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# Identification of cremains using X-ray diffraction spectroscopy and a comparison to trace element analysis<sup> $\ddagger$ </sup>

Elisa T. Bergslien<sup>a,\*</sup>, Mary Bush<sup>b</sup>, Peter J. Bush<sup>c</sup>

<sup>a</sup> Earth Sciences and Science Education, Buffalo State College, 271 Science Building, 1300 Elmwood Avenue, Buffalo, NY 14222, USA

<sup>b</sup> Department of Restorative Dentistry, School of Dental Medicine, SUNY at Buffalo, B1 Squire Hall, S. Campus, Buffalo, NY 14214, USA

<sup>c</sup> South Campus Instrument Center, School of Dental Medicine, SUNY at Buffalo, B1 Squire Hall, S. Campus, Buffalo, NY 14214, USA

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#### Abstract

The ability to distinguish human cremains from filler materials can be important in a variety of situations, the most notorious recent example being the Tri-State Crematorium incident. However, the majority of the papers in the recent literature present methods that rely on trace or minor element analysis, usually followed by a statistical or variable cluster analysis, to determine attribution. This approach is inherently risky, as there is significant natural variation in the trace and minor element body burdens within the human population and no real baseline for comparison.

Bones and teeth are a form of calcium phosphate that is part of the mineral group apatite, often referred to as bioapatite. X-ray diffraction (XRD) spectroscopy is a technique that is used to identify minerals by their crystalline structures rather than their elemental composition. The members of the mineral group apatite have a highly flexible hexagonal (6/m) structure that is able to incorporate small amounts of a wide variety of elements. However, its structure, and therefore its X-ray diffraction pattern, is distinct from the crystalline structures of all of the commonly reported filler materials, most of which are composed of some combination of Portland cement, limestone aggregate and quartz sand.

XRD has several advantages over other analytical techniques for the identification of cremains. It is non-destructive, requires relatively small amounts of material, is unaffected by the elemental variations found in bioapatite, and can be used to semi-quantify the components of a mixture, thus determining the relative level of contamination of a sample. This paper presents the results of X-ray diffraction spectroscopy analysis of human cremains and a variety of common filler materials.

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Keywords: Forensic geoscience; Forensic anthropology; Cremains; X-ray diffraction; Elemental analysis

#### 1. Introduction

The ability to distinguish between cremated human remains (cremains) and other powdered materials of similar appearance can be of great importance in a variety of situations, the Tri-State Crematorium incident in Noble, GA, USA [1] being only the most highly publicized recent example. In early 2002, it was discovered that rather than performing the cremations contracted, the owner of Tri-State was dumping bodies unceremoniously around the property. More than 330 bodies were eventually recovered, while the urns many families had received often contained cement dust, silica, rock or other materials. To confuse matters, most bodies received prior to a certain date were actually cremated, and later on, some bodies may have been sent to other facilities for proper cremation. Hundreds of families were uncertain as to the contents of the urns in their possession.

Most of the tools applied to this problem, such as ICP-OES [2], PIXE [3], and AA-MS [4] perform a partial set elemental analysis that must be followed by principle component or cluster analysis to determine whether or not the material qualifies as cremains. There is an inherent liability in this approach that lies not in the analytical technique applied but in the underlying presumption that all cremains will have approximately the same trace element composition. This presumption ignores the intrinsic natural variability of biologic mineral tissues.

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<sup>\*</sup> Corresponding author. Tel.: +1 716 878 3793.

E-mail address: bergslet@buffalostate.edu (E.T. Bergslien).

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Bones and teeth are mineralized tissues composed of calcium phosphate that is similar in composition and structure to the mineral group apatite, thus frequently referred to as bioapatite. The geologically occurring mineral that bioapatite most closely resembles is hydroxylapatite, which has an idealized unit cell formula of  $Ca_{10}(PO_4)_6(OH)_2$  [5,6]. The hexagonal crystalline structure of apatitic minerals is extremely flexible and allows a wide range of substitutions, though each of these substitutions much fulfill the overall charge balance of the mineral and fit structurally into the crystalline lattice. Geologic apatite can incorporate half of the elements in the periodic table into its structure [6].

