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Pacific Northwest
National Laboratory
Operated by Battelle for the
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A Graphite Isotope Ratio Method Primer—A Method for Estimating Plutonium Production in Graphite Moderated Reactors

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Prepared for the U.S. Department of Energy
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Summary

The Graphite Isotope Ratio Method (GIRM) is a technique used to estimate the total plutonium production in a graphite-moderated reactor. The cumulative plutonium production in that reactor can be accurately determined by measuring neutron irradiation induced isotopic ratio changes in certain impurity elements within the graphite moderator. The method does not require detailed knowledge of a reactor's operating history, although that knowledge can decrease the uncertainty of the production estimate. The basic premise of the GIRM is that the fluence in non-fuel core components is directly related to the cumulative plutonium production in the nuclear fuel (Reid et al. 1999). This report provides a basic description of the physical basis and practical implementation of the Graphite Isotope Ratio Method.

Glossary

Burnup – The *burnup* is the total energy released by a given quantity of nuclear fuel in units of megawatt-days/metric ton (MWd/MT).

Cross-Section – The total neutron *cross-section* is defined as the probability *per unit path length traveled* that a neutron will interact with a nucleus in the background media. There are specific cross sections for different reactions including scattering, capture, and fission. Cross-sections are typically denoted with the symbol Σ, and have units of inverse length (cm^{-1}). In general, cross sections are complex functions of the neutron energy and the composition of the background media. See *reaction rate* and *mean free path*.

Fissile – A *fissile* nuclide, such as U^{235} or Pu^{239}, can undergo fission following the absorption of a zero-energy neutron.

Fluence – The *fluence* is the time integral of the scalar flux in units of neutrons/cm^2. If the flux is constant in time, the fluence is simply the product of the flux and time.

Flux – The *flux* is the product of the neutron density and the neutron speed with units of neutrons/cm^2-second. The flux is often a very complex function of position (and energy).

Mean free path (MFP) – The mean distance a neutron can be expected to travel between collisions with the background media. The *mfp* is equal to the inverse of the total cross-section ($1/\Sigma$).

Moderator – Neutrons are produced in fission with very high energies. Fission cross-sections, however, are typically much larger at low neutron energies. Therefore, many nuclear reactors contain low atomic mass materials that serve to decrease average neutron energy through collisions. This material is referred to as *moderator*. Graphite, light water, and heavy water are frequently used as moderators.

Reaction Rate – A *reaction rate* is the rate at which neutrons interact with the nuclei in the background media in units of reactions/cm^3-sec. It is the product the *scalar flux* and the *cross-section* for the reaction of interest.

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1.0 Introduction

1.1 Physical Basis

Graphite-moderated reactors have been used to produce plutonium since the 1940s. These simple reactors, which include the U.S. Hanford Site Production Reactors, the French Marcoule G-series Reactors, and the British Calder-Hall Reactors, have remarkably similar designs. They use natural or low-enriched uranium metal for fuel and light water or gas (often CO_2) for coolant. The cylindrical fuel rods are clad with a thin layer of protective metal (typically alloys of aluminum, magnesium, or zirconium) and are loaded into channels in the graphite moderator blocks as shown in Figure 1.1.

A complete core can contain up to 2000 fuel channels, each about 20 feet long, yielding a total uranium mass of between 50 and 200 metric tons. While the fuel is frequently discharged and replaced, the graphite moderator is resident in the reactor throughout its lifetime.

Neutrons produced from fission reactions maintain the chain reaction by causing additional fissions in the fuel. These neutrons are also parasitically absorbed in non-fuel components such as reactor structural material, control rods, coolant, and the graphite moderator. The fluence (see the glossary) in the graphite moderator is proportional to the total number of fissions that have occurred in the fuel. This, in turn, can be directly related to the total plutonium production over the lifetime of the reactor. Therefore, if the fluence in the graphite can be determined, the cumulative plutonium production can be inferred.

