

A Comparison of Several Commercially Available Methods for the Geochemical Analysis of Rare Earth, Rare Metal and High Field Strength Elements in Geological Samples

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KEYWORDS: REE, RM, HFES, geochemical analysis, gold deposits

INTRODUCTION

Rare earth elements (REE: La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu), rare metals (RM: Sc, Nb, Ta) and high field strength elements (HFSE: Y, Zr, Hf) are important components in a wide range of industries such as the manufacture of computers, wind turbines and hybrid cars. They are also used extensively in geoscience research as a geochemical tool for discriminating different rock types or petrotectonic environment. Industry and geoscience research need an accurate estimation of REE, RM and HFSE content of rock and ore samples to satisfy both economic and scientific credibility. Fortunately, today, there are a number of analytical methods that satisfy this requirement. Some of the techniques, such as x-ray fluorescence (XRF) described by Potts and Webb, 1992, and instrumental neutron activation (INAA) described by Hoffman, 1992, and El-Taher, 2006 are non-destructive and are considered to produce an accurate determination of REE, RM and HFSE values. Other methods such as a fusion, sinter or acid digestion (Longerich *et al.*, 1990; Hall and Pelchat, 1990, Bayon *et al.*, 2009) are, by contrast, destructive and generate elemental values that range from near total to a partial estimate depending on the ability of the fusion or the digestion technique to completely release an element from rock-forming minerals in the sample. A reliable estimation of a rare earth-rare metal concentration before an economic resource requires a method to be accurate and precise, but not necessarily to be particularly sensitive because economic grades greatly exceed detection limits. However, high accuracy, good precision and low detection limits are all desirable criteria for a technique that will be used for litho-geochemical research.

Hall and Plant (1992) carried out a comprehensive

and detailed study of the accuracy and precision of RE and HFS elements obtainable from XRF, INAA, lithium metaborate fusion - inductively coupled plasma mass spectrometry (ICPMS), and 4 acid (hydrofluoric-nitric-perchloric-hydrochloric) digestion-ICPMS analysis of bedrock samples and 8 reference standards. The aim of their study was to assess the reliability of REE and HFSE data produced by commercial laboratories. This paper describes a similar study using commercial laboratory analysis of bedrock samples from the Spanish Mountain Au deposit and the Galore Creek porphyry Cu-Au deposit in British Columbia and a reference standard, for REE, RM and HFSE elements by INAA, sodium peroxide sinter and inductively coupled plasma mass spectrometry (sinter-ICPMS), lithium metaborate-tetraborate fusion-inductively coupled plasma mass spectrometry (LMB-ICPMS), 4 acid digestion-ICPMS, XRF and AR (hydrochloric-nitric acid) digestion-ICPMS.

ANALYTICAL METHODS

All samples were jaw crushed in a Rhino TM[™] jaw crusher, split into a subsample with a Jones splitter and a 100-150 gram subsample milled to 95 percent - 150 mesh in a Rocklabs[™] ring and puck mill in the laboratory of the British Columbia Geological Survey, Victoria. Milled subsamples and quality control samples (sample duplicates, milled quartz blanks, a CANMET reference standard) were analyzed for REE, HFSE and RM at several laboratories by the following methods:

- 1) XRF analysis: La, Y, Nb and Zr were determined by x-ray fluorescence using a lithium metaborate-tetraborate pressed pellet (1 g sample: 5 g lithium metaborate-tetraborate) and Siemens model 3000 x-ray fluorescence spectrometer at Global Discovery Laboratories (now Acme Analytical Laboratories), Vancouver British Columbia.
- 2) INAA analysis: La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Sc, Ta, Cs were determined by irradiating 1-2 g of the milled rock sample for 20 minutes in a neutron flux (10^{11} neutrons/cm²/second) and then, after a decay period of approximately 1 week, measuring the gamma-ray emissions from the sample with a gamma-ray spectrometer

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equipped with a high resolution, coaxial germanium detector (Hoffman, 1992).

- 3) Sinter-ICPMS analysis: La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y, Nb, Zr, Ta and Hf were determined by sintering 0.2 g of milled rock with 0.8 g of sodium peroxide for 1 hour at 480°C in a closed nickel crucible (Longerich *et al.*, 1990). After dissolution of the sinter cake in 8M nitric acid the solution was analyzed for elements using an HP 4500 plus ICPMS at the Department of Earth Sciences, Memorial University, Newfoundland.
- 4) LMB-ICPMS analysis: La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Cs, Y, Sc, Ta, Nb, Zr were determined by fusing 0.2 g of milled rock with lithium metaborate-lithium tetraborate flux at 980°C in a graphite crucible, dissolving the fused bead with weak hydrofluoric and hydrochloric acids and analyzing the solution by ICPMS at Acme Analytical Laboratories, Vancouver.
- 5) 4 acid digestion-ICPMS: La, Ce, Y, Hf, Nb, Zr, Ta, Sc were determined by digesting 0.5 g of milled sample in Teflon test tubes with HF-HClO₄-HNO₃-HCl acids and ICPMS analysis of the solutions at Acme Analytical Laboratories, Vancouver, British Columbia.
- 6) AR-ICPMS: La, Sc, were determined by digestion in HNO₃-HCl-H₂O and ICPMS analysis at Acme Analytical Laboratories, Vancouver, British Columbia.

