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Major and Trace Element Chemical Compositional Signatures of Some Granitic Rocks Related to Metal Mineralization in Japan

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Abstract

We analyzed the major and trace element chemical compositions of 66 granitic rocks from 15 different areas in Japan. The intrusions from which the samples were collected were associated with Pb-Zn, Mo, Cu-Fe, Sn, or W mineralization and, for comparison, samples were also collected from intrusions not associated with any metal mineralization. The analyses indicated that the granitic rocks associated with Pb-Zn, Mo, or Cu-Fe mineralization were granites, granodiorites, or diorites, and that they were all I-type and formed in a volcanic arc tectonic setting. The granitic rocks associated with Sn or W mineralization and barren granitic rocks were classified as granites and as I-type with the exception of a few S-type granitic rocks. Most of the Sn- or W-associated granitic rocks and barren granitic rocks are thought to have formed in a volcanic arc tectonic setting. The Pb-Zn-, Mo-, or Cu-Fe-associated granitic rocks rarely shows negative Eu anomalies and a few of them are adakitic rocks, whereas all of the Sn- or W-associated granitic rocks and barren granitic rocks show negative Eu anomalies. For these Japanese granitic rocks, the contents of K_2O, La, Y, Rb, Ta, Pb, Th, U, and REEs other than Eu increase with increasing SiO_2. Conversely, the contents of major components other than Na_2O and K_2O and the trace components V, Zn, Sr, Eu, and Sc decrease with increasing SiO_2. The Zr, Sn, and Hf abundances increase with increasing SiO_2 up to 70 wt%, but their abundances decrease when the SiO_2 exceeds 70 wt%. This suggests that granitic magma is saturated with these elements at 70 wt% of SiO_2, approximately.

Keywords

Granitic Rock, Hydrothermal Mineralization, Chemical Composition, Tectonic Setting, Japan

1. Introduction

Uchida *et al.* (2007) investigated the relationship between the chemical composition of biotite and mineralization type associated with representative granitic rocks in Japan. It was found that the average total Al content of biotite, listed by mineralization type, was Pb-Zn = Mo < Cu-Fe < Sn < W < no mineralization. In addition, the study found that the total Al content in biotite increased with the granite's solidification pressure. However, Uchida *et al.* (2007) only measured the major elements in the granitic rocks; trace elements were not analyzed. In this paper, we determined the whole rock chemical compositions, including trace elements and rare earth elements, for samples of granitic rocks from the same intrusions studied by Uchida *et al.* (2007). With these analyses, we aim to confirm and clarify the relationships between the chemical composition of the granitic rocks and 1) the type of metal mineralization and 2) the tectonic settings in which the granitic rocks were emplaced (e.g., [1] [2]).

2. Granitic Intrusions Investigated

The granitic rocks analyzed for this study are from the same 15 areas studied by Uchida *et al.* [3] (**Figure 1**). **Table 1** lists the names of the areas and mining districts from which the samples were collected, rock type, age, associated metal type, and sample number for the samples.

Intrusions in the Taishu [4], Obira (granite porphyry) [5] and Chichibu mining districts were designated as granitic rocks related to Pb-Zn mineralization. We studied samples from the Ohkawame [6] and Daito-Yamasa [7] mining districts as granitic rocks related to Mo mineralization. As for Cu-Fe mineralization, granitic rocks in the Kamaishi [8] [9] and Yaguki mining districts and granitic rocks in the Tanzawa area [10] were selected for study. The granitic rocks from the Yaguki mining district were the Eastern granodiorite (the Ohisa granodiorite [11]) and the Central granodiorite. For intrusions related to Sn mineralization, samples from biotite granite in the Obira mining district [5] and granitic rocks in the Osuzu [12] and Suzuyama mining districts were selected. As for granitic rocks related to W mineralization, we studied granitic rocks in the Yakushima and the Fujigatani-Kiwida (the Habu granodiorite and the Osogoe complex), Ohtani (the Gyojayama granite [7]) and Yaguki mining districts as well as the Inada coarse-grained granite [13] in the Tsukuba area. In the Yaguki mining district, samples were collected from intrusions of the Western granodiorite (the Yokokawa granodiorite [11]). Barren granitic rocks were collected from the Hidaka metamorphic belt (the Toyonidake cordierite tonalite and hornblende tonalite [14]), the Tsukuba area other than the Inada coarse-grained granite [13] and the Fujigatani-Kiwada mining district (the Nakayamagawa complex and the Shimokuhara granite).

The granitic rocks associated with Pb-Zn, Mo, or Cu-Fe mineralization are almost magnetite-series but some are ilmenite-series whereas the granitic rocks with Sn or W mineralization and those without mineralization are all ilmenite-series (**Table 1**) [1].

3. Sample Preparation, Analysis, and Results

Whole-rock chemical analyses were carried out on 66 samples from the granitic rocks mentioned above (Table 1). Broken down by metal type, there were 10 samples related to Pb-Zn mineralization, 12 samples related to Mo mineralization, 11 samples for Cu-Fe mineralization, 9 samples for Sn mineralization, 13 samples for W mineralization, and 11 samples for barren granitic rocks. Samples

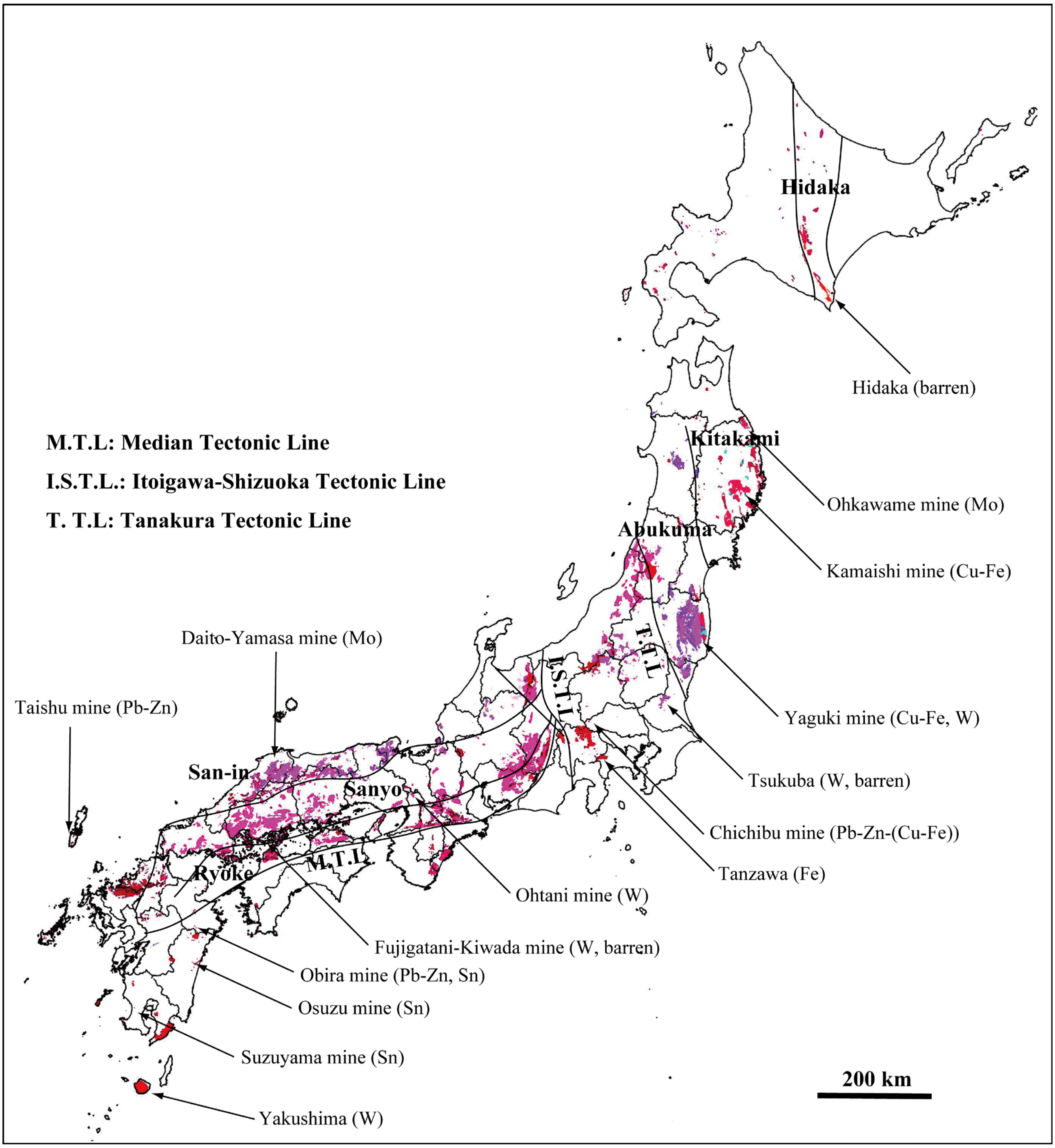


Figure 1. Map showing the localities of studied areas and distribution of Mesozoic and Cenozoic granitic rocks in Japan (Seamless digital geological map of Japan by Geological Survey of Japan).

