

Characterisation of Memory Effects and Development of an Effective Wash Protocol for the Measurement of Petrogenetically Critical Trace Elements in Geological Samples by ICP-MS

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High sensitivity and low detection limits would seem to make inductively coupled plasma-mass spectrometry (ICP-MS) an ideal analytical tool for determining low (sub- $\mu\text{g g}^{-1}$) concentrations of the rare earth elements (REE), Y, Zr, Nb, Hf, Ta, Sn, W, Mo, Th, and U in most mafic materials (e.g. Hall and Plant 1992). However, the generally "sticky" nature exhibited by most of the high field strength elements (HFSEs: Zr, Nb, Hf, Ta, Th and U) as well as Sn, W and Mo can result in spurious results due to memory effects transmitted between unknowns and calibration samples. This, in turn, can seriously compromise the sensitivity, accuracy, and precision of ICP-MS analyses for these elements in geological materials. Data resulting from analyses with poor accuracy and precision can lead to erroneous interpretation and misleading petrogenetic modelling. To resolve this problem, we propose an effective wash protocol for these critical trace elements.

Two sets of experiments were performed. In the first, pure elemental standards and international reference materials (BIR-1, a basalt and DTS-1, a peridotite) were analysed by pneumatic (Meinhardt) nebulisation ICP-MS using external calibration and internal standardisation procedures in order to identify the extent and nature of memory effects. Samples were diluted to concentrations between 1 and 500 pg g^{-1} and three replicates per sample analysis were utilized for measurement of each element. Using a wash sequence between samples consisting of three separate 90 second stages, each stage using 5% v/v HNO_3 , accuracy and precision of REE determinations were maintained at concentrations down to 5 pg g^{-1} for both pure element and rock solutions. For HFSEs, pure element solutions were accurate down to 10 pg g^{-1} and the rock solutions were accurate down to 50

Sa grande sensibilité et ses limites de détection très basses semblent faire de l'ICP-MS un outil idéal pour l'analyse de faibles concentrations (autour du $\mu\text{g g}^{-1}$) des terres rares, de Y, Zr, Nb, Hf, Ta, Sn, W, Mo, Th et U dans la plupart des roches basiques. Néanmoins, le comportement "adhésif" adopté par la plupart des éléments à fort champ ionique (HFSE: Zr, Nb, Hf, Ta, Th, et U) et par Sn, W et Mo donne parfois d'étranges résultats dus en fait à des effets de mémoire transmis entre échantillons inconnus et échantillons de calibration. Ce phénomène peut donc affecter gravement la sensibilité et la justesse des analyses de ces éléments par ICP-MS dans les matériaux géologiques. En effet, des données imprécises et fausses ne peuvent que conduire à des interprétations fausses et des modèles pétrogénétiques erronés. Pour résoudre ce problème, nous proposons un protocole de lixiviation efficace de ces éléments critiques.

pg g^{-1} . For low levels of HFSEs in rock solutions (i.e. ng g^{-1}), the relative standard deviations (RSDs) for three counting cycles were as high as 24%. However, for pure elemental solutions at the same levels the RSDs did not exceed 5%. These differences are due to adherence of the "sticky" HFSEs to the surfaces of the sample introduction system, which are subsequently remobilized by the trace amounts of hydrofluoric acid (HF) present in the rock solution, but not in the pure elements solutions. Such effects are not observed with the REE.

A second set of experiments was conducted using varying strengths of acid washes in order to minimise such memory effects, thus increasing the precision and accuracy of measured concentrations. A comparison of an original wash protocol using three 90 second flushes of 5% v/v HNO_3 and an improved method of using a

90 second flush of 10% v/v HNO₃ with 2 drops of HF per 300 ml, followed by a 90 second flush of 10% v/v HNO₃ only and a final 90 second flush of 5% v/v HNO₃ exhibited dramatic improvement in abundance determinations. This method was applied to USGS basaltic reference material BHVO-1 and basalts from the Ontong Java Plateau (SW Pacific) to illustrate the effectiveness of the new wash procedure in removing memory and producing accurate, precise data.

Accurate and precise determination of trace elemental abundances in geological materials is critical for constraining ratios (such as La/Yb, Sm/Eu, Zr/Nb, Nb/Ta, Nb/La etc.) which can be used to discriminate between source regions, degree of partial melting, and to evaluate multi-component mixing in igneous systems (Pearce and Norry 1979, Jenner *et al.* 1990, Rollinson 1993). For example, La/Ta, Hf/Ta, and Th/Ta have been used to differentiate between E- and N-Type MORB (Wood *et al.* 1979). Also, discrimination diagrams using various combinations of the high field strength and rare earth elements (HFSEs and REEs) can draw distinctions between MORBs, back-arc tholeiites, within-plate basalts, and various types of volcanic arc magmas (Pearce and Cann 1973, Rollinson 1993).

Development of new techniques for the precise and accurate determination of the trace elements at low abundance (pg g⁻¹ - ng g⁻¹) is required to obtain meaningful data from, for example, ultramafic rocks and arc lavas. Conventionally, the determination of these elements in rocks is achieved by a combination of techniques such as X-ray fluorescence (XRF: e.g. Zr and Nb) requiring at least 3-6 g of rock sample which is pressed into a pellet for each analysis and instrumental neutron activation analysis (INAA: e.g. Hf, Ta, Th, U and REEs). For INAA, long count times to accommodate isotopes with both long and short half lives (Potts 1993) are required as well as access to a nuclear reactor to irradiate samples, adding time and inconvenience to the analysis. Detection limits are 0.5-5 µg g⁻¹ (Potts 1987). However, quantification of Sn, Mo, and W abundances are difficult using XRF and INAA. Spark source mass spectrometry provides lower detection limits, but a potential difficulty arises from incomplete equilibrium between spike and sample, as the elemental spike in aqueous solution is in a very different chemical form to the element in the rock, and multi-element analysis is extremely slow (Jochum *et al.* 1988, Fassett and Poulson 1989).

Inductively coupled plasma-mass spectrometry (ICP-MS) is the only analytical technique capable of rapid multi-element analysis (Jarvis *et al.* 1992) of geological

materials which includes the HFSEs (Zr, Nb, Hf, Ta, Th, U) and REEs, as well as Y, Sn, W and Mo. Furthermore, it is the preferred technique for geochemical analysis due to the low (pg g⁻¹) detection limits for most elements (e.g. Jarvis *et al.* 1992), low required sample mass of ≤ 0.1g, and relatively simple sample digestion for most rock types (Hall and Plant 1992, Jenner *et al.* 1990, Potts 1993).

Determination of REE abundances by ICP-MS in rock samples is well documented (e.g., Lichte *et al.* 1987, Longerich *et al.* 1990, Jarvis 1990, Fedorowich *et al.* 1993) and although detection limits for all fourteen REE depend on the abundance of the quantified isotope (Jenner *et al.* 1990), superior detection limits (on average at the pg g⁻¹ level) relative to INAA have been achieved. However, HFSE determination using ICP-MS or any technique requiring sample dissolution and liquid introduction is problematic (Xie *et al.* 1994). For example, HFSEs 1) are often contained in refractory minerals which are resistant to conventional acid attack; 2) have a tendency to precipitate from the solution; and 3) are, along with W, Mo and Sn, notoriously "sticky" causing memory effects, a problem that becomes more significant for low abundance samples (Jain *et al.* 1994, McGinnis *et al.* 1996). During the analysis of an unknown sample, varying amounts of these elements, previously deposited during the analysis of calibration samples and other samples, can be extracted from tubing and glassware surfaces and incorporated into the sample solution. Once in the sampling system, the concentrations of these elements measured in the sample are elevated. Therefore, the accuracy of the analysis is adversely affected and as the incorporation of such elements can vary over time as well as on the particular element in question, repeat analysis of a particular sample will yield imprecise results. Such a scenario will adversely affect element ratios calculated for the sample, and, as the analysis is both inaccurate and imprecise, this can lead to erroneous petrogenetic interpretations.

Although other problems related to HFSE analysis by ICP-MS have been addressed in many laboratories, to our knowledge there is no systematic study about memory effects associated with ICP-MS analysis. Furthermore, few laboratories have routinely included Mo, Sn and W in their analytical package. The objective of the present study is to determine the cause of memory effects during ICP-MS analysis using pneumatic (Meinhardt) nebulisation. This paper reports

the development of an analytical procedure which minimizes memory effects associated with the analysis of basaltic samples. Only basaltic samples are considered in order to avoid complications caused by incomplete dissolution of refractory minerals. The procedure used in this study involves the analysis of forty trace elements (see Table 1). We concentrate on the petrogenetically important elements: Y, Zr, Nb, Hf, Ta, Sn, W, Mo, Th, U, and the REEs.