Table 1 lists elements determined by methods 1 to 6 and detection limits reported by the laboratories for each element.

ORIGIN OF THE SAMPLES

Two groups of samples were used in the study. One group of 60 bedrock samples and diamond drill core samples were collected from the Spanish Mountain Au deposit and analysed as part of a University of Victoria B.Sc. Honours Thesis project (Paterson, 2009). Results of the project are also described by Paterson *et al.* (2009). All of the samples from Spanish Mountain were analysed for major, minor and trace elements by INAA, 4-acid-ICPMS, AR-ICPMS and by XRF. Selected samples were also analyzed for REEs by sinter-ICPMS and by LMB-ICPMS. Figure 1 shows the location of the Spanish Mountain and Galore Creek deposits and Figure 2 shows the distribution of mainly argillite and greywacke samples collected from the Spanish Mountain property. A second group of 27 volcanic and mineralized intrusive bedrock samples were collected by Logan, 2005, during a previous study of Galore Creek Cu-Au deposit.

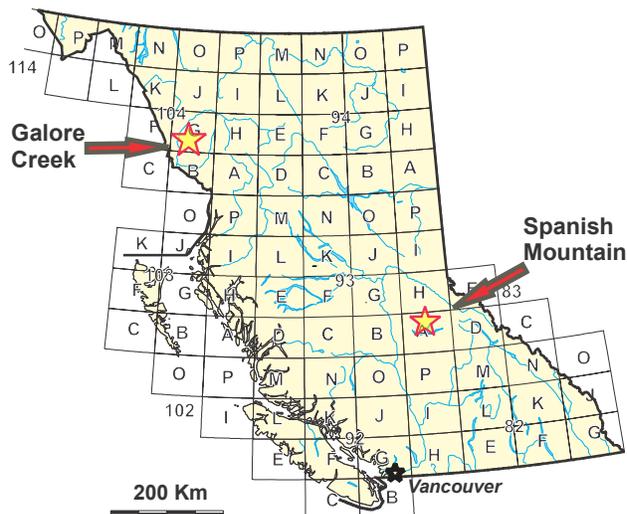


Figure 1. Locations of the Spanish Mountain Au and Galore Creek Cu-Au deposits.

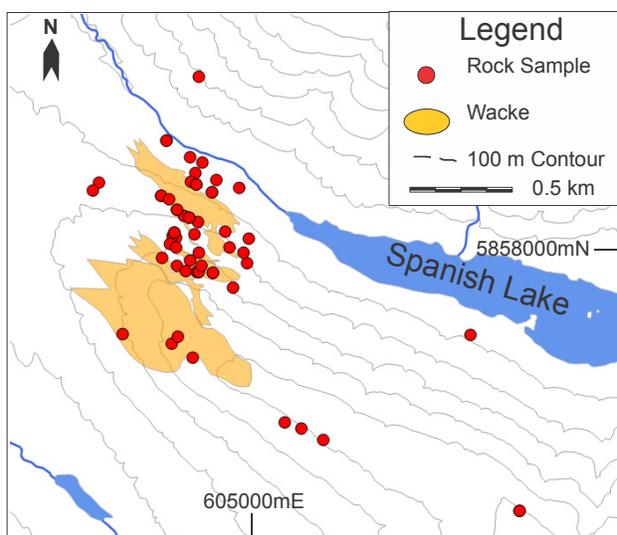


Figure 2. Location of bedrock and diamond-drill core samples collected by Paterson (2009), from the Spanish Mountain property.

ACCURACY AND PRECISION

As part of the British Columbia Geological Survey quality control program, the CANMET diorite gneiss standard SY4 (Bowman, 1995) is analysed routinely for REE, RM and HFSE by XRF, INAA, sinter-ICPMS, LMB-ICPMS and 4 acid-ICPMS. While the number of SY4 repeat determinations by each method is small (4-6 analyses), the analytical results allow a direct comparison of accuracy and precision for elements by different methods. For example, SY4 is analysed for La, Ce, Hf and Ta by all methods except AR – ICPMS. Figure 3 compares the mean value for La in SY4 by sinter-ICPMS, INAA, LMB-ICPMS and 4 acid-ICPMS, and the ± 2 standard deviation (2σ) range from multiple analyses, with the La content in SY4 (58 ppm) recommended by Bowman (1995). Mean La values by sinter-ICPMS, LMB-ICPMS

Table 1. Instrumental detection limits for elements described in this study by XRF, INAA, sinter-ICPMS, LMB-ICPMS, 4 acid-ICPMS and AR-ICPMS. Elements are grouped into REE, RM and HFSE.

