



A TEST OF A NON-CONSUMPTIVE NUCLEAR FORENSICS TECHNIQUE USING PHOTON ACTIVATION ANALYSIS OF FOSSILS AND SOURCE MATRICES

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ABSTRACT

Destructive elemental analysis techniques are common tools in paleontological studies. This study successfully tested the non-destructive technique of photon activation analysis (PAA) for multi-element analysis of fossils and their source matrices. Sample pairs were tested to determine if provenance of fossils could be correlated through their elemental composition. PAA was applied to four pairs of samples, a fossil and a source matrix, each with a different stratigraphic/geographic provenance. Thirty-one total elements were identified: Na, Mg, Ca, Ti, Cr, Mn, Co, Ni, Zn, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ag, Cd, Sn, Sb, Te, I, Cs, Ba, Ce, Sm, Tl, Pb, U. In each sample 19-26 elements were identified. The lowest concentration detected was 150 ng/g for tellurium. Principal component analysis was applied to the trace elements of the samples. The potential for provenance determination was inconclusive, due to the small number of samples; however, sample pairs showed some separation based on provenance and fossils and matrices were readily distinguishable after analysis.

Keywords: Elemental concentration analysis; photon activation analysis; nuclear forensics; non-destructive; non-invasive; non-consumptive; fossil provenance

RESUMO [in Portuguese]

As técnicas de análises elementares destrutivas são ferramentas comuns nos estudos paleontológicos. Este estudo testou com sucesso a técnica não-destrutiva de análise por ativação de fótons (AAF) para análises multi-elementares de fósseis e da suas matrizes rochosas. Pares de amostras foram testados para determinar se a proveniência dos fósseis poderia ser correlacionada através da sua composição elementar. AAF foi aplicada a quatro pares de amostras, um fóssil e a sua rocha matriz, cada um com uma proveniência estratigráfica/geográfica diferente. Foram identificados um total de trinta e um elementos: Na, Mg, Ca, Ti, Cr, Mn, Co, Ni, Zn, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ag, Cd, Sn, Sb, Te, I, Cs, Ba, Ce, Sm, Tl, Pb, U. Em cada amostra foram identificados 19-26 elementos. A concentração mais baixa detectada foi de 150 ng/g de telúrio. Análise do componente principal foi aplicada aos elementos traço das amostras. O potencial para determinação de proveniência foi inconclusivo devido ao número reduzido de amostras, no entanto, os pares de amostras mostraram alguma separação baseada na sua proveniência e os fósseis e matrizes foram facilmente distinguíveis após as análises.

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INTRODUCTION

The elemental composition of fossils can be analyzed to produce detailed information about the past. Elemental composition can provide information on fossil provenance, environmental and atmospheric conditions during deposition, and ecological and trophic information about various organisms.

There are several techniques for analyzing the elemental composition of fossils: X-ray fluorescence, neutron activation analysis, and various mass spectroscopy and chemical techniques. Most of these techniques are inherently destructive, while others are destructive for practical applications, such that samples need to be ground into a fine powder for bulk analysis of larger samples. Paleontology relies on the physical characteristics in addition to the elemental composition; thus, a non-destructive, or at least non-invasive, alternative is needed for analyzing the elemental composition of fossils without doing harm to this limited and valuable resource. Due to this requirement, samples cannot be altered to create more uniform geometries for analysis. Internal monitors, which provide more accurate measurements in activation analysis techniques, also cannot be used.

Photon activation analysis (PAA) is a reliable technique that has been shown, in certain applications, to be non-destructive and useful. This study focused on the utility of PAA for determination of stratigraphic and geographic provenance of fossils. Provenance determination is important for many reasons. Many fossils are collected illegally from Federal land. It would be useful to develop a reliable method to determine provenance of fossils and determine if they were illegally obtained. Museum collections also contain many unidentified fossils. This is due to the lack of standardized collection procedures in the past, as well as the collection and donation of fossils by amateur collectors. Reliable provenance determination would allow these unidentified fossils to be properly matched to similar fossils in collections. Finally, PAA could allow for correlation of geological formations. PAA may be able to determine the stratigraphic origin of a fossil with more precision, which would create better stratigraphic and temporal resolution.

Fossil Provenance

Published research on the provenance of fossils tends to focus on the rare earth element (REE) patterns of fossils (Trueman, 1999; Patrick et al.,

2007; Suarez et al., 2007). The focus on these elements is due to the overall stability of the REEs after the initial diagenetic uptake. The REE concentrations may change over time, but the ratios mimic the average composition of the early diagenetic environment, excluding cerium and europium, which are sensitive to redox conditions (Moses, 2010). Typical REE concentrations are well above the typical concentrations detected with PAA (Trueman et al., 2004, 2008). Although REEs have been shown to be important for provenance determinations, this study looked at concentrations of all the elements identified for provenance determination, in addition to REE patterns.

