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Sidonie Révillon, D. Hureau-Mazaudier. Improvements in Digestion Protocols for Trace Element and Isotope Determinations in Stream and Lake Sediment Reference Materials (JSd-1, JSd-2, JSd-3, JLk-1 and LKSD-1). *Geostandards and Geoanalytical Research*, 2009, 33 (3), pp.397-413. 10.1111/j.1751-908X.2009.00008.x . insu-00422107

HAL Id: insu-00422107

<https://insu.hal.science/insu-00422107>

Submitted on 8 Feb 2010

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Improvements in Digestion Protocols for Trace Element and Isotope Determinations in Stream and Lake Sediment Reference Materials (JSd-1, JSd-2, JSd-3, JLk-1 and LKSD-1)

Sidonie Révillon^{(1, 2,)*} and Danièle Hureau-Mazaudier⁽¹⁾

¹ Université de Brest, CNRS, UMR 6538 Domaines Océaniques, Institut Universitaire Européen de la Mer, Place Copernic, 29280 Plouzané, France

² IFREMER, Département Géosciences Marine, BP 70, 29280 Plouzané, France

*: Corresponding author : email : sidonie.revillon@ifremer.fr

Abstract:

Total dissolution is a critical step in geochemical analysis. Despite the number of published protocols, this issue still draws attention for sediment samples, which are particularly difficult to dissolve due to the common occurrence and high abundance of refractory phases such as zircon. We present tests of different chemical digestion procedures carried out on reference materials (RM) of stream (JSd-1, JSd-2 and JSd-3) and lake (JLk-1 and LKSD-1) sediments from the Geological Survey of Japan (GSJ) and the Canadian Certified Reference Material Programme (CCRPM). We demonstrate that the fusion technique is not appropriate for our studies as not all elements of interest were recovered and blank levels were too high to permit further Sr and Pb isotopic composition measurements. Similarly, conventional HF+HNO₃ dissolution methods were not efficient enough for detrital samples. Our preferred method involved using high pressure Teflon® vessel bombs in association with HClO₄. This protocol ensured a complete dissolution of the powder, as well as a complete recovery of trace elements. Moreover, blank levels were sufficiently low that Sr or Pb isotope compositions could be measured from the same mother solution. We also tested the homogeneity of RM powders by performing tests on various amount of powder.

Keywords: RM • HR-ICP-MS • acid digestion • fusion • sediment

Résumé:

La dissolution totale d'un échantillon est une phase critique pour toute analyse géochimique. Malgré le nombre de protocoles publiés, la mise en solution d'échantillons de sédiments reste problématique en raison de la présence de phases réfractaires comme les zircons. Nous présentons des tests de différentes procédures chimiques réalisés sur des Matériaux de Référence (RM) de sédiments de ruisseau (JSd-1, JSd-2 et JSd-3) et de lac (JLk-1 et LKSD-1) du Service Géologique de Japon (GSJ) et de Canadian Certified Reference Material Programme (CCRPM). Nous montrons que la technique de fusion utilisée n'est pas appropriée à nos études car tous les éléments d'intérêt ne sont pas récupérés quantitativement et le niveau des blancs est trop élevé pour permettre l'analyse des compositions isotopiques de Sr et de Pb à partir des mêmes solutions. De même, les techniques de mise en solution conventionnelles par attaque acide HF+HNO₃ sur plaque chauffante ne sont pas suffisamment efficaces pour une mise en solution complète de sédiments détritiques. Notre méthode préférée implique l'utilisation de bombes en téflon et de HClO₄. Ce protocole permet la mise en solution totale des échantillons et la récupération de tous les éléments trace intéressants. De plus, les blancs de chimie sont suffisamment bas pour que les compositions isotopiques, e.g., Sr, Pb puissent être mesurées à partir du même aliquot. Par ailleurs, nous avons aussi testé l'homogénéité des RM utilisés en appliquant notre protocole d'attaque sur des quantités de poudre variables.

Mots-clés: matériel de référence • HR-ICP-MS • dissolution acide • fusion • sédiments

Sample digestion is a critical stage in the process of chemical analysis of geological material. Especially since developments of modern multi-element measurement instrumentation, such as ICP-MS, HR-ICP-MS or MC-ICP-MS, which allow fast and highly precise solution analysis but require purest solution for the analytes. Despite the multitude of digestion techniques, complete dissolution of some sample types is still problematic. This is particularly true for sediment samples, which are especially difficult to dissolve due to the occurrence of refractory minerals such as zircons. Numerous studies have been published in the past, presenting various methods including conventional HF + HNO₃ acid dissolution procedures, HF + HNO₃ + HClO₄ procedures, with or without the use of high pressure digestion vessels or fusion techniques (Toutain and Meyer 1989, Townsend, *et al.* 1998, Toutain and Meyer 1989, Makishima and Nakamura 1997, Taicheng, *et al.* 2002, Liang, *et al.* 2000, Yamamoto, *et al.* 2005, Yokoyama, *et al.* 1999, Dulski 2001, Yu, *et al.* 2001, Münker 1998, Weis, *et al.* 2006, Pretorius, *et al.* 2006). However, few studies were specifically dedicated to sediment RM and there is a need for an efficient and reliable method for detrital sediment dissolution.

Sediment geochemistry is an increasingly attracting domain for the scientific community and numerous marine and continental paleo-environmental and paleo-climatic researches now involve geochemical studies. A usually limiting factor to the use of geochemical data, such as trace element analyses or radiogenic isotope compositions, in sediment provenance or climatic cycle's studies is the number of samples involved. Depending on the sediment accumulation rates, high-resolution investigations of environmental or climatic changes at various time scales require analysing hundreds of samples. Moreover, numerous proxies, used in those investigations, such as stable isotopes or biostratigraphy data, are usually analysed at a cm-scale. In order to consistently compare the various sets of data, it is therefore necessary to achieve similar resolution. In addition, complexity of such natural systems implies multi-

proxy approaches that involve the use of numerous geochemical tracers (e.g. trace elements, Sr, Nd, Pb, Hf isotope compositions).

Hence, it is critical to improve chemical procedures so that large numbers of sedimentary samples can be analysed. Rather than focussing on diminishing the time of sample dissolution, we chose in this study to improve the efficiency of the dissolution procedure together with diminishing as much as possible the blank level so that all trace elements and isotope compositions (including Pb) could be analysed from the same mother solution.

Several methods were fully tested and we propose a complete protocol for the dissolution of detrital sediment samples.

Analytical methodology

We have performed tests on various sediment Reference Materials (RM): 3 stream sediments from the Geological Survey of Japan (GSJ, JSd-1, JSd-2, and JSd-3); two lake sediments from the GSJ and the Canadian Certified Reference Material Programme (CCRMP, Jlk-1 and LKSD-1) as well as on a well-characterized granite RM (GS-N from the Centre de Recherches Pétrographiques et Géochimiques, CRPG) and a dolerite (CRPG, WS-E).

Reagents

Water was deionized and purified on a millipore water system (mixed-bed resin and filters by Milli-Q®). Hydrochloric (Merck PA) and nitric acid (Merck PA) were distilled on a Quartex® apparatus. Hydrofluoric (Merck Suprapur®) acid was distilled on a Teflon® Picrotrace® apparatus. Perchloric (Merck Suprapur®) acid was subboiled using a two-bottle Teflon® apparatus (Analab, Cleanacid®). All reagents were diluted following the various procedures with Milli-Q® water.

Digestion techniques

Five distinct digestion methods were tested in order to determine the most efficient procedure for sedimentary material digestion. The first one is a fusion method and the four others are conventional acid digestion procedures.

Alkaline fusion

We tested the alkaline fusion technique developed by Taicheng, et al. (2002) for soils and sediment samples and further tested by Bayon, *et al.* (In press). It involves alkaline fusion with NaOH-Na₂O₂ as the flux followed by pre-concentration of trace element using Fe(OH)₃-Ti(OH)₄ prior to ICP-MS analyses. About 100 mg of sediment RM were weighted and placed in the crucible with 1.2g Na₂O₂ (pro analysis, Fluka) and 0.6g NaOH (pellets, Riedel-de-Haën) and fused in a furnace at 650°C for 15 minutes. After cooling, the melt is dissolved and iron hydroxides are precipitated by adding 10ml of ultra-pure water.

Acid digestion procedures

100 mg of powdered sample were carefully weighted in 30 ml Savillex® PFA Teflon® beaker (Method A) or 30 ml PTFE Teflon® vessels designed for our high pressure digestion apparatus (Methods B through D).

Method A:

This first protocol is a classical acid HF-HNO₃ dissolution method. 3 ml of HF (24 mol l⁻¹) and 1 ml of HNO₃ (14 mol l⁻¹) were slowly added to the weighted sample to avoid drastic reaction. The Savillex® beakers were tightly closed and agitated for 20 mn in an ultrasonic bath. Beakers were placed on a hot plate at 130°C for 48h. Solutions were dried at 80°C for about 12h to ensure complete evaporation of HF. The temperature of the hot plate was then

increased to 120°C until complete dryness. The dried residue was dissolved in 1 ml HCl (6 mol l⁻¹), heated for about 12h on a hot plate at 120°C and dried again at 120°C. The dried residue was then dissolved in a mother solution of 40 ml HCl (3 mol l⁻¹) (Figure 1).

Method B:

In method B, 3 ml HF (24 mol l⁻¹) and 1 ml HNO₃ (14 mol l⁻¹) were carefully added to the weighted sample in PTFE Teflon® vessels and agitated for 20 mn in an ultrasonic bath. Teflon® lids were adjusted on the vessels and transferred into stainless steel high-pressure digestion apparatus. We placed them in an oven to cook at 160°C for 7 days. Solutions were then transferred into 30 ml concave bottom Savillex® PFA beakers and, as in Method A, a two-step evaporation procedure was adopted (80°C for 12h and 120°C until complete dryness). The dried residue was dissolved in HCl (6 mol l⁻¹), heated and dried before making the mother solution in 40 ml HCl (3 mol l⁻¹) (Figure 1).

Method C and D are identical except for the amount of HClO₄ added to the weighted sample.

In both methods, 5 ml of HF (24 mol l⁻¹) and 1 ml of HNO₃ (14 mol l⁻¹) were added to the sample and 0.2 ml and 1 ml of HClO₄ were added in method C and D, respectively, in PTFE Teflon® vessels. Closed vessels were agitated for 20 mn in an ultrasonic bath, placed in stainless steel high-pressure apparatus and oven-cooked for 7 days at 160°C. Solutions were then transferred into 30 ml concave bottom Savillex® PFA beakers, dried at 80°C for about 12h and 120°C for about 4h. Savillex® PFA beakers were then tightly closed and heated in an Analab Evapoclean® apparatus at 160°C for about 12h. Solutions were then dried at 160°C for about 12h and 180°C until complete dryness in an Analab Evapoclean® apparatus. The dried residue was dissolved in HCl (6 mol l⁻¹), heated and dried before the mother solution was made in 40 ml HCl (3 mol l⁻¹) (Figure 1).

Trace element analysis

Measurements were performed on an Element 2 HR-ICP-MS equipped with an ASX 100 auto-sampler at the Institut Universitaire Européen de la Mer (IUEM, Brest, France) using a Tm addition spike technique (Barrat, *et al.* 1996). The mother solutions in HCl 3 mol l⁻¹ are made up at least 48h prior to analysis so that the solutions are properly homogeneous and stable. The day before analysis, 0.95 ml of the mother solution (HCl, 3 mol l⁻¹) was carefully weighted; 0.07ml of Tm spike was added in Savillex® beakers and dried down on a hot plate. Dried residues were dissolved in 0.1 ml concentrated nitric acid and diluted with 14 ml Milli-Q® water just before analysis on the ICP-MS. International rock standard solutions of BHVO-2 or B-EN were used as reference solutions and run after every batch of three samples for the correction of instrumental drift. The measurement settings and calculations using Tm addition follow those of Barrat, *et al.* 1996) and are further described in Bayon *et al* (In press).