Bioapatite also contains many elements and molecular species other than calcium and phosphate, but from a more limited subset than geological apatite. For example, fluorine  $(F^-)$  and chlorine  $(Cl^-)$  commonly substitute for the hydroxyl ion  $(OH^-)$ . Modern use of fluoridated tooth paste and water alters tooth enamel to fluorapatite, which is more resistant to acid. This can also occur postmortem in bioapatite that is exposed to fluoridated water. Chorine, on the other hand, is rarely found in significant amounts in bioapatite. The reported or known ions substituting for calcium  $(Ca^{2+})$  in bioapatite include Na<sup>+</sup>, K<sup>+</sup>, Fe<sup>2+</sup>, Zn<sup>2+</sup>, Sr<sup>2+</sup>, Mg<sup>2+</sup>, Cd<sup>2+</sup> Ba<sup>2+</sup>, Mn<sup>2+</sup>, Pb<sup>2+</sup> and ions reported or known to substitute for phosphorous  $(P^{5+})$  include As<sup>5+</sup>, V<sup>5+</sup>, Si<sup>4+</sup>, S<sup>6+</sup>, and Sb<sup>5+</sup> [6,7]. Many of these elements are essential nutrients that are stored in the skeleton while others are toxic. Due to the wide range of possible substitutions, elemental analysis of human remains, especially when the test set is limited, can be ambiguous. The level of trace elements available to be incorporated into the mineralized tissues of an individual is highly dependent on two main factors. First is local geology, which governs the trace element loads found in the local water supply, in the soils in which local crops are grown, and in the dust particulates in the air that you breathe.

It had been assumed by some that the food distribution systems that now exist in the United States and other industrialized nations, would homogenize trace element loads in the various nations, but more recent work shows that this is not truly the case. Local geology still plays a significant role in determining the trace element loads of individuals living in industrialized nations and is arguably the primary factor for individuals living in pre-industrialized nations or in isolated rural areas [8].

Diet does play an important role in determining bodily trace element loads. Studies in animals have demonstrated that

Table 1

Listing of average peak position in  $2\theta$  (°) and relative peak intensity<sup>a</sup> for the **three greatest intensity XRD peaks** (noted in **bold**) of each of the study materials, plus any peaks located near the diagnostic apatite peaks described in the text

Rel. Int. (%)	Position (2 $\theta$ (°))	Rel. Int. (%)	Position (2 $\theta$ (°))	Rel. Int. (%)	Position (2 $\theta$ (°))	Rel. Int. (%)	Position (2 $\theta$ (°))
Bone average		Dentin		Synthetic hydroxylapatite		Plaster of paris	
16.2	10.989	18.3	10.879	1.9	11.010	100.0	14.829
36.9	26.021	47.3	25.941	100.0	18.317	47.2	25.744
100.0	31.920	100.0	31.809	11.9	26.128	3.7	26.711
49.7	32.270	65.0	32.234	24.0	31.977	76.1	29.815
46.8	32.662	58.8	32.944	14.6	32.432	5.6	31.002
49.5	33.306	24.0	34.094	12.9	33.154	1.3	31.461
22.3	49.625	30.7	49.510	6.5	49.707	12.8	32.036
						3.0	33.054
Polyblende		Quick crete		Charcoal ash		Wood ash	
2.4	11.722	66.9	26.683	16.5	26.728	5.9	26.712
0.6	25.329	82.9	29.486	100.0	29.501	100.0	29.542
8.9	27.523	8.7	30.962	3.3	31.588	1.9	31.958
100.0	29.509	8.4	32.274	0.3	34.866	1.8	32.318
33.8	31.042	10.3	32.707	15.5	39.532	1.1	33.168
14.9	32.223	2.8	33.289			1.9	34.142
11.0	32.313	19.4	34.447			14.3	39.556
13.0	32.607	100.0	36.601			13.8	47.627
13.4	34.389	62.4	75.666			14.1	48.638
Sheetrock, light		Sheetrock, regu	lar	Versabond mor	tar	Post set	
1.3	8.540	98.3	14.837	7.2	11.734	3.6	10.565
88.2	14.886	50.8	25.761	46.7	26.741	100.0	20.964
59.9	25.814	16.2	26.901	100.0	29.525	3.3	26.322
2.9	26.753	100.0	29.822	26.7	31.063	8.3	26.750
50.7	29.567	46.0	29.917	36.3	32.234	14.5	29.468
100.0	29.867	10.2	31.885	26.4	32.323	4.2	31.041
14.2	31.928	2.6	33.046	31.0	32.622	4.5	32.357
3.7	33.081	9.8	49.369	6.4	33.476	5.4	32.766
12.9	49.403	4.6	49.509	31.9	40.389	2.6	33.349
8.7	49.535					1.6	33.925
						76.2	42.543
						36.6	42.662