Photon Activation Analysis (PAA)

Applications

No published research was found on the use of PAA with fossils; however, as mentioned in the introduction, PAA has been used in many applications (Segebade et al., 2017). It has been used to analyze rock and ore samples (Kato et al., 1973; Alsufyani et al., 2014; Tickner et al., 2015), atmospheric particulates (Aras et al., 1973; Alian and Sansoni, 1985), sediment (Masumoto and Yagi, 1987; Mizera and Randa, 2009), and meteorites (Ebihara et al., 2000; Randa et al., 2003), as well as some geochemical studies (Randa et al., 2007; Randa et al., 2007). Typical applications of PAA can readily identify 10-15 metal elements per sample; however, it has been used to identify 20 elements in marine sediment and lobster hepatopancreas materials (Landsberger and Davidson, 1985), and 30 elements in market-garden soils (Chattopadhyay and Jervis, 1974). Detection limits for PAA depend on some nuclear parameters of the element, sample, irradiation conditions and the detector efficiency of the spectrometer. Depending on the half-life and background present, the detection limit has been shown to be as low as 1.0 ng/g (Schulze and Segebade, 2005). Another advantage of PAA is that in some cases it can be used not only to determine concentrations of each element as a whole, but concentrations of individual isotopes, too. In many cases PAA is non-destructive (Borgwardt and Wells, 2017) macroscopically. It can cause microscopic damage to organic samples, but has been shown to do a negligible amount of damage to samples with a solid crystal structure (Thompson, 2005), when used at energies similar to those used in this work. However, all samples have a higher level of radioactivity after use of PAA. This

reduces over time, but it can impact further handling and analysis.

Description

Photon activation analysis requires high flux of energetic photons which can be produced with electron accelerators equipped with a bremsstrahlung converter (Starovoitova and Segebade, 2016). The photons induce photo-nuclear reactions with the nuclei of the atoms in the sample. These reactions eject various nucleons from the nucleus, mostly turning a stable nuclide into an unstable one. The products of the reaction eventually beta-decay to a stable nuclide. Typically, this stable nuclide is first populated to an excited state by the beta-decay and gives off photons to reach its ground state. These characteristic photons of each nuclide can be detected using a germanium detector. Most radionuclides emit a characteristic set of photon energies with varying probabilities. These sets of energies, probabilities, and lifetimes can be used to determine which nuclear species are represented in the spectrum.

Such spectra can be used to calculate concentrations in each sample if a calibration material of well-known element concentrations is irradiated with the samples. If the specific isotope concentrations of the calibration material are known, then individual isotope concentrations can also be calculated for some elements.

Potential Applications in Paleontology

PAA's ability for non-consumptive, multi-element analysis makes it a suitable technique for many studies in paleontology and geology. In addition, select cases allow for the potential isotopic resolution of PAA (Peisach, 1973), making it a useful tool for several other types of paleontological studies. Isotopes of various elements have been used to study an organism's trophic level, diet, migration patterns, and associated climate (Kohn et al., 1999). Stable isotopes have also been used for paleoenvironmental reconstruction (Keatings et al., 2002). In addition to these, trace elements have been used in numerous paleontological studies (Bar-Matthews et al., 1993; Kohn et al., 1999; Schutkowski et al., 1999; Keatings et al., 2002; Trueman and Tuross, 2002). PAA is a broad spectrum multi-element analysis tool with low detection limits. These factors, including the non-destructive nature of the technique, make PAA a very promising tool for paleontology.

EXPERIMENTAL METHODS

Sample Preparation

Four sample pairs of a fossil and its corresponding source matrix were examined. A bulk analysis of the samples was performed; no aliquots were analyzed. The provenances of the samples are listed hereafter, with ages and method of dating in parentheses. The samples were cleaned at the excavation site and not subject to any post-excavation cleaning or preparation. No adhesives or stabilizers were used.

The first pair was a small fragment of mammalian limb bone and its consolidated matrix from the upper Eocene Chadron Formation (~36-34 million years old, faunal assignment; Ostrander, 1985; Prothero and Emry, 2004), found at Raben Ranch, Nebraska. The second pair, from Flint Hill, South Dakota, consisted of a small horse tooth and its consolidated matrix sample from the lower Miocene Batesland Formation (~19-17.5 million years old, faunal assignment) (Martin, 1976; Tedford et al., 2004). The third pair was from 13 miles west of Sundance, Wyoming. It was from the upper Jurassic Morrison Formation (~approximately 153-145 million years old, faunal correlation and provenance) (Kowallis et al., 1991; Foster and Martin, 1994). This pair contained a fragment of sauropod dinosaur limb bone and a matrix sample of indurated mudstone. The final pair was acquired approximately 50 km northwest of Chamberlain, South Dakota. It was from the upper Cretaceous (~approximately 81-75 million years old, provenance) (Obradovich, 1993). It contained a fragment of mosasaur and a matrix of iron-manganese concretion from the black shale of the DeGray Formation, Pierre Shale Group. This information is summarized in Table 1.