General analytical method

Stock solutions containing 1000 µg g⁻¹ each of Zr, Nb, Hf, Ta, Th, U, and REE as well as Ru, In, Re, and Tl (for internal standards) were obtained from Inorganic Ventures Inc. (Lakewood, NJ, USA). The solutions of Zr, Nb, Hf and Ta also contained precious metals, as well as a trace of HF in HCl; the rest of the elements were in a 5% v/v nitric acid matrix. Acids were purchased from Fisher Scientific and all were doubly distilled in-house. Nanopure (18 MΩ, Barnstead, Newton, MA, USA) water was used for the preparation of reagents and diluting samples.

Sample digestion consisted of three phases. Rock powder (50-100 mg) was initially treated with 60 drops of 60% v/v HF and 50 drops of 16 mol l⁻¹ HNO₃ in screw-top Teflon™ (Savillex®) beakers and placed on a hot plate for forty eight hours until a clear solution resulted. The solution was then dried to a white powder which was then treated with forty drops of HNO₃ to convert fluorides to nitrates. The residue was dissolved on a hot plate for twenty four hours, dried again and treated with a further 40 drops of HNO₃. The sample was then allowed to dissolve at room temperature for twenty four hours. After completing a third drying stage, the final residue was again dissolved in HNO₃ and then transferred to a 125 ml Nalgene LDPE bottle and diluted to 100 g using a 5% v/v HNO₃ matrix. Sample preparation was conducted under a clean lab (Class 1000) setting. Contamination was monitored by the use of procedural blanks with each analytical run.

A VG Elemental PlasmaQuad model PQII-STE ICP-MS was used for all data acquisition. Details of operating conditions are given in Table 1. Samples were introduced using a Gilson peristaltic pump at 1.0 ml min⁻¹ in conjunction with a Gilson auto-sampler (Model 221-222).

Characterisation of memory effects

Calibration and analytical procedures

To obtain the best possible results for any analysis, calibration blank counts must be at the instrument noise level. This is extremely important when dealing with the analysis of low abundance trace elements. A large blank subtraction in the case of low sample counts introduces uncertainty in the analysis and, therefore, affects accuracy. The analysis sequence used in this study was as follows: 1) calibration blank (2% v/v HNO₃); 2) calibration samples to generate a calibration curve; 3) calibration blank; 4) ten samples; 5) calibration blank; 6) repetition of the calibration samples; and 7) calibration blank. If the run included more than ten samples, a tube containing an element standard solution followed by calibration blank was inserted after the tenth sample. A wash sequence (see below) followed each sample/calibration sample/blank. Internal standards Ru, In, Re and Tl at 10 ng g⁻¹ each were used to correct for any matrix effects and instrumental drift (Ru or In for low mass HFSEs and REEs; Re or Tl was used for high mass elements). Suitability of Ru and Re for the analysis of HFSEs has been shown in the literature (Hall and Pelchat 1990, Perkins *et al.* 1992). Indium and Tl were included to check the response on Ru and Re, respectively. The oxide formation for most of the REE and Ba in the instrumental operating conditions used was less than 2%. Xie *et al.* (1994) observed that other isobaric interferences on the analytes of this study from rock

Table 1.
ICP-MS operating conditions

Instrument	VG PlasmaQuad II
Forward Power	1350 W
Reflected Power	2 W
Cooling Gas Flow	15.5 l min ⁻¹
Auxiliary Gas Flow	1.6-2.0 l min ⁻¹
Nebuliser Gas Flow	0.850 l min ⁻¹
Sample Pump Rate	1.0 ml min ⁻¹
Nebuliser	Meinhardt
Spray Chamber	Double-pass scott-type water cooled (4°C)
Sampler Cone	nickel 1 mm orifice
Skimmer Cone	nickel 0.75 mm orifice
Vacuum:	
Expansion Stage	2.2 mbar
Intermediate stage	< 10 ⁻⁴ mbar
Analyser stage	3.0 x 10 ⁻⁶ mbar
Measurement Mode	PC, Peak jump
Dwell Time	10.4 ms
Points/Peak	3
Measuring Time	60 s
Autosampler	Gilson 221-222

matrix were negligible. As the primary aim was to assess memory effects, and as oxide levels were low, no corrections for isobaric interferences were made during data reduction. However, while this *modus operandi* is adequate for this type of study, when quantifying trace element abundances in geological samples, interference corrections should be applied.

Effect of the wash cycle

Initial efforts were devoted to studying wash cycle effects on the background counts after the analysis of samples and/or calibration sample solutions. A generic three stage wash sequence was modified for this study. Three separate wash reservoirs of acid were used in the autosampler in order to prevent sample build up in the wash reservoir due to drops of sample solution adhering to the autosampler probe. While this may occur in the first reservoir during extended run times, such effects are reduced by approximately one order of magnitude for each subsequent wash stage. In this experiment, the concentration of the calibration samples ranged from 1 ng g⁻¹ to 100 ng g⁻¹ and a 25 ng g⁻¹ test solution was used between sets of ten unknown samples in conjunction with acid blanks. Three 90 second washes, each consisting of 5% v/v HNO₃ (Wash Cycle 1) were employed in between each analysis. (Note: one analysis means three 60 second data acquisitions for each sample/calibration sample/blank). General instrument background was monitored at ²²⁰Bk (for actual background counts see Tables 2 and 3). The data (Table 2) indicate that the counts on the HFSE isotopes in the blank acid solution are much higher when compared with background counts (from here on, "counts" refers to counts per second or cps). However, counts for REE in the same acid blank solution are comparable to background levels, which demonstrate a significant memory effect for the HFSEs. Note that HFSE blank counts approximate those for ²²⁰Bk when a blank solution is run prior to samples/standards. Therefore, we modified the wash sequence to comprise two separate 90 second washes with 10% v/v HNO₃ followed by one 90 second wash with 5% v/v HNO₃ (Wash Cycle 2) (Table 2). Although the use of a stronger acid in the wash cycle reduced the HFSE blank counts at the masses of interest, the new counts are still higher than the background measured at ²²⁰Bk.

Effect of calibration sample solution concentration

To test if the memory effect is concentration dependent, the concentrations of calibration samples

Table 2.
General instrument background (cps) at ²²⁰Bk to demonstrate the effects of wash strength on background counts obtained from 5% v/v HNO₃ acid blanks

Elements	Wash Cycle 1	Wash Cycle 2
La	45	25
Nd	21	14
Gd	25	12
Er	22	13
Lu	28	15
Zr	51	39
Nb	155	83
Hf	42	27
Ta	159	47
Th	84	33

Wash Cycle 1: Three separate 90 second washes with 5% v/v HNO₃.
 Wash Cycle 2: Two separate 90 second washes with 10% v/v HNO₃ followed by a 90 second wash with 5% v/v HNO₃.
 Background counts for 5% v/v HNO₃ acid blank on ²²⁰Bk = 17 cps.

Table 3.
Effect of calibration sample solution concentration on background counts (cps) from 5% v/v HNO₃ acid blank

Elements	Standard 1	Standard 2
La	25	19
Nd	14	10
Gd	12	11
Er	13	11
Lu	15	10
Zr	39	12
Nb	83	21
Hf	27	13
Ta	47	11
Th	33	10

Concentrations used: Standard 1 = 1-100 ng g⁻¹; Standard 2 = 1 pg g⁻¹ to 1 ng g⁻¹. Background counts for 5% v/v HNO₃ acid blank on ²²⁰Bk = 17.

were reduced. The concentrations used to generate new calibration curves were between 1 pg g⁻¹ and 1 ng g⁻¹ and the wash sequence used was Wash Cycle 2. A 1 ng g⁻¹ test solution was used in place of that containing 25 ng g⁻¹ in between sets of unknowns. It is evident from the data presented in Table 3 that the memory effect of HFSEs has been completely eliminated and the new calibration blank counts are at the instrument background level. This also confirms that the higher blank counts seen in the preceding study (Table 2) are due to memory effects

and eliminates the remote possibility of contamination from the reagents, laboratory environment, and labware used, resulting in counts higher than background for the HFSE isotopes in the blank solution.

