

THE USE OF MULTI-ELEMENT NEUTRON ACTIVATION ANALYSIS OF ORGANIC LAKE SEDIMENT IN GEOCHEMICAL EXPLORATION FOR GOLD

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ABSTRACT

Gold in organic lake sediment is a useful guide to areas of gold potential at the regional scale, although background and threshold values are low (<1 and 4 mg/t Au, respectively). Direct neutron activation analysis (NAA) of lake sediment can provide gold analyses adequate for geochemical exploration, and, in addition, gives data on a large number of other elements (e.g., Ag, As, Ba, Br, Cd, Ce, Co, Cr, Cs, Eu, Fe, Hf, Hg, Ir, La, Lu, Mo, Na, Ni, Rb, Sc, Se, Sm, Sn, Ta, Tb, Te, Th, U, W, Yb, Zn and Zr). The method has the advantage of being nondestructive.

The results of NAA analyses of about 1500 lake sediment samples from Newfoundland and Labrador, including a large number of replicates and control reference samples, indicate that the method provides good quality data for As, Ba, Br, Ce, Co, Cr, Cs, Eu, Fe, Hf, La, Lu, Mo, Na, Ni, Rb, Sc, Sm, Ta, Tb, Th, U, Yb and Zn. The detection limits for Ag, Cd, Hg, Ir, Sn and Te are too high to measure their abundances in typical lake sediment. Data for Se, W, Au and Zr are quite significantly truncated by their detection limits, but are still of value in geochemical exploration. The results for Co, Fe, Mo, Ni and Zn by NAA compare well with data acquired by atomic absorption; NAA data for Ba, Ce, La, Th and Zr show good overall correlations with results by ICP/OES.

Although the technique is nondestructive, when material is irradiated and analyzed a second time by NAA, long-lived isotopes lead to spuriously high results for elements such as Co, Cs, Eu and Sc. For Au, this 'memory' effect is negligible, and by reanalyzing the same material it is possible to isolate analytical variability from sample variability due to inhomogeneity. In general, organic lake sediment is remarkably homogeneous in its Au content, strongly suggesting that most of the Au is evenly dispersed (adsorbed ?) throughout the material.

INTRODUCTION

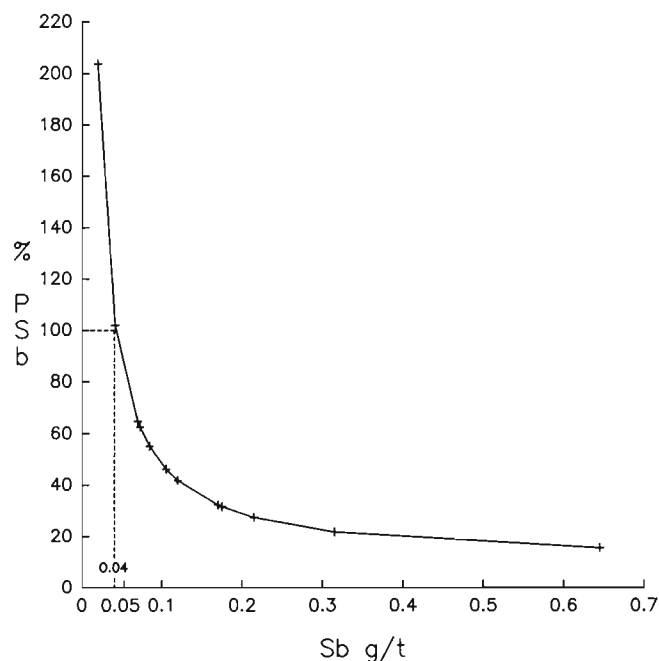
Direct neutron activation analysis (NAA) is capable of measuring, at reasonable cost, Au abundances in organic lake sediment at levels low enough to measure dispersion patterns from Au deposits (McConnell, 1987; Davenport and Nolan, 1987). As typically offered by commercial laboratories, the method provides data for over 30 elements in addition to Au: e.g., Ag, As, Ba, Br, Cd, Ce, Co, Cr, Cs, Eu, Fe, Hf, Hg, Ir, La, Lu, Mo, Na, Ni, Rb, Sb, Sc, Se, Sm, Sn, Ta, Tb, Te, Th, U, W, Yb, Zn and Zr for the results discussed here. In this article, the quality and usefulness of these multi-element data in lake sediment for geochemical exploration will be discussed, as well as some features of the method and suggestions for an approach to monitoring analytical quality and assuring analytical consistency.

MEASUREMENT AND MONITORING OF ACCURACY AND PRECISION

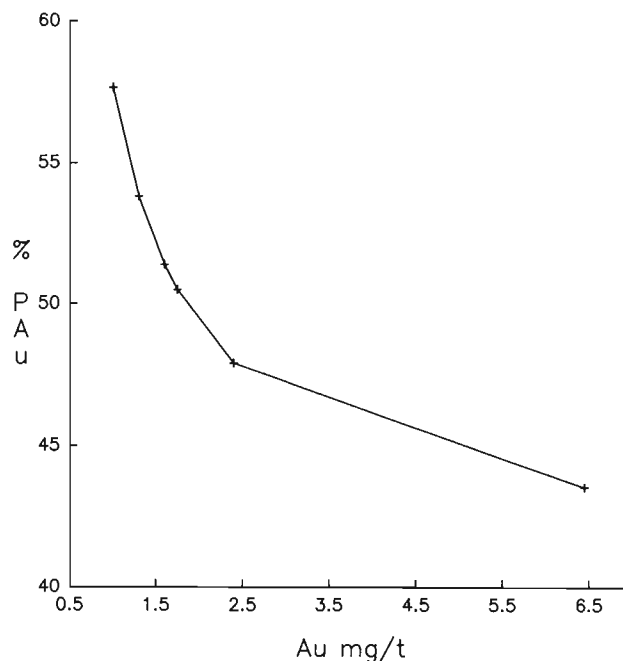
The determination of absolute accuracy presents considerable problems for most of the elements in the NAA suite, since there are few, if any, reference standards available

for many of them, and certainly none of lake sediment. Fortunately, for mapping geochemical patterns in surficial materials, absolute accuracy is not of paramount importance, providing the results for a particular element are directly proportional to the actual levels of the element in the samples, the results are consistent in level from one analytical batch to another, and the reproducibility (precision) for any sample is sufficiently good to allow differences in level between samples to be measured. In the absence of reference materials, the proportionality of results for an element to its real concentration in a sample can be estimated by comparing the results of two different analytical techniques—such as NAA, which depends on the nuclear properties of an atom, and atomic absorption spectrophotometry, which depends upon an atom's electronic properties. The likelihood of two such very different techniques giving closely proportional results by chance is remote.