In addition to these samples, 2.5 cm squares of nickel foil with a thickness of 25 μm were used as flux monitors. The whole samples were stacked in a line, with these foils placed between the samples, as well as on the ends. All of these samples had their masses determined using a high precision scale. A schematic of the setup can be seen in Figure 1. A calibration material was also inserted in the stack and the entire stack was wrapped in aluminum foil to hold samples in place during irradiation. The calibration material (URM-1) used was a waste incineration fly ash from Berlin (Schmitt et al., 1980). The fly ash contained over 50 elements with varying, well-known concentrations. The ash was in an

aluminum container and had dimensions similar to the samples.

Irradiation and Analysis

Two separate irradiations were performed. Each irradiation consisted of two of the sample pairs using the external flux monitor method (Segebade et al., 2013). These were performed at the Idaho Accelerator Center. One hour irradiations were performed with nominal electron beam energy of 21.3 MeV and a power of 1.02 kW using the 25B accelerator. The beam current was 80 μ A with a 150 Hz pulse rate and a 4 μ s pulse width. A tungsten converter was used.

After the irradiation, the samples were allowed to cool for approximately 18 hours before spectra were obtained. Multiple counts were performed with a Canberra GC3318 high purity germanium detector approximately one day, one week, and one month after the irradiation for each sample. The detector had an efficiency of 33% and a resolution of 1.8 keV (FWHM) at 1.3 MeV. Count times were approximately one hour, 16 hours, and 16 hours, respectively. These counts were done at position A of detector D at the IAC, which is right next to the detector. Detector calibration and efficiencies were determined with standard gamma ray sources including thorium. The spectra were analyzed to match each peak to a corresponding reaction and parent nuclei. Spectra were analyzed by hand using the MPA3 software (Fast ComTec, 2010) and checked with the automatic peak fitting software GammaW (Westmeier, 2009). After this, concentrations in each sample were calculated for every element possible. Calculations were done by hand and checked with the PAAS software (Sun et al., 2012). By hand calculations were done using the

single peak fitting function in the MPA3 software. This information was then placed into an excel spreadsheet and used to calculate concentrations and uncertainties.

Data Processing and Analysis

For a comprehensive review of the process for calculating concentrations, see the book or review papers by Segebade and others (Segebade et al., 1988; Schulze and Segebade, 2005; Masumoto and Segebade, 2006). PAA data analysis is straightforward when using a calibration material and external flux monitors. The final equation (1) used to calculate concentrations using the external flux monitor method with a calibration material is:

$$c_s = \frac{P_s m_{CM} c_{CM} e^{-\lambda t_{CM,d}} (1 - e^{-\lambda t_{CM,c}}) \phi_{CM}}{m_s P_{CM} e^{-\lambda t_{s,d}} (1 - e^{-\lambda t_{s,c}}) \phi_s} \quad (1)$$

Here, the subscripts *s* and *CM* correspond to the sample being analyzed and the calibration material with well-known concentrations. *P* is the counts in the peak in the gamma spectrum, *m* is the mass, *c* is the concentration of the element which corresponds to the peak being analyzed. Times are denoted by *t*, the subscripts *d* and *c* denoting decay time between irradiation and counting and counting time, respectively. ϕ 's are the flux scaling factors, which are used to correct for different intensities of photon flux seen by samples. Due to different thicknesses and positions relative to the beam, the flux, and subsequent induced radiation, will vary for each sample. This is monitored and corrected for using flux monitors. See Segebade et al., (2013) for the procedure for determining flux scaling factors.

Table 1: Table of the four sample pairs used in this research. The geographic and stratigraphic provenances are listed. The masses for the fossil and source matrix of each pair are listed as well.

