INAA trace element analysis of stream sediments collected from the northeastern areas of Aichi Prefecture, central Japan

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ABSTRACT

Geochemistry and Cosmochemistry Laboratory, Nagoya University, started a geochemical mapping project in 1994 to make environmental assessment of the Chubu area in Japan. During ten years from 1994 to 2004, stream sediment samples of 1,563 were collected in the northeastern parts of Aichi Prefecture. Major element data of these samples by X-ray fluorescence spectrometry (XRF) and the discussion on their regional spatial distributions have been published. Here we report 22 element analysis (Sc, Cr, Fe, Co, Zn, As, Rb, Sb, Cr, Ba, La, Ce, Sm, Eu, Tb, Yb, Lu, Hf, Ta, Au, Th and U) of the sediment samples by instrumental neutron activation analysis (INAA), together with discussion on the accuracy and precision of our analytical method by INAA.

A new automated γ-ray counting and data processing system for INAA and postal-delivery system of irradiated samples from Japan Atomic Energy Research Institute were utilized. The INAA system enables us simple and rapid INAA analysis of a large number of samples. By using this system, nine GSJ rock reference samples (JB-1a, JB-2, JA-1, JG-1a, JG-2, JLk-1, JSd-1, JSd-2 and JSd-3) and one USGS rock standard G-2 were analyzed to examine accuracy and precision of analytical results. The results show good agreement with the reference values, indicating that our analytical system is effective for analysis of stream sediments with various bedrock geology. On the other hand, in order to evaluate accuracy of the values obtained by INAA, comparison of analytical results of stream sediments by INAA with the previously analyzed data by inductively coupled plasma atomic emission spectrometry (ICP-AES), atomic absorption spectrometry (AAS) and XRF was made. The result indicates that the data by the ICP-AES and AAS methods, which need HF digestion of samples, could be lower than the true values for some elements due to partly incomplete decomposition of samples. The INAA method, which needs no HF digestion, is suitable for accurate analysis for a large number of samples in the geochemical mapping project.

We have collected stream sediments collected at the same site every year since 1994 to 2004. The samples were used to evaluate sample heterogeneity of the sediment collected at the same site. Most of trace elements, except for Cr, Zn, Hf and Au, of the samples show the concentrations with ±(30~50) % deviations, a little larger than the analytical errors. The Cr, Zn, Hf and Au concentrations have larger deviations, indicating the heterogeneous distribution of small accessory minerals at the sampling site and even in sample aliquots of 100 mg.

INTRODUCTION

Investigation of spatial distribution of element concentrations on the earth's surface is important for an environmental assessment from geochemical viewpoints. In recent years, many geochemical maps covering wide regions have been made to assess the environment of the ground. The geochemical maps in Japanese islands have been made for Akita Prefecture (Shiikawa et al., 1984), Northern Kanto area (Itoh et al., 1991; Kamioka et al., 1991), Fukuoka Prefecture (Takamoto et al., 2005), and nationwide regions in Japan (Imai et al., 2004; Ohta et al., 2004a, b). In 1994 we started a study of geochemical mapping based on chemical data of stream sediments in the area of Seto and Toyota Cities, mainly in the northeastern Aichi prefecture, central Japan, in order to make geoenvironmental assessment of the area (Tanaka et al., 1994) and to provide inexperienced students in geochemistry and geology with the training of sample collection and chemical analysis of geological samples (Tanaka et al., 2001). The distribution of element concentrations in stream sediments is mainly controlled by the surface geology of the drainage area. The geochemical mapping with high sampling density could give strict distribution of natural background concentrations of elements, and could also reveal artificial addition caused by a variety of different pollutants arising from human and industrial activities to the background. Trace elements in nature could be highly affected by anthropogenic contamination because their concentrations are low in natural substances while anthropogenic materials often contain trace elements with high concentration. For example, positive gadolinium anomalies in rare earth element patterns were observed in river waters in densely populated and industrialized areas (e.g., Bau and Dulski, 1996; Nozaki et al., 2000). The excess Gd may be derived from Gado-pentetic acid as medical agent for magnetic resonance imaging, which contains high concentration of Gd.

Among pollutants, heavy metals such as Cr, Cd, Pb, As, Cu, Ni, Zn and Co are the subjects of particular attention because of their long-standing toxicity when exceeding specific thresholds. For example, Cr is an essential engineering metal used in dozens of products such as stainless steel, and Cr^{6+} is a dangerous ion lethal to man. Uncontrolled development in industry, agriculture and urbanization accelerates the input of these heavy metals into the environment. Investigation of spatial distribution of the trace-element concentrations of stream sediments, therefore, is important for an environmental assessment.

During 10 years from 1994 to 2004, we have collected stream sediments of 1,563 samples in the northeastern Aichi prefecture, and some regionally limited geochemical maps were reported (Tanaka et al., 1994, 1995, 1996; Togami et al., 1997; Yamamoto et al., 1998; Asahara et al., 2006). It is important to officially present data of element concentrations in the stream sediments for further geochemical investigations and geoenvironmental assessments. All of major-element concentrations in the stream sediments by X-ray fluorescence spectrometry (XRF) were summarized in Minami et al. (2005), and geochemical investigations were made in Yamamoto et al. (2006) based on the major-element data. In this study, trace-element data of the stream sediments by instrumental neutron activation analysis (INAA) is reported. A part of trace-element concentrations in some sediment samples have been already measured

for Ce, Co, Cr, Cu, Ni, Sr, V and Zn by inductively coupled plasma atomic emission spectrometry (ICP-AES) and for Fe by atomic absorption spectrometry (AAS) in Tanaka *et al.* (1994, 1995, 1996), Togami *et al.* (1997), and Yamamoto *et al.* (1998). However, the elemental concentrations by the ICP-AES and AAS methods could be lower than the true values for a part of elements when sample digestion with $HF-HNO_3-HClO_4$ is partly incomplete. The adequate decomposition for a longer time is needed to get more reliable data but difficult, because many elements of a large number of stream sediment samples have to be analyzed for a limited time for geochemical mapping. On the other hand, the INAA is a method with non-destructive preparation, and provides the simultaneous measurement of many elements with adequate precision in widely varying concentration. Here we discuss on (1) precision and accuracy for the INAA system based on analytical results of several Geological Survey of Japan (GSJ) and United States Geological Survey (USGS) reference rocks, (2) comparison of the INAA data of stream sediments with data by ICP-AES, AAS and XRF, and (3) sampling heterogeneity in the stream sediment analysis, and (4) results of the INAA study of 1,563 stream sediment samples collected in the northeastern parts of Aichi Prefecture during 1994 to 2004.