Even high purity, reactor-grade graphite contains elemental impurities at parts per million levels. The isotopes of these elements are transmuted by neutron irradiation in a predictable manner. While measuring the change in a particular isotope's *concentration* is possible, it is difficult to correlate to fluence because the initial concentration of that element may not be known. However, if the *ratio* of two isotopes of the same element can be measured, the fluence can then be determined without knowing the absolute concentration of that impurity, since the initial ratio is known (it is simply the natural ratio). This is the fundamental principle underlying the GIRM.

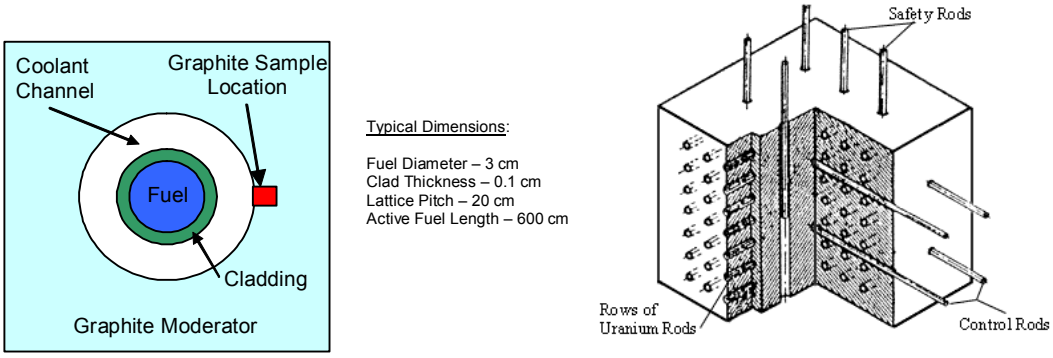

Figure 1.1. Graphite Reactor Fuel Channel and Simplified Reactor Core

Graphite reactors possess several characteristics that make this method particularly appealing.[i] The underlying physics of these reactors often result in fluence profiles that tend to be relatively smooth and predictable. This simplifies the correlation between the total number of fissions and the graphite fluence and results in a corresponding reduction in the uncertainty of the plutonium production estimate.

2.0 Indicator Elements

Suitable indicator elements for GIRM applications should exist in graphite in sufficient quantities to be accurately measured, have stable activation products, and have cross-sections of suitable magnitude to result in meaningful isotope ratio changes for the fluence range in question. For high-fluence reactors, the Ti^{48}/Ti^{49} ratio has been used very successfully.[(a)] For low-fluence measurements, the B^{10}/B^{11} ratio is an excellent indicator element.[(b)] A wide variety of uranium and plutonium ratios are appropriate both low- and high-fluence applications. The use of multiple indictor elements, such as boron and uranium, tends to reduce the overall uncertainty associated with a GIRM plutonium production estimate. Table 2.1 summarizes the characteristics of several useful indicator elements.

Table 2.1. GIRM Indicator Elements

Element	Primary Measured Ratios	Fluence Range
Boron	B^{10}/B^{11}	Low
Lithium	Li^{6}/Li^{7}	Low-Intermediate
Titanium	Ti^{48}/Ti^{49}	Intermediate-High
Uranium	U^{235}/U^{238}, U^{236}/U^{238}	Low-High
Plutonium	Pu^{240}/Pu^{239}, Pu^{241}/Pu^{239}, Pu^{242}/Pu^{239}	Low-High

(a) Reid BD, DC Gerlach, PG Heasler, and JV Livingston. 1997. "Trawsfynydd Plutonium Estimate," Unpublished PNNL Report, Pacific Northwest National Laboratory, Richland, Washington.

(b) Gerlach DC, CJ Gesh, DE Hurley, and SL Peterson. 2002. *Standard Low-Fluence Graphite Sample Preparation and Measurement Protocol for SIMS/TIMS GIRM Analysis, Rev. 2*. Unpublished PNNL Report, Pacific Northwest National Laboratory, Richland, Washington.