<sup>a</sup> Relative intensity (Rel. Int. (%)) is calculated by dividing the intensity of the peak at the indicated angle by the intensity of the highest peak and multiplying by 100.

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103 Sr/Ca ratios generally decrease as one moves from bedrock  $\rightarrow$  soil  $\rightarrow$  plants  $\rightarrow$  herbivores  $\rightarrow$  carnivores [9]. Since 104 humans are typically omnivores, their Sr/Ca ratio should lie 105 somewhere between that of herbivores and carnivores, though 106 107 marine and fresh water shellfish, and marine fish, have very 108 high levels of strontium, thus a diet rich in seafood would elevate Sr levels. Based on this vegans should have higher 109 strontium levels than someone who eats a significant amount of 110 111 red meat, and people who eat large quantities of seafood should also have very high strontium levels. Kuo et al. [10] found 112 113 significant positive correlation between the levels of Ni, Co, Mn, Cr, Mg, Al, Ag, and Ca in bone and seafood consumption. 114 They also found a negative correlation between Zn and 115 frequency of alcohol consumption, and a positive correlation 116 between Cu and fruit consumption. Thus significant variations 117 in diet, such as macrobiotics or veganism, or high levels of 118 seafood or meat consumption, should have a discernable impact 119 on an individuals trace element load. 120

The other major source of trace elements is the anthropogenic load in the environment, from such sources as power plant, automobile and industrial emissions [11]. In general, people who live in urban areas will have higher loads of heavy metals in their bodies than people who live in rural areas. This is also true of people who live in close proximity of a factory, mine or power plant, and obviously people who work in one of these industries can have a significant body burden of associated trace elements. However, taking even a detailed personal history may not reveal why any one person might have an unexpectedly high level of a particular trace element. For people other than industrial workers, they may never even know if they had been exposed. As noted by Brooks et al. [2] metals carried in the body in the form of bullets, and presumably other metal fragments as well, also increase the bodily loads.

Thus, the total trace element load of any one individual is the summation of a variety of exposures over the course of their life. The rate at which the bodily trace element load changes is a 138



Fig. 1. XRD diffractograms from  $2\theta 30^{\circ}$  to  $40^{\circ}$  showing diagnostic  $31.9^{\circ}$  apatite peak followed by three additional peaks (long bone1 sample), and comparison to other study materials.

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139 point of contention, though most authors suggest bone remodeling rates of 7-10 years. However, for people who 140 have had a high level of exposure to bone seeking elements, the 141 elemental "half-life" can be significantly longer. Trace 142 143 elements can be released from bone into the blood stream only to be re-incorporated into bone. The best understood 144 example of this is with lead, which is commonly recycled 145 through the blood stream back into bone, giving it a "half-life" 146 147 of between 15 and 30 years [12]. Similar behavior is believed to exist with other trace elements, though the rates of exchange are 148 149 thought to be significantly different.

This means that someone who has recently moved into an 150 area from a significantly different environment could have a 151 notably different body burden of trace elements than the locals, 152 and that will take years or even decades to equilibrate with the 153 local environment. A pilot study by Gulson and Gillings [13,14] 154 using permanent and deciduous teeth demonstrated that 155 individuals from eastern Europe, southern Europe, and 156 Australia showed completely different lead isotope composi-157 tions. Someday, with the development of a sufficient reference 158

database, trace elemental analyses may have several interesting potential applications. Unfortunately, at the current time, reliable and well-sourced data on the minor and trace element composition of human bone is quite scarce [15,16]. Thus, with no reliable baseline for comparison and relatively little understanding of how trace element loads vary in populations, relying on such analysis for identification of cremains is fraught with uncertainty. One significantly more reliable method would be to determine the mineralogy of a sample using X-ray diffraction spectrometry.

