

Sadanagaite and subsilicic ferroan pargasite from thermally metamorphosed rocks in the Nōgō-Hakusan area, central Japan

TAKAYUKI SAWAKI

Department of Earth Sciences, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya 464-01, Japan

Abstract

High-alumina subsilicic calcic amphiboles, including sadanagaite and subsilicic ferroan pargasite, are found in rock samples from the contact aureole in the Nōgō-Hakusan area, central Japan. They occur in the reaction zones between dark fragments and the surrounding crystalline limestone of the pyroxene hornfels facies zone. The dark fragments which underwent K-metasomatism are originally basaltic rocks. The sadanagaite and subsilicic ferroan pargasite have high Al_2O_3 (16–19 wt. %) and K_2O (3.6–4.3 wt. %) contents. The Si value ranges from 5.38 to 5.64 and the total Al ranges from 3.10 to 3.43 when cation ratios are calculated on the basis of O = 23. The calculated unit cell parameters of sadanagaite are a 10.00 (1), b 18.06 (2), c 5.355 (4) Å, β 105.52(7)°, V 932(1) Å³. The A-sites of the amphiboles is occupied almost entirely by K and Na; the amphiboles are saturated with the edenite component. The amphiboles show a larger extent of tschermakite-type substitution [(Mg,Fe)Si = AlAl] than does ordinary pargasite. Sadanagaite is probably stable at the temperature above the upper amphibolite facies.

KEYWORDS: sadanagaite, reaction zone, pyroxene hornfels facies, Nōgō-Hakusan area, Japan.

Introduction

SADANAGAITE is a subsilicic alumina-rich calcic amphibole with Si < 5.5 for O = 23. It was first reported by Shimazaki *et al.* (1984) in skarns of the amphibolite facies ($T = 600^\circ\text{C}$) in the Ryōke Metamorphic Belt. Recently van Marcke de Lummen and Verkaeren (1985) found sadanagaite in amphibole veins of a skarn in Cornwall. The formation of these skarns took place at 500–600°C and the sadanagaite is rich in chlorine (up to 1.3 wt. %) and in fluorine (up to 1.0 wt. %). Mogessie *et al.* (1986) found sadanagaite in eclogites, garnet amphibolites and metacarbonates in the Eastern Alps. Two types of the subsilicic amphibole are recognized; one was formed under the conditions of $P = 6\text{--}10$ kbar, $T = 550\text{--}700^\circ\text{C}$, and the other at a retrograde stage of the high-pressure event.

Sadanagaite and subsilicic ferroan pargasite occur in the thermally metamorphosed rock in the Nōgō-Hakusan area, central Japan. This paper describes their mode of occurrence, the mineral paragenesis and the physical and chemical properties of the subsilicic amphiboles, and discusses

especially the conditions for the formation of these amphiboles.

Geological setting and mode of occurrence

The sketch map of the Nōgō-Hakusan area is shown in Fig. 1. This area is underlain by the sedimentary and volcanic sequence of Jurassic age and is a part of the Mino Terrane. The sequence was buriedly metamorphosed under conditions of the prehnite-pumpellyite facies (Hattori, 1978) and thermally metamorphosed by the Cretaceous-Paleogene granodiorite intrusion. A hypersthene + K-feldspar + biotite assemblage in siliceous psammitic hornfels and spinel + forsterite + periclase + calcite assemblage in impure crystalline limestone are present in some parts within about 100 m of the contact. These assemblages indicate that the metamorphic grade reaches the pyroxene hornfels facies (cf. Turner, 1981). Basic hornfels in the pyroxene hornfels facies zone are composed mainly of plagioclase, biotite, clinopyroxene, orthopyroxene, calcic amphibole and olivine, and are characterized by a large amount of biotite.