SAMPLING POINTS AND GEOLOGY

The studied area is located in the northeastern Aichi Prefecture, a part of the south of Gifu Prefecture, and a part of the west of Shizuoka Prefecture. Sample locations and their geological features in this study are shown in Minami *et al.* (2005). The various geological features with variable distributions of background elements are situated in the sampling areas, and the area is proper for basic study about assessment of background element concentrations.

The Mino Terrane, which comprises a Jurassic accretionary complex of sandstone, mudstone and chert, is distributed in the northwest of the study area. The Cretaceous Ryoke belt, which comprises mafic to felsic plutonic rocks and low P/T metamorphic rocks, is distributed throughout southwest to northeast in the area. Four different Cretaceous granitic rocks, Naegi-Agematsu, Inagawa, Busetsu, Obara Granites, are exposed in the area. These volcanic, plutonic and metamorphic basements are covered by Miocene sedimentary and volcanic rocks (the Mizunami and Shitara Groups) and by Pliocene non-marine sediments (the Seto Group). Quaternary sediments also cover the basements in the southwestern part.

ANALYTICAL METHODS

We have already set up a new automated γ-ray counting and data processing system for INAA (Shibata *et al.*, 2001), following the INAA system of Tanaka *et al.* (1988). The system is equipped with a computer-controlled sample changing apparatus, which enables sequential analysis of twenty samples. Measurements and analyses of γ-ray spectra are made automatically using a personal computer connected to a multi-channel analyzer in INAA at Radioisotope Center in Nagoya University. Furthermore, we have set up to get irradiated samples as postal delivery materials with L-typed radioactivity

Table 1   Analytical results for various standard rocks standardized with a USGS rock standard BCR-1 and their referenced values (Imai et al., 1995, 1996; Gladney et al., 1990, 1992).

element	Basalt				Andesite		Granite						Stream sediment						Lake sediment	
	JB-1a[1]	*JB-1 ref.[2]*	JB-2	*JB-2 ref.[2]*	JA-1	*JA-1 ref.[2]*	JG-1a	*JG-1a ref.[3]*	JG-2	*JG-2 ref.[3]*	G-2	*G-2 ref.[4]*	JSd-1	*JSd-1 ref.[3]*	JSd-2	*JSd-2 ref.[3]*	JSd-3	*JSd-3 ref.[3]*	JLk-1	*JLk-1 ref.[3]*
Sc (ppm)	27.9	27.0±0.65	55.6	53.5	27.7	28.5	5.99	6.21	2.2	2.42	3.32	3.5	10.7	0.25	18.1	17.5	11.0	10.5	15.5	15.9
Cr (ppm)	380	433±11.4	28	28.1	9	7.83	18	17.6	10	6.37	10	8.7	24	21.5	105	108	36	35.3	63	69
Fe (%)	6.25	6.14±0.17	10.2	9.97	4.76	4.95	1.33	1.4	0.650	0.68	1.79	1.88	3.48	3.54	8.13	8.15	3.02	3.05	4.69	4.85
Co (ppm)	37.1	36.1±0.9	37.6	38	10.5	12.3	5.0	5.9	4.1	3.62	4.1	4.6	10.4	11.2	48.1	48.4	12.2	12.7	17.4	18
Zn (ppm)	96	92.4±19	130	108	120	90.9	41	36.5	15	13.6	63	86	80	96.5	1400	2056	110	136	120	152
As (ppm)	2	0.93±0.13	2	2.87	2	2.78	n.d.	0.43	n.d.	0.68	n.d.	0.07	1.6	2.42	30.0	38.6	187	252	18.3	26.8
Rb (ppm)	40	33.1±5.31	n.d.	7.37	n.d.	12.3	160	178	280	301	160	170	60	67.4	30	26.9	280	285	140	147
Sb (ppm)	n.d.	n.d.	n.d.	0.25	n.d.	0.22	n.d.	0.048	n.d.	0.057	n.d.	0.07	0.5	n.d.	14	12.5	2.1	2.78	2	1.68
Cs (ppm)	1	1.31	n.d.	0.85	0.9	0.62	10	10.6	7	6.79	1	1.34	2	1.89	0.9	1.07	30	30.6	10	10.9
Ba (ppm)	540	462±37	190	222	300	311	480	470	100	81	1900	1882	510	520	1200	1199	530	462	610	574
La (ppm)	31.5	36.1±0.87	n.d.	7.78	n.d.	5.24	31.2	21.3	43.9	42.2	69.7	89	13.1	18.1	n.d.	11.3	21.9	19.8	47	40.6
Ce (ppm)	66.7	63.6±2.36	8	6.76	14	13.3	51.3	45	49.2	48.3	158	160	33.7	34.4	22	23.4	42.0	42	86.4	87.9
Sm (ppm)	4.76	5.14±0.14	1.82	2.31	2.21	3.52	4.13	4.53	7.47	7.78	5.87	7.2	2.42	3.48	2.12	2.68	2.39	3.26	5.79	7.87
Eu (ppm)	1.5	1.41±0.1	0.9	0.86	1.1	1.2	0.74	0.7	0.1	0.1	1.5	1.4	0.99	0.925	0.83	0.81	0.80	0.686	1.4	1.27
Tb (ppm)	0.6	0.62±0.12	0.6	0.6	0.6	0.75	0.8	0.81	1.8	1.62	0.5	0.48	0.5	0.431	0.4	0.44	0.5	0.368	1	1.23
Yb (ppm)	1.9	1.97±0.08	2.5	2.62	2.5	3.03	2.7	2.7	7.7	6.85	0.89	0.8	1.2	1.18	1.7	1.67	1.5	1.4	3.6	3.99
Lu (ppm)	0.35	0.29±0.02	0.41	0.4	0.42	0.47	0.49	0.44	1.4	1.22	0.13	0.11	0.22	0.186	0.33	19.2	0.201	0.196	0.63	0.571
Hf (ppm)	3.3	3.45±0.18	2	1.49	2.4	2.42	3.9	3.59	7.0	4.73	8.79	7.9	3.5	3.55	3.4	2.7	3.9	3.21	3.7	3.78
Ta (ppm)	2	2.12±0.18	n.d.	0.13	n.d.	0.13	2	1.9	2	2.76	0.8	0.88	0.8	0.893	0.4	0.515	0.6	0.687	1	1.57
Au (ppb)	n.d.	n.d.	n.d.	0.564	n.d.	0.16	n.d.	0.21	n.d.	0.059	n.d.	1.03	n.d.	0.064	65	54.6	8	5.66	6	5.42
Th (ppm)	8.82	9±0.35	n.d.	0.35	0.7	0.82	12.5	12.8	27.8	31.6	23.7	24.7	4.4	4.44	2.3	2.33	7.29	7.79	18.6	19.5
U (ppm)	2	1.47±0.17	n.d.	0.18	n.d.	0.34	4	4.69	9	11.3	2	2.07	0.8	1	2	1.1	2	1.66	3	3.83

1) Data from Shibata et al. (2001)
2) Recommended values from Imai et al. (1995)
3) Recommended values from Imai et al. (1996)
4) Recommended values from Gladney et al. (1992)
5) n.d.: not determined

(<5μSv/h at the surface of the pack) using the postal transportation directly from Japan Atomic Energy Research Institute (JAERI), where samples are irradiated. The condition that 10~20 samples with about 120 mg each are irradiated for 5 minutes in the JRR-3 or JRR-4 reactor of JAERI is proper for the postal system of irradiated samples and also for adequate measurements of γ-rays in samples after irradiation. The postal-transportation system enables us the INAA analysis of many samples, several hundreds of samples per year, because we do not have to go to JAERI at every irradiation of samples.