Site	Age (Myr)	Fossil Mass (g)	Matrix Mass (g)
Raben Ranch, NE	36-34	26.17	12.82
Flint Hill, SD	19-117.5	11.86	11.07
Sundance, WY	153-145	16.26	56.37
Chamberlain, SD	81-75	12.64	3.51

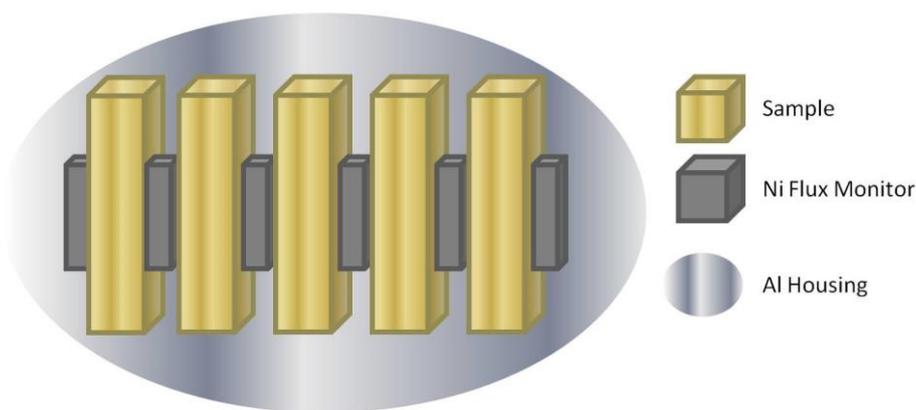


Figure 1: Schematic of the samples and flux monitors during irradiation.

Principal Component Analysis (PCA)

For forensic data analysis, Principal Component Analysis (PCA) (Jolliffe, 2002) was chosen as a statistically robust, multivariate analysis tool. Common elements to all samples were analyzed with PCA using the Excel add-in Multibase package (Numerical Dynamics, Japan). In addition to this, elemental concentration plots were made for the samples. Concentration plots allowed for a visual representation of the variation between samples. Pair-wise elemental concentration plots were also created for the samples. This allowed for a smaller scale of paired elements' contributions to provenance determination to be explored.

PCA is a data reduction technique that finds correlations in the data and can reduce the dimensionality by finding principal axes that can account for most of the variance in the data. PCA has many applications; the one used here is its ability to transform a multidimensional plot into two dimensions. PCA uses an orthogonal transformation to create principal axes of the data set. These axes are linear combinations of the original variables. These principal axes reduce the data by first finding which combination of the original variables preserves the maximum amount of variance in the data, then repeating the process to find a second axis which is orthogonal to the first principal axis and has the maximum amount of variance. Typically, most of the variance in data can be described by two or three of these principal axes. This allows a multidimensional space to be reduced to a two-dimensional plot by projecting the data onto the plane created by these principal axes.

Typically, clustering of similar samples is seen in the graph. This clustering shows that some variables are correlated and responsible for the clustering of similar samples. A positive correlation between two variables indicates that when one of the variables has a larger value in a sample, the other variable will also have an increased value. Negative correlations between variables indicate that if one variable is larger in a sample, the other will have a decreased value. Correlation coefficients are given for each variable. If the product of the two correlation coefficients has a positive/negative value, there is a positive/negative correlation. Correlation coefficients range from -1 to 1. If the product of two variables' correlation coefficient is 1 or -1, then the two variables have a perfect positive or negative correlation, respectively.

RESULTS AND DISCUSSION

We successfully demonstrated PAA as a potentially useful non-destructive and/or non-invasive multi-element analysis tool with fossils and their source matrices. The use of PAA identified 31 total elements in all: Na, Mg, Ca, Ti, Cr, Mn, Co, Ni, Zn, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ag, Cd, Sn, Sb, Te, I, Cs, Ba, Ce, Sm, Tl, Pb, U. In each sample 19-29 elements were identified. Concentrations of all elements for each sample can be seen in Table 2. Asterisks (*) in Table 2 denote elements which were identified but whose concentrations couldn't be calculated with confidence due to different counting geometries for the initial count. Elements labeled ND were not detected in that sample. The reactions used for calculations are also listed. For more detailed information on the reactions, see (Segebade et al.,

Table 2: Concentrations in $\mu\text{g/g}$. Asterisks denote identified elements whose concentrations weren't calculated. Non-detected elements were labeled with "ND".