An alternative method for reducing memory effects is that of "surrogate calibration" (Jenner *et al.* 1990). These authors eliminated Nb and Ta from the calibration samples to reduce the memory of these elements. Their protocol utilized previously determined Nb/Zr and Ta/Hf ratios to calculate the concentrations of Nb and Ta, respectively. This approach would be effective if the ratios of analytes to the elements used for surrogate calibration were constant throughout the run, but this is not always true. In one typical run we observed variations in $^{181}\text{Ta}/^{177}\text{Hf}$ ratio from 4.5 to 5.1 and $^{93}\text{Nb}/^{90}\text{Zr}$ ratio from 1.48 to 1.62 over a twelve hour period. Furthermore, these ratios may be dependent on instrumental operating parameters and sample matrix, and can introduce more uncertainty if not determined prior to each analysis.

Detection limits and accuracy

The detection limits in ICP-MS analysis are controlled by the sensitivity of the instrument and the abundance of the isotope measured. To constrain the lower limit of detection of the Notre Dame ICP-MS for precise determination of REEs and HFSEs, pure elemental solutions were prepared ranging in concentration from 1 pg g^{-1} to 500 pg g^{-1} . A series of dilutions of the low-level international rock reference material BIR-1 were also made and analysed during the same run with the pure elemental solutions. Since

Table 4.
Detection limits calculated as concentration equivalent to 3σ from the calibration blanks analysed during the run

Elements	Detection limits (ng g^{-1})
La	0.50
Sm	0.52
Dy	0.52
Er	0.54
Lu	0.34
Zr	0.48
Nb	0.50
Hf	0.80
Ta	0.29
Th	0.75

the concentration of these elements in the BIR-1 stock solution varies from less than a ng g^{-1} (Nb, Hf) to 15 ng g^{-1} (Zr and some REE), calibration sample solutions of between 10 pg g^{-1} and 25 ng g^{-1} of each element were prepared. Three replicates per individual sample analysis were used for the measurement of each element.

Accurate results were obtained for REE at concentrations down to 5 pg g^{-1} (Figure 1), a concentration about ten times higher than detection limits (Table 4). However, HFSEs determinations were only accurate above 25 pg g^{-1} (Figure 1), except data for Th and Nb which were accurate down to 10 pg g^{-1} . In the case of rock solutions, the accuracy of REE was maintained at the same levels as the pure elemental solutions, but it was poor for the HFSEs (Table 5).

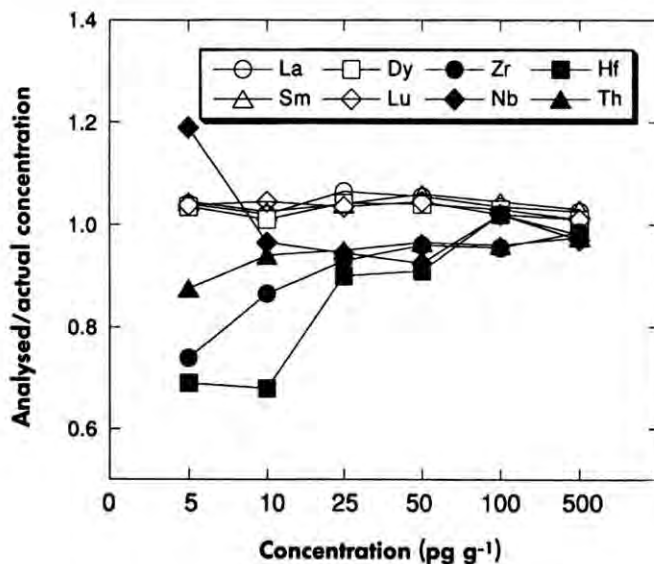


Figure 1. Analysis of single element standard solutions. Concentrations are calculated on blank subtracted counts. Lower values of the ratio analysed/actual concentration observed in the case of the HFSEs are the result of high blank counts (Table 2).

Table 5.
Analyses of diluted BIR-1 aliquots ($\mu\text{g g}^{-1}$)

Elements	Recommended values	Undiluted	Dilution factor		
			10x	100x	1000x
La	0.61	0.64	0.67	0.71	5.5
Sm	1.14	1.06	1.15	1.23	8.24
Dy	2.63	2.10	2.27	2.54	6.5
Lu	0.259	0.21	0.28	0.37	2.8
Zr	15.7	14.4	14.5	14.8	25.6
Nb	0.73	0.70	0.76	1.18	7.9
Hf	0.63	0.58	0.63	0.95	5.7
Th	0.06	0.05	0.1	0.35	3.1

Statistically, BIR-1 yielded HFSE concentrations greater than recommended values where actual abundances in the analysed solution were below 50 pg g^{-1} . Previous studies (Jochum *et al.* 1990, Xie *et al.* 1994) have indicated that rock solutions containing low-level HFSE concentrations tend to yield abundances of these elements which are elevated above the actual value. This was attributed to increased uncertainty in measurement from the lower counts and/or memory effects (Xie *et al.* 1994). Longerich (personal communication 1996) pointed out that the deposition and subsequent erosion of solution elements from sampler cone are greatly controlled by the composition of the solution. The differential memory effect shown by the pure elemental solution and rock solution further confirms this assumption.

Relative standard deviation of three counting cycles

Analytical precision is calculated here as the relative standard deviation (RSD) on replicate analyses and are used here to study memory effects. In a prior study of memory effects derived from external calibration samples on a BIR-1 solution, Jain *et al.* (1994) observed that for Zr and Hf concentrations below 5 ng g^{-1} , the relative standard deviations (RSD) for three counting cycles were as high as 80%. This phenomenon was, however, only observed for the first sample run after the external calibration sample solution. In contrast, pure elemental and sodium peroxide fused samples did not exhibit such behaviour. Surprisingly, high RSDs were not observed elsewhere in this study, irrespective of the position of analysis even though the most diluted BIR-1 solution (Table 5) analysed contained less than a pg g^{-1} of the HFSEs. All the dilutions of BIR-1 analysed (Table 5) exhibited $\leq 5\%$ RSDs for three counting cycles. Similar results were

also obtained for pure elemental solutions down to concentrations as low as 1 pg g^{-1} (Table 6). The different observations on the precision of analysis for BIR-1 in the present study and that of Jain *et al.* (1994) seem to be due to instrumental sensitivity; the present study uses a machine with approximately one order of magnitude higher sensitivity than the ICP-MS used by Jain *et al.* (1994). Furthermore, the concentrations of analytes in the calibration sample solutions in this study are comparatively lower.

The above results led us to repeat this experiment using the rock sample containing lower levels of HFSEs than BIR-1, for which the international rock reference material DTS-1 (a peridotite produced by the USGS) was chosen. The calibration curve was generated using concentrations in calibration sample solutions of between 10 pg g^{-1} and 25 ng g^{-1} . Interestingly, the RSDs of the three counting cycles for the first DTS-1 were all $> 7\%$ (Table 7). However, in the case of subsequent DTS-1 samples the RSDs were $\leq 5\%$ for all HFSEs (Table 7). These results are in agreement with Xie *et al.* (1994) who observed a similar decay of memory signal during continued analysis of BIR-1 rock solution.

Two conclusions can be drawn from this experiment. First, as pure elemental solutions and diluted BIR-1 solutions did not exhibit high RSDs on individual samples, the memory effect is not entirely concentration dependent. Secondly, the memory effect is more visible only on the first low level rock sample which is analysed subsequent to the calibration samples. Pure elemental solutions and diluted rock solutions analysed immediately after the calibration standards did not exhibit similar effects, thus eliminating the possibility of cross contamination of one sample with another due to insufficient wash time between samples. Since this is a memory problem, the magnitude of the

Table 6.
Analyses of pure HFSE solutions

Solutions Elements	1 pg g ⁻¹		5 pg g ⁻¹		10 pg g ⁻¹	
	Mean	%RSD	Mean	%RSD	Mean	%RSD
Zr	20	2.3	67	1.6	133	5.2
Nb	30	1.9	161	5.5	294	3.2
Hf	12	4.3	32	2.7	55	5.2
Ta	12	2.8	35	5.6	50	4.7
Th	13	1.6	90	2.3	150	4.5

Results represent counts per second and %RSD is the average of three analyses.

Table 7.
Analysis of rock (DTS-1) reference material solutions

Elements	Sample 1 replicates				Sample 2 replicates			
	I	II	III	%RSD	I	II	III	%RSD
Zr	2673	2378	2081	12	2071	1961	1992	2.3
Nb	749	692	643	7.6	646	624	621	1.8
Hf	63	51	38	24	37	40	43	5.1
Ta	387	365	314	10	319	333	325	1.8
Th	117	97	83	17	89	78	96	4.9

Results represent counts per second.

effect may also depend on the prior history of the machine interface.

