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Ishida, Kiyotaka
Department of Evolution of Earth Environments, Graduate School of Social and Cultural Studies, Kyushu University

https://doi.org/10.15017/8564

出版情報：比較社会文化. 1, pp.87-96, 1995-04-28. 九州大学大学院比較社会文化研究科
バージョン：
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『比較社会文化』第1巻（1995）87～96頁
Bulletin of the Graduate School of Social and Cultural Studies, Kyushu University
vol.1 (1995), pp.87～96

Cation site-occupancies and infrared spectra for Na-Ca and alkali amphiboles in manganese ore deposits from Japan and India

Kiyotaka ISHIDA*

Keywords: Mn-bearing amphibole, Cation site-occupancy, A-site occupancy, Infrared spectra

Abrstract: With the combination of Mössbauer spectroscopy and an electron probe microanalysis, the relationships between the cation site-occupancies and infrared spectra for Na-Ca and alkali amphiboles in manganese ore deposits from Japan and India have been investigated. The fractionation ratios of Na, Ca, and Mn in their M(4) site are closely related to the A-site alkali metal occupancy: for amphiboles nearly unoccupied with alkali metal at A site (0.00～0.25 Na+K, per formula unit) Mn is strongly concentrated in the M(4) site; in A-site partially occupied (0.25～0.75 p.f.u.) amphiboles Mn content becomes to decrease whereas the populations of Na and Ca become to be predominant; and in A-site fulfilled (0.75～1.00 p.f.u.) amphiboles Na and Ca are also predominant. The distribution of manganese in their M(1)・M(2)・M(3) sites increases with increasing the A-site alkali metal occupancy. A-site occupancies estimated by means of the chemical analysis are roughly proportional to those values calculated from infrared OH stretching bands. The frequencies and intensities of almost all their infrared absorption bands are closely related to the A-site occupancies in these amphiboles.

Introduction

Amphiboles are the most chemically complex silicates among major rock-forming mineral groups, consisting of Si-O double chains and M(1), M(2), M(3) and M(4) cation sites similar to that of pyroxene structure with Si-O single chain and M(1) and M(2) cation sites, and also of the interlayer A cation site and structural $(OH)^-$ ions alike sheet silicates. According to the nomenclature of amphiboles proposed by Leake (1978), the principal groups are classified mainly on the basis of the kinds of M(4) site cation: iron-magnesium-manganese (Fe-Mg-Mn), calcic (Ca), sodic-calcic (Na-Ca), and alkali amphiboles.

As there are various ionic substitutions in their various cation sites, many spectral studies for amphiboles — not only X-ray crystal structural analysis but also Mössbauer, infrared, Raman, electronic absorptions, etc. — have been undertaken to obtain mineralogical information. Among these many experimental techniques that were used to derive site-populations for amphiboles, the three most common techniques are the X-ray diffraction, Mössbauer and infrared spectroscopies, as reviewed by Hawthorne (1983).

Manganese ion is usually contained in all kinds of amphiboles, and many mineralogical and petrological studies for Mn-bearing amphiboles which occur in contact or regionally metamorphosed manganese ore deposits in India, Japan, and U.S.A. have been made (Roy and Purkait, 1968; Nambu et al., 1980; Klein, 1966). Numerous spectral studies for amphiboles have been made, however, those for Mn-bearing ones are rather scarce. Mottana and Griffin (1986) have reported infrared OH -stretching bands of some Sr-containing richterites. In their crystal structural and chemical analyses for Li-containing manganoan alkali amphiboles, Ghose et al. (1986) and Hawthorne et al. (1992) have reported that the Li is concentrated at the M(3) site, and the Fe^{3+} at the M(2) site.

In this study, the site-population schemes of Mn-bearing amphiboles were reported by means of the Mössbauer and infrared spectroscopies and chemical analyses: the relationships between the A-site occupancy of alkali metal ions (Na+K) and the M(4)-site Ca-Na-Mn population, the distributions of Mn among their M(1) ～M(4) sites, and especially the frequency shifts of infrared absorption bands in relation to A-site occupancies of alkali metal ions.

Materials and experimental

Most samples used in this study have already been described in Ishida (1989), and the additional samples are also examined (Table 1). Oxide mineral which co-

*Department of Evolution of Earth Environments, Graduate School of Social and Cultural Studies, Kyushu University, Ropponmatsu, Fukuoka 810, Japan

Table 1. Material examined.

Sample	No. (EPMA)	Locality	Meneral assemblages Amphiboles	clinopyroxenes	Pyroxenoids	Other minerals
TN1	29	Tanohata	brown Mrf	brown Agt	Nm	Ccp
TN2	189	〃	Kozulite	brown Ae	Rn, Nm	Br
ND1	27,174	Noda-Tamagawa	dark-brown Mrf	brown Agt	Rn, Nm	Phl, Kfs, Tp, Hem, Jb
ND3	19	〃	dark-brown Mrf	—	Rn	
ND4	20	〃	dark-brown Mrf	—	Rn	
ND5	340	〃	pale-bluish Tir	—	Rn	
HW	22	Hanawa	brown Mrf	brown Agt	Rn	Kfs, Chl, Bm, Ap(Sr), Brt, Pr
GS	18	Gos(z)aisho	yellow Mrb	yellow Ae	—	Kfs
TG8A	823	Taguchi	greenish Win	—	Rn	Ab, Kfs, Hem
TG8B	826	〃	greenish Mrb	—	—	Kfs(Ba), Yo, Qtz
TG13	822	〃	greenish Win	—	Rn	Qtz, Rds
TG64	26,478	〃	pale-greenish-yellow Ric	—	Pxm	Qtz, Yo, Kfs(Ba)
TG67	844	〃	pale yellowish-green Mrf	—	Pxm	Qtz, Kfs(Ba)
TG68	28	〃	dark-greenish Mrf	—	Rn	Yo, Kfs
KM	61	Kamisugai	fiberous Win	brown Agt	Rn	Hem, Br, Qtz, Kfs
TR1	25	Tirodi	pale-brownish Tr	—	—	
TR2	24	〃	pale-purplish Mrb	—	—	Br
TR3	482a	〃	pale-purplish Mrb	—	—	Br
TR4	482b	〃	pale-purplish Mrb	—	—	Br
TR5	492	〃	yellow Tir	—	—	Mc
TR6	487	〃	yellow Tir	—	Rn	Ab, Ap, Ktn, Br, Brt
TR7	647	〃	purplish Win	—	—	Ab, Qtz, Cal(Ba)
TR8	649	〃	yellowish Tir	brown Agt	Rn	Kfs(Ba), Rds(Ba), Pen
JN1	481	Junawani	red Mrf	—	—	Qtz, Ap(Sr)
JN2	486	〃	pale-purplish Mrb	—	—	Br, Ap(Sr)
JN3	498	〃	violet Mrb	blue Agt	—	Mc, Br, Wit, Ap(Sr)
JN4	499	〃	yellow Tir	—	Rn	Cal(Sr)
JN5	500	〃	yellow Tir	—	Rn	Cal(Mn), Cal(Sr), Grt, Br, Hem
JN7	510	〃	pale-brown Tr	brown Di	—	Kfs, Cal
JN9	501	〃	violet-Mrb	blue Agt	—	Ab, Br, Qtz
JN10	485	〃	blue Mrf	blue Di	—	Phl, Cal(Sr), Brt