Results and discussion

All concentration results are given in Table 1. Mean Values (MV) are reported with the number (n) of solutions made as duplicates. Precision are reported as RSD %. To test the accuracy of our different procedures, we compared our data with compilations of published reference values. For each RM, published values (n, number of published values used) are averaged and the RSD % is reported. Differences between our results and averaged published values are also reported as Δ (%). We also report averages (in ppb) of total procedural blanks (alkaline fusion and Method D) in Table 1. Our results are also illustrated together with

published values as spidergrams normalised to UCC (Upper Continental Crust, Taylor and McLennan 1995) (Figures 1-4).

Fusion procedure:

The main advantage of fusion techniques is to ensure rapid and complete digestion of all rock-forming minerals, including highly resistant minerals. The main limitation of this method is, however, potential contamination problems related to the use of impure reagents and metal crucible and incomplete recovery of all elements of interest. As reported in Table 1, blank levels are very high for some elements like Ba, Sr, Pb, metals and to a lesser extent Nb, Zr, and La. Such elevated values rule out any further measurement of Sr and Pb isotope compositions but also do not allow the use of these elements for geochemical interpretations. However, we did not use selected very high purity fluxes and it is likely that lower blank values could be obtained by utilizing higher grade reagent (S. Gallet, pers. com.). It is also clear that the preconcentration procedure does not allow a complete recovery of all elements. In particular, most of U, Nb, Pb, Cu and Zn are missing and V, Cr and Ga are not recovered (Figure 1, JSd-1 and Jlk-1). On the other hand, REE, Th, Hf or Y, are fully recovered and blank values are low. This technique can therefore be easily used in the case of geochemical studies focused on these specific elements or dedicated to Nd and Hf only isotope compositions analyses.

Despite the rapidity of the technique and its efficiency for some elements (mainly the REE), we decided not to carry on using this procedure because of two main limitations: (1) blank levels and (2) the lack of recovery for some element of interest in our sediment geochemistry studies.

Methods A through C:

We performed these three methods in order to test whether a total dissolution could be achieved with a conventional HF + HNO₃ digestion procedure (Method A), a high pressure digestion apparatus would increase the efficiency of an HF + HNO₃ procedure (Method B) and the minimum amount of HClO₄ needed to ensure a complete dissolution in high pressure digestion vessels (Method C).

The most significant difference between results of method A and the others is that Zr and Hf are not recovered. This clearly indicate that the Method A is unable to dissolve highly refractory minerals and most likely zircons as previously shown for granite RM (Yu, *et al.* 2001). It is particularly seen in RM JSd-1 in which respectively ~21% and ~ 28% of Zr and Hf are recovered (Table 1). For RM JSd-2 and JSd-3, 75% Zr, 72% Hf and 65% Zr and Hf are recovered respectively.

Results obtained with Method B are even worse compared with Method A. Many elements, including the REE are lost during the digestion procedure (Figure 2) and none of the RM gave satisfactory results. We do not expect any problems related to storage duration of the diluted solutions as they were systematically prepared immediately prior to measurements. An explanation to this feature may be that insoluble phases precipitate at high temperature when HF and HNO₃ only are used or that 1 ml of HCl is insufficient to remove all the fluorides. Such an effect has already been noticed for mafic silicate rocks in which many trace element including the REE precipitate as insoluble fluorides (Yokoyama, *et al.* 1999). We can also note that the amount of insoluble phase precipitating is probably highly variable as reflected by the relatively high RSD % values calculated for Method B analyses (Table 1). Another likely possibility is that 3ml of HF was not sufficient to dissolve all the silicates resulting in a partial dissolution of the silicate phases. During the course of this set of experiments, we noticed a relationship between the amounts of sample dissolved (varying between 100 and

110 mg) and the low quality of the results. Whenever the sample weight was slightly higher, the quality of the recovery was worse. We concluded that increasing the volume of HF would probably improve the procedure and 5ml of HF was used for methods C and D.

Method C gave satisfactory results for reference material JSd-1, JSd-2 and JSd-3 compared to published values (Table 1, Figure 2). However, we noted that Zr and Hf results with this method were still slightly lower than the published values and concluded that zircon may have not been completely dissolved (Table 1). In contrast, reference material Jlk-1 gave mitigated results. It is clear from Figure 2 that Jlk-1 was only partially dissolved with method C or that an insoluble phase formed during the dissolution process leading to a partial recovery of the sample in the solution.

Method D:

For each analysed RM, method D gave the most accurate results compared to the published values. Numerous duplicate solutions were made for each RM (between 6 and 16, Table 1) in order to check the reliability and the reproducibility of the method. We also tested this protocol on well-measured international standards such as dolerite WS-E and granite GS-N (Table 1, Figure 2). Results for WS-E and GS-N are in very good agreement with certified values and RSD % for our measurements are less than 10% for most elements. Exceptions to this are mainly Cs, Nb and to a lesser extent Pb for GS-N and Nb for WS-E (Table 1).

Results for JSd-1 are in fairly good agreement with published values and RSD % are below 15% except for Rb and Nb (Table 1). Results for JSd-2 are in good agreement with published values and RSD % for all elements are below 10% with the exception of Nb and Ta, which are however, still below 15%. Similarly, to JSd-2, results for JSd-3 are in good agreement with published values and have RSD values below 10% for most elements. Exceptions to this are Cs and Nb, which are about 15%. For an unknown reason, one solution for JSd-2 and one

for JSd-3 gave very high Pb contents compared to the others, which drastically increased the calculated RSD to 33% and 31% respectively. As these two solutions were run on the same day, one can suspect a contamination problem or a memory effect in the machine at this precise time. Results for Jlk-1 are overall less satisfactory than measurements on stream sediment samples. Calculated RSD are slightly higher around 10 to 15%. An explanation to these results might reside in the fact that this lake sediment sample contains a consequent amount of organic material (~15 000 ppm, Imai, *et al.* 1996) and may therefore decrease the stability of the solution.

As already noticed by Yamamoto *et al.* (2005), compiled published values for JSd-1 and JSd-2 show clear derivations from smooth REE patterns, particularly within the HREE. We compared our results with those of Yamamoto *et al.* (2005) who performed a two-steps procedure using first an acid dissolution method followed by an alkali fusion method and a cation exchange column for REE separation. Our results are in very good agreement with their results and confirm the fact that compiled published values for HREE may not be the most reliable. This also demonstrates that our method is efficient to recover REE in sedimentary rocks without the use of an alkali fusion step and without separating REE from the matrix (Figure 3).

Results of trace metals analyses (mainly V, Co, Cu, and Ga, Table 1) are overall in good agreement with the published values. Calculated RSD are mostly within 10 to 15% and below 10% for reference material WS-E (Table 1). Results for Ni (JSd-1) and Zn (JSd-2 and Jlk-1) are less satisfactory and contamination problems cannot be completely ruled out. Measured Cr contents are not only highly variable but also very different from published data. On average, 50% of Cr is lost during the dissolution process and this method can therefore not be used for this element.

Are some reference powders heterogeneous?

In order to check the homogeneity of RM powders we performed several sets of analyses with variable amount of sample (Table 1, Figure 4). For reference material JSd-1, JSd-2, JSd-3 and Jlk-1, there is a good agreement between results obtained for 100 mg, 200 mg and 400 mg of sample. Slight differences observed in the concentrations are mostly within analytical errors and we concluded that powders for these standards were homogeneous (Table 1, Figure 4). In contrast, reference material LKSD-1 gave highly variable concentrations depending on the amount of sample dissolved. Concentrations are clearly higher in experiments carried with 100 mg (4 duplicates, Table 1) than with 200 mg and 400 mg (two duplicates each, Table 1). Careful examination of the spidergrams, reveals that patterns are strictly parallel suggesting a dilution process (Figure 4). We suggest that the powder contain variable amounts of quartz that can dilute trace element content without fractionation of trace element between each other.

Conclusion

Sample digestion is a critical stage to ensure high quality geochemical analyses of geological material. It is particularly relevant for sediment analyses, as this type of material is naturally highly heterogeneous and highly resistant to acid dissolution. Occurrence of refractory minerals such as zircon makes it difficult to obtain a complete dissolution of the samples. In this study, we compare various methods of sediment dissolution using different acid associations and high pressure-high temperature Teflon® vessels as well as a fusion technique. We show that the fusion procedure is efficient and rapid but does not allow analysing all element of interest. Moreover, blank levels are very high for some elements ruling out any further Sr or Pb isotope composition analyses from the solution. We show that

HF + HNO₃ digestion procedures are not sufficient to ensure a complete dissolution of refractory phases (Method A), even when placed at high temperature and high pressure for a long period (7 days, method B). We achieve a complete dissolution of our Reference Materials (RM) by adding HClO₄ and using stainless steel Teflon® vessels. We also demonstrated that a minimum amount of HClO₄ is necessary to ensure a full dissolution (Methods C and D). In order to check its reliability and reproducibility, we have tested our preferred method (method D) on five sediment RM powders: stream sediments JSd-1 (16 duplicates), JSd-2 (7 duplicates) and JSd-3 (6 duplicates) and lake sediments Jlk-1 (8 duplicates) and LKSD-1 (4 duplicates). We further confirmed the reproducibility of our method on well characterised international RM for granite (GS-N, from the Centre de Recherches Pétrographiques et Géochimiques, CRPG) and basalt (WSE, CRPG). Our results indicate that our method allow to obtain a complete dissolution of the sample and a complete recovery of the trace element. Our measured blanks are also very low, which permit to undertake chemical separations for further radiogenic isotope analyses (Sr, Nd, Pb, Hf). Although this protocol seems time-consuming, including numerous steps, we strongly suggest its use for sediment geochemistry studies. The main advantage of our method is that once a mother solution is made up, one can undertake any type of analyse including Sr, Nd and Pb isotope work.

During the course of these experiments, we have also tested the homogeneity of RM powders. We noticed that RM LKSD-1 might be heterogeneous, containing variable amount of quartz that entrains a dilution of trace element content.

Acknowledgments:

This work was supported by IFREMER and the French CNRS through funding of SR.

Authors are grateful to M. Benoit and C. Bassoulet for their assistance in running the ICP-MS

at the IUEM, Brest, France. The authors greatly acknowledge N. Mattielli and S. Gallet for their careful and detailed reviews, which significantly improved the quality of the manuscript.

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Table and Figure captions

Table 1:

Concentrations measured in reference material JSd-1, JSd-2, JSd-3, Jlk-1, LKSD-1, GS-N and WS-E (ppm) together with average blank values (ppb). MV: mean value; n: number of

duplicate solutions analysed; RSD: relative standard deviation; Δ (%): differences expressed as % between our results and averaged published values.

Figure 1:

Flow chart illustrating the different digestion procedure tested in this study.

Figure 2:

Concentrations normalised to UCC (Upper Continental Crust, Taylor and McLennan 1995) for RMs JSd-1, JSd-2, JSd-3, Jlk-1, LKSD-1, GS-N and WS-E in comparison with published values. For RMs JSd-1, JSd-2 and JSd-3, published values are represented as grey shaded area and are from Yamamoto, *et al.* 2005, Dulski 2001, Imai, *et al.* 1996, Garbe-Schönberg 1993, Govindaraju 1994, Sahoo, *et al.* 2001.