Removal of memory

To identify which component of the acid digested rock solution is responsible for eluting memory from the machine, a synthetic rock solution in 2% v/v HNO₃ was prepared using single element standards. Major and trace element concentrations of the synthetic rock solution were in the range of basaltic rocks and the HFSEs were excluded. The analysis was carried out in identical conditions as those described above for DTS-1. The data (Table 8) indicate that no significant increase in detectable signal of HFSEs was observed for the synthetic rock solution versus DTS-1. The different behaviour between DTS-1 and the synthetic rock solution could be due to trace amounts of hydrofluoric acid remaining from the dissolution procedure in DTS-1 solution (see above). To confirm this, 50 µl of hydrofluoric acid were added to 10 ml of the synthetic rock solution and the experiment was repeated; higher counts were observed for all HFSEs analysed in the presence of trace HF (Table 8).

The above findings indicate that any trace of HF remaining after rock dissolution causes those "sticky"

Table 8.
Memory removal during ICP-MS analysis

Sample sequence	Average counts per second			
	Zr	Nb	Hf	Th
1	17,740	30,465	6,647	17,183
2	33	28	17	19
3	55	48	31	47
4	289	158	103	166

- Results represent counts per second for the indicated element.
- 1 Calibration sample - concentration between 10 pg g⁻¹ and 25 ng g⁻¹.
 - 2 Calibration blank (5% v/v HNO₃).
 - 3 Synthetic rock solution - prepared using pure elements in 5% v/v HNO₃ and the concentration of major and trace elements was comparable to BIR-1.
 - 4 Rock solution + HF - 50 µl of HF was added to 10 ml of the synthetic rock solution.

HFSEs adhering to the surfaces of sample introduction system to be remobilized. The fact that the diluted rock solutions do not exhibit a memory effect is because, in diluted samples, HF concentration drops below an effective level. On the other hand, if the concentration of analytes is very high (e.g. undiluted BIR-1 solution), then the signal enhancement caused by memory effects is within analytical error.

It could be argued that use of HClO₄ in conjunction with HF in the dissolution stage would effectively remove all traces of HF from the rock solution. This would then solve the problem of remobilisation by the rock solution of "sticky" HFSEs from the tube walls and glass surfaces. However, we recommend NOT to do this because the HFSEs (especially Nb and Ta) require at least a trace of HF in order to stay in solution. Total removal of HF could mean that abundances in the rock would be low due to element loss through precipitation; (Note that the calibration solutions used contain a trace of HF in the matrix of the Zr, Nb, Ta and Hf standard solutions). Furthermore, if the trace of HF is eliminated from the samples, build up of these elements on tube walls and glass surfaces during sample introduction may reach a critical level during extended runs, such that they are released intermittently in an unpredictable manner even with a HF acid-free matrix. This would result in meaningless results during at least the latter stages of an extended run. An alternative to total HF removal has been proposed by Wu *et al.* (1996), who demonstrated the use of boric acid to mask free fluoride ions in the solution for ICP-MS analysis. The feasibility of this approach for minimizing the memory effect in low-level analysis of the HFSEs requires further investigation.

One obvious question is how does regular use of HF in the ICP-MS affect performance? We have been "spiking" the first stage of our wash sequence routinely with 2 drops of HF per 300 ml of 10% v/v HNO₃ (see below) for > 12 months and have seen no degradation of machine glassware or performance. Scandium was monitored in our blank solutions and no elevation in its concentration was detected, as one would expect if SiOH were being produced from dissolution of the glassware. While effectively removing HFSE (and other) memory effects, HF acid has to be handled with extreme caution when "spiking" the wash reservoir although, once diluted, it may be run as any other wash stage.

Testing of memory removal techniques

Analytical method

Machine operating conditions are given in Table 1. All Teflon™ tubing was changed before each run, and a complete set of clean glassware and cones was used. Counts were corrected for drift using internal standardisation procedures. Internal standards As, Rh, In, Re, and Tl were spiked into every test tube (standard, blank, and sample) at a concentration of

20 ng g⁻¹. Note that chlorine abundances were negligible, allowing the use of As as an internal standard solutions. Calibration standard solutions of 1, 2, 5, 10, 25, 50, 75, and 100 ng g⁻¹ were run at the beginning of each run, and international basaltic reference material BHVO-1 (Totland *et al.* 1992, Govindajaru 1994) was used to monitor the accuracy of the analyses.

Understanding and either eliminating or correcting for potential interferences is just as important as elimination of memory effects from previously run samples and/or calibration samples. In order that potential interferences can be monitored, two solutions were run periodically throughout each run to monitor for oxide interferences (Jenner *et al.* 1990); these were "Standard A" and "Standard B" (Table 9), with both being in a 5% v/v HNO₃ matrix. The elements present

Table 9.
Concentrations in calibration sample solutions used in analyses (ng g⁻¹)

Element	Standard A	Standard B	Oxide Interference
Y	20	-	-
Zr	40	-	-
Nb	20	-	-
Mo	20	-	-
Sn	20	-	-
Ba	200	-	-
La	20	-	-
Ce	20	20	-
Pr	20	-	-
Nd	-	40	-
Sm	-	40	-
Eu	-	40	¹³⁷ BaO
Gd	-	40	¹⁴¹ PrO
Tb	40	-	¹⁴⁵ NdO
Dy	20	-	¹⁴⁷ SmO
Ho	20	-	¹⁵¹ EuO
Er	40	-	-
Tm	20	-	¹⁵³ EuO
Yb	20	-	¹⁵⁷ GdO
Lu	-	40	¹⁵⁹ TbO
Hf	-	20	¹⁶³ DyO
Ta	-	20	¹⁶⁵ HoO
W	-	20	¹⁶⁷ ErO
Th	20	20	-
U	20	-	-

After Jenner *et al.* (1990).

in each solution were not affected by oxide interferences from any other element in that particular solution. For example, in Standard A, Eu is absent from the solution, while Ba, whose oxide produces an interference on Eu, is present. Any counts detected on the Eu peak at mass 153 are the result of a BaO interference. The percent interference caused by Ba on Eu is defined by the counts on Eu due to BaO divided by the counts on Ba. Eight Standard A and Standard B solutions were placed throughout each run, and the average percent interference used to correct for oxide interferences on rock solutions and calibration standards.

Wash protocols

A sequence of three separate 90 second washes of 5% v/v HNO₃ was first used as a wash protocol for the experiments evaluating memory effects. Acid blanks (5% v/v HNO₃) were placed between each

sample pair to monitor for memory effects. Analyses incorporating the 5% v/v HNO₃ wash sequence exhibited elevated blank levels (Figure 2a) especially for Nb and Ta. Experiments were conducted with varying strengths of nitric acid washes; however, elevated sample and blank concentrations persisted. Notable improvement was made when a trace of hydrofluoric acid was added to a first wash of 10% v/v HNO₃. This wash sequence consisted of three 90 second washes in the order: 10% v/v HNO₃ + 2 drops HF per 300 ml, 10% v/v HNO₃, and 5% v/v HNO₃ to re-equilibrate with the sample matrix. By adding a trace amount of HF to only the first 10% v/v HNO₃ wash, we could maintain low blank levels (Figure 2b). There appeared to be little difference in the blank levels or memory of the REE between the two wash protocols used (Figure 3). By reducing memory effects, exaggerated element concentrations in samples are prevented (Figures 4 & 5), while simultaneously limiting the time of exposure of

