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Magnesiosadanagaite, a new member of the amphibole group from Kasuga-mura, Gifu Prefecture, central Japan

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Abstract: Magnesiosadanagaite, ideally $NaCa_2[Mg_3(Al, Fe^{3+})_2]Si_5Al_3O_{22}(OH)_2$, is a new member of the amphibole group occurring as rims of zoned amphibole in rock samples from the contact aureole in Kasuga-mura, central Japan. The amphibole is associated with phlogopite, titanite, calcite, pyrrhotite and chalcopyrite, and composed of an $^{[4]}$Al-poorer core and $^{[4]}$Al-richer rim. The core and rim are classified into pargasite [$^{[4]}$Al = 1.84-2.19 atoms per formula unit (apfu); for O = 23] and pargasite-magnesiosadanagaite ($^{[4]}$Al = 2.45-2.84 apfu), respectively. Both have relatively high $^{[A]}$Na (0.67-0.96 apfu) and low K content (< 0.29 apfu). The high $^{[A]}$Na (0.70-0.92 apfu) and low K (0.09-0.28 apfu) values of magnesiosadanagaite refute the view that high K substitution at the A site is an essential feature of Si-poor calcic amphiboles. The crystal structure of magnesiosadanagaite was refined for two compositionally different samples. Magnesiosadanagaite has the lowest O(5)-O(6)-O(5) angles (160.4° and 161.8°) ever reported in *C*2/*m* amphiboles, indicating maximal kinking of the double-chain of tetrahedra.

Key-words: magnesiosadanagaite, new mineral species, Si-poor amphibole, structure refinement, Japan.

Introduction

The silica-poor [Si < 5.5 atoms per formula unit (apfu) for O = 23] calcic amphibole sadanagaite and its Mg-rich analogue, magnesiosadanagaite, were both first identified and described by Shimazaki *et al*. (1984) from skarns of the amphibolite facies in the Ryoke metamorphic belt. Their ideal chemical formulae were defined as $(K,Na)Ca_2(Fe^{2+},Mg,Al,Fe^{3+},Ti)_5(Si,Al)_8O_{22}(OH)_2$ for sadanagaite and $(K,Na)Ca_2(Mg,Fe^{2+},Al,Fe^{3+},Ti)_5(Si,Al)_8O_{22}(OH)_2$ for magnesiosadanagaite. Sadanagaite was also found from skarns in Cornwall (van Marcke de Lumen & Verkaeren, 1985), thermally metamorphosed rocks in the Nogo-Hakusan area (Sawaki, 1989) and Caledonian metamorphic rocks in the Western Baikal region (Savel'eva & Korikovskii, 1998). Magnesiosadanagaite was also reported from metabasites and metacarbonates in the Eastern Alps (Mogessie *et al*., 1986) and a ruby deposit in China (Wang *et al*., 1997). These amphiboles, except for those from the Eastern Alps and China, characteristically show a high K_2O content (K = 0.43-0.84 apfu). Recently, amphibole nomenclature was revised by the Amphibole Subcommittee of the International Mineralogical Association Commission on the New Minerals and Mineral Names (CNMMN) (Leake *et al*., 1997). According to the current nomenclature, sadanagaite and magnesiosadanagaite are defined as $^{[A]}$Na (Na in the A site)-dominant and Si-poor (< 5.5 apfu) calcic amphiboles, ideally $NaCa_2[Fe^{2+}_3(Al,Fe^{3+})_2]Si_5Al_3O_{22}(OH)_2$ and $NaCa_2[Mg_3(Al,Fe^{3+})_2]Si_5Al_3O_{22}(OH)_2$, respectively. Moreover this nomenclature scheme defines prefixes (*e.g.*, fluoro, potassic) that are an essential part of an amphibole name. The prefix "potassic" is related to K > 0.5 apfu and applies to all amphibole groups (Leake *et al*., 1997). According to this new definition, "sadanagaite" and "magnesiosadanagaite", which were once approved by CNMMN (Nos. 80-27 and 82-102) and reported by Shimazaki *et al*. (1984), have been redefined into potassic-sadanagaite and potassic-magnesiosadanagaite, respectively because they are potassium-dominant-species. The amphiboles described initially as sadanagaite in the literature are potassicsadanagaite except for those from Cornwall (van Marcke de Lumen & Verkaeren, 1985), whereas the amphiboles reported initially as magnesiosadanagaite (*e.g.*, Mogessie *et al*., 1986; Wang *et al*., 1997) possess more

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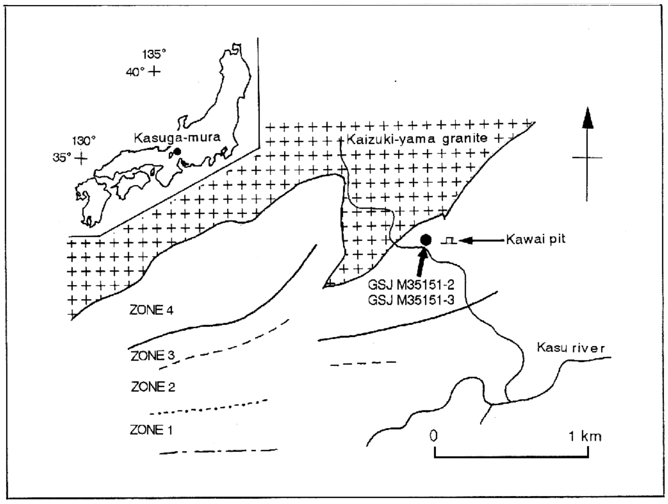

Fig. 1. Schematic metamorphic zone map of the Kasuga-mura area after Suzuki (1977), showing the sample localities.

