Determination of abundances of 52 elements in natural waters by ICP-MS with freeze-drying pre-concentration

Que Dinh Hoang, Tak Kunihiro, Chie Sakaguchi, Masahiro Yamanaka, Hiroshi Kitagawa, and Eizo Nakamura*

The Pheasant Memorial Laboratory for Geochemistry and Cosmochemistry
Institute for Planetary Materials, Okayama University at Misasa Tottori
682-0193, Japan
*Corresponding author. e-mail: eizonak@misasa.okayama-u.ac.jp

Abstract

To precisely determine the abundances of 52 elements found within natural water samples, with concentrations down to fg g^{-1} level, we have developed a method which combines freeze-drying pre-concentration (FDC) and isotope dilution internal standardization (ID-IS). By sublimation of H_2O, the sample solution was reduced to <1/50 of the original volume. To determine element abundance with an accuracy better than 10%, we found that for solutions being analyzed by mass spectrometry the HNO_3 concentration should be >0.3 mol l^{-1} to avoid hydrolysis. Matrix-affected signal suppression was not significant for the solutions with NaCl concentrations lower than 0.2 cg g^{-1} and 0.1 cg g^{-1} for quadrupole ICP-MS and sector field ICP-MS, respectively. The recovery yields of elements after FDC were 97−105%. The detection limits for the sample solutions prepared by FDC were ≤10 pg g^{-1}, except for Na, K, and Ca. Blanks prepared using FDC were pg-level, except for 11 elements (Na, Mg, Al, P, Ca, Mn, Fe, Co, Ni, Cu, and Zn). We determined the abundances of 52 elements within bottled drinking water from five different geological sources with concentrations ranging from fg g^{-1} to μg g^{-1} level with high accuracy.

Keywords: pre-concentration, freeze drying, ID-IS, natural water, drinking water

1 Introduction

The chemical characteristics of natural fluids such as hot-spring water and groundwater are the consequence of interactions between fluids and solids on the surface and within the crust of the Earth (Shevenell and Goff 1993, Lee *et al.* 2011). Thus element abundances in these fluids provide physiochemical characteristics of an aqueous system and can indicate the origin and evolution of these fluids. Determination of element abundances of natural fluids is, however, difficult because of the small quantities of elements that they contain, as low as fg g^{-1} level (Kalacheva *et al.* 2015). To determine element abundances in natural waters, therefore, the elemental pre-concentration of elements prior to analysis has been proposed. Various pre-concentration techniques have been developed; these include sub-boiling evaporation (Görlach and Boutron 1990), coprecipitation (Umashankar *et al.* 2002), solid-phase or liquid-phase extraction (Esser *et al.* 1994), and freeze-drying (Harrison *et al.* 1975, Stössel and Prange 1985). The advantages of pre-concentration using freeze-drying include good recovery yield and low procedural blanks. Thus it has been applied to the analysis of natural waters and combined with INAA (Ndiokwere 1982), AAS (Hall and Godinho 1980), and total-reflection XRF (Stössel and Prange 1985). However, the number of elements determined by these studies was limited.

To determine the abundances of 52 elements found within natural water with pre-concentrations down to fg g^{-1} level, we have developed a method which combines freeze-drying pre-concentration (FDC) and isotope dilution internal standardization (ID-IS). Recovery yields for FDC were estimated through analyses of reference solutions with and without FDC. The effect of acidity on hydrolysis of cations and the effect of NaCl concentration on matrix-affected signal suppression on mass spectrometry were examined. To determine the Eu concentration accurately, the contribution of $^{135}BaO^+$ interference on the $^{151}Eu^+$ spectrum was estimated. To demonstrate performance of the FDC-ID-IS method, the river water CRM SLRS5 and bottled drinking water from five geological sources were analyzed.

2 Experimental

2.1 Spike, reagent, and reference solutions

The reagents H_2O, $HClO_4$, HCl, HF, and HNO_3 were prepared according to Moriguti *et al.* (2004). Four isotopic spike solutions enriched in ^{149}Sm, ^{10}B, ^{91}Zr-^{179}Hf, and ^{97}Mo-^{119}Sn-^{121}Sb were prepared with reference to Makishima and Nakamura (2006), Makishima *et al.* (1997), Makishima *et al.* (1999), and Lu *et al.* (2007), respectively. To estimate the recovery yields of elements after FDC, two reference solutions X1 and X2 were prepared. To investigate the effect of hydrolysis and matrix-affected suppression, two additional reference solutions TE and ME were prepared. These four reference solutions are detailed as below.

Reference solutions X1 and X2: To determine element abundances by mass spectrometry, elements in solution must be in the form of soluble ions or stable complexes. Elements Li, Be, Na, Mg, Al, P, K, Ca, Sc, V, Mn, Fe, Ni, Co, Cu, Zn, Ga, Rb, Sr, Y, Cd, In, Cs, Ba, REE, Tl, Pb, Bi, Th, and U (group I elements) form soluble ions in HNO_3 and elements B, Ti, Zr, Nb, Mo, Sb, Sn, Hf, and Ta (group II elements) form soluble oxo- and fluoro-complexes in HF (Nagender Nath *et al.* 2009). Silicate rock powder (JB3, Geological Survey, Japan) was decomposed, dried, redissolved following Yokoyama *et al.* (1999) and Makishima and Nakamura (2006), then diluted with 0.5 mol l^{-1} HNO_3 to make a solution with dilution factor of 1000, which was referred as reference solution X1. To demonstrate the performance of Ba oxide correction, a solution of Ba (Wako pure chemical industries, Ltd, Japan) was mixed with reference solution X1 to generate a series of solutions that varied in Ba/Eu ratio from 182 to 5×10^5. The silicate rock powder JB3 was also prepared for another reference solution, X2, following Lu *et al.* (2007), then diluted with 0.5 mol l^{-1} HF to make a solution with a dilution factor of 1000. To suppress evaporation of B during decomposition (Nakamura *et al.* 1992), mannitol solution (Ishikawa and Nakamura 1990) was dropped on the silicate rock powder before decomposition.