The sediment samples were collected from the bottom of small streams branching upward from the main rivers, with high sampling density of one sediment sample per about 1.5 km^2. The collected sediment samples were passed through 16 mesh (1 mm) sieve with stream water once, passed through 80 mesh (160 μm) sieve with stream water twice, and then filtered using commercial paper filters. The detailed sampling method of stream sediments is shown in Tanaka et al. (2001). Trace-element composition in the sediment samples was measured by INAA. About 120 mg of a sample was put into a plastic bag and irradiated for 5 minutes together with the standards in the JRR-3 (f=1×10^{14} n/cm^{2}s) or JRR-4 (f=8×10^{13} n/cm^{2}s) in JAERI. The γ-rays were detected by the Ge detector (GEM359150, EG&G ORTEC) energized at 3500V at Radioisotope Center in Nagoya University. The measurement of γ-rays was performed twice: The first measurement (6000–8000s per one sample) was performed at about 5 to 7 days after irradiation, and the second (12000–15000s per one sample) was performed after cooling of about 3 weeks to 2 months. The standards used in the INAA are basalt JB-1a, one of the GSJ reference rocks, for measurements of all elemental concentrations except for As, Sb and Au in stream sediments, and a standard solution containing As, Sb and Au with concentration of 20 ppm each (As-Sb-Au standard solution) was used because JB-1a has comparatively low As, Sb and Au concentrations. The more detailed procedure of the INAA system is shown in Shibata et al. (2001).