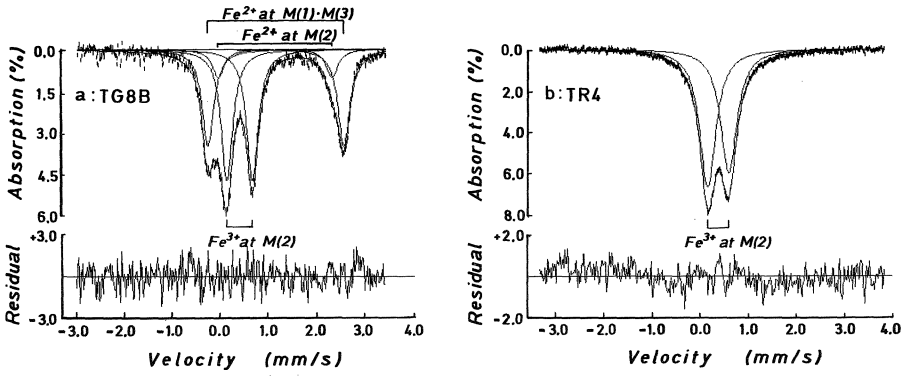
Amphiboles: Mrf, manganoan magnesioarfvedsonite; Mrb, manganoan magnesioriebeckite; Win, manganoan ferri-winchite; Tir, tirodite; Ric, manganoan richterite; Tr, manganoan tremolite.
Clinopyroxenes: Ae, manganoan aegirine; Agt, manganoan aegirine-augite; Di, diopside.
Pyroxenoids: Rn, rhodonite; Pxm, pyroxmangite; Bs, bustamite; Nm, natronambulite.
Other minerals: Kfs(Ba), Ba-bearing potassium feldspar; Ab, albite; Mc, microline; Phl, manganoan phlogopite; Chl, manganoan chlorite; Grt, garnet; Tp, tephroite; Yo, yoshimuraite; Qtz, quartz; Rds, rhodochrosite; Cal(Sr), Sr-bearing calcite; Ktn, kutnahorite; Wit, witherite; Ap(Sr), Sr-bearing apatite; Brt, baryte; Br, braunite; Hem, hematite; Jb, jacobsite; Pr, pyrophanite; Ccp, chalcopyrite; Py, pyrite; Pen, penwithite

exists with amphiboles of the Indian ores is braunite accompanying with a trace amount of hematite, whereas those of the Japanese ores are braunite, magnetite, hematite, jacobsite, and pyrophanite. In general, the Indian ores studied are poor in Fe, and the fugacity of oxygen at a mineral formation stage is supposed to be much higher than that of Japanese ones.

The chemical analyses were made using a scanning electron microscope JEOL SEM35CF-II with a LINK SYSTEM 800-2-500 energy-dispersive spectrometer (using 15kV, a specimen current of 1.5 nA on iron metal, and the ZAF-4/FLS quantitative analysis software system) (Shinno and Ishida, 1983).

The Mössbauer spectra were recorded with an Elcint Associates spectrometer, using 512 channels of a 1024-channel Nuclear Data multichannel analyzer of Toshiba Co. Ltd., and 10 mCi ^{57}Co in a Pd matrix. The velocity scale calibration was made against the spectrum of iron foil. The spectra were fitted to Lorentian curves using a Basic program coded by Akasaka and Shinno in 1991 (unpublished).

Infrared spectra were recorded with a JASCO A-302 spectrophotometer with a data processor JASCO DP-300 of the Department of Earth and Planetary Sciences, Kyushu University, using the KBr disc method (Ishida, 1989).



Figs. 1a and 1b Mössbauer spectra of Mn-bearing amphiboles. 1a: TG8B, greenish manganoan ferri-winchite from the Taguchi mine, Aichi Pref., Japan. 1b: TR4, pale-purplish manganoan magnesioriebeckite from the Tirodi mine, Madhya Pradesh, India.

Table 2. Chemical compositions and structural formulae of manganoan and/or manganian calcic, sodic-calcic, and alkali amphiboles.