Reference solutions ME and TE: To investigate the effect of acidity on ion hydrolysis and the effect of NaCl concentration on matrix-affected signal suppression, two reference solutions were prepared. Reference solution ME includes Na, Mg, Al, K, Ca, V, Mn, Fe, Co, Ni, Cu, Zn, Ga, and Sr, and was created by dilution of a multi-element calibration standard 2A (Agilent Technologies, USA) with 0.5 mol l^{-1} HNO_3. Reference solution TE includes Li, Rb, Sr, Y, Cs, Ba, REE, Pb, Th, and U, and was created by dilution of a mixture of a “PM solution” (Makishima and Nakamura 1997), Li solution (Kanto Chemical Co, Japan) and Pb solution (Kanto Chemical Co, Japan) by 0.5 mol l^{-1} HNO_3. Reference solution TE was mixed with 16 mol l^{-1} HNO_3, and diluted with H_2O to give a series of solutions that varied in HNO_3 concentration from 0.1 to 1.0 mol l^{-1}. Reference solutions ME and TE were mixed with a NaCl solution to give a series of solutions that varied in NaCl concentration from 0 to 0.6 cg g^{-1} and from 0 to 2 cg g^{-1}, respectively. The NaCl solution was created by dissolving NaCl solid (Merck KGaA 64271 Darmstadt, Germany) in 0.5 mol l^{-1} HNO_3.

2.2 Pre-concentration, collection, and spiking

Sample solutions (100−125 ml with 0.05 mol l^{-1} HNO_3) were loaded in two polypropylene bottles (125 ml bottle, Thermal Scientific, USA) for group I and II elements. The sample solutions were frozen at 10^5 Pa and −70 °C for 8 hours in a freezer MDF-C8V1 (Sanyo Electric, Japan). Then the solids were dried at 2 Pa and −60 °C for

45 hours in a dryer DC800 (Yamato Scientific, Japan). By sublimation of H_2O, the volume of a given sample was reduced to <1/50. The solids were then thawed at room temperature. Following freeze-drying pre-concentration (FDC), the sample was collected, digested, dried, and redissolved in a different solvent (see Figure 1).

After FDC, the sample for group I elements was transferred into a 7 ml Teflon beaker (Savillex). To collect elements that may adsorb on the bottle wall, the following procedures were repeated twice: (1) Solutions of 6 mol l^{-1} HCl (1.5 ml) and 30 mol l^{-1} HF (0.15 ml) were dropped on to the 125 ml bottle. (2) The 125 ml bottle was vigorously shaken. (3) The solution in the bottle was transferred into the 7 ml beaker. The sample solution was mixed with 7 mol l^{-1} $HClO_4$ (0.5 ml) and 30 mol l^{-1} HF (0.3 ml), and agitated in an ultrasonic bath at 70 °C for 8 hours, and dried according to Yokoyama *et al.* (1999). The residue after drying was redissolved in 0.5 mol l^{-1} HNO_3 to give a sample solution of 0.7−2 ml. The sample solution was agitated in the ultrasonic bath at 70 °C for 1 hour.

After FDC, the sample solution for group II elements was transferred into a 8 ml polypropylene beaker (Thermal Scientific). To collect elements that may adsorb on the bottle wall, the following procedures were repeated twice: (1) Solutions of 0.1% mannitol (0.12 ml) and 10 mol l^{-1} HF (1.2 ml) were dropped into the 125 ml bottle. (2) The 125 ml bottle was vigorously shaken. (3) The solution in the bottle was transferred into the 8 ml beaker. To suppress coprecipitation of group II elements with CaF_2, Al-solution (Alfa Aesar, USA) was mixed with the sample solution to adjust the Al/(Al+Ca) ratio to ≥ 0.9 (Tanaka *et al.* 2003, Lu *et al.* 2007). The sample solution was agitated in an ultrasonic bath at 70 °C for 8 hours, and dried at 70 °C following Lu *et al.* (2007). The residue after drying was redissolved by 0.5 mol l^{-1} HF to give a sample solution of 0.7−2 ml. The sample solution was agitated in the ultrasonic bath for 1 hour.

To determine element abundances using the ID-IS, the optimum amount of spike solutions (^{149}Sm for group I elements and ^{10}B, ^{91}Zr-^{179}Hf, and ^{97}Mo-^{119}Sn-^{121}Sb for group II elements) were mixed with the sample solutions. Before addition of the spike solutions, element abundances of samples solutions semi-quantitatively determined through examination of the ion signal intensities generated by a 0.3 ml sample of each solution. The sample solutions were agitated in the ultrasonic bath at 70 °C for 30 minutes after addition of the spike solutions. The supernatant of the sample solutions was analyzed by mass spectrometry. We define a pre-concentration factor C as the difference between the relative quantity of the sample solution before FDC to that fed into mass spectrometry. The sample solution that fed into the mass ICP-MS typically had $C = 50 - 185$.

2.3 Mass spectrometry

The abundance of the 52 elements were determined in six difference acquisitions using ICP-MS. The abundances of group I elements were determined in four acquisitions Ia (Li, Be, Rb, Sr, Y, Cs, Ba, REE, Pb, Th, and U), Ib (Cd, In, Tl, and Bi), Ic (Na, Mg, Al, P, Ca, V, Mn, Fe, Co, and Sr), and Id (K, Sc, Ni, Cu, Zn, Ga, and Sr). The abundances of group II elements were determined in two acquisitions IIa (B, Zr, Nb, Mo, Sn, Sb, Hf, and Ta) and IIb (Ti). Acquisitions Ia, Ib, and IIa, and acquisitions Ic, Id, and IIb were conducted by ICP-QMS Agilent 7500cs (Yokogawa Analytical Systems, Japan; Makishima and Nakamura 2006, Makishima *et al.* 2011, Lu *et al.* 2007) and ICP-SFMS Element-XR (Thermo Scientific, Germany; Makishima and Nakamura 2006, Lu *et al.* 2007), respectively. To minimize overestimation of element abundances resulting from interferences, the high-mass-resolution technique was applied for acquisitions Ic, Id, and IIb with M/ΔM 4000, 10000, and 4000, respectively. The oxide-correction technique was also applied for acquisitions Ia and Ib. To estimate the contributions of $^{95}MoO^+$ and $^{135}BaO^+$ interference on $^{111}Cd^+$ and $^{151}Eu^+$ spectra, Mo solution without Cd (1 µg g^{-1}; Makishima *et al.* 2011) and Ba solution without Eu (1 µg g^{-1}) were analyzed periodically. The analytical conditions are detailed in Supporting Information (SI) Tables S1 and S2. Total yields and atomic yields on mass spectrometry are shown in SI Appendix A.

