

Geochemical mapping of the northern area of Toyota City, Aichi Prefecture, central Japan: Distinct chemical characteristics of stream sediments between granitic and sedimentary rock areas

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ABSTRACT

Our study of geochemical mapping in the area of Toyota and Seto Cities, Aichi Pref., central Japan, has been further extended. This geochemical mapping, started in 1994 for the purpose of environmental assessment of this area, is based on chemical data of stream sediments of drainage systems distributed over the area. Cretaceous granitic basements occur widely in the eastern part, whereas late Cenozoic sedimentary rocks cover the basements in the western part. In 1996, we have extended the mapped area to the northeastern part of Toyota City, and collected new 66 samples. Since 1994, we have sampled stream sediments from 352 different locations in the area of approximately 25 km × 25 km. All the samples have been analyzed for Al, Ti, P, Ni, Co, V, Sr, Cu, Cr, Ce and Zn by ICP-AES and for K, Na, Fe, Ca, Mg and Mn by AAS. In addition, representative samples of three different types of Cretaceous granites and their biotite mineral separates were analyzed. It turned out that chemical compositions of stream sediments in the areas of Cretaceous granitic basements are systematically different from those in the areas of sedimentary rocks: (1) The Ca/Ti ratio and Ca, Na and Sr abundances in Cretaceous granitic basements are higher than those in the areas of the sedimentary rocks. (2) Cr, Co, Cu, Ni, V and Zn are depleted in the stream sediments from the granitic basements relative to the sedimentary rock areas. (3) The areal distribution patterns of the Ca/Ti ratio and the elemental abundances coincide with the distribution of the Cretaceous granitic basements.

The geochemical results are fairly reasonable, because the sedimentary rocks have experienced much more intensive weathering reactions than the Cretaceous granitic rocks. During weathering of granitic rocks, plagioclase is more readily decomposed than biotite. Hence, as the weathering proceeds, the abundance of biotite relative to plagioclase increases in weathered rocks. As a result, the clastic materials transported into sedimentary basins tend to be depleted in Ca, Sr and Na because these cations are contained mainly in plagioclase. But such clastics become enriched in Ti, Cr, Co, Cu, Ni, V and Zn because biotites still accommodate these cations. This inference is consistent with our analyses of representative samples of granites and their biotite

mineral separates. The areal distribution of Ce, however, does not show such a systematic difference between the two geologically different areas. Finer grains of Ce-rich rare phases such as monazite, allanite and/or sphene may be responsible for the areal distribution pattern of Ce abundance in the stream sediments.

INTRODUCTION

Geochemical mapping is useful for environmental assessment of the earth's surface from geochemical viewpoints. In European countries, nation-wide surveys for geochemical mapping have been conducted (Webb et al., 1978; Fauth et al., 1985; Kautsky and Bolviken, 1986; Thalmann et al., 1988). In Japan, geochemical maps for Akita Prefecture (Shiikawa et al., 1984) and for Northern Kanto area (Itoh et al., 1991; Kamioka et al., 1991) have been reported. Geochemical maps as to various chemical elements can illustrate areal variations of natural background abundances of respective elements. Such data are important not only to understand the distribution of elements in the area but also to investigate geochemical processes occurring at or near the earth's surface. They help us identify anthropogenic chemical pollutions as well.

In 1994 we started a study of geochemical mapping based on chemical data of stream sediments for the purpose of environmental assessment of the area of Seto and Toyota Cities, Aichi Prefecture, central Japan (Tanaka et al., 1994 and 1995). There are reasons why we selected this area as a test field: The first reason is that the surface geology of this area is rather simple (Fig. 1). In the eastern part of this area, Cretaceous granitic basement rocks outcrop widely. In the western part, such basements are covered by Neogene sedimentary rocks. The basement rocks of Triassic to Jurassic cherts and clastics occur only in a very limited area of the northern part. The second reason is that this area is famous for production of chinaware from old times. There are many chinaware factories in and around Seto City. In recent years, the population of this area is rapidly increasing, since it is located in the north-eastern suburb of a large city of Nagoya. Hence, possible environmental effects due to anthropological activities might be found in stream sediments of this area. The third reason is that the local government of Aichi Prefecture is planning to invite an international exposition in 2005 to this area. If this is accomplished, natural environments of this area will be modified more or less. It seems important to have the data for geochemical mapping before and after such modifications.

We have already reported analytical data of 286 stream sediments collected in this area until 1995 (Tanaka et al., 1995). It is pointed out that stream sediments in granitic rock basements show higher Ca, Sr, Na, K and Al contents and lower Fe, Mn, Cr, Co, Ni, Cu, V, Zn and P contents than those in the areas of Miocene and Pliocene sedimentary rocks. We commented that such contrasting chemical features of stream sediments may possibly be related to the

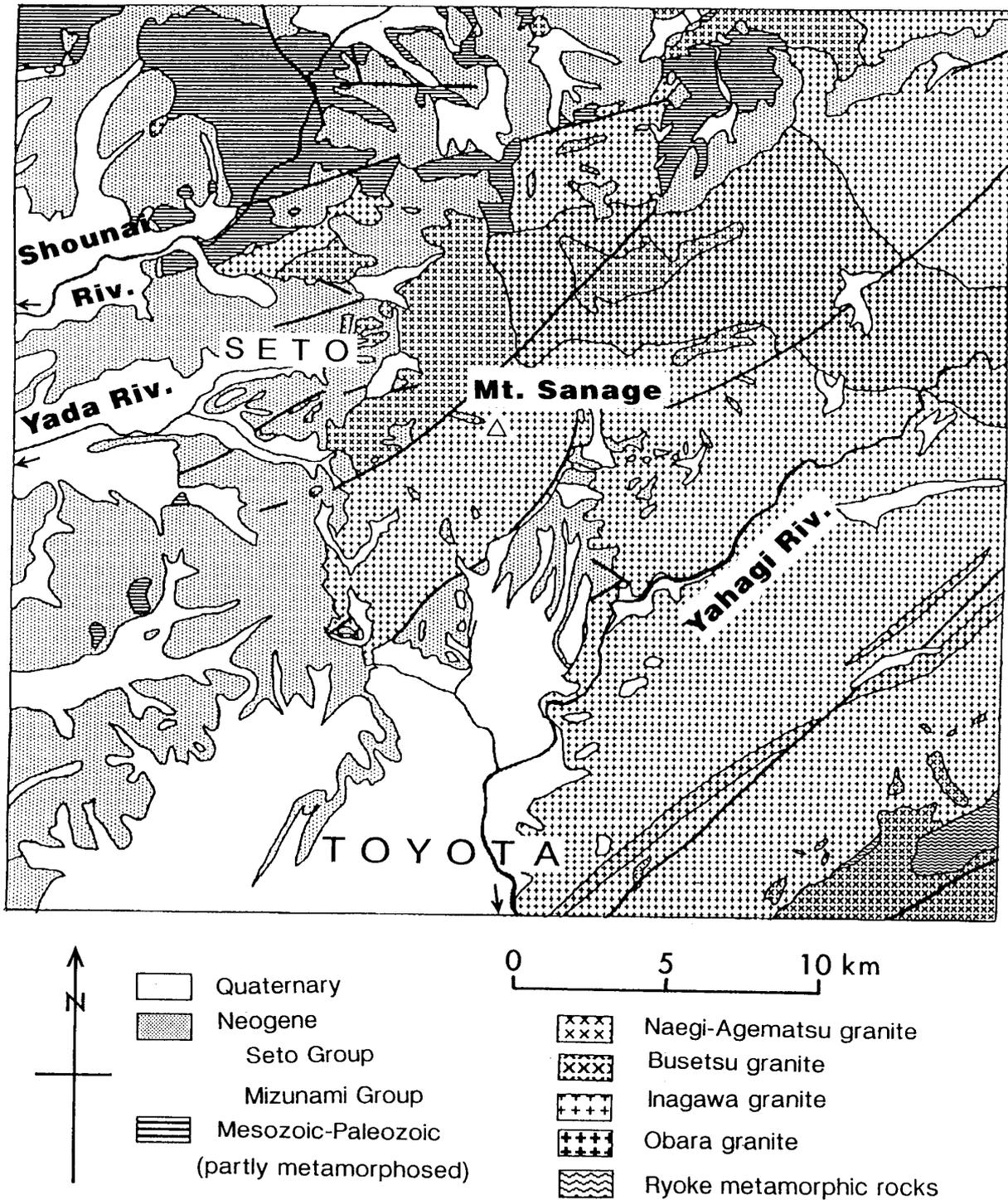


Fig. 1. Surface geology of the studied area, which is modified from Yamada et al. (1987).

different degrees of weathering between the two types of surface rocks (Tanaka et al., 1995). In April, 1996, we extended our mapping area to the northeastern part of Toyota City, where basement rocks of Cretaceous granites are exposed widely. A few representative samples of the Cretaceous basement granites were collected along with additional stream sediments

from 66 locations. We separated biotites from the granite samples in order to know how elemental abundances are different among the bulk granites, their biotite mineral separates and stream sediments. In this paper we report areal distributions of elemental abundances in the northern area of Toyota and Seto Cities on the basis of chemical analyses of 352 stream sediment samples collected by us in recent three years. The interesting geochemical contrast in stream sediments between the Cretaceous granitic basements and Neogene sedimentary basins is further discussed in conjunction with our new data.

