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Non-Destructive Photon Activation Analysis in Paleontology †

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Abstract: Paleontological samples are rare and non-renewable, which makes their study require non-destructive methods. Of interest to paleontologists are both the physical and chemical characteristics. Physical characteristics are routinely studied with non-destructive methods; however, chemical studies tend to require destructive methods unless samples are very small or only the surface compositions are of interest. One potential technique for non-destructive elemental analysis is photon activation analysis (PAA). PAA is a versatile, broad-spectrum, multi-element analysis tool with low sensitivities, capable of analyzing large samples without any alteration, preserving the physical characteristics.

Recent work has applied PAA to fossils and their source matrices in an attempt to correlate provenance through trace element analysis. PAA was shown to be non-consumptive and able to identify 20+ elements in samples with sub-ppm sensitivities. From that work, several lessons were learned and the non-destructivity of the technique was better characterized. PAA doesn't have one standardized methodology, as it varies depending on the sample type. As such, from the lessons learned from the previous research, a standard method of applying PAA non-destructively to paleontological samples has been developed and will be presented in the following paper.

Keywords: fossils; non-destructive elemental analysis; photon activation analysis; trace element; provenance

1. Introduction

Paleontology is a field where both the chemical and physical pathways of information are important. The external morphology, internal structure, and chemical composition can all provide valuable insights. Overall, a plethora of techniques exist for retrieving information from each pathway; however, chemical analyses are typically destructive [1], making them less than ideal candidates for use. Recent work [2] has shown photon activation analysis (PAA) as a potentially non-destructive elemental analysis technique in paleontology. PAA is a technique that is impossible to develop a general, standardized methodology for use [3]. Each type of sample may require a different methodology. As such, this paper will present a standardized methodology for the non-destructive use of PAA with paleontological samples. It should be noted that the word "non-destructive" is used with a plethora of meanings. The usage in this paper will follow the criteria and definitions laid out in [1].

The main factor limiting chemical analysis of paleontological samples is that they are a rare and non-renewable resource. As such, any analysis that is done needs to be non-destructive. For many chemical analysis techniques, this requirement is either impossible to meet, or limits analysis in some other manner. For example, common techniques used are x-ray fluorescence (XRF) and neutron activation analysis (NAA). These techniques can be used non-destructively, but the size of sample they can analyze non-destructively is limited, unless only a surface analysis is desired.

The non-destructive requirement has several consequences for chemical analysis. First, the samples can't be modified in any manner, because the external morphology and internal structure all provide information. This creates samples with odd, varying geometries and sizes, as the samples can't be cut or shaped to be more uniform. This requirement also means samples can't be ground into a fine powder, which is a common, destructive [4] preparation technique. This limits the overall mass that can be analyzed, as well as the bulk analysis capabilities. Lastly, since the internal structure is also a source of information in paleontology, any analysis needs to do a negligible amount of damage to the internal structure.

Photon activation analysis in many cases can be used non-destructively (one notable exception is organic samples). It has a long history of applications with a variety of different sample types in many fields [3]. It is a broad spectrum, multi-element analysis technique with low sensitivities. In this regard it is very similar to NAA, however, each technique has different sensitivities for each element, making them complementary tools.

Compared to NAA though, PAA offers several advantages. First is the equipment required. NAA requires a nuclear reactor, the availability of which is expected to decrease in the future [5], while PAA requires a particle accelerator. Accelerators are expected to find an increased importance in science, particularly in America, in the coming years [6]. These two facts combined, should create more accessibility and importance for PAA as an analysis tool, particularly in provenance studies, where NAA has been the main tool for decades [5, 7]. PAA uses high energy photons as an irradiation source. This gives the technique a large penetrability compared to other techniques. This allows bulk analysis of large samples, 100's of grams or more, with no special considerations. In addition to this, the ability to control the radiation source allows much larger samples to be analyzed using equipment such as collimators and electron beam scanners. The bulk analysis capabilities are of particular importance for the non-destructive considerations of paleontology. Techniques such as NAA are generally limited to sample sizes of around 0.5 grams or less [8], unless destructive sample preparation is employed. As paleontological samples can be found in a wide range of sizes, PAA is a suitable tool for a general non-destructive analysis technique. Lastly, the bulk analysis capabilities of PAA allow a thorough analysis of inhomogeneous materials. Sample size and inhomogeneity are common constraints for trace element analysis of fossils [4], thus PAA provides a technique with great potential. When used in conjunction with surface techniques, it also has the potential to help study migration mechanisms of elements [9].

