected the other elements of interest for the Peiting Woman. Each of the elements of interest demonstrates elemental concentration levels, as well as CIs, that are noticeably, if not exceedingly, greater than levels found in normal human bone, except for Sr (Tables 2 and 3). Such noticeable increases in elemental concentrations suggest that elemental incorporation occurred within the bone and dental remains.

As discussed previously, the Sr concentration levels were affected by bog diagenesis and appears unusable as biogenic indicators of geographic origin and migration for the bog body. From the levels reported, it seems leaching has occurred and the levels are greatly reduced compared to what they were in life for these individuals. This may be supported by Peiting Woman's Sr concentration range demonstrating that its maximum (40.00 ppm) is the minimum range of 40.00 ppm in normal human bone (Table 3). Incorporation due to free Sr ionic exchange is also possible. As the majority of the Sr was leached from the bones, free Sr ions may have also been incorporated. One can suggest that the wooden coffin enclosing the body of Peiting Woman impeded the process of leaching and ionic exchange of free Sr ions, creating a disparity between the surrounding bog Sr levels and the body itself.

Element of Interest	CIs
Cu	17.06 – 71.30
Fe	97.36 - 304.77
Mn	288.03 - 362.61
Mo	5.83 - 14.54
Pb	1.33 - 76.17
Sr	33.90 - 48.90
Zn	389.75 - 1336.36
Zr	30.75 - 52.23

Table 2: 95% Confidence Intervals (CIs) for the mean of Elemental Readings

Element of Interest	Normal HBR* (ppm)	ECR
Cu	0 – 19.63	0 – 100.33
Fe	100.00 – 300.00	58.00 – 463.67
Mn	2.00 – 10.00	231.00 – 457.67
Mo	< 1.00	3.67 – 16.67
Pb	0 – 4.00	6.67 – 147.00
Sr	40.00 – 400.00	29.33 – 40.00
Zn	164.00 – 256.00	251.33 – 1575.33
Zr	0 – 5.00	24.67 – 60.00

*HBR = Human Bone Range
Data sources[19]

Table 3: Elemental Composition of the Peiting Woman

Post-Discovery Preservative Implementation

The remains of the Peiting Woman demonstrate post-discovery preservative implementation. The bone and teeth measured exhibit elevated levels for certain elements of interest at specific sites, which suggests elemental incorporation occurred (Table 4). This bog body may also demonstrate exceedingly high levels of metallic or metalloid elements that are usually found in lower concentrations in human bone and are not found in high concentrations in the raised bog environment. These elements include Co, Sb, and Ti. These specific elements are absent or do not reach levels minimally detectable by the pXRFS analyzer in the raised bog body bones and teeth not treated post-discovery with preservatives (Table 5).

The particular sites on the remains of Peiting Woman that exhibit excessively high elemental concentrations are both capitates, right hamate, right second metacarpal, left first metacarpal, fourth and fifth medial phalanx of the right hand, second proximal phalanx of the left hand, both trochleae of the humeri, both radii, and both ulnae. Concentrations of both Fe and Mn are elevated (Table 4). Comparing CIs between treated and untreated bone statistically supported Fe as an element of differing intervals, but revealed a general overlap when comparing the CIs for Mn (Tables 2 and 6). Co was also found at excessively high concentrations at these specific sites (Table 5). These sites of enhanced elemental levels correspond with the areas of the body wrapped in metal coiling.

Conclusion

Applying pXRFS to the analysis of the Peiting Woman has provided much valuable information about the interactions between the bog environment and the remains of this bog body, and verified that post-discovery preservative treatment occurred during the conservation process. Because diagenesis may have occurred in this raised bog body, we conclude that one cannot apply data involving Sr concentrations to geographic origin and migration studies.