To monitor the precision and accuracy of NAA analyses of Newfoundland lake sediment, analytical splits and control reference materials were inserted in all batches. In addition, site duplicate samples were included, which allow the



A



B

Figure 1. Plots of precision (PSb , PAu) as a function of concentration for (A) Sb and (B) Au by NAA, based on 136 pairs of replicate analyses. The calculated detection limit (0.04 g/t) where $PSb = 100$ percent and the quoted detection limit (0.05 g/t) are shown in Figure 1A.

determination of the combined sampling and analytical variance. Both controls and duplicates were included 'blind'; that is, they were indistinguishable from the normal samples.

Sample Splits

If chosen randomly, the sample splits will comprise a representative subset of the sample suite being analyzed. Being representative, they will give the best measure of analytical reproducibility for the sample set, in contrast to the control reference material, which usually is specially prepared from a different area and from a different medium having a different chemical and mineralogical composition.

Thompson and Howarth (1978) devised a method for calculating analytical precision from duplicate pairs of analyses (at least 50), which recognizes that analytical precision varies with absolute concentration. This approach allows the effective detection limit of the analytical method to be determined in many cases; this detection limit may be higher in the particular sample material being used than that quoted by the laboratory.

Briefly, the method of Thompson and Howarth (1978) involves the following steps:

- 1) calculate the means and absolute values of the differences of the pairs of duplicate analyses, $(X_1 + X_2)/2$ and $|X_1 - X_2|$ respectively;

- 2) sort the values in order of increasing mean value;
- 3) assign the sorted results to groups of eleven, ignoring the last group if it contains less than eleven results;
- 4) for each group obtain the overall mean concentration and the median difference;
- 5) calculate the linear regression equation of the median difference (dependent variable) on the mean group value (independent variable); and
- 6) from the regression equation, the value of the median difference $|X_1 - X_2|$ at any mean concentration X_c can be taken as the standard deviation (s) and the precision (P_c) at that concentration (X_c) is given by $P_c = 200s/X_c$ (at the 95 percent confidence level).

Analytical values less than the detection limit have been set here to a value of one half of the detection limit that was quoted by the laboratory. This leads to a slightly optimistic value for the precision at low levels (Thompson and Howarth, 1978), but this is not regarded as a major problem; the choice of some other value would be even more arbitrary.

Examples of the application of this approach are shown in Figures 1A and 1B for Sb and Au by NAA. These results are based on 136 pairs of laboratory splits from the orientation

study of McConnell (1987) in the White Bay area, the analyses of archived samples in the Port aux Basques and White Bay area (Davenport and Nolan, 1987), and the analyses of lake sediment from other parts of Newfoundland and Labrador carried out in 1987. Figure 1A shows a common form of plots of precision with concentration (Fletcher, 1981, Fletcher *et al.*, 1987). The quoted detection limit and the actual detection limit (the concentration where the precision is ± 100 percent) are marked for Sb. In the case of Au (Figure 1B), the rounding of the values below the detection limit has significantly increased the precision measured in this manner, and a true assessment of the actual detection limit is not possible from this approach. Estimates of the detection limits for As, Cs, Co, Eu, Hf, Ni, Rb and Yb can be obtained, however, in addition to that of Sb. The range of values for several other elements in the duplicate samples is generally well above their detection limits, so for these elements too, this approach does not yield estimates of their detection limits.

Although this method gives an overall assessment of analytical precision where a reasonably large number of duplicate analyses (> 50) is available, it is neither particularly useful for monitoring precision, nor for identifying outliers which might indicate the need for reanalysis. This can be done in another way from the results of analyses of laboratory splits.

For each pair of analytical duplicates a precision parameter, p , is calculated from the ratio of the absolute value of the difference between the two values to the mean of the two values,

$$\text{i.e., } p = |X_1 - X_2| / \frac{1}{2} (X_1 + X_2)$$

The value of p is expressed as a percentage, and as in Thompson and Howarth's (op. cit.) approach relates analytical variance to absolute concentration, but for each individual pair rather than generally for all pairs. The values of p can be compared to a table of pre-established tolerances such as in Table 1 for Sb. The tolerances at lower concentrations increase progressively to a value of ± 100 percent (cf. Figure 1A).

In establishing tolerances such as those in Table 1 for a new analytical method, it is necessary to analyze the distribution of p values with concentration. This can be done by assigning the results for the duplicate pairs into four to six groups that span the range of concentrations. For each group the mean and standard deviation of the p values and maximum p value are tabulated. The mean, mean plus one standard deviation and maximum value of p can be plotted against the midpoint value of each group (Figure 2) to obtain a general impression of the relationship between p and concentration. Values for p can then be selected based on what the analytical method can be reasonably expected to achieve. This table of precision tolerances should be compared to the range of concentrations to be measured in the sample set. If the precision over most of observed range of concentrations is not adequate to characterize the geochemical patterns in the data, another method should be sought (if available). In

Table 1. Tolerances for pairs of replicate analyses for Sb by concentration range.

| Concentration Range (g/t) | Tolerance* 'p' |
|------------------------------|-------------------|
| 0.1–0.2 | 100% |
| 0.21–0.5 | 67% |
| 0.51–1.0 | 50% |
| > 1.0 | 30% |

$$*p = \frac{|X_1 - X_2| \times 100\%}{(X_1 + X_2)/2}$$

Where X_1 and X_2 are the first and second values from a duplicate pair of samples.

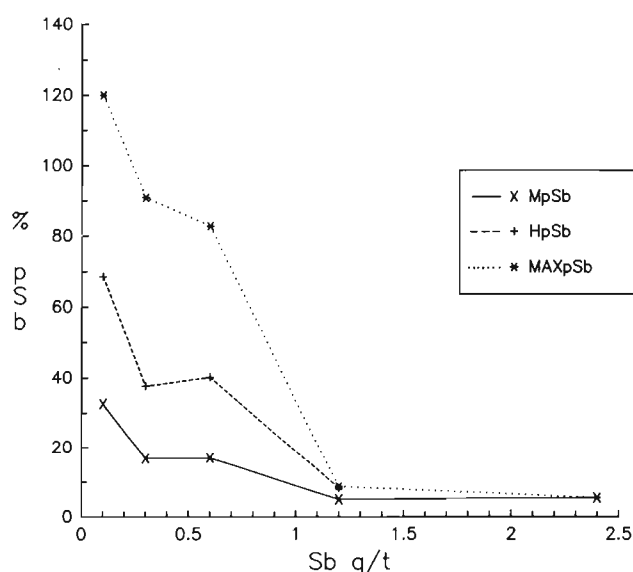


Figure 2. Plot of difference (pSb) between pairs of Sb values from 136 duplicate samples against their average concentration in five groups (< 0.2 , $0.2-0.4$, $0.4-0.8$, $0.8-1.6$, > 1.6). $MpSb$ is the mean difference in each group, $HpSb$ is the mean plus one standard deviation of the differences in each group, and $MAXpSb$ is the maximum (worst) difference between pairs in each group.

the case of Au, for example, both the precision and the detection limit are higher than is desirable in relation to the observed levels and range of Au in lake sediment, but a better practical alternative is lacking.