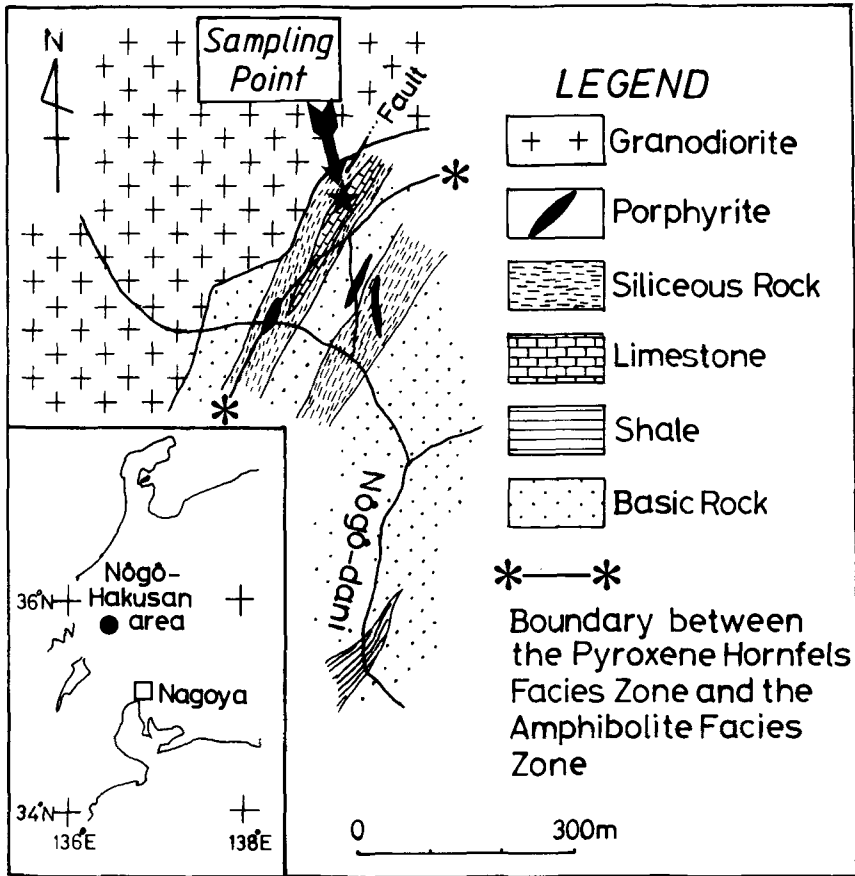


FIG. 1. The locality map and geological sketch map of the Nōgō-Hakusan area.

There are three kinds of calcic amphibole in the pyroxene hornfels facies zone of this area. The first is sadanagaite and subsilicic ferroan pargasite which occur in the reaction zones around the dark fragments in crystalline limestone, and will be described in detail. The second is a pargasitic amphibole ($5.6 < Si < 6.2$) which occurs around calcareous veins in the basic hornfels. The calcareous veins consist mainly of prehnite, anisotropic grandite, epidote, calcite, and K-feldspar. The third is a non-subsilicic amphibole ($6.2 < Si$) which is found in the basic hornfels, and is not associated with the veins.

The rock containing sadanagaite and subsilicic ferroan pargasite was sampled at the outcrop about 50 m away from the contact. Brownish dark fragments up to 20 cm in size are scattered in greenish white crystalline limestone in the pyroxene hornfels facies zone (Fig. 2a).

The crystalline limestone consists mainly of

calcite, clinopyroxene, grandite and wollastonite. Calcite measures 0.5–1 mm in size. Clinopyroxene, grandite and wollastonite are disseminated among the calcite grains.

The dark fragments consist mainly of Ti-grandite, clinopyroxene, K-feldspar, biotite, and titanite. The amount and size of Ti-grandite decreases toward the centre of the dark fragments. Muscovite, apatite, zircon, pyrite, chalcopyrite, pyrrhotite and quartz are also found. Quartz forms secondary veins.

Reaction zones developed between the dark fragments and the surrounding crystalline limestones (Fig. 2b). The zones are divided into four subzones 0.5–2 mm thick on the basis of the main constituent minerals. From the crystalline limestone to the dark fragment, they are;

