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Pacific Northwest
National Laboratory
Operated by Battelle for the
U.S. Department of Energy

Feasibility of Isotopic Measurements: Graphite Isotopic Ratio Method

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Prepared for the U.S. Department of Energy
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Summary

This report addresses the feasibility of laboratory measurement of isotopic ratios for selected trace constituents in irradiated nuclear-grade graphite, based on the results of a proof-of-principal experiment recently completed at Pacific Northwest National Laboratory (PNNL). These ratios are of interest in characterization of reactor operational histories, and in particular estimation of the neutron fluence (cumulative neutron flux) that has been experienced by a given sample. This estimation scheme was hypothesized under the name of Graphite Isotopic Ratio Method (GIRM) within the Nuclear Archeology Project at PNNL, and has been in development during FY-93 and FY-94, under the sponsorship of the Office of Research and Development, Office of Non-Proliferation and National Security of the U.S. Department of Energy (DOE NN-20). GIRM is based on the concept that the isotopic ratios of impurity elements in graphite will change as a function of reactor fluence and that the change in isotopic ratios can be measured to an acceptable degree of accuracy. Accurate measurement of the isotope ratios of key elements present in an unknown sample of reactor graphite would then permit the estimation of total fluence. Combined with reactor design and fuel information, such measurements can be used to estimate life-cycle energy and special nuclear materials (SNM) production in graphite-moderated reactors. This method has the important advantage that graphite moderator material is not replaced during the life of a graphite reactor. The isotopic signature that remains after a given operation period is characteristic of all reactor operations to that point, in contrast to methods based on fuel examination, or examination of components which can be easily replaced such as process tubes.

GIRM, as a method of estimating SNM production based on sample data, requires the ability to acquire samples and protect their chemical integrity, to prepare samples for isotopic analysis, to adequately measure isotopic ratios of interest, and to interpret these measurements in terms of reactor physics. Based on early studies (FY-92), the key uncertainties in this sequence were the ability to obtain good measurements for ratios which were adequately sensitive to fluence over the appropriate fluence ranges.

For this reason, the initial proof-of-principle experiment for GIRM was structured around the laboratory measurements step. The experiment used archived samples of a nuclear-grade graphite irradiated in a test location in C Reactor (one of several production reactors) at Hanford, and from the moderator of the French G-2 reactor at Marcoule. These samples were very large by chemical analysis standards, are from well known reactor locations, and the basic qualitative composition of trace impurities is known; however they were halide - purified nuclear grade materials, with lower impurity levels than are necessary for nuclear reactor construction. Thus, these relatively pure graphites represented a challenge to the GIRM methodology. The initial steps of the estimation process (e.g., sample collection and protection) were assumed to be feasible, and the proof-of-principle experiment focused on measuring selected ratios in this graphite.

This report documents the procedures for and results of this experiment insofar as measurement of the isotopic ratios are concerned. A subsequent, classified report dealing with the estimation of neutron fluence and SNM production based on these samples is scheduled as the final FY-94 deliverable for the Nuclear Archeology Project this year, and a reactor-scale demonstration of

GIRM is being planned for FY-95. This reactor-scale demonstration would integrate all the required capabilities, including a non-destructive sampling technique, to demonstrate the utility of the technique in a realistic setting.

As discussed in greater detail in the report, elemental impurities were found to be present in samples of reactor grade graphite in sufficient concentrations to permit measurement of isotope ratios with acceptable degrees of accuracy and precision. Furthermore, measurements of graphite irradiated in both C Reactor and the French G-2 Reactor indicate that isotope ratios for the measured impurity elements vary as a function of total reactor fluence. The measurement of isotope ratios in the irradiated graphite were also achieved with an acceptable degree of measurement uncertainty.

The overall results from the initial proof-of-principle experiment are very encouraging. Very good measurements were obtained for several ratios of interest in both in both samples, establishing the ability to obtain useful measurements at impurity levels that will be encountered in relatively pure nuclear graphite. The sample preparation methods developed in the project during FY-94 circumvent the apparent contamination problems experienced with earlier methods, and the use of Thermal Ionization/Mass Spectrometric (TIMS) methods allows element-specific analysis. The result is that precise, replicable measurements can be obtained for fluence-sensitive ratios in Ca, Ti, Sr and Ba. Measurement precision (based on integration statistics for a given MS measurement) for the ratios of interest is typically on the order of a few tenths of a percent to just over 1 percent. Replicability of the measurements is also very good, with measured values for key ratios typically differing less than 0.5 percent.

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1.0 Introduction

1.1 Overall Objectives of GIRM

The Graphite Isotopic Ratio Method (GIRM) was proposed as a way to estimate neutron fluence and associated special nuclear materials (SNM) production during the scoping phase of the Nuclear Archeology Project. This method seeks to exploit the shifts in isotopic composition that occur in some elements as a result of neutron irradiation. Earlier proposals to estimate fluence by measuring absolute levels of neutron activation products (Federation of American Scientists 1991) were found to suffer from the high degree of variability in trace impurities in nuclear graphite. In order to make use of such measurements, the original quantities of precursor isotopes would have to be accurately known. Since the absolute levels of impurity elements vary both from lot-to-lot, bar-to-bar within a lot, and spatially within a given bar of graphite, the practical utility of using absolute measurements to estimate fluence is nil. Table 1 illustrates the range of impurities for several grades of Hanford nuclear graphite. This difficulty is circumvented by measurement of isotopic ratios, which do not depend on varying initial impurity levels.