ENVIRONMENTAL CHARACTERISTICS OF STUDIED AREA

Three different Cretaceous granitic rocks called the Inagawa, Obara and Naegi-Agematsu types are distributed widely in this area (Fig. 1). They are exposed mainly in the eastern part, whereas the granitic basements are covered by Miocene sedimentary rocks (the Mizunami group) and by Pliocene non-marine sediments (the Seto group) in the western part. Quaternary sediments also cover the basements in the southwestern part. Another type of basement rocks, which are cherts and clastic rocks of the early Mesozoic, are exposed in only small areas of the northern part.

The provenance of Miocene or Pliocene sedimentary rocks is the Cretaceous granites and the basement rocks of the early Mesozoic clastics occurring more widely in the further north of this area. The Neogene sedimentary rocks were formed in local basin structures developed on the basement rocks. Kaolins and other clay deposits are found in the Seto group. Open-cut mines of such clay deposits as the raw materials for chinaware and pottery are distributed in and around Seto City.

River drainage systems develop in this area (Figs. 1 and 2). The Shounai and Yada Rivers run across this area toward the Ise Bay in the southwest. The Yahagi and Asuke Rivers merge with each other in the further south of this area and flow into the Mikawa Bay. Small streams branching upward from large rivers are our sampling sites for sediments. Sediments in the smaller stream represent the average for exposed rocks in the more restricted area belonging to its drainage subsystem.

SAMPLES AND ANALYTICAL METHOD

We have collected new stream sediments from 66 locations in the northeastern of Toyota City in April, 1996. The locations are indicated in Fig. 2, together with their sample numbers. The sampling sites of 286 stream sediments collected and analyzed in 1994 and 1995 are also shown in Fig. 2. In these three years, we have collected a total number of 352 stream sediments from different locations in an area of approximately 25 km \times 25 km. The average density of sampling sites is about one location per 2 km². The sampling method of stream sediments is the same as described in Tanaka et al. (1994 and 1995). Fine sediment particles were sieved with stream water at each

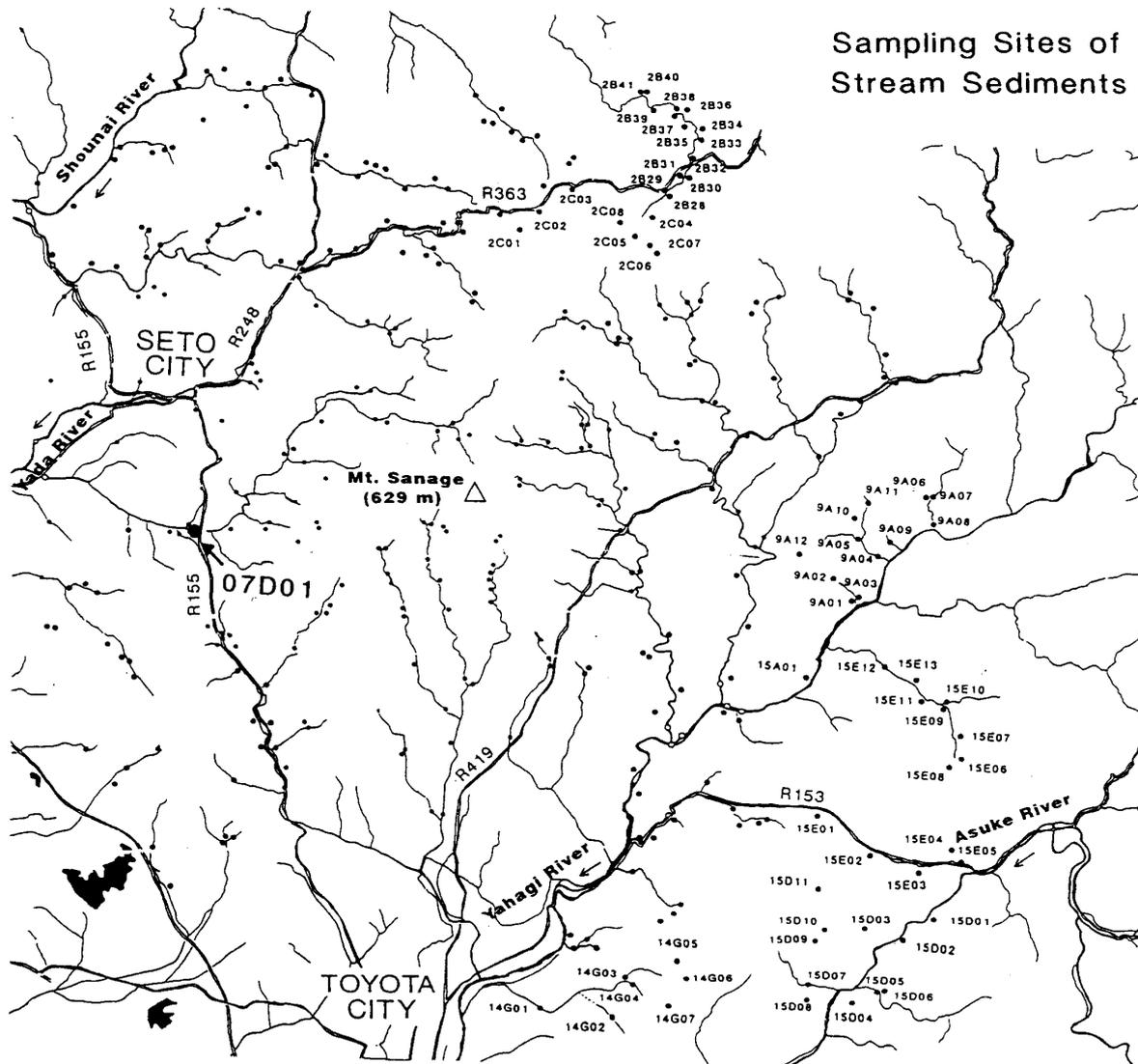


Fig. 2. Sampling sites of stream sediments in this study, together with our previous ones (Tanaka et al., 1994, 1995). Sample numbers are given to the sites where they were collected in April, 1996. This map covers an area of approximately 25 km × 30 km.

sampling site by using an 80 mesh (180 μm) sieve. They were dried at about 30°C before their chemical analyses.

We also collected representative samples of Inagawa, Obara and Naegi-Agematsu type granites in the north and south of Mt. Sanage. For each granite sample, we prepared a pulverized sample for its bulk chemical analysis and its mineral separates. Although separations of biotite, plagioclase, K-feldspar and Fe-Ti oxides were attempted by using magnetic and heavy liquid methods, only biotite grains were successfully purified for each granite sample. We also collected a special sample of stream sediment at the site 07D01 shown in Fig. 2, where Yada River is crossed by Route 155 in Seto City (Tanaka et al., 1994), without sieving in order to prepare a sample for its bulk

analysis and biotite mineral separates. One bulk sample and biotite separate of each type of the three Cretaceous granites and the stream sediment from Site 07D01 were analyzed by the same method as the ordinary samples of stream sediments.

The stream sediments, granites, and biotite separates have been analyzed for Al, Ti, P, Ni, Co, V, Sr, Cu, Cr, Ce and Zn by ICP-AES (Seiko SPS-1500R) and for K, Na, Fe, Ca, Mg and Mn by AAS (Perkin-Elmer 5100 PC). The analytical method is reported by Tanaka et al. (1995). In brief, each aliquot of about 0.5 g weighed in a Teflon beaker was digested by conc. HNO₃ (4 ml), conc. HClO₄ (3 ml) and HF (10 ml). After being dried up under infrared lamps, it was dissolved in 3 ml of 6M HCl. The mostly insoluble organic materials were removed by filtering. Finally, it was made up to 50 ml with 0.35 M HCl, which was the sample solution for ICP-AES. The sample solution for AAS was prepared by taking an aliquot (5 ml) from the sample solution for ICP-AES. And, being added 6 M HCl (15 ml) and 4% SrCl₂ solution (25 ml) to the aliquot, it was made up to 250 ml. The addition of SrCl₂ solution was also made for all the standard solutions for AAS, because Sr is the agent for matrix matching between samples and standards. The analytical results of new samples of 66 stream sediments are listed in Table 1. The results for bulk granites and biotite separates are summarized in Table 2, together with the results for the stream sediments at Site 07D01.

RESULTS AND DISCUSSIONS

1. Precision and accuracy of analytical method

In order to evaluate the precision and accuracy of our analytical method, two reference rocks of JG-1a and JB-1a distributed by Geological Survey of Japan (GSJ) have been analyzed three times in ordinary runs for stream sediments. The results of replicate analyses are listed in Table 1 and compared with compiled values for the two GSJ reference rocks (Imai et al., 1995). The precisions of our analyses for the seventeen elements are mostly less than 5%, except for a few cases. The analyses for 10 to 11 elements are within the deviation of $\pm 10\%$ from the compiled values. However, our analyses for Al, Ce, and Cr negatively deviate by about 20–30% from the respective compiled values (Imai et al., 1995). This is attributed to incomplete sample digestion, because samples were digested by using HF-HNO₃-HClO₄ in an open Teflon beaker. The systematic bias in our Al, Ce and Cr data must be kept in mind when their distributions are discussed. This drawback of our sample digestion is partly inevitable from the constraint of our present study as to available instruments and working time for both field sampling and chemical analysis.