Element	XRF	AR ICPMS	4 ACID ICPMS	INAA	Sinter-ICPMS	LMB-ICPMS
Units	ppm	ppm	ppm	ppm	ppm	ppm
REE						
La	3	0.5	0.1	0.5	0.03	0.1
Ce			1	3	0.14	0.1
Pr					0.02	0.02
Nd				5	0.03	0.3
Sm				0.1	0.8	0.05
Eu				0.2	0.04	0.02
Gd					0.07	0.05
Tb				0.2	0.01	0.01
Dy					0.06	0.05
Ho					0.01	0.02
Er					0.06	0.03
Tm					0.01	0.01
Yb				0.2	0.08	0.05
Lu				0.05	0.01	0.01
RM						
Cs				1		0.1
Sc		0.1	1	0.1		
Ta			0.1	0.5	0.08	0.1
HFSE						
Hf			0.1	1	0.09	0.1
Nb	3		0.1		0.08	0.1
Y	3		0.1		0.04	0.1
Zr	3		0.1		0.07	0.1

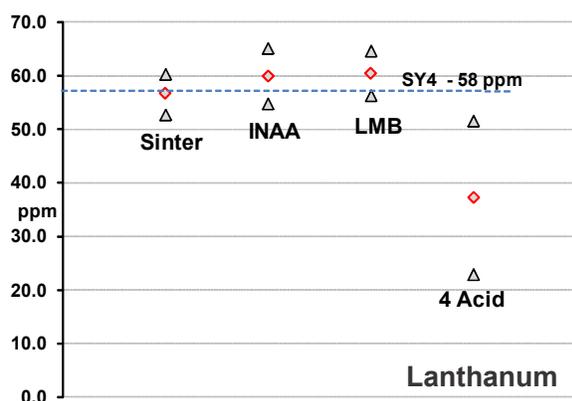


Figure 3. Determinations of La in SY4 by sinter-ICPMS, INAA, LMB-ICPMS and 4 acid - ICPMS. The mean value is indicated by a diamond symbol. The ± 2 standard deviation range from the repeat analyses is shown by the triangle symbols and the recommended average La content (58 ppm) in SY4 (Bowman, 1995) is a broken line.

and INAA are within ± 3 ppm of the recommended value and the ± 2 standard deviation range is 4.5 ppm. However, the mean La value by 4 acid-ICPMS is 20 ppm lower than the recommended value and the ± 2 standard deviation range is 14 ppm indicating that not all of the La is recovered by acid digestion from the standard matrix and there is a greater variation in values.

Figure 4 similarly compares the mean Ce value ± 2 standard deviations in CANMET SY4 by the same four analytical methods with the recommended value for Ce in SY4 (122 ppm; Bowman, 1995). Cerium by sinter-ICPMS, INAA and LMB-ICPMS is within ± 13 ppm of the recommended values for SY4 (122 ppm) with the INAA Ce having the largest variation. The Ce mean by 4 acid digestion ICPMS is much lower than by the other methods. In general, the precision estimate from the mean ± 2 standard deviation range decreases in order from sinter-ICPMS > INAA > LMB-ICPMS => 4 acid digestion ICPMS.

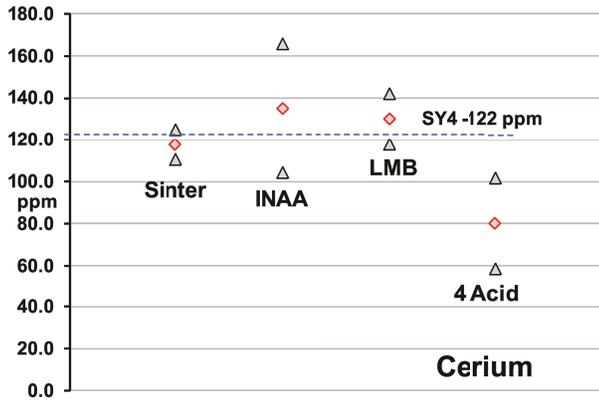


Figure 4. Determinations of Ce in SY4 by sinter-ICPMS, INAA, LMB-ICPMS 4 acid-ICPMS. symbols are the same as Figure 3. the recommended average Ce content (122 ppm) in SY4 (Bowman, 1995) is a broken line.

Precision and accuracy for Hf, Zr, Nb and Y from analyses of SY4 by multiple methods are compared in Figures 5, 6, 7 and 8. Only Hf is determined by INAA, whereas Zr, Y and Nb are measured by XRF. Mean Hf values are within 1.2 ppm of the CANMET recommended value (10.6 ppm) and the departure of the mean values from the standard are in the order INAA < sinter-ICPMS < LMB-ICPMS < 4 acid-ICPMS Hf. The Hf content in SY4 by LMB-ICPMS is clearly higher than the recommended value and the 4 acid-ICPMS Hf value is much lower (Figure 5). Hafnium precision estimated from the +/- 2 standard deviation range is in the order sinter-ICPMS > LMB > INAA > 4 acid-ICPMS.