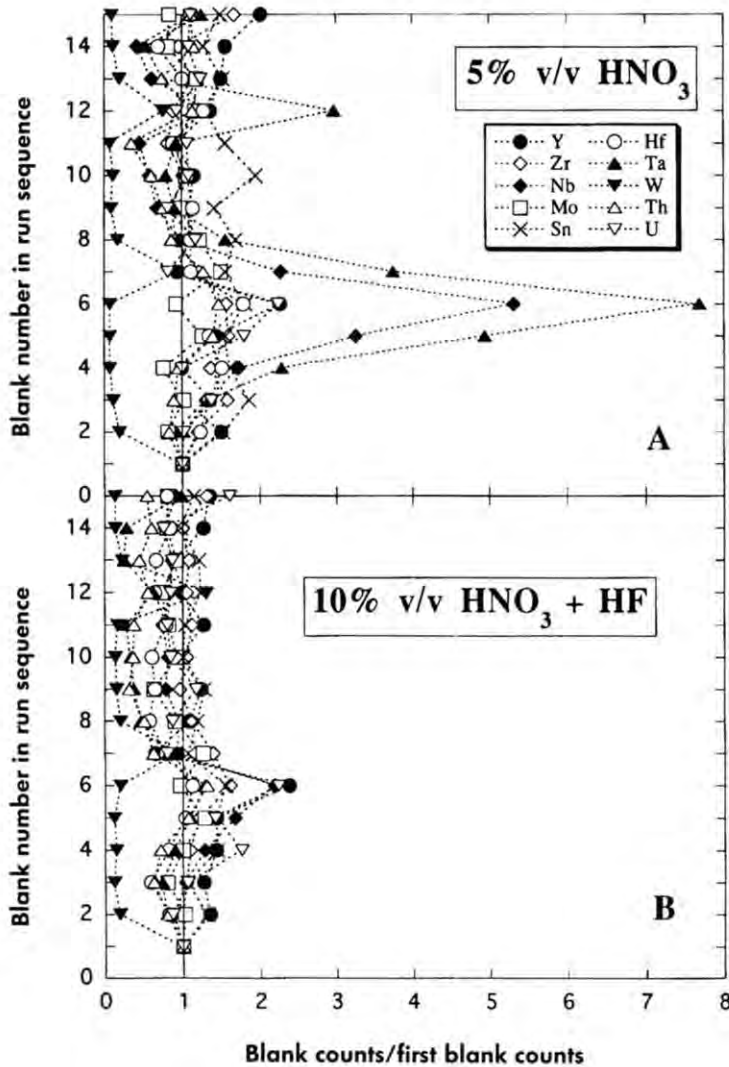


Figure 2. Progression of blanks for Y, Zr, Nb, Mo, Sn, Hf, Ta, W, Th and U. Counts (cps) are normalized to the first blank of each run under (A) 5% v/v HNO₃ wash protocol, and (B) 10% v/v HNO₃ + HF wash protocol. In each case, the same sample order and uptake times are used. Samples include calibration samples ranging from 1 to 100 ng g⁻¹, several replicates of BHVO-1, and unknown rock solutions. Memory effects in the blanks are improved under the 10% v/v HNO₃ + HF wash, especially for Nb and Ta. Memory effects are strongest in blanks following highly concentrated solutions. The scale is kept the same for both plots for ease of comparison.

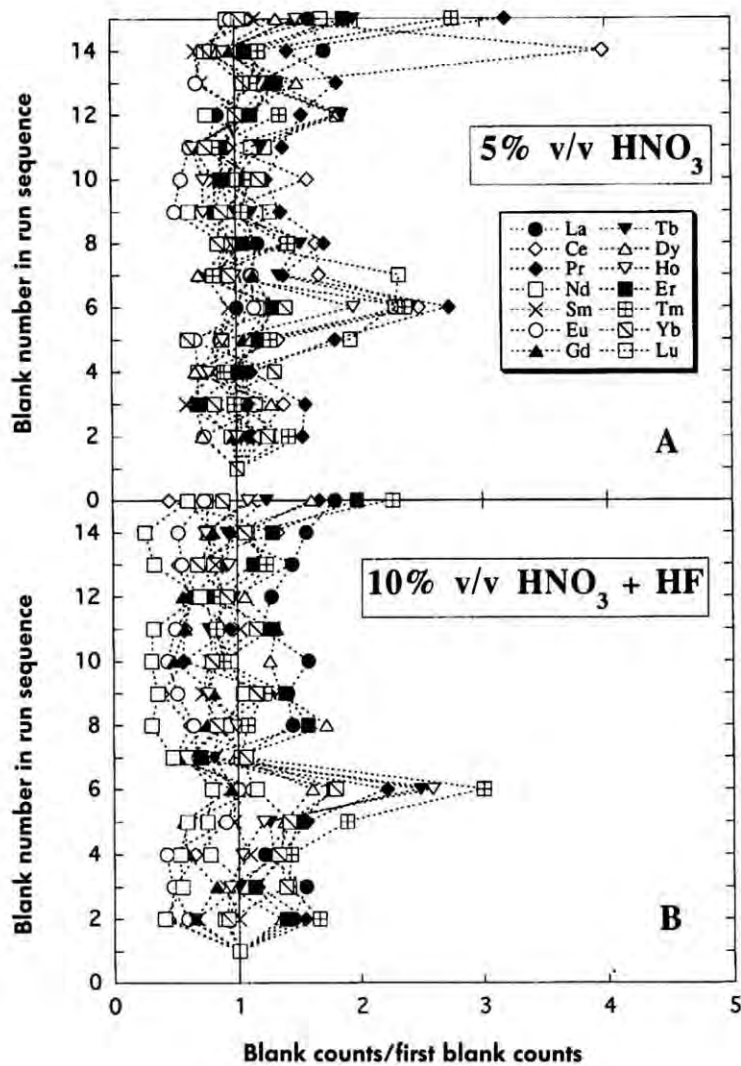


Figure 3. Progression of blanks for Y, Zr, Nb, Mo, Sn, Hf, Ta, W, Th and U as in Figure 2. Counts (cps) are normalized to the first blank of each run under (A) 5% v/v HNO₃ wash protocol, and (B) 10% v/v HNO₃ + HF wash protocol. In each case, the same sample order and uptake times are used. Memory effects in the blanks for the REE show little difference between the wash protocols. The scale is kept the same for both plots for ease of comparison.

the apparatus to HF. The three stage wash sequence was continued because of the possibility of wash reservoir contamination, especially during extended runs, as discussed above.

From the above work and that of Jain *et al.* (1994), it is evident that: 1) HFSEs tend to adhere to the sides of the sample introduction apparatus; and 2) these elements are remobilized by the trace amounts of HF persisting in the rock samples even after treatment with concentrated HNO₃ washes, to the point where they are still being removed during the next sample acquisition. Therefore, by placing a trace amount of HF in the first wash, any residual elements would be removed from the sample introduction apparatus before it came into contact with the next sample. Indeed, blank levels throughout the run sequence were similar to the initial blank, indicating no build up of residual HFSEs (Figure 2b). As noted earlier, visible

deterioration of the glassware as a result of HF use has not been seen in over twelve months of operation.

By reducing the memory effects, calculated detection limits (3σ above blank levels) remained low throughout the entire run under the 10% v/v HNO₃ + HF wash protocol. These detection limits (generally 5-20 pg g⁻¹) were two orders of magnitude lower than those obtained using the 5% v/v HNO₃ wash protocol (300-800 pg g⁻¹) (see above) and are also significantly lower than the concentrations expected in basalt samples, even after dilution prior to analysis.

USGS basaltic reference material BHVO-1

Experiments using the two wash protocols were conducted on USGS basaltic reference material BHVO-1. Element concentrations were determined and normalized to the recommended concentrations for

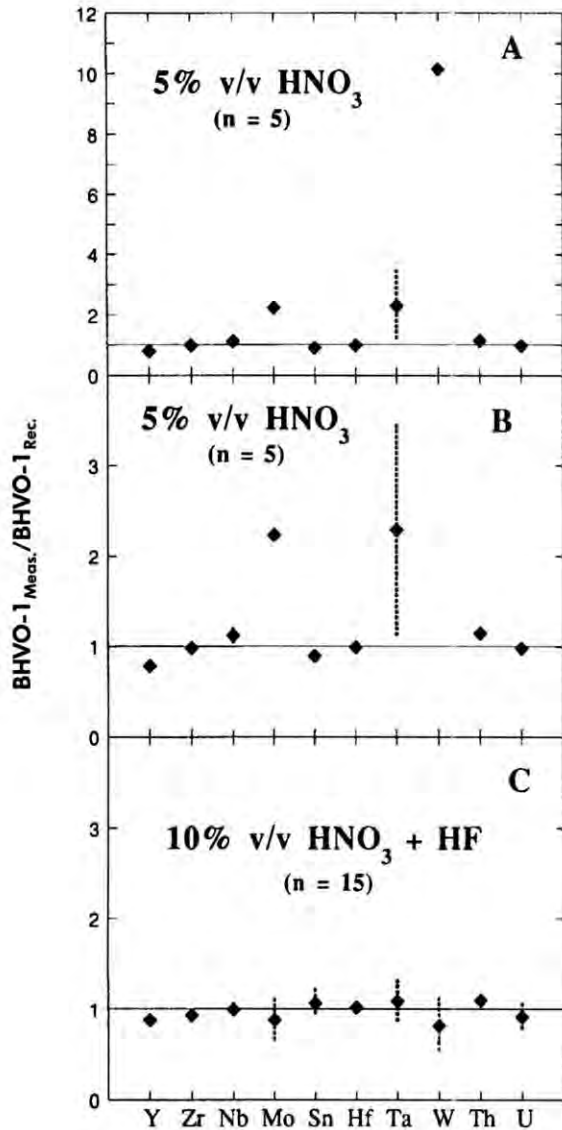


Figure 4. Abundances of Y, Zr, Nb, Mo, Sn, Hf, Ta, W, Th and U for BHVO-1 analysed using (A) and (B) 5% v/v HNO₃ wash protocol, and (C) 10% v/v HNO₃ + HF wash protocol. (B) is an expanded scale of (A) to allow ease of comparison with the 10% v/v HNO₃ + HF results depicted in (C). All measured (meas.) data are normalized to recommended (rec.) values. Note the decrease in bias when the more rigorous wash protocol is used.