Elements with ionic potential (IP ≡ charge/radius ratio) >30 nm^{-1} strongly bond with O^{2-} in water and therefore form stable oxyhydroxides or aquocomplexes, which tend to turn into minerals (Railsback 2003). Such hydrolysis results in inhomogeneous distribution of cations in solution (e.g., Milkey 1954) and consequently, the delivery rate of elements to the ICP-MS may be biased. Elements such as Pb, Th, and U are not hydrolyzed with pH <0.3 (e.g., Nagender Nath *et al.* 2009) but are hydrolyzed with pH >4.2, >3.7, and >5.6 (e.g., Milkey 1954). In order to find out the minimum acidity that ensures that cation hydrolysis does not occur, the reference solutions TE was varied in concentrations of HNO_3 from 0.1 to 1.0 mol l^{-1}, were analyzed in the same way as the samples. Ion signals of Li, Be, Rb, Sr, Y, Cs, Ba, REE, Pb, Th, and U were measured.

Matrix-affected signal suppression in ICP-MS is a phenomenon in which the signal from analytical target ions is suppressed by the presence of abundant ions of a major element. Natural waters (hot-spring water, river water, and sea water) contain abundant major elements such as Na and Cl up to µg g^{-1} level. By performing FDC both the trace elements and the major elements were concentrated. To find the maximum NaCl concentration that did not cause matrix-affected signal suppression, reference solutions ME and TE were varied in concentration of NaCl from 0 to 0.6 cg g^{-1} and from 0 to 2 cg g^{-1}, respectively, were analyzed in the same way as the samples. Ion signals of the elements Na, Mg, Al, K, Ca, V, Mn, Fe, Co, Ni, Cu, Zn, Ga, and Sr and the elements Li, Be, Rb, Sr, Y, Cs, Ba, REE, Pb, Th, and U were measured.

Contribution of $^{135}BaO^+$ to the $^{151}Eu^+$ signal at m/z = 151 becomes significant when the Ba/Eu ratio is $>10^3$, such as in hot-spring water and river water (Nakamura *et al.* 2015, Aries *et al.* 2000). Aliaga-Campuzano *et al.* (2013) tried to suppress generation of BaO using high efficiency sample introduction and membrane-desolvation. However, when the Ba/Eu ratio became $>4\times10^4$, the aperture on the sample-introduction cone was partially closed by the deposit of salts, and memory effects, derived from the membrane-desolvator system, became significant. Nakamura *et al.* (2015) estimated the contribution of BaO^+ interference on the Eu^+ spectrum by analysis of Ba solution, but without showing the uncertainty. We determined [Eu] accurately and estimated the uncertainty propagated from uncertainties on the intensity ^{151}I, intensity ^{137}I, and the Ba oxide-to-atomic-yield Θ_{BaO^+/Ba^+}. The uncertainty is detailed in SI Appendix B. To demonstrate the performance of Eu determination, reference solutions X1 that varied in Ba/Eu ratio from 182 to 5×10^5, were analyzed in the same way as the samples.

2.4 Performance of freeze-drying pre-concentration

The recovery yield, of the elements after FDC, was examined. Reference solutions X1 and X2 were diluted 50 times by H_2O, then pre-concentrated by FDC. Reference solutions X1 and X2 with and without the FDC step were analyzed in the same way as the sample. To demonstrate applicability of the method, reference river water SLRS5 from Ottawa (National Research Council Canada, Canada) was analyzed with and without undertaking FDC, and drinking waters from five geological sources were also analyzed in the same way.

3 Results and discussion

3.1 Optimization of method for natural-water analyses

The range of HNO_3 concentrations for which hydrolysis does not occur were examined by analysis of a series of reference solutions TE, which varied in their concentration of HNO_3 from 0.1 to 1.0 mol l^{-1}. Hydrolysis was detected as a decrease in the ion signal relative to that in a solution of 0.5 mol l^{-1} HNO_3. The decrease in ion signal as a function of concentration of HNO_3 is shown in Figure 2. Hydrolysis of elements was ≤10% for all HNO3 concentrations except for Th which had >10% when the concentration of HNO_3 was <0.3 mol l^{-1}. Thus all solution measured by ICP-MS had a HNO_3 concentration ≥0.3 mol l^{-1}.

The range in concentrations of NaCl which did not cause matrix-affected signal suppression was examined by analysis of a series of reference solutions ME and TE that varied in concentrations of NaCl from 0 to 0.6 cg g^{-1} and from 0 to 2.0 cg g^{-1}, respectively. The existence of matrix-affected signal suppression was detected as a decrease in ion signal relative to that in a solution without added NaCl (Figure 3). The maximum concentrations of NaCl, which ensured matrix-affected signal suppression ≤10%, were ≤0.1 cg g^{-1} and ≤0.2 cg g^{-} for ICP-SFMS and ICP-QMS, respectively. We conclude that to have less than 10% signal suppression, solutions fed into ICP-SFMS and ICP-QMS should have NaCl concentrations of ≤0.1 cg g^{-1} and ≤0.2 cg g^{-1}, respectively.

To estimate the abundance of Eu precisely, $\Theta_{\mathrm{BaO^+/Ba^+}}$ was estimated from the $^{151}I/^{135}I$ ratio, that corresponds to the $I_{^{135}\mathrm{BaO^+}}/I_{^{135}\mathrm{Ba^+}}$ ratio, from analysis of a Ba solution without Eu. The mean and relative standard deviation (1σ) of $\Theta_{\mathrm{BaO^+/Ba^+}}$ among eleven sessions was 2.48×10^{-3} and 4%, respectively. Reference solutions X1, that varied in Ba/Eu ratio from 182 to 5×10^5 were analyzed The deviation of the Eu concentration relative to that of the reference solution X1 with a Ba/Eu ratio of 182 as a function of the Ba/Eu ratio is shown in Figure 4, which shows that the Eu concentration could be determined with an uncertainty <10% when the Ba/Eu ratio $<5\times10^4$.

3.2 Recovery yields after freeze-drying pre-concentration

The recovery of elements through FDC was estimated by analysis of the reference solutions X1 and X2 with and without FDC. The recovery yields for the 52 elements were 97−106% and shown in SI Table S4 and Figure 5.