Table 1. Lithology, age, and associated metal for 66 granitic rocks collected from 15 different localities in Japan.

Area	Granitic rock	Age	Mgt/Ilm series	Metal type	Sample No.
Hidaka	Toyonidake cordierite tonalite	Paleogene to Neogene	Ilm	No mineralization	HD02
	Toyonidake hornblende tonalite	Neogene	Ilm	No mineralization	HD05
Ohkawame mine	Granitic rocks in the zones I and II	Cretaceous	Mgt	Mo	OK01, OK04, OK05, OK07, OK11
Kamaishi mine	Ganidake granodiorite	Cretaceous	Mgt	Cu-Fe	KM03, KM04
	Ganidake diorite/diorite porphyry	Cretaceous	Mgt	Cu-Fe	KM05, KM09
Yaguki mine	Eastern granodiorite	Cretaceous	Mgt	Cu-Fe	YG01, TG04
	Central granodiorite	Cretaceous	Mgt	Cu-Fe	YG08
	Western granodiorite	Cretaceous	Mgt	W	YG16, YG17
Tsukuba	Tsukuba two mica granite	Paleogene	Ilm	No mineralization	TK01
	Inada coarse-grained granite	Paleogene	Ilm	W	TK08, TK09
	Kamishiro fine-grained granodiorite	Paleogene	Ilm	No mineralization	TK11
	Inada medium-grained granodiorite	Paleogene	Ilm	No mineralization	TK12, TK14
	Inada fine-grained granite	Paleogene	Ilm	No mineralization	TK13, TK15
	Tsukuba porphyritic granodiorite	Paleogene	Ilm	No mineralization	TK16
Chichibu mine	Chichibu quartz diorite	Neogene	Mgt	Pb-Zn(-Cu-Fe)	CC03, CC04, CC08
Tanzawa	Yushin tonalite	Neogene	Mgt	Fe	TZ05, TZ08
	Azegamaru tonalite	Neogene	Mgt	Fe	TZ10, TZ11
Ohtani mine	Ohtani or Gyojayama granite	Cretaceous	Ilm	W	OT02, OT03
Daito-Yamasa mine	Yamasa leucocratic granite	Paleogene	Mgt	Mo	DY03, DY04
	Renge granodiorite	Paleogene	Mgt	Mo	DY07, DY08
	Leucocratic granite complex	Paleogene	Mgt	Mo	DY11
	Kawai Hb-Bi hybrid rock	Paleogene	Mgt	Mo	DY10, DY14
Fujigatani-Kiwada mine	Nakayamagawa complex	Cretaceous	Ilm	No mineralization	IW02
	Habu granodiorite	Cretaceous	Ilm	W	IW07, IW08
	Shimokuhara granite	Cretaceous	Ilm	No mineralization	IW13
	Osogoe complex	Cretaceous	Ilm	W	IW18, IW19
Taishu mine	Uchiyama granitic rock and others	Neogene	Mgt-Ilm	Pb-Zn	TS05, TS07, TS08, TS13
Obira mine	Obira granite porphyry	Neogene	Ilm	Pb-Zn	OB02, OB09, OB10
	Obira biotite granite	Neogene	Ilm	Sn	OB01, OB04, OB06
Osuzu mine	Osuzu granodiorite/granite porphyry	Neogene	Ilm	Sn	OS02, OS03, OS04
Suzuyama mine	Suzuyama granite porphyry	Neogene	Ilm	Sn	SZ03, SZ04, SZ05
Yakushima	Yakushima granite	Neogene	Ilm	W	YK01, YK04, YK07

were pulverized using a tungsten carbide rod mill. About 5 g of the pulverized samples were sent to Activation Laboratories Ltd. (Ancaster, Canada) for analysis by their code "4 Litho" lithogeochemistry package. For those analyses, the granitic rock powders were fused using lithium metaborate/tetraborate and digested in dilute nitric acid. Analyses for a total of 55 elements were then obtained by analyzing the aqueous solutions thus prepared using inductively coupled plasma optical emission spectrometer (ICP-OES) and inductively coupled plasma mass spectrometer (ICP-MS). The analytical results are shown in Table 2. Because the samples were contaminated with Co and W by the tungsten carbide rod mill during grinding, Co and W values are not listed in Table 2.

Table 2. Major, minor, and trace element chemical compositions for 66 granitic rocks collected from 15 different localities in Japan.

Mineralization	Sn											W										No mineralization											
	Obira			Osuzu			Suzayama			Tsukiba		Ohtani		Fijigatani-Kiwada				Yakishjoma			Yaguki		Hidaka		Tsukiba							Fijigatani-Kiwada	
Sample No.	OB01	OB04	OB06	OS02	OS03	OS04	SZ03	SZ04	SZ05	TK08	TK09	OT03	OT04	IW07	IW08	IW18	IW19	YK01	YK04	YK07	YG16	YG17	HD02	HD05	TK01	TK11	TK12	TK13	TK14	TK15	TK16	IW02	IW13
SiO_2 (wt%)	75.14	76.06	73.15	67.34	67.23	73.17	67.93	70.93	68.63	77.69	74.16	68.75	68.75	66.81	70.98	72.08	74.84	68.85	68.61	70.33	70.57	73.26	71.54	69.09	68.92	70.04	71.54	70.22	69.84	72.32	69.34	75.53	70.52
Al_2O_3	12.47	12.28	12.96	14.72	14.83	14.2	14.13	14.16	14.08	12.34	13.44	15.34	15.34	15.7	14.95	13.6	13.56	14.32	15.15	14.04	14.85	12.44	14.81	15.4	14.9	15.3	14.28	14.3	15.02	14.67	15.18	12.94	14.11
Fe_2O_3(T)*	1.22	1.16	1.63	5.02	5.37	2.6	4.04	2.76	3.4	1.65	1.84	3.15	3.15	4.01	2.96	2.11	2.05	3.52	3.51	3.58	2.92	3.07	2.36	3.34	2.82	3.32	2.85	2.55	2.45	2.62	3.06	1.17	2.95
MnO	0.022	0.018	0.027	0.087	0.08	0.055	0.029	0.023	0.038	0.031	0.03	0.067	0.07	0.096	0.082	0.039	0.047	0.079	0.067	0.067	0.066	0.07	0.046	0.065	0.072	0.063	0.058	0.054	0.053	0.07	0.058	0.063	0.086
MgO	0.14	0.14	0.2	1.55	1.69	0.75	1.21	0.96	1.06	0.16	0.19	0.93	0.93	1.12	0.74	0.33	0.45	0.92	0.92	0.97	0.81	0.84	1.04	1.75	0.69	0.6	0.57	0.42	0.45	0.52	0.88	0.13	0.61
CaO	0.71	0.88	0.87	2.73	2.85	1.09	2.61	2.16	2.49	1.89	1.89	2.04	2.04	3.24	2.2	1.24	1.6	2.41	2.78	1.79	3.2	2.23	2.79	3.91	2.32	2.8	2.56	2.28	2.33	2.23	2.93	0.81	1.94
Na_2O	3.25	3.21	3.19	3.02	2.93	2.76	2.75	2.78	2.84	3.06	3.03	2.95	2.95	3.53	3.27	2.9	2.94	3.33	3.45	2.79	3.42	2.61	3.13	3.36	3.36	3.8	3.36	3.39	3.43	3.22	4.02	3.43	3.07
K_2O	4.78	4.52	5.02	3.3	3.23	4.24	3.69	3.98	3.56	3.48	4.41	3.92	3.92	3.22	3.98	4.89	4.12	3.62	3.28	3.82	2.92	3.64	3.06	1.88	3.84	2.75	3.12	3.62	3.93	4.18	1.51	4.34	3.33
TiO_2	0.149	0.138	0.21	0.803	0.87	0.373	0.524	0.495	0.483	0.143	0.164	0.438	0.44	0.364	0.269	0.186	0.247	0.525	0.533	0.517	0.309	0.327	0.318	0.483	0.326	0.355	0.32	0.283	0.271	0.302	0.429	0.074	0.289
P_2O_5	0.03	<0.01	0.02	0.17	0.17	0.17	0.1	0.09	0.1	0.03	0.03	0.23	0.23	0.13	0.1	0.01	0.08	0.17	0.13	0.17	0.06	0.08	0.06	0.08	0.14	0.13	0.13	0.1	0.08	0.12	0.06	0.02	0.06
LOI	0.65	0.33	0.84	1.38	1.08	1.46	1.72	2.14	2.11	0.3	0.6	2.07	2.07	1.02	0.92	0.89	0.8	0.92	0.73	1.11	0.7	0.74	0.79	1.23	0.78	0.94	0.46	1.14	0.91	0.67	0.94	0.75	1.23
Total	98.57	98.99	98.11	100.4	100.3	100.9	99.23	100.5	98.89	100.8	99.8	100.2	100.2	99.24	100.4	98.27	100.8	98.65	99.14	99.17	99.81	100.4	99.94	100.6	98.18	100.1	99.24	98.35	98.78	100.9	98.42	99.26	98.18
Sc (ppm)	6	6	7	13	14	7	15	15	14	5	5	7	7	8	7	5	6	9	9	8	6	6	8	11	6	8	6	6	5	6	8	4	6
Be	3	2	2	2	3	3	2	3	3	2	2	4	4	3	3	3	3	4	4	7	2	1	1	2	5	2	3	2	3	3	2	4	4
V	17	17	13	65	77	34	46	46	43	10	12	33	33	50	32	16	22	35	38	34	40	36	28	58	30	19	16	15	15	28	44	7	20
Ba	216	187	261	494	559	426	515	562	482	958	1314	513	513	513	695	224	351	189	295	248	395	523	811	315	464	867	480	766	760	828	146	235	333
Sr	43	49	54	158	179	85	180	168	166	159	189	229	229	230	182	84	103	133	176	115	213	159	300	262	236	361	290	275	292	247	307	70	116
Y	32	24	34	27	30	19	29	28	31	18	21	17	17	15	13	26	19	28	27	23	13	13	28	13	20	15	22	17	23	22	19	44	31
Zr	105	102	112	232	293	127	188	204	182	120	140	115	115	99	81	63	100	142	183	165	96	103	62	59	122	195	145	155	164	137	205	76	86
Cr	<20	<20	<20	50	50	40	30	30	30	20	<20	<20	<20	<20	30	<20	20	20	20	30	<20	<20	<20	50	<20	<20	<20	20	<20	<20	<20	<20	<20
Ni	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	30	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20
Cu	<10	10	<10	<10	10	<10	80	90	40	<10	<10	<10	<10	<10	<10	<10	<10	<10	30	<10	<10	10	<10	<10	<10	<10	<10	<10	<10	<10	<10	20	<10
Zn	40	<30	<30	60	70	40	50	<30	40	40	40	70	70	50	70	<30	30	60	50	50	40	60	40	40	60	50	70	60	60	40	50	50	70
Ga	18	18	17	19	19	19	20	17	19	16	16	19	19	19	18	18	18	20	20	21	15	14	13	13	19	20	20	19	19	16	20	17	18
Ge	2	2	2	2	2	2	2	3	2	1	2	1	1	2	2	2	1	2	2	2	2	1	2	2	2	2	2	1	2	2	2	3	2