Figure 3:

Chondrite-normalised REE patterns of RMs JSd-1 and JSd-2 compared to published reference values and results obtained by Yamamoto *et al.*, (2005).

Figure 4:

Concentrations normalised to UCC for reference material JSd-1, JSd-2, JSd-3, Jlk-1 and LKSD-1 using 100 mg, 200 mg or 400 mg of powder for the dissolution procedure.

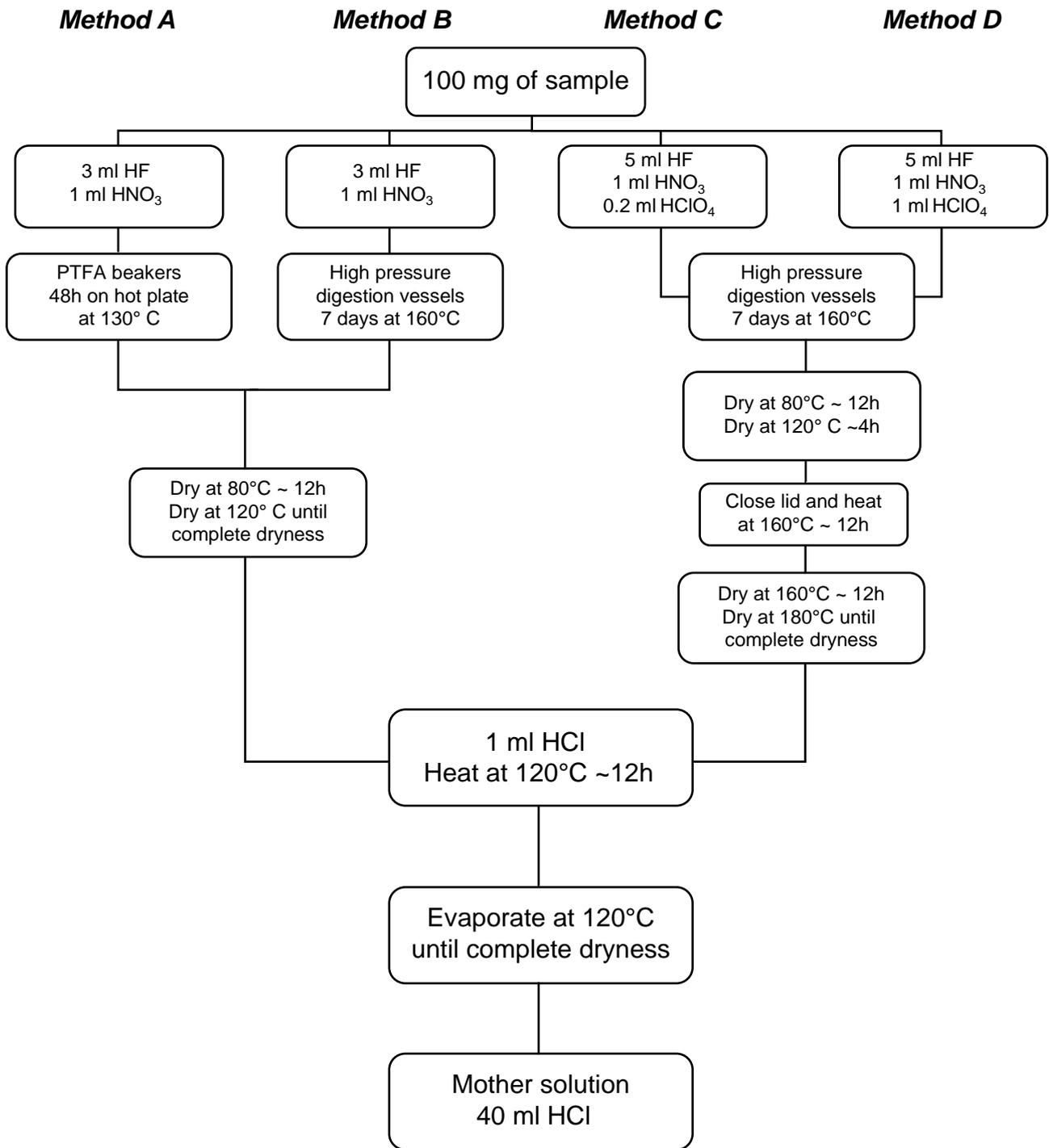


Figure 1

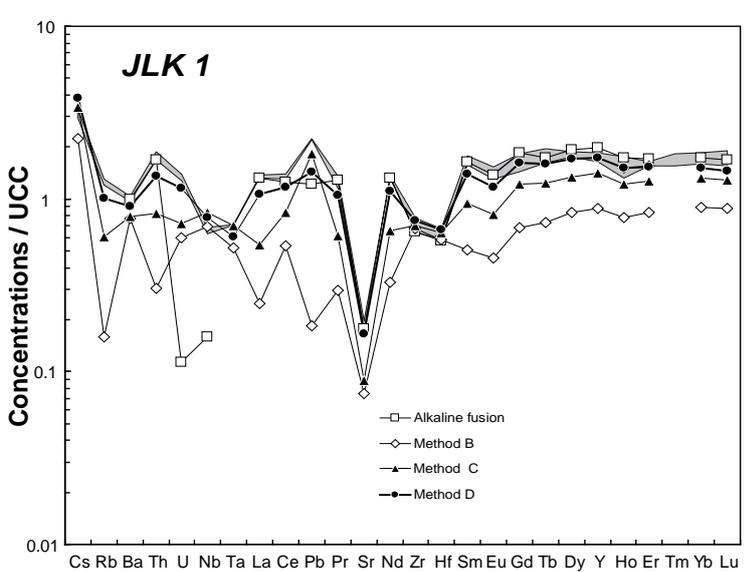
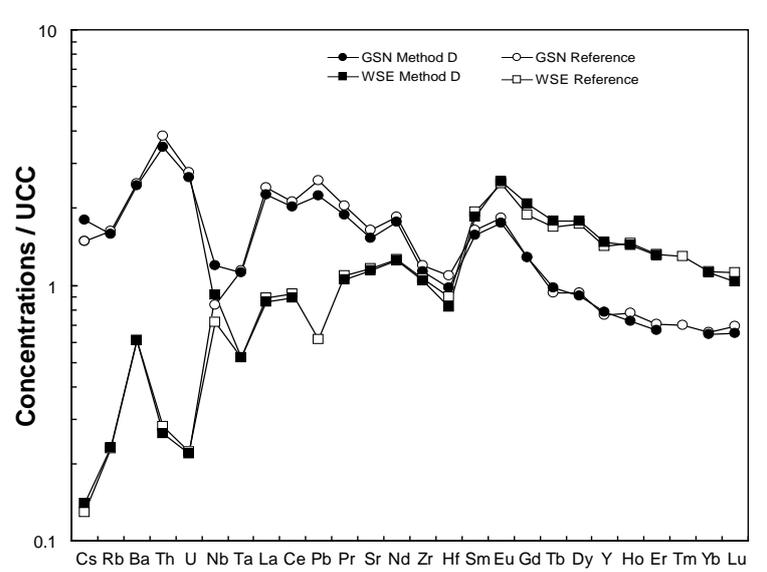
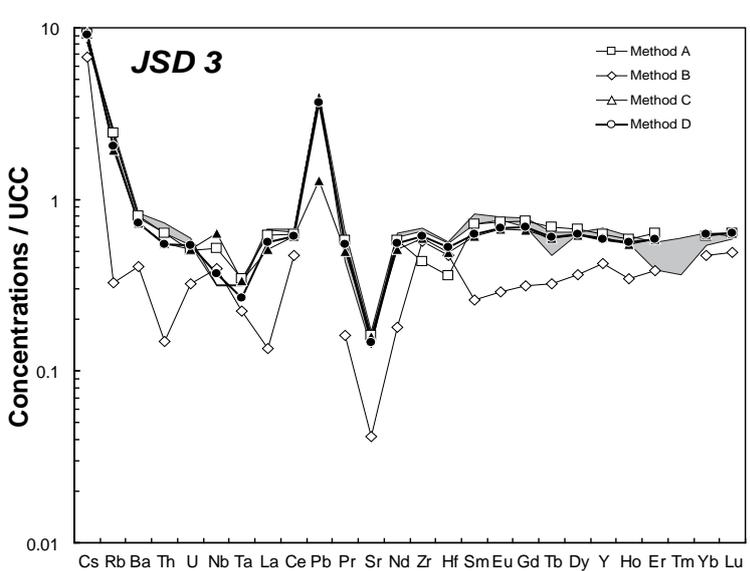
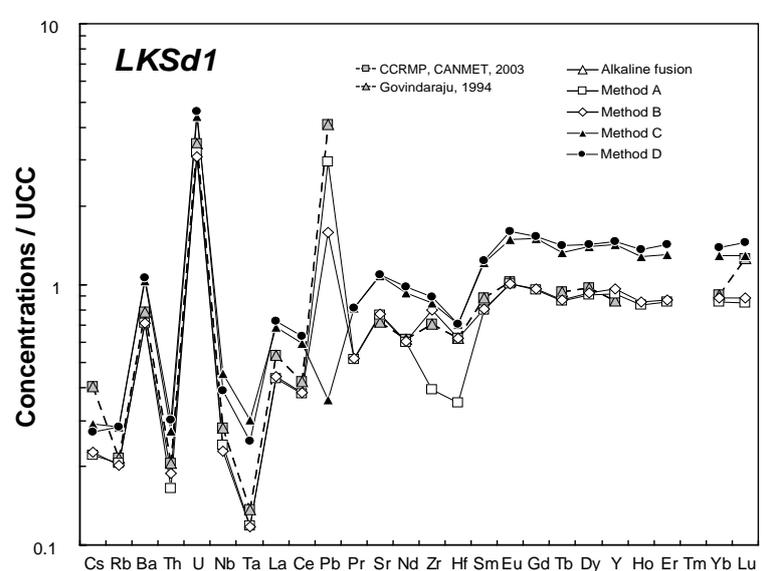
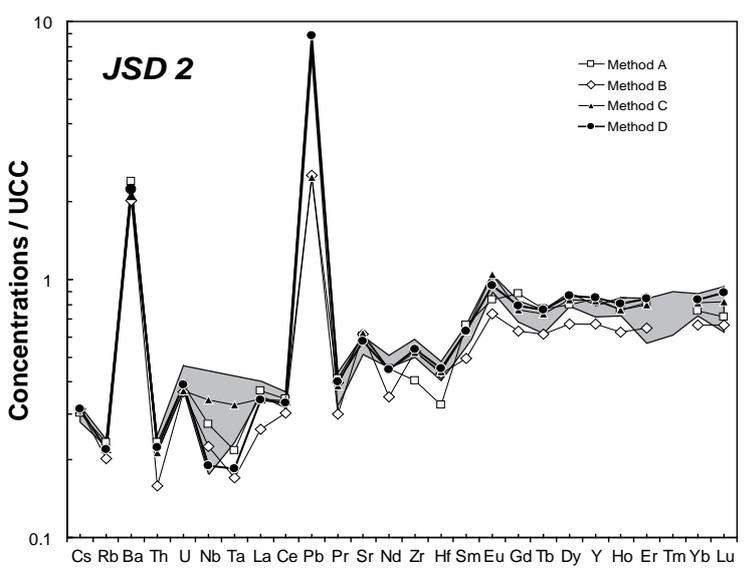
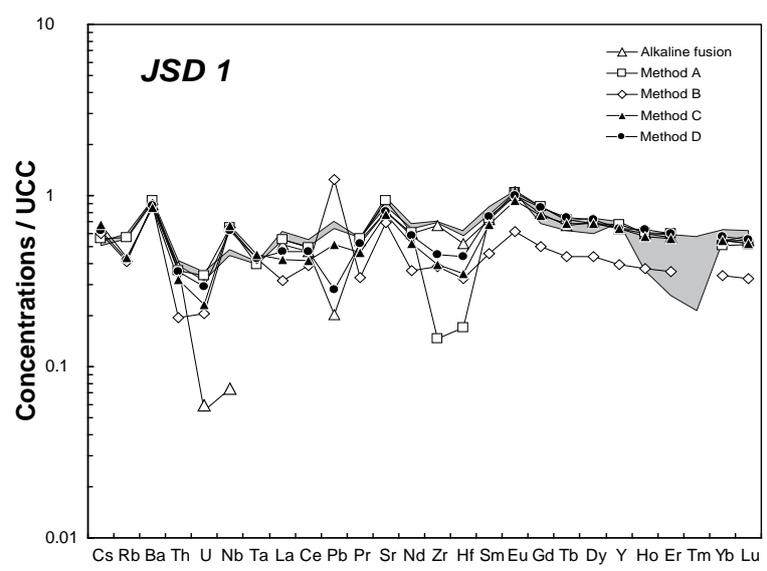