3.0 Graphite Sampling, Preparation and Measurement

Engineers in the United States, the United Kingdom, and Russia have performed extensive graphite sampling campaigns to study graphite performance. Automated graphite reactor sampling (trepanning) machines are commercially available. These devices are inserted into fuel channels and extract samples of about 1-cm in diameter and 2-cm in length from virtually any location in the core. The relative position of the sample in the core can be precisely measured during sampling. The sampling locations and the number of samples needed to achieve a desired accuracy in the total plutonium production estimate can be optimized. This optimization is described in the GIRM Estimation and Error Analysis Report (Heasler, et al. 2003)

A graphite sample from a reactor that has operated for a significant time may have been exposed to a variety of contaminants. Uranium, plutonium, and fission products from failed fuel elements may be present on or near the surface of a sample taken from a fuel channel wall. Additionally, environmental contamination with boron and lithium, which are ubiquitous, is also a concern. Therefore, careful preparation and cleaning of the graphite samples is required prior to performing an accurate mass-spectrometry measurement.[(a)] Preliminary screening measurements may be necessary to evaluate the levels of surface contamination. Effective surface decontamination methods include vacuuming, CO_2 bead blasting and plasma-etching.

Three mass-spectrometry measurement techniques are used to support GIRM analysis:

- Secondary Ionization Mass Spectrometry (SIMS) is primarily used to analyze boron isotopic ratios.
- Thermal Ionization Mass Spectrometry (TIMS) is used to evaluate titanium, uranium, and plutonium ratios.
- Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is used to screen samples for U/Pu content prior to TIMS analysis.

Note that while SIMS is a non-destructive procedure only requiring a small, conductive surface to evaluate, TIMS is a destructive method that can require relatively large samples (depending on the amount of the indicator element in the sample).

(a) Gerlach DC, CJ Gesh, DE Hurley, and SL Peterson. 2002. *Standard Low-Fluence Graphite Sample Preparation and Measurement Protocol for SIMS/TIMS GIRM Analysis, Rev. 2*. Unpublished PNNL report, Pacific Northwest National Laboratory, Richland, Washington.

4.0 Local and Global Plutonium Production Estimates

The total plutonium production estimate is constructed in two basic steps. First, the isotopic ratio measurements for each sample are used to produce a *local* plutonium production estimate for that sample location. Secondly, the local plutonium estimates are combined to estimate the total plutonium production in the reactor. In essence, the local plutonium production values at known locations (that is, the sample locations) are used to estimate the plutonium production throughout the rest of the core.

It is not strictly necessary to construct a three-dimensional computer model of the reactor core in a GIRM analysis.[ii] However, three-dimensional computer models of the reactor that are based on *accurate operational data* can significantly reduce the uncertainty of the global plutonium production estimate or reduce the number of samples required to obtain a certain level of uncertainty. The statistical methods used in GIRM analysis are described in (Heasler et al. 2003).

4.1 Local Plutonium Production Estimates

To estimate the local plutonium production from an individual graphite sample, a two-dimensional computer model of a unit cell, like the one shown in Figure 1.1, must be constructed. Using a lattice physics code such as WIMS (AEA 1995), the spatial and energy dependence of the neutron flux in the unit cell can be calculated using the geometric and material specifications of the reactor. The result of these calculations is a precise relationship *at a specific location* between the cumulative plutonium production in the fuel and the isotopic ratios in the graphite moderator.

A typical set of curves is shown in Figure 4.1 for the British Experimental Pile Zero Energy (BEPO) reactor (Wickham 2003). Here, the calculated ratios of B^{10}/B^{11} and U^{235}/U^{238} are plotted as a function of cumulative grams of plutonium per centimeter of fuel length. Note that the B^{10}/B^{11} ratio is read on the left and the U^{235}/U^{238} ratio is read on the right. Mass spectroscopy results, indicated by single data points overlaid on the calculated curves, indicate that the fuel in this location produced a total of about 0.16 grams of plutonium per centimeter of fuel length. Uncertainties in the isotope ratio measurements result in uncertainties in the cumulative plutonium production, and the error bars on data points in Figure 4.1 correspond to approximately one standard deviation. The measured isotope ratios correspond to a cumulative fuel burnup of 1700 MWd/MT and a graphite fluence of approximately 1×10^{21} n/cm^2.[iii] The fluence value agrees well with the peak value reported in (Wickham 2003) for the BEPO core.