	JN4	TR5	TR6	JN5	KM	TR4	TR1	JN7	ND5	TR8	TR2	JN2	TR3	GS	JN3
SiO_2	56.51	57.11	56.73	55.87	56.12	57.35	54.75	56.95	54.74	55.16	57.43	56.68	57.09	55.16	57.40
Al_2O_3	0.22	0.32	0.25	0.40	0.10	0.43	2.12	0.38	0.16	0.05	0.23	0.36	0.21	0.41	0.47
TiO_2	0.02	0.04	0.02	0.03	0.06	0.40	0.08	0.06	0.17	0.59	1.25	0.94	1.31	0.14	0.92
MgO	20.14	18.05	18.62	19.47	15.89	16.00	20.44	20.49	16.33	16.29	16.39	15.94	15.57	15.75	17.36
FeO*	–	–	–	–	–	–	–	–	9.99	–	–	–	–	–	–
Fe_2O_3**	1.42	7.62	4.93	2.54	8.10	13.19	3.58	1.99	–	6.15	9.93	9.21	9.08	10.58	8.39
MnO	16.91	9.11	12.20	14.11	6.60	1.29	2.47	5.91	14.23	9.62	3.31	3.23	4.29	6.10	1.99
CaO	2.27	2.28	2.92	3.27	6.01	1.81	10.71	10.55	2.23	2.43	1.77	1.72	1.76	0.92	2.55
Na_2O	0.53	3.06	2.23	1.15	3.28	5.85	1.51	1.49	0.83	3.77	5.83	5.89	5.67	6.48	6.51
K_2O	0.02	0.05	0.05	0.04	0.16	0.46	0.22	0.10	0.24	0.89	1.51	1.49	1.61	0.18	0.98
Total	98.04	97.64	97.96	96.88	96.33	96.79	95.87	97.92	98.91	94.93	97.64	95.45	96.58	95.73	96.56
Si	8.006	8.033	8.009	7.982	8.034	8.053	7.723	7.926	7.961	8.056	8.049	8.108	8.105	7.968	8.065
Al	–	–	–	0.018	–	–	0.277	0.062	0.028	–	–	–	–	0.032	–
ΣT	(8.006)	(8.033)	(8.009)	(8.000)	(8.034)	(8.053)	(8.000)	(7.988)	(7.989)	(8.056)	(8.049)	(8.108)	(8.105)	(8.000)	(8.065)
Al	0.036	0.053	0.042	0.050	0.018	0.071	0.077	–	–	0.008	0.038	0.060	0.035	0.038	0.077
Ti	0.003	0.005	0.002	0.004	0.009	0.043	0.008	0.006	0.019	0.065	0.131	0.101	0.139	0.015	0.097
Mg	4.255	3.785	3.917	4.147	3.391	3.350	4.298	4.249	3.535	3.547	3.425	3.398	3.295	3.392	3.635
Fe^{2+}	–	–	–	–	–	–	–	–	1.220	–	–	–	–	–	–
Fe^{3+}	0.151	0.807	0.525	0.273	0.872	1.394	0.380	0.208	–	0.676	1.049	0.900	0.970	1.150	0.886
Mn	0.555	0.350	0.514	0.526	0.710	0.142	0.237	0.537	0.226	0.704	0.357	0.392	0.515	0.405	0.237
M(123)	(5.000)	(5.000)	(5.000)	(5.000)	(5.000)	(5.000)	(5.000)	(5.000)	(5.000)	(5.000)	(5.000)	(4.941)	(4.954)	(5.000)	(4.932)
Mn	1.474	0.736	0.946	1.182	0.092	0.012	0.058	0.160	1.530	0.486	0.034	–	–	0.341	–
Ca	0.345	0.344	0.439	0.502	0.923	0.273	1.619	1.573	0.347	0.380	0.268	0.265	0.267	0.142	0.384
Na	0.145	0.833	0.612	0.316	0.909	1.592	0.323	0.267	0.123	1.068	1.586	1.633	1.561	1.517	1.616
M(4)	(1.964)	(1.913)	(1.997)	(2.000)	(1.924)	(1.877)	(2.000)	(2.000)	(2.000)	(1.934)	(1.888)	(1.898)	(1.828)	(2.000)	(2.000)
Na	–	–	–	0.002	–	–	0.090	0.135	0.111	0.000	–	–	–	0.299	0.157
K	0.003	0.008	0.009	0.007	0.030	0.081	0.039	0.009	0.045	0.165	0.268	0.271	0.292	0.033	0.175
ΣA	(0.003)	(0.008)	(0.009)	(0.009)	(0.030)	(0.081)	(0.129)	(0.144)	(0.156)	(0.165)	(0.268)	(0.271)	(0.292)	(0.332)	(0.332)
Total	14.973	14.954	15.015	15.009	14.988	15.011	15.129	15.132	15.145	15.155	15.205	15.218	15.179	15.332	15.329

* : Total iron as FeO.
** : Total iron as Fe_2O_3.

Table 2. (continued)

	TG13	TG8A	TG8B	JN1	TR7	HW	JN10	TG68	TG64	TG67	ND3	ND4	ND1	TN1	TN2
SiO_2	53.96	54.91	55.36	57.03	56.25	54.82	56.86	54.63	55.58	55.33	54.45	53.35	50.55	53.90	50.43
Al_2O_3	0.02	0.01	0.00	0.21	0.00	0.09	0.05	0.20	0.01	0.00	0.04	0.02	2.39	0.03	0.00
TiO_2	0.38	0.16	0.55	1.41	0.96	0.74	0.01	0.30	0.02	0.08	0.66	0.59	0.60	0.55	0.22
MgO	13.81	12.88	12.61	15.41	19.42	14.46	21.96	14.04	17.51	13.69	12.20	11.36	11.90	12.47	4.81
FeO*	9.96	10.50	10.25	–	–	–	–	–	–	9.29	–	–	–	–	–
Fe_2O_3**	–	–	–	8.07	2.85	8.08	1.29	8.73	4.07	–	7.46	7.19	6.42	5.51	2.23
MnO	10.32	8.19	8.88	1.73	1.61	7.94	0.60	9.56	6.81	6.65	12.06	13.11	12.60	12.53	26.69
CaO	2.89	3.92	2.08	2.29	5.40	2.35	7.72	1.64	3.48	2.02	1.34	1.29	2.84	2.60	1.50
Na_2O	4.09	5.14	6.19	6.93	5.30	6.89	4.48	6.98	4.12	5.25	7.61	7.56	7.32	7.20	7.77
K_2O	0.73	1.34	1.53	1.64	1.52	1.65	2.82	1.24	4.37	4.42	2.22	2.16	1.03	2.15	1.06
Total	96.16	97.05	97.45	94.59	93.31	97.01	95.79	97.31	95.97	96.73	98.03	96.62	95.63	96.94	94.69
Si	8.000	8.000	8.000	8.181	8.119	7.951	8.049	7.965	8.081	8.000	7.977	7.975	7.614	7.986	8.095
Al	–	–	–	–	–	0.015	–	0.035	–	–	0.006	0.003	0.386	0.005	–
ΣT	(8.000)	(8.000)	(8.000)	(8.181)	(8.119)	(7.966)	(8.049)	(8.000)	(8.081)	(8.000)	(7.983)	(7.978)	(8.000)	(7.991)	(8.095)
Al	0.003	0.002	0.000	0.035	0.000	–	0.008	–	0.002	0.000	–	–	0.037	–	–
Ti	0.043	0.017	0.059	0.152	0.104	0.081	0.001	0.033	0.003	0.009	0.072	0.066	0.068	0.061	0.026
Mg	3.052	2.790	2.716	3.295	4.179	3.127	4.634	3.052	3.795	2.948	2.664	2.531	2.670	2.755	1.147
Fe^{2+}	0.827	0.801	0.605	–	–	0.247	–	0.499	0.145	0.425	–	–	–	–	–
Fe^{3+}	0.408	0.486	0.633	0.874	0.309	0.881	0.137	0.618	0.321	0.700	0.823	0.809	0.726	0.614	0.268
Mn	0.667	0.904	0.987	0.209	0.197	0.911	0.077	0.850	0.754	0.814	1.441	1.594	1.499	1.570	3.559
M(123)	(5.000)	(5.000)	(5.000)	(4.565)	(4.789)	(5.000)	(4.857)	(5.000)	(5.000)	(4.896)	(5.000)	(5.000)	(5.000)	(5.000)	(5.000)
Mn	0.612	0.105	0.100	–	–	0.065	–	0.332	0.085	–	0.056	0.066	0.110	0.003	0.073
Ca	0.458	0.610	0.323	0.353	0.834	0.365	1.172	0.256	0.542	0.313	0.211	0.206	0.442	0.413	0.258
Na	0.930	1.285	1.577	1.647	1.166	1.570	0.828	1.412	1.162	1.471	1.733	1.728	1.448	1.584	1.669
M(4)	(2.000)	(2.000)	(2.000)	(2.000)	(2.000)	(2.000)	(2.000)	(2.000)	(1.789)	(1.784)	(2.000)	(2.000)	(2.000)	(2.000)	(2.000)
Na	0.246	0.168	0.156	0.279	0.315	0.368	0.401	0.561	–	–	0.428	0.464	0.687	0.482	0.750
K	0.138	0.247	0.281	0.301	0.279	0.305	0.365	0.231	0.810	0.816	0.415	0.412	0.198	0.408	0.216
ΣA	(0.385)	(0.415)	(0.437)	(0.580)	(0.594)	(0.673)	(0.766)	(0.792)	(0.810)	(0.816)	(0.843)	(0.876)	(0.885)	(0.890)	(0.966)
Total	15.385	15.415	15.437	15.326	15.502	15.639	15.672	15.792	15.680	15.496	15.826	15.854	15.885	15.881	16.061