Element (Z)	Reaction Measured	Sample Concentration ($\mu\text{g/g}$)									
		Raben Ranch Fossil	Raben Ranch Matrix	Flint Hill Fossil	Flint Hill Matrix	Chamberlain Fossil	Chamberlain Matrix	Sundance Fossil	Sundance Matrix		
Na (11)	$^{23}\text{Na}(\text{Y,n})^{22}\text{Na}$	2790 ± 90	2600 ± 100	2800 ± 100	2800 ± 100	4000 ± 100	2200 ± 200	3900 ± 100	2630 ± 80		
Mg (12)	$^{25}\text{Mg}(\text{Y,p})^{24}\text{Na}$	*	5400 ± 300	1700 ± 100	*	*	7700 ± 400	*	*		*
Ca (20)	$^{48}\text{Ca}(\text{Y,n})^{47}\text{Ca}$	334000 ± 7000	228000 ± 4000	266000 ± 5000	101000 ± 3000	470000 ± 10000	108000 ± 2000	470000 ± 10000	44000 ± 1000		
Ti (22)	$^{49}\text{Ti}(\text{Y,p})^{48}\text{Sc}$	ND	1100 ± 100	280 ± 40	ND	ND	1500 ± 200	ND	4700 ± 600		
Cr (24)	$^{52}\text{Cr}(\text{Y,n})^{51}\text{Cr}$	ND	21 ± 7	170 ± 40	ND	ND	23 ± 10	ND	40 ± 4		
Mn (25)	$^{55}\text{Mn}(\text{Y,n})^{54}\text{Mn}$	820 ± 60	1300 ± 70	700 ± 40	180 ± 20	10800 ± 800	19000 ± 1000	10700 ± 800	110 ± 10		
Co (27)	$^{59}\text{Co}(\text{Y,n})^{58}\text{Co}$	ND	ND	ND	ND	2.6 ± 0.7	12 ± 1	ND	5.8 ± 0.6		
Ni (28)	$^{58}\text{Ni}(\text{Y,p})^{57}\text{Co}$	ND	ND	43 ± 19	9.4 ± 2.5	27 ± 5	68 ± 11	23 ± 3	7.8 ± 0.6		
Zn (30)	$^{66}\text{Zn}(\text{Y,n})^{65}\text{Zn}$	32 ± 6	100 ± 25	860 ± 170	640 ± 140	1100 ± 400	53 ± 7	140 ± 14	52 ± 4		
As (33)	$^{75}\text{As}(\text{Y,n})^{74}\text{As}$	500 ± 20	150 ± 6	200 ± 7	25 ± 2	29 ± 1	37 ± 3	30 ± 1	8.1 ± 0.4		
Se (34)	$^{76}\text{Se}(\text{Y,n})^{75}\text{Se}$	ND	ND	7.5 ± 3.4	ND	ND	11 ± 4	ND	ND		ND

Table 2: continued.

Element (Z)	Reaction Measured	Sample Concentration ($\mu\text{g/g}$)									
		Raben Ranch Fossil	Raben Ranch Matrix	Flint Hill Fossil	Flint Hill Matrix	Chamberlain Fossil	Chamberlain Matrix	Sundance Fossil	Sundance Matrix		
Br (35)	$^{59}\text{Co}(\gamma, n)^{58}\text{Co}$	280 ± 100	ND	310 ± 90	170 ± 60	1200 ± 300	ND	930 ± 230	ND		
Rb (37)	$^{85}\text{Rb}(\gamma, n)^{84}\text{Rb}$	ND	37 ± 2	10 ± 2	46 ± 2	5.1 ± 0.9	42 ± 3	5.1 ± 0.8	89 ± 4		
Sr (38)	$^{84}\text{Sr}(\gamma, n)^{83}\text{Sr}$	ND	300 ± 30	570 ± 50	ND	4000 ± 1700	2400 ± 900	ND	ND		
Y (39)	$^{89}\text{Y}(\gamma, n)^{88}\text{Y}$	390 ± 20	260 ± 30	220 ± 20	84 ± 5	230 ± 10	23 ± 4	230 ± 10	17 ± 1		
Zr (40)	$^{90}\text{Zr}(\gamma, n)^{89}\text{Zr}$	6.6 ± 0.8	50 ± 3	23 ± 2	94 ± 7	19 ± 3	50 ± 4	15 ± 2	270 ± 20		
Nb (41)	$^{93}\text{Nb}(\gamma, n)^{92\text{m}}\text{Nb}$	ND	4.8 ± 1.1	ND	6.5 ± 0.8	1.5 ± 0.4	6.2 ± 1.4	1.6 ± 0.4	12 ± 1		
Mo (42)	$^{96}\text{Mo}(\gamma, p)^{95}\text{Nb}$ $^{99}\text{Mo}(\beta\text{-decay})$	30 ± 5	14 ± 2	42 ± 5	9.0 ± 2	16 ± 4	10 ± 3	15 ± 4	15 ± 3		
Ag (47)	$^{107}\text{Ag}(\gamma, 2n)^{105}\text{Ag}$	ND	ND	ND	ND	ND	18 ± 8	ND	7.4 ± 2		
Cd (48)	$^{115}\text{Cd}(\beta\text{-decay})$	77 ± 15	ND	110 ± 30	44 ± 17	ND	130 ± 60	ND	32 ± 9		
Sn (50)	$^{112}\text{Sn}(\gamma, p)^{111}\text{In}$	ND	ND	ND	ND	ND	232 ± 74	ND	ND		

Table 2: continued.