Figure 2

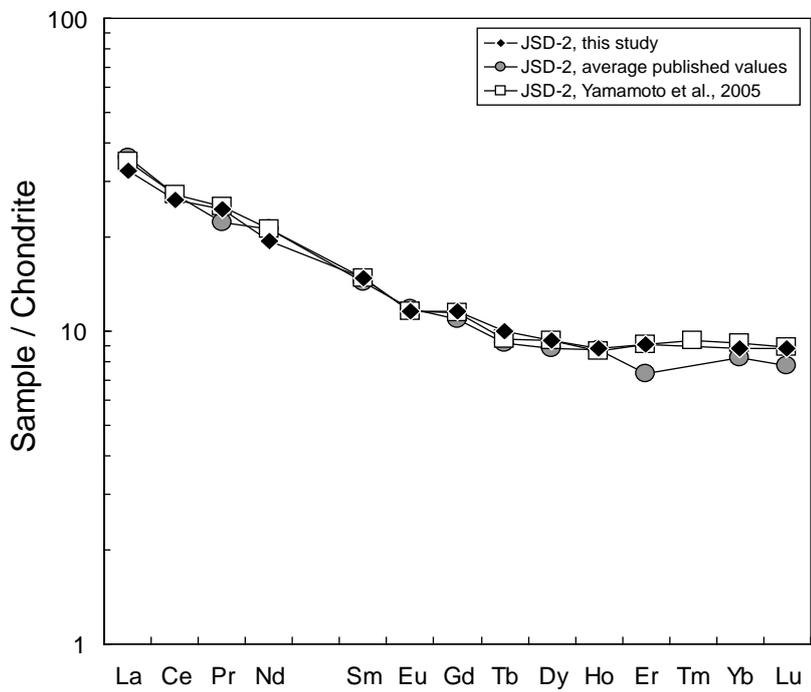
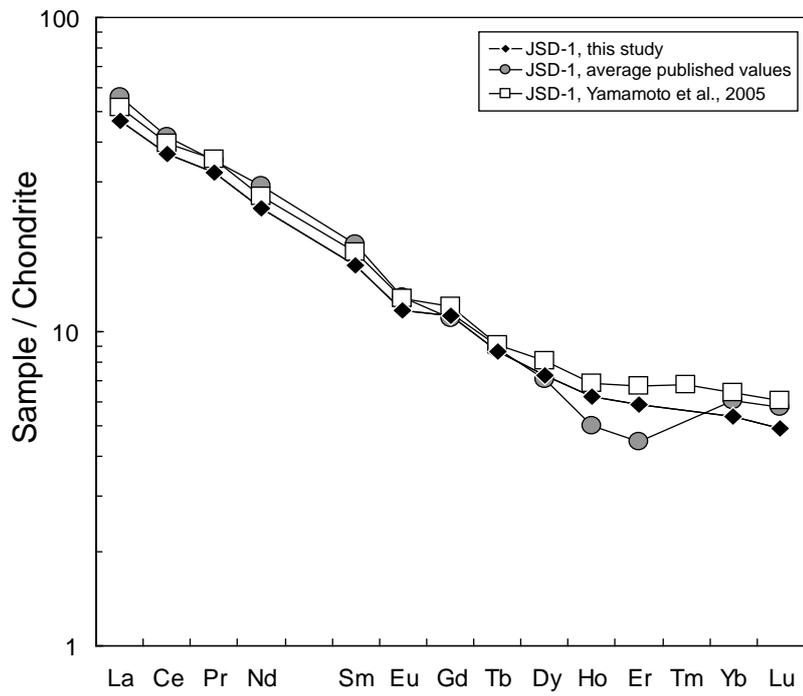


Figure 3

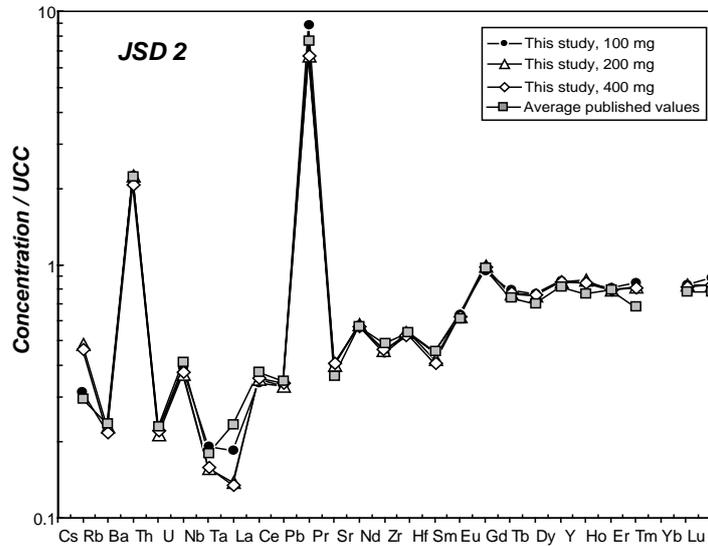
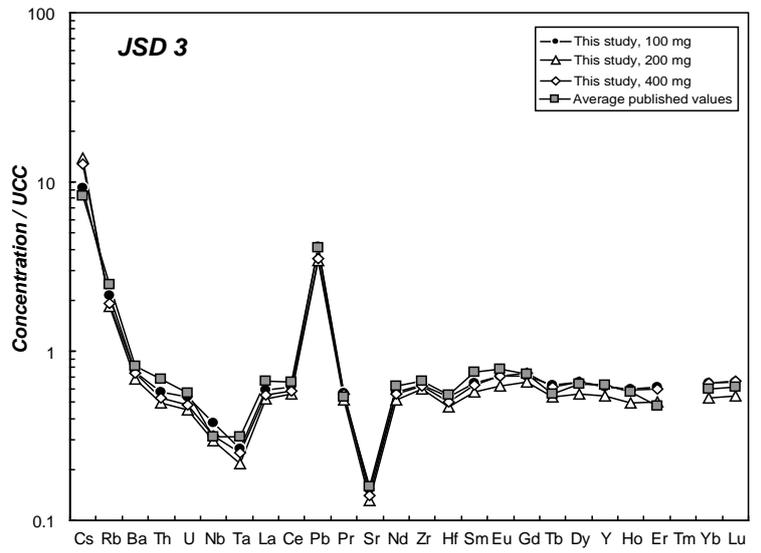
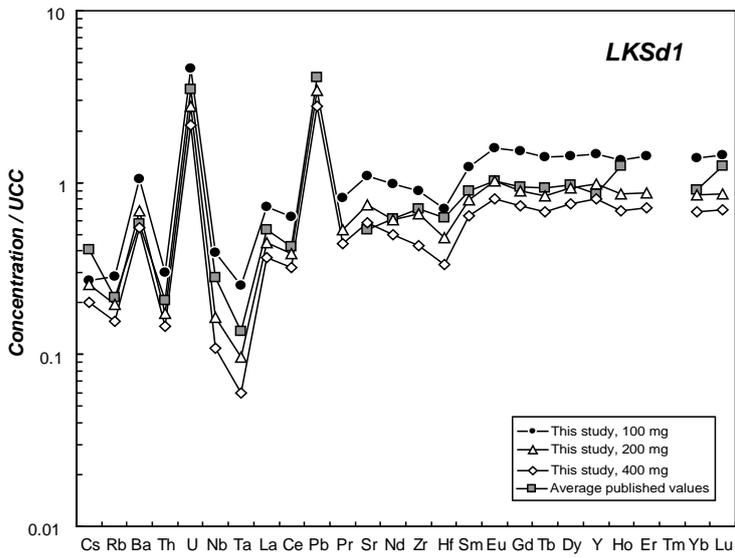
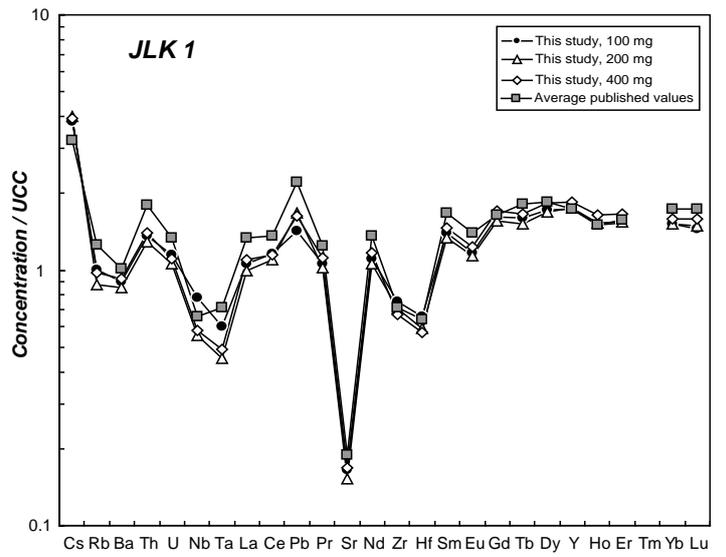
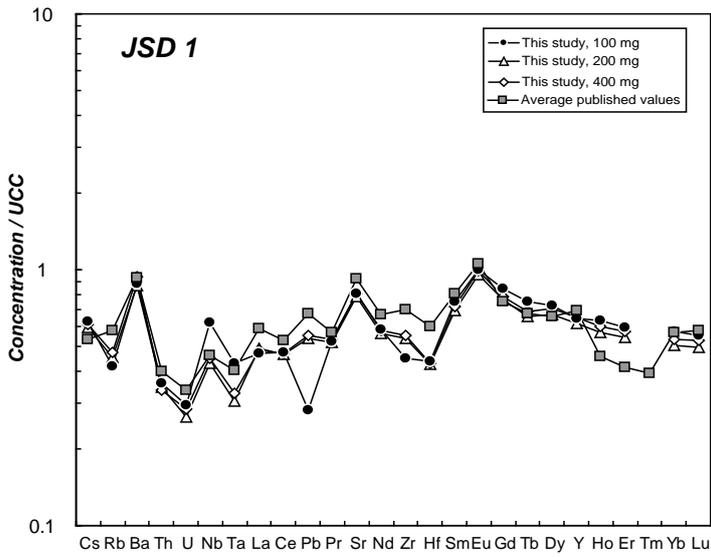