- Subzone 1: wollastonite
- Subzone 2: Ti-grandite

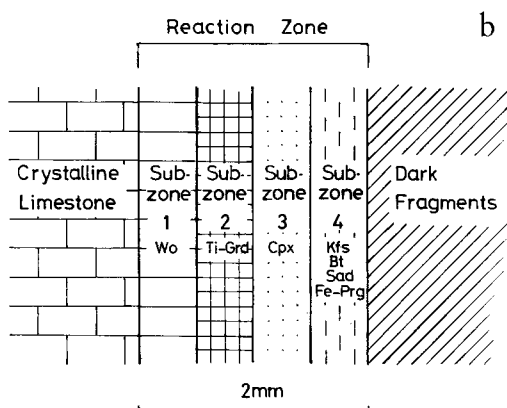
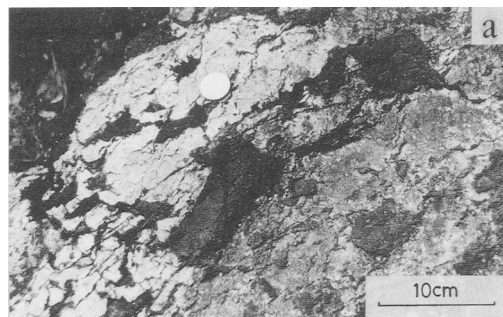


FIG. 2. (a) Occurrence of dark fragments in crystalline limestone. (b) Sketch of the reaction zone: Wo, wollastonite; Ti-Grd, Ti-grandite; Cpx, clinopyroxene; Kfs, K-feldspar; Bt, biotite; Sad, sadanagaite; Fe-Prg, subsilicic ferroan pargasite.

Subzone 3: clinopyroxene

Subzone 4: K-feldspar, biotite, sadanagaite and subsilicic ferroan pargasite.

Titanite occurs sporadically in Subzone 4. Wollastonite is replaced in places by pectolite. Small amounts of pyrite, chalcopyrite and pyrrhotite occur in every subzone.

The sadanagaite and subsilicic ferroan pargasite occur in Subzone 4. The amphibole forms prismatic crystals less than 1.3 mm in length (Fig. 3) and is pleochroic: X = greyish yellow to pale greenish yellow, Y = yellowish orange to light olive brown, Z = light olive brown to dark yellowish orange. It is optically biaxial negative with $2V_x = 70-80^\circ$.

Biotite associated with the amphibole in Subzone 4 is generally reddish brown, and occurs as short prisms and plates about 0.1–0.2 mm in length, and minute crystals. The fine biotite replaces the amphibole sporadically. Green biotite (lepidomelane) is also present in small amounts.

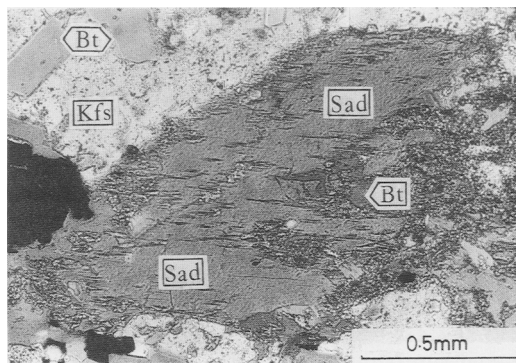


FIG. 3. Photomicrograph of sadanagaite: Sad, sadanagaite; Bt, biotite; Kfs, K-feldspar.

Table 1. Bulk chemical composition of the dark fragment including the reaction zone, in which sadanagaite and subsilicic ferroan pargasite are found

Sample	TS86081403
SiO ₂	38.49
TiO ₂	1.96
Al ₂ O ₃	14.37
Fe ₂ O ₃	4.26
FeO	4.59
MnO	0.06
MgO	3.86
CaO	17.59
Na ₂ O	0.10
K ₂ O	6.77
P ₂ O ₅	0.17
H ₂ O(+)*	6.35
H ₂ O(-)	0.88
Total	99.45

* Ignition loss (including CO₂).

The short prismatic and platy biotite grains in Subzone 4 are generally larger than the biotite grains of less than 0.1 mm in length in the dark fragments. The amphibole and biotite are embedded in an interstitial matrix of K-feldspar.

A wet chemical analysis of the dark fragment including some of the reaction zone material (Table 1) shows high Al₂O₃ and K₂O contents relative to SiO₂ and Na₂O. The high CaO content is ascribed to contamination of the crystalline limestone in the preparation of the sample for the analysis.