Continued

As	<5	<5	<5	5	16	<5	13	45	137	<5	<5	<5	<5	<5	<5	<5	<5	9	12	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Rb	226	206	224	113	116	192	188	181	155	95	113	169	169	145	156	263	192	176	158	201	95	126	65	59	180	97	125	110	138	143	101	176	162
Nb	14	14	11	12	12	11	13	11	13	5	5	10	10	10	9	16	9	12	12	14	5	7	2	1	9	13	9	8	9	8	9	7	9
Mo	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
Ag	<0.5	0.5	<0.5	1	1.6	1	0.9	1.3	0.8	1	0.6	<0.5	<0.5	<0.5	0.6	<0.5	0.7	0.7	0.7	0.7	<0.5	<0.5	0.7	<0.5	0.6	0.9	0.6	1	0.9	1	0.9	<0.5	<0.5
In	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Sn	8	2	2	2	4	4	2	7	3	2	1	4	4	3	3	4	4	9	11	5	2	3	2	3	8	2	3	2	3	4	4	8	17
Sb	1.2	0.5	<0.5	<0.5	0.6	1.1	<0.5	<0.5	0.5	0.8	<0.5	<0.5	<0.5	<0.5	0.8	<0.5	1.7	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0.9	<0.5	<0.5	<0.5	<0.5	<0.5
Cs	11.7	11.1	15.2	5.6	7.9	13.8	24.1	18	19.9	2.9	3.1	8.2	8.2	9.5	8.4	17.2	9	15.7	16.5	16.9	4.1	6.6	3.5	4.6	11.9	5	5.3	2.3	3.5	5.6	7.6	5.8	13.5
La	42.3	40.7	32.9	36.2	38.1	27.2	37.2	37.1	36.4	53.1	40.1	30.6	30.6	29.6	21.8	18.9	36.4	30.4	31.7	33.8	13.7	28.8	25	5	29.9	36.4	37.1	35	37.6	43.5	50.2	15.8	28.5
Ce	88.5	83.7	68.8	73.7	77.9	55.3	76.4	75	74.4	101	77.6	59.4	59.4	54.9	39.3	37.2	70.6	63	64.5	70.7	24.6	50.9	52	10.3	60	69	74.4	67.8	76.5	82.6	96.8	33.4	58.8
Pr	9.97	9.34	8.08	8.23	9.01	6.42	8.45	8.59	8.27	11.3	8.54	6.48	6.48	6.07	4.36	4.5	7.93	6.95	7.36	7.86	2.9	5.18	6.14	1.13	6.77	7.5	8.36	7.75	8.79	8.96	11	4.15	6.44
Nd	37.3	34.6	30.6	31.9	34.2	23.2	31.8	32.1	31.7	39.9	30.2	23.3	23.3	22.3	16.1	17.3	28.9	26.6	27.8	29.8	10.5	17.3	23.7	4.4	25.3	26.8	31.8	28.7	31.7	31.4	38.8	17.4	24.7
Sm	8.1	7	7.1	6.2	6.8	4.9	6.8	6.4	6.7	6.4	5.6	4.7	4.7	4.7	3.4	4.6	5.8	5.7	5.3	6.3	2.4	2.9	5	1.2	5	4.9	6.5	5.4	6.4	5.8	7.2	5	5.8
Eu	0.29	0.29	0.34	1.2	1.28	0.76	1.07	1.06	1.05	0.84	0.93	0.79	0.79	0.8	0.67	0.44	0.63	0.75	0.99	0.75	0.8	0.61	0.92	0.71	0.89	0.99	0.91	0.95	0.97	1.06	1.17	0.31	0.56
Gd	6.2	5.6	5.9	5.3	5.8	4.1	5.7	5.3	5.8	4.8	4.3	3.5	3.5	3.4	3.1	4.5	4.9	5	4.8	5	2.1	2.3	4.3	1.3	3.8	3.9	5.1	4.6	4.9	4.7	5.5	5.7	5.5
Tb	1	0.8	1	0.8	0.9	0.6	0.9	0.8	0.9	0.7	0.6	0.5	0.5	0.5	0.5	0.8	0.7	0.8	0.8	0.8	0.3	0.4	0.7	0.2	0.6	0.5	0.8	0.7	0.7	0.7	0.7	1.1	0.9
Dy	6.2	4.9	5.8	5.2	5.2	3.7	5.4	5.1	5.6	3.7	3.7	3.2	3.2	2.9	2.5	4.3	3.8	5.5	4.8	4.6	2.1	2.3	4.2	1.7	3.7	2.9	4.4	3.6	4.2	3.8	3.7	7.3	5.6
Ho	1.2	1	1.1	1	1	0.7	1.1	1	1.1	0.7	0.8	0.6	0.6	0.5	0.4	0.8	0.7	1.1	0.9	0.9	0.4	0.5	1	0.4	0.7	0.5	0.8	0.7	0.8	0.7	0.7	1.5	1.1
Er	3.7	2.8	3.3	3.1	3.1	2.3	3.4	2.8	3.4	2.1	2.2	1.9	1.9	1.3	1.2	2.2	2	3.2	2.7	2.6	1.3	1.5	2.9	1.2	2	1.5	2.3	1.9	2.2	2.1	1.9	4.1	3
Tm	0.58	0.43	0.5	0.45	0.47	0.37	0.5	0.45	0.52	0.3	0.34	0.33	0.33	0.19	0.17	0.32	0.3	0.48	0.44	0.39	0.22	0.24	0.42	0.21	0.31	0.2	0.33	0.28	0.34	0.33	0.26	0.64	0.44
Yb	3.7	2.7	3.3	2.9	3	2.5	3.1	3	3.2	1.9	2.3	2.1	2.1	1.3	1.1	2	1.8	3.2	2.9	2.4	1.5	1.6	2.5	1.5	2	1.3	2.1	1.7	2	2.2	1.7	4.1	2.7
Lu	0.52	0.4	0.45	0.44	0.45	0.38	0.48	0.45	0.5	0.29	0.33	0.29	0.29	0.19	0.16	0.31	0.26	0.45	0.4	0.36	0.23	0.25	0.37	0.23	0.31	0.18	0.3	0.23	0.3	0.33	0.27	0.6	0.38
Hf	4.5	4.5	3.4	6.5	6.5	4	5.6	4.9	5.8	4	3.9	3.8	3.8	2.8	3	1.9	3.5	4.5	4.4	5.4	2.4	3.2	1.5	1.6	3.2	4.3	4.5	4.6	4.3	3	5	2.9	2.7
Ta	2.3	2.4	2.2	1.2	1.3	2	1.4	1.6	1.6	0.8	1	1.5	1.5	2.2	2	2.8	1.9	1.7	2.1	2	1.3	1.4	0.9	0.7	1.9	2	1.5	1.1	1.6	1.4	1.9	2.8	2.9
Tl	1.2	1	1.2	0.6	0.7	0.6	1.2	1.4	1.1	0.4	0.7	0.8	0.8	0.8	0.7	1.4	0.9	0.9	1.1	1	0.5	0.6	0.3	0.2	1.1	0.7	0.6	0.4	0.7	0.9	0.7	0.9	0.9
Pb	38	28	24	16	16	21	11	10	12	17	17	27	27	20	27	37	31	23	22	21	15	16	20	13	22	20	21	22	23	19	14	34	20
Bi	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	1.3	0.5	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	0.5	1.7
Th	24.2	25.8	17.7	11.9	13.1	10.6	15.5	15.8	15.7	14.8	11.4	12.7	12.7	14.8	11.4	13.8	22.8	12.6	12.5	13.5	10.5	15.4	10.7	0.6	12	8.9	11	8.7	11.1	15.7	21.8	11.1	18.6
U	5.1	4.8	3.7	2.5	2.6	3.9	3.7	4.8	4.1	2	1.8	2.8	2.8	4.3	2.8	3.5	3.3	5.4	5	4	2.2	2.4	1.6	1.7	3.4	1.3	2.2	1.1	1.6	5.5	2.7	2.8	5