Table 1. Concentrations of Selected Impurities in Hanford Reactor Graphite

			Concentration, ppm				
Element	**Detection Limit,(a) PPM**	**KSO**	**KCF**	**CSO**	**CSF**	**GBF**	**SGBF**
Al	0.007	0.59	0.06	0.36	0.09	0.15	0.83
B	0.005	3.0	0.08	2.8	0.13	0.04	0.10
Ba	0.0005	2.6	0.02	2.6	0.03	0.04	0.007
Ca	0.002	210.0	0.13	135.0	0.27	0.59	0.22
Cr	0.003	1.1	BDL	0.34	BDL	0.005	BDL
Cu	0.001	0.68	0.15	0.19	0.28	0.06	0.68
Fe	0.001	5.6	0.33	2.8	0.28	3.1	0.19
Li	0.001	0.37	0.002	0.21	0.003	0.003	0.003
Ni	0.005	0.31	0.02	2.5	0.06	0.20	0.05
S	0.02	31.0	0.04	33.0	0.07	0.07	0.05
Si	0.005	1.3	0.67	6.0	1.3	0.07	1.25
Sr	0.0005	4.0	0.003	3.1	0.002	0.008	BDL
Ti	0.001	7.5	0.001	8.2	0.01	0.02	0.001
V	0.001	11.0	BDL	12.0	0.004	0.12	0.015
Zn	0.001	5.4	0.06	160.0	0.16	0.08	0.43

(a) Approximate, for the sample size and dilution factors used for these samples.
BDL = not detected, concentration below detection limit.

In addition to the elements listed in Table 1, the following elements either were not detected or were present in concentrations below 1 ppm: Be, Na, Mg, P, K, Mn, As, Se, Zr, Mo, Ru, Cd, Sd, Sn, Te, La, Ce, Nd, Sm, Gd, and Pb.

The immediate goal of the Nuclear Archeology Project is to develop GIRM sufficiently well to validate declared SNM production or detect SNM production in reactors ostensibly operated for other purposes. This measurements feasibility report discusses some of the feasibility issues associated with employing this measurement method for these purposes.

The feasibility of the GIRM requires that elemental impurities in graphite are present in sufficient quantities so that isotope ratios can be measured with acceptable uncertainties. The feasibility of GIRM also requires that isotope ratios of measurable impurity elements change predictably and perceptibly as a function of fluence over the fluence range of interest.

The overall objective is to provide an estimation method that can be used to objectively and accurately bound SNM production quantities in graphite reactors. This method could be used with extensive, large size samples in validating production declarations for graphite production reactors which are shut down, permitting destructive sampling. Such reactors have been in widespread use in several countries for decades and account for a sizeable fraction of worldwide weapons SNM inventory. If it can be established that small, non-destructive samples can also provide reliable information, this technique could also be used to estimate neutron fluence and SNM production in graphite reactors without compromising the ability for continued operation.

1.2 Fluence Estimation and Elements of Interest

There are several potential elements and isotopes that could be employed to estimate the special nuclear materials production of reactors using the graphite isotope ratio measurement concept. Potential ratio measurements include, a) variation in isotope ratios of impurity elements in the graphite, b) ratios of fission products from uranium impurities in graphite, and c) ratios of higher actinides resulting from successive neutron captures that originated with uranium impurities in graphite. The initial GIRM proof-of-principle efforts have focused on measuring the variations in isotope ratios of impurity elements in the graphite since this was considered to represent the best promise for success.

As will be discussed in some detail in Section 2.0, nuclear-grade graphite contains small amounts of many different elemental impurities. Each of these impurities are typically present in concentrations of less than a few parts per million. Under beginning of life conditions, prior to reactor irradiation, the isotopic ratios of each elemental impurity are consistent with natural abundances in the precursor materials, because the graphitization process does not alter isotopic ratios. During irradiation, each isotope of the impurity element has different rates of production and destruction. The production and destruction rate can be calculated for each isotope based on the reactor flux spectrum and nuclear cross section data. Therefore, after a period of irradiation, the isotope ratios of the impurity elements will have been changed from the natural abundance ratios. Measurement of these changed isotope ratios will permit the determination of the total neutron fluence required to produce the measured ratios, provided the reactor flux spectrum is known. Once the GIRM method has estimated the change in isotopic ratio for impurity elements in the graphite, a full core reactor physics model can be used to estimate the total neutron fluence and to translate this to an estimated SNM production.

In theory, isotope ratio measurements of any element can provide a fluence estimate. However, within a given range of fluences, some elements represent much better fluence estimators than others. As an example, the ratio of boron-10 to boron-11 varies rapidly as a function of fluence, but after a short period of irradiation the boron-10 has been completely destroyed and the boron isotopic ratio measurements provide no useful information after this point. Alternately, isotopes that have small net rates of production or destruction reflect only small changes in isotopic ratios as a function of fluence. Other elements represent poor choices for fluence estimation because there are large uncertainties in the tabulated nuclear data for these elements or there are inherently large measurement uncertainties due to their peculiar physical attributes. Moreover, the impurity element of interest must be present in the graphite in sufficient concentrations so that isotopic measurements can be performed on reasonable sizes of graphite samples. However the choice of sample size, precision of the chosen measurement method, and alternative choices of isotopic ratios can extend the useful application range of the GIRM methodology.

Based on the considerations discussed above, selection criteria were generated to assist in identifying elements for evaluation using the GIRM method that would have the greatest potential for success with the readily available irradiated graphites. Selection criteria included the following considerations, a) the element should be present in nuclear grade graphites in concentrations of at least a few tenths of ppm, b) the element should exhibit nuclear reaction cross sections that would result in perceptible changes in isotope ratios over the fluence range of interest, c) the nuclear data for the element should be well characterized, and d) laboratory measurement procedures should be available or could be developed to obtain acceptably low measurement uncertainty. Since both the range of concentrations of various impurities in graphite and the laboratory measurement uncertainties were less well quantified, the list of elements considered to have the greatest potential for providing the desired fluence estimation capability was generated primarily based on neutronics considerations. Reactor physics cell calculations were performed to provide the basis for determining, from the neutronics perspective, which elements would be most suitable for supporting GIRM. Each of the fourteen elements identified in the following list exhibit perceptible changes in isotope ratios over the fluence ranges of interest and are considered to have the most promise: 1) Chlorine, 2) Calcium, 3) Titanium, 4) Chromium, 5) Iron, 6) Cobalt, 7) Strontium 8) Niobium, 9) Barium, 10) Neodymium, 11) Europium, 12) Hafnium, 13) Tungsten, and 14) Rhenium.