Element (Z)	Reaction Measured	Sample Concentration (µg/g)									
		Raben Ranch Fossil	Raben Ranch Matrix	Flint Hill Fossil	Flint Hill Matrix	Chamberlain Fossil	Chamberlain Matrix	Sundance Fossil	Sundance Matrix		
Sb (51)	$^{123}\text{Sb}(\gamma, n)^{122}\text{S}$ b	46 ±6	34 ±6	25 ±6	21 ±4	140 ±20	75 ±10	130 ±20	10 ±2		
Te (52)	$^{122}\text{Te}(\gamma, n)^{121}\text{T}$ e	1.6 ±0.2	3.0 ±0.3	0.15 ±0.04	3.3 ±0.4	0.9 ±0.2	0.8 ±0.2	2.0 ±0.3	1.6 ±0.2		
I (53)	$^{127}\text{I}(\gamma, n)^{126}\text{I}$	870 ±50	250 ±20	200 ±20	37 ±3	3.9 ±0.6	190 ±20	2.0 ±0.6	1.5 ±0.3		
Cs (55)	$^{133}\text{Cs}(\gamma, n)^{132}\text{C}$ s	ND	ND	ND	ND	1.0 ±0.3	2.7 ±0.3	0.9 ±0.2	3.7 ±0.4		
Ba (56)	$^{132}\text{Ba}(\gamma, n)^{131}\text{B}$ a	2900 ±500	1100 ±200	9700 ±700	990 ±200	2700 ±700	1800 ±500	4600 ±1200	690 ±190		
Ce (58)	$^{140}\text{Ce}(\gamma, n)^{139}\text{C}$ e	110 ±6	79 ±6	230 ±20	81 ±5	160 ±10	15 ±2	150 ±10	20 ±1		
Sm (62)	$^{154}\text{Sm}(\gamma, n)^{153}\text{Sm}$	*	3.6 ±0.8	10 ±2	*	*	11 ±3	*	*		
Tl (81)	$^{203}\text{Tl}(\gamma, n)^{202}\text{Tl}$	ND	ND	ND	ND	2.0 ±1	0.4 ±0.2	ND	1.2 ±0.3		
Pb (82)	$^{204}\text{Pb}(\gamma, n)^{203}\text{P}$ b	*	32 ±7	59 ±4	*	*	ND	*	ND		
U (92)	$^{238}\text{U}(\gamma, n)^{237}\text{U}$	68 ±8	33 ±6	120 ±21	18 ±2	9.3 ±1.4	3.5 ±0.8	9.1 ±1.1	4.2 ±0.6		
# : 31		19	22	25	22	25	29	22	26		

1988). PAA was used non-destructively and the lowest concentration detected was 150 ng/g for tellurium. Optimization of irradiation and counting conditions should allow for more elements to be identified with a lower detection limit.

Three rare earth elements were identified. All samples contained all three of these REE: yttrium, cerium, and samarium. These alone were not sufficient to use for provenance determination, as one of the common REE in the samples was cerium which is sensitive to redox conditions. Samarium concentrations could not be calculated for several samples due to different counting geometries in relation to the calibration material and lack of reliable efficiency data. The samarium concentrations also had relatively high uncertainties due to interference from a uranium peak, as well as a small peak to background ratio. All these factors contribute to the inability to reliably examine the REE patterns.

There are several options for analysis of concentrations. These include, univariate, bivariate, multivariate analyses, as well as concentration plots. Concentration plots are typically the first step in analysis as it is simple and straightforward. This was the first step taken for this research. The concentration plots showed significant variations between individual samples. Some similarities, such as similar ratios between certain elements were seen for sample pairs, as well as the groupings of fossils and matrices. These similarities and variations showed some potential for the provenance postulate (Glascok and Neff, 2003) to be satisfied in this case. In addition to this, bivariate analysis was performed, where concentrations of two elements were plotted with all samples on the same plot. Univariate analysis, i.e. looking at distributions for a single element over all samples, was not performed as the number of samples was very small. The final type of analysis performed was a multivariate analysis, described in detail below.

The analysis of concentrations, or compositional data, requires special handling. Most statistical techniques were developed for unconstrained data; however, concentrations are a type of constrained, or closed, data, due to the fact that they sum to a constant (i.e. 1, 100%, 10^6 ppm, etc.).