Results and discussion

Mössbauer spectra

The obtained Mössbauer spectra show that pale-bluish tirodite (ND5), green, greenish-yellow, and dark-green (TG8A, TG8B, TG13, TG64, TG67 and TG68), and brownish (ND3, ND4 and HW) amphiboles contain both Fe^{2+} and Fe^{3+} ions (Fig. 1a), and the spectra are much similar to those for Na-Ca and Fe^{3+}-rich alkali amphiboles. On the other hand, the peaks due to only

Fe^{3+} ions were observed in all samples from India, and in yellow (GS), golden yellow (ND1), reddish brown (TN1 and TN2) amphiboles from Japan (Fig. 1b).

From the peak areas of Fe^{2+} and Fe^{3+} absorptions, the calculated ratios of Fe^{2+}/Fe^{3+} were as follows: ND5, total iron as FeO; TG8A, 62.26/37.74; TG8B, 48.86/51.14; TG13, 66.98/33.02; TG64, 32.58/67.42; TG67, 53.12/37.88; TG68, 46.88/53.12; ND3, 28.12/71.88; ND4, 26.98/73.02; HW, 28.04/71.96; others, total iron as Fe_2O_3.

The chemical composition dependence on Mössbauer parameters will be discussed in another paper (Ishida et al., in preparation).

Chemical composition

The structural formulae were calculated on the basis of the analytical data by EPMA and the iron oxidation state data by Mössbauer spectra (Table 2). Because the Al_2O_3 contents of almost all of the amphiboles studied are very small, the tetrahedral (T) sites are predominantly occupied by Si ion. Almost all of the amphiboles are rich in MgO, hence Mg in their M(1)～M(3) sites exceeds 3.0 per formula unit of 5.0 p.f.u. except the sample TN2. The M(4) sites consist of Na, Ca, and Mn ions with various proportions.

M(4)-site cations

The proportions of M(4)-site cations calculated from the structural formulae are plotted in the Na-Ca-Mn triangles (Figs. 2a, 2b and 2c). A-site vacant (0.00～0.25 Na+K p.f.u. in A site) manganoan amphiboles are grouped due to the kind of ions which mainly occupy the M(4) site; Ca, manganoan tremolite-ferroactinolite series (TR1 and JN7); Mn, tirodite-dannemorite series (ND5, JN4, TR5, TR6 and JN5); Na, manganoan glaucophane-riebeckite series (TR4); Ca/Na=1, manganoan winchite (KM and TR8). In these amphiboles, the proportions of M(4)-site Na-Ca-Mn ions have much wide variations with each other.

A-site partially occupied (0.25～0.75 Na+K p.f.u.)

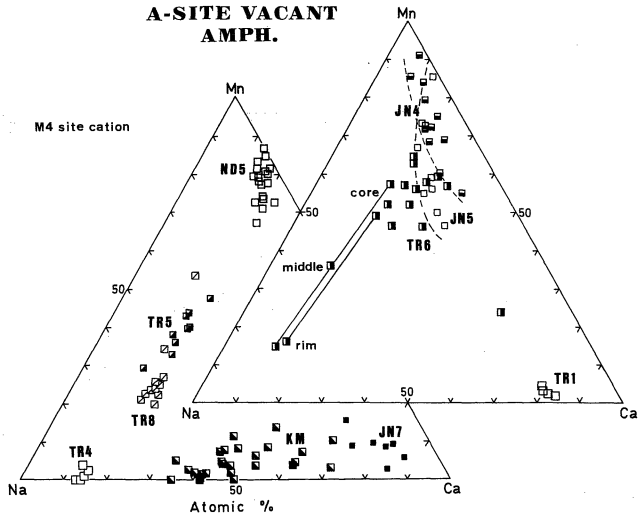


Fig. 2a M(4)-site populations of Na, Ca, and Mn for A-site nearly vacant (0.00～0.25 p.f.u. Na and K) Mn-bearing amphiboles.