As described in more detail in Section 2.0, two samples of irradiated graphite were readily available to support the GIRM proof-of-principle. Irradiated graphite samples were available from the Y Test Hole at C Reactor and the moderator of the French G-2 Reactor. To support the GIRM proof-of-principle, reactor physics cell calculations were performed for both reactors so that isotope measurements of the graphite samples could be compared to analytical predictions.

The cell calculations provided the basis for determining the neutron spectrum in the graphite in each reactor. Absorption cross sections for 207 isotopes of potential interest were obtained from the Evaluated Nuclear Data File, Version VI (ENDF/B VI). Using the ENDF/B VI cross section data, 89 group cross sections were computed for the neutron energy spectrum in the graphite. Using the 89 group, spectrum averaged cross sections, isotopic abundances for each graphite sample were calculated for the exposure times estimated from the reactor's operating history. These calculations account for transmutation from isotope to isotope, but do not consider transmutation from element to element. For the purposes of evaluating the fourteen elements identified in the above list, there are no errors introduced by not accounting for element to element transmutation as long as there are no elemental impurities of adjacent atomic mass that can decay to the element of interest.

In summary, the reactor cell calculations indicate that there are several elements which exhibit the desired neutronic properties that would permit their use as fluence estimators. Further, several of this identified elements are known to be present as impurities in reactor grade graphite. The neutronics studies indicated that the GIRM represented a technically feasible means of estimating fluence and SNM production.

1.3 Early Mass Spectrometry Results

The first attempts at measuring the isotopic ratios of interest for fluence estimation in irradiated graphite were conducted using Glow Discharge Mass Spectrometry (GDMS) in 1992. The GDMS technique was chosen because it required essentially no sample preparation and made use of the conductive nature of graphite to provide an ion source for spectrometry. The initial set of measurements was conducted at Y-12 laboratory, using samples irradiated in the moderator of the C Reactor and the G-2 Reactor from the same source as the samples used in the current study.

The resulting GDMS measurements were unsatisfactory for this application. Measurement precision was often in the 10% range, and replicates often differed by even larger fractions. Most importantly, however, many of the measurements showed little statistically significant variation from natural abundance ratios, even for isotope pairs in which neutronics predictions indicates that very noticeable change would have occurred. Furthermore, the ratios measured were inconsistent with each other - the pattern of ratios measured was not clearly consistent with *any* fluence level. Finally, some of the measured ratios were by themselves inconsistent with any fluence level - they indicated *negative* fluences.

Because these measurements were made on an instrument that was undergoing calibration and acceptance testing at the Y-12 laboratory, and the radiation history of the samples was well known, additional measurements were taken using another GDMS instrument, with the assistance of the instrument maker. These measurements were also of limited precision and were biased toward natural abundance ratios, and therefore of marginal use.

Based on these results, and the fact that several unirradiated samples had been analyzed just prior to the Y-12 analysis, it was concluded that the ratios measured using GDMS had been biased in the direction of natural (e.g., pre-irradiation) ratios due to contamination of the instruments. It was at this point in the project that the current approach was formulated. This approach involved ashing to concentrate the impurities, chemical separation of the individual impurity elements, and TIMS analysis of the resulting sub-samples. This set of procedures is described in the following sections.

1.4 Experimental Concept for Proof-of-Principle Measurements

The proof-of-principle experiment reported here is the first step in the development of GIRM as a working technique for validation of SNM production in graphite reactors. As such, it does not address all of the issues involved, but focuses on the feasibility of obtaining useful measurements from irradiated graphites of high nuclear purity. Other issues relating to sample acquisition and integrity, extended or different target elements, and minimization of sample quantity requirements are being addressed in ongoing work.

A central feature of the proof-of-principle experiment was the isolation of elements of interest by chemical processing prior to analysis. The procedures for this processing were adapted from various standard analytical practices and combined in a fashion that produced pure elemental fractions for several elements that were both present as impurities-in the test materials and sufficiently sensitive to neutron capture and transmutation. In order to allow the work to proceed reasonably quickly without an overly complex separations scheme, the work was focused on the elements Ca, Ti, Sr, Ba. These elements were selected based on a combination of analytical chemistry and neutronics considerations, and the available data on chemical composition of the test graphites. It is emphasized that application of GIRM on other graphite materials may require measurement of isotope ratios for other elements and development of separation/purification methods for these additional elements.

The existing data reporting levels of trace element impurities in graphite reveals wide variations in contents ranging from less than 1 ppb ($<10^{-9}$g/g) to more than 100 ppm (10^{-4}g/g). The chosen elements of interest in our study thus far (Ca, Ti, Sr, Ba,) occur in concentrations that do not exceed a few ppm, with the exception of Ca, which is found at levels exceeding 200 ppm in some types of graphite. Based on the analytical technique used to measure isotope ratios, some minimum amount of each elemental impurity is necessary. With present instrumentation and methods (TIMS), minimum amounts of each element of interest extracted and purified are in the range from 100 ng (10^{-7}) to 1 μg (10^{-6} g). These are considered minimum requirements for current methods; larger amounts will usually yield somewhat more precise results. These minimum analytical quantities can be used with concentrations of elemental impurities in any specific graphite to determine required sample sizes for application of GIRM. In this respect, it is also significant that the desired precision is inversely proportional to the sensitivity or usefulness of the ratio in fluence estimation calculations. For example, Ti and Cr are more sensitive than Sr, which is more sensitive than Ba, and a small amount of extracted Ti yielding an isotope ratio measurement precision typical of those measured in this experiment is more useful than a larger amount of Ba with a much better measurement precision. In the proof-of-principle experiment, there was no attempt made to demonstrate very small sample performance, and large (gram size) samples were used.