2. Methods

To set the stage for the discussion of the methods, a brief overview of photon activation analysis in general will be given. For a more detailed treatment, see [10, 11]. Photon activation analysis is a technique that induces radioactivity in samples by using photons (high energy light). This radioactivity is measured, and when a material with well known concentrations of the elements of interest is irradiated at the same time, concentrations can be calculated.

If photons are high enough energy, they can be absorbed by a nucleus of an atom in the sample, causing (most likely) a neutron to be ejected. When a nucleus loses a neutron, it will oftentimes become radioactive, giving off a unique set of photons, which can be measured with a detector such as a high purity germanium detector. These radioactive nuclei also have a unique half-life (the time for half of the nuclei to decay). These differing half-lives play an important role in allowing elements to be differentiated, as well as optimizing experimental parameters.

Due to large uncertainties in the probabilities of these nuclear reactions (absorption of a photon and subsequent ejection of a neutron) and the photon flux, direct calculations of concentrations are difficult, but easily overcome by using some sort of standard reference material and taking ratios. In PAA terms, the material with well known concentrations that is used in the ratios is referred to as a calibration material, whereas a reference material is also used. The reference material is treated as an unknown sample, calculating the concentrations and comparing to the certified values for quality assurance. In addition, the photon flux isn't homogeneous due to varying sample sizes and distances from the source, so typically a monitor is used to calculate correction factors.

2.1. Sample Preparation

For sample preparation, no special handling is required, apart from the typical handling procedures for such samples. As the analysis is non-destructive, no sampling, chemical separation, or altering of the sample should be done. Samples should be handled with care as flaking or other breakage is possible with fragile samples. Gloves should be used when handling the samples to avoid adding contaminants to the surface.

As a limited number of samples can be irradiated at a time, samples with similar sizes and geometries should be grouped and analyzed together. This helps limit the uncertainties caused by the non-destructive requirements that samples can't be altered. Once samples have been grouped, they should be organized and have their masses measured with a high precision scale.

Besides the sample, three other items are needed: flux monitors, calibration material, reference material. Flux monitors are used to correct for individual samples receiving an inhomogeneous flux of irradiation. In general, internal and external monitors can be used, the former giving better results [12]; however, the need for non-destructive analysis forces the use of external monitors. Typically thin foils (~25 μm) of high purity nickel or copper are used, cut to match the geometry of the samples and then placed on both sides of the sample with respect to the beam direction. Given the non-uniform geometries of paleontological samples, copper is the better choice, as it is malleable, allowing the flux monitor to be wrapped around the entire sample, conforming to the sample geometry. The copper foil should be cut, such that it can cover and conform to the entire sample. After the irradiation, foils and samples will be separated for counting, so the foils should be labeled with a marker to identify them later. During this procedure, the masses of each foil should be recorded with a high precision scale, either before or after wrapping them around the samples.

Calibration and reference materials are used to calculate concentrations and assure data quality, respectively. In reality, they can be similar materials. The choice of which material to use depends on the application. The main requirement is that the calibration and reference materials contain all of the elements of interest with a well-known concentration. Oftentimes, a general purpose material, such as URM-1 [13], is suitable, as it contains 50+ elements of varying, well-known concentrations. If only a few elements are of interest, a general purpose material will give results with more uncertainties, as the large number of elements will create a substantial background. In this case, a more specialized material would be ideal, containing only the elements of interest.