2. Inhomogeneity effects in stream sediment samples

Inhomogeneity effects not only in the *in situ* stream sediment but also in the collected sample are important for our study. Tanaka et al. (1995) evaluated such effects in stream sediments by comparing analytical results for

Table 1. The analytical results of stream sediments in the northeastern part of Toyota City in April, 1996. The replicates analyses of JG-1a and JB-1a in this study are also summarized, together with the compiled values ("REF." in this table) for the two GSJ reference rocks by Imai et al. (1995).

sample	Na (%)	K (%)	Mg (%)	Ca (%)	Al (%)	Fe (%)	Mn (%)	Ti (%)	P (%)	Ce (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Ni (ppm)	Sr (ppm)	V (ppm)	Zn (ppm)
09A01	2.49	2.24	0.08	1.33	5.92	1.0	0.029	0.073	0.010	34.6	1.4	2.2	2.3	1.1	91	6.1	34
09A02	3.49	2.36	0.03	1.17	6.33	0.7	0.016	0.032	0.009	22.5	0.7	2.0	1.7	1.2	60	2.2	41
09A03	2.51	2.14	0.08	1.39	5.56	1.0	0.037	0.163	0.012	90.8	1.1	3.2	1.2	1.3	121	8.1	66
09A04	2.55	2.27	0.05	1.22	3.54	0.6	0.033	0.095	0.009	57.2	1.0	8.1	3.2	1.9	98	4.6	30
09A05	2.89	2.52	0.05	1.19	5.07	0.6	0.016	0.037	0.014	20.9	0.8	5.3	5.7	3.0	66	4.0	85
09A06	2.39	2.54	0.03	1.37	5.31	0.5	0.025	0.166	0.008	61.5	0.7	1.7	1.8	1.1	107	3.9	38
09A07	2.50	2.64	0.16	1.57	6.17	1.0	0.029	0.104	0.011	38.4	2.0	3.4	1.6	1.3	125	11.0	37
09A08	2.71	2.17	0.09	1.61	6.24	0.7	0.017	0.078	0.010	37.4	1.1	2.5	1.5	1.2	137	6.6	24
09A09	3.05	1.75	0.12	2.02	6.57	1.1	0.026	0.127	0.012	29.3	1.5	2.8	3.1	1.2	149	10.1	35
09A10	2.34	3.47	0.02	0.66	3.48	0.4	0.013	0.038	0.007	14.1	0.9	2.1	0.8	1.1	46	2.7	20
09A11	2.44	2.70	0.08	1.22	5.30	0.6	0.013	0.108	0.013	48.2	1.7	8.0	3.6	2.8	101	8.4	21
09A12	3.26	1.90	0.02	1.25	5.57	0.8	0.011	0.043	0.008	16.8	0.6	1.7	3.5	1.3	45	2.5	25
15A01	2.34	1.97	0.30	2.15	4.52	2.1	0.037	0.175	0.027	32.7	4.1	6.5	4.9	2.6	129	29.7	66
02B28	1.10	3.90	0.16	0.42	4.53	1.1	0.023	0.130	0.020	16.9	2.2	9.1	15.8	4.5	33	13.9	41
02B29	1.30	2.79	0.33	0.88	3.97	1.7	0.047	0.209	0.066	25.7	23.7	34.5	47.2	12.2	71	27.4	166
02B30	1.38	3.76	0.20	0.78	3.38	1.1	0.041	0.121	0.014	13.1	2.8	4.5	5.0	2.1	47	15.9	43
02B31	1.28	2.50	0.33	1.11	3.85	1.8	0.072	0.174	0.032	20.9	4.9	12.0	15.9	4.2	65	26.7	104
02B32	0.39	1.65	0.21	0.29	2.73	1.1	0.032	0.160	0.020	17.1	5.6	33.6	16.6	16.9	35	24.8	62
02B33	0.90	3.37	0.11	0.12	4.61	1.8	0.077	0.143	0.018	25.0	5.9	8.9	16.8	6.5	20	21.1	78
02B34	1.06	2.04	0.15	0.41	7.56	11.0	0.936	0.137	0.081	55.2	8.1	9.6	9.6	5.5	47	23.1	104
02B35	0.65	3.52	0.20	0.12	5.87	2.2	0.068	0.327	0.048	22.5	7.4	11.8	29.7	7.2	35	33.0	161
02B36	1.50	2.62	0.23	0.56	7.18	3.4	0.815	0.151	0.090	24.0	15.5	12.9	17.3	6.6	41	28.4	101
02B37	2.06	3.33	0.17	0.56	3.52	1.2	0.042	0.143	0.022	24.8	2.9	4.8	10.5	3.0	66	20.7	51
02B38	1.46	3.14	0.27	0.68	3.89	1.6	0.078	0.147	0.033	17.0	5.3	10.1	11.8	5.1	58	22.4	86
02B39	1.56	3.72	0.18	0.29	4.64	1.3	0.039	0.140	0.018	12.2	3.2	7.0	6.3	2.6	32	20.4	53
02B40	1.44	3.89	0.10	0.16	4.62	1.2	0.037	0.106	0.011	13.0	2.6	2.9	3.8	1.9	26	13.5	43
02B41	1.27	4.81	0.09	0.23	5.97	1.2	0.050	0.094	0.014	11.3	3.0	4.4	6.3	3.3	30	14.7	49
02C01	1.94	2.73	0.31	1.33	6.41	1.7	0.057	0.173	0.017	15.9	3.9	5.0	3.2	2.4	91	23.4	51
02C02	1.97	2.37	0.58	2.31	6.15	3.2	0.114	0.408	0.026	52.2	6.1	6.0	16.0	2.2	112	41.2	70
02C03	1.92	2.36	0.35	1.67	4.56	2.0	0.057	0.177	0.026	21.1	4.7	7.8	6.5	2.8	93	28.9	55
02C04	1.01	4.30	0.26	0.59	5.79	1.6	0.050	0.200	0.018	30.4	3.8	4.1	64.4	2.3	56	20.0	49
02C05	1.26	3.16	0.33	1.18	5.59	3.5	0.055	0.179	0.016	30.3	4.3	6.7	4.6	2.4	67	27.8	44
02C06	1.51	3.91	0.04	0.30	4.79	0.5	0.027	0.046	0.009	12.7	1.4	3.5	11.5	1.6	27	5.1	21
02C07	1.23	4.58	0.08	0.23	5.77	0.8	0.026	0.071	0.014	9.4	2.2	3.1	6.7	1.9	33	8.7	34
02C08	1.82	2.47	0.27	1.01	5.65	1.8	0.046	0.162	0.020	10.6	3.8	4.9	7.3	2.4	68	22.8	59
15D01	2.69	1.10	0.48	3.00	6.10	2.9	0.061	0.358	0.076	21.3	5.8	6.7	5.6	2.6	182	40.5	66
15D02	2.40	1.22	0.54	2.74	6.06	3.4	0.072	0.376	0.057	21.9	6.8	8.4	6.8	3.8	148	47.3	83
15D03	2.58	0.94	0.22	3.66	5.89	2.1	0.054	0.258	0.029	30.4	3.3	5.1	3.1	1.6	246	31.8	50
15D04	1.99	1.35	0.62	2.47	6.34	5.3	0.153	0.469	0.088	35.2	9.3	9.3	10.3	4.0	142	55.9	113
15D05	1.97	1.56	0.48	2.65	6.26	3.2	0.071	0.352	0.034	37.2	5.6	7.4	6.4	3.0	162	45.0	73
15D06	2.22	1.21	0.50	3.05	5.89	3.4	0.082	0.396	0.042	21.1	6.6	8.5	6.8	3.1	144	49.4	87
15D07	2.49	1.54	0.13	2.93	5.79	1.4	0.049	0.173	0.018	49.9	2.1	4.0	3.0	1.6	249	18.2	41
15D08	2.39	1.24	0.44	3.11	5.98	2.7	0.083	0.270	0.044	19.9	5.3	11.2	9.8	3.4	196	40.0	80
15D09	2.34	1.34	0.18	2.70	6.47	2.0	0.075	0.223	0.026	38.1	3.0	4.4	3.2	1.7	260	24.6	84
15D10	2.66	1.08	0.23	3.44	6.22	1.9	0.032	0.193	0.037	57.5	3.3	4.6	5.3	2.0	314	23.0	74
15D11	2.14	2.40	0.16	2.40	7.38	1.7	0.026	0.133	0.014	58.3	2.7	4.3	2.5	1.6	245	17.0	44
15E01	1.84	2.34	0.10	1.40	5.62	1.7	0.065	0.094	0.027	35.6	2.8	4.7	7.8	3.1	137	12.8	47
15E02	2.44	1.40	0.31	3.23	6.36	2.9	0.072	0.404	0.020	119.8	4.0	5.9	2.7	3.4	262	35.8	67
15E03	2.38	1.10	0.24	3.61	7.52	2.2	0.040	0.202	0.030	27.0	3.7	6.2	3.8	2.2	278	30.1	52
15E04	2.46	1.11	0.22	2.78	5.45	2.4	0.067	0.526	0.021	145.7	3.3	5.1	2.4	1.7	245	32.4	55
15E05	2.35	1.12	0.17	2.81	6.08	1.7	0.049	0.212	0.035	47.1	3.1	5.1	5.3	3.5	248	21.7	55
15E06	2.37	1.09	0.15	2.89	6.63	1.5	0.046	0.279	0.019	174.5	2.2	3.4	2.0	1.5	268	20.5	40
15E07	0.99	0.58	0.17	1.95	5.47	25.8	0.683	0.127	0.071	184.5	8.5	4.5	6.9	4.1	248	20.9	66
15E08	2.33	1.03	0.15	2.81	5.48	1.8	0.056	0.304	0.014	105.1	2.4	3.8	1.6	0.9	227	22.6	41
15E09	2.50	1.15	0.09	2.46	6.05	2.4	0.124	0.087	0.021	42.7	2.5	2.5	2.3	1.3	258	11.0	36
15E10	2.40	1.20	0.20	2.73	5.84	2.0	0.076	0.313	0.029	158.1	3.1	4.6	5.4	1.7	241	26.0	57
15E11	2.17	1.40	0.03	1.68	3.90	0.5	0.011	0.066	0.007	38.2	1.0	1.2	1.0	0.5	126	4.7	18
15E12	2.27	1.24	0.09	2.33	3.33	1.0	0.049	0.087	0.011	37.5	1.6	2.0	3.1	0.8	159	11.3	31
15E13	1.85	0.93	0.17	2.72	5.44	5.9	0.899	0.189	0.218	122.6	4.8	9.6	9.8	5.5	200	20.8	128
14G01	1.86	2.36	0.46	1.61	6.52	2.5	0.039	0.248	0.034	41.9	6.3	15.0	16.8	6.5	130	43.6	71
14G02	1.70	2.10	0.36	1.95	6.53	2.7	0.087	0.195	0.027	25.5	5.6	9.2	6.4	4.0	139	37.1	74
14G03	2.04	1.74	0.50	2.53	6.62	3.2	0.086	0.335	0.050	49.1	6.0	14.9	15.3	4.5	156	48.1	90
14G04	1.62	2.17	0.25	1.64	5.97	2.1	0.055	0.193	0.037	28.9	5.2	9.2	8.4	4.7	131	31.3	65
14G05	2.31	1.52	0.33	2.48	5.70	2.5	0.071	0.182	0.018	39.9	4.7	8.8	4.6	4.6	179	38.5	61
14G06	2.67	1.07	0.29	2.45	6.45	2.1	0.051	0.179	0.024	40.3	3.7	5.9	3.6	3.8	157	30.8	57
14G07	1.43	1.95	0.22	1.43	5.86	3.3	0.075	0.191	0.041	57.6	5.7	9.1	10.6	25.0	136	28.8	87
JG-1a-1	2.44	3.53	0.38	1.35	4.57	1.3	0.030	0.135	0.035	28.3	4.8	15.4	1.7	6.8	139	20.7	36
JG-1a-2	2.44	3.50	0.37	1.41	6.04	1.3	0.041	0.132	0.037	32.9	5.1	14.2	1.8	5.2	147	20.4	38
JG-1a-3	2.39	3.33	0.40	1.45	5.69	1.3	0.036	0.132	0.036	31.0	5.0	14.2	1.9	5.4	145	20.4	38
AVE	2.42	3.45	0.39	1.40	5.43	1.3	0.036	0.133	0.036	30.8	5.0	14.6	1.8	5.8	144	20.5	37
S.D.	0.03	0.11	0.01	0.05	0.77	0.0	0.005	0.001	0.001	2.3	0.1	0.7	0.1	0.8	4	0.1	1
REF.	2.53	3.33	0.42	1.52	7.53	1.4	0.047	0.150	0.035	47.1	5.7	18.6	1.3	6.4	185	23.0	39
JB-1a-1	1.71	1.16	3.50	5.91	5.32	6.0	0.088	0.776	0.101	51.1	31.9	283.9	49.2	113.6	370	181.9	75
JB-1a-2	1.95	1.22	4.65	6.72	7.28	6.4	0.										