Zirconium precision and accuracy from the analysis of SY4 is similar to Hf except that XRF replaces INAA as the non destructive method of analysis (Figure 6). From a comparison of the mean Zr value by XRF (513 ppm) to the recommended value (517 ppm) this is clearly the most precise and accurate of the four analytical methods. The Zr mean by sinter-ICPMS is 69 ppm above the recommended value whereas the Zr mean by LMB-ICPMS is 42 ppm higher than the recommended value. By contrast to LMB-ICPMS and sinter-ICPMS analysis, the 4 acid digest-ICPMS only recovers 48 ppm Zr from the standard. Although XRF is most accurate of the methods for Zr at a concentration similar to the standard the analytical error may be larger close to the XRF 3 ppm detection limit. Sinter-ICPMS and LMB-ICPMS have an advantage over XRF in that they can detect Zr to a lower detection limit (0.1 ppm) and consequently, have a higher accuracy at a lower concentration.

Unlike other REEs and HFSEs, the Nb content in SY 4 determined by XRF, LMB and 4 acid-ICPMS is very similar and is within 1 ppm of 13 ppm (Figure 7). However, the sinter-ICPMS Nb mean is more than 3 ppm higher than the recommended value. The larger ±2 standard deviation range for Nb by XRF, compared to the other methods, most likely reflects a value close to the 3 ppm Nb-XRF detection limit. Among common rock forming minerals zircon is known to be a host for Nb, but

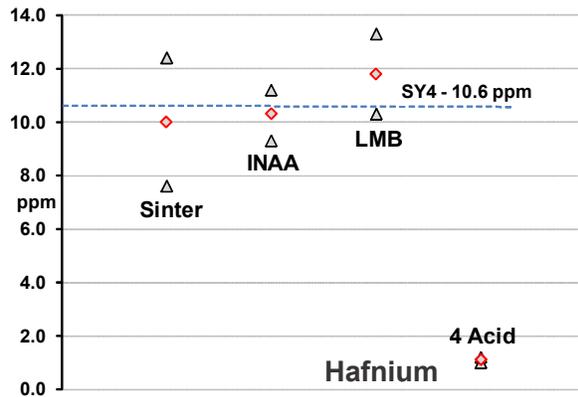


Figure 5. Determinations of Hf in SY4 by sinter-ICPMS, INAA, LMB-ICPMS and 4 acid digestion-ICPMS. Symbols are the same as Figure 3. The recommended average Hf content (10.6 ppm) in SY4 (Bowman, 1995) is a broken line.

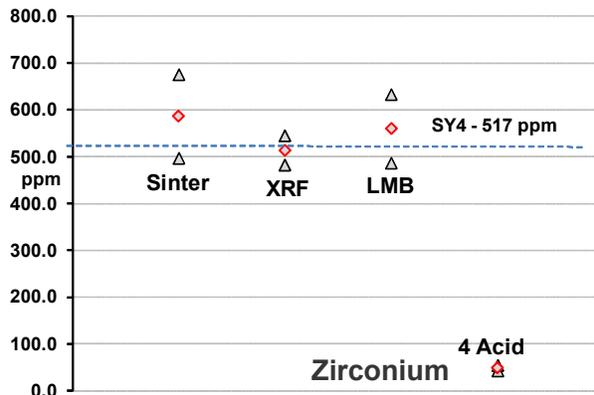


Figure 6. Determinations of Zr in SY4 by sinter-ICPMS, XRF, LMB-ICPMS and 4 acid digestion-ICPMS. Symbols are the same as Figure 3. The recommended average Zr (517 ppm) content in SY4 (Bowman, 1995) is a broken line.

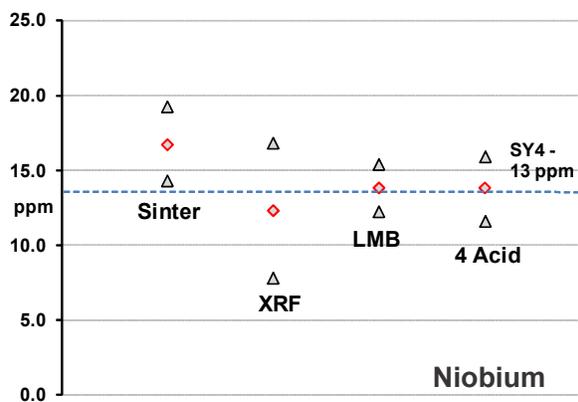


Figure 7. Determinations of Nb in SY4 by sinter-ICPMS, XRF, LMB-ICPMS and 4 acid digestion-ICPMS. Symbols are the same as Figure 3. The recommended average Nb content (13 ppm) in SY4 (Bowman, 1995) is a broken line.

the similar Nb mean by 4 acid-ICPMS compared to a much lower Zr mean suggests other rock forming mineral (e.g. Fe-Ti oxides) hosts the Nb. Figure 8 shows that the accuracy and precision for Y in SY4 follows the order of XRF > LMB-ICPMS > sinter-ICPMS > 4 acid-ICPMS.