The rock containing the dark fragments occurs also in the upper amphibolite facies zone, and is similar to the rock in the pyroxene hornfels facies zone. In the upper amphibolite facies zone, the dark fragments consist mainly of clinopyroxene,

K-feldspar and very fine biotite, and are also surrounded by reaction zones consisting of anisotropic grandite, epidote, biotite and clinopyroxene. The dark fragments have a hyalo-ophitic texture, where pseudomorphous plagioclase laths, however, are embedded in a matrix of very fine biotite and K-feldspar. The pseudomorphous plagioclase was replaced by K-feldspar, clinopyroxene and biotite. Amygdales are filled with clinopyroxene, K-feldspar and biotite. These textures suggest that the dark fragments in crystalline limestone were originally basaltic rocks. The high K₂O content of the dark fragments and the presence of the pseudomorphous plagioclase replaced by K-feldspar and biotite suggest that the dark fragments have been subjected to potassium-metasomatism during the thermal metamorphism.

X-ray crystallography and chemistry

Sadanagaite in specimen No. TS86081410 was examined on a Rigaku RU-200(P) X-ray microdif-

fractometer with position sensitive proportional counter (PSPG/MDG system), using V-filtered Cr-K α radiation ($\lambda = 2.29092 \text{ \AA}$): accelerating voltage 50 kV, current 200 mA. The X-ray diffraction pattern was obtained from the selected area of about 30 μm in diameter using a single crystal in thin section.

The unit cell parameters obtained from 11 reflection peaks of $2\theta = 30\text{--}110^\circ$ are: monoclinic, a 10.00 (1), b 18.06 (2), c 5.355 (4) \AA , β 105.52 (7) $^\circ$, V 932(1) \AA^3 .

Chemical analyses of the minerals were performed on a JOEL JCXA-733 electron-probe microanalyser. Accelerating voltage, specimen current and beam diameter were 15 kV, $1.2\text{--}1.3 \times 10^{-8} \text{ A}$ and $3 \mu\text{m}$, respectively. The chemical formulae of the amphibole were calculated on the basis of 23 oxygens.

Selected analyses for the sadanagaite and subsilicic ferroan pargasite are given in Table 2, and all analytical results (Rock and Leake, 1984) are plotted in Fig. 4. The amounts of Fe²⁺ and Fe³⁺

Table 2. Chemical composition of the sadanagaite and subsilicic ferroan pargasite

Sample	(1) TS84081410	(2) TS86081410	(3) TS84081411	(4) TS86081403
SiO ₂	34.4	35.0	36.3	36.6
TiO ₂	3.15	3.28	2.91	1.84
Al ₂ O ₃	18.4	18.5	17.7	17.5
FeO*	18.4	15.7	17.6	15.9
MnO	0.24	0.16	0.17	0.23
MgO	6.11	7.61	7.40	8.43
CaO	11.9	12.0	11.8	12.1
Na ₂ O	0.73	0.85	0.92	0.87
K ₂ O	4.21	4.00	3.67	3.88
Total	97.5	97.1	98.5	97.4
O=23				
Si	5.360	5.412	5.564	5.617
Al ^{IV}	2.640	2.588	2.436	2.383
Al ^{VI}	0.738	0.783	0.762	0.781
Ti	0.369	0.381	0.335	0.212
Fe ^{3+*}	0.228	0.088	0.000	0.201
Fe ^{2+*}	2.168	1.941	2.256	1.839
Mn	0.032	0.021	0.022	0.030
Mg	1.418	1.753	1.691	1.928
Ca	1.986	1.987	1.938	1.989
Na	0.220	0.255	0.273	0.259
K	0.836	0.789	0.718	0.759
X _{Mg}	0.395	0.475	0.428	0.512

* Total iron as FeO.

** Fe³⁺/Fe²⁺ ratios are estimated with adjustment of total cations to 16 for O=23.

- (1) & (2) Potassium titanian sadanagaite
 (3) Potassium titanian subsilicic ferroan pargasite
 (4) Potassium subsilicic ferroan pargasite

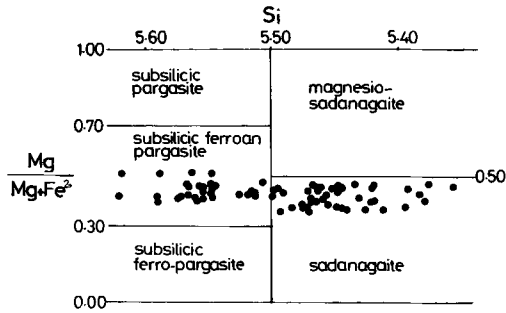


FIG. 4. Subsilicic amphiboles in the Nōgō-Hakusan area.