The laboratory analysis of each sample provides a set of isotopic ratios (B^{10}/B^{11}, U^{235}/U^{238}, Pu^{240}/Pu^{239}, etc.) at a specific point in the reactor. Using the WIMS code results, each set of isotopic ratios is statistically combined into a single *local* plutonium production estimate associated with that sample. When this step is complete, the result is a set of local plutonium production values (corresponding to the sample locations) and their associated uncertainties. It is clearly not practical to sample every fuel channel at numerous axial locations. In fact, it is not even realistic to sample each fuel channel at a

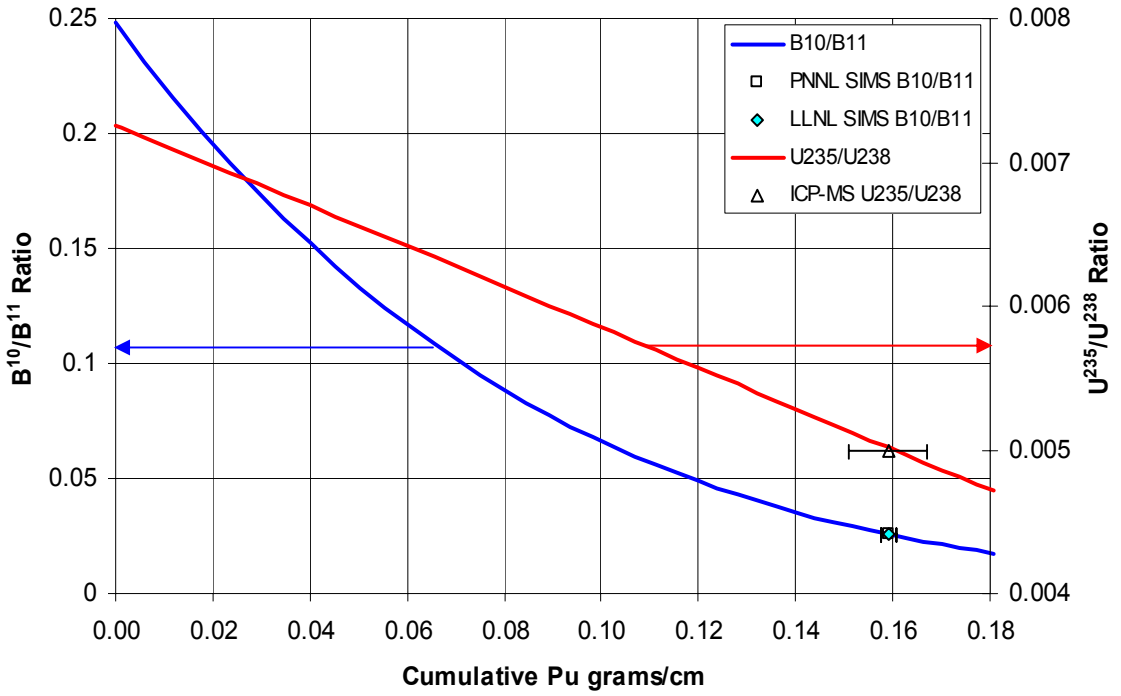

Figure 4.1. Isotope Ratios as a Function of grams Pu/cm for BEPO

few axial locations. Therefore, a relatively small set of local plutonium production values must be used to estimate the total plutonium production throughout the reactor.

4.2 Global Plutonium Production Estimate

To produce the total plutonium production estimate, the local values are used to construct a three-dimensional plutonium production map using a standard statistical method known as regression (U.S. National Institute of Standards and Technology). The regression technique produces a three-dimensional map that most closely fits all of the local plutonium production values.[iv] The samples with the lowest uncertainties are given more weight in the total plutonium production estimate. The details of this procedure are described in (Heasler et al. 2003).