*Total Fe as Fe_2O_3

4. Discussion

4.1. Chemical Compositions and Granitic Rock Classification

According to the classification of plutonic rocks based on the SiO_2 vs. (Na_2O + K_2O) diagram (**Figure 2**) [15] [16], most of the granitic rocks associated with Sn or W mineralizetion and barren granitic rocks are classified as granites except some of them deviate into granodiorite. The samples associated with Pb-Zn or Mo mineralization fall into granite, diorite and diorite fields, whereas the samples associated with Cu-Fe mineralization are mainly in the diorite to granodiorite fields except one sample fall into granite field.

According to the A/NK vs. A/CNK diagram (**Figure 3**), A/CNK values for the granitic rocks associated with Pb-Zn, Mo or Cu-Fe mineralization range from 0.7 to 1.1; this means that they are metaluminous to slightly peraluminous. They were all classified as I-type granitic rocks [17]. The A/CNK values for the granitic rocks associated with Sn or W mineralization and barren granitic rocks range from 1.0 to 1.3, which corresponds to peraluminous. Most of these rocks are I-type granitic rocks but some are S-type granitic rocks.

4.2. Tectonic Setting

Based on the Rb vs. (Yb + Ta) diagram (**Figure 4**) [18], most of the granitic

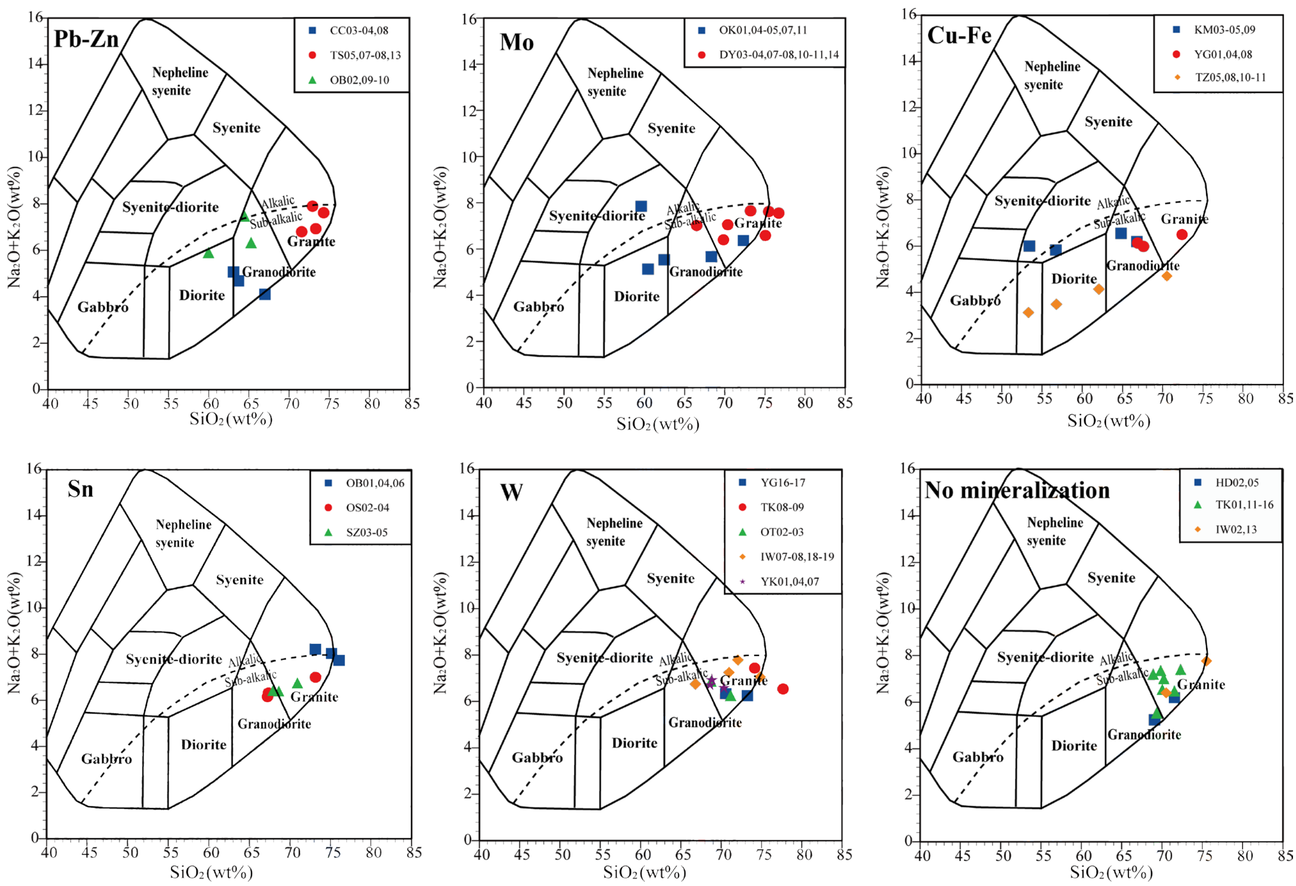


Figure 2. Classification of the analyzed granitic rocks from Japan: Total alkali vs. SiO_2 diagrams (classification boundaries after Cox *et al.* [15]; Wilson [16]).