Control Reference Materials

Control reference materials (lake and stream sediment) prepared by the Geological Survey of Canada and the Canadian Centre for Mineral and Energy Technology (GSC/CANMET) and bulk samples of lake sediment prepared by the Newfoundland Department of Mines were used to monitor both precision and batch to batch consistency. Altogether these control reference materials were included 173 times (labelled as though normal samples) throughout

CURRENT RESEARCH, REPORT 88-1

the analytical batches. The identity and number of analyses for each of the 19 controls are given in Table 2.

Table 2. Control reference materials used to measure analytical consistency of multi-element neutron activation data.

| Source | Sample I.D. | Type of Material | Number of times analyzed |
|------------------------------|-------------|------------------|--------------------------|
| Mineral Development Division | C-21 | lake sediment | 7 |
| | C-22 | lake sediment | 14 |
| | C-23 | lake sediment | 4 |
| | C-24 | lake sediment | 7 |
| | C-25 | lake sediment | 3 |
| | C-26 | lake sediment | 15 |
| | C-27 | lake sediment | 6 |
| | C-28 | lake sediment | 12 |
| | C-29 | lake sediment | 4 |
| | C-30 | lake sediment | 4 |
| | C-31 | lake sediment | 2 |
| GSC/CANMET | LKSD-1 | lake sediment | 11 |
| | LKSD-2 | lake sediment | 16 |
| | LKSD-3 | lake sediment | 19 |
| | LKSD-4 | lake sediment | 19 |
| | STSD-1 | stream sediment | 13 |
| | STSD-2 | stream sediment | 12 |
| | STSD-3 | stream sediment | 2 |
| | STSD-4 | stream sediment | 3 |
| TOTAL | | | 173 |

The results obtained from these controls for Sb, Hf and Au are plotted in Figure 3. For each element the controls are ranked in order of increasing geometric mean value; the geometric mean and a bar extending one standard deviation unit (log) above and below the mean (a one sigma range) are also plotted for each control. The scale bar on the right-hand side indicates a range of ± 0.2 log units about any mean value. For a mean of 100 g/t, the top and bottom of the bar would plot at 158 and 63 g/t respectively; this range is roughly equivalent to a precision of ± 100 percent. Where the one sigma range is greater than this range, it suggests the element concentration is below the effective detection limit.

For Sb (Figure 3A), with the exception of control C-24, the one sigma ranges are all considerably smaller than ± 0.2 log units, and there is a general decrease in the standard deviations with increasing concentration. The control C-24 has two high analyses of 0.23 and 0.35 g/t, compared to the remainder in the range 0.07 to 0.11 g/t. These two high values are based on rather small samples (1.4 g) compared to samples yielding the other results for this control (6.6 to 10.4 g). Three subsequent analyses of this control gave results of 0.11, 0.11 and 0.12 g/t, confirming that the two high results are spurious.

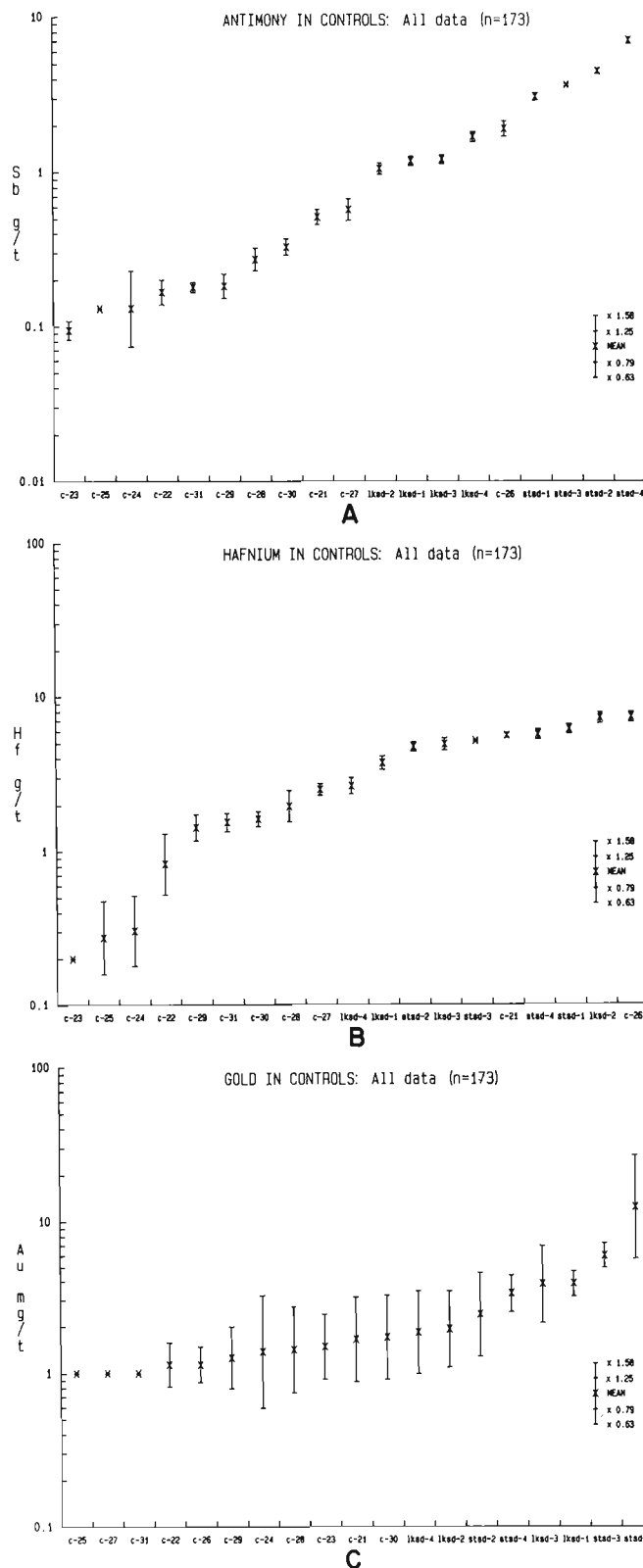


Figure 3. Plots of geometric means and one standard deviation ranges for (A) Sb, (B) Hf and (C) Au contents in control reference materials (173 samples) used for batch to batch monitoring of accuracy of NAA analyses.

For Hf (Figure 3B), the precision improves generally from low to high values. The controls C-25 and C-24 have one sigma ranges greater than ± 0.2 log units, indicating that they are below detection limit, whereas control C-22 shows a one sigma range of about ± 0.2 , so its mean value of 0.8 g/t is probably close to this limit. Control C-23 has values consistently below detection, and so all values were assigned an arbitrary value of 0.2 g/t, leading to the apparent absence of analytical variance.

Gold (Figure 3C) shows a trend similar to the left side of the plot for the Hf controls (C-23 to C-28). The controls with the lowest Au content (C-25, C-27 and C-31) show no apparent variance, as all values were below the detection limit, and were assigned values of 1 mg/t (cf. control C-23 for Hf, Figure 3B). As the mean values increase from C-22 to C-24, there is an apparent increase in variance. This reflects an increase in the proportion of values above the detection limit to those below. The controls C-26 to STSD-2 show similar and large one sigma ranges, indicating that these controls are below the effective detection limit. Of the five controls with the highest mean Au values, only three (STSD-4, LKSD-1 and STSD-3) have acceptable precision.