each element (Figures 4 and 5) as reported in Totland *et al.* (1992) and Govindaraju (1994). The accuracy and precision of Y, Zr, Nb, Mo, Sn, Hf, Ta, W, Th and U determinations for BHVO-1 are dramatically improved using the more rigorous 10% v/v HNO₃ + HF wash protocol (Figure 2). Most notable is the substantial improvement in Mo, Ta, and W, with Y and Nb

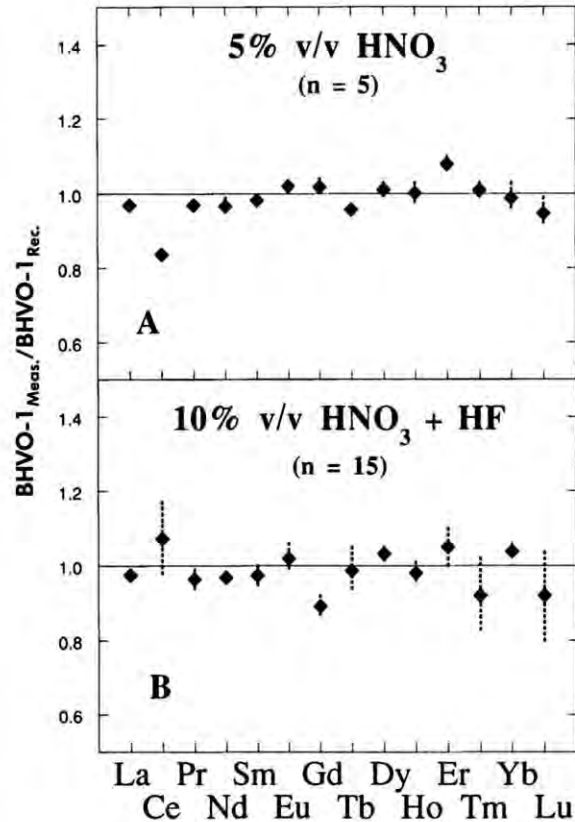


Figure 5. Abundances of the REE for BHVO-1 analysed using (A) 5% v/v HNO₃ wash protocol, and (B) 10% v/v HNO₃ + HF wash protocol. Thulium and Lu exhibit poor precision for the more rigorous wash protocol, but the accuracy of Ce is improved. Otherwise, little difference is noted in the results of the different experiments.

moderately improved (Table 10). With regard to the REE, there is similar accuracy and precision for most of these elements using either wash protocol, although the low abundance elements Tm and Lu display less precision using the 10% v/v HNO₃ + HF wash protocol (Table 10). Cerium is very precise using the 5% v/v HNO₃ wash protocol, but has poor accuracy relative to the results for the 10% v/v HNO₃ + HF wash. Absolute abundances of the target group of elements for BHVO-1 are shown in Figure 6 for both wash protocols. The REE exhibit similar average abundances irrespective of the wash protocol used, but the effect of the more rigorous wash protocol on Y, Zr, Nb, Mo, Sn, Hf, Ta, W, Th and U is dramatic. Most notable are Nb, Mo, and W, although accuracy is improved for almost all of these elements using the 10% v/v HNO₃ + HF wash protocol (Figure 6, Table 10). Such improvements caused by the removal of memory demonstrate the value of this wash protocol.

Table 10.
Concentrations ($\mu\text{g g}^{-1}$) of BHVO-1 reference material determined under 5% v/v HNO_3 + HF wash protocols compared with the recommended values

Element	10% v/v HNO_3 + HF (n = 15)	1 σ	5% v/v HNO_3 (n = 5)	1 σ	Recommended values
Y	24.16	1.49	21.84	1.09	27.6
Zr	166.21	10.07	176.48	9.23	179.0
Nb	18.97	1.11	21.38	1.47	19.0
Mo	0.90	0.23	2.28	0.01	1.02
Sn	2.24	0.31	1.89	0.05	2.10
Hf	4.47	0.10	4.36	0.14	4.38
Ta	1.34	0.29	2.82	1.42	1.23
W	0.22	0.08	2.74	0.01	0.27
Th	1.19	0.07	1.24	0.03	1.08
U	0.38	0.06	0.41	0.01	0.42
La	15.41	0.14	15.32	0.11	15.80
Ce	41.84	3.93	32.68	0.10	39.0
Pr	5.49	0.13	5.52	0.06	5.70
Nd	24.41	0.28	24.37	0.36	25.2
Sm	6.04	0.15	6.09	0.05	6.20
Eu	2.10	0.08	2.10	0.01	2.06
Gd	5.70	0.17	6.51	0.13	6.40
Tb	0.95	0.06	0.92	0.01	0.96
Dy	5.37	0.08	5.26	0.12	5.20
Ho	0.97	0.03	0.99	0.03	0.99
Er	2.52	0.13	2.59	0.05	2.40
Tm	0.30	0.03	0.33	0.01	0.33
Yb	2.10	0.04	2.00	0.08	2.02
Lu	0.27	0.03	0.28	0.01	0.29

Application to geological research

Ontong Java Plateau basalts

Oceanic basalts from the Ontong Java Plateau, which outcrop in the Solomon Islands, south west Pacific, are relatively homogeneous in incompatible trace element ratios (e.g. Mahoney and Spencer 1991, Mahoney *et al.* 1993, Tejada *et al.* 1996, Neal *et al.* 1997). Knowing that these samples have, for example, a well constrained Zr/Nb ratio of ~ 17 makes these an ideal suite of rocks to test the new wash procedure for the elimination of memory effects.

Malaita, Solomon Islands

A suite of seventeen previously analysed plateau basalts were used in this study. This allowed a comparison of the 5% v/v HNO_3 wash sequence and the 10% v/v HNO_3 + HF wash sequence in order to

highlight the benefits of the new wash protocol on research samples. Using the 10% v/v HNO_3 + HF wash procedure, concentrations of all the studied elements appear reduced relative to those obtained from the 5% v/v HNO_3 wash (Figure 7), although the REE generally yield similar abundances for both wash protocols. Occasionally, the decrease is significant (i.e. Zr, Nb, W, Th; Figure 7 and Table 11). More importantly, elimination of memory effects thereby alters element ratio calculations thus affecting modelling and petrogenetic interpretations. The effect is demonstrated dramatically when Zr ($\mu\text{g g}^{-1}$) is plotted against Nb, Y, and Hf (Figure 8 a-c) and where Nb is plotted against Ta, Th and Y (Figure 9a,b,c). The new wash protocol decreases the Zr, Nb, Hf, Ta and Th concentrations and thus, for example Zr/Nb and Zr/Hf ratios are increased (Figure 8a,c) and the average shifts from ~ 14 to ~ 17 and ~ 32 to ~ 35.5 , respectively, in keeping with previous analyses of the Ontong Java Plateau basalts (Mahoney and Spencer 1991, Mahoney