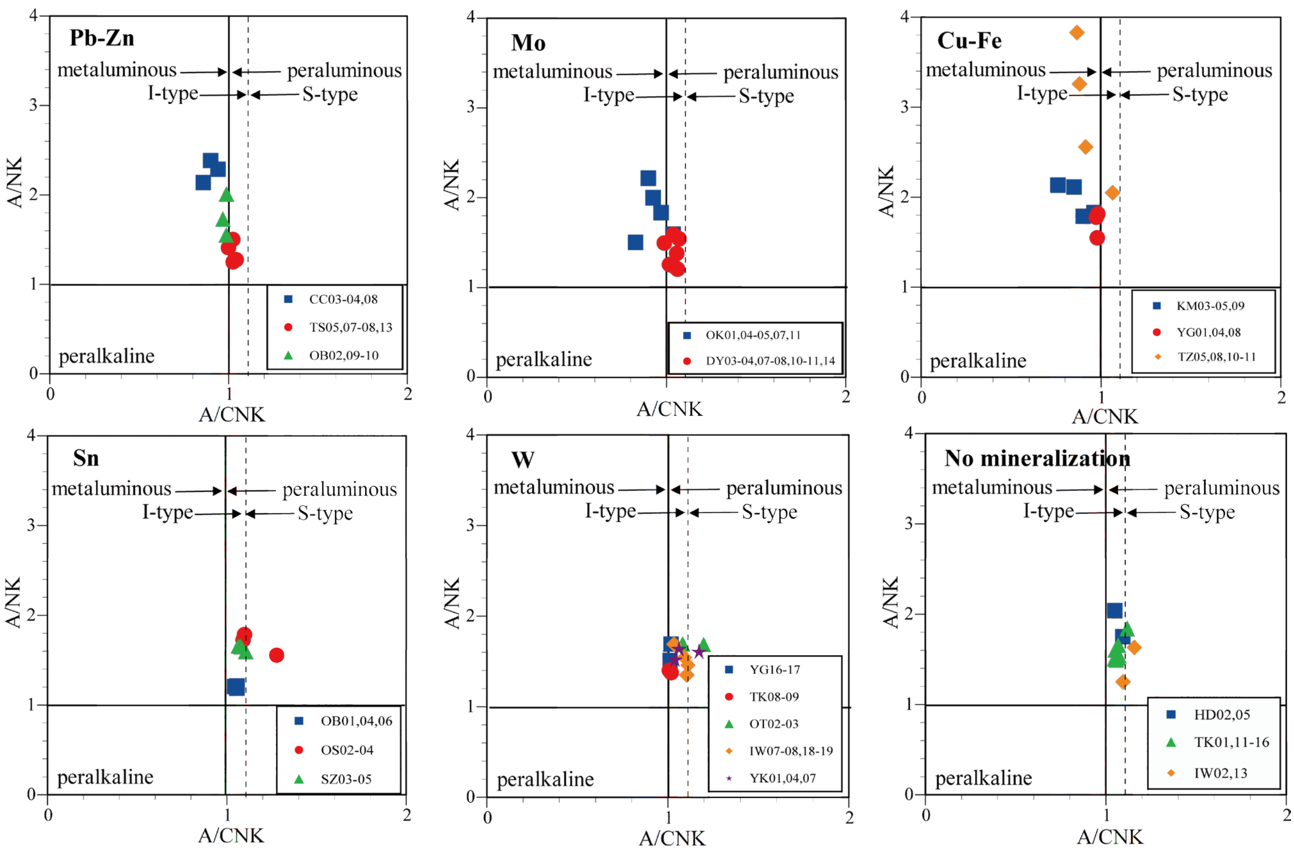


Figure 3. Classification of the analyzed granitic rocks from Japan: $Al_2O_3/(Na_2O + K_2O)$ vs. $Al_2O_3/(CaO + Na_2O + K_2O)$ diagrams.

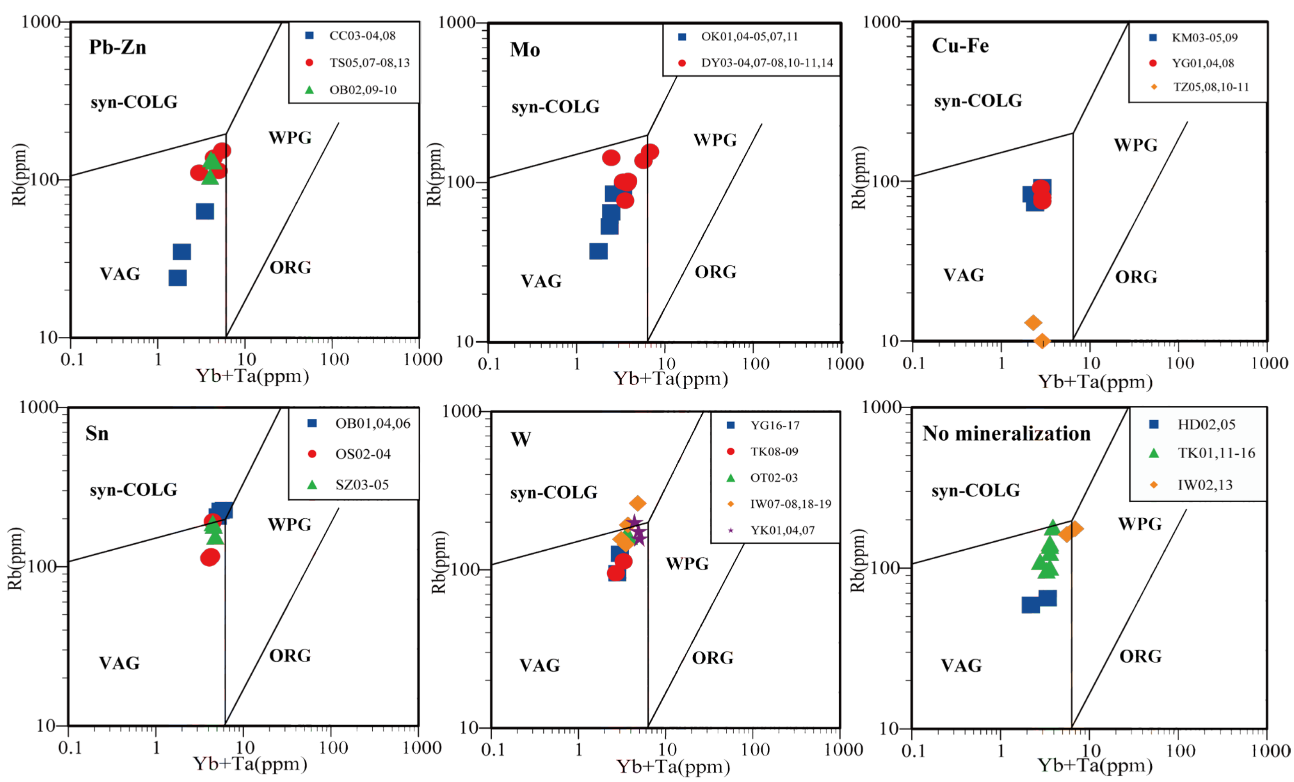


Figure 4. Rb vs. (Yb + Ta) tectonic discrimination diagrams (after Pearce *et al.* [18]) for the granitic rocks from Japan. ORG: ocean ridge granitic rocks, VAG: volcanic arc granitic rocks, WPG: within plate granitic rocks, and syn-COL: syn-collision granitic rocks.

rocks analyzed were classified as volcanic arc granitic rocks. However, some granitic rocks associated with Sn or W mineralization (some Obira and some Fujigatani-Kiwada mining districts samples) were plotted in syn-collision granitic rock field. Because the Rb content of the Tanzawa granitic rocks is extremely low, they were classified as M-type granitic rocks [19]. As the Chichibu granitic rocks are also depleted in Rb, although not as depleted as the Tanzawa granitic rocks, they were also classified as M-type granitic rocks.

According to the Sr/Y vs. Y diagram by Defant and Drummond [20] (**Figure 5**), most of the granitic rocks analyzed in this study are non-adakitic, but a few adakitic rocks are present in the granitic rocks in the Ohkawame and Kamaishi mining districts [21]. For the adakitic rocks analyzed, all the Al_2O_3 content are greater than 15 wt% except for one sample (OK11 at 14.59 wt%). On the SiO_2 vs. Zr/TiO_2 diagram (**Figure 6**) [22], most of these adakitic rocks were classified as true adakitic rocks which were produced by the partial melting of young subducting oceanic crust.

4.3. REE Patterns

Chondrite-normalized REE patterns for the granitic rocks organized by type of associated metal are shown in **Figure 7**.

All of the granitic rocks associated with Sn or W mineralization show negative Eu anomalies. The Eu anomalies for the biotite granites associated with Sn mineralization in the Obira mining district are particularly large. Barren granitic rocks also show negative Eu anomalies except for the hornblende granodiorite in

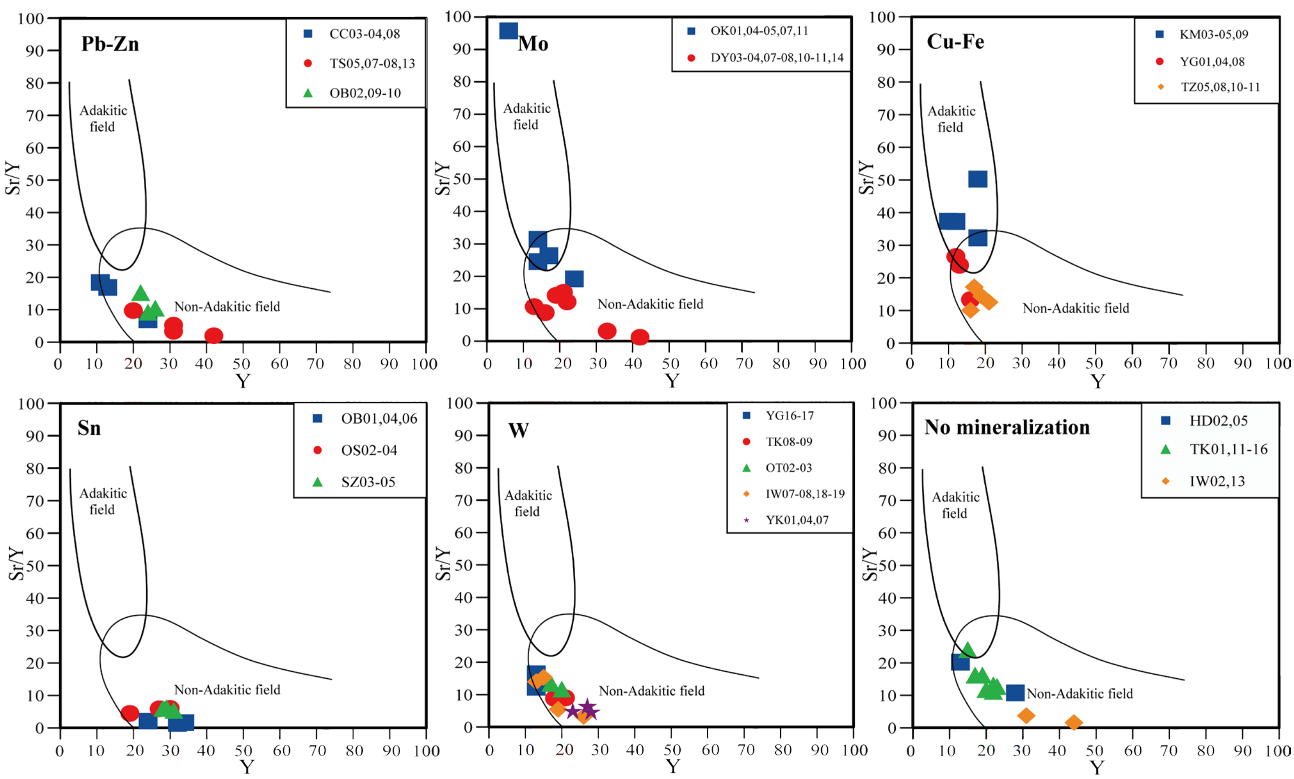


Figure 5. Sr/Y vs. Y diagrams (after Defant and Drummond [20]) for the granitic rocks from Japan.