These materials require some preparation. They should be similar to the dimensions of the samples, so they should be placed in appropriate containers to assure that. Aluminum foil is typically a good choice as a housing for the calibration and reference materials. It is malleable, such that it can be formed into a container of the appropriate dimensions. It also mostly contains short lived isotopes after irradiation, thus the calibration and reference materials can remain in the housing during counting without any significant effect on the results, unless a count is done shortly after irradiation and aluminum is an element of interest. Once the containers have been made, an appropriate amount of material should be placed to fill it. The mass of both the calibration and reference material should be recorded using a high precision scale.

2.2. Irradiation

Once all the appropriate materials are prepared, they need to be prepared for irradiation. Two options are generally used: creating a stack of samples along the direction of photon flux or placing samples on a rotating table. A stack of samples, typically wrapped in aluminum foil to keep samples in place, will require less irradiation time to achieve the same activity, while a rotating table gives the benefit of a more homogeneous irradiation of all samples. The choice depends on several factors, such as the thickness of samples and how many samples will be irradiated. If the sample thickness makes the total length of the stack around 15 cm or less, this method will typically be fine. If the length is too long, attenuation from the beam of photons will cause a much lower flux to be seen by the samples in the end of the stack, creating less activity, which makes the experiment less sensitive, with more uncertainties. If a large number of samples need irradiation, a rotating table can be used to rotate samples in and out of the center of the flux during irradiation. This allows more samples to

be more homogeneously irradiated at one time, but also has the drawback that more irradiation time is required to achieve a similar dose as compared with a stack.

Once the irradiation setup has been decided, the power of the beam needs to be decided. A power of approximately 1 kW with a maximum energy of approximately 20 MeV is a good choice. 20 MeV is on the lower end of the typical range for PAA, but at the current time, is the best recommendation for non-destructive use in this context. Due to internal structure being of interest in paleontology, this needs to be preserved during the analysis. Some work [14] has been done on examining the damage done to the internal structure of steel using this type of irradiation. It found that up to 20 MeV there was negligible damage. Future research, however, should be done in this area to see if the maximum energy can be increased while maintaining non-destructivity, as well as characterize the material dependence.

After the beam parameters have been set, the irradiation time should be decided. From a radiological standpoint, a 60 second irradiation can be done to assess how radioactive samples will be after a full irradiation. This knowledge gives an idea of how active the samples will be and how/when they can be handled after the irradiation. The irradiation time will depend on the elements of interest. Unless very short-lived isotopes are of interest, an irradiation time of 1-5 hours is suitable in general. If specific element(s) are of interest, the time can be optimized for detecting them, as the induced activity is close to its saturated value after 2-3 half-lives of the element. The longer the irradiation, the more total activity will be induced in the sample. This increases the background, which reduces the detection limits (DL), which can be quantified as [15]:

$$DL \propto \frac{\sqrt{Background}}{Yield}$$

Where the yield is essentially a product of induced activity and the detector efficiency. Recent work [16] has derived a more accurate induced activity equation, lowering the theoretical detection limits.

2.3. Counting

After irradiation samples, as well as calibration/reference materials and flux monitors, need to be counted. The flux monitors can be counted consecutively, separately from the samples and other materials, typically around 12 hours after the irradiation for roughly 5 minutes each. Different methods for the subsequent calculations can be found in [10, 17].

The induced activity has a symmetrical behavior during and after irradiation. Activity will have mostly decayed away after 2-3 half-lives of the isotope of interest. For a general, multi-element survey, a good rule to go by is to count after 12-24 hours, 1 week, and 1 month. The longer counts give the benefit of reducing the background from all the elements with shorter half-lives, thus giving a cleaner signal to detect and calculate concentrations of longer half-life elements.