2. Methods

X-ray diffraction (XRD) spectrometry is one of the most powerful analytical tools available for identifying unknown crystalline substances [17]. All crystals are composed of regular, repeating planes of atoms that form a lattice. When coherent X-rays are directed at a crystal, the X-rays interact with each atom in the crystal, exciting their electrons and causing them to vibrate with the frequency of the incoming radiation. The electrons become secondary sources of X-rays, re-radiating this energy in all directions at the same wavelength as the incident beam, a phenomenon called coherent



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Position [°2 Theta]

Fig. 2. XRD diffractograms from  $2\theta 20^{\circ}$  to  $30^{\circ}$  showing diagnostic  $26^{\circ}$  apatite peak (long bone1 sample), and comparison to other study materials.

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Fig. 3. XRD diffractograms from  $2\theta$  5° to 15° showing diagnostic 11° apatite peak (long bone1 sample), and comparison to other study materials.

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scattering. These secondary, or diffracted X-rays, which can be thought of as waves traveling in all directions, form interference patterns, much like interference patterns formed by dropping two rocks into water. This interference may be constructive, forming larger waves, or destructive, canceling out the waves entirely. The pattern of interference created depends on the distance between atomic layers, chemical composition, and the angle that the



Fig. 4. Detailed comparison of XRD diffractograms for geological and biological apatite. Note peak sharpness and intensity of geological sample in comparison to cremains.

X-rays diffract away from the atoms, thus it indirectly reveals a crystals structure.

Using an XRD spectrometer, the diffraction pattern created by constructive interference is recorded by a beam detector as the X-ray tube and the detector are rotated around the sample. The relationship between angle at which diffraction peaks occur  $(2\theta(^{\circ}))$  and the inter-atomic spacing of a crystalline lattice (*d*-spacing) is expressed by Bragg's law:  $n\lambda = 2d \sin \theta$ . For historical reasons, XRD-traces, or diffractograms, are expressed in degrees two theta  $(2\theta(^{\circ}))$ .

Since each crystalline structure is unique, the angles of constructive interference form a unique pattern. By comparing the positions and intensities of the diffraction peaks against a library of known crystalline materials, samples of unknown composition can be identified. This works even with mixtures of materials, where each separate crystalline material can be identified and semi-quantified.

Crystallographically, apatite is easily distinguished from the commonly used filler materials, such as concrete or sand. X-ray diffraction has several advantages to many of the other methods currently employed for cremains identification. It is not destructive, which means that the same sample can be examined multiple times by various laboratories, if necessary, and little to no sample preparation is required. If the sample is identified as being cremated remains it can be returned to a family in essentially its original condition.

The bone and dentin samples used were sub-samples from cadavers donated to the University at Buffalo medical program that were cremated at 1010 °C (1850 °F) for 2.5 h and then processed into a coarse powder. The comparison samples were collected individually from packages purchased at local hardware

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Fig. 5. Comparison of XRD diffractograms from  $2\theta 60^{\circ}$  to  $90^{\circ}$  for geological and biological apatite. Some points of distinction are highlighted with ovals.

stores, from a home fireplace, and from a barbeque grill in a public park. Each of the samples was sieved through a No. 4 (4750  $\mu$ m) screen, to remove and separate out the coarsest particles, but otherwise untreated.

All of the samples were then loaded directly into back-mounted aluminum sample trays and analyzed using a theta-theta PANalytical X'Pert MPD X-ray diffractometer equipped with a Cu-tube. The system uses a X'Celerator High Speed Detector system and has a diffracted beam monochromomator. Each sample was analyzed at 45 kV and 40 mA from 5° to 120° in scanning mode with a step time of 200 s. Identification was performed using X'Pert Highscore Software and the ICDD database.