Element of Interest	PDPI Sites ECR	Unaffected Sites ECR
Cu	13.00 – 29.00	13.00 – 100.33
Fe	76.00 – 112978.67	58.00 – 463.67
Mn	101.50 – 786.67	231.00 – 457.67
Mo	5.33 – 26.33	3.67 – 16.67
Pb	9.00 – 89.00	6.67 – 147.00
Sr	22.00 – 49.67	29.33 – 57.00
Zn	68.67 – 1758.67	251.33-1575.33
Zr	26.00 – 51.67	24.33 – 60.00

Table 4: Elemental Concentration Ranges of Post-Discovery Preservative Implementation (PDPI) Sites vs. Unaffected Sites

Element of Interest	Normal HCR	ECR
Co	0.01 – 0.04	38.00 – 127.00
Sb	0.01 – 0.6	<LOD 218.00
Ti	0 – 40.00	<LOD 2435.00

Data sources[20]

Table 5: Additional Elements of Interest in PDPI Analysis

Element of Interest	CIs
Cu	13.74 – 26.16
Fe	333.35 – 1534.26
Mn	236.23 – 368.81
Mo	9.00 – 17.33
Pb	15.51 – 42.91
Sr	32.14 – 39.64
Zn	232.81 – 736.04
Zr	36.54 – 45.46

Table 6: CIs for PDPI Elemental Values

Sr measurement ranges of bone and teeth for the Peiting Woman are not similar to those of the local geochemical soil standards. The similar ranges of Sr for both the teeth and bone of Peiting Woman may affirm leaching occurred to the body, but that the difference between those levels and the surrounding environment may also suggest that incorporation by ionic exchange was impeded, thwarting equilibrium of Sr concentrations between the body and the bog. Thus, it is likely she was not native to her burial site.

Each of the elements of interest demonstrates much higher elemental concentration levels than those found in normal human bone. These findings suggest that elemental incorporation occurred to this raised bog body during interment within the bog. Thus, pXRFS can assist with developing further understanding of the diagenetic effects of the bog to the bog bodies and augment the concept of chemical processes occurring within the bog.

Excessively high elemental values on specific sites on the remains of Peiting Woman suggest post-discovery preservative implementation occurred. PXRFS improves comprehension of archival collection history of bog bodies by identifying sites of post-discovery preservation implementation. This information could aid future preservation efforts by allowing curators to know the elemental composition of undocumented treatment conducted on the bodies. It can also allow one to assess the possibility of reversing or lessening the effects of detrimental preservative treatments to the bog bodies.

Endnotes:

1 Arai 2006, 1-2; Granite and Bauerochse 2010a, 69; Bonizzoni et al. 2011, 252; Kenna et al. 2011, 395; Polikreti et al. 2011, 2889-2890.
2 Haas-Gebhard et al. 2009, 239.
3 Haas-Gebhard et al. 2009, 240.
4 Pestka et al. 2010, 396.
5 Pestka et al. 2010, 396-398.
6 Haas-Gebhard et al. 2009, 240.
7 Pestka et al. 2010, 396.
8 Rehbein et al. 2009, 320.
9 Fauth et al. 1985; Granite and Bauerochse 2010b, 98.
10 Granite, G. 2012, 60; Granite and Bauerochse 2010a, 71.
11 Budd et al. 1998, 121; Nafplioti 2008, 2310.
12 Slovak et al. 2009, 159.
13 Fowler 2007, 22.
14 Granite, G. 2012, 28, 228.
15 Katzenberg 1984, 4; Price 1989, 126-130; C. Vogt, personal communication, May 11th, 2011
16 Price 1989, 150.
17 Granite, G. 2012, 45.
18 Granite, G. 2012, 181.
19 Budd et al. 1998, 132; Emsley 2003, 30, 451; Fauth et al. 1985; Gilbert, Jr. 1977, 92-93; Katzenberg 1984, 14-15; Kenna et al. 2011, 395; Lambert et al 1979, 119; Miculescu et al. 2011, 1118, 1122; Nafplioti 2008, 2311; Polikreti et al. 2011, 2894; Price 1989, 135; Scancar et al 2000, 195; Wildman and Medeiros 2000, 278-280.
20 Barbalace 2006, June 9a; Barbalace 2006, June 9b; Barbalace 2006, June 9c; Budd et al 1998, 132.

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