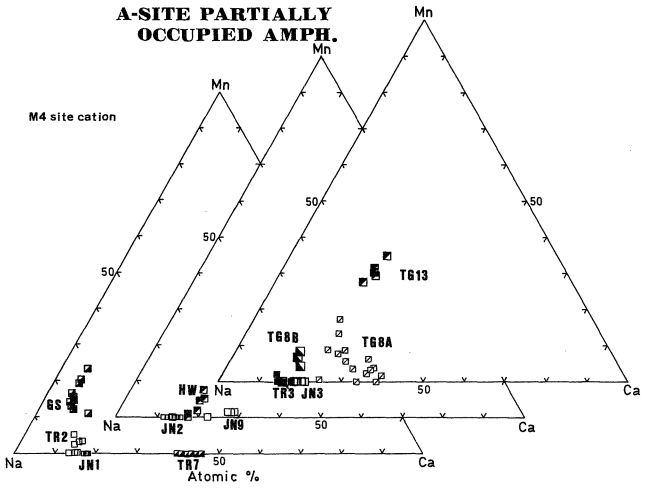


Fig. 2b M(4)-site populations of Na, Ca, and Mn for A-site partially occupied (0.25～0.75 p.f.u. Na and K) Mn-bearing amphiboles.

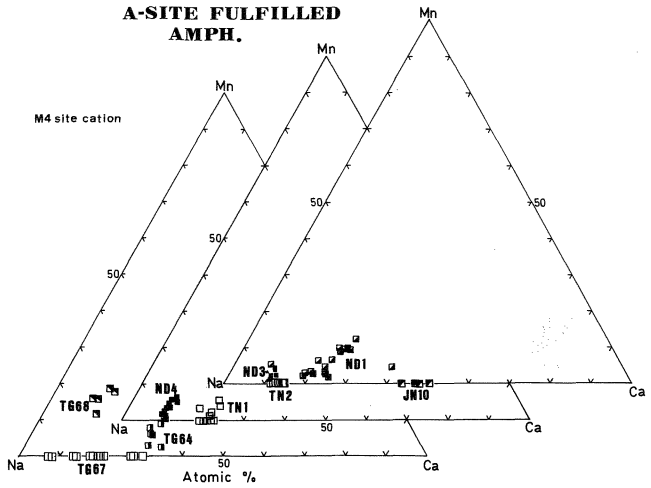


Fig. 2c M(4)-site populations of Na, Ca, and Mn for A-site nearly fulfilled (0.75 ~1.00) Mn-bearing amphiboles.

manganoan amphiboles are grouped to manganoan magnesio-riebeckite (GS, TR2, TR3, JN2, JN3, JN9 and TG8B), manganoan magnesio-arfvedsonite (JN1 and HW), and manganoan winchite (TR7, TG8A and TG13). Most amphiboles are poor in Mn in the M(4) sites, which are occupied by less than 50 mol% Ca and Mn.

A-site nearly fulfilled (0.75~1.00 Na+K p.f.u.) manganoan amphiboles are grouped to manganoan magnesio-arfvedsonite (TG67,TG68,ND1,ND3,ND4, TN1 and JN10), manganoan richterite (TG64) and kozulite (TN2). These amphiboles contain up to 20 mol % Mn at M(4) sites, which are mainly occupied by both Na (50~95 mol%) and Ca (5~50 mol%).

In conclusion, the amphiboles studied usually contain two or three kinds of cations in their M(4) sites. In the A-site partially occupied and nearly fulfilled amphiboles, Na ion is predominant in the M(4) site. It can be pointed out that the Mn content in the M(4) site decreases markedly with increasing occupancy of the A-site alkali metal ions.

Mn distribution

The Mn ions in the M(4) and (M(1)・M(2)・M(3)) sites are plotted in Figs. 3a, 3b and 3c. The Mn content of amphiboles obtained from metamorphosed manganese ore deposits is strongly controlled by the physical and chemical conditions, because Mn ion has various valence states and forms various minerals as a minor or major constituent. The A-site vacant amphiboles which coexist with pyroxenoids (samples ND5, JN4, JN5, TR6

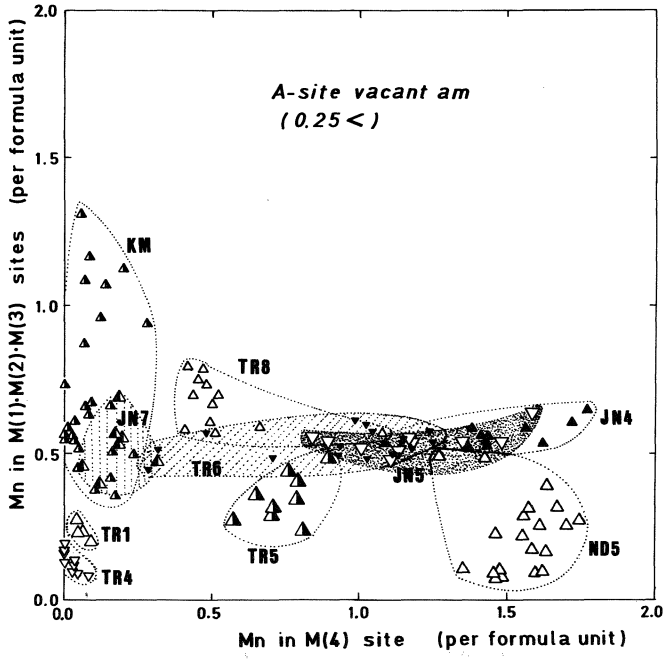


Fig. 3a Distribution of Mn ion between the M(4) and M(1)·M(2)·M(3) sites for A-site nearly vacant (0.00~0.25 p.f.u. Na and K) Mn-bearing amphiboles.

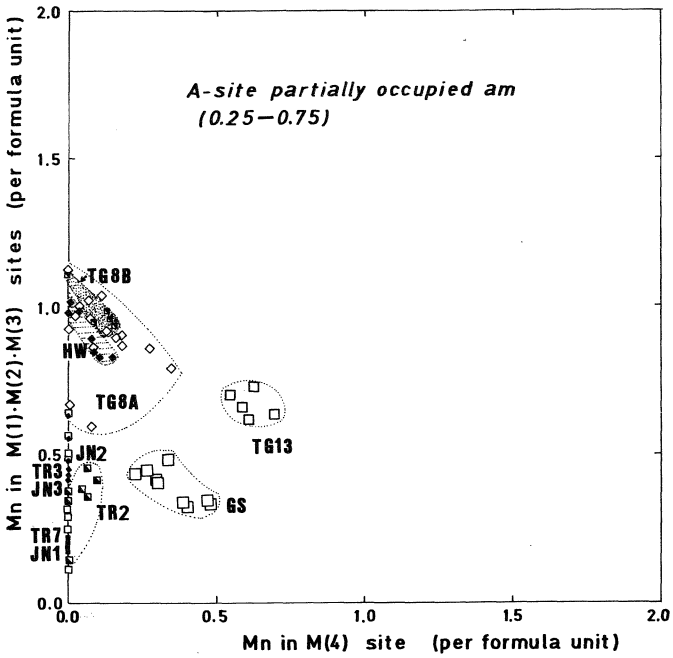


Fig. 3b Distribution of Mn ion between the M(4) and M(1)·M(2)·M(3) sites for A-site partially occupied (0.25~0.75 p.f.u. Na and K) Mn-bearing amphiboles.