Earlier in this project, the elements of interest were identified based on several factors: 1) their sensitivity and usefulness in the fluence estimate calculations, 2) their detectable occurrence at reasonable levels (ppb to ppm) in the readily available irradiated graphites, and 3) prior experience and published research results by others which suggested the feasibility of mass spectrometric measurements for the elements of interest. Basically, the TIMS measurements are performed by loading a small amount of an element in solution onto a metal ribbon or filament which is heated under a high vacuum to produce ions that are accelerated into the mass spectrometer and separated on a mass-to-charge basis. The first experiments consisted of trials to determine the best filament material to use for each element, the loading medium, and the effects of any supplemental loading media on ion yield and sustainability of the run. These trials were conducted using high-purity standard solutions of the elements of interest. The element is gradually 'burned' off during the analysis; a longer run with a larger amount of sample yields higher measurement precision. Further tests were conducted to determine minimum and optimum amounts of each element required for a successful measurement and a desired precision. By using standard solutions with natural or 'normal' isotopic compositions, other factors affecting precision and accuracy were also evaluated as outlined below.

2.0 Sample Description

The samples labeled Y@C were cut from a bar of graphite that was irradiated in the Y Test Hole of C Reactor between August 1954 to April 25, 1969. It was retrieved from Y Test Hole on October 5, 1987, and has been stored under controlled conditions since that time. Although not documented, the bar is believed to be nuclear grade TSGBF graphite that was manufactured for the construction of KW Reactor.

The samples labeled G-2 were cut from a semi-cylinder furnished to us by the French Committee Energie Atomique. The semi-cylinder was part of a segment (Section 13) of a moderator block, core-drilled from the maximum flux region of the G-2 Reactor in February 1988. Like the bar from the Y Test Hole, this segment has been stored in sealed plastic bags in a controlled repository since it was received at Hanford.

2.1 Impurity Concentrations

Arrangements are being made to measure the concentrations of impurity elements in small samples of these two graphites by neutron activation analysis techniques; however, those results are not yet available. The primary source of impurities for these graphites is the petroleum coke that is used as the filler; lessor, but still significant, amounts of impurities can be contributed by the coal-tar pitch used as binder. The filler-coke used in both grades of graphite was produced at the Lockport, Illinois, refinery of the Texas Company[1] during the mid-1950s; thus, one could expect a similarity in the impurities for the two graphites. However, there were differences in the sources for the coal-tar pitch binders, the graphitization temperatures, and the processes used to purify the graphites. Each of these differences can alter the impurity concentrations, and concentration ratios, (but not isotopic ratios) in the final product.

The binder used in TSGBF was number 30 coal-tar pitch produced by the Barrett Co., and the maximum graphitization temperature was about 2450°C. During the graphitization run, chlorine was injected into the furnace during the heating period between 1000 and 2000°C, freon-12 was injected while the furnace temperature was above 2000°C, and chlorine was again injected until the furnace cooled to 1000°C. Chlorine removes most impurity elements; however, the fluorine from disassociated freon is more effective in removing the boron.

The binder used in the G-2 graphite was a coal-tar pitch was produced by Saar, and the maximum graphitization temperature was about 2900°C. Layers of NaF salt were deposited above and below the bars in the graphitization furnace; the distance between the outer-most bars and the NaF was chosen such that the NaF would begin to vaporize when the furnace reached about 2000°C. This process reduces the impurity content, but not as effectively as does a flow of chlorine gas. The neutron-capture cross-section of the graphite produced for the G-2 Reactor averaged 4.03 mb, significantly higher than the 3.74 mb cross-section of the TSGBF that was used in the construction of the KW Reactor.

Some information is available regarding the impurity concentrations in SGBF graphite (produced for use in the KE Reactor) and in the graphite produced for use in the G-3 Reactor. These two

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[1] Now Texaco Inc., Morristown, NJ 07960.

grades of graphite are, essentially, identical twins to TSGBF and the G2 graphite, respectively. Table 2 shows measured concentrations of important impurity elements in samples of SGBF and G-2 graphite. It should be noted, however, that the impurity concentrations in a particular sample of graphite may not be typical of the average concentrations in that grade of graphite.

2.2 Sample Machining

Machining of the cylindrical samples was done inside a HEPA-filtered glove box that is dedicated to the preparation of irradiated graphite samples. A diamond-tipped cutting tool was used to shape the samples, and about one-eight inch of material was removed from all surfaces to ensure against the retention of surface contamination. Platinum foil was used to ensure that the turned surfaces did not contact the lath chuck, or any other parts of the machinery.

The machined samples were then transferred to precleaned (acid washed) glass tubes for transport to the analytical laboratory for ashing, chemical separation, and TIMS analysis.

Table 2. Measured Impurity Concentrations (ppm) in Graphite Samples

	SGBF Graphite	**G-2 Graphite**
Total Ash	10.	220.
Barium	0.007	nm
Boron	0.10	0.20
Calcium	0.22	30.0
Chlorine	7.8	3.5
Chromium	0.003	nm
Dysprosium	< 0.001	0.010
Europium	nm	0.0007
Iron	0.19	2.0
Lithium	0.003	nm
Samarium	< 0.01	0.017
Strontium	0.002	nm
Titanium	0.001	5.0
Vanadium	0.015	32.0

nm = not measured by technique used.

3.0 Sample Preparation

Several factors in this project require much care to be taken in the sample preparation procedures. TIMS measurements are more successful when the elements isolated from the sample are as pure as possible, i.e., free of elements with overlapping isotopes which will result in isobaric interferences, during the measurement (e.g., the interference of ^{48}Ca or ^{50}Cr on ^{48}Ti and ^{50}Ti, respectively), and free of other major or matrix elements which may tend to suppress thermal ionization of the element of interest. Early experiments which consisted of loading finely powdered graphite onto a filament resulted in detection of several of the elements of interest, however, the overall signal for an element such as Ti was insufficient for any useful amount of data acquisition and suffered from the presence of significantly higher amounts of Ca which produced isobaric interferences and possibly partial suppression of the Ti ion signal. The very low contents of trace element impurities in the graphite provide limited amounts of each element of interest, and significant contamination by natural elements during sample preparation could bias the isotope ratio measurements conducted on irradiated graphite samples. Thus, any sample preparation procedure undertaken must involve a significant extraction and preconcentration of the trace element impurities as a group and their separation from one another while maintaining a high extraction yield of each element throughout the process. Contamination control during the procedure is also very important and is accomplished by several means as outlined below.