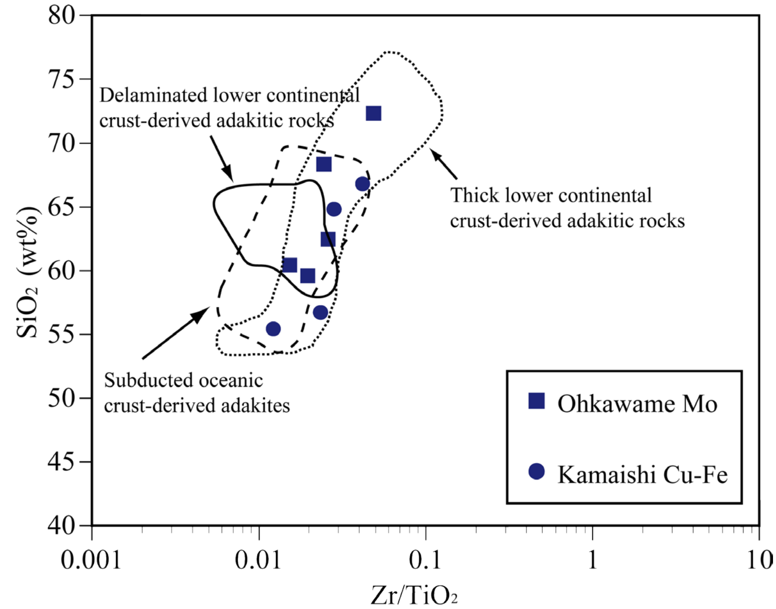


Figure 6. SiO_2 vs. Zr/TiO_2 discrimination diagram for adakitic rocks (after Wang *et al.* [22]), showing plots for the granitic rocks from the Kamaishi and Ohkawame mining districts, Japan.

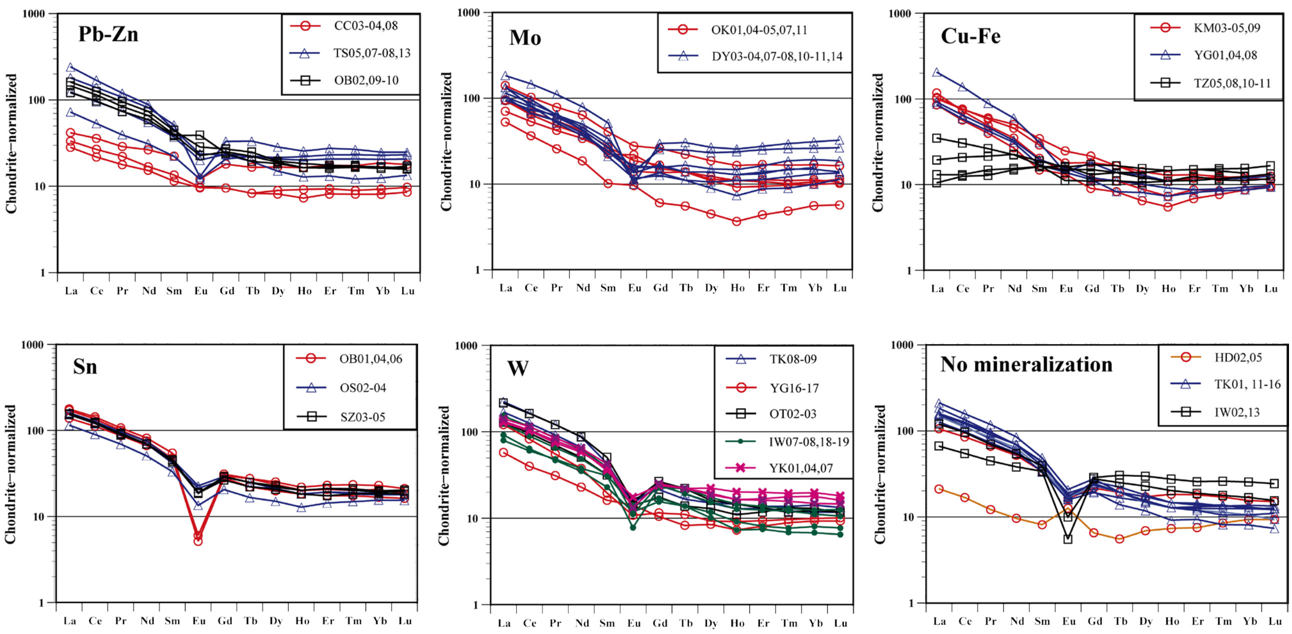


Figure 7. Chondrite-normalized REE patterns for the granitic rocks from Japan.

the Toyonidake area in the southern part of the Hidaka metamorphic belt. This indicates that the Sn- or W-associated granitic rocks and barren ones were formed by the fractional crystallization of plagioclase from granitic magma under reducing conditions where divalent Eu was stable. The hornblende granodiorite in the Toyonidake area shows a pronounced positive Eu anomaly and it is relatively depleted in REEs. These observations suggest that plagioclase may have accumulated during hornblende granodiorite formation.

Conversely, the majority of the granitic rocks with Pb-Zn, Mo, or Cu-Fe mineralization do not show pronounced negative Eu anomalies. This suggests that these rocks formed under oxidizing conditions where trivalent Eu was stable. The samples associated with Pb-Zn, Mo, or Cu-Fe mineralization that do show significant negative Eu anomalies, the Uchiyama sample TS05 (Pb-Zn) and the Yamasa sample DY04 (Mo), are rich in SiO_2 (>74%) and relatively enriched in REEs. This suggests that they formed from differentiated magmas. The REE patterns for the granitic rocks from the Tanzawa area (TZ samples, Cu-Fe) are almost flat, consistent with the features of M-type granitic rocks [20] [23]. The REE patterns for the granitic rocks from the Chichibu mining district (CC samples, Pb-Zn) are also relatively flat and show the features of M-type granitic rocks.

Figure 8 shows the relationship between the magnitude of the negative Eu anomaly and the differentiation index. The vertical axis in Figure 9 shows the distance (Eu/Eu*) from the line connecting Sm and Gd on the chondrite-normalized REE pattern to Eu in Figure 8. The Eu/Eu* is defined by the following equation:

$$\frac{\text{Eu}}{\text{Eu*}} = \log\left(\frac{\text{Eu}}{\text{Eu}_{\text{cn}}}\right) - \frac{1}{2}\left(\log\left(\frac{\text{Sm}}{\text{Sm}_{\text{cn}}}\right) + \log\left(\frac{\text{Gd}}{\text{Gd}_{\text{cn}}}\right)\right),$$

where REE with subscript of cn indicates each REE concentration of chondrite.

Figure 8 indicates that the magnitude of the negative Eu anomalies increase as the differentiation index increases.