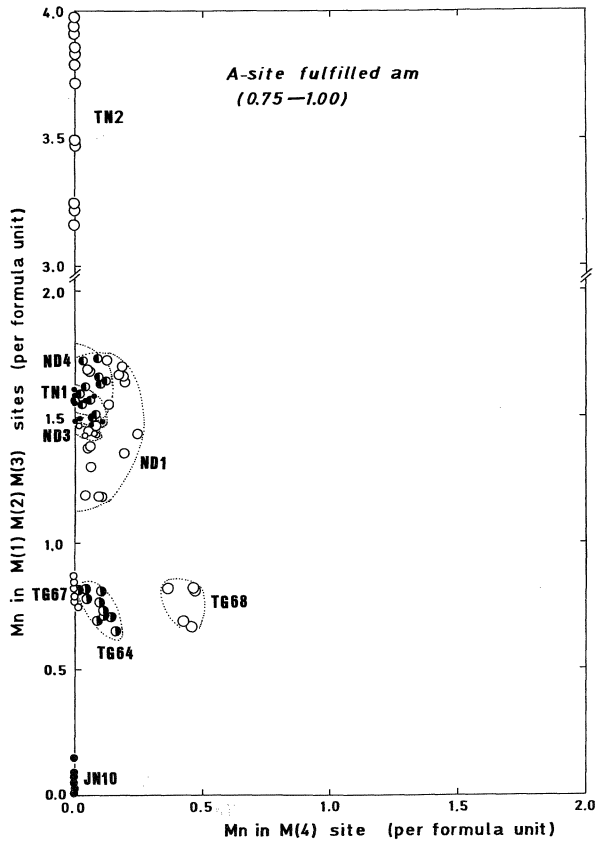


Fig. 3c Distribution of Mn ion between the M(4) and M(1)·M(2)·M(3) sites for A-site nearly fulfilled (0.75~1.00) Mn-bearing amphiboles.

and TR8) contain up to 1.8 Mn p.f.u. in their M(4) sites, whereas in their (M(1) · M(2) · M(3)) sites these amphiboles contain less than 0.8 Mn p.f.u. (Fig. 3a). Thus, these A-site vacant amphiboles accommodate up to 2.5 Mn p.f.u. in their structure. The A-site partially occupied amphiboles, coexisting with pyroxenoids (TG8

A and TG13), contain up to about 1.2 Mn p.f.u. in their (M(1)・M(2)・M(3)) sites, whereas the amphiboles contain less than 0.7 Mn p.f.u. in their M(4) sites (Fig.3b). These A-site partially occupied amphiboles accommodate up to 1.5 Mn p.f.u. in their structure.

With increasing A-site occupancy, amphiboles which coexist with pyroxenoids contain up to about 1.8 Mn p.f.u. in their (M(1)・M(2)・M(3)) sites, whereas the amphiboles contain less than 0.5 Mn p.f.u. in their M(4) sites. Thus, these A-site occupied amphiboles (samples ND1, ND3, ND4 and TN1) except TN2, which coexists with braunite, accommodate up to 2.0 Mn p.f.u. (Fig. 3c).

Irrespective of their A-site occupancies, amphiboles which do not coexist with pyroxenoids but with mainly quartz and/or manganoan clinopyroxenes accommodate less than 1.2 Mn p.f.u. in their structure. Most amphiboles from India can contain a rather small amount of Mn. The amounts of Mn in these amphiboles markedly increase when over 80% of the A-site formula units are occupied by Na and K (Fig. 4).

Infrared spectra

The infrared spectra obtained in the range of 5040 ~330 cm^{-1} are similar to each other and show characteristic bands in four regions (Fig. 5) : 1) several bands between 3750 and 3600 cm^{-1} (OH stretching vibrations) ; 2) a group of strong bands between 1150 and 800 cm^{-1} (Si-O stretching vibrations) ; a group of weaker bands between 800 and 580 cm^{-1} (vibrations of silicate chains and OH librational bands) ; and 4) a group of strong bands between 580 and 330 cm^{-1} (Si-O bending and M-O stretching vibrations).

The relations between the frequencies and A-site alkali occupancies for the studied amphiboles are shown in Fig. 6.

1) OH stretching vibration region

Hydroxyl stretching bands in the range of 3750 ~3600 cm^{-1} can be further divided into two regions: the lower frequency bands between 3685 and 3600 cm^{-1} (L-bands), and the higher frequency bands above 3685 cm^{-1} (H-bands). With increasing A site alkali metal ions, the intensity of H-bands also increases, because the electric field of A-site alkali metal ions causes an increase in the OH stretching energy (Rowbotham and Farmer, 1973). Thus, hydroxyl configurations of L- and H-bands can be expressed by (M(1)・M(1)・M(3))-OH-V (vacant A site) and (M(1)・M(1)・M(3))-OH-A (A site alkali ions), respectively, using notations similar to those used by Maresch and Langer (1976).

The relationships between the intensity ratio (areal ratio of the absorption bands) of H-bands to L-bands and the number of A-site Na+K ions per formula unit calculated by chemical analyses are shown in Fig. 7. The A-site alkali occupancy estimated by infrared OH stretching bands is in accord with that of chemical analysis in most samples.

The fine structures of these H- and L-bands were also observed. For example, TG67 shows four well-resolved bands A' ~ D' and A ~ D, respectively, which ascribed to hydroxyl vibrations close to 3Mg (A',A), 2Mg + (Fe^{2+}+Mn^{2+}) (B',B), Mg+2(Fe^{2+}+Mn^{2+}) (C', C), and 3 (Fe^{2+}+Mn^{2+}) (D', D).