are calculated by means of adjustment of the total cations to 16 for O = 23 by redistribution of total Fe. The calculated Fe³⁺ content is less than about 0.31 and Fe³⁺/(Fe²⁺ + Fe³⁺) ratio is less than 0.14. The calculated Mg/(Mg + Fe²⁺) values of the 'sadanagaites' are less than 0.50, indicating the 'sadanagaite' and not 'magnesio-sadanagaite' composition of Shimazaki *et al.* (1984).

Compositional zoning in the sadanagaite and

subsilicic ferroan pargasite is not observed, but appreciable chemical variations, e.g. from 5.38 to 5.64 Si (O = 23 and total iron as FeO), are found between individual rock specimens; the variation, however, is very small in a single rock specimen.

Fig. 5 shows that the Si values of the sadanagaite and subsilicic ferroan pargasite of this area are much higher than those of sadanagaite in the Ryōke Metamorphic Belt (4.52–5.24, Shimazaki *et al.*, 1984), and are similar to those of Eastern Alps (Mogessie *et al.*, 1986). The Al content of the sadanagaite and subsilicic ferroan pargasite of this area ranges from 3.10 to 3.43, and is far lower than those of the Ryōke metamorphic belt (3.64–4.46, Shimazaki *et al.*, 1984). The chemical composition of the sadanagaite from the Ryōke metamorphic belt is extraordinary when compared with other sadanagaites, and with high-alumina and subsilicic pargasites.

The K₂O content of the sadanagaite and subsilicic ferroan pargasite of this area is 3.6–4.3 wt. %, and the K/(K + Na) values are about 0.7–0.8. The high K₂O content and X_K value of the sadanagaite and subsilicic ferroan pargasite are similar to those

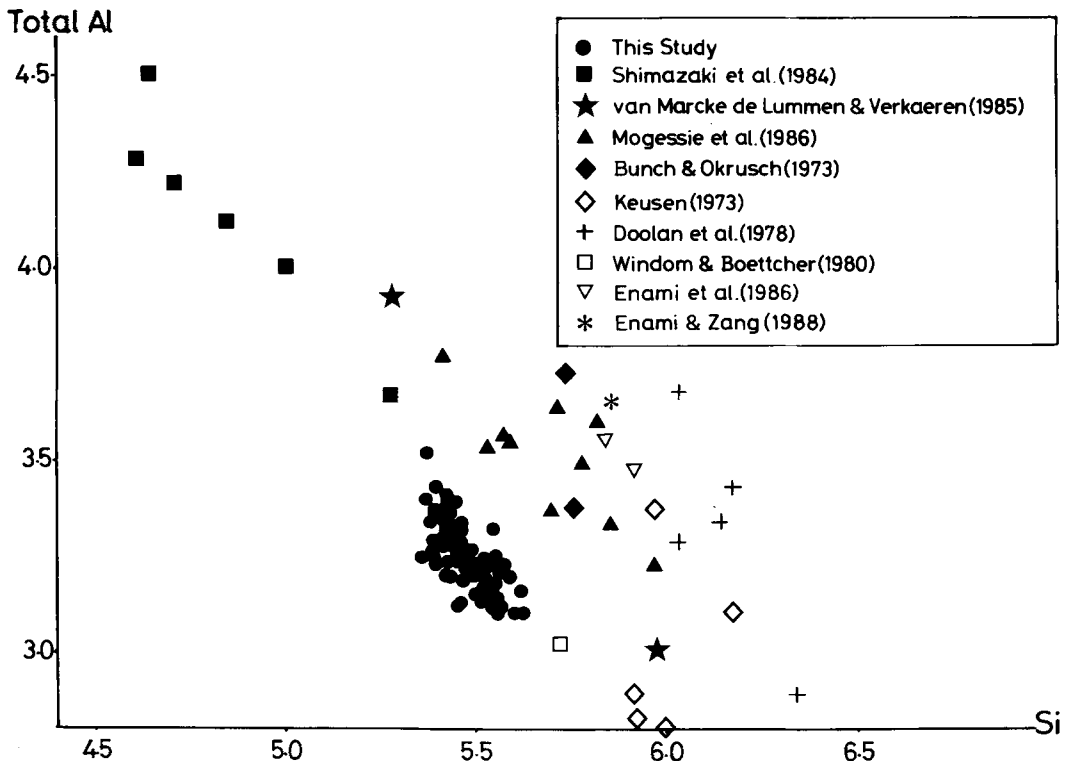


FIG. 5. Si vs. total Al plots for sadanagaites, and high-alumina and subsilicic pargasites. The chemical formulae are calculated on O = 23, and the total irons are recalculated as FeO.