RESULTS AND DISCUSSION

1. Precision and accuracy of the INAA method

In order to evaluate the precision and accuracy of our INAA method, various GSJ reference samples, basalts JB-1a and JB-2, andesite JA-1, granites JG-1a and JG-2, stream sediments JSd-1, JSd-2 and JSd-3, and lake sediment JLk-1, and one USGS reference rock, granite G-2 were analyzed by use of a USGS rock standard basalt BCR-1 and the As-Sb-Au standard solution as the INAA standards. The results are listed in Table 1, together with recommended or preferable values in the GSJ and USGS rocks (Imai et al., 1995, 1996; Gladney et al., 1992). The elemental concentration data for USGS BCR-1 is from Gladney et al. (1990). In Table 1, the data with analytical errors of <3% are shown in three significant digits, those with errors of 3% to 10% are in two significant digits, and those with errors of >10% are in one significant digit. The precision of the INAA method is mostly <3% for Sc, Fe, Co, La, Ce, Sm and Th, and several % for Cr, As, Eu, Yb, Lu, Hf and Au. The data of Zn, Rb, Sb, Cs, Ba, Tb, Ta and U often have large analytical errors of 10% to 20%.
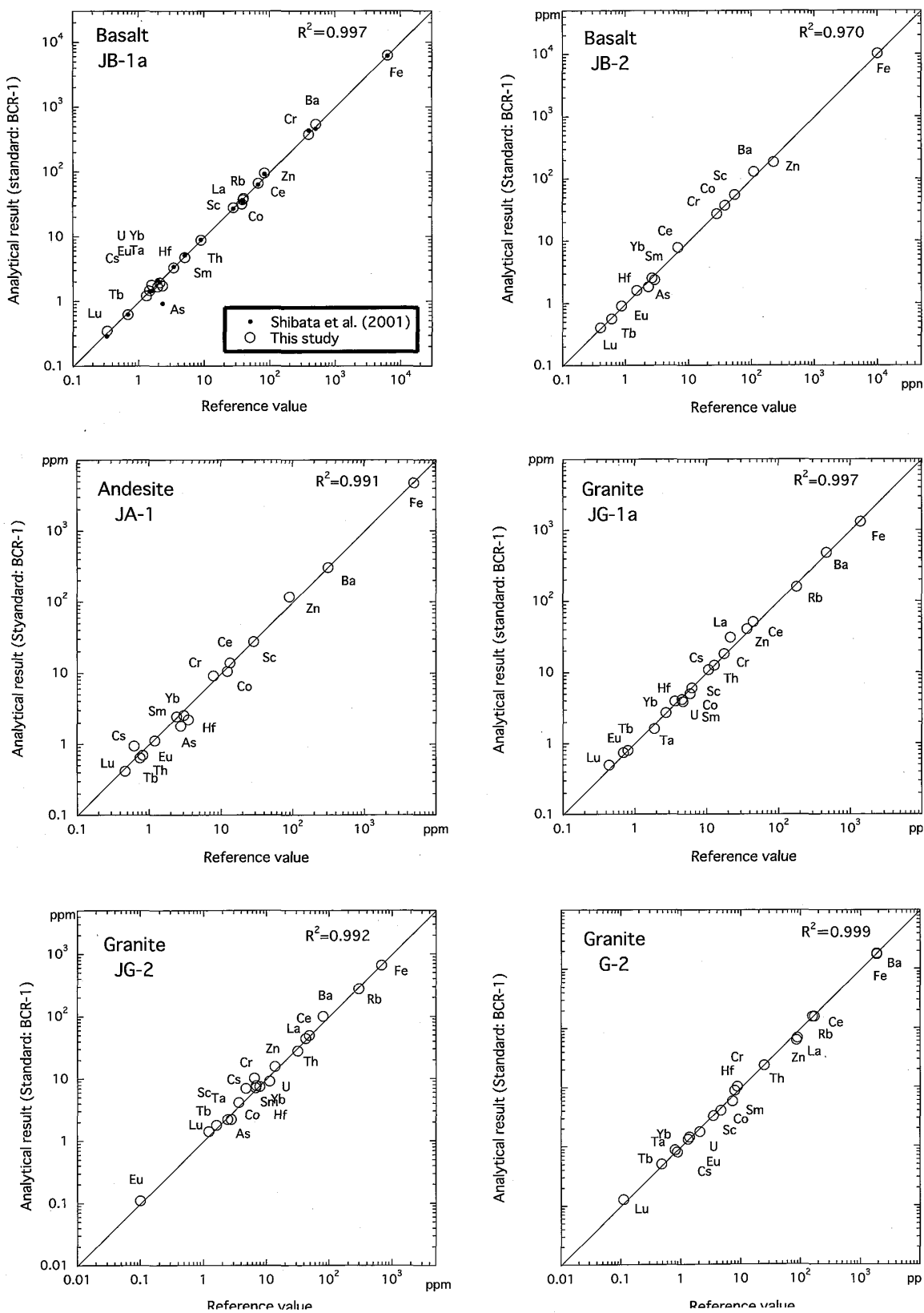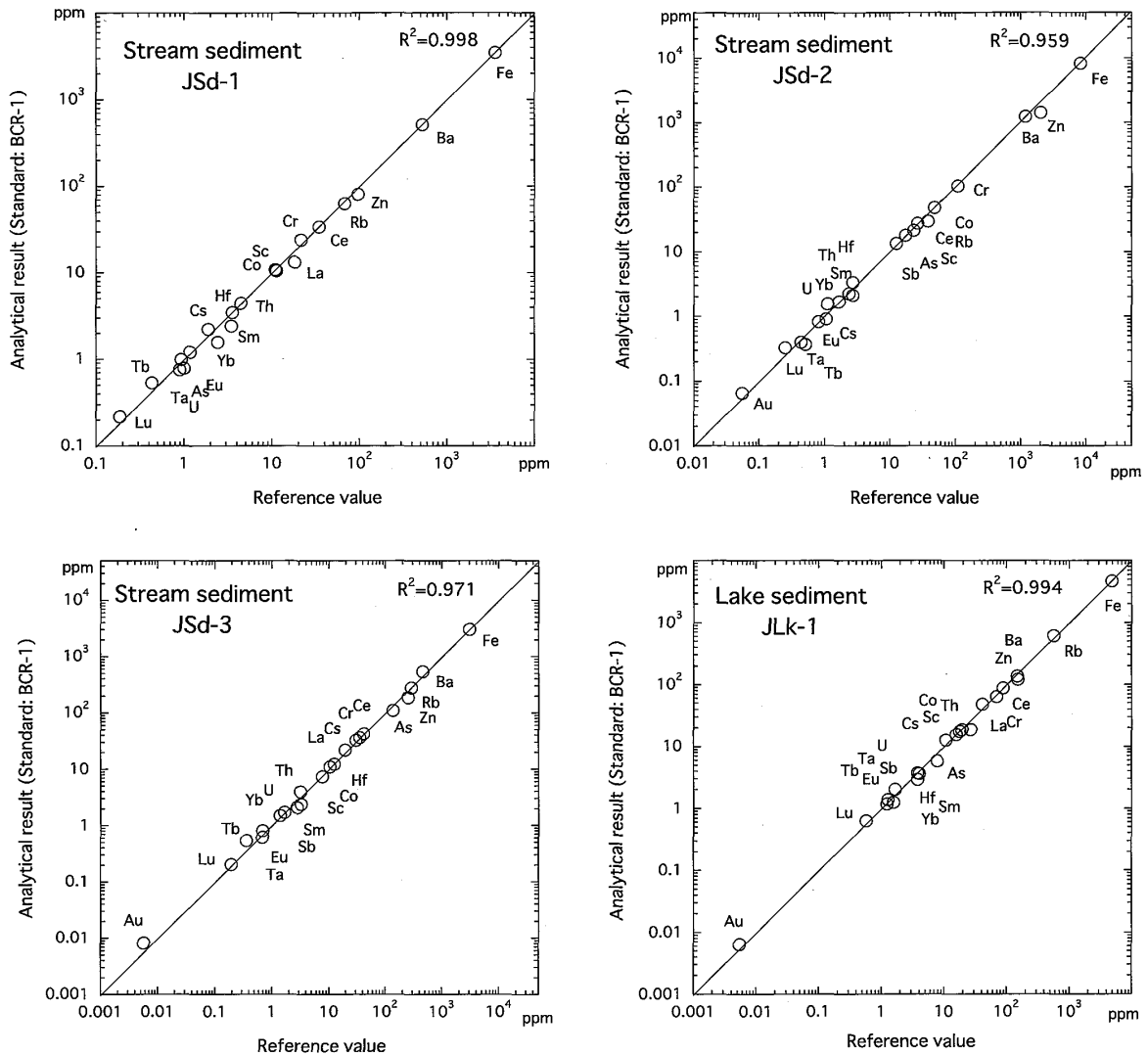
Fig. 1-1

Fig. 1-2

Fig. 1 Comparison of analytical results for various standard rocks standardized with a USGS rock standard BCR-1 and their referenced values (Imai *et al.*, 1995, 1996; Gladney *et al.*, 1990, 1992).

Analyzed values and the recommended values in nine GSJ and one USGS standard rocks are compared in Fig. 1. The correlation coefficient between the analyzed and recommended values is also shown in Fig. 1. The analytical results of the standard rocks are mostly consistent with the reference values. The slightly scattered values from the reference values might be due to analytical errors on INAA, sample hetero-geneity of the standard rocks, and partly uncertain preferable values of elemental concentrations in the BCR-1 standard. For example, the scattered values for Ba and Zn might be derived mainly from analytical errors in the INAA. The larger scattering in correlation plots in stream sediment reference rocks, JSd-2, JSd-3, might be derived from sample heterogeneity in the standard rocks, and the reference value of As con-centration in BCR-1 standard may be uncertain. The compiled value of As in BCR-1, 0.65 ppm (Gladney *et al.*, 1990), could be lower than its true value, and so the As

concentration for JB-1a by Shibata *et al.* (2001) is lower than the GSJ reference value, 2.3 ppm (Imai *et al.*, 1995), where BCR-1 was used for INAA as the standard. In this study, the As-Sb-Au standard solution was used for determining of As concentrations in ten standard rocks, and the results are consistent with the reference values. The use of the standard solution enables us more accurate measurement on As.

Our results show that the various rocks such as basalt, andesite, granite, lake sediments and stream sediments can be analyzed with adequate accuracy by the INAA system using a basalt standard and the As-Sb-Au standard solution. In the measurements of stream sediments, we used JB-1a, which is basalt similar to BCR-1, and the As-Sb-Au standard solution. The elemental concentrations determined by the INAA system for stream sediments could be enough reliable on any stream sediments with various bedrock geology of the sampling points.