The five highest controls have median values of 3.1, 4.6, 3.8, 6.8 and 8.9 mg/t Au, at which levels, from the reproducibility of the laboratory duplicates, precision should be acceptable. This contradiction calls into question the homogeneity of the controls for Au, due to the possibility of the 'nugget' effect. For example, the control STSD-1 is almost certainly inhomogeneous in Au, with values ranging from 4.8 to 44.0 mg/t, and with no obvious outliers. The control is homogeneous for all other elements examined, but its use as a control reference material for Au is dubious. For the control LKSD-3, 19 of 22 values fall in the range 2.1 to 5.9 mg/t Au (median of 4.7 mg/t), but there are three outliers; two values of <1 and one of 11.0 mg/t Au. Outliers occur in the data for STSD-2 (a value of 7.8 mg/t Au compared to its median value of 2.4 mg/t), and for C-24 (a value of 9.3 mg/t Au compared to a median value of <1 mg/t).

These outliers suggest that the controls LKSD-3, STSD-2 and C-24 might also be inhomogeneous, although the outliers could also be due to analytical imprecision. To determine whether control sample inhomogeneity or analytical error was the problem, the capsules containing these controls giving dubious results were relabelled and resubmitted for analysis, together with several other capsules containing controls where consistent Au values had been reported. Altogether 19 capsules of material were reanalyzed.

The possible problems with the carry-over of radioactive isotopes produced in an initial neutron activation on results from a second irradiation and analysis are dealt with later in this report. For Au this is not a very serious problem, as the isotope produced from it during activation has a fairly short half-life. The results for Au from the first and second analysis are listed in Table 3.

Of the five suspected outliers, all three high values were confirmed on reanalysis of the same sample material. The

Table 3. Comparison of initial Au results by NAA with results from a second irradiation and analysis of the same material after a four-month interval.

| Control | 1st Au values mg/t | 2nd Au values mg/t |
|---------|-----------------------------|----------------------------|
| C-22 | <1 <1 <1 <1 2.4 | <1 <1 <1 <1 <1 |
| C-26 | 1.8 | <1 |
| C-24 | <1 9.3* | <1 11.0* |
| C-28 | 3.0 4.2 | <1 <1 |
| C-30 | <1 | <1 |
| LKSD-2 | <1 <1 | <1 <1 |
| STSD-2 | 7.8* | 7.7* |
| LKSD-3 | <1* <1* 11.0* | 4.0 5.1 8.2* |
| LKSD-1 | 5.2 | <1 |

* outliers

values for the two low outliers for LKSD-3 on reanalysis (4.0 and 5.1 mg/t Au) are close to the median for the control (4.4 mg/t). For most other samples the second analysis confirmed the earlier determination, although one value of 5.2 mg/t dropped to <1 mg/t on reanalysis. From these results it is apparent that the controls are somewhat inhomogeneous, although probably usable (in contrast to STSD-1). The controls do not provide as good a measure of precision for Au as the laboratory duplicates. Both the control and duplicate data suggest that Au values greater than 6 to 7 mg/t are consistently reproducible. Results between 2 to 4 mg/t are less reliable, as the effective detection limit for Au is in this range, and the effective detection limit for Au in lake sediment by this NAA method is about 2 mg/t.

COMPARISON OF NAA WITH OTHER ANALYTICAL METHODS

Since the control reference materials used have no generally accepted values for Au (or any of the element suite analyzed), analyses of some of the samples by other techniques were carried out to get an idea of how well the

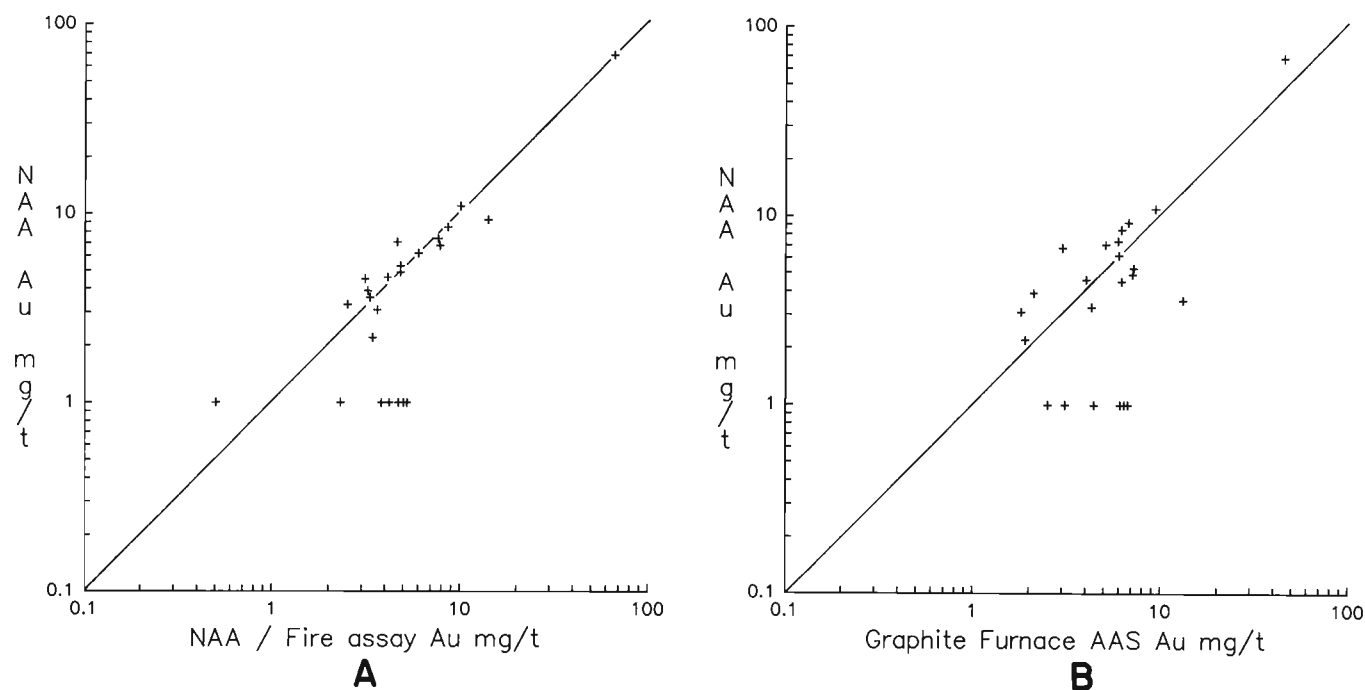


Figure 4. Plot of Au content analyzed by multi-element NAA against Au content analyzed by (A) neutron activation, fire assay and neutron counting (24 lake sediment samples) and (B) graphite furnace atomic absorption (23 lake sediment samples).