Table 2. The analytical results of bulk samples and biotite mineral separates for the Naegi-Agematsu, Obara, Inagawa type granites and one stream sediment at Site 07D01.

sample	Na (%)	K (%)	Mg (%)	Ca (%)	Al (%)	Fe (%)	Mn (%)	Ti (%)	P (%)	Ce (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Ni (ppm)	Sr (ppm)	V (ppm)	Zn (ppm)	
Naegi bulk	1.67	4.46	0.01	0.33	2.78	0.21	0.000	0.017	0.003	6.5	0.4	0.4	0.6	4.0	0.4	31	0.7	8
Naegi biotite	0.21	6.07	1.56	0.28	7.93	16.11	0.419	1.532	0.018	169.4	26.5	4.7	139.1	6.4	1.5	49.8	454	
Obara bulk	2.28	2.72	0.65	2.37	6.13	3.30	0.067	0.262	0.045	49.3	5.9	9.3	1.7	2.1	146	34.2	65	
Obara biotite	0.22	4.30	4.25	1.67	6.24	18.73	0.427	1.870	0.067	208.1	36.8	26.5	14.4	10.2	16	208.5	406	
Inagawa bulk	1.81	2.83	0.29	1.18	3.56	1.41	0.040	0.133	0.018	22.2	3.4	3.5	1.6	1.0	83	18.7	38	
Inagawa biotite	0.24	6.37	4.23	1.29	6.58	20.10	0.551	1.799	0.077	216.3	37.0	22.1	13.6	7.9	12	232.5	459	
Sediment bulk	1.34	3.95	0.08	0.15	2.87	0.60	0.017	0.055	0.009	8.0	2.0	3.1	2.9	1.8	39	6.6	29	
Sediment biotite	0.15	3.58	2.69	0.69	8.13	19.55	0.478	1.575	0.073	108.3	33.9	17.0	29.2	11.5	41	136.2	731	

several samples collected at the same location (Site 07D01) by different members of our group in April, 1995. The analytical data for most of the seventeen elements are in agreement within $\pm 20\%$, but Ti analyses significantly fluctuate by a factor of about two. This suggests that the *in situ* distribution of small grains of Ti-rich minor minerals such as Fe-Ti oxide and sphene may be inhomogeneous. The inhomogeneity of each sample in its sample bottle was also checked from standard deviations of replicate analyses of aliquots (0.5 g) for selected samples (Tanaka et al., 1995). Although such standard deviations are different from one sample to another, the standard deviations of Na, K, Mn, Co and Ni analyses were within $\pm 20\%$, but those for the others are within $\pm 50\%$.

In this study we re-analyzed the five samples collected at the same site (Site 07D01) by different members in 1995. Before each aliquot (0.5 g) was taken, we mixed each sample split of about 15g by using ball mills made of agate for 5 minutes. The analytical results for well-mixed samples in this study were compared with the results obtained last year without mechanical mixing (Tanaka et al., 1995). The averages and one- σ standard deviations calculated for respective elements are shown in Fig. 3, together with the previous results without mixing procedure. Each standard deviation in Fig. 3 represents the total effects due to (1) the analytical error, (2) the *in situ* inhomogeneity of stream sediments at the sampling site, and (3) the sample inhomogeneity inside each sample bottle. The first and second effects are common between the sets of the present results and those reported in Tanaka et al. (1995). Only the third effect is different between them. From the comparison of Fig. 3, the standard deviations for most of the seventeen elements decreased only slightly by intensive mixing with the ball mill. However, the resultant standard deviations are still larger than the analytical errors for respective elements. This means that the *in situ* inhomogeneity of stream sediments at the sampling site is much larger than the other effects. In the case of Ce analyses, however, its standard deviation decreased greatly by a factor of 1/5 after mechanical mixing of samples. This may be the "nugget effect" due to the presence of Ce-rich minor phase grains. They may be monazite, allanite and/or sphene.

3. Chemical compositions of three granites, a stream sediment and their biotite mineral separates

The analytical results for the bulk samples of three granites, one sample of stream sediment from Site 07D01 and their biotite mineral separates are summarized in Table 2. Enrichment factors for respective elements in biotites relative to bulk samples of granites and the stream sediment are shown in Fig. 4. In all the cases of three granites, Mg, Fe, Mn, Ti, Ce, Co, Cr, Cu, Ni, V and Zn are enriched in biotites relative to the respective bulk samples by factors of 10 to 100. In contrast, Na and Sr are so depleted in biotites relative to their bulk samples. Large enrichments of Mg and the transition metals and significant depletions of Na and Sr in biotites are reasonable from cation substitution relations in biotites and feldspars of granitic rocks: The metal cations

of Mg and the transition elements except Ce can be accommodated at the octahedral cation sites of biotites. Biotite is the most important major Mg-Fe mineral that can incorporate such transition metals among constituent minerals of the granites. Substitutions of Na^+ , Sr^{2+} and Ca^{2+} for K^+ -sites in biotites are fairly limited, but these large cations are allowed to substitute extensively