Three common types of transformations are used for compositional data (Filzmoser and Hron, 2009). Of these, however, the isometric log-ratio (ILR) (Egozcue et al., 2003) is considered the best option (Filzmoser et al., 2009) because it is

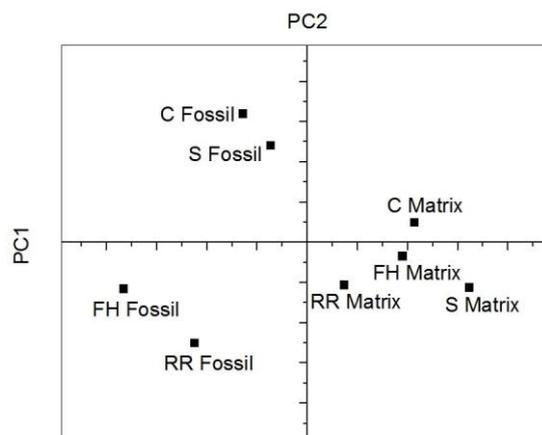


Figure 2 : Principal Component Analysis of the elements identified in all samples. The figure shows that the matrices and fossils are readily distinguished by their position relative to the second principal component (PC2) axis. Fossils have positive first principal component (PC1) values, while matrices have negative PC1 values.

isometric and subcompositionally coherent, meaning correlations will be the same regardless of any subset of the data chosen.

PCA is largely affected by subcompositional decoherence (Greenacre, 2011), so the first step in the analysis was to close the data because subcompositions were analyzed. After this the next step is to apply an ILR transformation. Before this, PCA was applied to the unclosed, untransformed data, of the common elements in all samples, as this is valid if groupings of the samples are known a priori (fossils and matrices). This analysis showed a clear separation of the fossils and matrices. The elements with the two highest positive and negative correlation coefficients (four in total: Ca, Zr, Ce, Te) were subsequently removed, as they dominated the analysis, which is one way to deal with over-influential components (Greenacre and Lewi, 2009). See Figure 2 for the PCA results of this analysis.

After the over-influential components (those separating the matrices and fossils in the analysis) were identified, they were removed, and a new analysis was done. This time the analysis consisted of closing the data and applying the ILR transformation. This was done in CoDaPack (Thió-Henestrosa and Martín-Fernández, 2005; Comas and Thió-Henestrosa, 2011). The subsequent PCA was done using Multibase with centering of the results and no scaling and with the PAST (Hammer et al., 2001) software to verify the results. The results show each pair of

samples occupying a quadrant on the graph of the first and third principal components, see Figure 3.

Another option for data analysis would be a robust version of PCA to deal with outliers (Filzmoser et al., 2009, 2011). There is an R-package for this type of PCA with compositional data (Templ et al., 2011); however, analysis of the data in this work was not possible using this because the number of samples was too small. This limitation in the software is likely to avoid any horseshoe effects (Diaconis et al., 2008) that can occur in these types of analysis if the number of samples is much less than the number of variables.

To obtain a more conclusive result about provenance determination, more samples need to be examined and lower detection limits achieved, of which are both readily achievable. This work only had a single sample pair from each of four different stratigraphic/geographic provenances. To more conclusively determine if provenance determination is possible, multiple samples need to be examined from each provenance. Approximately 10-30 samples should be examined for each provenance and multiple provenances should be studied. With an expanded sample set, the data analysis presented here should be able to more reliably determine if provenance can be verified by the elemental composition of a fossil and its source matrix.

Future work needs to determine systematic uncertainties and reduce detection limits. The work presented here only factored in uncertainties from counts in the spectra. The uncertainties associated with use of the external flux monitor method also need to be fully characterized. Some work has been done to assess the accuracy and precision of the external flux monitor method (Sun et al., 2014), but a more thorough study is needed so that it can be optimized. In particular, the geometric arrangement of the samples/monitors needs improvement. Optimization of the irradiation parameters also needs to be examined. Beam energies of 20-40 MeV are common, with 30 MeV being a typical value. However, selection of the beam energy has to be done on a case-by-case basis (Segebade et al., 2017), as increased beam energy will increase activity and thus lower sensitivities, but can also introduce more background. Depending on the elements of interest, as well as what elements are in the sample, the beam energy should be selected to maximize sensitivity in the areas of interest. This will allow a larger set of elements to be identified and possibly a lower detection limit. Irradiation