3.1 Sample Ashing and Digestion

Our present method of sample preparation involves slow combustion and ashing of the graphite as a first step. The ash content of graphites under study varies from a few ppm to a few hundred ppm, and this ashing step effectively preconcentrates the elements of interest by a factor of about 10^6. The ashing was accomplished in a horizontal muffle tube furnace lined with a high purity quartz glass tube of approximately 1-inch diameter.

The graphite samples were enclosed in a 'boat' made of high-purity Pt foil, chosen for its purity and refractory properties, and a new piece of Pt foil was used for each sample to avoid cross-contamination between samples. The Pt-wrapped graphite sample was centered at the center of the quartz furnace tube and ashed in pure O_2 at 700° C, and the CO_2 reaction product was trapped in Ascarite so Carbon-14 was not released to the atmosphere. The temperature and O_2 flow rate were previously found to be optimum for samples of unirradiated test graphite. These procedures may require some adjustment for ashing of different graphites, because too high a temperature may cause too rapid combustion, buildup of too much water vapor and plugging of the $C0_2$ trap, or alloying of the ash residue with the Pt foil. All graphite samples that we processed in this manner so far contained variable amounts of black refractory particles that were apparent in the ash residue.

Upon completion of ashing, the samples were allowed to cool completely in the furnace, still under O_2 flow. The samples were removed from the quartz furnace tube and carefully transferred to a clean working area in a fume hood. Transfer of the ash from the Y@C sample to a capped, screw-top Teflon beaker was accomplished by pipetting 0.2-0.3 ml portions of nitric acid ($HN0_3$) onto the Pt foil. The G-2 sample yielded a number of black inclusions which adhered tightly to the Pt foil, possibly due to inadvertently heating the sample to a higher temperature than required. To remove these inclusions the surface of the Pt foil was etched with warm aqua regia ($HCL:HN0_3$=3:1 mixture). After transferring to a capped Teflon beaker, the nitric acid or aqua regia from each sample was evaporated under a heat lamp in the fume hood. Approximately 1 ml of $HN0_3$ and 0.3 ml of tetrafluoroboric acid (HBF_4) were added to the sample residue, the beaker capped, and left under low heat overnight. Subsequent evaporation of this mixture further reduced the mass of the sample residue by loss of volatile SiF_4 from the sample, however using hydrofluoric acid (HF) can cause precipitation of insoluble fluorides such as CaF_2, and HBF_4 prevents this. After evaporating to dryness, three 0.5 ml portions of HCl were added to each sample residue, evaporating to dryness in between, in order to convert most or all of the sample to soluble chlorides for subsequent ion exchange chemistry. The sample was redissolved in 0.5 ml of 1.6M HCI, and transferred to a small pre-cleaned centrifuge tube and centrifuged to separate the undissolved particles, because only the portion of the sample in solution could be used in ion exchange purification processes.

Several precautions were taken for contamination control throughout the sample preparation. Sources of potential contamination include reagents used, leaching from containers used during processing, and airborne dust in the laboratory. All reagents used for sample removal, digestion, and ion exchange are the highest purity commercially available, and are typically purified by sub-boiling distillation. Trace element impurities in these acids are typically only a few ng (10^{-9}g) to pg (10^{-12}g) per ml and contribute negligible amounts of normal elements to the sample trace element impurities. Water used is purified in the laboratory by a commercial, high-efficiency physical and chemical filtering system. Highly significant amounts of trace element impurities are easily leached from laboratory glassware even by dilute acids. Chemically inert containers composed of Teflon or similar materials were used in the process wherever possible, and plastic labware used for various other tasks. All Teflon and plastic labware was cleaned by soaking first in a solution of 50% NH_40H for a few days, rinsed thoroughly in distilled water, leached for a few days in a 50% $HN0_3$ bath, rinsed again, dried in air, and sealed and stored in an airtight bag until just prior to use. All reagents are stored in containers cleaned and leached in this manner. Ion exchange resins are stored in Teflon bottles in dilute HCl; this equilibrates or converts the resins to chloride form and leaches trace impurities from the material.

3.2 Ion Exchange Chemistry

The ion exchange procedure for purifying and extracting trace impurity elements of interest from the graphite sample ash residue is based partly on previous or established methods. The method basically depends on the different relative retention/complexation of trace element cations or anions by the resins in various types and strengths of reagents. This phenomenon permits the separation of elements of interest from each other and also from major, or matrix elements making up the ash sample, in order to improve quality of measurements and to eliminate isobaric interferences in the mass spectrometric analyses. Ion exchange columns were made up of pre-cleaned polyethylene tapered squeeze transfer pipets with the tops removed, and fitted with a plastic, permeable frit at the bottom. The columns were filled with ion exchange resin to a desired height and flow rate, and the resin was cleaned further with successive rinses of concentrated HCl. For a particular medium, elements are eluted or removed from the resin in order of increasing affinity. Some elements are not retained, while others may strongly complex with the resin, and a typical elution scheme would employ increasingly stronger acid as an elutant, either in a smooth or stepwise gradient elution.

It was expected that the graphite ash residue would be broadly similar to geological samples such as rocks or soils, and prior experience suggested an elution scheme using the cation exchange resin and HCl as the elutant. The first column thus consists of approximately 3 cc of cation exchange resin (Dowex AG50X8) and multiple trials were conducted to determine optimum elutions for the elements of interest. An analog 'sample' was made up by combining small amounts of pure standard solutions of K, Ca, Ti, Cr, Fe, Ni, Co, Rb, Sr, and Ba; this mixture included the 4 elements of interest in addition to other elements with potential isobaric interferences in order to determine an effective separation from each other, e.g., Rb from Sr due to an overlapping isotope at mass 87. This mock 'sample' solution (and also graphite ash samples as mentioned earlier) was dried down and redissolved in 1.6M HCl. Each trial consisted of loading a small amount of this 'sample' solution on the cation resin column equilibrated earlier in 1.6M HCl, followed by certain volumes of 1.6M HCl, 2.0 M HCl, and finally 6M HCl as predicted by specific element distribution coefficients for the resin. Each HCl fraction was allowed to drain from the column before the next, and throughout the entire elution, 1 ml volumes were collected and later analyzed by inductively coupled plasma mass spectrometry (ICP-MS), a sensitive method of multi-elemental analysis. The ICP-MS results for each trial revealed the intervals and peaks at which the various elements were eluted from the column. The final elution scheme was further tested with an actual sample solution of dissolved ash produced from an unirradiated graphite sample.