NAA results compared with these other more widely used methods.

Gold

Two comparative methods were employed for comparison with the NAA data for Au. First, 24 samples were analyzed by a different NAA technique at another laboratory in which the sample (5 to 10 g) was first irradiated, then fire assayed and the resulting doré bead counted. This alternative neutron activation analysis technique can achieve lower detection limits for Au (0.2 mg/t was quoted) as most other elements that interfere with the determination of Au are removed by the fire assay step. Furthermore, as the Au in the sample is irradiated prior to fire assaying, any Au contamination introduced in the flux is not irradiated, and hence cannot influence the Au result.

The results of the two methods are shown in Figure 4A. There is a good correspondence between the methods above about 4 mg/t (overall correlation 0.74). The scatter at low values is probably due both to poor precision and lack of sensitivity by the multi-element method, and increasing problems of sample representivity at these very low levels.

The very sensitive neutron activation, fire assay, neutron counting method may be superior for Au in comparison with the multi-element NAA method, but it has several drawbacks. The sample material is destroyed, it provides data only for Au, and the method is more costly. Moreover, since the technique requires the handling of radioactive material during the fire assay step, it is not really a routine procedure for large numbers of samples.

A second comparison is afforded from the results of 23 of the same samples that were analysed by a graphite furnace, atomic absorption technique, following the digestion of 10 g of sample in *aqua regia*, and extraction of the Au into methyl isobutyl ketone (Figure 4B). There is an overall correlation between the two methods ($r = 0.57$), but the correspondence is not as good in Figure 4A. A similar plot of the graphite furnace, atomic absorption data against the neutron activation, fire assay, neutron counting data, was similar to Figure 4B (correlation $r = 0.55$), implying that the two neutron activation methods show the best correspondence.

Atomic Absorption Analysis for Ag, Co, Fe, Mn, Ni and Zn

A total of 1279 lake sediment samples analysed by NAA had been analyzed previously by atomic absorption for the elements Ag, Co, Fe, Mn, Ni and Zn, using the methods described by Wagenbauer *et al.* (1983). Correlations (based on log-transformed data) and the slope and intercept of the regression for the NAA data on the AA data are given in Table 4, and plots for Co, Fe, Mo, Ni and Zn are shown in Figure 5. No plot is included for Ag as there is no significant correlation between the two sets of data; the AA data with a detection limit of 0.2 g/t is considered to be better, as the NAA method has a detection limit of 1 ppm, which is above the 95th percentile for lake sediment in Newfoundland. The very good correspondence between the Co and Fe data suggest that both methods give good data for these elements. The lower correlations for Mo, Ni and Zn are due to the higher detection limit for these elements by NAA, which causes a scatter of points at lower values. For these elements the AA data are better.

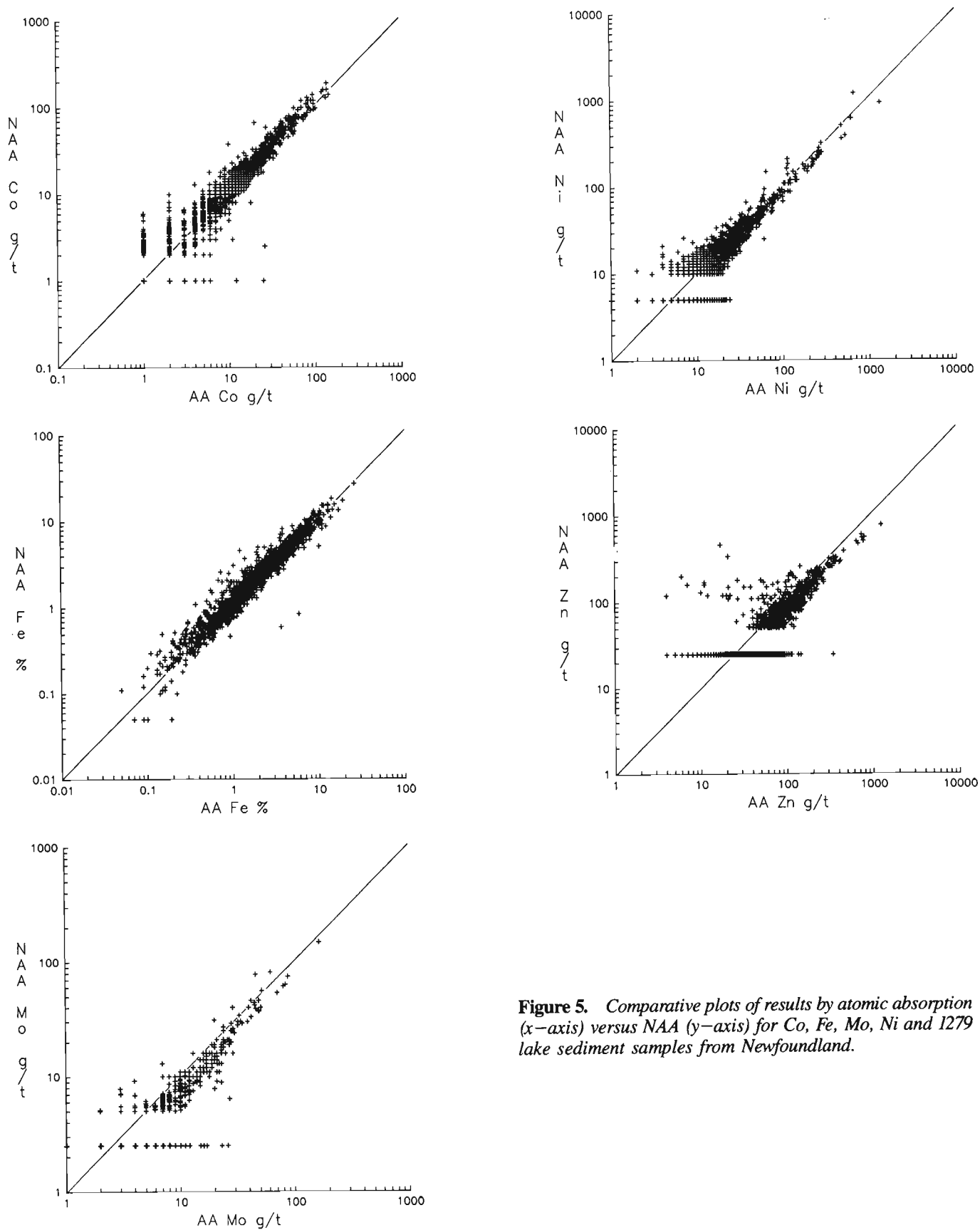


Figure 5. Comparative plots of results by atomic absorption (x-axis) versus NAA (y-axis) for Co, Fe, Mo, Ni and 1279 lake sediment samples from Newfoundland.