This is illustrated in Figures 4.2a and 4.2b. In Figure 4.2a, the red line is the function $2.0\cos(\pi x/60) + 0.3\sin(\pi x/15)$, which is a completely arbitrary function used only to demonstrate the idea of regression. The diamonds correspond to *simulated data* points that have up to 10% random error with respect to the function. In Figure 4.2b, the simulated data is used to produce a simple, polynomial regression. The result, shown as a black line in Figure 3b, is the best fitting polynomial to the simulated data. Note that the polynomial regression closely matches the true function. The actual error between the "true" function and polynomial fit produced by the regression procedure is less than 1%. The functions used to produce the global plutonium production estimate in GIRM analysis are developed in a similar way and are discussed in (Heasler et al. 2003) and endnote **iv**.

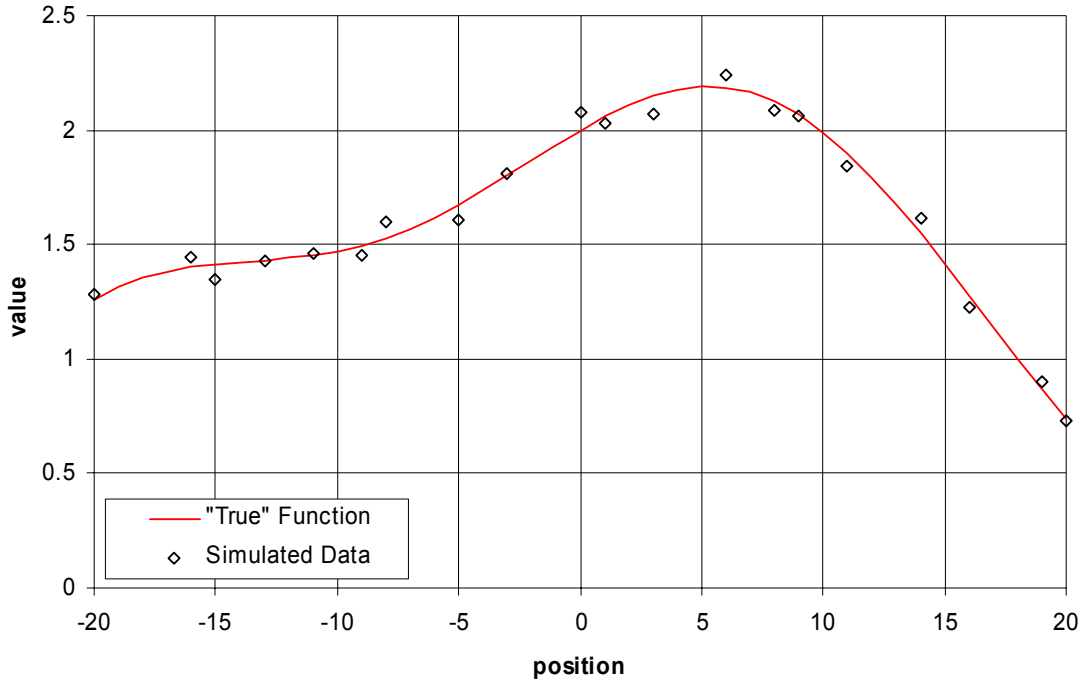

Figure 4.2a. Example of a "True" Function and Simulated Data to Illustrate Regression