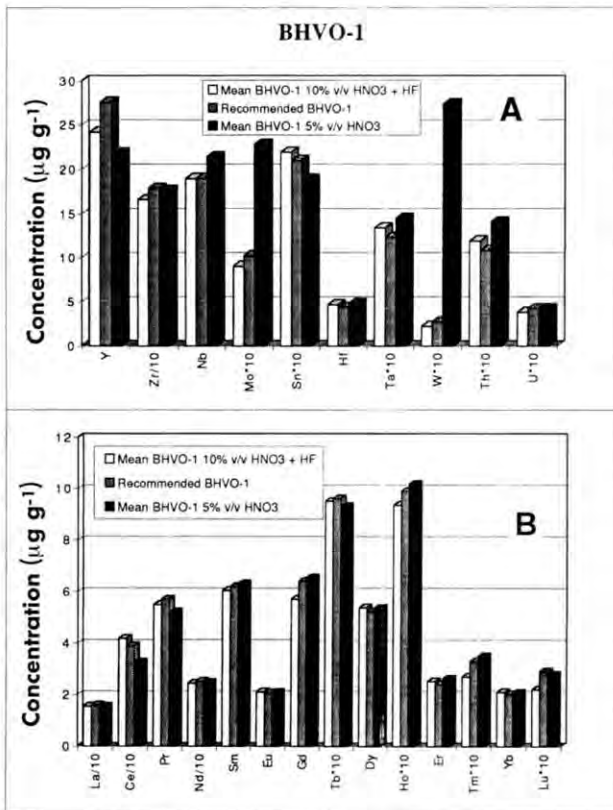


Figure 6. BHVO-1 concentrations ($\mu\text{g g}^{-1}$) represented in bar graph form for ease of comparison between the two wash protocols and the recommended values. Note the dramatic improvement in using the 10% v/v HNO_3 + HF protocol for Y, Zr, Nb, Mo, Sn, Hf, Ta, W, Th and U in (A), whereas in (B) there is little difference between the wash protocols for the REE. Elements of low abundance are exaggerated by 10x (Mo, Sn, Ta, W, Th, U, Tb, Ho, Tm, Lu) and those of high abundances (Y, Zr, La, Ce, Nd) have been reduced by a factor of ten so that they can be compared on the same scale.

et al. 1993, Tejada *et al.* 1996, Neal *et al.* 1997). However, a dramatic decrease in Th abundance of up to 30% between the 5% v/v HNO_3 and the 10% v/v HNO_3 + HF wash protocols is observed (Figure 9b). These data unambiguously demonstrate the effect of memory on analyses of geological samples using solution ICP-MS. However, the abundances of Y actually increase with the more rigorous wash protocol (Figures 8b and 9c), causing a decrease in Zr/Y and Nb/Y ratios from ~ 3.6 to ~ 3.2 and from ~ 0.25 to ~ 0.20 , respectively. This is also witnessed for BHVO-1 (Figure 6, Table 10), bringing the analysed concentration closer to the recommended value.

Makira, Solomon Islands

A suite of seventeen plateau-type basalts were analysed from Makira (San Cristobal), Solomon

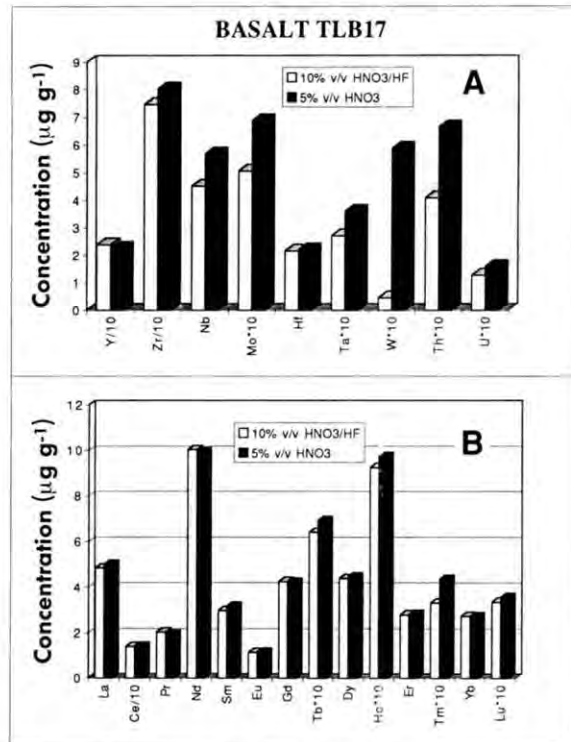


Figure 7. Malaita sample TLB 17 illustrates the effect of the 10% v/v HNO_3 + HF in removing memory. concentrations ($\mu\text{g g}^{-1}$) appear elevated under the 5% v/v HNO_3 wash compared to results from the 10% v/v HNO_3 + HF wash. As in Figure 6, elements of low abundance are exaggerated by 10x (Mo, Ta, W, Th, U, Tb, Ho, Tm, Lu) and those of high abundances (Y, Zr, Ce) have been reduced by a factor of ten so that they can be compared on the same scale. No tin data is presented because it was not quantified in the 5% v/v HNO_3 wash experiment, no single element calibration sample being available at the time.

Islands, under the 10% v/v HNO_3 + HF wash protocol (Pettersen *et al.* 1995, Birkhold-VanDyke *et al.* 1996). The Makira basalts are very similar to the Malaita basalts, but exhibit a larger range in HFSE concentrations (Figures 8 and 9). However, this suite demonstrates the repeatability of HFSE ratios using the new wash protocol, since ratios defined by the Malaita suite (using the more rigorous wash protocol) are preserved by Makira basalts. It is evident that Makira basalts have identical ratios to the Malaita suite for other HFSEs (Figures 8 and 9).

Summary and recommendations

While ICP-MS has the sensitivity to quantify the HFSEs and REEs to low pg g^{-1} levels, memory effects

Table 11.
Element concentrations ($\mu\text{g g}^{-1}$) in oceanic plateau basalts from Malaita, Solomon Islands,
determined using (1) 10% v/v HNO_3 + HF wash and (2) 5% v/v HNO_3 wash protocols

(1)	Y	Zr	Nb	Mo	Sn	La	Ce	Sm	Eu	Hf	Ta	W	Th	U
tlb 2	21.30	84.71	5.44	0.48	0.97	5.06	15.18	2.99	1.16	2.43	0.51	0.01	0.46	0.10
tlb 3	22.28	71.97	4.45	0.37	1.11	4.96	14.62	3.02	1.23	2.28	0.30	0.07	0.41	0.06
tlb 4	24.91	79.98	4.84	0.79	1.16	4.91	14.17	2.96	1.21	2.25	0.28	0.05	0.39	0.07
tlb 5	22.01	71.35	4.40	0.42	0.89	4.81	13.11	2.87	1.10	2.10	0.35	0.10	0.40	0.09
tlb 8	22.67	73.60	4.11	0.27	0.80	4.86	13.05	2.79	1.13	2.02	0.27	0.13	0.38	0.08
tlb 10	25.38	83.82	5.16	0.38	1.17	4.91	13.58	3.06	1.18	2.27	0.33	0.11	0.45	0.10
tlb 11	23.77	74.47	4.42	0.69	1.28	5.00	14.10	3.09	1.19	2.18	0.34	0.09	0.42	0.10
tlb 15	25.27	79.52	4.78	0.27	0.57	4.90	13.99	3.03	1.21	2.30	0.32	0.09	0.42	0.08
tlb 17	25.34	78.24	5.00	0.48	1.21	4.64	13.08	2.93	1.07	2.15	0.52	0.03	0.37	0.07
tlb 18	26.21	79.65	4.94	0.31	0.98	4.88	13.79	2.92	1.14	2.15	0.32	0.05	0.44	0.08
tlb 19	24.03	77.78	4.94	0.64	0.72	4.89	13.56	3.06	1.17	2.25	0.62	0.06	0.40	0.07
tlb 22	22.43	67.52	4.11	0.77	0.88	3.49	10.33	2.53	1.01	1.83	0.34	0.05	0.28	0.06
tlb 24	21.45	68.69	3.89	0.22	0.59	3.70	11.02	2.73	1.05	2.02	0.29	0.03	0.27	0.05
tlb 26	22.92	75.13	4.55	0.27	1.25	5.14	14.09	3.00	1.17	2.27	0.31	0.05	0.38	0.06
tlb 28	24.54	80.80	5.00	0.42	0.99	5.06	13.77	3.09	1.20	2.30	0.35	0.07	0.45	0.08
(2)	Y	Zr	Nb	Mo	Sn	La	Ce	Sm	Eu	Hf	Ta	W	Th	U
tlb 2	21.45	94.99	6.70	1.09		5.36	14.95	3.22	1.24	2.59	0.45	1.36	0.55	0.15
tlb 3	22.59	83.77	5.81	1.35		5.31	14.74	3.18	1.22	2.86	0.40	5.93	0.73	0.12
tlb 4	22.85	81.90	5.70	1.52		5.40	14.88	3.18	1.18	2.42	0.41	0.17	0.56	0.13
tlb 5	22.76	81.94	5.82	0.76		5.19	14.44	3.13	1.14	2.23	0.37	1.73	0.56	0.11
tlb 8	23.40	85.33	5.98	1.34		5.42	14.70	3.21	1.23	2.30	0.38	7.32	0.77	0.11
tlb 10	22.73	83.11	5.99	0.62		5.18	14.55	3.21	1.20	2.40	0.37	0.79	0.61	0.14
tlb 11	23.55	81.99	5.80	1.22		5.35	14.73	3.36	1.20	2.29	0.37	2.06	16.49	3.81
tlb 15	23.78	86.21	5.96	1.05		5.39	14.99	3.39	1.25	2.59	0.40	7.32	0.84	0.12
tlb 17	22.61	80.10	5.68	0.69		4.98	14.01	3.16	1.15	2.20	0.36	0.59	0.66	0.16
tlb 18	25.03	84.70	6.08	1.00		5.37	14.73	3.30	1.27	2.21	0.37	2.10	0.55	0.14
tlb 19	22.71	82.27	5.87	1.29		5.16	14.36	3.31	1.22	2.28	0.38	6.30	0.69	0.13
tlb 22	20.42	70.26	4.74	1.46		3.73	10.75	2.73	1.00	1.91	0.29	1.05	0.39	0.12
tlb 24	20.58	74.26	4.87	0.39		3.91	11.71	2.85	1.07	2.09	0.33	1.71	0.39	0.09
tlb 26	22.38	83.69	6.05	0.98		5.38	15.02	3.20	1.23	2.66	0.40	6.93	0.76	0.12
tlb 28	21.72	80.57	5.68	0.53		5.30	14.51	3.18	1.19	2.32	0.37	0.99	0.59	0.13