CURRENT RESEARCH, REPORT 88-1

Table 4. Comparison of multi-element NAA data for Ag, Co, Fe, Mo, Ni and Zn with results by atomic absorption for regional lake sediment samples. All data were log transformed.

| Element | Number of samples | Correlation coefficient r | Regression equation (slope) (intercept) | |
|---------|-------------------|------------------------------|--|--------|
| Ag | 1279 | 0.036* | 0.086 | -0.760 |
| Co | 1279 | 0.926 | 0.857 | 0.094 |
| Fe | 1279 | 0.967 | 0.981 | -0.052 |
| Mo | 1275 | 0.748 | 1.096 | -0.042 |
| Ni | 1279 | 0.882 | 0.902 | 0.138 |
| Zn | 1279 | 0.754 | 0.815 | 0.377 |

* not significant ($p = 0.68$)**Analysis of Ba, Ce, La, Th and Zr by ICP Spectrometry**

Replicate determinations of 101 lake sediment samples were performed by inductively coupled plasma (ICP) spectrometer for Ba, Ce, La, Th and Zr, following the digestion of 1 g of sample in an $\text{HF-HClO}_4\text{-HNO}_3$ acid mixture. The results are plotted in Figure 6, and the correlation coefficients, and slopes and intercepts of the regression equation from log-transformed data (NAA on ICP data) are given in Table 5. For Ce, La and Ba the correlations between the two methods are very good. For Th, the higher effective detection limit of ICP (approximately 5 g/t) and, for Zr, the relatively high detection by NAA (approximately 100 g/t), lead to considerable scatter at lower concentrations. The Ce, La and Ba data are satisfactory by either method, whereas Th is better by NAA and Zr by ICP.

Table 5. Comparison of multi-element NAA data for Ba, Ce, La, Th and Zr with results by ICP spectrometer for 101 lake sediment samples. All data were log transformed.

| Element | Correlation coefficient r | Regression equation (slope) (intercept) | |
|---------|------------------------------|--|--------|
| Ba | 0.979 | 1.073 | -0.205 |
| Ce | 0.983 | 0.895 | 0.244 |
| La | 0.976 | 0.929 | 0.124 |
| Th | 0.753 | 0.365 | 0.769 |
| Zr | 0.844 | 0.890 | 0.601 |

EFFECT OF DOUBLE IRRADIATION ON NAA RESULTS

One of the advantages of NAA is that sample material is conserved, and can be used for further chemical analyses. The sample is altered, however, by the transmutation of a small proportion of the atoms into new radioactive isotopes

during irradiation, which forms the basis of the analytical method. Some of these radioisotopes have half-lives of months or years, and although the proportions of new isotopes to their precursors are very small, a measurable amount of these radiation products with longer half-lives may be retained for months or years. If such irradiated material is subjected to a second irradiation and analysis, the products of the second irradiation will be added to those remaining from the initial irradiation, and the results will be erroneously high. Moreover, the amount of the enhancement will vary depending on the half-life of the isotope, the time between irradiations, and the neutron fluxes and exposure times in each case. In general, these parameters are not known by the person requesting the analysis.

This long-lasting effect is particularly important if a repeat NAA analysis is required on a sample, and all the material has been irradiated in the initial analysis. This effect also precludes the use of the same portion of standard reference material more than once to monitor analytical accuracy.

To gain an appreciation of the effect of double irradiation of material on the reported analytical results, samples that had been irradiated and analyzed at two laboratories were reanalyzed. Set A was analyzed by laboratory A in April 1986 and set B was analyzed by laboratory B in April 1987. Both sets were reanalyzed at laboratory B in August, 1987 (the same aliquot of material was re-irradiated and analyzed again). Set A samples (numbering 28) were typical lake sediments, and set B were control reference samples (17 lake sediment, 2 stream sediment). In Table 6, the means of the reported element content for singly and doubly irradiated samples are given, together with the probability that the paired values are, on average, different, using Student's 't' test for paired data. For set A, for almost all elements, the reported values for the doubly irradiated material are from slightly higher to very much higher than the 'true' values, as revealed by the singly irradiated set (the exceptions are Lu, Se, Ta, Yb). The 't' test results show that significant (i.e., $p < 0.05$) differences are shown by Au, Co, Cs, Eu, Ni, Sc and Zn, with the doubly irradiated values being from 1.2 to 15.7 times higher.

There is no general trend of increased levels of element values in the doubly irradiated material for set B, although Co, Cs, Eu, Sc and Zn are significantly higher (as they were in set A). In addition, La, Lu, Mo, Ta and Tb are also significantly higher in the doubly irradiated material in set B, but these elements showed no significant difference in Set A. Overall, the increases due to the double irradiation in set B (from 1.1 to 2.2 fold) are much lower than in set A (from 1.2 to 15.7 fold).

Since all the data in Table 6 were determined at the same laboratory in one analytical project, the observed differences between the values for doubly and singly irradiated samples in sets A and B must reflect their different irradiation histories. The irradiation used at laboratory B appears to have less of a lasting effect than that used for laboratory A. From