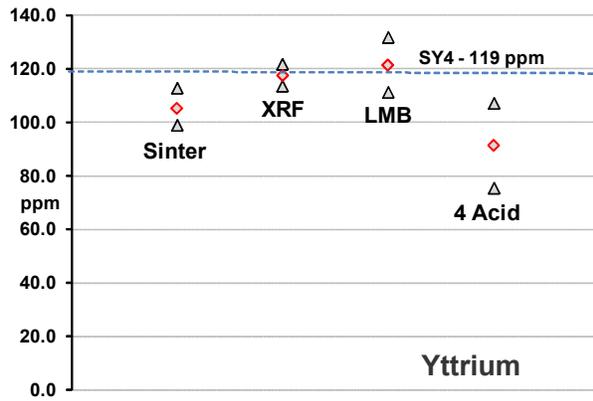


Figure 8. Determinations of Y in SY4 by sinter-ICPMS, XRF, LMB-ICPMS and 4 acid digestion-ICPMS. Symbols are the same as Figure 3. The recommended average Y content (119 ppm) in SY4 (Bowman, 1995) is a broken line.

Mean values and ± 2 standard deviation ranges of Eu and Lu (typical of the heavier REEs) in SY4 by sinter-ICPMS, INAA and LMB-ICPMS are shown in Figures 9 and 10. Both elements display similar patterns

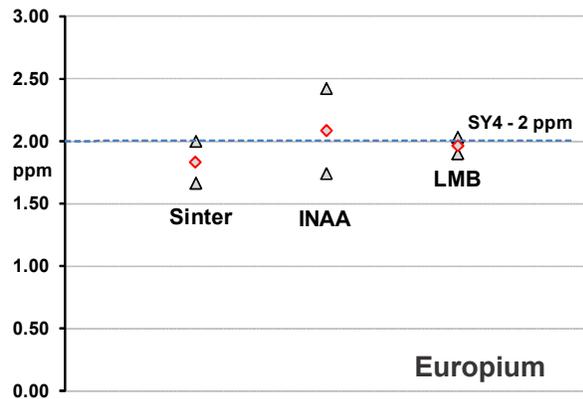


Figure 9. Determinations of Eu in SY4 by sinter-ICPMS, INAA and LMB-ICPMS. Symbols are the same as Figure 3. The recommended average Eu content (2 ppm) in SY4 (Bowman, 1995) is a broken line.

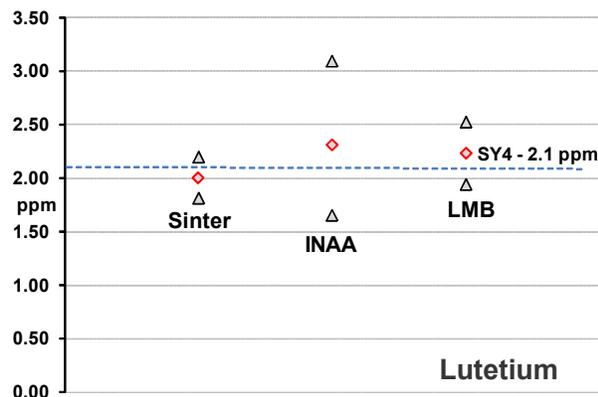


Figure 10. Determinations of Lu in SY4 by sinter-ICPMS, INAA and LMB-ICPMS. Symbols are the same as Figure 3. The recommended average Lu content (2.1 ppm) in SY4 (Bowman, 1995) is a broken line.

with mean values close to those recommended (Eu = 2 ppm, Lu = 2.1 ppm). The wider ± 2 standard deviation range for INAA Eu and Lu could reflect values closer to the INAA detection limit compared to the sinter and LMB-ICPMS detection limits.

COMPARISON OF PARTIAL AND NEAR TOTAL METHODS FOR ANALYSIS

Aqua regia (HCl-HNO₃) or a similar mineral acid reagent (e.g. HCl-HNO₃-H₂O) is commonly used to dissolve soil, drainage sediment and rock samples before analysis by ICPMS for a range of ore indicator, mineralization pathfinder and other trace elements. Rare-earth element analyses produced by such acid digestions can be useful for outlining areas of mineralized bedrock. However, the determinations must be used cautiously if REE data are applied to geological research because accurate element values are essential for a confident interpretation of lithochemical results. There is often only a partial REE recovery by the acid digest from the different rock-forming minerals in the sample, limiting the usefulness of the results. An example of variable REE release is illustrated in Figure 11 by a scatter graph of La determined by AR-ICPMS (partial recovery) plotted against La determined by INAA (near-total estimate) from analyses of the rock samples from Spanish Mountain. A poor correlation between AR-ICPMS La and INAA La (correlation coefficient, $R^2 = 0.422$) and the analyses are scattered along a trend line of increasing La concentration. The scatter of values and the 0.3326 regression coefficient suggest that a varying, partial amount of the INAA determined La is liberated from individual samples by the AR-ICPMS acid digestion.