In previous studies using FDC, recovery yields of K, Al, Cu, Mo, Sb, Cd, V, Cd, Ce, and Eu were significantly lower of higher than 100% (Lieser *et al.* 1977, Hall and Godinho 1980, Grotti *et al.* 2008) This was probably due to incomplete collection of elements during sample transfer after FDC or due to contamination from impurity of quartz tubes on non-destructive neutron activation (Lieser and Neitzert 1976, Lieser *et* *al.* 1977) and flasks (Hall and Godinho 1980). The recovery yields of these elements (K, Al, Cu, Mo, Sb, Cd, V, Ce, and Eu) in this study were 100−104%, which demonstrates that the elements were completely collected and contamination from apparatus was not significant.

3.3 Detection limit and blank

The detection limit was defined as the variation (3σ) of mean ion signals of 10 acquisitions of 0.5 mol l^{-1} HNO_3 and 0.5 mol l^{-1} HF, and typically expressed in units of counts per second. Using atomic yield, isotope ratio, and *C*, the detection limit was converted into concentration for the original solution before pre-concentration. As *C* gets larger, the sample detection limit becomes smaller. The sample detection limits achieved with *C*=50 are shown in Table 1. The sample detection limits were ≤10 pg g^{-1}, 100 pg g^{-1}, 89 pg g^{-1}, and 16 pg g^{-1} for 49 of the elements, Na, K, and Ca, respectively. Since the abundances of Na, K, and Ca in natural waters such as river water SLRS5 are at μg g^{-1} level, the detection limits of these elements are still about 6 orders of magnitudes smaller than their expected abundances in the sample. By FDC-ID-IS method, element abundances down to fg g^{-1} level can be determined.

To determine the blank, two empty polypropylene bottles (125 ml) were prepared for group I and II elements, and the chain of operations were conducted in the same way as for the samples, including FDC, before ICP-MS analysis. Estimated blanks are shown in Table 1. Most elements (32) had a blank ≤10 pg, with 9 elements with 10 pg−1 ng, and 11 elements with >1 ng. The origin of blanks was from impurities in the $HClO_4$, mannitol, and Al solutions. When the relative contribution of the blank to the sample was ≥1%, a blank correction was applied. When the relative contribution of the blank was >50%, the acquisition was not considered.

3.4 Analytical precision and accuracy

The river water CRM SLRS5 was analyzed with ($C = 50$) and without FDC, although on acquisitions Ic, Id, and IIb, sample solutions were diluted to $C \leq 1$ to avoid matrix-affected signal suppression. Analytical precision was calculated as the standard deviation of quadruplicate analyses. The results are shown in Table 2 and SI Figure S1.

Analytical precision without FDC was ≤10% and >10% for 41 and 9 elements, respectively. Analytical precisions for two elements (Be and Ta) were not determined because concentrations were lower than detection limit. The 9 elements with precision > 10% (Ga, Zr, Nb, Cd, In, Sn, Eu, Lu, and Hf) were all measured close to detection limits (detection limits divided by element abundances are 19, 24, 129, 8, 23, 87, 12, 15, and 262%). Analytical precisions for analyses with FDC were all ≤10%, except for Sn which was 21%. The value for Sn was attributed to a significant contribution from the blank (35% of measured signal). Analytical precisions for analyses with FDC were better for the 33 trace elements (determined by acquisitions Ia, Ib, and IIa, except for U) and were consistent for the 16 major- and the transition-elements (determined by acquisitions Ic and Id, and IIb).

Element abundances of SLRS5 using ICP-MS determined without FDC by five laboratories were extracted from data compiled by Yeghicheyan *et al.* (2013), all of which are consistent with the limited certified data (Table 2). Analytical precision of analyses taken with FDC in this study were 1.7−31 times better for the 32 trace elements, except for Sn, and were consistent for the 16 major- and the transition-elements compared to the data from Yeghicheyan *et al.* (2013). Note that In, Hf, and Ta were not listed in Yeghicheyan *et al.* (2013).

Analytical precision of analyses with FDC in this study were better than those without FDC (this study and data from Yeghicheyan *et al.* 2013) for the trace elements because of the improvement in counting statistics resulting from a significant increment in ion signal. For major- and transition-elements, analytical precision with FDC were similar to those without FDC (this study; Yeghicheyan *et al.* 2013), because the pre-concentrated solutions were diluted to avoid the matrix effects.

The values determined by analyses without FDC (this study; Yeghicheyan et al. 2013) were also compared to those determined with FDC, with the relative difference compared to the analyses with FDC shown in Figure 6. Taking into account the analytical precision, analyses without FDC (this study; Yeghicheyan *et al*. 2013) were consistent within 10% for all elements except P, Ga, and Sn. Results for P, Ga, and Sn deviated by 40%, ≤10%, and ≤10% for this study, and by 13%, 68%, and 43% for Yeghicheyan *et al*. (2013). The relatively large deviation for P was due to difficulty in measurement with its low ionization efficiency in comparison to other major elements during ICP-SFMS (Makishima and Nakamura 2006). The relatively large deviation of Ga by Yeghicheyan *et al.* (2013) probably resulted from interferences caused by sulfur, because of lack of sufficient mass resolution during mass spectrometry (May and Wiedmeyer 1998). The abundance of Sn determined without FDC in this study is consistent with the abundance determined with FDC, suggesting that the blank is properly corrected in this study. Since the abundance of Sn is reported by only one laboratory in Yeghicheyan *et al*. (2013), the inconsistency of Sn should further be evaluated. We also compared of the values determined FDC-ID-IS in this study compared to the compilation means by Yeghicheyan *et al.* (2013), using ISO recommended statistical methods (ISO 13528, 2005), and found that all elements were consistent within uncertainty, except for P and Sn.

Abundances of REE of the reference river water SLRS5 determined by this study (FDC-ID-IS), Yeghicheyan *et al.* (2013), and Heimburger *et al.* (2013) were normalized ($_n$) by abundances in CI chondrite (Anders and Grevesse 1989) and shown in SI Figure S2. The normalized patterns for each dataset are identical when analytical precision is considered, and show enrichment in light REE (LREE, $[La/Lu]_n$=13) with negative anomalies for Ce ($Ce/Ce^*=Ce_n/[La_n \times Pr_n]^{0.5}=0.60$) and Eu ($Eu/Eu^*=Eu_n/[Sm_n \times Gd_n]^{0.5}=0.63$). Abundances of heavy REE (HREE) determined by Heimburger *et al.* (2013) were slightly lower (3-19%) than those determined in this study and by Yeghicheyan *et al.* (2013), however the differences are not significant.