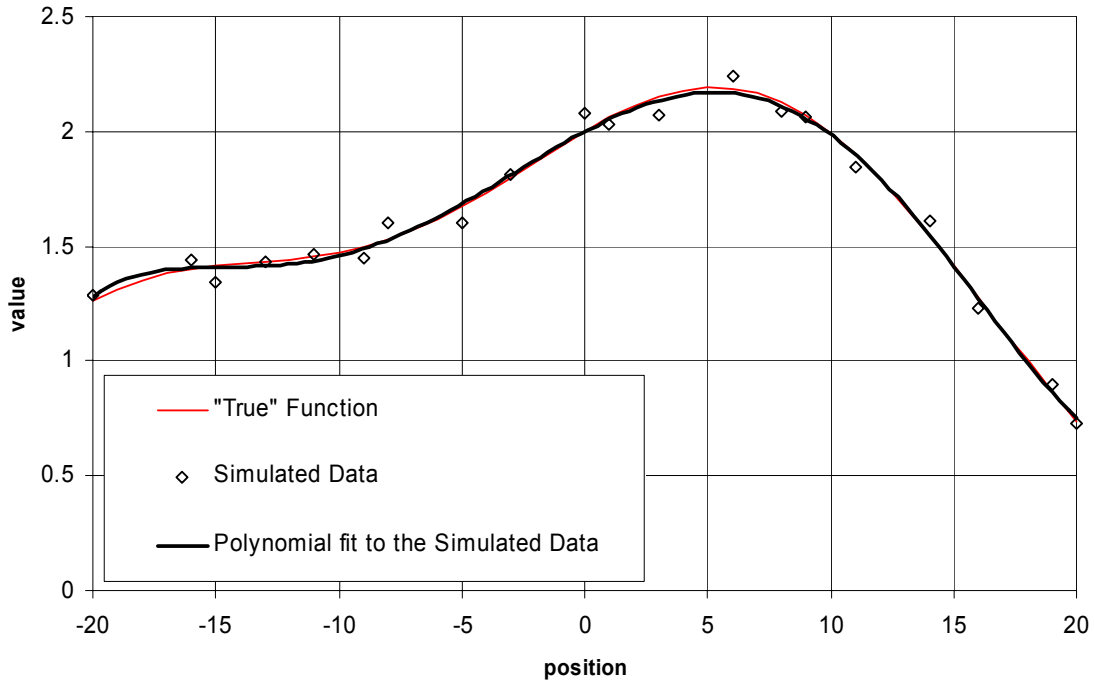

Figure 4.2b. Example of a "True" Function, Simulated Data, and Polynomial Fit to Illustrate Regression

5.0 Uncertainty and Error Analysis

Several studies have evaluated the uncertainty in GIRM calculations (Gerlach et al. 1998, Heasler et al. 2003, Reid et al. 1997). The most recent estimation procedure (Heasler et al. 2003) produces two separate local plutonium production estimates from the three primary indicator elements (boron, and uranium/plutonium). A final algorithm is then used to combine the three sets of local estimates into a global estimate. Numerous sources of uncertainty are considered and modeled by the algorithm. Several Monte Carlo calculations have been performed to test the uncertainty analysis methodology on simulated, though realistic, data. The major sources of error include sample position/orientation uncertainties, mass spectrometry measurement uncertainties, regression error, and uncertainties associated with the reactor design and operational parameters.

A full-scale demonstration of the GIRM procedure was performed on the Trawsfynydd reactor in Wales.[(a)] In a blind test, using only titanium isotopic ratio measurements from 90 sample locations throughout the core, a total plutonium estimate and uncertainty were calculated. The results agreed with the value provided by the reactor operator (based on actual fuel reprocessing records) to within their stated uncertainty.

(a) Reid BD, DC Gerlach, PG Heasler, and JV Livingston. 1997. "Trawsfynydd Plutonium Estimate," Unpublished PNNL Report, Pacific Northwest National Laboratory, Richland, Washington.

6.0 Conclusions

The GIRM is an experimentally proven, robust tool for accurately predicting the cumulative plutonium production in a graphite reactor. It is based on sound physical principles and is resistant to tampering since only neutron irradiation can induce the isotopic ratio changes that GIRM analysis depends on. In the future, it may be possible to apply this method to other reactor types if some structural component can be identified for sampling.

7.0 References

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Endnotes

[i] Because of the large neutron *mean free path* in graphite, the shape of the flux is relatively smooth. Therefore, constructing the global fluence profile will often be straightforward. Additionally, the concentration of impurities in reactor-grade graphite is so low that they do not measurably perturb the spatial or energy flux shape in the graphite. That is, the impurities are *infinitely dilute* [Duderstadt and Hamilton 1976]. Finally, because of the low fissile (i.e. U^{235}) content of the natural uranium fuel, the burnup in graphite reactors is typically low (<1500MWd/MT) so that the plutonium production rate changes very little over the course of a fuel cycle.