2) Si-O stretching region

In the range of 1200~800 cm^{-1}, all samples give similar three to five strong Si-O stretching bands with some

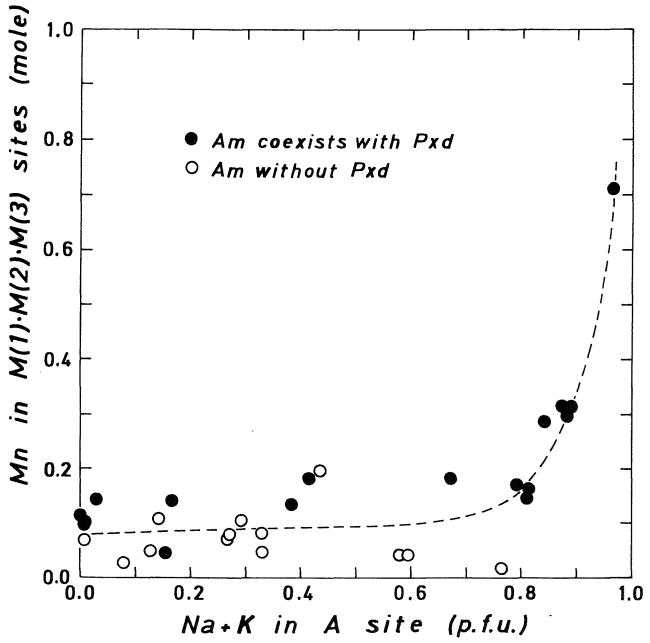


Fig. 4 Relationship between A-site occupancy and Mn ion in M(1)·M(2)·M(3) sites for Mn-bearing amphiboles.

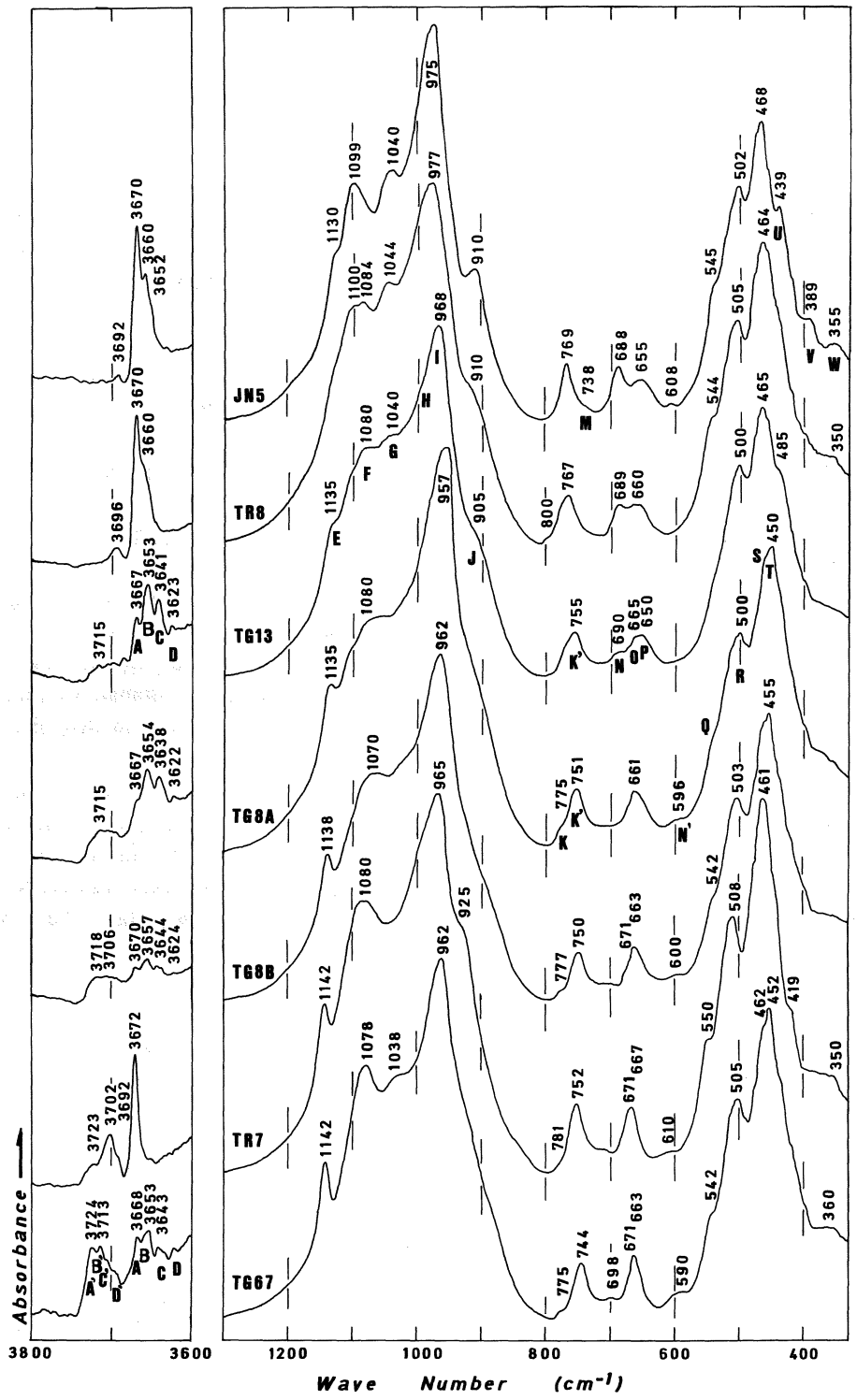


Fig. 5 Infrared spectra of Mn-bearing amphiboles.

differences: a band E near 1130 cm^{-1} in the spectrum of JN5 and 1140 cm^{-1} band in the spectra from TG13 to TG 67 were observed (Fig. 5). With increase in A-site occupancy, the frequencies of these Si-O stretching bands except band E tend to shift to the lower frequency side up to about 40 cm^{-1} (Fig. 6).