The stronger 4 acid digestion improves the La recovery from rock samples. For example, in Figure 12, La determined by the 4 acid digestion is plotted against La determined by INAA for the same samples. The values are more closely grouped along a common trend and the

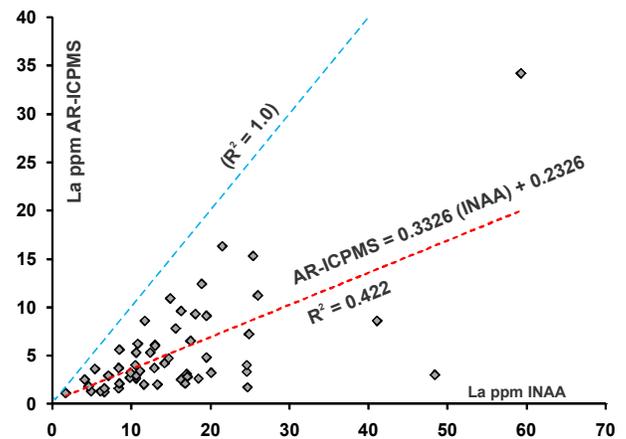


Figure 11. Scatter plot for La determined by AR-ICPMS and INAA in rock samples from Spanish Mountain. A least mean squares trend line, a regression equation and the correlation coefficient are shown on the graph and the trend line for a 1:1 correlation.

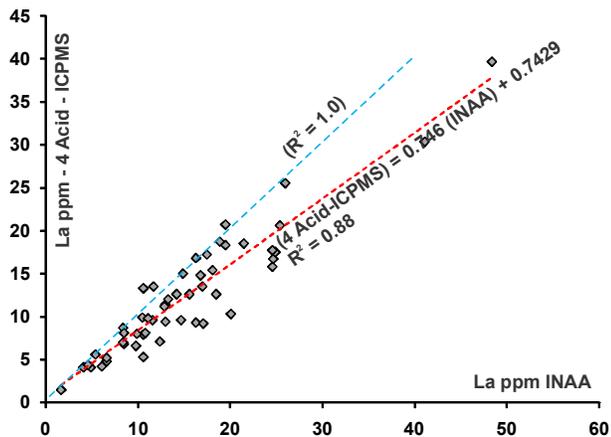


Figure 12. Scatter plot for La determined by 4 acid - ICPMS and INAA in rock samples from Spanish Mountain. A least mean squares trend line, a regression equation and the correlation coefficient are shown on the graph and the trend line for a 1:1 correlation.

correlation coefficient for the two populations is now $R^2 = 0.88$. However, the coefficient of 0.746 for the La-INAA – La 4 acid-ICPMS regression equation suggests that the acid still fails to release all of the La from samples. Although there are only 9 samples from Spanish Mountain analysed for La by INAA and LMB-ICPMS the correlation between the two populations is high (coefficient of $R^2 = 0.996$) with negligible scatter along the regression line (Figure 13). The coefficient of 0.9668 for the La-LMB-La-INAA regression equation indicates that virtually all of the La is determined by the two methods from the same samples.

While the rock samples from Galore Creek have only been analysed for REE elements by sinter-ICPMS and LMB-ICPMS the larger number of samples (29) allows comparison of results by the two methods over a different concentration range and in different rock types. Scatter graphs for La by sinter-ICPMS vs. La by LMB-ICPMS; Eu by sinter-ICPMS vs. Eu by LMB-ICPMS and for Lu

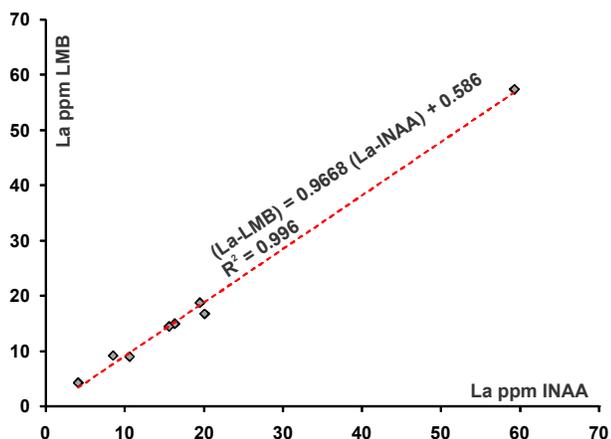


Figure 13. Scatter plot for La determined by LMB-ICPMS and INAA in the 9 rock samples from Spanish Mountain. A least mean squares trend line, a regression equation and the correlation coefficient are shown on the graph and the trend line for a 1:1 correlation.

by sinter-ICPMS vs. Lu by LMB-ICPMS in Figures 14, 15 and 16 all show that values cluster close to a trend line. Correlation coefficients are close to 1 and, similarly, the coefficients for the LMB-ICPMS – sinter-ICPMS equation are also close to 1.