3.5 Analyses of drinking waters

To demonstrate capability and applicability of the FDC-ID-IS method, commercially available bottled drinking waters from five different locations were analyzed as examples of natural water analyses. The bottled waters were sources from: the foothills of young Holocene basaltic volcanoes (Mt. Fuji, Shizuoka prefecture, Japan and Volvic, Auvergne-Rhone-Alpes, France), the foothills of the a young dormant andesite-dacite volcano (Mt. Daisen, Tottori Prefecture, Japan), a Tertiary granitic rock terrain (Akaishi Mountains, Yamanashi Prefecture, Japan), and a Permian meta-sedimentary rock layer (Nishiki-cho, Yamaguchi Prefecture, Japan). The drinking waters were pre-concentrated by FDC reducing the weight of drinking waters from ~125 g to ~0.7 g, resulting in a pre-concentration factor C of ~180. Elements determined by acquisitions Ia (Li, Be, Rb, Sr, Y, Cs, Ba, REE, Pb, Th, and U), Ib (Cd, In, Tl, and Bi), and IIa (B, Zr, Nb, Mo, Sn, Sb, Hf, and Ta) were determined with C ~ 180, while elements determined by acquisitions Ic (Na, Mg, Al, P, Ca, V, Mn, Fe, Co, and Sr), and Id (K, Sc, Ni, Cu, Zn, Ga, and Sr), and IIb (Ti) were determined with $C < 1$ after re-dilution to avoid matrix-affected signal suppression. The analyses of five drinking waters were duplicated, and their element abundances were shown in Table 3.

To evaluate the reliability of acquisitions through FDC-ID-IS for unknown water samples, relative differences among duplicated acquisitions are plotted as a function of the abundances of 52 elements, and shown in Figure 7. Of the 260 acquisitions, 80%, 10%, and 10% of total acquisitions have relative differences of <10%, 10−20%, and

>20%, respectively. Among the acquisitions with relative differences >10% are 29 elements, which correspond to 12% of total acquisitions and have concentrations at fg g^{-1} level. The difference may be caused by over addition of spike more than the optimum quantity and low intensity signals with high background noise during acquisitions. In addition, tiny suspended particles (such as colloid, clays, and zircons which are enriched in specific elements) can pass through membrane filter during filtration of natural waters (Sholkovitz, 1992; Elderfield et al., 1990; Nozaki et al., 2000). If this is the case, then the effect can be mitigated by addition of small amounts of acid such as HNO_3 and HF to the original bottled water to dissolve the tiny particles before taking aliquots for FDC-ID-IS. It is noteworthy that 80% of the duplicate analyses have <10% deviation among duplicates irrespective of elements and concentrations, which range from several tens of µg g^{-1} down to the fg g^{-1} level indicating that the FDC-ID-IS method is a powerful tool for the comprehensive trace element analyses of fluids with extremely low element abundances.

Abundances of major elements (Na, Mg, K and Ca) given on the labels are consistent with those determined by this study (see Tables 3 and S5), although it is noted that the abundances of major elements on labels are not certified values. The labels for water from Mt. Daisen and the Akaishi Mountains infer that the abundances of the major elements on them have variations of ±50% and our data fit within in this range. Such large variations probably result from the weather (rainy and dry seasons), time, and location of collection. The results also suggest that determination of abundances of major elements is accurate, even though the water samples were diluted to $C<1$ after pre-concentration of C to ~180.

Abundances of the 52 elements were normalized to those of the upper continental crust as a function of the solubility of the elements estimated from partition coefficients between seawater and upper-crust (Taylor and McLennan 1985, Rudnick and Gao 2003, Li *et al.* 2011), and are shown in Figure 8. The element abundances of the drinking waters vary by nine orders of magnitude, from fg g^{-1} (e.g., [In]=8.98 fg g^{-1}) to µg g^{-1} concentrations (e.g., [Ca]=19.6 µg g^{-1}). Abundances of 44 of the 52 elements (77% of elements measured) in the drinking waters are sub-pg g^{-1}. Indeed, element abundances for Li, Be, Ti, Mn, Sc, Ga, Zr, Nb, Cd, In, Sn, Cs, REE, Hf, Ta, Pb, Bi, and Th could only be determined after FDC. Depending on the samples, elements such as Be, Sc, Ti, Zn, Ga, Hf, and Ta are below the sample detection limit, even with a C of ~180. If further pre-concentration with FDC is carried out until the detection limits are exceeded and assuming the blank corrections are carried out properly, then these extremely low element abundances should be able to be determined.

Abundances of REEs in the drinking water samples were normalized to those of CI chondrite (Anders and Grevesse 1989) and shown together with the reference river water SLRS5 in Figure S3. Compared to SLRS5, LREEs such as La and Ce are lower by two to four orders of magnitude. The abundances of LREEs are down to 0.0167 pg g^{-1} in the drinking water samples and HREEs are variable within two orders of magnitude (0.0826 to 6.28 pg g^{-1}). The REE patterns are smooth with variable negative spikes of Ce and Eu, indicating that the analyses were properly carried out. The slope $(La/Lu)_n$ and the negative spikes of Ce and Eu (Ce/Ce^*, and Eu/Eu^*) range from 0.001 to 4.7, 0.02 to 0.6, and 0.2 to 0.9, respectively. These geochemical characteristics reflect ground water processes such as permeability, residence time, redox and the chemical properties of the host rocks.

Recently, Bulia and Enzweiler (2018) determined REE abundances of drinking water from São Paulo state, Brazil and reported concentrations ranging from pg g^{-1} down to fg g^{-1} level. They pre-concentrated the water sample by C=100 using solid phase extraction with bis-(2-ethyl-hexyl)-phosphate. However, the abundance of Gd is not quantitatively determined by the bis-(2-ethyl-hexyl)-phosphate, because the Gd chelates dissociated slowly in the acid media to produce free ions during extraction (de Campos and Enzweiler 2016). In the results from our study, there is no significant Gd anomaly in these drinking water samples, which indicates that Gd is quantitatively determined by our method, and there is no significant anthropogenic contamination (de Campos and Enzweiler 2016). The blanks in Bulia and Enzweiler (2018) range from 2 pg (Tm) to 189 pg (Ce), which are ten to one hundred times higher than those in this study using FDC. We infer that the FDC-ID-IS method is a better technique to determine trace element abundance comprehensively and precisely for fluids with extremely low element abundances.