Table 3. Chemical compositions of some minerals coexisting with the subsilicic amphiboles (TS84081411)

	(1)	(2)	(3)	(4)	(5)	(6)
SiO ₂	28.0	36.5	45.7	38.8	34.8	32.5
TiO ₂	16.6	2.25	0.24	3.53	3.06	0.47
Al ₂ O ₃	4.73	12.3	7.80	14.5	17.0	14.9
Cr ₂ O ₃	0.16	0.00	0.00	0.00	0.00	0.17
Fe ₂ O ₃ *	17.2	14.7	9.70	13.9	19.7**	37.9**
MnO	0.08	0.33	0.45	0.18	0.17	0.25
MgO	0.68	0.33	11.0	6.05	11.2	0.65
CaO	32.9	33.6	24.8	23.7	0.04	0.14
Na ₂ O	0.10	0.04	0.09	0.31	0.03	0.05
K ₂ O	0.12	0.00	0.00	0.00	9.81	9.04
Total	100.6	100.1	99.8	101.0	95.8	95.6
	O=12		O=6		O=22	
Si	2.309	2.894	1.713	1.463	5.312	5.454
Al ^{IV}	0.460	0.106	0.287	0.537	2.688	2.546
Fe*	0.231	---	---	---	---	---
Al ^{VI}	---	1.038	0.071	0.108	0.380	0.404
Ti	1.030	0.134	0.007	0.100	0.351	0.059
Cr	0.011	0.000	0.000	0.000	0.000	0.000
Fe*	0.839	0.876	0.274	0.395	2.522**	5.317**
Mn	0.005	0.022	0.014	0.006	0.022	0.035
Mg	0.083	0.039	0.616	0.340	2.561	0.164
Ca	2.910	2.849	0.997	0.956	0.007	0.025
Na	0.015	0.007	0.007	0.022	0.009	0.015
K	0.013	0.000	0.000	0.000	1.910	1.933

* Total iron as Fe₂O₃.

** Total iron as FeO.

(1) dark red schorlomite in the dark fragment;

(2) pale pink melanite in Subzone 2;

(3) fassaite in crystalline limestone; (4) fassaite in Subzone 3;

(5) biotite in Subzone 4; (6) green biotite in Subzone 4.

of K-Cl-bearing amphiboles of Primorye, Far East USSR (2.56-4.21 wt. %; Gulyaeva *et al.*, 1986); Einstodingen, East Antarctica (2.94, 3.19 wt. %; Matsubara and Motoyoshi, 1985); and West Ongul Island, East Antarctica (2.98-3.32 wt. %, Suwa *et al.*, 1987). Qualitative analyses of the sadanagaite of the last area, however, show small amounts of chlorine.

Chemical compositions of some minerals coexisting with the subsilicic amphibole are shown in Table 3. The Ti content of the granitides reach 19 wt. %, melanite and schorlomite being the appropriate names. The clinopyroxene containing 4-8 wt. % Al₂O₃ in the crystalline limestone is fassaite to salite. The clinopyroxene in Subzone 3 and in the marginal part of the dark fragment contains 8-14 wt. % Al₂O₃ and is enriched in the fassaite molecule. The chemical composition of reddish brown biotite in the reaction zones is similar to that in the dark fragments. The green biotite in Subzone 4 is enriched in FeO and depleted in MgO.