In the calibrated elution scheme currently in use, Ti and Cr are removed immediately, i.e., pass through the cation exchange column in 1.6M HCl and are collected in a Teflon beaker for subsequent separation on a second column step described below. This is likely due to a lack of affinity of Cr and especially Ti for this particular resin; we later observed this effect to be enhanced in the presence of residual F from the HBF_4 used in the sample digestions. The elutant is then changed to 2 M HCl which removes K, Ca, Fe, Ni, Rb, and Cs. For our studies, the Ca fraction was collected for mass spectrometric analysis at this point. This is followed by 6M HCl which elutes Sr first, followed by Ba, and these two fractions were collected in Teflon beakers for mass spectrometric analysis. For the irradiated graphite ash samples, all elution fractions not reserved for mass spectrometric analysis were also collected but were combined and saved for possible future use in radiochemical counting analyses. The Ca, Sr, and Ba fractions were dried to a residue in their respective Teflon beakers and converted to nitrates by addition of 0.2ml of $HN0_3$ followed by evaporation. Teflon beakers with an inner conical shape are used to concentrate each of these fractions to a small visible portion which facilitates handling prior to mass spectrometric analyses. The early Ti and Cr fraction contained Na, Si, Al, K, and some Ca and was unsuitable for analysis due to this extra material and also the interference of ^{50}Cr on ^{50}Ti.

The presence of F after the first cation exchange column greatly reduces or even reverses any subsequent anion exchange procedures for Ti and Cr separations, and F must be removed. The initial fraction containing Ti and Cr from sample graphite ash collected on the first cation exchange column was evaporated and 0.2 ml of perchloric acid ($HCl0_4$) added.

This was evaporated at a higher temperature under heat lamps to ensure removal of the more volatile F and conversion of the Ti+Cr fraction to chlorides for separation on the second anion exchange column.

A second anion exchange resin (Dowex AG1X4) column consisting of approximately 1 cc of resin was used to separate Ti and Cr. At high molarity HCl, Ti has a high affinity for the resin, and Cr even higher, whereas other elements such as Ca and K are immediately eluted, thus purifying the Ti fraction for analysis. In initial trials, the elution peak for Ti was detected by collecting 0.5 ml elution fractions into beakers containing 0.5 ml of hydrogen peroxide (H202); Ti was apparent as the highly colored Ti perchlorate ion. Titanium was removed after a few ml of 12M (concentrated) HCl, and Cr (and any traces of other transition metals) was later removed in 6M HCI. This final Ti fraction was dried in a conical beaker and treated with $HN0_3$ prior to later mass spectrometric analyses which confirmed the successful removal of Cr from the Ti fraction in this procedure. Analysis of the Ti fraction also confirmed the successful removal of Ca, which is accomplished mainly on the first cation column, and to a lesser degree on the second (anion) column.

3.3 Summary

In summary, the sample preparation methods developed and used to date are meeting present desired performance objectives for the four elements selected. Future development or application of GIRM project will undoubtedly involve preparation and analysis of smaller graphite samples with unknown trace element impurity contents. Where sample sizes permit, a small portion of samples should be used for bulk chemical analysis to determine impurity contents to judge feasibility, and to guide, further sample preparation and mass spectrometric analyses. In anticipation of smaller samples, even more rigorous approaches to contamination control during preparation are under development. To identify and control sources of contamination, sample preparation blanks will be prepared and run using isotope dilution analysis; this is a sensitive method which involves preparation, analysis, and calibration of a spike solution consisting of a nearly pure isotope of each element of interest. The unused portions of the ion exchange elutions may be useful in radiochemistry and counting analyses; this removes significant background for detection of many elements by gamma- and beta-counting. Finally, ion exchange separations and mass spectrometric analysis procedures are being developed for additional elements of interest, especially Cr, which were identified earlier as potentially useful based on neutronics perspectives.

4.0 Mass Spectrometric Analysis

Each of the elemental fractions purified by ion exchange chemistry as outlined above was redissolved in a few microliters of 1% $HN0_3$, and a small portion of the sample, usually 1 µl, was taken up and loaded onto a filament. High-purity zone-refined Ta filaments were found to be most effective for running Ca, Sr, and Ba, and zone-refined Re filaments were determined to be best for analyzing Ti. Filaments were then heated under vacuum to higher temperatures than employed during analyses in order to 'outgas' the filaments and remove surface contamination. Rhenium filaments used for Ti are 'carburized' after this initial high-temperature outgassing, by re-heating at a lower current under vacuum with a slow bleed of benzene. Carburized Re filaments have been found to be useful for several elements such as Ti which do not thermally ionize efficiently. The ion yield for Ti is further inhibited by the tendency for Ti ions to recombine readily with oxygen even under high vacuum; the thin film of carbon on the carburized Re filaments reverses this effect by minimizing the oxides produced and increasing the production of metal ions which are preferred for analysis. The Ca, Sr, and Ba samples were carefully loaded in one µl aliquots onto the center of Ta filaments, evaporated in air by applying a low current; one µl of 0.7 N phosphoric acid (H_3P0_4) was applied over the sample, evaporated, and the filament brought slowly up to a dull red heat, and then cooled. The Ti fractions were simply loaded onto the Re filaments, evaporated, and slowly brought up to a dull red heat also. The loading 'blank' for each of these loading methods was qualitatively evaluated using a filament and the same amounts of loading media but no sample. The signal intensities for each element of interest on the 'blank' filament were negligible even at currents and temperatures higher than those used for analysis, and in most cases decreased rapidly.