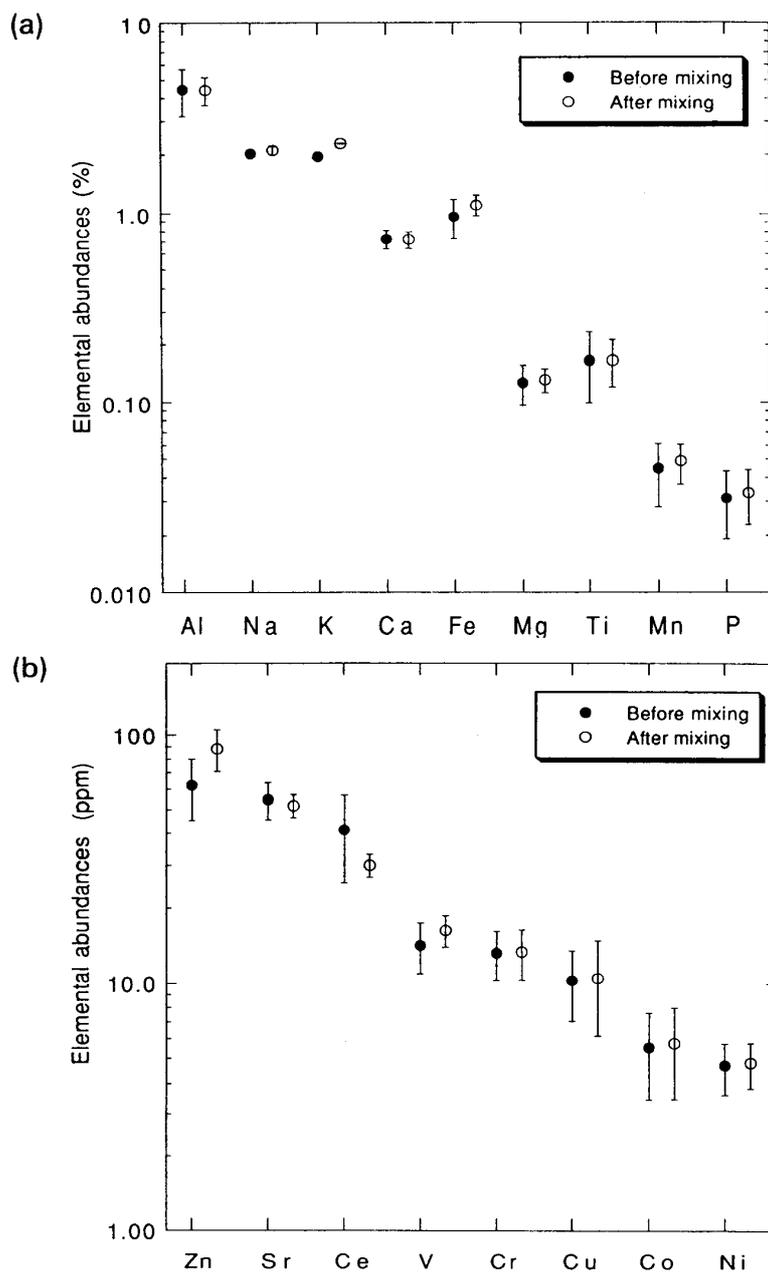


Fig. 3. Means and one- σ standard deviations for determinations of seventeen elements in five stream sediments collected in the same location (Site 07D01). The analyses of aliquots of the respective sediment samples taken before and after vigorous mechanical mixing by agate ball mills are compared. Comparisons in nine major elements in (a) and eight minor and trace metals in (b). The analyses of the aliquots taken before mechanical mixing were cited from Tanaka et al. (1995).

for the cation sites of feldspars of granitic rocks.

In the case of the stream sediment from Site 07D01, metal enrichments in biotite relative to the bulk sample exactly coincide with those in the three granites. Tanaka et al. (1995) noted that Ca, Sr, Na, K and Al concentrations in stream sediments are high in granitic basements but Fe, Mn, Cr, Co, Ni, Cu, V, Zn and P concentrations are high in the areas of Miocene and Pliocene sedimentary rocks. This contrast in elemental abundances seems to be analogous to the metal enrichments in biotites relative to bulk samples in Fig. 4. If stream sediments in the area of Neogene sedimentary rocks are more enriched in biotites and more depleted in plagioclase feldspars than those sediments in granitic basements, the areal contrast in chemical characteristics of stream sediments between the two geologically different areas can be explained.

In weathering reactions of granitic rocks, plagioclase feldspars are readily altered into clay minerals via their hydrolysis reactions with surface water, but biotites cannot be altered so rapidly as plagioclase feldspars (Mason, 1966). Hence, weathered granites and clastics derived from weathered rocks are more likely to have lower plagioclase contents but higher biotite contents. The ratio of biotite/plagioclase may be a mineralogical index of the weathering effect. In the light of our results of Fig. 4, the mineralogical index is a key to understanding the observed difference in chemical compositions of stream sediments between the granitic basements and Neogene sedimentary basins. In this context, we will make more detailed examinations of our analytical

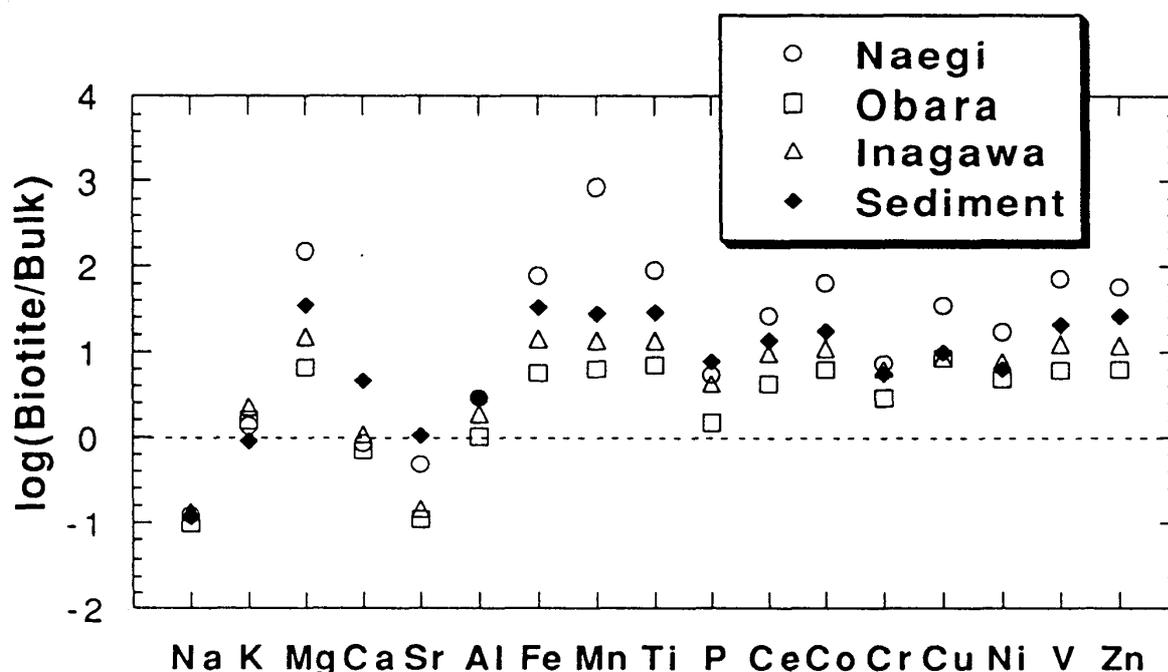


Fig. 4. The enrichment factors of seventeen elements in biotites relative to bulk samples of the Inagawa, Obara and Naegi-Agematsu type granites and one stream sediment collected at Site 07D01.

results of stream sediments in the next section.

4. *Two distinct trends in Ca/Al vs. Ti/Al plots of all the stream sediments*

Ca-rich plagioclase is decomposed in the earliest stage of chemical weathering of granitic rocks (Mason, 1966). Ca is depleted in weathered products since surface waters transport dissolved Ca^{2+} during weathering. Although Al is also a constituent of the plagioclase, Al remains as the constituent of clay minerals in weathered rocks. Hence the Ca/Al ratio of a stream sediment may reflect the modal abundance of remaining plagioclase as an index of chemical weathering. Ti found in bulk samples of granitic rocks is not present in felsic minerals but in ferro-magnesian minerals like biotite, as is shown by our chemical analyses of biotites separated from three granites. It is well-known that Ti substitutes for the octahedral cation sites of biotites to some extents (Deer et al., 1962). Since Al is also an essential constituent of biotites, the Ti/Al ratios of biotites are not so high but still significantly higher than those ratios of bulk granites: In Table 2, the Ti/Al ratios of the bulk granites and their biotite separates are 0.01–0.04 and 0.2–0.3, respectively. Ti is also the essential constituent of ilmenite. Since Al is not allowed to substitute for the cation sites of ilmenites, Ti/Al ratios of ilmenites in granitic rocks are as high as about 100 according to Haggerty (1976). Hence, Ti/Al ratios of stream sediments are related to enrichments of biotite and Fe-Ti oxide in the sediments relative to bulk granites samples.

The Ca/Al and Ti/Al ratios of stream sediments are plotted in Figs. 5a and b, in which those ratios of the bulk granites and their biotite separates are also shown for comparison. In Figs. 5a and b, we classified the stream sediments into four groups according to different surface rock types in the respective sampling locations. We can see two clearly different variation trends in the Ca/Al vs. Ti/Al plots of all the stream sediments. The stream sediments in Cretaceous granitic basements show one trend characterized by high Ca/Ti ratios. This trend appears to coincide with the compositional variations in the three different types of Inagawa, Obara and Naegi-Agematsu granites. The stream sediments in the areas of Mesozoic and Tertiary sedimentary rocks and the Quaternary sediments show another trend with lower Ca/Ti ratios, which are approximately equal to the Ca/Ti ratios of biotite mineral separates from the three granites. The Ca/Ti ratio is a good parameter to distinguish the two types of stream sediments whose bedrocks at sampling locations are Cretaceous granites or the others.