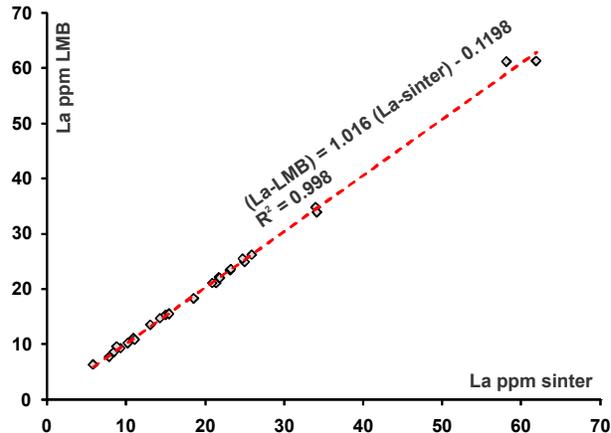


Figure 14. Scatter plot of La by LMB-ICPMS and by sinter-ICPMS in 29 rock samples from Galore Creek.

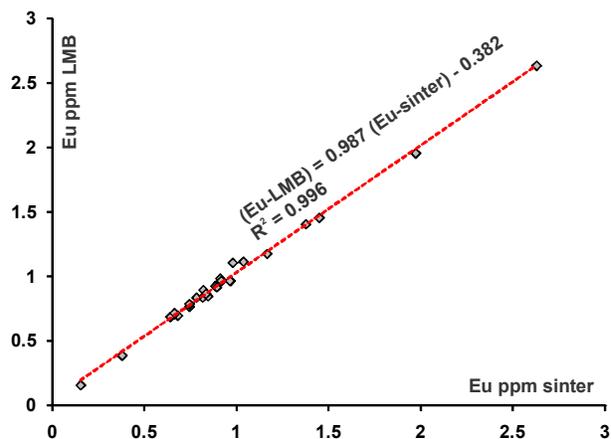


Figure 15. Scatter plot of Eu by LMB-ICPMS and by sinter-ICPMS in 29 rock samples from Galore Creek.

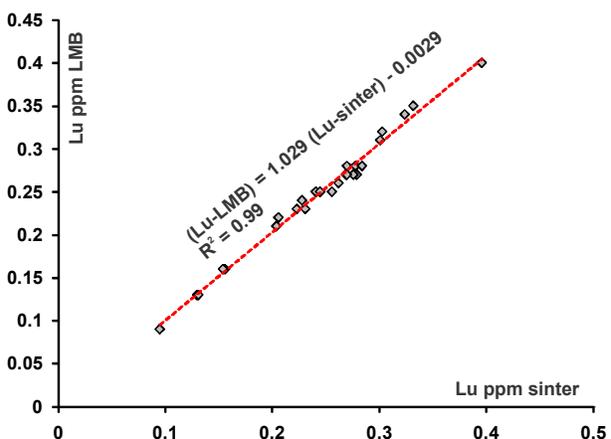


Figure 16. Scatter plot of Lu by LMB-ICPMS and by sinter-ICPMS in 29 rock samples from Galore Creek.

A practical application of comparing REE analyses using different digestions and sinter-ICPMS/fusion-ICPMS methods is to select the most suitable technique in terms of sensitivity, accuracy and economy for producing the data needed to create chondrite-normalized and other discrimination diagrams. Figure 17 is an example of a REE diagram from two argillite samples from the Spanish Mountain suite analysed by LMB-ICPMS and INAA. The only obvious divergence along the common REE plot for Argillite 1 is for Ce where the chondrite-normalized INAA Ce value is noticeably higher than LMB-ICPMS Ce value. Argillite 2 has much lower REE content and there is a greater difference between the INAA and LMB-ICPMS plots largely due to the Eu and Tb levels below the INAA detection limit. This emphasizes a requirement that an REE analytical method must have a detection limit able to cover a concentration range anticipated in all rock types.

A second comparison of chondrite-normalized values for a wacke and argillite from Spanish Mountain is shown in Figure 18. Plots for argillite and a wacke samples by sinter-ICPMS and LMB-ICPMS show a marked difference in the REE signature of the two rock types that

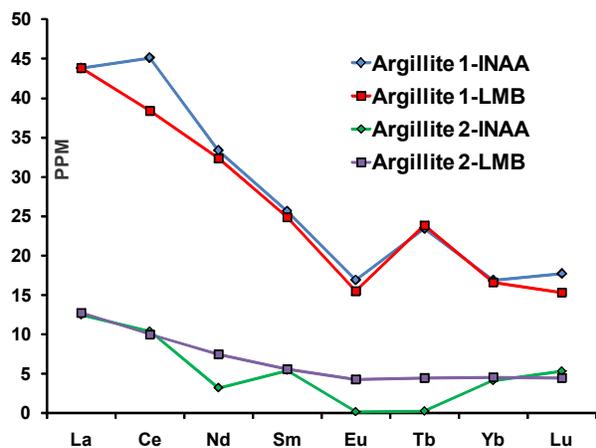


Figure 17. Chondrite-normalized (Nakamura, 1974) REE plot of two argillite samples from Spanish Mountain analysed by LMB fusion-ICPMS and INAA.