Discussion

Chemical environment for formation of sadanagaite. Al^{IV} vs. total (Na+K) and Al^{IV} vs. Al^{VI} plots for the calcic amphiboles in the pyroxene hornfels facies zone are shown in Fig. 6a and b, respectively. The total (Na+K) of the sadanagaite, subsilicic ferroan pargasite and the pargasitic amphiboles is 1.0-1.1 for O = 23, and their Ca is over 1.9, suggesting saturation in the edenite component. On the other hand, the total (Na+K) of the non-subsilicic amphiboles are below 0.9, suggesting undersaturation in the edenite component. The plots for the subsilicic amphiboles on the Al^{IV} vs. Al^{VI} diagram show positive correlation between Al^{IV} and Al^{VI}. This suggests that the subsilicic amphiboles resulted from a large extent of tschermakite-type substitution, (Mg,Fe)Si ⇌ AlAl. The subsilicic amphiboles were subjected to a greater tschermakite-type substitution than the non-subsilicic amphibole, in which little correlation between Al^{IV} and Al^{VI} is found. Sadanagaite is

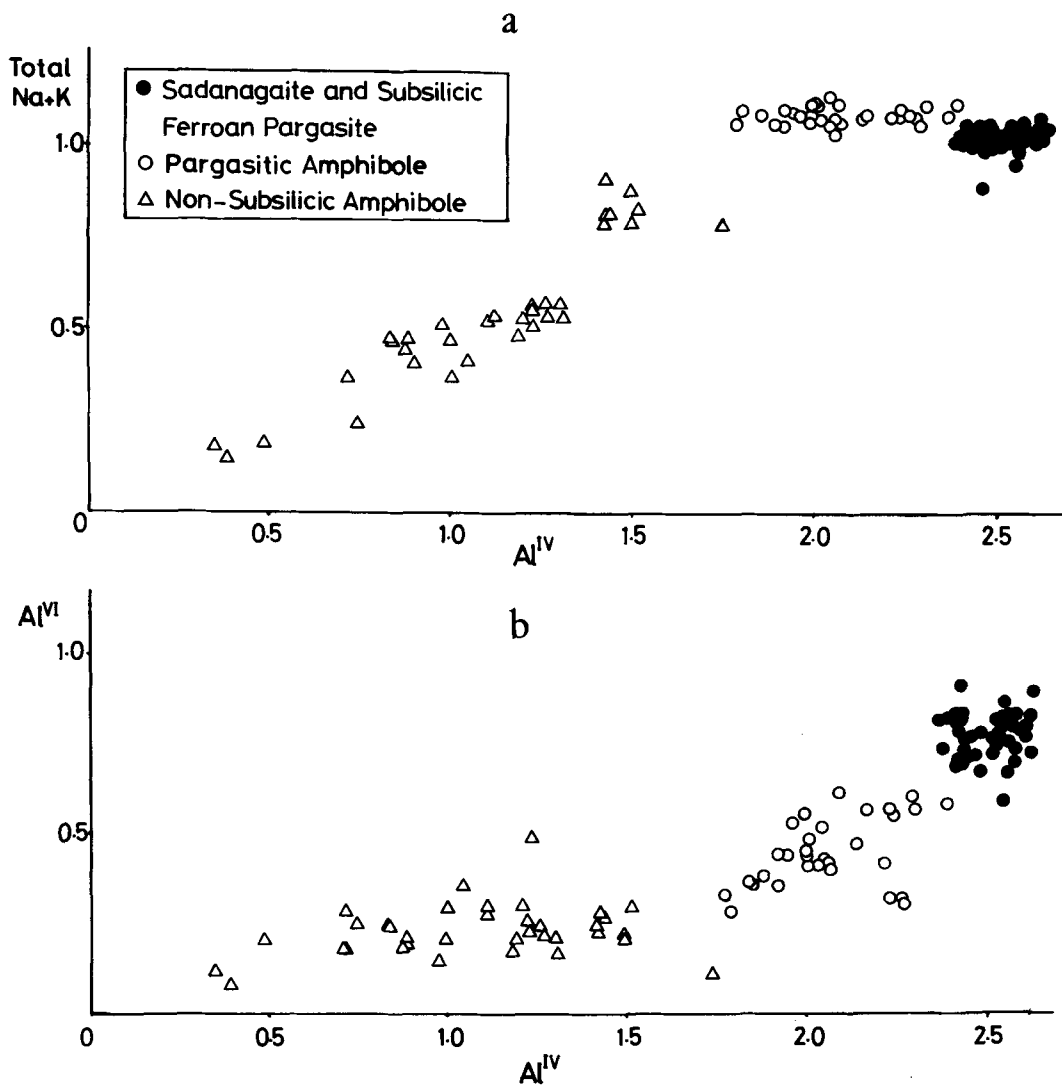


FIG. 6. (a) Al^{IV} vs. total Na + K plots for the calcic amphiboles in the pyroxene hornfels facies zone in the Nōgō-Hakusan area. The chemical formulae are calculated on O = 23 and total iron as FeO. (b) Al^{IV} vs. Al^{VI} plots for the amphiboles. The symbols are the same as in Fig. 6a.