By combing geological and isotopic characteristics with fluid properties (e.g., pH, Eh, and temperature) and the FDC-ID-IS method which we have developed to determine the element abundances in natural water samples down to fg g^{-1} level, our understanding of the origin and evolution of aqueous systems will be further improved.

4 Conclusions

A FDC-ID-IS method was developed to determine the abundances of 52 elements found within natural water samples. The method was able to detect concentrations down to the fg g^{-1} level. To minimize overestimation of element abundances resulting from interferences, the high resolution ICP-SFMS (M/ΔM = 4000 or 10000) and oxide-correction techniques were applied for some elements. Hydrolysis of Th was avoided by dissolution of the sample in 0.5 mol l^{-1} HNO_3, and matrix-affected signal suppression was avoided by dilution of the sample solution to a NaCl concentration of $\leq$0.2 cg g^{-1} and $\leq$0.1 cg g^{-1} for ICP-QMS and ICP-SFMS analyses, respectively.

The sample solution (100–125 ml) was reduced to 0.7–2.0 g through freeze-drying, producing concentrated sample solutions with $C = 50-180$. The recovery yields of the 52 elements after FDC were 97–106%, which demonstrates that the elements were fully collected without significant contamination. Detection limits in a sample solution with FDC were $\leq$10 pg g^{-1}, except for Na (100 pg g^{-1}), K (89.0 pg g^{-1}) and Ca (15.6 pg g^{-1}). Blanks with FDC were at pg-level, except for 11 elements, which at the ng-level (Na, Mg, Al, P, Ca, Mn, Fe, Co, Ni, Cu, and Zn). Compared with other pre-concentration techniques for the determination of REEs in drinking water (e.g., solid phase extraction by Bulia and Enzweiler 2018), blanks using FDC-ID-IS are ten to one hundred times smaller.

The analytical precision of determinations of element abundances of river water SLRS5 with FDC were $\leq$10% and 21% for 51 elements and Sn, respectively. Analytical precision with FDC relative to those without FDC by Yeghicheyan *et al.* (2013) were 1.7−31 times better for 32 trace elements except Sn, and consistent for the 16 major- and transition-elements.

We determined the abundances of 52 elements in bottled drinking water from five geological sources, which ranged in concentration by nine orders of magnitude from fg g^{-1} to µg g^{-1} concentrations by the FDC-ID-IS method. Major-element abundances indicated on the labels were consistent with values determined in this study. The CI-normalized REE patterns are smooth, with variable negative spikes of Ce and Eu suggesting that the analyses were properly conducted for the samples with various matrices and extremely low element abundances. These results indicate that the FDC-ID-IS method is an appropriate technique to determine extremely low trace-element abundances accurately and precisely for natural water samples.

5 Acknowledgements

We would like to thank Potiszil Christian for useful discussions. We are grateful to all members of PML for technical supports during the lab works. We thank Dr. Kathryn Linge and the two anonymous reviewers for their constructive comments. This study was funded by Tottori prefecture through the program “Environmental Research Promotion” and Ministry of Education, Culture, Sports, Science and Technology (MEXT, Japan) through the program “Establishment of the international research-education center for pioneering planetary material science”.

References

Aliaga-Campuzano M.P., Bernal J.P., Briceno-Prieto S., Pérez-Arvizu O. and Lounejeva E. (2013)
Direct analysis of lanthanides by ICP-MS in calcium-rich water samples using a modular high-efficiency sample introduction system–membrane desolvator. **Journal of Analytical Atomic Spectrometry**, **28**, 1102–1109.

Anders E. and Grevesse N. (1989)
Abundances of the elements: Meteoritic and solar. **Geochimica et Cosmochimica Acta**, **53**, 197–214.

Aries S., Valladon M., Polvé M. and Dupré B. (2000)
A routine method for oxide and hydroxide interference corrections in ICP-MS chemical analysis of environmental and geological samples. **Geostandards Newsletter**, **24**, 19–31.

Bulia I.L. and Enzweiler J. (2018)
The hydrogeochemistry of bottled mineral water in São Paulo state, Brazil. **Journal of Geochemical Exploration**, **188**, 43–54.

de Campos F.F. and Enzweiler J. (2016)
Anthropogenic gadolinium anomalies and rare earth elements in the water of Atibaia River and Anhumas Creek, Southeast Brazil. **Environmental Monitoring and Assessment**, **188**, 281.

Elderfield, H., Upstill-Goddard, R. and Sholkovitz, E.R. (1990)
The rare earth elements in rivers, estuaries, and coastal seas and their significance to the composition of ocean waters. **Geochimica et Cosmochimica Acta, 54**, 971-991.

Esser B.K., Volpe A., Kenneally J.M. and Smith D.K. (1994)
Preconcentration and purification of rare earth elements in natural waters using silica-immobilized 8-hydroxyquinoline and a supported organophosphorus extractant. **Analytical Chemistry**, **66**, 1736–1742.

Görlach U. and Boutron C.F. (1990)
Preconcentration of lead, cadmium, copper and zinc in water at the pg g^{-1} level by non-boiling evaporation. **Analytica Chimica Acta**, **236**, 391–398.

Grotti M., Soggia F. and Todoli J.L. (2008)
Ultratrace analysis of Antarctic snow samples by reaction cell inductively coupled plasma mass spectrometry using a total-consumption micro-sample-introduction system. **Analyst**, **133**, 1388–1394.

Hall A. and Godinho M.C. (1980)
Concentration of trace metals from natural waters by freeze-drying prior to flame atomic absorption spectrometry. **Analytica Chimica Acta**, **113**, 369–373.

Harrison S.H., LaFleur P.D. and Zoller W.H. (1975)
Evaluation of lyophilization for the preconcentration of natural water samples prior to neutron activation analysis. **Analytical Chemistry**, **47**, 1685–1688.

Heimburger A., Tharaud M., Monna F., Losno R., Desboeufs K. and Nguyen E.B. (2013)
SLRS-5 elemental concentrations of thirty-three uncertified elements deduced from SLRS-5/SLRS-4 ratios. **Geostandards and Geoanalytical Research**, **37**, 77–85.

Ishikawa T. and Nakamura E. (1990)
Suppression of boron volatilization from a hydrofluoric acid solution using a boron-mannitol complex. **Analytical Chemistry**, **62**, 2612–2616.

ISO 13528 (2005)
Statistical methods for use in proficiency testing by interlaboratory comparisons. **International Organization for Standardization (Geneva)**, 66pp.