2. Trace-element concentrations of stream sediment samples

Trace-element concentrations in the sediment samples are not listed here in the limited space of this Journal, but they can be distributed on request. See the note in the end of this paper. The INAA data by Togami *et al.* (1997) are also combined together with our data. The sample irradiation condition of Togami *et al.* (1997) is different from our experiment: about 350 mg of a sediment sample was put into a plastic bag, and irradiated for 6 hours in the TRIGA-II reactor (f=1×10^{12} n/cm^{2}s) of Institute for Atomic Energy, Rikkyo University. Their data might have different precision from our data, and the published data are put as it is in our data.

Twenty-four samples were analyzed two times. The duplicated analyses started with pack of samples from the same sample bottle into each plastic bag, and the irradiation and γ-ray counting were made separately. The duplicated analytical results are consistent well with each other. The deviation of duplicated results is mostly less than 5%, though some elements such as Au and U show deviations of about 10%.

The variations of elemental concentrations classified according to the bedrock geology of the sampling points are shown in Fig. 2. The stream sediments sampled from granitic areas have higher concentrations of rare earth elements, Hf, Th and U and lower concentrations of As, Au, Co and Cr than those from areas of sedimentary bedrock. The stream sediments sampled from different granitic rock areas of Naegi-Agematsu, Inagawa, Busetsu, Obara Granites tend to have different variations of the elemental concentrations. Detailed geochemical discussion on the distribution of the elemental concentrations in stream sediments will be made elsewhere.

3. Comparison of analytical data by ICP-AES, AAS and XRF with those by INAA

Some of the samples were already measured for Ce, Co, Cr and Zn by ICP-AES and for Fe by AAS and XRF in previous studies (Tanaka *et al.*, 1994, 1995, 1996; Togami *et al.*, 1997; Yamamoto *et al.*, 1998; Minami *et al.*, 2005). The analytical method for ICP-AES and AAS is as follows: A sediment sample is digested with HF-HNO$_3$-HClO$_4$ in an open Teflon beaker, and after dryness it is dissolved in HCl, and then insoluble materials in the sample solution are removed by filtering. In order to evaluate precision and accuracy of the INAA method, the analytical results of Cr, Co,
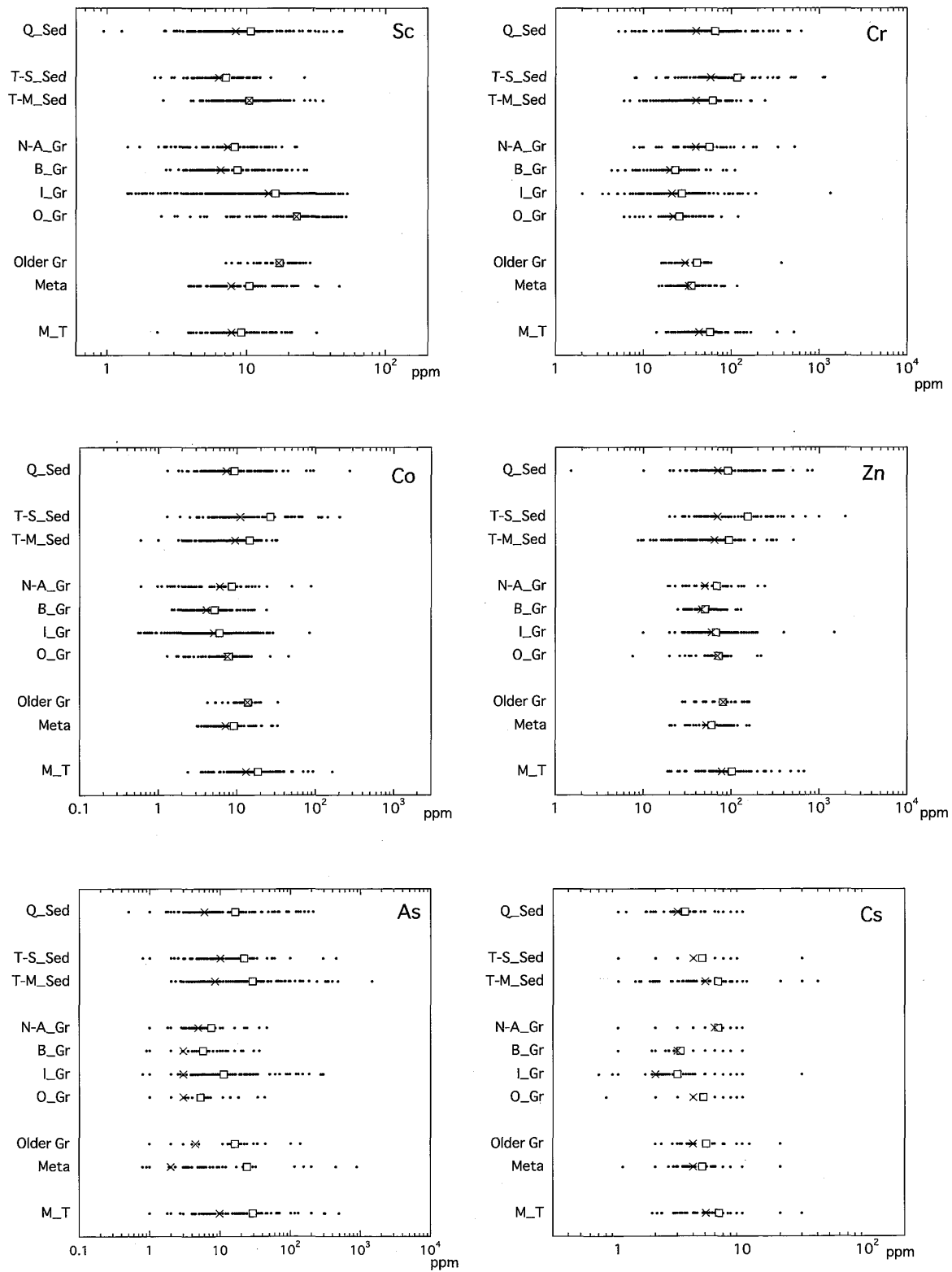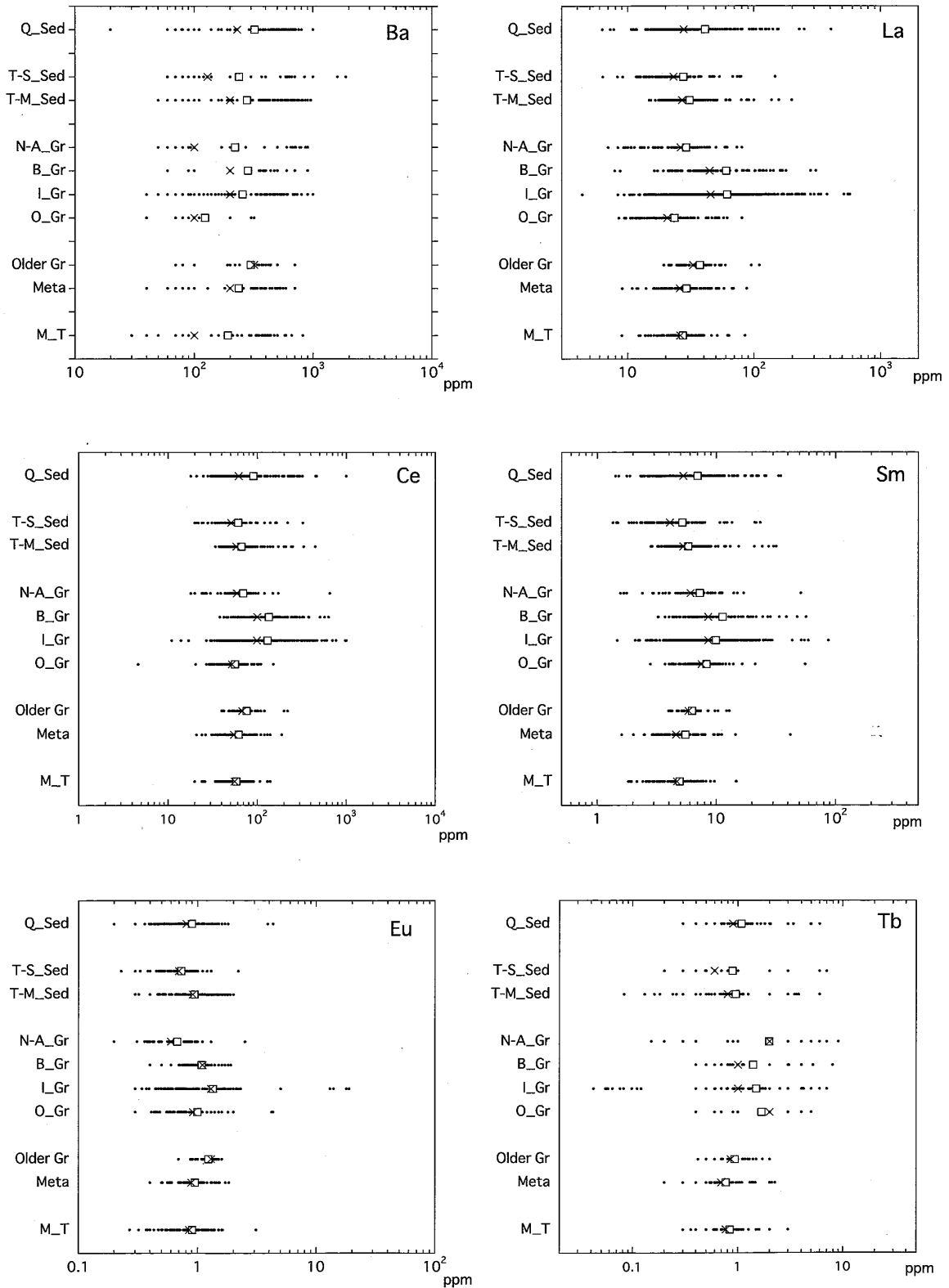
Fig. 2-1