3) Chain vibration and OH librational region

Two or three medium strong bands with some weak bands and shoulders are observed in the 800～580 cm^{-1} region. The medium strong bands K and K' in the range of 800～740 cm^{-1} are particularly sensitive to the nature of the A-site alkali ions and the M(4)-site octahedral cations. In Al^{IV} (tetrahedral Al) -free monoclinic amphiboles with vacant A site, the frequencies of these bands vary with the M(4)site cations: Na, 789～773 cm^{-1}; Mn, 768～762 cm^{-1}; Ca, 756～745 cm^{-1} (the slight frequency decrease in the same series depends mainly on $Fe^{2+}+Mn^{2+}$ contents in the M(1)・M(2)・M(3)sites). Amphiboles with A-site partly occupied by alkali ions

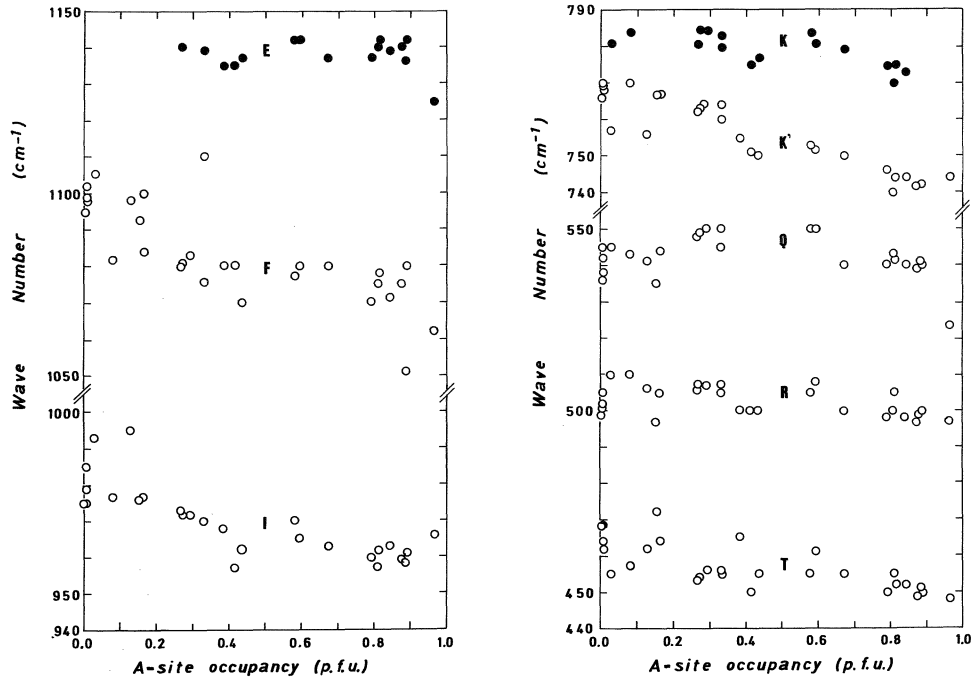


Fig. 6 Relationship between the frequencies of infrared absorption bands and A-site occupancies for Mn-bearing amphiboles.

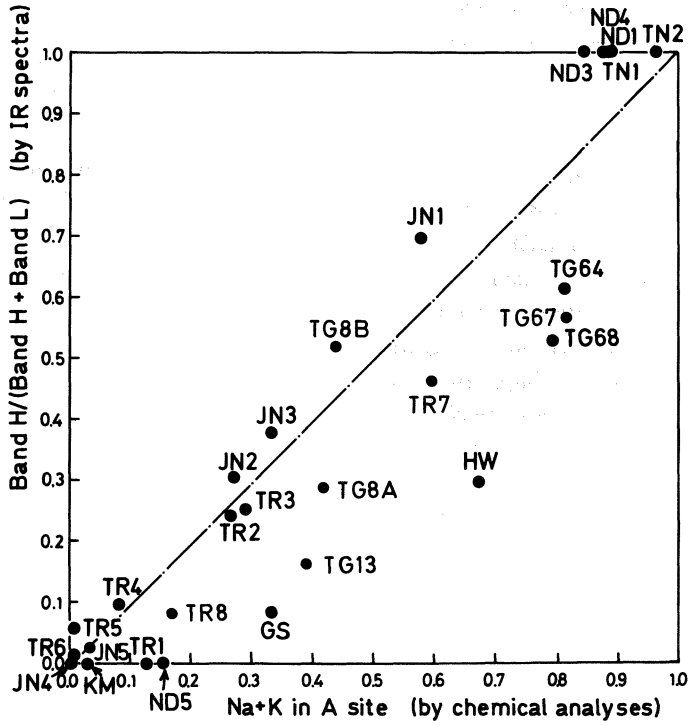


Fig. 7 Relationship between the H-band intensity ratio to the total OH stretching band intensity and the A-site occupancy for Mn-bearing amphiboles.

show split or broad bands. With increasing A-site alkali occupation, the band K' which splits on the lower frequency side decreases further in frequency but increases in intensity. The higher frequency one K is, therefore, attributed to a vacant A site cell of which M(4)site ions are predominantly Ca or Mn.

Two OH librational band N near 700 cm^{-1} and band N' near 600 cm^{-1} were determined by comparison of the spectra with those of deuterated forms (Ishida, 1984). The band N near 700 cm^{-1} is a little shifted by the substitution of M(1) cations to M(4) cations, but the band N' near 600 cm^{-1} tends to shift to the lower frequency side with increasing the content of A site alkali ions. With A -site alkali occupations, the band N near 700 cm^{-1} be-

comes weaker in intensity, and a broad band N' near 600 cm^{-1} stronger. Thus the former band is ascribed to a librational of (M(1) · M(1) · M(3))-OH-V configuration, while the latter band to that of (M(1) · M(1) · M(3))-OH-A configuration.

4) Si-O bending and M-O stretching region

Bands ascribed to the bending vibrations of the silicate chain and to the M-O stretching vibrations are observed below 580 cm^{-1}, broadly divided into three bands: medium strong or weak shoulder bands Q near 540 cm^{-1}, strong bands R near 505 cm^{-1}, and very strong bands T near 455 cm^{-1}. The frequencies of these bands tend to decrease up to 20 cm^{-1} with increase in A-site alkali metal contents (Fig. 6).

Concluding remarks

For manganoan Na-Ca and alkali amphiboles, it is worth noting that their infrared spectra have strongly dependent on their A-site occupancy, which varies only up to 1.0 per 16.0 cations in amphibolic structure. To characterize the A-site in amphiboles, further studies on chemical and physical properties of these amphiboles will be necessary by, for example, chemical analysis on Li and F ions, structural and electronic spectral analyses.

Acknowledgements — The author wishes to thank Prof. Kazuhisa Yoshimura of Kyushu University for his critical reading of the manuscript. This is a part of my doctoral thesis, and thanks are also due to Profs. Yoshikazu Aoki, Isamu Shinno and Nobutaka Shimada of Kyushu University for their advice and encouragement, and to associate Prof. Masahide Akasaka of Shimane University for his kind permission to use his analysing program of Mössbauer spectra. This study was supported by Grant-in-Aid for Scientific Research (C) (No. 04640743).

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(Received January 9, 1995; Accepted January 24, 1995)