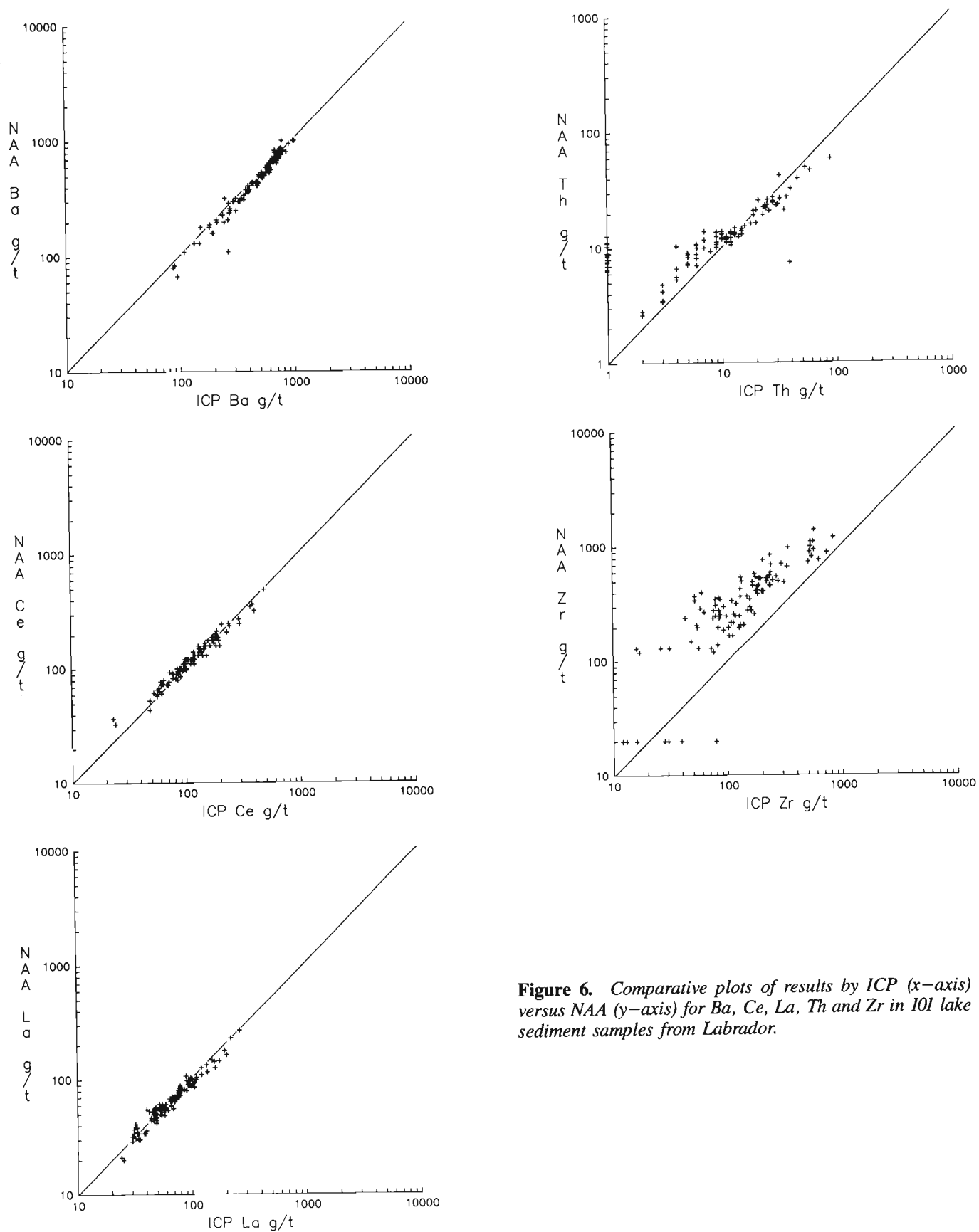


Figure 6. Comparative plots of results by ICP (x-axis) versus NAA (y-axis) for Ba, Ce, La, Th and Zr in 101 lake sediment samples from Labrador.

CURRENT RESEARCH, REPORT 88-1

Table 6. The effect on reported results when material subjected to an initial multi-element NAA analysis is subjected to a second irradiation and neutron count.

| Element | Unit | Set A Reanalysis of lake sediment samples | | | Set B Reanalysis of control samples | | |
|-----------------|------|---|--------|-------|---|--------|-------|
| | | Mean 1 | Mean 2 | p(t) | Mean 1 | Mean 2 | p(t) |
| Au ¹ | mg/t | 1.62 | 2.69 | 0.007 | 1.58 | 1.08 | 0.444 |
| As | g/t | 3.33 | 3.59 | 0.300 | 16.9 | 16.2 | 0.466 |
| Ba | g/t | 177 | 193 | 0.090 | 675 | 755 | 0.598 |
| Br | g/t | 13.3 | 13.8 | 0.531 | 35.2 | 35.2 | 0.998 |
| Ce | g/t | 38.5 | 42.3 | 0.084 | 178 | 169 | 0.335 |
| Co ² | g/t | 6.7 | 68.7 | 0.000 | 23.3 | 40.6 | 0.000 |
| Cr | g/t | 39.8 | 45.3 | 0.050 | 35.8 | 42.0 | 0.090 |
| Cs ² | g/t | 1.37 | 3.66 | 0.000 | 2.48 | 4.80 | 0.000 |
| Eu ² | g/t | 0.77 | 12.1 | 0.000 | 1.39 | 3.10 | 0.000 |
| Fe | % | 2.11 | 2.21 | 0.241 | 5.75 | 6.10 | 0.448 |
| Hf | g/t | 1.1 | 1.2 | 0.223 | 3.08 | 2.82 | 0.446 |
| La ³ | g/t | 36.8 | 41.1 | 0.223 | 57.5 | 63.1 | 0.023 |
| Lu ³ | g/t | 0.20 | 0.20 | 0.757 | 1.01 | 2.12 | 0.008 |
| Mo ³ | g/t | 3.62 | 3.89 | 0.276 | 9.8 | 12.7 | 0.021 |
| Na | % | 0.253 | 0.283 | 0.051 | 0.78 | 0.86 | 0.119 |
| Ni ¹ | g/t | 31.1 | 37.0 | 0.013 | 15.9 | 10.6 | 0.075 |
| Rb | g/t | 24.3 | 25.7 | 0.126 | 38.8 | 36.4 | 0.555 |
| Sb | g/t | 0.33 | 0.42 | 0.081 | 0.83 | 0.80 | 0.604 |
| Sc ² | g/t | 4.6 | 6.5 | 0.000 | 7.78 | 10.47 | 0.000 |
| Se | g/t | 1.15 | 1.13 | 0.919 | 1.81 | 1.55 | 0.596 |
| Sm | g/t | 4.65 | 4.86 | 0.390 | 9.07 | 9.07 | 1.000 |
| Ta ³ | g/t | 0.22 | 0.20 | 0.192 | 0.54 | 0.86 | 0.005 |
| Tb ³ | g/t | 0.49 | 0.50 | 0.600 | 1.87 | 2.42 | 0.032 |
| Th | g/t | 3.61 | 3.82 | 0.067 | 11.6 | 12.0 | 0.425 |
| U | g/t | 2.61 | 2.78 | 0.197 | 30.8 | 34.6 | 0.115 |
| W | g/t | 1.0 | 1.1 | 0.356 | 1.31 | 1.43 | 0.357 |
| Yb | g/t | 0.94 | 0.91 | 0.648 | 4.12 | 5.55 | 0.077 |
| Zn ¹ | g/t | 140 | 467 | 0.000 | 198 | 356 | 0.005 |
| Zr | g/t | 105 | 151 | 0.062 | 175 | 230 | 0.489 |

NOTE: Set A is for 28 normal lake sediment samples, where Mean 1 represents the average for each element for pristine sample material for the element at lab B, whereas the Mean 2 column gives the average results reported by lab B on splits of the same samples which had been analyzed previously by NAA at lab A. Set B is for 19 control samples (17 lake sediment and 2 stream sediment) where again Mean 1 for each element is for pristine material, and Mean 2 is for doubly irradiated material, in this case with all sample irradiation conducted by lab B. The columns p(t) are the probability that the paired values for singly and doubly irradiated material are the same using Students 't' test for paired data. All results in this table were from lab B in the same analytical batch.

- ¹ significantly higher in twice-irradiated duplicate samples; first irradiation at N.A.S., second analysis by Becquerel.
- ² significantly higher in twice-irradiated control samples; both irradiations and analyses by Becquerel.
- ³ significantly higher in both twice irradiated duplicate and control samples.

the data in Table 6, it is not clear whether the enhancements to La, Lu, Mo, Ta and Tb in set B would become negligible if the length of time between irradiations was the same as for set A (16 months rather than 4).

To determine whether the bias between singly and doubly irradiated samples in set A is sufficient to impair data interpretation, the doubly and singly irradiated data were

compared using the Mann-Whitney U test (a nonparametric equivalent of Student's 't' test). Using this test, only Cs, Eu, Zn and Zr were significantly different (higher) in the doubly irradiated samples ($p < 0.05$).