Kalacheva E., Taran Y. and Kotenko T. (2015)
Geochemistry and solute fluxes of volcano-hydrothermal systems of Shiashkotan, Kuril islands. **Journal of Volcanology and Geothermal Research**, **296**, 40–54.

Lee S.-G., Kim T.-K. and Lee T.J. (2011)
Strontium isotope geochemistry and its geochemical implication from hot spring waters in South Korea. **Journal of Volcanology and Geothermal Research**, **208**, 12–22.

Li Y.-H., Sohrin Y. and Takamatsu T. (2011)
Lake Biwa and the ocean: geochemical similarity and difference. **Limnology**, **12**, 89–101.

Lieser K., Calmano W., Heuss E. and Neitzert V. (1977)
Neutron activation as a routine method for the determination of trace elements in water. **Journal of Radioanalytical and Nuclear Chemistry**, **37**, 717–726.

Lieser K. and Neitzert V. (1976)
Determination of trace elements in water by non-destructive neutron activation. **Journal of Radioanalytical Chemistry**, **31**, 397–405.

Lu Y., Makishima A. and Nakamura E. (2007)
Coprecipitation of Ti, Mo, Sn and Sb with fluorides and application to determination of B, Ti, Zr, Nb, Mo, Sn, Sb, Hf and Ta by ICP-MS. **Chemical Geology**, **236**, 13–26.

Makishima A., Kitagawa H. and Nakamura E. (2011)
Simultaneous determination of Cd, In, Tl and Bi by isotope dilution-internal standardisation ICP-QMS with corrections using externally measured MoO^+/Mo^+ ratios. **Geostandards and Geoanalytical Research**, **35**, 57–67.

Makishima A. and Nakamura E. (1997)
Suppression of matrix effects in ICP-MS by high power operation of ICP: application to precise determination of Rb, Sr, Y, Cs, Ba, REE, Pb, Th and U at ng g^{-1} levels in milligram silicate samples. **Geostandards Newsletter**, **21**, 307–319.

Makishima A. and Nakamura E. (2006)
Determination of major/minor and trace elements in silicate samples by ICP-QMS and ICP-SFMS applying isotope dilution- internal standardisation (ID-IS) and multi-stage internal standardisation. **Geostandards and Geoanalytical Research**, **30**, 245–271.

Makishima A., Nakamura E. and Nakano T. (1997)
Determination of boron in silicate samples by direct aspiration of sample HF solutions into ICP-MS. **Analytical Chemistry**, **69**, 3754–3759.

Makishima A., Nakamura E. and Nakano T. (1999)
Determination of zirconium, niobium, hafnium and tantalum at ng g^{-1} levels in geological materials by direct nebulisation of sample HF solution into FI-ICP-MS. **Geostandards Newsletter**, **23**, 7–20.

May T.W. and Wiedmeyer R.H. (1998)
A table of polyatomic interferences in ICP-MS. **Atomic Spectroscopy -Norwalk Connecticut**, **19**, 150–155.

Milkey R.G. (1954)
Stability of dilute solutions of uranium, lead, and thorium ions. **Analytical Chemistry**, **26**, 1800–1803.

Moriguti T., Makishima A. and Nakamura E. (2004)
Determination of lithium contents in silicates by isotope dilution ICP-MS and its evaluation by isotope dilution thermal ionisation mass spectrometry. **Geostandards and Geoanalytical Research**, **28**, 371–382.

Nagender Nath B., Makishima A., Noordmann J., Tanaka R. and Nakamura E. (2009)
Comprehensive analysis for major, minor and trace element contents and Sr-Nd-Pb-Hf isotope ratios in sediment reference materials, JSd-1 and MAG-1. **Geochemical Journal**, **43**, 207–216.

Nakamura E., Ishikawa T., Birck J.-L. and Allègre C.J. (1992)
Precise boron isotopic analysis of natural rock samples using a boron-mannitol complex. **Chemical Geology**, **94**, 193–204.

Nakamura H., Chiba K., Chang Q., Nakai S., Kazahaya K. and Iwamori H. (2015)
Rare earth elements of the Arima spring waters, southwest Japan: Implications for fluid-crust interaction during ascent of deep brine. **Journal of Geology & Geophysics**, **2015**.

Ndiokwere C.L. (1982)
Determination of trace elements in rain water by neutron activation analysis. **Radioisotopes**, **31**, 583–586.

Nozaki, Y., Lerche, D., Alibo, D.S. and Tsutsumi, M. (2000)
Dissolved indium and rare earth elements in three Japanese rivers and Tokyo Bay: evidence for anthropogenic Gd and In. **Geochimica et Cosmochimica Acta, 64**, 3975-3982.

Railsback L.B. (2003)
An earth scientist's periodic table of the elements and their ions. **Geology**, **31**, 737–740.

Rudnick R.L. and Gao S. (2003)
Composition of the continental crust. **Treatise on Geochemistry**, **3**, 659.

Shevenell L. and Goff F. (1993)
Addition of magmatic volatiles into the hot spring waters of Loowit Canyon, Mount St. Helens, Washington, USA. **Bulletin of Volcanology**, **55**, 489–503.

Sholkovitz, E.R. (1992)
Chemical evolution of rare earth elements: fractionation between colloidal and solution phases of filtered river water. **Earth and Planetary Science Letters, 114, 77-84.**

Stössel R.P. and Prange A. (1985)
Determination of trace elements in rainwater by total-reflection X-ray fluorescence. **Analytical Chemistry**, **57**, 2880–2885.

Tanaka R., Makishima A., Kitagawa H. and Nakamura E. (2003)
Suppression of Zr, Nb, Hf and Ta coprecipitation in fluoride compounds for determination in Ca-rich materials. **Journal of Analytical Atomic Spectrometry**, **18**, 1458–1463.

Taylor S.R. and McLennan S.M. (1985)
The continental crust: its composition and evolution. **Oxford: Blackwell Press**, **1**, 312.

Umashankar V., Radhamani R., Ramadoss K. and Murty D.S.R. (2002)
Simultaneous separation and preconcentration of trace elements in water samples by coprecipitation on manganese dioxide using D-glucose as reductant for $KMnO_4$. **Talanta**, **57**, 1029–1038.