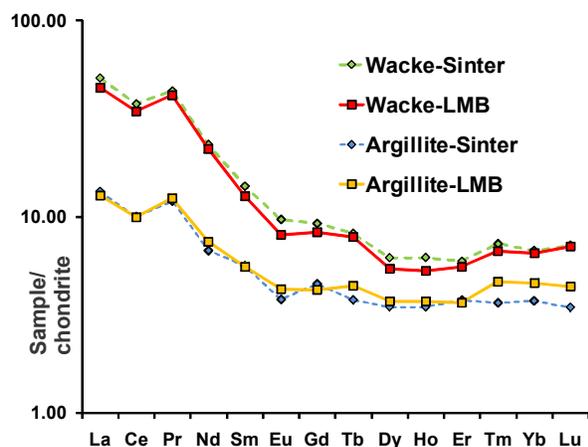


Figure 18. Log transformed chondrite-normalized (Nakamura, 1974) REE plot of argillite and wacke samples from Spanish Mountain analysed by LMB fusion-ICPMS and sinter-ICPMS.

possibly reflects a difference in the geochemistry of continental derive sediment (wacke) and island arc derived sediment (argillite). However, the two methods do produce very similar REE plots for each rock type. The only significant difference between the plots is for the heavier REEs, (Tm, Yb, Lu) in the argillite sample. A third example of sinter-ICPMS and LMB-ICPMS REE analysis (Figure 19) shows chondrite-normalized diagrams for three rock samples from Galore Creek. The two biotite-monzonite dikes show increasing light REE enrichment compared to the basalt and the only noticeable difference between the plots for the heavier REEs in the dike samples.

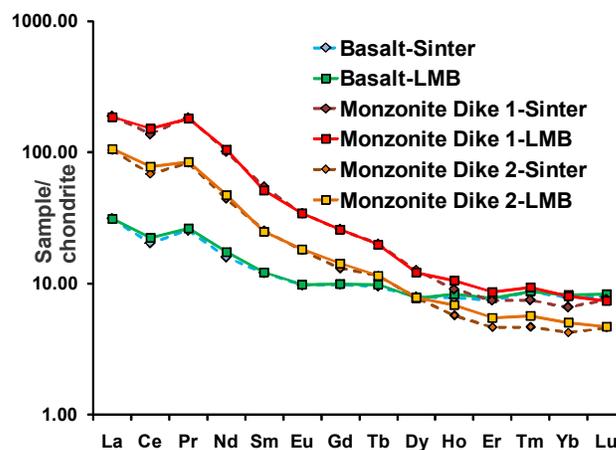


Figure 19. Log transformed chondrite-normalized (Nakamura, 1974) REE plot of a basalt and two biotite-monzonite dike samples from Galore Creek analysed by LMB fusion-ICPMS and sinter-ICPMS.

CONCLUSIONS

A study of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Nb, Ta, Y, Zr, Hf accuracy and precision determined by the analysis of the CANMET diorite gneiss standard SY4 and bedrock samples from two mineral deposits by several commercially available methods has revealed that:

- Sodium peroxide sinter-ICPMS, LMB fusion-ICPMS, INAA and XRF are preferred methods for geochemical research because they produce the most accurate and precise data. Both 4 acid-ICPMS and AR-ICPMS analyses, while sufficiently precise for mineral exploration purposes, are inaccurate due to the inability of the acid to fully digest all rock-forming minerals and release all of the element in a sample.
- X-ray fluorescence is the most accurate technique for Zr, Hf, Y and Nb, but has a disadvantage of higher detection limits compared to sinter-ICPMS and LMB fusion-ICPMS analysis. Accuracy and precision of lithium metaborate-tetraborate fusion-ICPMS approaches that of XRF and elements can be determined to lower detection limits. Mean values for Zr and Hf in the standard SY4 by 4

acid digest-ICPMS are much lower than the recommended value indicating that there is only a partial recovery of these elements from the standard.

- Instrumental neutron activation produces sufficiently accurate data for creating chondrite-normalized REE plots, but the high detection limits for some elements (Eu, Tb) are problematic for samples with low REE concentrations.
- Sodium peroxide sinter-ICPMS and LMB fusion-ICPMS analysis generate very similar chondrite-normalized REE profiles in contrasting rock types for all elements except for Ce.
- Analysis of other standard reference materials by the same methods would be a valuable complement to this study so that accuracy and precision of REE, RM and HFES elements can be determined over a wider concentration range.

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