4.1 Instrumentation and Data Acquisition

A 12-inch radius single-stage, magnetic sector mass spectrometer originally manufactured by Consolidated Electrodynamics Corporation (CEC) was used for measurements thus far in this study. The ion detection system consists of a discrete-dynode electron multiplier coupled to a Carey Vibrating Reed Electrometer and a Digital-Analog Converter. The software for instrument control and data acquisition was written in-house under contract, and is currently being modified or updated to later enhance measurement capabilities in this project. Appropriate magnet settings for each of the four elements of interest were determined and analysis menus composed as summarized in Table 3.

The most abundant isotope of each element is underlined. For some elements, additional masses were monitored to check for potential isobaric interferences, e.g., ^{85}Rb is scanned to check for ^{87}Rb interference on ^{87}Sr. In Ba extracted from irradiated graphite samples, mass 133 is monitored to check for ^{133}Ba and a potential ^{133}CS interference, although Cs is quite well separated from Ba in the first cation exchange purification step. For Ca, there is the possibility of a significant ^{40}K interference on ^{40}Ca, and the chosen approach was simply to 'burn off' the more readily ionized K, which was usually present to a small degree, before acquiring data for Ca.

Table 3. Mass Spectrometric Settings

	Ca	**Ti**	**Sr**	**Ba**
	40	44(Ca)	84	130
masses	41	46	85(Rb)	132
	42	47	86	133(Cs)
of	43	48	87	134
	44	49	88	135
interest	46	50		136
	48	52(Cr)		137
				138
(baseline)	41.5	45.5	84.5	130.5
peak integration time	1 sec	1	1	1
magnet settling time	3 sec	3 sec	2 sec	2 sec

Isotope ratio data were acquired by peak-jumping, whereby the magnet current is periodically switched to a predetermined setting corresponding to a mass of interest, allowed to settle, and the measured ion current converted to counts, integrated, and recorded/stored on a computer. For each element, the selected mass range is jumped or scanned up mass, then down mass in one cycle, and in between cycles the baseline mass is counted. Data from each cycle yields one set of isotope ratio measurements, and up to 10 cycles per block of data may be specified. A single block of data (10 ratio measurements) is adequate for many nuclear applications, however for this project, it was desirable to attain maximum measurement precision possible, and several blocks of data were collected until the sample was exhausted.

Isotope ratio measurements of each of the 4 elements of interest extracted from graphite samples were accompanied by isotope ratio measurements of corresponding 'normal' or natural elements. The latter were usually run first to check instrument settings and were loaded onto the filament in exactly the same way as samples. Running normal elements or standards in this manner also serves to evaluate and quantify small amounts of instrument bias, i.e., measured deviations from certified or reference values for normal isotopic ratios. The amount of instrument bias, and also within-run thermal fractionation of light isotopes relative to heavier isotopes of each element, appears to be negligible with respect to measurement precisions attained so far. In a further attempt to make standard and sample runs closely comparable, one μg (10^{-6} g) of Ca standard was loaded, whereas an average of .5 μg of each of the other element standards (Sr, Ba, and Ti) was used. At this time, sufficient trace element bulk compositional data is not available for either of the irradiated samples analyzed, though in the future samples will be analytically screened when possible to guide our sample preparation efforts and to judge how much of each element is available for mass spectrometric analysis. The success of the isotope ratio analyses in this study suggests that the amounts loaded and run for elements actually extracted from the samples were equal to or greater than those amounts loaded and run from standard solutions.

4.2 Results and Summary

Results of mass spectrometric analyses are presented in Tables 4 and 5 for each of the two irradiated graphites analyzed thus far. Isotope ratios for Ca, Ti, Sr, and Ba are expressed relative to the major isotope of each element. In most cases, replicate sample analyses were conducted to evaluate potential variations arising from possible different amounts of within-run fractionation, slight variations in running currents/temperatures, or from loading different amounts of sample. Most of these replicate analyses were well within analytical uncertainty. The analytical precision for the measured isotope ratios, especially for Ti, is insignificant relative to other sources of uncertainty in calculations for fluence estimates and is more than adequate for such applications. As described earlier, the greater sensitivity of some elements over others in the calculations, e.g., Ti is more sensitive than Ba, requires less analytical precision in these more sensitive elements, whereas the use of less sensitive elements such as Ba and Ca may always be somewhat limited both by neutronics uncertainties despite a very high obtainable mass spectrometric analytical precision.

In summary, our initial mass spectrometric analyses of trace element impurities extracted from two irradiated graphite samples were very successful and show much promise for future applications in fluence calculations and estimates of SNM production. Present and future developments in the mass spectrometric analytical effort must also strive for acceptable isotope ratio measurement precision on smaller amounts of the trace elements of interest. These developments include 1) modification of present software on the CEC instrument for more efficient data acquisition, 2) modification or development of filament loading methods to improve ionization efficiency of more difficult elements such as Ti, Cr, or Fe, and 3) possible acquisition of a new multi-collector instrument (via another funded program) capable of even more efficient data acquisition and lower detection limits.

Table 4. Results for Y@C Graphite

Titanium

ratios measured	natural Ti	sample Ti(1)	sample Ti(2)
^{46}Ti/^{48}Ti	0.1088(12)	0.1245(13)	0.1242(16)
^{47}Ti/^{48}Ti	0.09908(80)	0.1091(8)	0.1094(12)
^{49}Ti/^{48}Ti	0.0740(7)	0.2217(15)	0.2229(15)
^{50}Ti/^{48}Ti	0.0715(7)	0.0862(9)	0.0871(9)

	natural %			
mass/atom %	reference	measured		
46	8.0	8.039	8.077	8.046
47	7.3	7.321	7.078	7.087
48	73.8	73.89	64.87	64.78
49	5.5	5.468	14.39	14.44
50	5.4	5.283	5.592	5.643

Strontium

ratios measured	natural Sr	sample Sr(1)	sample Sr(2)
^{84}Sr/^{88}Sr	0.006759(66)	0.006444(10)	0.006497(20)
^{86}Sr/^{88}Sr	0.11966(46)	0.11460(50)	0.11463(55)
^{87}Sr/^{88}Sr	0.08461(21)	0.05712(22)	0.05713(42)

	natural %			
mass/atom%	reference	measured		
84	0.56	0.558	0.547	0.551
86	9.86	9.881	9.727	9.729
87	7.02	6.987	4.848	4.849
88	82.56	82.57	84.88	84.87