Figure 4

	Blank (n=14) Method D ppb	Blank (n=2) Alkaline fusion ppb	GS-N					WS-E				
			Method D			Published		Method D			Published	
			MV (n=6)	% RDS	Δ (%)	MV (n=4)	%RDS	MV (n=5)	% RDS	Δ (%)	MV (n=12)	% RDS
Cs	6.08	23.14	7	14.6	21.7	5.5	1.6	0.5	5.6	8.6	0.5	5.0
Rb	21.66	143.28	178	15.8	-3.0	183	1.2	26.0	6.7	1.5	25.6	5.4
Ba	42.57	11533.23	1354.6	4.5	-1.6	1376.3	1.3	336.0	3.4	0.5	334.3	5.1
Th	0.12	5.88	37.3	5.0	-9.1	41	1.7	2.8	6.4	-6.1	3.0	2.8
U	0.11	1.20	7.4	8.3	-3.7	7.7	2.1	0.6	3.3	-1.3	0.6	3.1
Nb	2.35	204.53	30	25.0	42.4	21		22.9	9.7	27.0	18.0	6.1
Ta	0.64	85.68	2	19.9	-1.9	2.5	5.5	1	12.6	0.4	1.1	3.0
La	1.31	142.51	68.0	7.8	-5.6	72	3.0	25.9	2.7	-3.6	26.8	2.3
Ce	2.58	46.44	129.4	4.4	-4.7	135.9	2.3	57.1	4.6	-3.2	59.0	7.8
Pb	25.86	2141.07	44.7	7.5	-13.2	51.5	4.1				12.3	9.2
Pr	0.31	6.09	13.4	5.5	-7.2	14.5	3.1	7.4	3.8	-3.6	7.7	3.0
Sr	16.18	49095.68	533.9	6.5	-7.3	576	1.5	401.0	3.2	-1.5	406.9	4.2
Nd	1.21	23.21	45.9	5.9	-4.5	48	2.4	32.5	4.3	-0.7	32.7	2.1
Zr	4.89	687.76	214.2	5.0	-5.4	226.5	8.7	198.6	6.1	-1.8	202.2	5.8
Hf	1.12	4.19	5.6	4.2	-10.4	6.3	4.0	4.8	9.3	-8.4	5.2	4.5
Sm	0.36	5.04	7.1	4.6	-3.8	7.4	2.2	8.3	5.9	-4.7	8.7	3.2
Eu	0.45	7.89	1.5	4.1	-4.7	1.6	4.0	2.2	6.0	1.6	2.2	3.7
Gd	1.26	6.95	5	13.8	-0.3	4.9	7.3	7.9	7.6	11.2	7.1	4.0
Tb	0.09	1.37	0.6	1.3	5.0	0.6	6.7	1.1	5.8	5.4	1.1	3.5
Dy	0.21	3.70	3.2	6.1	-2.5	3.3	6.6	6.3	6.7	3.6	6.1	2.9
Y	1.38	26.74	17.3	4.8	2.7	16.8	7.7	32.4	5.2	3.3	31.4	6.4
Ho	0.05	0.49	0.6	7.0	-7.1	0.6	9.4	1.1	1.8	-1.9	1.2	4.2
Er	0.20	1.74	1.5	3.4	-5.4	1.6	9.9	3.0	4.9	-0.9	3.0	3.4
Yb	0.19	1.82	1.4	9.0	-1.7	1.4	2.2	2.5	5.2	-0.3	2.5	2.7
Lu	0.04	0.56	0.2	6.2	-6.1	0.2	3.5	0.3	6.6	-7.4	0.4	4.6
Sc	1.47	12.08	7.2	6.3	1.1	7.2	3.6	30.0	7.0	8.8	27.6	3.8
Ti	0.11	1.13	0.7	9.3				2.4	5.7			
V	12.01	188.38	60	14.8	-8.2	65		340.6	3.8	3.2	330.0	4.2
Cr	143.53	1078.21	34	59.5	-38.8	55.2	0.7	133.8	8.6	40.7	95	11.6
Mn	62.94	7745.07	422.1	8.6	-2.7	434		1349.5	5.1			
Co	7.21	158.38	66.4	6.8	1.0	65.7	1.8	47.1	3.9	5.5	44.7	4.6
Ni	279.04	12918.06	35	11.7	7.6	33	5.2	57.1	5.6	5.2	54.3	4.5
Cu	46.77	4096.80	20	12.1	1.3	20		71.5	3.0	7.3	66.6	2.0
Ga	2.74	9.51	20.0	6.3	-9.2	22		22.2	2.8	1.4	21.9	4.3
Zn	604.18	38338.68	50	17.1	4.2	48		134.0	9.9	18.1	113.4	7.4

**Cs
Rb
Ba
Th
U
Nb
Ta
La
Ce
Pb
Pr
Sr
Nd
Zr
Hf
Sm
Eu
Gd
Tb
Dy
Y
Ho
Er
Yb
Lu
Sc
Ti
V
Cr
Mn
Co
Ni
Cu
Ga
Zn**

Table 1

Table

JSd-1																	
Alkaline fusion			Method A			Method B			Method C			Method D			Method D, 200mg		
MV (n=2)	% RDS	Δ (%)	MV (n=2)	% RDS	Δ (%)	MV (n=4)	% RDS	Δ (%)	MV (n=11)	% RDS	Δ (%)	MV (n=16)	% RDS	Δ (%)	MV (n=2)	% RDS	Δ (%)
			2.1	6.7	5.3	2.2	8.0	11.8	3	20.1	27.1	2.3	3.7	16.8	2.2		11.1
0	33.8	-99.9	63.3	3.3	-2.7	46	50.4	-29.1	49	42.9	-25.2	47	22.2	-27.6	50.9	4.1	-21.9
487.7	0.7	-4.6	511.6	6.8	0.1	484.4	3.9	-5.2	466	10.2	-8.8	483.2	7.2	-5.4	478.4	3.1	-6.4
4.3	0.4	-0.8	3.9	9.8	-8.8	2	21.3	-51.7	3	19.6	-19.7	3.9	7.8	-10.3	3.7	0.1	-13.8
0.2	0.5	-81.2	1	10.0	1.2	0.6	15.2	-39.9	1	30.6	-32.0	0.8	11.3	-12.5	0.7	4.4	-21.1
1.9	0.6	-83.3	16	12.4	39.9	16.3	5.7	41.3	17	49.9	44.4	16	18.9	35.1	11	12.5	-6.4
0	12.5	-100.0	0.9	7.1	-2.6	0.9	8.3	6.0	1	57.5	11.3	0.9	11.0	5.8	0.7	14.3	-24.3
15.4	0.4	-12.9	16.5	1.3	-6.6	10	19.6	-45.8	13	21.7	-28.0	14.2	8.1	-19.7	14.8	3.6	-16.3
30.1	0.7	-11.4	31.9	1.0	-6.1	24.9	9.0	-26.6	27	18.5	-21.1	30.3	5.1	-10.7	29.9	4.8	-12.0
4.1	1.5	-69.6				25	18.2	85.0	10	92.8	-22.7	5.6	6.9	-58.0	10.8	3.0	-19.6
3.9	0.9	-4.5	4.0	3.9	-2.4	2	20.0	-42.1	3	16.6	-19.1	3.7	6.3	-8.4	3.7	5.4	-8.6
283.2	3.2	-12.0	328.9	1.0	2.2	245	36.1	-24.0	269	28.0	-16.3	281	11.3	-12.6	273.6	3.1	-14.9
15.6	1.1	-10.3	15.9	5.7	-8.5	9	20.9	-45.5	14	16.0	-22.0	15.2	4.6	-12.4	14.7	4.0	-15.5
133.9	0.3	0.7	27.9	0.9	-79.0	73	39.9	-44.8	75	31.9	-43.6	86	12.5	-35.6	102.8	5.4	-22.7
3.2	1.0	-7.3	1.0	7.6	-71.9	2	31.0	-45.4	2	29.3	-41.2	2.5	9.9	-27.1	2.5	0.6	-28.5
3.3	0.4	-9.7	3.3	3.0	-8.9	2	21.3	-43.0	3	14.0	-15.9	3.4	5.6	-6.9	3.1	0.8	-14.4
0.9	1.7	-4.6	0.9	2.1	-1.4	0.5	23.1	-41.9	0.8	12.3	-11.2	0.9	5.7	-4.9	0.8	3.7	-9.2
3.0	1.4	4.2	3.3	6.3	14.0	1.9	22.2	-32.7	3	10.1	1.2	3.2	5.1	12.6	2.9	9.2	1.7
0.4	1.0	0.0	0.5	1.4	7.1	0.3	24.6	-34.4	0.4	8.0	1.7	0.5	3.5	11.2	0.4	2.7	-2.0
2.5	0.4	7.1	2.4	1.3	4.8	1.5	24.5	-32.9	2.4	7.8	4.2	2.5	4.3	10.8	2.3	3.7	2.2
14.2	0.4	-6.7	14.9	3.8	-2.2	8.7	26.2	-42.7	14.0	9.3	-7.9	14.1	4.3	-7.3	13.6	7.5	-11.1
0.5	0.7	33.1	0.5	1.1	33.4	0.3	25.0	-18.0	0.5	6.5	25.9	0.5	2.9	38.6	0.5	4.5	24.1
1.3	0.5	37.5	1.4	5.5	43.7	0.8	25.5	-13.4	1.3	5.1	34.7	1.4	4.4	43.4	1.3	2.9	30.9
1.2	0.4	-1.1	1.1	2.8	-10.4	0.7	25.0	-40.3	1.2	5.2	-5.0	1.3	3.7	0.4	1.1	1.7	-11.3
0.2	0.9	-3.1	0.2	3.7	-11.3	0.1	25.5	-43.2	0.2	5.5	-9.3	0.2	3.6	-4.2	0.2	3.3	-14.3
10.1	0.7	-9.1	11.6	9.3	5.1	8.1	12.5	-27.2	12	22.7	6.9	10.6	5.3	-4.3	9.7	4.7	-12.8
0.6	1.4	-12.0	0.7	15.1	11.2							0.7	10.7	6.7	0.6	8.9	-2.3
0	28.8	-99.9	74	13.8	-6.1	90.1	4.1	14.7	77.4	9.1	-1.4	73	11.2	-7.5	73.9	3.7	-5.9
			19	11.0	-14.8	22.8	21.4	0.4	21	59.9	-5.8	22	90.0	-4.1	10.5	6.6	-53.8
621.3	1.1		687.8	6.9								733.9	4.5		698.0	1.4	
9.3	0.5	-18.3	11	13.2	-7.2	12.7	5.9	12.1	10	19.1	-10.3	11.5	5.2	1.0	10.8	0.5	-4.9
3.8	4.9	-48.0	7.7	0.4	6.3	3.2	138.9	-56.0	8	28.0	5.8	11	48.8	48.7	6.6	5.6	-9.2
9.2	1.6	-59.6	24.3	3.0	6.3	29.8	2.1	30.3	24	15.8	4.4	25.3	3.9	10.9	22.1	5.3	-3.2
0.0	7.4	-99.8	16.7	3.4	-1.6	18.2	0.9	7.0	15.9	9.4	-6.5	17.0	3.8	0.0	16.3	2.7	-4.4
12.2	3.4	-87.6	100.6	4.5	2.2	142.1	9.7	44.3	96	17.9	-2.9	97	14.3	-1.6	86	10.2	-12.4