Fig. 2-2

Fig. 2 Plots of some elemental concentrations classified according to the bedrock geology of
sampling point. Q_Sed, Quaternary sediments; T-S_Sed, Sedimentary rocks of the Tertiary
Seto Group; T-M_Sed, Sedimentary rocks of the Tertiary Mizunami Group; N-A_Gr, Naegi-
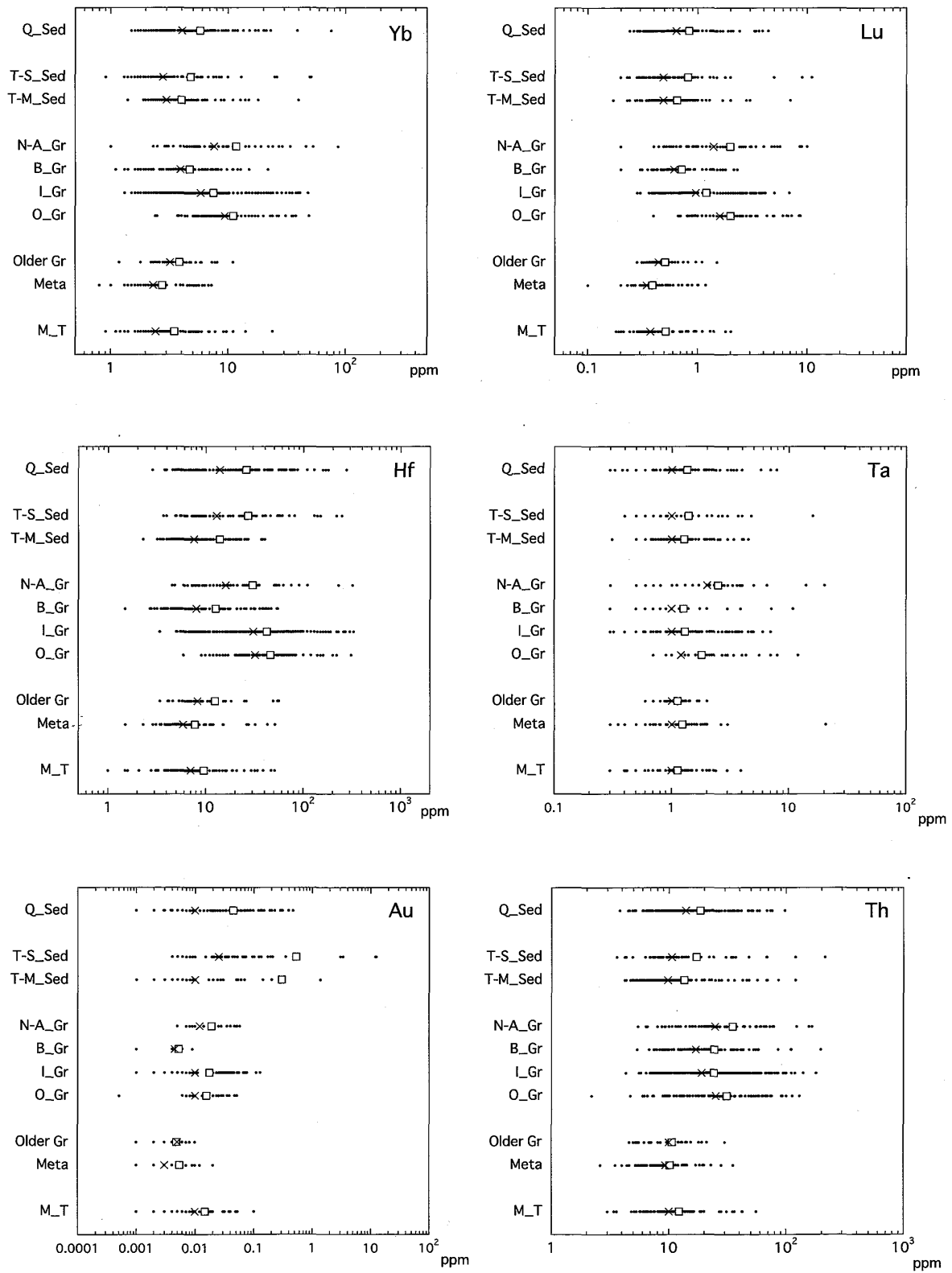Agematsu Granite; B_Gr, Busetsu Granite; I_Gr, Inagawa Granite; O_Gr, Obara Granite;