It seems interesting to compare Ca/Al ratios of stream sediments among the three areas of the sedimentary rocks of the Mesozoic, Tertiary, and Quaternary in Fig. 5b. The stream sediments in the areas of the early Mesozoic chert and clastic rocks show exclusively lowest Ca/Al ratios (0.0–0.1). In the areas of Tertiary sedimentary rocks, Ca/Al ratios of most of the stream sediments are limited in a range of 0.0–0.30. The Ca/Al ratios of stream sediments in the areas of Quaternary sediments show a slightly greater variation (0.0–0.40) than those in the Tertiary areas. Thus the variation range of Ca/Al

ratios in stream sediments systematically decreases with geological ages of the respective surface rocks at their sampling sites. The prolonged and repeated weathering which the surface rock materials have experienced is

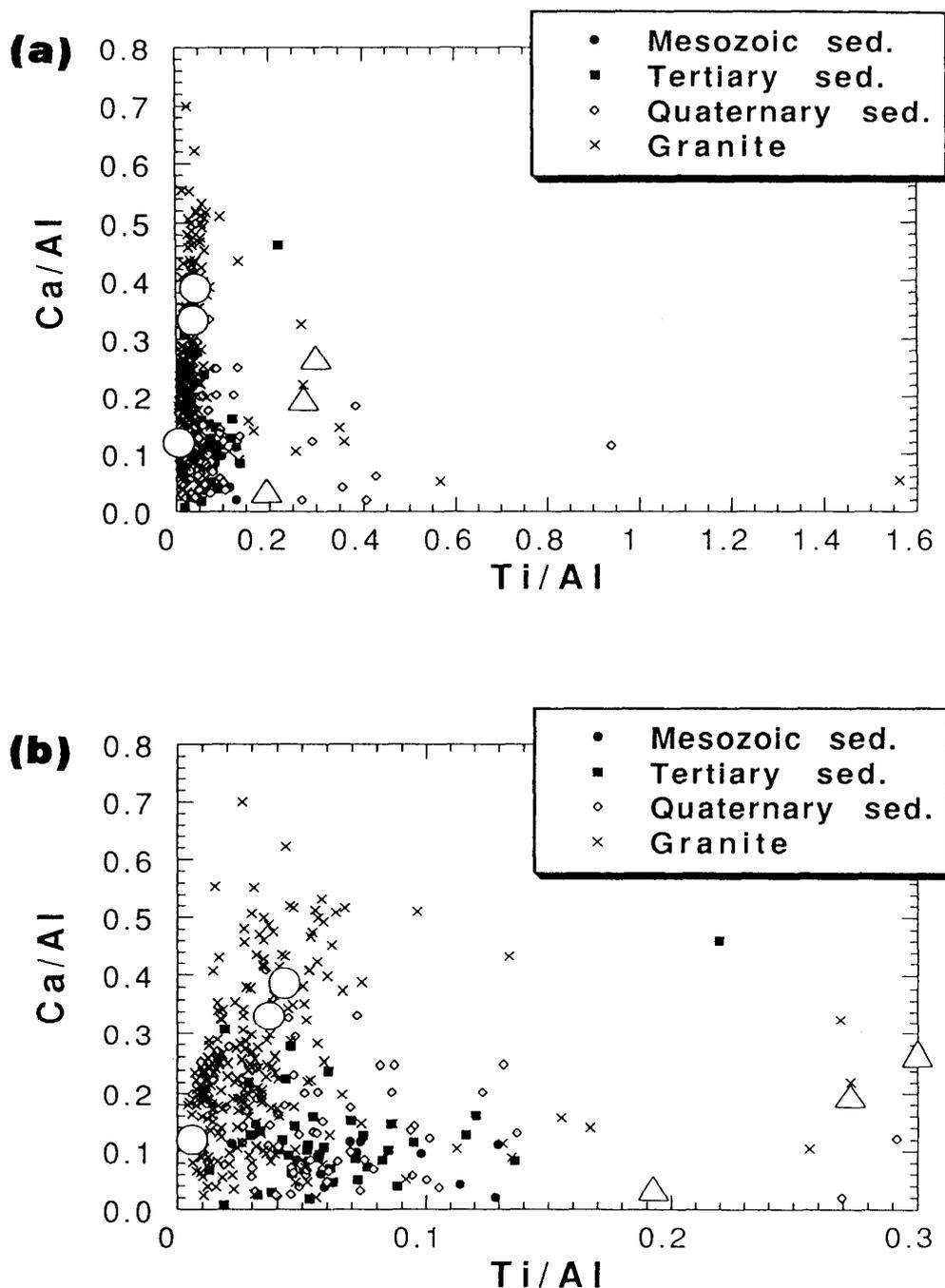


Fig. 5. (a): The plots of Ca/Al and Ti/Al ratios of all the stream sediments, the bulk samples of the Inagawa, Obara and Naegi-Agematsu type granites (large open circles), and their mineral separates of biotites (large open triangles). (b): Some samples of stream sediments having extremely high Ca/Al and Ti/Al ratios are omitted in order to see variation trends in the majority of the sediment samples, the bulk samples of granitic rocks and their biotites.

reflected in their Ca/Al ratios. The Ca/Al ratio is a good chemical index of weathering even when the chemical data of stream sediments are discussed.

The stream sediments having high Ti/Al ratios greater than those of biotites (~ 0.3) are so limited as seen in Fig. 5a. Hence, we expect that there are only a few sediment samples affected significantly by enrichments of ilmenite grains. The lower Ca/Ti ratios of most of the stream sediments collected from the three sedimentary rock areas, are indeed indicative of their high modal abundance ratios of biotite to plagioclase. The areal distribution of the Ca/Ti ratios of all the stream samples is consistent with the distribution of Cretaceous granitic basements (Fig. 6). This is a line of evidence supporting that our samples of stream sediments represent averages of rocks exposed in the local drainage subsystems assigned by the respective streams.

5. Areal distribution patterns of elemental abundances

The areal distributions of elemental abundances in stream sediments can be grouped into several types. The first type involves the Ca, Na and Sr distributions. The abundances of these elements are higher in Cretaceous granitic basements than those in post-Paleogene sedimentary basins and the basement of early Mesozoic clastics, just like the distribution pattern of Ca/Ti ratio of Fig. 6. The areal distribution of Ca abundances is shown in Fig. 7, along with their frequency distributions in classified areas from surface geology and in the whole area. The second type is the reverse pattern of the first one. The abundances of Cr, Co, Ni, V and Zn are clearly higher in post-Paleogene sedimentary basins and the basement of early Mesozoic clastics than in the Cretaceous granitic basements. The areal distributions of Fe, Mg, Mn, Ti and P abundances more or less exhibit this characteristics. The areal distribution pattern of Cr abundance shown in Fig. 8 is the most typical example of this type.

The first and second types of areal distributions of elemental abundances may also be understood in view of the averaged modal abundance ratios of biotite to plagioclase in surface rocks. The biotite/plagioclase ratio of a surface rock is systematically changed according to chemical weathering, as we discussed in relation to Ca/Ti, Ca/Al and Ti/Al ratios of sediments in the previous section. This mineralogical change inevitably accompanies systematic changes in the elemental abundances of Ca, Na, Sr, Cr, Co, Ni, V and Zn because of their enrichment factors in biotites (Fig. 4). This interpretation is basically applicable to either minor or major elements. In the cases of some trace transition metals, however, we must place some limitations on our interpretation as below.

There are analytical data for some trace transition metals that cannot be explained only by the elemental abundances in bulk granites and their biotite separates of Table 2. For example, Cr contents of the biotite mineral separates are less than 30 ppm. Bulk granites show low Cr contents less than 10 ppm. However, the frequency distributions of Cr abundance in Fig. 8 indicate that about a half of the stream sediments collected from the areas of Tertiary

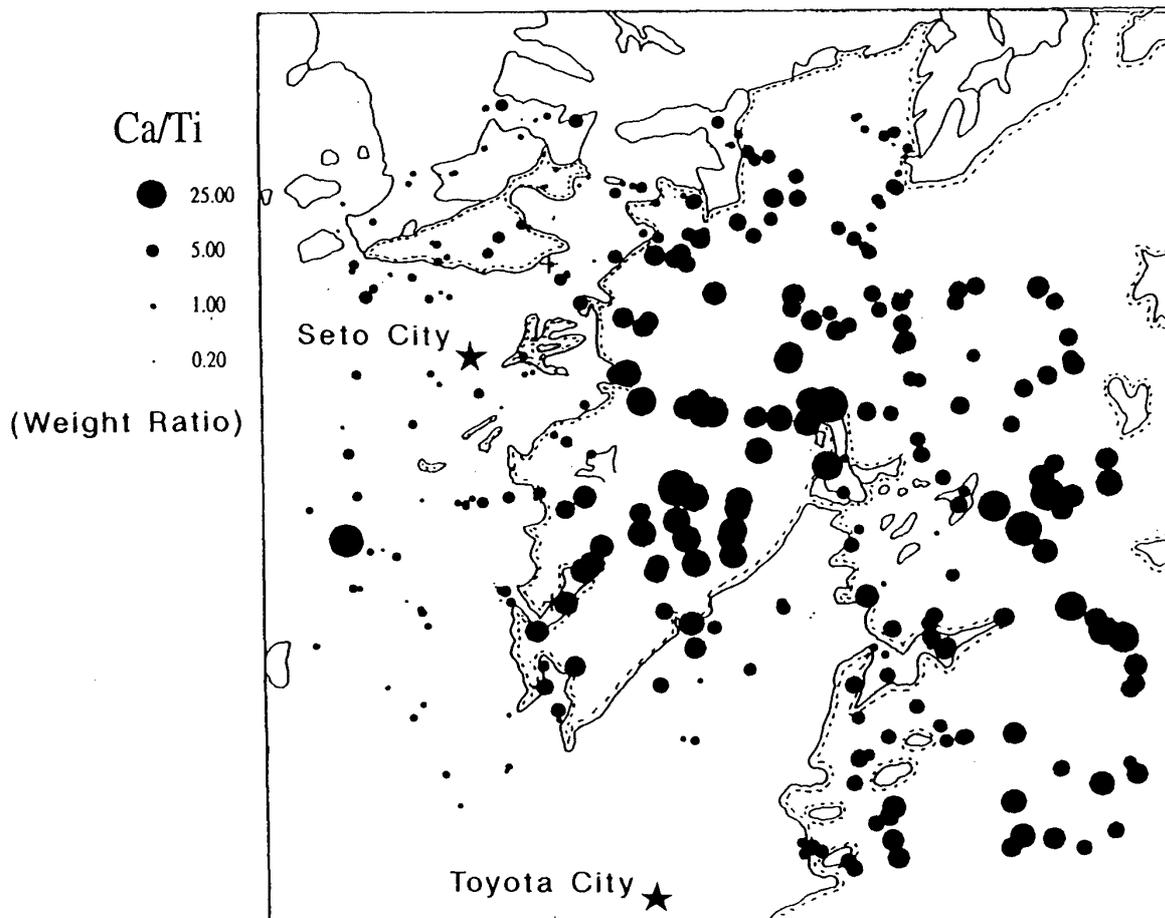


Fig. 6. The areal distribution of the Ca/Ti ratio of stream sediments in accordance with the distribution of Cretaceous granitic basements. The boundaries between Cretaceous granitic rocks and the other rocks or sediments are indicated by a pair of solid and dashed lines.

sedimentary rocks or of Quaternary sediments have high Cr contents greater than 30 ppm. Biotites are fairly enriched in trace transition metals relative to bulk granites (Fig. 4). Nevertheless, in order to account for the observed high Cr abundances in the sedimentary rock areas, we must postulate other phases more enriched in Cr than biotites.