: 1 continued

Method D, 400mg			Published	
MV (n=2)	% RDS	Δ (%)	MV (n=3)	% RDS
2.3		14.5	2.0	4.1
53.3	5.7	-18.1	65.1	3.5
516.4	3.2	1.0	511.0	2.5
3.6	1.7	-15.6	4.3	4.6
0.8	2.9	-15.2	0.9	8.2
11	13.6	-2.2	11.6	5.5
0.7	13.6	-18.7	0.9	
14.5	5.2	-17.7	17.7	6.8
30.2	4.3	-11.1	33.9	5.1
11.1	3.6	-17.4	13.4	4.1
3.8	6.2	-6.7	4.1	1.4
282.4	7.7	-12.2	321.7	5.9
15.0	4.4	-13.7	17.4	3.4
105.4	5.4	-20.7	133.0	1.1
2.5	0.6	-28.2	3.5	3.1
3.2	2.2	-10.8	3.6	5.8
0.9	2.3	-5.9	0.9	1.1
3	10.1	4.1	3	12.4
0.4	2.7	2.4	0.4	7.0
2.5	2.1	7.0	2	10.3
14.3	8.2	-6.4	15.3	4.2
0.5	4.3	30.8	0.4	27.1
1.3	1.7	37.7	1	40.0
1.2	0.9	-6.7	1.3	9.2
0.2	4.1	-8.5	0.2	8.1
9.6	5.8	-13.2	11.1	2.6
0.6	9.7	-5.4	0.6	0.8
71.5	3.8	-8.9	78.5	4.5
7.7	7.5	-66.3	22.8	7.8
658.1	2.7			
10.6	0.8	-6.8	11.4	5.0
6.9	7.1	-5.0	7.2	6.1
20.8	5.7	-8.8	22.8	5.6
16.4	4.9	-3.8	17.0	1.7
87.8	9.4	-10.8	98.5	1.8

	JSc									
	Method A			Method B			Method C			I
	MV (n=2)	% RDS	Δ (%)	MV (n=6)	% RDS	Δ (%)	MV (n=2)	% RDS	Δ (%)	MV (n=7)
Cs	1.1	5.9	2.8	1.2	6.7	6.5	1.2	0.1	7.0	1.2
Rb	26.3	5.6	-0.4	23	22.6	-14.0	24.9	1.2	-5.7	24.5
Ba	1316	14.7	7.7	1113.1	8.2	-8.9	1166.5	4.4	-4.5	1227.8
Th	2	13.9	2.2	2	27.9	-30.4	2.3	1.5	-6.7	2.4
U	1.1	5.8	-5.5	1.0	5.6	-10.8	1.0	7.1	-10.4	1.1
Nb	7	20.9	52.9	6	12.7	25.3	9	80.2	90.4	5
Ta	0.5	21.0	-6.9	0.4	11.5	-27.3	0.7	51.4	39.3	0.4
La	11	11.2	-1.3	8	21.6	-30.1	10.3	5.0	-8.9	10.2
Ce	22	13.0	-1.2	19.5	5.7	-12.5	21.6	3.4	-2.8	21.3
Pb				50.9	1.1	-66.5	49.6		-67.4	177
Pr	3	11.7	13.1	2	21.5	-17.4	2.7	4.6	6.6	2.9
Sr	211	10.2	6.2	214.2	2.6	7.6	216.0	4.1	8.6	201.5
Nd	12	13.0	-7.2	9	20.9	-28.1	11.6	3.1	-8.4	11.6
Zr	77	39.9	-24.8	99.8	3.5	-2.3	99.5	6.4	-2.7	101.9
Hf	2	43.5	-28.0	2.5	4.2	-5.2	3	15.5	-3.5	2.6
Sm	3.0	9.5	8.8	2	21.0	-19.0	2.8	1.2	3.2	2.8
Eu	0.7	5.6	-13.8	0.6	19.7	-23.9	0.9	18.5	8.1	0.8
Gd	3.3	6.6	18.5	2	23.5	-14.6	2.9	2.8	2.7	3.0
Tb	0.5	6.5	9.5	0.4	22.7	-12.2	0.5	1.0	5.1	0.5
Dy	2.8	7.1	-2.2	2	21.7	-17.5	2.9	0.1	2.2	3.0
Y	19	13.1	10.1	15	22.2	-12.2	18.1	6.6	7.5	18.6
Ho	0.6	7.1	-3.9	0.5	21.5	-21.3	0.6	0.8	-4.3	0.6
Er	1.9	9.7	19.9	1	21.6	-4.9	1.8	2.0	17.2	1.9
Yb	2	19.9	-2.8	1	22.4	-14.9	1.8	2.7	4.5	1.8
Lu	0.2	15.8	-8.5	0.2	22.8	-14.7	0.3	3.8	5.0	0.3
Sc	19.7	6.5	14.4	15	18.1	-11.8	19	12.3	9.1	18.1
Ti	0.7	8.2	19.2							0.6
V	146.8	5.2	17.9	144	10.9	15.5	128.0	8.3	2.8	122
Cr	134	28.9	28.2	94	25.7	-10.5	86	81.4	-17.4	87
Mn	1005.7	5.1								893.0
Co	54.2	8.6	12.0	46	16.2	-5.8	52	14.1	6.8	47.7
Ni	108	15.3	16.7	80	29.2	-14.4	96	15.1	3.4	92.1
Cu	1298	13.5	15.8	1224	14.1	9.3	1301.6	3.9	16.2	1037.7
Ga	14.7	9.1	-0.7	14.3	4.0	-3.4	14.6	7.6	-0.9	13.0
Zn	2411	14.5	17.9	2424	21.5	18.5	2136.3	1.9	4.4	1790

Table 1 continued

J- 2									
Method D		Method D, 200mg			Method D, 400mg			Published	
%RDS	Δ (%)	MV (n=2)	% RDS	Δ (%)	MV (n=2)	% RDS	Δ (%)	MV (n=5)	%RDS
9.7	6.6	2	34.0	64.5	2	33.4	57.3	1.1	6.8
4.6	-7.0	25.7	1.7	-2.6	24.3	3.4	-8.0	26.4	3.1
2.3	0.5	1227.9	1.4	0.5	1137.4	3.6	-6.9	1221.3	5.4
6.8	-2.5	2.3	0.2	-6.9	2.4	1.2	-3.4	2.4	6.6
8.2	-5.8	1.0	0.3	-10.6	1.1	1.7	-9.0	1.2	9.4
11.7	6.3	4	10.5	-12.2	4	11.5	-11.8	4.5	2.5
13.7	-21.4	0.3	14.8	-41.1	0.3	18.6	-42.3	0.5	
6.4	-9.4	10.6	1.2	-6.3	10.7	3.4	-5.1	11.3	5.5
5.4	-4.2	21.2	1.8	-4.7	21.9	3.1	-1.7	22.2	4.9
33.4	16.3	132.9	3.7	-12.6	132.8	8.7	-12.7	152.0	3.5
4.5	10.6	2.8	2.7	10.4	2.9	4.6	12.6	3	14.1
5.0	1.3	203.5	2.2	2.2	200.0	3.4	0.5	199.0	6.8
6.9	-8.2	11.9	2.5	-6.2	12.0	4.6	-5.3	12.7	4.4
7.2	-0.3	102.9	2.5	0.7	99.4	3.6	-2.7	102.2	8.3
9.0	-0.6	2.4	1.4	-7.3	2.4	2.5	-10.0	2.6	7.5
2.5	3.3	2.8	1.2	2.3	2.8	3.0	2.2	2.8	7.6
6.5	-2.4	0.9	2.3	1.7	0.9	4.6	1.0	0.9	6.1
6.8	6.8	2.9	6.9	3.6	2.9	8.4	4.7	2.8	7.3
4.6	8.9	0.5	1.4	7.1	0.5	3.9	8.0	0.4	7.8
2.5	5.9	3.0	1.4	4.8	3.0	3.2	4.8	2.9	4.9
7.0	10.3	19.2	3.7	13.6	18.6	5.7	10.4	16.9	4.4
7.1	1.2	0.6	2.4	-0.4	0.6	3.7	-0.6	0.6	7.1
3.0	24.1	1.9	1.9	20.2	1.9	2.4	19.1	2	16.7
7.0	6.6	1.8	2.9	6.2	1.8	4.1	4.8	1.7	8.4
2.9	13.2	0.3	3.4	6.5	0.3	5.6	6.3	0.3	14.4
5.3	5.2	18.9	1.1	10.0	18.3	3.1	6.6	17.2	2.1
6.5	-4.8	0.6	4.6	-9.0	0.6	5.1	-7.9	0.6	1.8
11.9	-1.7	126.3	0.8	1.4	121.0	1.8	-2.8	124.5	0.6
40.9	-16.9	67.7	4.3	-35.3	60.5	2.7	-42.2	104.7	2.9
2.8		899.9	0.5		870.3	0.7			
3.0	-1.6	48.7	0.5	0.5	46.5	0.9	-4.0	48.4	0.9
5.8	-0.9	92.2	1.4	-0.8	86.8	3.6	-6.5	92.9	1.1
9.4	-7.4	1062.9	4.7	-5.1	970.6	6.8	-13.4	1120.3	0.8
6.5	-11.9	13.4	0.9	-9.2	13.1	1.1	-11.2	14.8	5.3
13.1	-12.5	1842.6	9.0	-9.9	1701.1	8.7	-16.8	2045.3	1.5

	Method A			Method B	
	MV (n=2)	% RDS	Δ (%)	MV (n=3)	% RDS
Cs	34.0	5.7	11.7	25	13.1
Rb	274.0	3.0	-0.8	37	31.3
Ba	441.0	5.0	-1.1	224.0	9.9
Th	6.8	0.6	-7.6	1.6	4.6
U	1.4	9.7	-11.3	0.9	8.1
Nb	13.0	3.9	66.3	9.8	4.1
Ta	0.8	6.5	10.4	0.5	5.5
La	18.7	6.9	-6.7	4	12.3
Ce	40.0	1.5	-5.0	30	11.7
Pb					
Pr	4.1	0.3	6.9	1.1	6.8
Sr	56.9	2.1	2.1	15	26.1
Nd	15.1	6.2	-7.3	4.7	9.8
Zr	82.4	9.5	-34.8	108.3	4.2
Hf	2.1	7.3	-34.8	2.7	2.9
Sm	3.2	5.1	-4.9	1	15.8
Eu	0.7	0.9	-5.1	0.3	23.8
Gd	2.8	0.6	1.1	1	17.6
Tb	0.4	5.1	23.0	0.2	17.4
Dy	2.4	0.0	5.6	1	17.1
Y	13.8	4.3	-0.7	9	14.0
Ho	0.5	2.7	2.1	0.3	16.5
Er	1.5	3.8	33.7	0.9	15.1
Yb	1.3	5.3	2.1	1	12.4
Lu	0.2	3.8	3.7	0.2	12.0
Sc	11.3	2.4	7.0	4	21.4
Ti	0.5	3.8	17.4		
V	79.8	0.1	12.1	78.1	5.2
Cr	47	29.1	30.1	31.1	6.4
Mn	1126.5	0.3			
Co	12.9	4.7	3.8	12.0	3.9
Ni	19.9	4.3	2.7	15	29.1
Cu	459.9	4.5	8.8	511.7	1.4
Ga	13.1	5.8	-2.9	13.6	2.1
Zn	151.3	1.8	10.7	148.0	7.8