Fig. 2-3

Older Gr, Older Ryoke Granite; Meta, Ryoke Metamorphic Rocks, and M_T show, the Mino Terrane belt. Mean and median values are expressed by open squares and crosses, respectively.
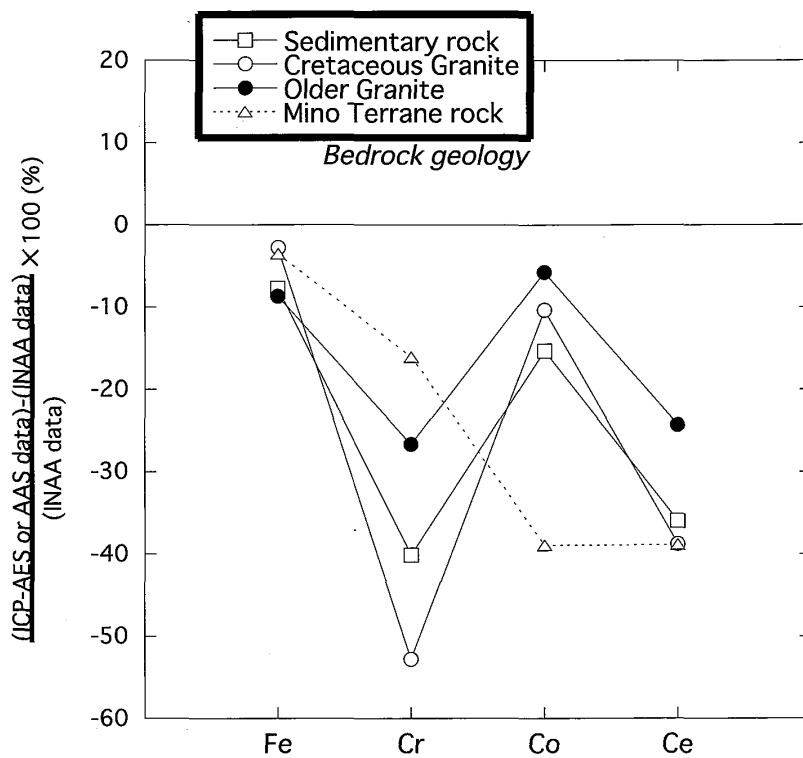
Fig. 3   The relative deviations of ICP-AES data from INAA data for sediment samples classified according to their bedrocks.
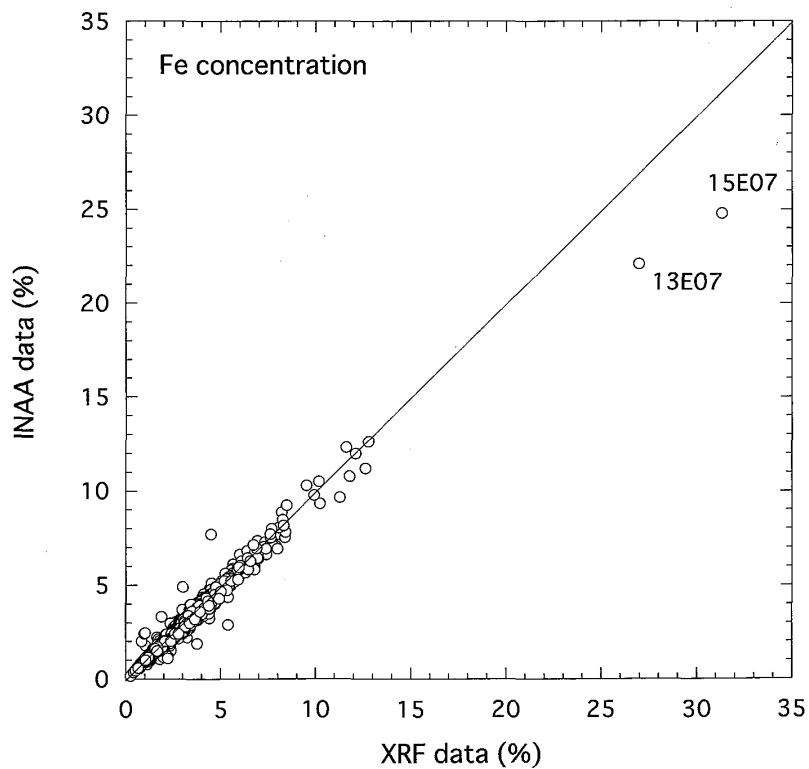
Fig. 4   Fe concentration data measured by INAA compared with those by XRF.

Ce and Fe, except for Zn with large analytical errors, by INAA are compared with those by ICP-AES and AAS. The deviation rate of the ICP-AES and AAS data from the INAA data for sediment samples collected from the various geological areas is shown in Fig. 3. The concentrations of Fe, Cr, Co and Ce by the ICP-AES and AAS methods are lower by <10%, 20~60%, 10~20% and 20~40% than those by our INAA method, respectively. The degrees of the deviations are hardly different among the samples collected from different geological bedrocks, but a little larger in samples collected from areas of sedimentary and Cretaceous granitic bedrocks. The results indicate that sample digestion by $HF-HNO_3-HClO_4$ was partly incomplete and the data by the ICP-AES and AAS methods could be lower than the true values for a part of elements. The larger deviation of Cr could be due to incomplete digestion of chromite and magnetite, which contain high Cr concentration, in samples, especially samples collected from areas of sedimentary and Naegi-Agematsu granitic bedrocks, where distribution of high Cr concentration is observed (Fig. 2). The heavy minerals such as chromite, magnetite and zircon are strong to digestion with HF. Tanaka *et al.* (1996) reported that analyses of JG-1a and JB-1a for Al, Ce and Cr by the ICP-AES method negatively deviate by about 20~30% from the reference values. The deviation value is roughly consistent with our result.