The Inagawa and Obara type granites contain subordinate amounts of amphiboles (Yamada et al., 1987). Weathered products of amphiboles and/or remaining amphiboles may be candidates for such phases enriched in Cr. The Cr analyses in Fe-Ti oxides in granitic rocks are compiled by Haggerty (1976). The Cr contents of Fe-Ti oxides are too low to be such candidates. Anyway there must be some mineral phases accommodating larger amounts of Cr and some other transition metals than biotites. In addition, possible effects of anthropological activities or pollutions may also be explored. For example, the sample from Site 07E03 shows the highest Cr abundance of 785 ppm, which is corresponding to the largest solid circle in Fig. 8. Tanaka et al. (1995) strongly suspected that this stream sediment is polluted by some anthropo-

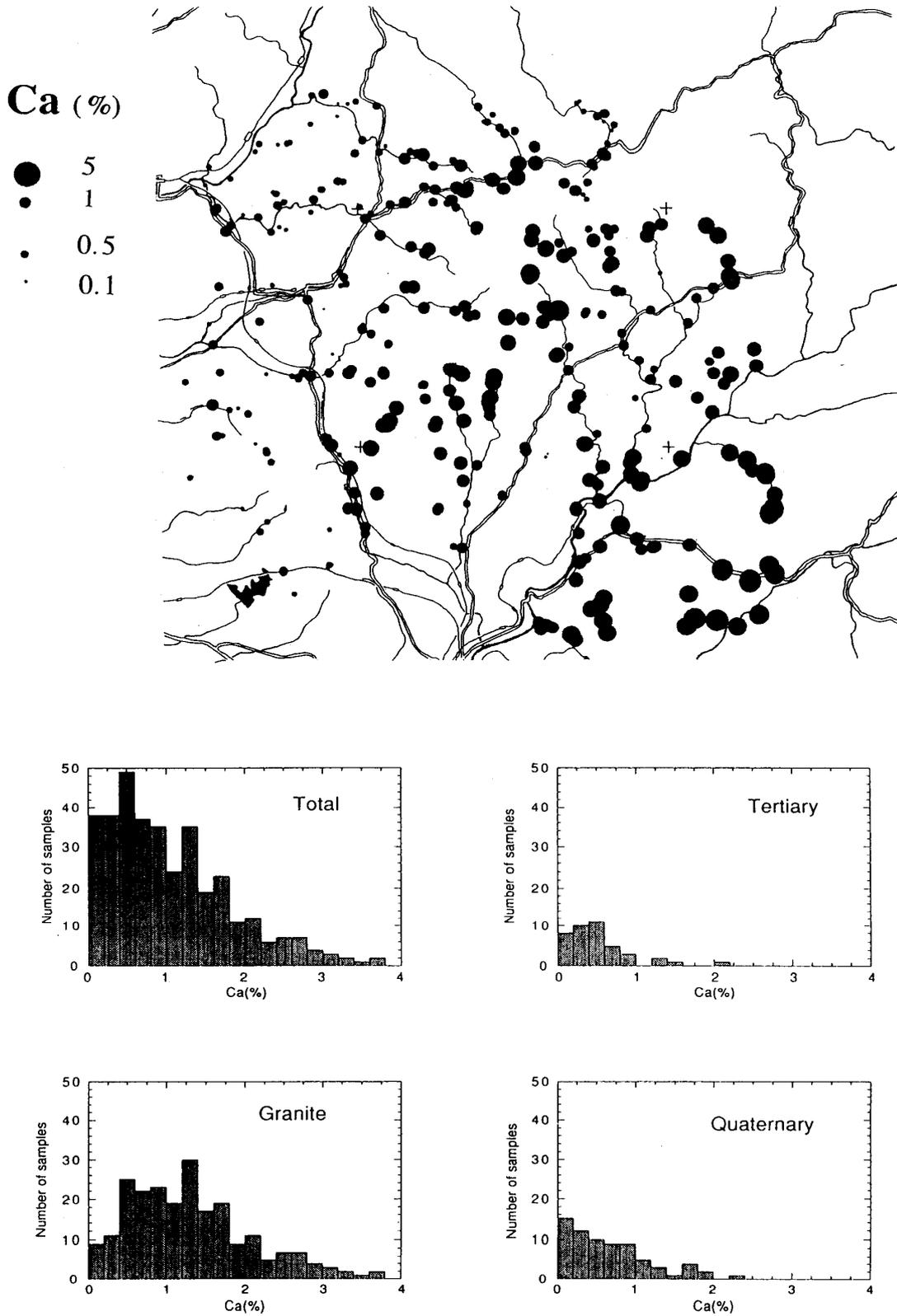


Fig. 7. The areal distribution of Ca content of stream sediments and the frequency distributions of Ca content in all the areas and in the respective areas of Cretaceous granitic rocks, Tertiary sedimentary rocks and Quaternary sediments.

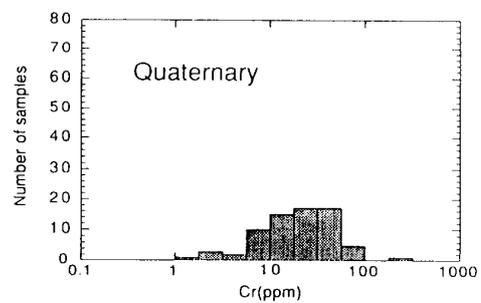
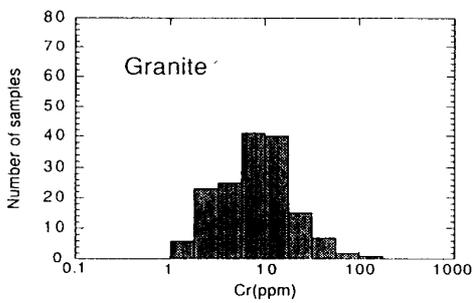
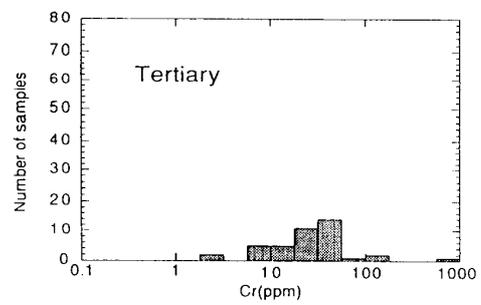
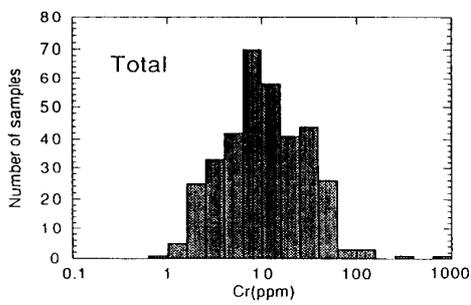
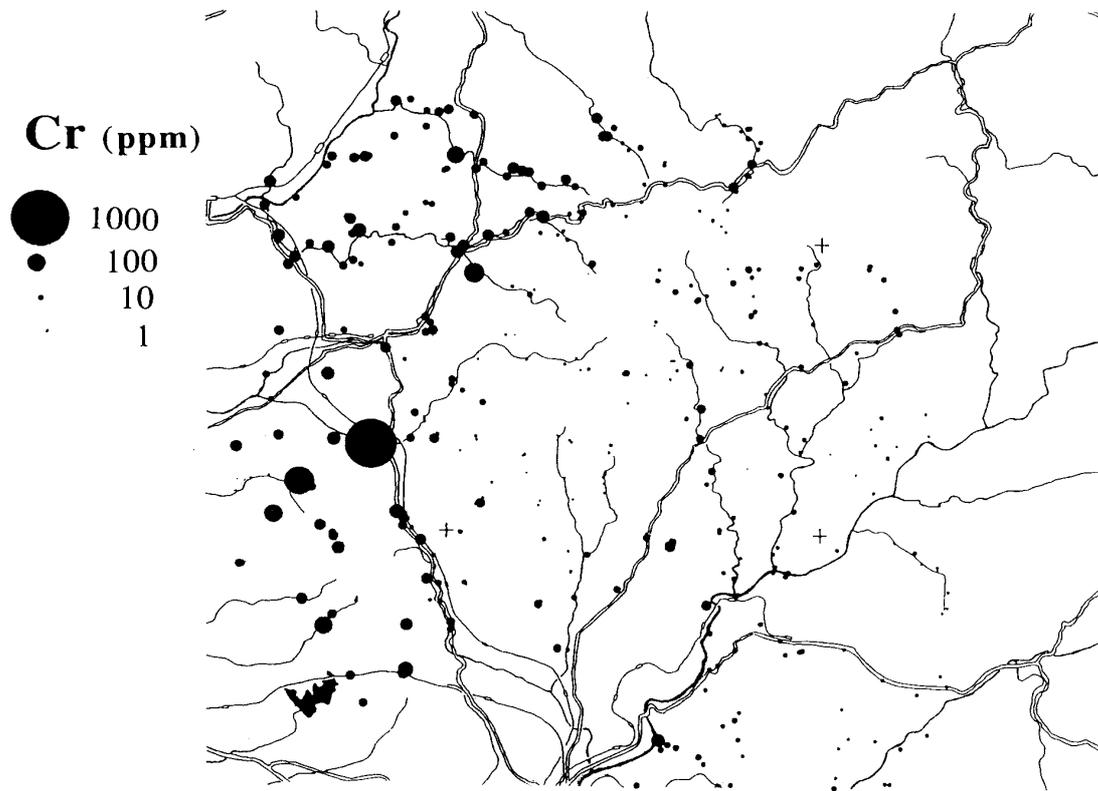


Fig. 8. The areal distribution of Cr content of stream sediments and the frequency distributions of the logarithmic Cr content in all the areas and in the respective areas of Cretaceous granitic rocks, Tertiary sedimentary rocks and Quaternary sediments.