4.4. Interelement Correlations and SiO_2 Content

Figure 9 shows graphs of SiO_2 vs. the major element oxides and graphs of SiO_2

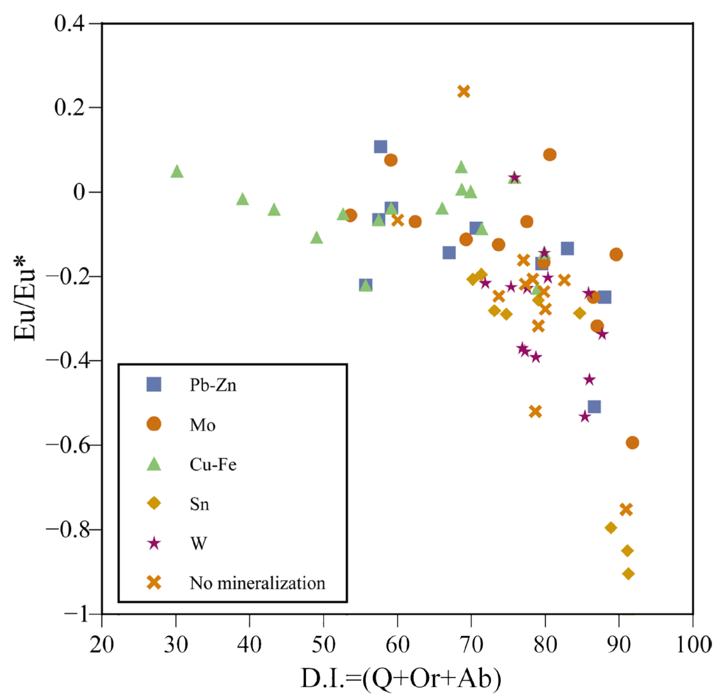
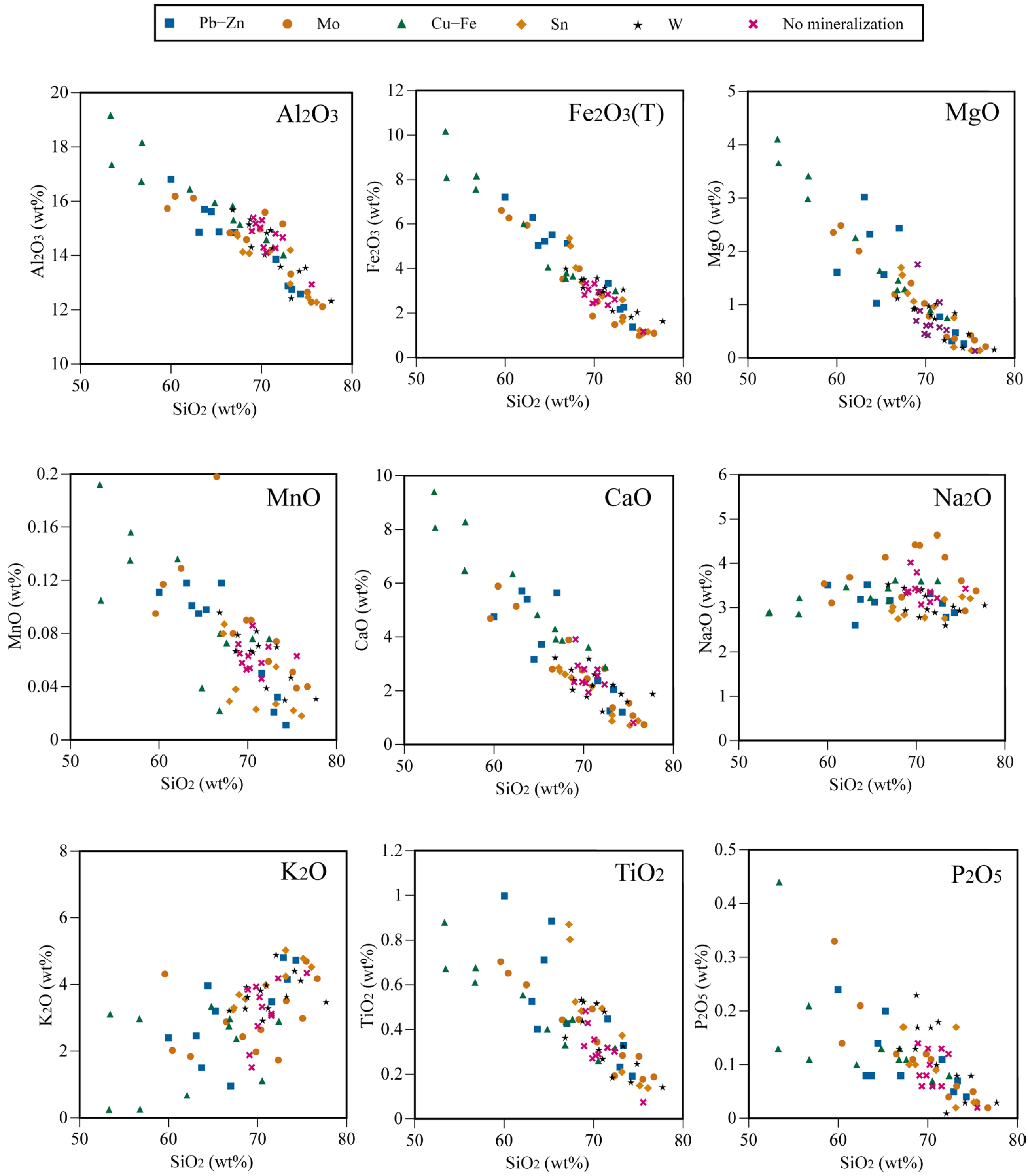
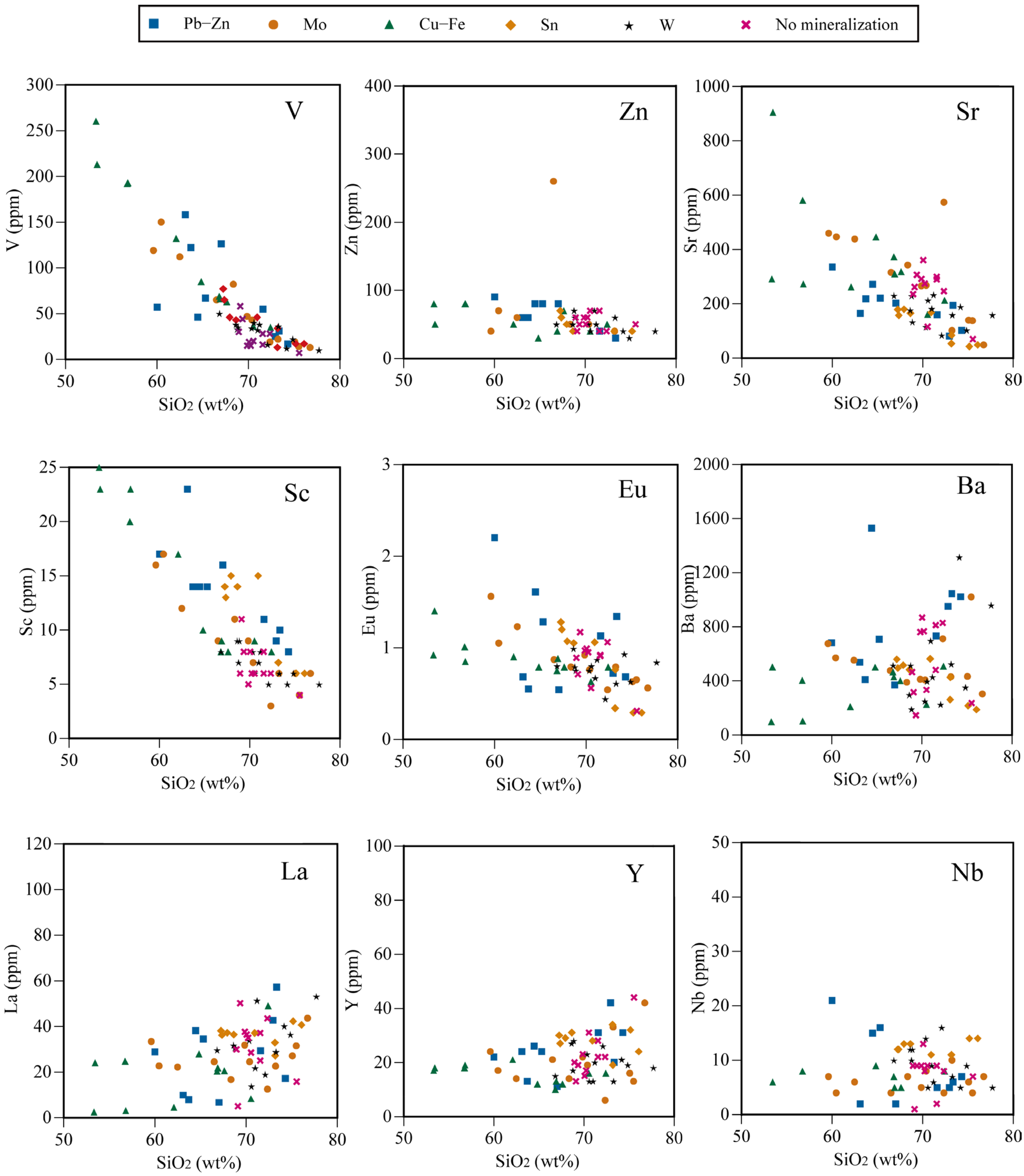


Figure 8. Eu/Eu* vs. differentiation index (D.I.) diagram for the granitic rocks from Japan.