In all samples examined to date, cremains can clearly be

differentiated from filler materials using XRD analysis. As seen

in Table 1, bioapatite, identified as the bone and dentin samples,

can be identified by a highest intensity peak located at

### 3. Results

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approximately  $2\theta$  31.9°, closely followed by three more high intensity peaks located between  $2\theta$  32° and 34° (Fig. 1). Apatite also has weaker intensity diagnostic peaks located at approximately  $2\theta$  26° (Fig. 2) and  $2\theta$  11° (Fig. 3). The locations and intensities of these peaks clearly differentiate apatite from the vast majority of the study materials that are for the most part composed of calcium carbonates, silicates, or sulfates. For example, plaster of paris, quick crete, charcoal ash, wood ash and both kinds of sheetrock all lack peaks near  $2\theta$  11° (Fig. 3). If a sample lacks any of the diagnostic peaks listed and/or the relative peak heights are significantly different, then the sample is not apatite, or the sample is contaminated. 223

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The only noteworthy difficulty encountered lies in clearly differentiating bioapatite from geologically occurring apatite. Here the differences are more subtle, but based on the examples studied to date, there are clear points of distinction. The first

Table 2

Q1 Listing of average peak position in  $2\theta$  (°) and relative peak intensity<sup>a</sup> for the **three greatest intensity XRD peaks** of some of the geological apatite samples examined, plus any peaks located near the diagnostic apatite peaks described in the text

Apatite powder	1	Geoapatite 2	eoapatite 2		Geoapatite 3		Geoapatite 4	
Rel. Int. (%)	Position (2 $\theta$ (°))	Rel. Int. (%)	Position (2 $\theta$ (°))	Rel. Int. (%)	Position (2 $\theta$ (°))	Rel. Int. (%)	Position $(2\theta (^{\circ}))$	
11.33	10.9569	6.99	10.9885	13.82	10.9864	4.04	11.0668	
11.33	10.9569	6.99	10.9885	13.82	10.9864	4.04	11.0668	
38.86	25.92	100	26.0037	75.49	25.9653	28.96	26.0148	
30.05	29.4768	61.45	31.9258	33.8	29.136	100	32.0781	
100	31.9365	29.12	32.0238	97.09	31.9596	46.12	32.1722	
48.23	32.0363	39.64	32.3209	43.57	32.0566	64.36	32.3892	
34.13	32.2817	52.45	33.0668	67.92	32.3147	28.84	32.4852	
46.26	33.099	91.9	53.3072	29.74	32.4112	62.81	33.2539	
57.02	49.5975	45.79	53.4523	38.48	33.1318	28.25	33.3515	
				39.52	34.1992			
				30.72	49.6149			
				68.56	53.2601			
				34.06	53.4058			
				100	63.2631			
				49 33	63 4377		11.0668 26.0148 <b>32.0781</b> 32.1722 <b>32.3892</b> 32.4852 <b>33.2539</b> 33.3515	

<sup>a</sup> Relative intensity (Rel. Int. (%)) is calculated by dividing the intensity of the peak at the indicated angle by the intensity of the highest peak and multiplying by 100.

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Fig. 6. Comparison of XRD diffractograms from  $2\theta 25^{\circ}$  to  $70^{\circ}$  for geological and biological apatite. Some points of distinction are highlighted with ovals.

point of distinction lies in peak shape and intensity. The better developed the crystalline structure of a material, the tighter the peaks and the higher the intensity. Poorly crystalline materials have wider peaks with lower overall intensity. Geologically occurring apatite is composed of well-developed crystals, while bioapatite is poorly crystalline (Fig. 4). This is especially apparent in the  $2\theta > 50^{\circ}$  section of a diffractogram where the geological apatite generally still displays additional well developed peaks while the biological apatite does not (Fig. 5, note the scale).

The second point of distinction is due to the greater chemical variation in geologically occurring apatite, which results in a greater number of peaks, and variations in peak location and intensity (Table 2) (Figs. 5 and 6). With the samples examined thus far, these points of distinction have been successfully used

to differentiate biological from geological apatite samples. However, geological apatite samples examined thus far have been prepared from pure apatite crystals. The colors of the powdered samples are aqua blue, pale green and pale red, which would be unusual, though not unheard of, colors for cremains. Commonly occurring geological apatite would be found as an accessory mineral intimately mixed with other minerals such as quartz, feldspars, opal, chert, calcite, dolomite, glauconite, illite, montmorillonite, and zeolites, which are easily distinguishable using XRD [18].