Table 1 continued

JSd-3														
Δ (%)	Method C			Method D			Method D, 200mg			Method D, 400mg			Published	
	MV (n=2)	% RDS	Δ (%)	MV (n=6)	% RDS	Δ (%)	MV (n=2)	% RDS	Δ (%)	MV (n=2)	% RDS	Δ (%)	MV (n=3)	% RDS
-17.6	35.1	2.3	15.3	39	24.7	29.0	41	35.3	35.5	40	27.3	30.3	30.4	0.9
-86.8	218	22.1	-21.2	236.8	8.9	-14.3	200.2	3.3	-27.6	216.6	0.4	-21.6	276.3	5.4
-49.8	402.6	8.3	-9.7	419.7	4.2	-5.9	364.0	4.3	-18.4	408.6	0.7	-8.4	446.0	5.1
-78.1	5.9	7.3	-18.9	6.4	8.3	-12.6	5.2	1.6	-28.4	5.7	0.5	-22.1	7.3	9.2
-43.1	1.4	2.9	-10.0	1.6	8.3	-0.8	1.3	0.5	-20.7	1.4	0.3	-14.6	1.6	6.7
26.1	16	61.8	104.0	9	15.5	14.2	6.7	13.2	-13.8	7.4	8.8	-4.5	7.8	
-28.5	1	51.5	8.2	0.6	6.4	-17.3	0.4	20.6	-39.9	0.5	14.8	-27.5	0.7	
-79.8	15	18.4	-23.7	17.5	4.5	-12.5	15.1	5.0	-24.5	16.3	1.7	-18.7	20.0	1.0
-27.9	39.3	1.3	-6.4	39.1	5.4	-6.9	34.2	5.7	-18.6	36.5	2.0	-13.2	42.0	1.5
	25.7		-68.7	64	30.9	-22.1	65.9	6.7	-20.0	67.3	5.8	-18.2	82.3	0.5
-70.2	4	21.4	-7.9	4.1	3.5	5.9	3.5	5.7	-8.7	3.9	3.2	1.0	4	19.7
-73.9	55.6	9.5	-0.2	50	10.0	-10.2	44.2	5.4	-20.7	48.9	0.9	-12.2	56	11.4
-71.3	13	22.5	-18.0	14.8	3.8	-8.6	12.8	5.5	-20.9	14.2	3.1	-12.4	16.2	2.8
-14.4	112	21.5	-11.1	114.4	6.8	-9.6	109.3	4.7	-13.6	115.8	2.4	-8.4	126.5	2.8
-14.7	3	21.9	-11.3	3.1	7.8	-2.3	2.7	2.5	-16.2	2.9	2.4	-10.6	3.2	0.2
-65.6	3	21.3	-19.8	3.0	4.4	-13.0	2.5	2.5	-25.3	2.8	0.6	-16.8	3.4	7.7
-62.7	0.6	10.2	-14.3	0.6	6.2	-7.6	0.5	4.5	-22.1	0.6	3.0	-10.0	0.7	2.2
-57.1	3	18.1	-10.4	2.7	7.2	-3.9	2	10.6	-16.6	2.7	7.5	-4.6	2.8	6.1
-42.3	0.4	13.6	6.6	0.4	4.8	11.7	0.3	3.6	-6.3	0.4	0.6	8.8	0.4	15.4
-42.6	2.2	8.0	-2.4	2.3	3.4	4.3	1.9	2.0	-13.6	2.3	0.8	2.1	2.2	1.4
-33.2	13.3	9.3	-4.0	13.2	7.5	-4.8	11.4	6.6	-17.9	13.4	3.3	-3.7	14	10.2
-40.0	0.4	6.6	-4.5	0.5	5.1	3.6	0.4	2.8	-16.4	0.5	3.0	0.9	0.5	7.3
-18.6	1.4	7.0	24.5	1.4	6.3	31.1	1.1	3.3	3.8	1.4	1.7	24.9	1	18.4
-20.6	1.4	2.3	5.0	1.5	4.7	11.9	1.1	5.1	-13.7	1.4	4.8	5.3	1.3	7.3
-20.0	0.2	2.5	3.7	0.2	3.2	9.2	0.2	6.2	-15.1	0.2	6.8	4.6	0.2	2.6
-60.6	9.8	25.1	-6.7	10.1	9.6	-4.0	8.2	3.8	-22.6	9.9	0.5	-6.3	10.5	2.4
-100.0				0.4	10.0	-3.8	0.4	4.7	-11.2	0.4	3.1	-7.7	0.4	2.9
9.7	63	26.9	-12.1	67	10.8	-5.5	67.1	1.0	-5.8	68.1	0.3	-4.3	71.2	1.6
-13.2	20	113.3	-44.8	31	25.6	-13.1	56.6	4.6	57.8	20.8	2.3	-42.1	35.9	3.5
				1023	11.8		991.4	0.6		1016.5	0.7			
-3.0	13.1	7.1	5.6	12	11.2	-7.1	11.4	0.2	-7.8	11.8	0.8	-4.5	12.4	2.9
-20.7	19	13.5	-4.1	19	13.2	-0.2	18.9	2.2	-2.2	18.0	1.1	-7.0	19.4	2.1
21.1	507.2	0.4	20.0	391	16.2	-7.4	393.1	8.0	-7.0	386.4	9.5	-8.6	422.7	1.4
1.3	13.5	0.1	0.7	12	10.5	-8.2	12.2	1.4	-9.2	12.6	1.6	-6.0	13.5	0.5
8.3	139.9	0.7	2.4	132	19.35	-3.5	120	11.0	-12.3	123	13.7	-10.4	136.7	1.5

Cs
Rb
Ba
Th
U
Nb
Ta
La
Ce
Pb
Pr
Sr
Nd
Zr
Hf
Sm
Eu
Gd
Tb
Dy
Y
Ho
Er
Yb
Lu
Sc
Ti
V
Cr
Mn
Co
Ni
Cu
Ga
Zn

Table

Jlk-1																	
Alkaline fusion			Method B			Method C			Method D			Method D, 200mg			Method D, 400mg		
MV (n=2)	% RDS	Δ (%)	MV (n=3)	% RDS	Δ (%)	MV (n=14)	% RDS	Δ (%)	MV (n=8)	% RDS	Δ (%)	MV (n=2)	% RDS	Δ (%)	MV (n=2)	% RDS	Δ (%)
0	11.4	-99.6	6.3	1.0	-47.4	13	29.3	9.4	14	12.8	18.1	15	21.8	23.9	15	16.0	21.3
0.4	0.6	-99.7	7.3	3.6	-94.8	72	80.6	-49.1	112	13.5	-20.0	98.6	1.8	-29.9	109.4	1.8	-22.1
550.6	1.0	-1.4	398.9	2.6	-28.6	438	19.4	-21.5	497.1	5.9	-11.0	469.4	1.9	-16.0	510.7	1.9	-8.6
18.0	1.1	-6.3	4.1	7.0	-78.9	9	68.7	-52.5	14.6	9.2	-24.2	13.8	1.9	-28.3	14.9	2.1	-22.3
0.3	0.8	-91.6	1.7	1.9	-54.8	2	50.4	-44.9	3.2	7.2	-14.1	3.0	0.6	-20.9	3.1	0.3	-17.1
4.0	3.0	-75.7	16.4	5.1	-0.2	22	57.4	33.5	20	36.9	19.1	14	11.5	-15.5	14.6	8.7	-11.5
	5.7		1	11.0	-27.5	2	66.7	2.9	1	25.5	-15.6	1	15.3	-36.8	1	13.7	-31.2
39.9	0.8	-0.8	8	19.5	-81.0	17	75.5	-58.2	31.9	9.0	-20.8	29.8	1.2	-25.9	33.1	1.2	-17.7
80.6	0.7	-7.4	20	11.5	-77.5	57	34.8	-34.8	74.5	5.9	-14.4	70.1	2.5	-19.4	73.4	1.5	-15.7
24.4	1.0	-44.8	3.7	5.2	-91.7	9	42.4	-79.9	29	25.0	-35.6	33.4	3.5	-24.5	32.6	4.2	-26.3
9.1	0.7	3.5	3	12.1	-70.0	4	64.9	-50.0	7.5	9.9	-14.9	7.3	4.2	-17.7	7.9	2.7	-10.4
61.9	1.0	-6.3	8	13.7	-87.4	33	68.5	-50.3	57.8	9.0	-12.6	53.3	1.6	-19.4	58.7	1.6	-11.2
34.5	0.8	-2.6	11.3	9.7	-68.0	17	59.7	-51.1	29	10.6	-18.7	27.6	3.7	-22.3	30.4	3.3	-14.3
123.1	0.7	-9.0	123.8	4.3	-8.6	132.6	8.0	-2.0	143	14.0	5.7	134.8	4.9	-0.4	127.8	5.1	-5.5
3.3	0.6	-9.8	3.4	4.2	-9.3	4	10.8	0.8	4	15.6	3.3	3.4	3.2	-7.2	3.3	2.0	-10.4
7.3	1.2	-3.1	3.3	6.5	-56.7	4	51.1	-44.2	6.3	8.4	-17.1	6.0	0.6	-20.5	6.6	1.6	-13.1
1.2	1.8	-2.3	0.6	5.7	-52.4	0.7	48.3	-42.3	1	11.9	-16.3	1.0	3.2	-19.1	1.1	3.0	-11.8
7.1	1.1	13.2	3.9	3.9	-36.9	5	44.7	-26.0	6	10.2	-1.2	6.0	8.7	-4.5	6.5	9.6	4.4
1.1	0.7	-4.8	0.7	4.0	-38.7	0.8	39.7	-32.9	1.0	9.0	-12.1	1.0	2.5	-16.7	1.1	2.6	-9.1
6.8	0.5	4.7	4.5	3.8	-30.5	5	36.2	-28.1	6	11.1	-6.9	5.9	2.1	-8.3	6.4	3.0	-0.9
43.9	0.2	14.9	29.4	3.8	-22.9	31	35.1	-19.5	38.3	9.0	0.2	38.5	5.3	1.0	40.7	4.7	6.6
1.4	0.1	15.7	1.0	3.2	-19.6	1	33.7	-19.8	1.2	9.4	0.3	1.2	4.5	2.1	1.3	4.3	9.3
3.9	0.2	9.2	3.0	3.5	-18.1	3	31.8	-20.3	3.5	8.9	-2.3	3.5	2.4	-1.8	3.8	3.4	6.2
3.8	0.1	-0.3	3.0	2.3	-20.7	3	27.9	-25.0	3.3	6.4	-12.8	3.3	4.8	-13.0	3.5	3.0	-8.9
0.5	1.0	-3.0	0.4	2.5	-21.2	0.4	27.0	-26.5	0.5	10.7	-16.7	0.5	5.9	-14.4	0.5	6.5	-8.7
13.8	9.8	-13.8	5.7	3.1	-64.3	11	55.8	-33.4	13.9	7.2	-13.5	13.8	1.7	-14.3	14.0	1.9	-13.2
1	13.9	-15.4							1	18.4	6.6	0.6	5.7	-7.5	0.6	7.2	-8.2
0	76.6	-99.9	106.8	3.2	-8.3	107.6	5.6	-7.6	115	11.6	-1.1	108.3	2.2	-7.0	106.2	2.1	-8.9
	2.2		41	26.5	-41.4	68	36.5	-3.2	49	23.3	-30.3	39.4	2.7	-44.3	42.2	4.1	-40.2
1507	23.9	-22.5							1932	11.4	-0.7	1805.5	1.8	-7.2	1817.4	0.4	-6.6
12	53.1	-34.5	9.2	6.7	-48.4	14	20.3	-22.5	18	12.8	0.0	16.9	0.1	-5.7	16.6	0.7	-7.3
39.0	0.6	6.8	16.1	0.0	-56.0	31	12.8	-14.9	37	11.8	2.0	35.6	1.4	-2.5	33.6	4.5	-8.0
25.3	4.6	-60.2	57.7	8.6	-9.5	62	10.1	-2.6	66	19.1	4.2	59.9	9.4	-6.0	56	10.3	-12.4
0.1	2.2	-99.8	20.4	3.5	-11.4	20.7	7.1	-10.1	23.0	9.4	0.1	21.8	0.2	-5.2	21.7	1.6	-5.6
25.3	4.5	-83.3	106	17.2	-30.2	107	26.8	-29.6	217	66.0	43.2	132	13.7	-13.0	123.6	13.6	-18.4