Yeghicheyan D., Bossy C., Bouhnik Le Coz M., Douchet C., Granier G., Heimburger A., Lacan F., Lanzanova A., Rousseau T.C., Seidel J.-L. *et al.* (2013)
A compilation of silicon, rare earth element and twenty-one other trace element concentrations in the natural river water reference material SLRS-5 (NRC-CNRC). **Geostandards and Geoanalytical Research**, **37**, 449–467.

Yokoyama T., Makishima A. and Nakamura E. (1999)
Evaluation of the coprecipitation of incompatible trace elements with fluoride during silicate rock dissolution by acid digestion. **Chemical Geology**, **157**, 175–187.

Tables

Table 1: Sample detection limit by *C*=50 and blank of FDC-ID-IS method.

Table 2: Element abundances of river water SLRS5 determined by analyses with and without FDC (this study, n=4), and those determined using ICP-MS without FDC (Yeghicheyan *et al.* 2013), together with certified values. A standard deviation of analyses by this study, that by Yeghicheyan *et al.* (2013), and that by certified values are also shown.

Table 3: Abundances of 52 elements of drinking waters from five geological sources determined by FDC-ID-IS. Acquisitions were duplicated (n=2).

Figures

Figure 1: Chain of operations under FDC-ID-IS method. Two batches of sample solution (river water SLRS5 and drinking waters) were acidified to 0.05 mol l^{-1} HNO_3 and freeze dried. Following freeze drying, the sample was collected, digested, dried, and redissolved. Then solutions was mixed with spike solutions and 6 acquisitions were conducted by ICP-MS.

Figure 2: Ion signal as a function of concentration HNO_3 from 0.1 to 1.0 mol l^{-1}. Ion signal is normalized to that obtained at HNO_3 0.5 mol l^{-1}. No hydrolysis of cation was observed with concentration of HNO_3 ≥0.3 mol l^{-1}. The grey area corresponds to a deviation of ± 10%.

Figure 3: Matrix-affected signal suppression as a function of concentration of NaCl. Ion signal is normalized to that obtained for solutions with no added NaCl. A standard deviation of duplicates is shown by the error bars. The dotted lines correspond to NaCl concentration of river water SLRS5 with or without pre-concentration. The grey area corresponds to a deviation of ± 10%. (a) Major- and transition-elements determined by ICP-SFMS. (b) Trace elements determined by ICP-QMS.

Figure 4: Determination of Eu in solutions that varied in Ba/Eu ratio from 182 to 5×10^5. The abundance is normalized to that obtained at Ba/Eu ratio of 182. The grey area corresponds to a deviation of ± 10%. Uncertainties of Eu abundance resulting from that of oxide-to-atomic-yield $\Delta\Theta_{\mathrm{BaO/Ba}}$ of ±1%, ±5%, and ±10% are shown by curves. Eu abundance is determined with uncertainty <10% when Ba/Eu ratio is $<5 \times 10^4$.

Figure 5: Recovery yield (Ω) of elements after freeze-drying pre-concentration. The grey area corresponds to a deviation of ± 10%.

Figure 6: Comparison of average results for river water SLRS5 with FDC (this study) and those without FDC (this study and 5 laboratories using ICP-MS from Yeghicheyan *et al.* 2013, Table 2). The difference is defined as deviation of element abundances

relative to that determined by analysis with FDC (this study). Data for P ($\Delta = -68\%$; Yeghicheyan *et al.* 2013) is located out of the plot. The grey area corresponds to a deviation of ± 10%. Note that on analysis with FDC (this study), element abundances of Na, Mg, Al, P, K, Ca, Sc, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, and Ga were determined by $C < 1$ after redilution from $C \sim 50$.

Figure 7: Relative differences of duplicated analyses applied to five geological sourced waters as function of element abundances. The grey area and dotted lines correspond to relative difference of 0–10% and 20%, respectively. Relative differences of > 20% are often observed in the range of ≤pg g^{-1}, but also in the range from pg g^{-1} to ng g^{-1} such as Zr, Co, Zn, and Fe. The observation implies that precision is not only controlled by signal intensity, but also by possible existence of particles, as described in the text.

Figure 8: Abundances of 52 elements of drinking waters from five geological sources determined by FDC-ID-IS method. Element abundances were normalized by those of upper crustal continents (Rudnick and Gao 2003) and aligned as a function of solubility of elements estimated from partition coefficient between seawater and upper crust (Taylor and McLennan 1985, Rudnick and Gao 2003, Li *et al.* 2011). The dotted line indicates sample detection limit for $C \sim 180$ and arrows indicate that the element abundances were below detection limit. Element abundances of Na, Mg, Ca, K, P, V, Ni, Cu, Zn, Mn, Co, Ga, Sc, Al, Ti, and Fe were determined by $C < 1$ after redilution from $C \sim 180$.

Supporting information

Tables

Table S1: Analytical condition by ICP-QMS

Table S2: Analytical condition by ICP-SFMS

Table S3: Total yields (Λ) and atomic yields (Ψ).

Table S4: Recovery yields Ω on FDC estimated by element abundances (ng g^{-1}) of reference solutions X1 and X2 determined with and without FDC (n=4).

Table S5: Abundances of major elements shown on labels of drinking waters from five geological sources. Unit is in μg g^{-1}.

Figures

Figure S1: Comparison of analytical precision on analyses of river water SLRS5 with FDC (this study) and those without FDC (this study and 5 laboratories using ICP-MS from Yeghicheyan *et al*. 2013, Table 2). Gray area corresponds to analytical precision from 0 to +10%. Note that on analysis with FDC, element abundances of Na, Mg, Al, P, K, Ca, Sc, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, and Ga were determined by $C < 1$ after redilution from $C \sim 50$.

Figure S2: Abundances and analytical precisions of REE determined by FDC-ID-IS compared with those by Yeghicheyan et al. (2013), and Heimburger et al. (2013). Element abundances are normalized by those of CI chondrite (Anders and Grevesse 1989). Standard deviation (1σ) and expanded uncertainty (U = kσR with k = 1 that described in Yeghicheyan et al. 2013) are shown for FDC-ID-IS and Heimburger et al. (2013), and Yeghicheyan et al. (2013), respectively.

Figure S3: Abundances of REE of drinking waters from five geological sources (n=2) and Ottawa river SLRS5 (n=4) determined by FDC-ID-IS. Relative difference of duplicates is shown by error bar. Analytical uncertainty of SLRS5 is within symbol. The dot line indicates sample detection limit (C~180). Element abundances were normalized by those of CI chondrite (Anders and Grevesse 1989).