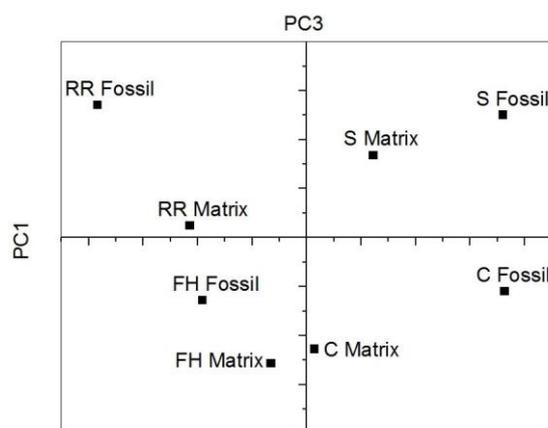


Figure 3: PCA done with properly transformed data of all common elements to the samples, excluding, Ca, Ce, Te, Zr. The results include centering of the results, but no scaling. Each pair is separated into a quadrant of the graph based on provenance. The result is inconclusive due to the small number of samples, but does provide some optimism for future study.

parameters can be tuned if only certain elements are of interest for a study.

Lower detection limits can also be obtained by reducing background. This can be achieved by counting in a low background lab, optimizing irradiation beam parameters, waiting to count, or counting longer. The latter of these options are useful on a case-by-case basis, because depending on half-lives, source of the background, etc., these options can have diminishing returns. Also, data quality can be enhanced significantly by improved bremsstrahlung flux monitoring, such as photon tagging (Sober et al., 2000) A future study should also be conducted using PAA to examine migration mechanisms of some elements between fossil and matrix in either direction, as similar work has been done in a different context with soils and ancient Roman pottery (Segebade and Lutz, 1976).

A comprehensive study of the measurement uncertainties needs to be done for paleontological samples. The equation (2) for the uncertainty is given as:

$$\Delta c_s \cong c_s \sqrt{\left(\frac{\Delta c_{CM}}{c_{CM}}\right)^2 + \left(\frac{\Delta P_{CM}}{P_{CM}}\right)^2 + \left(\frac{\Delta P_s}{P_s}\right)^2 + \left(\frac{\Delta \varphi_s}{\varphi_s}\right)^2 + \left(\frac{\Delta \varphi_{CM}}{\varphi_{CM}}\right)^2} \quad (2)$$

The main sources of uncertainty (Δ) are the concentration in the calibration material (c_{cm}), and the activities (peak counts) of the sample (P_s) and calibration material (P_{cm}), the flux factors (Segebade et al., 2013) of the sample (φ_s) and calibration material (φ_{cm}), the masses of the

sample (m_s) and calibration material (m_{cm}), and the decay constant (λ). The latter three of these uncertainties tend to be very small and can be considered negligible.

The flux factor assumes the spatial variation of the bremsstrahlung flux has the same distribution for all samples and only the intensity scales (Segebade et al., 1988), as is similar in NAA (Agostino et al., 2014). Included in the flux factor is a correction factor as samples were relatively thick and not a uniform distance from the converter. Each sample will receive a different intensity of photons, due to differences in thickness and position relative to the beam. This creates less induced activity, which needs to be accounted for in the calculations. See (Segebade et al., 2013) for more information.

A similar study to that mentioned in the previous paragraph has been done for NAA of biological materials (Moreira et al., 2006). This study showed that the sample activity was the main contributor to uncertainty; however, other quantities can have a significant effect, and it varies by element. Given the similarities between PAA and NAA, the results should be similar, but considering the differences between biological and paleontological samples, as well as the differences between NAA and PAA, a separate study should be conducted. A study of this nature would help to characterize which uncertainties need to be the focus of reduction efforts, which can provide useful information for irradiation parameter optimization.

CONCLUSION AND FUTURE WORK

Photon Activation Analysis has been shown to be a potential non-destructive tool for paleontological studies. As a tool for examining the elemental composition of fossils and rocks, it is a broad spectrum multi-element analysis tool. This work identified 31 elements, with the lowest concentration detected at 150 ng/g for tellurium. PAA's multi-element spectrum and low detection limits, along with its ability to do bulk analysis of large samples, makes it suitable for several types of paleontological studies. The non-destructive nature of PAA makes it a wise alternative to current analysis methods that are destructive.

Concerning provenance determination, this work is inconclusive, due to the small number of samples. Though this work was inconclusive, there were some hints that provenance determination may be possible. The work did show a clear

distinction between matrices and fossils, which was important for identifying which elements contributed the most to this distinction. This allowed these elements to be removed from the subsequent analysis of provenance, so that they didn't dominate the analysis. In addition to this, there was some separation of the sample pairs; however, multiple sample pairs from each provenance need to be examined to make any conclusive claims.

PAA has a lot of potential as a non-destructive elemental analysis technique for paleontology. To demonstrate its potential for provenance determination more samples need to be analyzed. In addition to this, the technique itself needs to have more research done into uncertainties as they apply to paleontological samples. This will allow better optimization of the technique for paleontological samples, thereby lowering detection limits and uncertainties.

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