Barium

ratios measured	natural Ba	sample Ba(1)	sample Ba(2)
^{130}Ba/^{138}Ba	0.001486(33)	0.001054(56)	0.001053(53)
^{132}Ba/^{138}Ba	0.001427(27)	0.001177(48)	0.001169(55)
^{134}Ba/^{138}Ba	0.03385(15)	0.03283(25)	0.03275(25)
^{135}Ba/^{138}Ba	0.09214(21)	0.07779(36)	0.07756(36)
^{136}Ba/^{138}Ba	0.10869(17)	0.12401(53)	0.12392(44)
^{137}Ba/^{138}Ba	0.15683(23)	0.14894(42)	0.14893(53)

Table 4. (contd.)

	natural%		sample %	
mass/atom%	reference	measured	reference	measured
130	0.101	0.107	0.076	0.076
132	0.097	0.102	0.085	0.084
134	2.42	2.426	2.369	2.364
135	6.59	6.603	5.613	5.598
136	7.81	7.861	8.949	8.945
137	11.32	11.24	10.75	10.75
138	71.66	71.66	72.16	72.18

Calcium ratios measured	natural Ca	sample Ca
^{48}Ca/^{40}Ca	0.002040(24)	0.001722(63)
^{41}Ca/^{40}Ca	0.0000302(36)	0.0000182(47)
^{44}Ca/^{40}Ca	0.02217(14)	0.02189(6)
^{43}Ca/^{40}Ca	0.001425(19)	0.001339(20)
^{42}Ca/^{40}Ca	0.006786(43)	0.006836(40)
^{41}Ca/^{40}Ca		0.006119(37)

	natural %		
mass/atom %	reference	measured	
40	96.97	96.86	96.35
41			0.590
42	0.64	0.657	0.659
43	0.145	0.138	0.129
44	2.06	2.147	2.109
46	0.0033	0.0029	0.0018
48	0.18	0.198	0.166

Notes

(1) Numbers in parentheses are errors on measured ratios representing 1 standard deviation in smallest significant figures.

(2) Data for Ca measurements were taken only after ^{39}K had decreased ('burned' off) to less than 30mV. The average signal for ^{40}Ca was 20V.

(3) None of the above results are corrected for within-run fractionation, although some of this effect is observed in Sr and Ti.

Table 5. Results for G-2 Graphite

Titanium

ratios measured	natural Ti	sample Ti(1)	sample Ti(2)
^{46}Ti/^{48}Ti	0.10768(69)	0.11079(35)	0.11112(45)
^{47}Ti/^{48}Ti	0.09840(54)	0.10106(36)	0.10145(61)
^{49}Ti/^{48}Ti	0.07447(38)	0.11408(26)	0.11461(38)
^{50}Ti/^{48}Ti	0.07224(45)	0.07560(27)	0.07622(41)

	natural %		sample %	
atom%	reference	measured	reference	measured
46	8.0	7.960	7.905	7.918
47	7.3	7.274	7.211	7.229
48	73.8	73.92	71.35	71.26
49	5.5	5.505	8.140	8.167
50	5.4	5.340	5.394	5.431

Strontium

ratios measured	natural Sr	sample Sr(1)	sample Sr(2)
^{84}Sr/^{88}Sr	0.006852(56)	0.006700(84)	0.006729(87)
^{86}Sr/^{88}Sr	0.12032(48)	0.11850(32)	0.11841(40)
^{87}Sr/^{88}Sr	0.08469(21)	0.07626(26)	0.07633(29)

	natural %		sample %	
atom %	reference	measured	reference	measured
84	0.56	0.565	0.558	0.560
86	9.86	9.929	9.863	9.855
87	7.00	6.988	6.347	6.353
88	82.58	82.52	83.23	83.23

Barium

ratios measured	natural Ba	sample Ba(1)
^{130}Ba/^{138}Ba	0.001488(12)	0.001360(22)
^{132}Ba/^{138}Ba	0.001421(16)	0.001347(32)
^{133}Ba/^{138}Ba		0.000036(21)
^{134}Ba/^{138}Ba	0.03392(9)	0.03385(14)
^{135}Ba/^{138}Ba	0.09230(14)	0.08814(26)
^{136}Ba/^{138}Ba	0.10983(18)	0.11396(22)
^{137}Ba/^{138}Ba	0.15696(21)	0.15457(26)

Table 5. (contd.)

	natural %		
atom %	reference	measured	
130	0.106	0.107	0.0976
132	0.101	0.102	0.0967
133			0.0026
134	2.42	2.430	2.430
135	6.593	6.612	6.326
136	7.85	7.868	8.179
137	11.23	11.24	11.09
138	71.70	71.64	71.77

Calcium ratios measured	natural Ca	sample Ca(1)
^{48}Ca/^{40}Ca	0.001692(48)	0.00149(11)
^{46}Ca/^{40}Ca	0.0000162(23)	0.0000130(28)
^{44}Ca/^{40}Ca	0.02173(14)	0.02123(14)
^{43}Ca/^{40}Ca	0.001385(15)	0.001321(24)
^{41}Ca/^{40}Ca	0.006679(39)	0.006568(86)
^{41}Ca/^{40}Ca		0.001715(24)

	natural %		
atom %	reference	measured	
40	94.941	96.95	96.87
41			0.166
42	0.647	0.648	0.636
43	0.135	0.134	0.128
44	2.086	2.107	2.057
46	0.004	0.0016	0.0013
48	0.187	0.164	0.144

Notes:

(1) Numbers in parentheses are errors on measured ratios representing 1 standard deviation in smallest significant figures.

(2) None of the results are corrected for within-run fractionation; some is observed in Sr and Ti measurements.

(3) Ca measurements were taken only after ^{39}K had decreased to <30mV; the average ^{40}Ca signal was 20V.

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5.0 Reference

Federation of American Scientists. 1991. "Ending the Production of Fissile Materials for Weapons - Verifying the Dismantlement of Nuclear Warheads."

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