: 1 continued

<i>Published</i>	
MV (n=5)	% RDS
12.0	6.0
140.5	4.2
558.7	4.1
19.2	4.4
3.8	3.7
16.5	5.6
1.6	
40.2	1.9
87.0	2.8
44.3	1.3
8.8	5.7
66.1	6.4
35.4	1.3
135.3	8.6
3.7	7.4
7.6	5.3
1.2	6.5
6.2	9.1
1.2	8.1
6.4	2.9
38.2	6.8
1	10.5
3.6	2.9
3.8	7.8
0.6	9.1
16.1	1.3
0.7	0.2
116.5	0.6
70.6	3.9
1945	10.5
17.9	2.3
36.6	2.9
63.7	6.1
23.0	9.8
151.5	0.4

	<i>LKSD-1</i>													
	<i>Method A</i>		<i>Method B</i>			<i>Method C</i>			<i>Method D</i>			<i>Method D, 200mg</i>		
	n=1	Δ (%)	MV (n=2)	% RDS	Δ (%)	MV (n=4)	% RDS	Δ (%)	MV (n=4)	% RDS	Δ (%)	MV (n=2)	% RDS	Δ (%)
Cs	1	-45.6	0.8		-44.2	1.1	2.0	-28.4	1.0	2.5	-33.4	1	17.9	-37.2
Rb	23.0	-4.0	22.7	5.9	-5.3	31.8	2.3	32.7	32	10.6	32.5	21.9	4.0	-8.7
Ba	390	13.6	389.0	3.0	13.2	568.7	2.4	65.4	581.2	3.1	69.1	377.3	2.1	9.8
Th	2	-20.0	2	14.1	-8.5	2.9	8.6	33.3	3.2	9.8	46.4	1.8	0.3	-16.1
U	9.0	-7.5	8.7	1.3	-10.7	12.3	3.2	26.8	12.9	2.8	33.1	7.7	2.0	-20.3
Nb	6	-13.7	5.7	5.0	-18.3	11	28.5	62.8	9.8	9.1	40.1	4	13.8	-41.3
Ta	0.3	-13.2	0.3	32.4	-13.9	1	23.9	121.0	1	40.0	84.2	0.2	18.0	-29.2
La	13	-18.7	13.3	7.5	-16.8	20.5	6.6	27.9	21.7	9.0	35.3	13.3	1.8	-16.7
Ce	24.4	-9.7	24.5	6.7	-9.1	38.2	5.6	41.4	40.6	8.2	50.3	24.7	1.4	-8.5
Pb	59	-28.8	31.8		-61.6	14.5	0.3	-82.5			-100.0	69.0	8.7	-16.6
Pr	3.7		3.7	5.4		5.8	2.6		5.8	6.0		3.8	3.8	
Sr	267	31.7	269.5	3.7	32.7	378.7	3.2	86.6	380.5	6.9	87.4	259.2	2.5	27.7
Nd	15.6	-2.5	15.7	4.1	-1.8	24.2	1.6	51.0	25	11.2	59.0	15.8	3.3	-1.0
Zr	75	-44.3	151.4	0.7	13.0	161	30.7	20.2	169	23.6	26.5	125.5	4.3	-6.3
Hf	2	-43.6	3.6	2.6	0.3	4	30.4	13.3	4	24.9	13.1	2.8	6.5	-23.0
Sm	3.6	-10.3	3.6	3.8	-9.6	5.5	0.5	36.4	5.6	2.5	39.2	3.6	1.6	-10.7
Eu	0.9	-2.0	0.9	1.6	-1.9	1.3	2.1	45.9	1.4	1.5	55.5	0.9	4.6	-0.1
Gd	3.6	0.6	3.6	2.4	1.3	5.7	2.8	57.8	5.8	3.6	60.6	3.4	7.6	-5.4
Tb	0.6	-8.2	0.6	1.4	-7.0	0.8	3.0	41.0	0.9	5.6	50.9	0.5	1.0	-10.3
Dy	3.2	-6.2	3.2	0.7	-4.6	4.9	4.6	43.9	5.0	5.2	46.0	3.3	1.6	-4.1
Y	20.3	6.6	21.2	3.4	11.7	31.3	4.3	64.9	32.1	2.5	68.7	21.5	4.7	13.4
Ho	1	-33.1	0.7	1.3	-31.8	1.0	4.8	2.1	1.1	3.2	8.8	0.7	2.6	-31.5
Er	2.0		2.0	1.4		3.0	3.9		3.3	6.9		2.0	1.2	
Yb	1.9	-6.1	1.9	0.5	-2.6	2.8	4.5	42.0	3.0	4.6	51.8	1.9	2.9	-7.3
Lu	0.3	-32.4	0.3	1.3	-29.4	0.4	3.0	2.7	0.5	6.9	15.5	0.3	5.1	-31.2
Sc	8	-11.8	7.9	5.1	-11.9	11.5	3.7	28.0	12.1	6.2	34.0	8.0	1.7	-10.9
Ti						1	18.9		0.8	4.1		0.5	5.8	
V	51	26.1	50.6	3.7	24.1	81	15.7	99.8	80.6	2.5	97.6	46.9	0.5	15.0
Cr	16	-31.1	20	28.3	-12.3	25	58.8	9.3	35.8	5.0	54.1	5.8	4.1	-74.9
Mn						980.4	2.9		1016.9	5.1		663.0	1.4	
Co	9.1	-6.9	10	10.5	2.1	15.4	3.2	57.0	16.3	2.4	66.7	10.5	0.0	7.0
Ni	9	-35.6	9.0		-35.4	21.9	9.0	56.2	24.8	6.2	76.9	15.8	3.4	13.0
Cu	39.3	-9.9	43	10.7	-0.9	70.4	4.0	61.5	70.5	6.1	61.6	42	10.6	-3.2
Ga	9.1	-8.6	9.0	6.4	-10.2	12.7	3.6	26.8	13.0	6.2	30.3	8.8	3.4	-11.7
Zn	479	45.3	385	16.8	17.0	460.1	9.9	39.7	533.9	4.6	62.1	303	16.1	-8.1

Table 1 continued

Method D, 400mg			Published	
MV (n=2)	% RDS	Δ (%)	MV (n=2)	% RDS
1	22.6	-50.2	1.5	
17.6	1.7	-26.9	24.0	
301.4	2.5	-12.3	343.8	50.2
1.6	0.3	-29.0	2.2	
6.0	0.6	-37.7	9.7	
2.7	13.7	-61.0	7.0	
0.1	32.2	-56.5	0.3	
10.9	2.3	-31.7	16.0	
20.6	3.4	-23.8	27.0	
55.8	7.9	-32.7	82.8	1.3
3.1	5.1			
205.1	2.9	1.0	203	46.3
12.9	3.0	-19.2	16.0	
82.2	6.0	-38.7	134.0	
1.9	6.4	-46.4	3.6	
2.9	3.2	-28.0	4.0	
0.7	5.0	-21.1	0.9	
3	11.0	-22.9	3.6	
0.4	2.3	-28.0	0.6	
2.6	3.8	-22.5	3.4	
17.8	5.6	-6.3	19.0	
0.6	5.0	-44.9	1.0	
1.6	4.1			
1.5	3.3	-25.8	2.0	
0.2	5.7	-44.4	0.4	
6.7	2.0	-25.9	9.0	
0.3	6.6			
39.5	1.7	-3.3	40.8	30.9
6.1	4.4	-73.6	23.2	46.1
535.2	0.1			
8.4	0.3	-14.7	10	16.8
13.0	2.9	-7.3	14	19.6
32.6	9.1	-25.2	43.6	2.1
7.1	0.9	-29.3	10	
235	15.8	-28.7	329.4	3.3

Improvements in Digestion Protocols for Trace Element and Isotope Determinations in Stream and Lake Sediment Reference Materials (JSd-1, JSd-2, JSd-3, JLk-1 and LKSD-1)

Sidonie Révillon^{(1, 2,)*} and Danièle Hureau-Mazaudier⁽¹⁾

¹ Université de Brest, CNRS, UMR 6538 Domaines Océaniques, Institut Universitaire Européen de la Mer, Place Copernic, 29280 Plouzané, France

² IFREMER, Département Géosciences Marine, BP 70, 29280 Plouzané, France

*: Corresponding author : email : sidonie.revillon@ifremer.fr

Abstract:

Total dissolution is a critical step in geochemical analysis. Despite the number of published protocols, this issue still draws attention for sediment samples, which are particularly difficult to dissolve due to the common occurrence and high abundance of refractory phases such as zircon. We present tests of different chemical digestion procedures carried out on reference materials (RM) of stream (JSd-1, JSd-2 and JSd-3) and lake (JLk-1 and LKSD-1) sediments from the Geological Survey of Japan (GSJ) and the Canadian Certified Reference Material Programme (CCRPM). We demonstrate that the fusion technique is not appropriate for our studies as not all elements of interest were recovered and blank levels were too high to permit further Sr and Pb isotopic composition measurements. Similarly, conventional HF+HNO₃ dissolution methods were not efficient enough for detrital samples. Our preferred method involved using high pressure Teflon® vessel bombs in association with HClO₄. This protocol ensured a complete dissolution of the powder, as well as a complete recovery of trace elements. Moreover, blank levels were sufficiently low that Sr or Pb isotope compositions could be measured from the same mother solution. We also tested the homogeneity of RM powders by performing tests on various amount of powder.

Keywords: RM • HR-ICP-MS • acid digestion • fusion • sediment

Résumé:

La dissolution totale d'un échantillon est une phase critique pour toute analyse géochimique. Malgré le nombre de protocoles publiés, la mise en solution d'échantillons de sédiments reste problématique en raison de la présence de phases réfractaires comme les zircons. Nous présentons des tests de différentes procédures chimiques réalisés sur des Matériaux de Référence (RM) de sédiments de ruisseau (JSd-1, JSd-2 et JSd-3) et de lac (JLk-1 et LKSD-1) du Service Géologique de Japon (GSJ) et de Canadian Certified Reference Material Programme (CCRPM). Nous montrons que la technique de fusion utilisée n'est pas appropriée à nos études car tous les éléments d'intérêt ne sont pas récupérés quantitativement et le niveau des blancs est trop élevé pour permettre l'analyse des compositions isotopiques de Sr et de Pb à partir des mêmes solutions. De même, les techniques de mise en solution conventionnelles par attaque acide HF+HNO₃ sur plaque chauffante ne sont pas suffisamment efficaces pour une mise en solution complète de sédiments détritiques. Notre méthode préférée implique l'utilisation de bombes en téflon et de HClO₄. Ce protocole permet la mise en solution totale des échantillons et la récupération de tous les éléments trace intéressants. De plus, les blancs de chimie sont suffisamment bas pour que les compositions isotopiques, e.g., Sr, Pb puissent être mesurées à partir du même aliquot. Par ailleurs, nous avons aussi testé l'homogénéité des RM utilisés en appliquant notre protocole d'attaque sur des quantités de poudre variables.

Mots-clés: matériel de référence • HR-ICP-MS • dissolution acide • fusion • sédiments