Comparison of Fe concentration data measured by INAA with data by XRF is shown in Fig. 4. The INAA data are very good agreement with the XRF data, though the samples 15E07 and 13E07 with high Fe concentrations have different INAA values from the XRF ones. The XRF data are calibrated by some GSJ reference rocks with Fe concentration of 0.5% to 11% in this study, and thus Fe calibration curve should not be used out of the concentration range. The XRF values of 15E07 and 13E07 are 24.8% and 22.1%, 6.5% and 4.5% lower than the INAA values respectively, are not reliable because they are out of the calibration range. Therefore, the INAA data are preferable in case of determination of very high Fe concentrations of stream sediments.

A large number of samples should be analyzed in a short time for the geochemical mapping project, and adequate decomposition of each sample for a long time is difficult. The INAA method, which needs no HF digestion of a sample and gives data of many elemental concentrations with adequate precision and accuracy, is suitable for the geochemical mapping project.

4. Representativeness of stream sediments in the sampling areas

Stream sediment samples mostly represent the averaged chemical characteristics of bedrocks in the upstream area. The previous papers ascertained that chemical compositions of stream sediments in the area of granitic bedrocks are systematically different from those in the area of sedimentary rocks (Tanaka *et al.*, 1994, 1995, 1996, 2001; Togami *et al.*, 1997; Yamamoto *et al.*, 1998, 2007). However, analytical results of the sediment samples contain some errors due to analytical procedure, sample heterogeneity inside a sample collected in a bottle, and heterogeneous distribution of sediment at a sampling site (Tanaka *et al.*, 1995; Togami *et al.*, 1997). Tanaka *et al.* (1996) reported that the analytical errors are smaller than the deviation caused by the heterogeneity in a stream sediment, and that heterogeneity of mineral particles in a stream sediment at the sampling site could affect largely to the deviation.
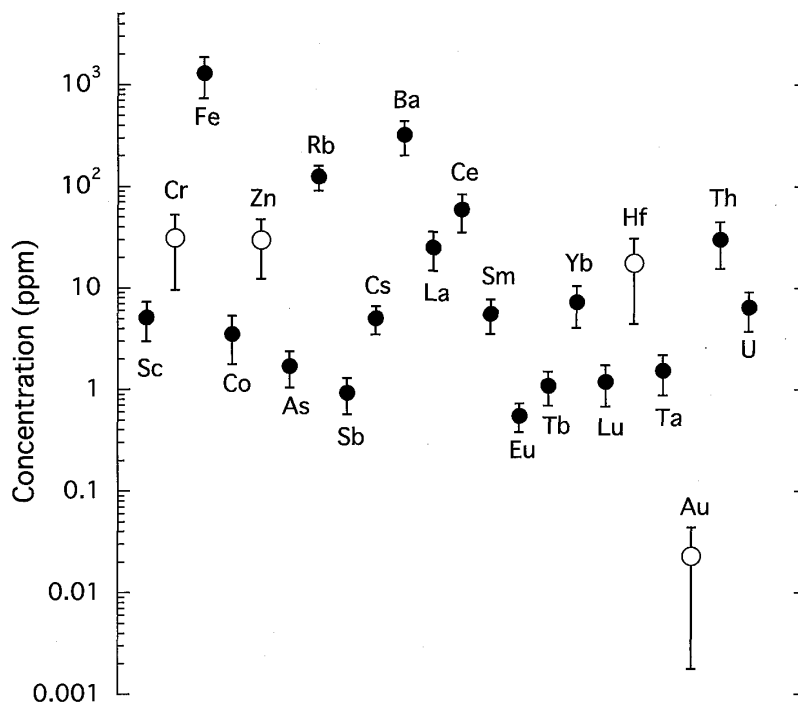
Fig. 5   Analytical data of stream sediments collected at same sampling site every
year from 1994 to 2004. Bars show standard deviations (1σ).

In order to evaluate sampling heterogeneity in a stream sediment, we have collected
stream sediments at the same spot for sampling (35° 11' 43" N, 137° 6' 8" E), where
Quaternary sedimentary bedrocks are distributed, every year since 1994 to 2004. Most
of major elements of the sediments at the site showed the concentrations with ±20%
deviations while Ti and P showed relatively fluctuated concentrations (Minami et al.,
2005), while most of trace elements, except for Cr, Zn, Hf and Au, of the samples
showed the concentrations with ±(30~50) % deviations, a little larger than the analyti-
cal errors (Fig. 5). The data are not listed here in the limited space, but they can
be distributed on request, as will be noted in the end of this paper. The Cr, Zn, Hf
and Au concentrations have larger deviations, probably by the heterogeneity of the
stream sediment but analytical errors. Trace-element concentrations in a sediment
sample could be significantly perturbed by heterogeneous distribution of the elements
at the sampling site, and even in the collected sample in a bottle, when compared
with major-element concentrations. The amount of sediment samples used in XRF
is about 700 mg, whereas that in INAA is about 120 mg, and the values obtained by
INAA is relatively affected by sample heterogeneity. The high deviations in Cr, Zn,
Hf and Au might be caused by heterogeneous distribution of small accessory miner-
als such as chromite, magnetite and zircon at the sampling site, and heterogeneous
sample aliquots used in INAA analysis.

Furukawa et al. (2004) reported that major elements and most of trace elements,
except for Th, Y and Zr, in stream sediments show no seasonal changes. Our sampling
of stream sediments has been usually carried out in every April, and therefore the
fluctuations of elemental concentrations might not contain seasonal change but secular

change. We need study in detail about secular change of elemental concentrations in the stream sediments at the same spot. Discussion on fluctuated concentrations of trace elements together with major elements according to sampling year and month will be made elsewhere.

SUMMARY

We have utilized a postal-delivery system of irradiated samples directly from JAERI, in addition to the automated γ-ray counting and data processing system for INAA (Shibata et al., 2001) for simple and rapid INAA analysis of a large number of sediment samples in the geochemical mapping project. Analytical results of several rock reference samples have ensured that our INAA analytical system show acceptable accuracy and precision. Analysis of many elements of a large number of stream sediment sampled with high sampling density is most important for reliable geochemical mapping and detection of anthropogenic contamination. Our INAA system is most suitable for rapid, simple and accurate analysis of a large number of sediment samples.

By our INAA system, more than 1,500 sediment samples collected in the northeastern parts of Aichi Prefecture, central Japan were analyzed for 22 elements (Sc, Cr, Fe, Co, Zn, As, Rb, Sb, Cs, Ba, La, Ce, Sm Eu, Tb, Yb, Lu, Hf, Ta, Au, Th and U). The data of elemental concentrations for all of the sediments together with geological information were presented for database to geochemical mapping. The database is useful for detection of an anthropogenic contamination. Detailed geochemical discussion on the distribution of trace-elemental concentrations in stream sediments will be made elsewhere soon.

The database in this paper could be distributed to everyone by e-mail or by the medium of CD-ROM. The person who wants to use the database, please contact to the following personnel:

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