Any standard gamma spectroscopy setup will work for counting samples. High purity germanium detectors are preferred, as they have enough resolution to separate individual peaks. Samples should be placed at the closest geometry possible to the detector that doesn't create much dead time in the detector. A rate of less than 1000 counts per second is a rough limit, with around 500 counts per second being ideal [18].

Before beginning counting, all samples should be tested at various positions to see what sort of counting rate they create in the detector. It is best to place all samples in the same position when counting, to limit uncertainties due to different counting geometries and detector efficiencies at different positions. Therefore, if any of the samples has a rate higher than 1000 counts per second at the closest position, the second closest position should be checked, and so on, until a position is found such that all counting rates are acceptable. Grouping samples by similar size/mass should mitigate this issue if the amount of flux received by each sample is fairly homogeneous.

2.4. Calculations

After counting, the peaks in the spectrum obtained need to be identified. Once this is done, the peaks can be fit to obtain the number of counts (photons). With this information, as well as other readily available parameters such as time of irradiation (t_i), time between irradiation and counting

(t_d) and time of counting (t_c), as well masses/peak counts of the sample (m_s/P_s) and the material with well known concentrations (i.e. calibration material) (m_{CM}/P_{CM}), and the decay constant of the produced radioactive nuclei (λ). If these are known, as well as the flux correction factors (φ) from the flux monitors (see [17]) and the concentration of the element of interest in the calibration material (c_{CM}), the concentration (c_s) of each element identified can be calculated with:

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

This can be repeated for all the peaks mutually identified in a sample and the calibration material. Once concentrations are calculated, the uncertainty can be calculated:

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

3. Applications

As far as elemental analysis is concerned, paleontology typically looks at three areas: isotopic ratios, trace elements, and rare earth element ratios. Though photon activation analysis does have, in principle, some potential for isotopic analysis, up to this point, it has only been tried in rare cases, with destructive methods. Further theoretical characterization and experimental tests need to be conducted to examine the potential of this type of analysis. Rare earth element ratios are often utilized for provenance studies. The REEs typically increase greatly in concentration during diagenesis [19, 20], but their ratios stay the same, making them good indicators of provenance [21]. This uptake creates concentrations high enough for PAA to detect; however, some REEs aren't detectable, or reliably measured, via PAA [11].

Despite having no sensitivity to some REEs, PAA still can routinely detect 30+ elements, including several REEs used in provenance studies [21] with sensitivities typically in the ppm range. Recent work [2] has shown multivariate statistical analysis of the trace elements measured using PAA to have potential for provenance determination. Though the number of samples was too low to make any provenance claims, it did show PAA as a suitable tool to measure a broad spectrum of elements with sub-ppm sensitivities, making it suitable for trace element analysis at the very least.

Trace elements are important in a plethora of paleontological studies. Trace elements can help characterize the amount of diagenesis that took place. This is important, as it also characterizes the stability of the isotopic ratios in the sample during that time. Samples with unaltered ratios are useful for studying the chemical evolution of the oceans, which includes a host of different global processes [22]. In addition, trace elements are useful for Paleolimnology studies [23], Paleodiet [24] and Paleonutritional studies [25]. In addition, as previously mentioned, trace elements are possibly useful for provenance determination, which scientifically is useful for providing better alignment of geological formations and timelines, as well as matching unknown or improperly collected specimens to an origin, giving them scientific value. In addition, a reliable provenance determination tool would be useful in law enforcement, in particular, concerning the removal of items illegally from Federal land [26].

4. Conclusions

Photon activation analysis offers a unique, non-destructive elemental analysis technique for paleontological studies. The broad multi-element spectrum, coupled with low sensitivities makes it a potential tool for several paleontological studies, including provenance, paleoenvironment reconstruction and taphonomic studies. In order to use PAA non-destructively, care must be taken, as such, this work presents the needed information for the non-destructive use of PAA with (non-organic) paleontological samples. This standard methodology resulted from the first application of PAA to fossils and their source matrices, wherein a provenance study was conducted.

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