Pb–Zn
Mo
Cu–Fe
Sn
W
No mineralization
Al2O3
Al2O3 (wt%)
Fe2O3(T)
Fe2O3 (wt%)
MgO
MgO (wt%)
MnO
MnO (wt%)
CaO
CaO (wt%)
Na2O
Na2O (wt%)
K2O
K2O (wt%)
TiO2
TiO2 (wt%)
P2O5
P2O5 (wt%)
SiO2 (wt%)


Pb–Zn
Mo
Cu–Fe
Sn
W
No mineralization
V
V (ppm)
Zn
Zn (ppm)
Sr
Sr (ppm)
Sc
Sc (ppm)
Eu
Eu (ppm)
Ba
Ba (ppm)
La
La (ppm)
Y
Y (ppm)
Nb
Nb (ppm)
SiO2 (wt%)
50
60
70
80
0
50
100
150
200
250
300
400
800
1000
1600
2000
10
15
20
25
1
2
3
20
40
60
80
120
30

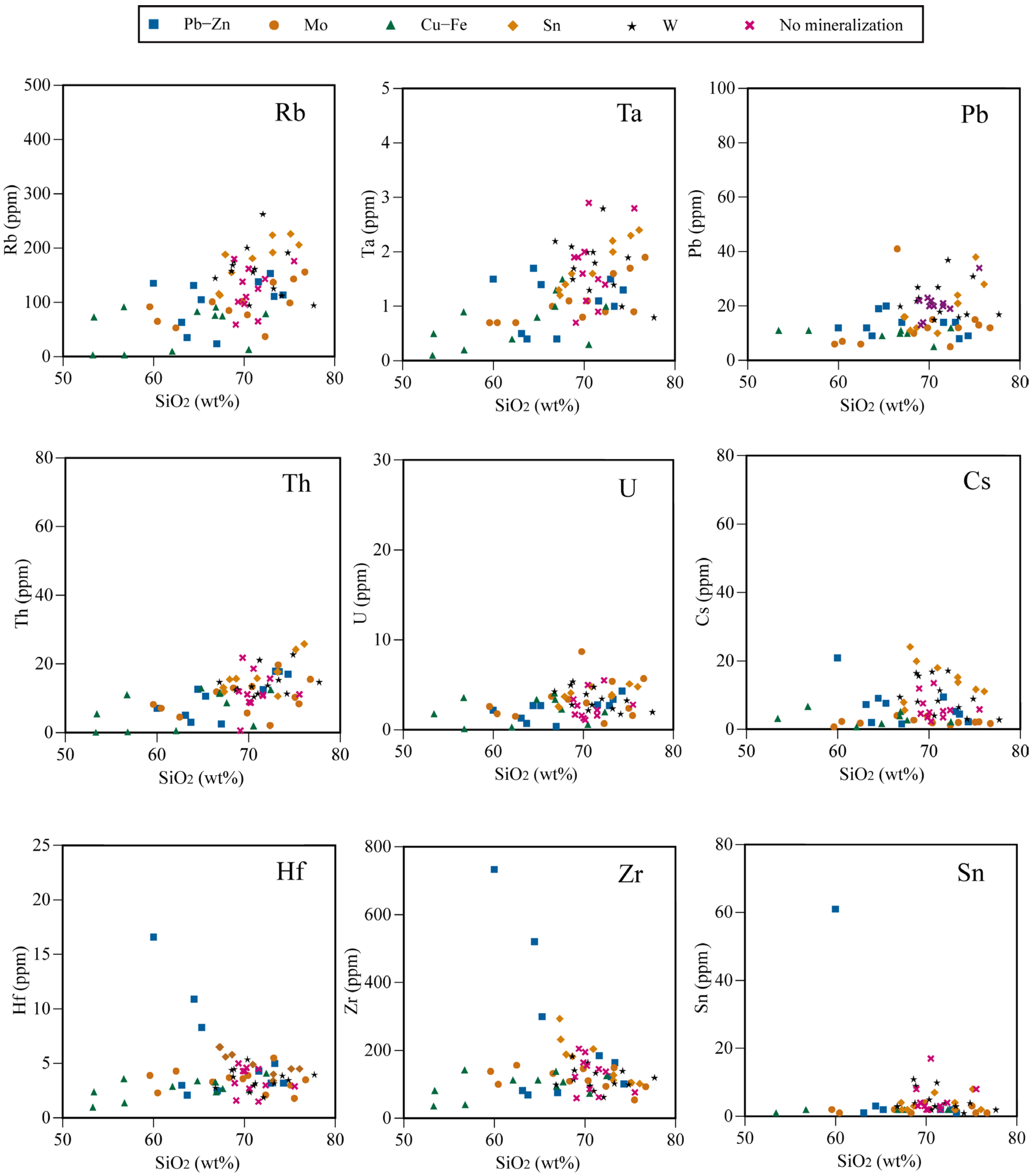


Figure 9. Variation diagrams for the granitic rocks from Japan. Data points are coded for the metal association.

vs. trace elements. The relationships illustrated in **Figure 9** are discussed below.

The Al_2O_3, Fe_2O_3(T), MgO, MnO, CaO, TiO_2, and P_2O_5 show a tendency to decrease with increasing SiO_2, whereas, despite a lot of scatter in the data, K_2O seems to increase. The granitic rocks in the Tanzawa area and the Chichibu mining district have low K_2O and are high in CaO (**Table 2**), suggesting that they are M-type granitic rocks. It seems that Na_2O content increase slightly or is almost constant with increasing SiO_2.

The elements V, Zn, Sr, Eu, and Sc decrease as SiO_2 increases. Vanadium is commonly incorporated in magnetite but is also partitioned into mafic minerals like pyroxenes, amphiboles, and biotite [24]. Because Sc^{3+} is close to Fe^{2+} and Mg^{2+} in ionic radius [25], it is thought that Sc^{3+} is incorporated in mafic minerals in a similar way to Zn and V. In contrast, Sr is incorporated in plagioclase by substituting Ca.

Yttrium, Nb, Rb, Ta, Pb, Th, U, and REEs other than Eu are elements that increase as SiO_2 increases. Among the REEs, Ce, Pr, Nd, and Sm behave like La, and Ga, Tb, Dy, Ho, Er, Tm, Yb, and Lu behave like Y. The granitic rocks associated with Sn or W mineralization and barren granitic rocks have higher SiO_2 contents compared to the granitic rocks associated with Pb-Zn, Mo, or Cu-Fe mineralization, so there is a tendency for La, Y, Nb, Rb, Ta, Pb, Th, U, and REEs other than Eu to be enriched in the Sn- or W-associated granitic rocks and barren granitic rocks (e.g., [1] [26] [27] [28]).

Zirconium, Sn, and Hf increase with increasing SiO_2, but start to decrease when the SiO_2 content exceeds 70 wt%. Zirconium concentrates in the magma during crystal differentiation. However, when the SiO_2 content reaches around 70 wt%, it is likely that magma will be saturated with Zr and zircons will precipitate [29]. Thus above 70 wt% SiO_2, the Zr content in the remaining magma tends to decrease. As shown in **Figure 9**, the distribution of Hf data points mimics the distribution of the Zr points, indicating that Hf is concentrated in zircon. Tin behaves similarly to Zr and Hf and it is concentrated in the magma as crystal differentiation progresses. Magmas will be saturated with Sn when the SiO_2 content reaches about 70 wt%. A granite porphyry accompanied by Pb-Zn mineralization in the Obira mining district is enriched in Zr, Hf, and Sn compared with other granitic rocks.

The behavior of Ba on **Figure 9** is complicated. On the whole, Ba shows a similar behavior to the REEs including La with a larger ionic radius, and Ba content increases as SiO_2 increases. At the same time, however, the Ba content tends to decrease similarly to the alkali earth elements such as Ca and Sr as SiO_2 increases.

5. Conclusions

Major and trace element contents were determined for 66 samples of granitic rocks from 15 different areas in Japan. The samples were from intrusions that were either associated with Pb-Zn, Mo, Cu-Fe, Sn, or W mineralization or were barren. Examination of the analytical results for the studied granitic rocks allows the following conclusions to be drawn.

The studied granitic rocks associated with Pb-Zn, Mo, or Cu-Fe mineralization were classified as granite to diorite and were magnetite-series and I-type granitic rocks. However, the granitic rocks in the Tanzawa area and the Chichibu mining district were classified as M-type granitic rocks. The granitic rocks in the Ohkawame and Kamaishi mining districts are adakitic rocks and were generated from the partial melting of a subducting oceanic plate. It is thought that all the granitic rocks formed in a volcanic arc tectonic setting. Only a few REE analyses for rocks of this type show negative Eu anomalies.

Most of the studied granitic rocks associated with Sn or W mineralization and the barren granitic rocks were classified as granite and were ilmenite-series and I-type granitic rocks. A few of these rocks are S-type granitic rocks. It is likely that most of the granitic rocks formed in a volcanic arc tectonic setting. None of these granitic rocks is adakitic and most of their chondrite-normalized REE pattern show negative Eu anomalies.

The contents of K_2O, La, Y, Nb, Rb, Ta, Pb, Th, U, and REEs other than Eu in the granitic rocks increase with increasing SiO_2. These elements tend to be enriched in the high SiO_2 granitic rocks associated with Sn or W mineralization and the high SiO_2 barren granitic rocks.

The major components other than Na_2O and K_2O, Sr, Eu, and Sc in the granitic rocks tend to decrease as SiO_2 increases.

Barium has two different trends. For some sets of analyses, Ba tends to increase with increasing SiO_2, for other sets Ba decreases with increasing SiO_2.

The contents of Zr, Sn, and Hf increase with increasing SiO_2 up to approximately 70 wt%, but then decrease when the SiO_2 content exceeds 70 wt%. This phenomenon is thought to be related to the melt becoming saturated with these elements.

Acknowledgements

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