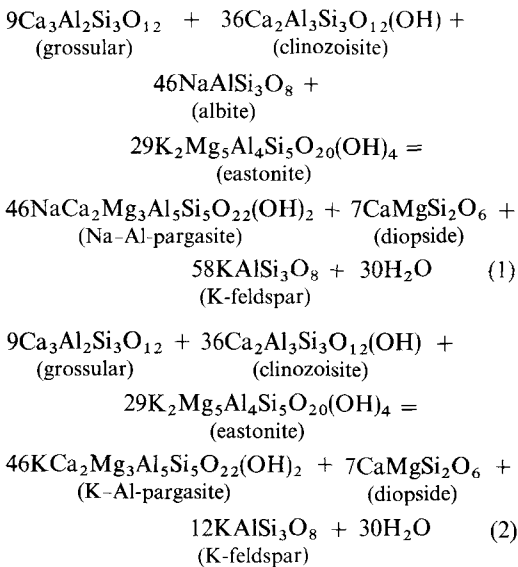
considered to have been formed only when calcic amphibole becomes enriched in the edenite component and simultaneously a large extent of tschermakite-type substitution occurs.

Shimazaki *et al.* (1984) considered that the sadanagaite-bearing rock had been originally derived from Al-rich sediments such as laterite intercalated into limestone. Si contents of sadanagaite for the Ryōke Metamorphic Belt is 4.52–5.24 (Shimazaki *et al.*, 1984), for Cornwall 5.24–5.50 (van Marcke de Lummen and Verka-

eren, 1985), for Eastern Alps 5.34–5.47 (Mogessie *et al.*, 1986), and for the Nōgō-Hakusan area 5.38–5.50 (this paper). This is ascribed probably to the difference between the bulk chemical compositions of the original rocks. The alkali enrichment of sadanagaite suggests that its formation requires not only Si-depleted and Al-enriched conditions but also alkali-enriched conditions. Sadanagaite will probably be discovered in the future in other skarns subjected to intensive alkali-metasomatism at high temperatures.

Physical environment for formation of sadanagaite. Fig. 6b shows that the Al^{VI} in the subsilicic amphiboles is well below the maximum possible Al^{VI} for a given Al^{IV} content demonstrated by Leake (1971). Leake (1971) stated that Al^{VI} content is high when amphiboles crystallize under high-pressure conditions. The depletion of Al^{VI} of the present subsilicic amphiboles may suggest that these amphiboles were formed under low-pressure conditions. In fact, the present subsilicic amphiboles were formed under the low-pressure environment of the pyroxene hornfels facies.

The dark fragments in crystalline limestone are surrounded, as described above, by reaction zones. In the pyroxene hornfels facies zone, Subzone 2 is composed mainly of Ti-grandite, Subzone 3 of clinopyroxene, and Subzone 4 of subsilicic amphibole, K-feldspar and biotite, and the dark fragments of Ti-grandite, clinopyroxene, K-feldspar and biotite. Similar reaction zones develop around dark fragments in the upper amphibolite facies zone. They include anisotropic grandite, clinopyroxene, epidote and biotite, and dark fragments are composed mainly of K-feldspar, biotite, clinopyroxene. From these mineral assemblages, the following reactions of the formation of the sadanagaite are suggested:



In those equations, Al-pargasite (Bunch and Okrusch, 1973) is taken as the end component of the sadanagaite. Grossular, clinozoisite, eastonite and diopside represent grandite, epidote, biotite and clinopyroxene, respectively. Albite is probably

derived from the albite component in K-feldspar. Reactions (1) and (2) are considered to progress with increasing metamorphic temperature, and the sadanagaite becomes stable at high temperatures.

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