are a serious problem for analysis of low HFSE abundance samples. Build-up of the "sticky" HFSEs on the walls of the sample introduction system occurs during the analysis of calibration sample solutions made up of pure element solutions. These adhering HFSEs are remobilized during the first rock analysis because of the trace of HF inherent in these solutions after rock dissolution. Minimizing such memory effects is essential for precise and accurate determination of HFSE abundances in, for example, ultramafic and arc-related igneous rocks.

It is evident that the rigorous wash protocol involving HF used for the analysis of HFSEs with ICP-MS greatly affects the accuracy of the measured

concentrations without any adverse effects on the hardware. When element ratios are studied, small inaccuracies in the concentrations can alter the field in which the ratios plot on discrimination diagrams, thereby making it difficult or impossible to model petrogenetic trends accurately. By decreasing or eliminating memory effects associated with the HFSEs, concentrations are more accurate and precise, and produce ratios that can show distinct variations that would otherwise be masked.

The recommendations of this study are to follow the HF/ HNO_3 dissolution procedure *without* HClO_4 . This will result in a trace of HF in the final rock solution, thus maintaining the HFSEs in solution without any

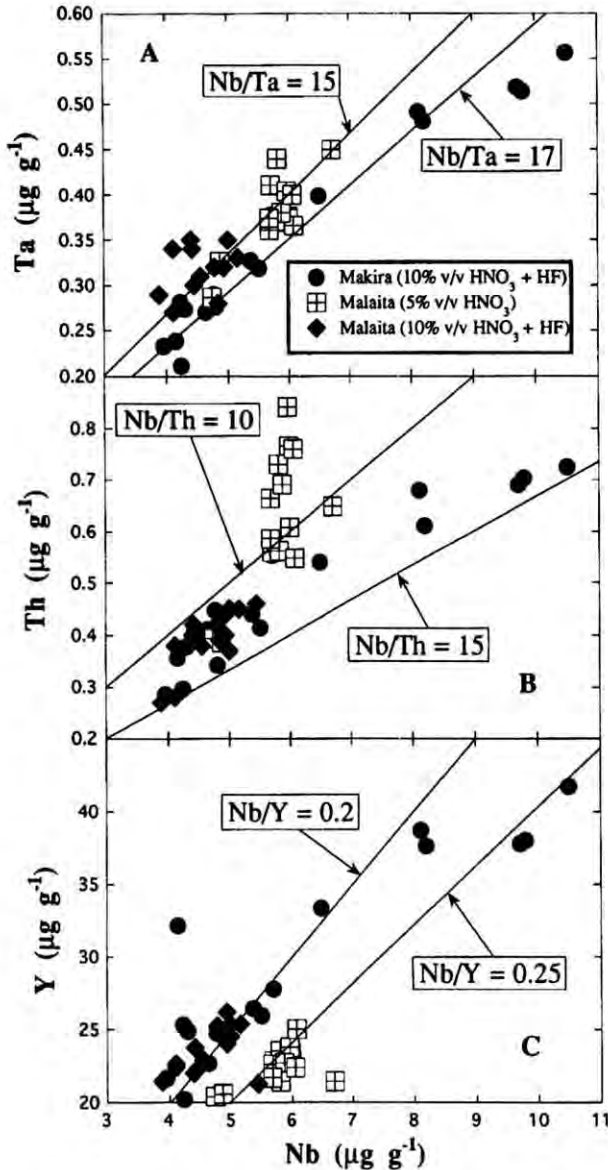


Figure 8. Ontong Java Plateau basalts (from Malaita and Makira) exhibit similar HFSE ratio characteristics. The 5% v/v HNO_3 wash procedure produces measured element concentrations that are elevated relative to those measured with the 10% v/v HNO_3 + HF wash for the Ontong Java Plateau basalts from the Solomon Islands. This results in erroneous element-element ratios: (A) Zr vs. Nb; (B) Zr vs. Y; and (C) Zr vs. Hf. Zirconium, Nb and Hf exhibit decreases in abundances when the 10% v/v HNO_3 + HF wash is used, whereas Y exhibits an increase.

apparent major effect on the REE precipitating out as fluorides. Minimisation of the HFSE memory effects can be accomplished by: 1) cleaning all the glassware and cones, and changing sample introduction tubes prior to analysis thereby eliminating the possibility of

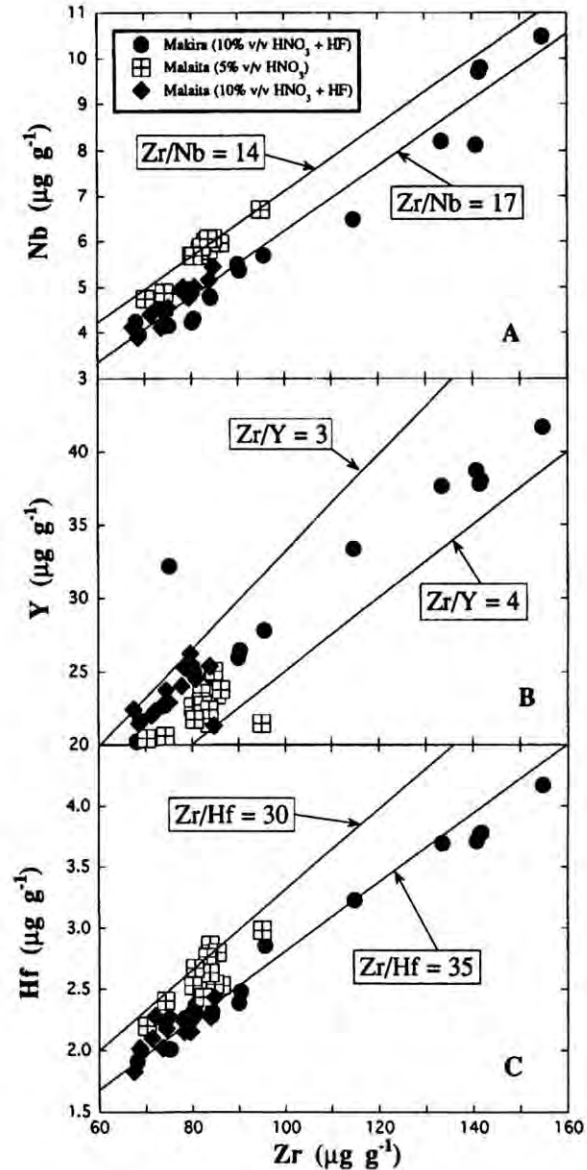


Figure 9. Similar to Figure 8, but featuring niobium: (A) Nb vs. Ta; (B) Nb vs. Th; and (C) Nb vs. Y. Niobium, Ta, and Th all exhibit decreases in abundance when the 10% v/v HNO_3 + HF wash protocol was used. The increase in Y using the more rigorous wash protocol is again observed in (C).

contamination from a previous run; 2) inclusion of rock solution (digested in identical conditions to the sample) immediately following the calibration standards thereby reducing the memory effects on subsequent samples; and 3) inclusion of an HF stage in the wash procedure.

The above experiments demonstrate that the new protocol can be applied to basaltic rocks very easily and allows sub- $\mu\text{g g}^{-1}$ abundances to be determined -

a vast improvement over using a combination of XRF and INAA. This new protocol can be used to yield high quality (accurate and precise) data from which robust petrogenetic models can be developed.

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