Though it seems unlikely that someone would secure a large amount of pure apatite crystals to grind into powder in order to fill an urn, a trace elemental analysis can be coupled with XRD in order to clearly separate geological apatite from biological apatite. The trace elements that occur in geologic samples are

Table 3 Selected results from laboratory X-ray fluorescence elemental analysis of study materials

	Cremated bone	Enamel	Geologic apatite	Wood ash	Charcoal ash	No mix concrete	Sheetrock (light)	Quick crete	Grout (white)	Versabond mortar	Plaster of paris
Ag		93	124 😑					62			
Ba			406 🖵	121	284	189		155			73
Bi			33		6						
Ca	558237	451672	550228	430120	289285	411599	310781	356499	706723	474210	320157
Co								178			
Cr			140		46	84					
Cu	ND	70	ND	360	44	ND	ND	40	ND	ND	ND
Fe	145	231	780	2305	9710	11086	1904	11948	786	715	1497
Hg		62									
Κ	2605	3812		108084	23177	9997	8322	7104			1635
Mn			98	344	1513	210	37	281			
Mo	ND	29	ND	13	12	ND	ND	ND	ND	ND	12
Ni		85	241								
Р	437047	302432	312334	161125							
Pb		22	89	200	15					11	
S				34792			237518				419432
Sr	85	79	2680	1476	276	643	530	242	237	130	1130
Ti					1738	844		1252	32296	409	
Zn	31	560	32	1150	149	94	26	82	59	17	38

All values in parts per million, a blank space means that element was at less than the lower limit of detection for the instrument.

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Fig. 7. XRD diffractogram from  $2\theta 24^{\circ}$  to  $42^{\circ}$  of the *in situ* trabecular material of a fossilized Ursus (bear) vertebrate. Note silica infill and recrystallization of bioapatite. The poor quality of the trace is due to the unpowdered, spongelike nature of the interior of the vertebrae.

different in character and in amount than those that occur in bioapatite [6,7] (Table 3).

#### 4. Discussion

273 Though the sample set examined thus far is relatively small, it is clear that XRD can be used to easily differentiate cremains 274 275 from the vast majority of common filler materials. For the majority of conditions, XRD would be a more appropriate technique to apply than a trace element analyses, where the natural variation in human trace element loads could cause significant ambiguity. In instances where biological apatite must be differentiated from geological apatite, elemental analysis can be coupled with XRD to conclusively determine an unknown samples source. An additional strength of XRD is that exposure of cremains to chemical weathering, often referred to as digenesis in some of the literature, does not significantly alter the crystalline structure while the trace element composition 285 can be extensively altered. This is true even for some fossilized 286 287 bone that has truly undergone significant digenesis, or

chemical, physical and biological change after deposition Q1 and through lithification (transformation into sedimentary rock) (Fig. 7). This example also demonstrates that XRD cannot be used to differentiate human cremains from the powdered cremains of other vertebrates.

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Brooks et al. [2] raised a significant point concerning the definition of cremains as contaminated, i.e. what percent of filler material would render the whole sample non-cremains, and how to tell. One of the advantages of XRD analysis is that it is semi-quantitative, thus the relative proportions of biologic apatite to filler material can be established. Each of the materials used in the study, excluding geological apatite, was mechanically mixed 50-50 by volume with cremains.

Unsorted, untreated samples of each mix were packed into a back-mounted aluminum sample stage and analyzed as previously described. Differences in particle size do significantly effect the accuracy of semi-quantitative XRD analysis, but this initial run was intended to simulate simply taking a subsample directly from an urn for examination. In all cases, XRD analysis could clearly distinguish apatite in the mixtures, with semi-quantification values ranging from 32 to 64%. For example, an analysis of a 50-50 by volume mixture of wood ash collected from a residential fireplace with cremated human remains returned values of 64% fluorapatite, 32% calcium carbonate and 4% lime using ICDD reference files. The resultant diffractogram is a composite of the diffractograms for wood ash and for cremains (Fig. 8). If such measures are called for, quantification results can be improved by grinding and sieving the samples, or by performing an analysis using quantification reference materials. This is another instance were trace elemental analysis coupled with XRD could provide significant additional information where conditions necessitate.

As this work has demonstrated, XRD analysis has several significant advantages over trace elemental analysis for identification of human cremains. Significant advances in hardware, such as solid-state detectors and theta-theta configurations, plus the development of robust identification and database software,





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have greatly improved the speed and accessibility of XRD.
Hopefully this analytical technique will see greater application in
the field of forensic science in the future.

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