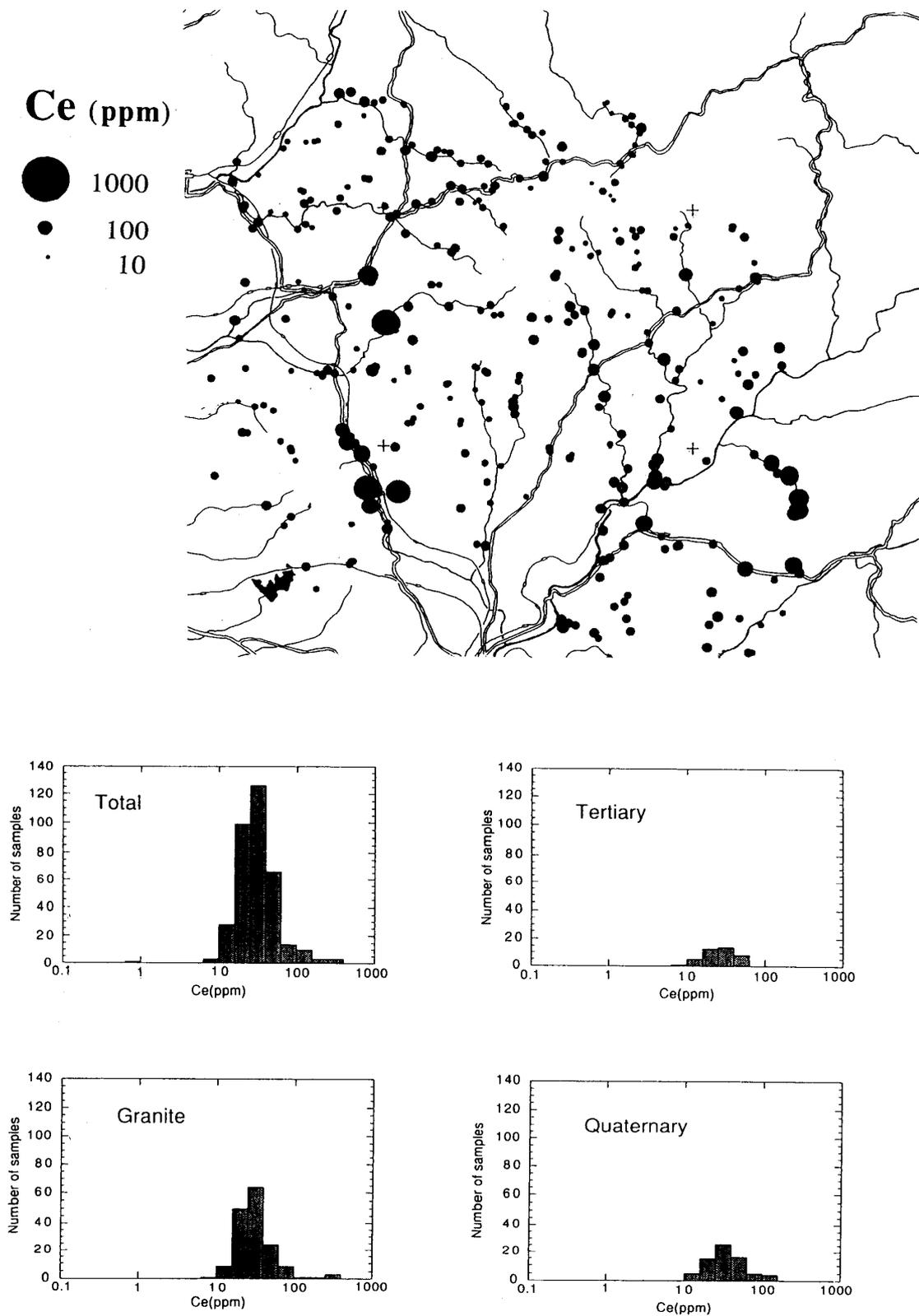


Fig. 9. The areal distribution of Ce content of stream sediments and the frequency distributions of the logarithmic Ce content in all the areas and in the respective areas of Cretaceous granitic rocks, Tertiary sedimentary rocks and Quaternary sediments.

logenic Cr source. More quantitative examinations as to these points are beyond the scope of the present study, and they will be made in future studies.

The third type of areal distributions of elemental abundances are those for K and Ce, in which no significant contrasts are apparent between the Cretaceous granitic basements and the other areas, unlike the first and second types. Figure 9 shows the areal distribution of Ce abundance and frequency distributions of Ce abundance in three different areas and in the whole area. The modal values of Ce abundance in the three geologically different areas are approximately the same (about 50 ppm). On the other hand, the average Ce contents for the three granites and their biotite mineral separates are 26 ± 22 ppm and 198 ± 25 ppm, respectively. If the modal abundance of these biotites is the major factor controlling the areal distribution of Ce abundance, a much larger contrast is expected in the areal distribution of Ce abundance. Hence, the biotite content is not the major factor controlling the areal distribution of Ce abundance.

In the discussion of relatively large inhomogeneity of Ce in bottled samples from the test sampling site (Site 07D01), we referred to the "nugget effect" in the stream sediments due to the presence of Ce-rich grains such as monazite, allanite and/or sphene. The inhomogeneity of Ce and the unique areal distribution of Ce may suggest that the content of Ce-rich rare minerals is a possible major factor determining Ce contents of stream sediments in this area. In this respect, the attempt to separate Ce-rich minor phases is important in future studies. It is also necessary to examine possible effects due to the physical sorting of various mineral grains including minor heavy minerals by stream waters at normal and flooding conditions.

The rather uniform distribution of K abundance over the entire area can be understood from the following points: (1) alkali feldspar is the major phase containing K among felsic minerals of granitic rocks. Alkali feldspar is slightly more stable than plagioclase in chemical weathering of granitic rocks (Mason, 1966), and (2) K is the essential constituent not only of biotites in granitic rocks but also of clay minerals as the weathered products of the ferro-magnesian minerals of igneous origins. Hence, K contents of surface rocks in this area are not so sensitive to chemical weathering.

CONCLUSIONS

The results of geochemical mapping in Seto and Toyota Cities, Aichi Pref., central Japan, based on chemical analyses of 352 stream sediments for seventeen elements (Al, Ti, P, Ni, Co, V, Sr, Cu, Cr, Ce and Zn by ICP-AES and for K, Na, Fe, Ca, Mg and Mn by AAS), have been presented. Here are also reported the chemical analyses of representative samples of Cretaceous granitic rocks of Inagawa, Obara and Naegi-Agematsu types, together with their biotite mineral separates.

Stream sediments in the Cretaceous granitic basements are chemically distinct from those in the areas of late Cenozoic sedimentary basins and of early

Mesozoic sedimentary rock basements: (1) the Ca/Ti ratio and Ca, Na and Sr abundances in Cretaceous granitic basements are higher than those in the areas of the sedimentary rocks. (2) Cr, Co, Cu, Ni, V and Zn are depleted in the stream sediments of Cretaceous granitic basement areas relative to the sedimentary rock areas. (3) The areal distribution patterns of the Ca/Ti ratio and the elemental abundances mentioned as above, coincide with the distribution of the Cretaceous granitic basements in this area.

These characteristics can be explained as follows: Most of the stream sediments are chemically similar to the rocks exposed in local drainage areas assigned by the respective small streams. The constituent materials of sedimentary rocks have been subjected to more prolonged and intensive weathering than those of Cretaceous granitic rocks. The Ca/Al vs. Ti/Al plots of all the stream sediments, bulk granites, and biotite mineral separates, strongly suggest that biotite/plagioclase ratios of sediments in the sedimentary rock areas are greatly higher than those in the Cretaceous granitic rocks. The low Ca/Ti ratios of the sediments from the sedimentary rock areas, are approximately equal to those of biotites separated from three granites. Mg and transition metals are enriched in the separated biotites relative to the bulk granites by factors of 10 to 100. Hence, increasing biotite abundances due to weathering accompany the enrichments of transition metals, as we observe in the stream sediments from the sedimentary rock areas. However, in order to explain the areal distributions of some trace metals like Cr, the contribution by other mineral phases much more enriched in the transition metals than biotites is necessary.

Ce contents of stream sediments do not show any significant contrast between Cretaceous granitic basement areas and the other areas of sedimentary rocks. We also found relatively large inhomogeneity in the Ce concentration even in bottled stream sediments. This must be the "nugget effect" due to Ce-rich minor phases such as monazite, allanite and/or sphene. Thus the unique areal distribution of Ce may be related to the abundance of Ce-rich rare minerals in stream sediments.

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