[ii] This is generally true. However, in the case of Pu^{241}, which decays with a 14.4-year half-life, it is necessary to know the actual power history (specific power, time of operation and time since shutdown) at specific locations to appropriately calculate isotopic ratios involving Pu^{241} and Pu^{242}. This provides another potential check on declared operations. Other isotopic ratios of interest are not significantly affected by radioactive decay and can be calculated without a detailed power history.

The measured isotopic ratios and corresponding Pu production estimates will also be used to characterize the reactor configuration and operational history. By "bootstrapping" with the measurements, the final three-dimensional reactor model will produce essentially the same results as the GIRM procedure described in this document. This is, in fact, an alternate way to approach the GIRM method. Here, detailed three-dimensional calculations would be the basis for the total plutonium production estimate. Each sample would be used to set the *magnitude* of the total plutonium production by overlaying the calculated shape on the measured data point. By repeating this for several samples, an average plutonium production value and uncertainty would result.

[iii] Though the values from the WIMS calculation shown in Figure 2 are much more accurate, a simple hand calculation is illustrative. Consider the B^{10}/B^{11} ratio in graphite and note that B^{11}'s cross section is negligibly small, so that its concentration remains essentially constant. The differential equation governing the depletion of the B^{10} is:

$$\frac{dN^{10}}{dt} = -N^{10}\sigma^{10}\phi \;\Rightarrow\; N^{10}(t) = N^{10}(0)e^{-\sigma^{10}\phi t} \text{ thus,}$$

$$\frac{N^{10}}{N^{11}}(t) = \frac{N^{10}}{N^{11}}(0)e^{-\sigma^{10}\phi t} = 0.248e^{-\sigma^{10}\phi t}.$$

Here, N is the number density in atoms/barn-cm and σ^{10} is the microscopic absorption cross-section of B^{10}. Assuming a Maxwellian flux and a graphite temperature of 420K, the value of σ^{10} is approximately 2830 x 10^{-24} cm^2. Thus, if the Pacific Northwest National Laboratory SIMS value for B^{10}/B^{11} from BEPO Block 19 is 0.0261 (which was in the highest fluence portion of the core), we obtain an estimated peak fluence of:

$$0.0261 = 0.248e^{-\sigma^{10}\phi t} \;\Rightarrow\; \phi t \cong 0.8\times10^{21}\,\text{n/cm}^2.$$

The value from Wickham (2003) is 1x10^{21} n/cm^2.

[iv] In practice, virtually any set of functions can be used as the basis of the three-dimensional plutonium production map. Obviously, the closer the basis functions are to the actual shape, the better the fit will be. In the past, functions from the eigenfunction expansion solution to the neutron diffusion equation (Duderstadt and Hamilton 1976) have been successfully used as a basis for the regression. These functions are a series of trigonometric functions that have the ability to *fit nearly any shape*, provided enough are used. Additionally, they reflect the theoretical shape of the neutron flux in a bare, homogeneous reactor. Note that the maximum number of functions used in a regression must be less than the actual number of samples.

It is also possible to use shapes generated by three-dimensional code calculations of the specific reactor. If the reactor operational history and design features of the reactor are well-known, this could result in a very accurate global plutonium production estimate with a small uncertainty. However, if there are unknowns in either the reactor configuration or operational history, the uncertainties could be unacceptably large. It is likely that some combination of theoretical shapes and code-calculated shapes will produce the best results. This combination of shapes has the benefit of using a best estimate three-dimensional shape while also retaining the theoretical shapes as a contingency in the event there is incomplete or inaccurate knowledge of the reactor configuration or operating history. It should be stressed that selecting the best regression model has a large impact in the development of the sampling plan (that is, the number and locations of the samples to be extracted from the reactor).