These data show that in general sample material should not be sent for this type of multi-element neutron activation more than once, as for several elements the effect of the initial

irradiation will lead to errors in several elements in the subsequent analysis. If it is absolutely necessary to reanalyze sample material by neutron activation a second time because of lack of additional sample material, a sufficient number of replicates of unirradiated material should be included to fully assess the effects of the initial irradiation. This will vary from one laboratory to another, and may even vary from the same lab if their irradiation procedures change.

DISCUSSION AND CONCLUSIONS

Multi-element NAA does provide good-quality analytical data for many elements in lake sediment. An overall assessment for all 35 elements determined in the suite discussed here is given in Table 7. The abundances of As, Ba, Br, Ce, Co, Cs, Fe, Hf, La, Lu, Rb, Sc, Sm, Ta, Tb, Th, U and Yb

are determined satisfactorily by this method. For the elements Cr, Eu, Mo, Ni, Se, W, Zn and Zr, the detection limits are high enough to preclude their determination at the lower levels found in lake sediment. Nevertheless, the NAA data are useful in geochemical exploration. The detection limits for Ag, Cd, Hg, Ir, Sn and Te are too high to be useful.

The detection limit for Au by NAA (approximately 2 mg/t) is higher than the median Au content of lake sediment (<1 mg/t), and is therefore much higher than is desirable. There is, however, no obvious, cost-competitive alternative method that would offer significantly lower detection limits and be applicable to large sample sets. The method does seem to offer slightly better data than that acquired by graphite-furnace or atomic absorption. The absolute values for Au from both techniques compare well, and also from the more

Table 7. A summary of the data quality of multi-element neutron-activation analysis (NAA) for lake sediment samples from control reference samples and replicate analyses of sample splits.

| | Quoted Detection Limit | Actual Detection Limit | Abundance in the Lake Sediment Analyzed | | Assessment of Data Usefulness |
|-----------|------------------------------|------------------------------|---|------|---|
| | | | range | mean | |
| Au (mg/t) | 1 | 2-3 | <1-24 | 1.9 | fair to poor; anomalous values (>4-5 ppb) can be quantified |
| Sb (g/t) | 0.05 | 0.05 | <0.05-1.9 | 0.21 | fair; a lower real detection limit would improve the data |
| As (g/t) | 0.2 | 0.5 | <0.2-228 | 27 | good |
| Ba (g/t) | 20 | 50 | <20-1200 | 219 | good |
| Br (g/t) | 1 | 1 | 1.8-161 | 49 | good |
| Cd (g/t) | 2 | ? 2 | <2-9.1 | - | poor; detection limit 10 times too high |
| Ce (g/t) | 3 | 3 | 4.8-608 | 102 | good |
| Co (g/t) | 2 | 2 | <2-140 | 17 | good |
| Cs (g/t) | 0.5 | 0.5 | <0.5-12 | 1.6 | good |
| Cr (g/t) | 2 | 15 | <2-393 | 47 | fair; a lower detection limit would improve the data |
| Eu (g/t) | 0.2 | 0.5 | <0.2-5.3 | 1.2 | fair; a lower detection limit would improve the data |
| Fe (%) | 0.1 | 0.1 or lower | <0.1-15.6 | 3.1 | good |
| Hf (g/t) | 0.5 | 1 | <0.5-23 | 2.7 | good |
| Hg (g/t) | 1 | ? | <1 | - | useless; the detection limit is about 100 times too high |
| Ir (mg/t) | 20 | ? | <20 | - | useless; the detection limit is far too high |
| La (g/t) | 1 | 1 | 5.7-304 | 44 | good |
| Lu (g/t) | 0.05 | 0.05 | <0.05-3.5 | 0.4 | good |
| Mo (g/t) | 0.5 | 5 | <0.5-264 | 8.4 | fair; a lower real detection limit would improve the data |
| Ni (g/t) | 5 | 10 | <5-250 | 24 | fair; a lower real detection limit would improve the data |
| Rb (g/t) | 5 | 5 | <5-170 | 27 | good |
| Sm (g/t) | 0.1 | 0.1 | 0.34-53 | 7.3 | good; two noisy controls |
| Sc (g/t) | 0.1 | ? 0.1 | 0.7-22.1 | 7.2 | good |
| Se (g/t) | 1 | ? 3-5 | <1-6.5 | 1.2 | poor; a lower detection limit would improve the data |
| Ag (g/t) | 1 | ? 1 | <0.2-3 | - | useless; the detection limit is about 20 times too high |
| Na (%) | 0.05 | 0.05 | <0.05-4.00 | 0.62 | good |
| Ta (g/t) | 0.2 | 0.2-0.3 | <0.2-3.5 | 0.41 | good |
| Te (g/t) | 10 | ? | <10 | 10 | useless; the detection limit is far too high |
| Tb (g/t) | 0.5 | 0.5 | <0.5-9.3 | 1.1 | good |
| Th (g/t) | 0.1 | 0.1 | 0.68-41.5 | 7.6 | good |
| Sn (g/t) | 50 | ? | <50 | - | useless; the detection limit is far too high |
| U (g/t) | 0.1 | 0.1 | <0.1-180 | 13.5 | good |
| W (g/t) | 0.5 | 2 | <0.5-67.4 | 2.2 | fair; anomalous values (>5 ppm) can be reproduced |
| Yb (g/t) | 0.1 | 0.5 | <0.1-27.3 | 2.1 | good; precision falls off rapidly below 1 ppm |
| Zn (g/t) | 50 | 75 | <50-440 | 97 | fair to good; detection limit a little high |
| Zr (g/t) | 50 | 250 | <50-1100 | 173 | fair; real detection limit about 5 times too high |

sensitive neutron-activation, fire-assay, neutron-counting methods. The information on analytical precision for Au from the control samples, analyses of sample splits by three laboratories, laboratory replicates and site duplicates (not discussed here) suggest that Au in lake sediment is quite homogeneous. In fact, the routine samples seem to be more homogeneous than some of the control reference materials in Au. This suggests that the Au is probably complexed with the organic material and is not generally present as a discrete metallic phase. Thus organic lake sediments would seem to be a very good sample medium for regional Au exploration.

The nondestructive nature of the direct NAA method is a great advantage, since it permits further chemical analysis of the sample material. Some long-lived isotopes are created during irradiation which will cause spuriously high results if the material is subjected to a second neutron activation analysis. In general, therefore, a portion of sample material should be analyzed only once by NAA.

Careful monitoring of analytical precision is necessary for Au because values of interest are so close to the detection limit of the method. The inclusion of sample splits is essential, and these should be chosen randomly from the sample set and included without disclosing their identity as duplicates. At least 30 pairs are required to give a good estimate of precision, although as few as 10 pairs in small sample batches will give a qualitative idea. The inclusion of site duplicates as well as sample splits is also strongly recommended to allow assessment of overall sample to sample variance.

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