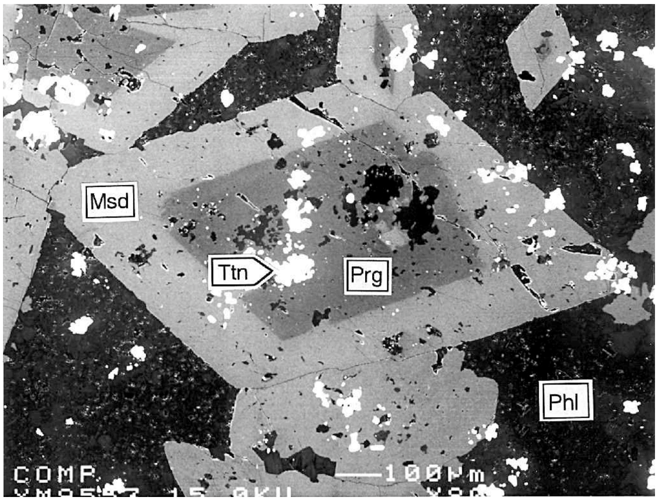

Fig. 2. Back-scattered electron image of zoned amphibole (GSJ M35151-2). Msd: magnesiosadanagaite; Prg: pargasite; Ttn: titanite; Phl: phlogopite.

$^{[A]}$Na than K except for those described by Shimazaki *et al.* (1984). However, the $^{[A]}$Na-rich members, sadanagaite and magnesiosadanagaite have not been formally described as a species until now. Recently, potassic-ferrisadanagaite was described as a new species from an alkaline complex in the Ilmen Mountains (Sokolova *et al.*, 2000).

The amphibole, which has chemical and structural properties that conform to the new nomenclature of magnesiosadanagaite (Leake *et al.*, 1997), was found in a granitic contact aureole in Kasuga-mura, Gifu Prefecture, central Japan. The mineral data and mineral name have been approved by CNMMN (No. 2002-051). In this paper, we will present the mode of the occurrence, chemistry and crystallographic data for magnesiosadanagaite from this locality. The type specimens of magnesiosadanagaite are deposited at the Geological Museum, Geological Survey of Japan, AIST, Tsukuba under the registered number GSJ M35151 and National Science Museum, Tokyo under the catalogue No. NSM-M28307.

Geological setting and petrography

The Kasuga-mura area comprises the Jurassic formation and Cretaceous Kaizuki-yama granite. The Jurassic formation consists of shale, sandstone and chert with a substantial amount of basic volcanic rocks, dolomite and limestone. The formation was thermally metamorphosed by the Kaizuki-yama granite. The contact aureole around the Kaizuki-yama granite was recognized with a width of more than 3 km. Its metamorphic grade ranges from the greenschist to amphibolite facies (Suzuki, 1975, 1977). Metamorphic zoning is shown in Fig. 1 after Suzuki (1977). The contact aureole is divided into four zones on the basis of mineral parageneses in siliceous dolomite; zone 1 is defined by the presence of talc, zone 2 by the dolomite-quartz-tremolite-calcite assemblage, zone 3 by the diopside-dolomite assemblage and zone 4 by the forsterite-diopside assemblage. Magnesiosadanagaite from three samples, sample numbers GSJ M35151-1, M35151-2 and M35151-3, was examined. The sample GSJ M35151-1 was collected from dump material in the Kasuga mine's Kawai pit, which had produced wollastonite and dolomite. Two other samples GSJ M35151-2 and M35151-3 were collected from basic nodules (up to about 1.5 m in length and 0.5 m in width), which locally occur in dolomite-calcite marble in zone 4 (Fig. 1). The dolomite-calcite marble commonly contains skarn minerals such as grossular, diopside and wollastonite.

All rock samples contain amphibole, phlogopite, titanite, calcite, pyrrhotite and chalcopyrite. Sample GSJ M35151-1 also contains scapolite and apatite with minor amounts of chlorite and pyrite. The other two samples contain minor spinel, pentlandite, ilmenite, apatite (only in GSJ M35151-2), and chlorite (only in GSJ M35151-3).

The amphibole occurs as prismatic crystals, up to 3 mm in length. Most amphibole crystals exhibit distinct optical zoning (Fig. 2). The rim is characterized by stronger pleochroism (yellowish brown to pale yellowish brown) than the core (pale greenish brown to pale brown). In some cases, the zoning is not concentric, and a part of the core contacts directly with the matrix. The boundary between the core and rim is sharp, and the rim has higher refractive indices than the core.

Phlogopite is pale brown and occurs as plates about 0.1-1 mm in length or aggregates of finer crystals (20-30 μm). The latter occurrence was found only in GSJ M35151-2 and M35151-3. Titanite is euhedral to subhedral < 0.2 mm in length. Spinel is green and subhedral in form (0.2-0.3 mm in grain size). Pentlandite occurs as lamellae in pyrrhotite.

Mineral chemistry

Chemical analyses of the minerals were performed on a JEOL JXA-8800R electron microprobe analyzer at AIST. Accelerating voltage and specimen current were kept at

Table 1. Chemical compositions of amphiboles.

	GSJ M35151-1				GSJ M35151-2				GSJ M35151-3		
	core Prg	rim Msd	rim Msd	rim Msd#	core Prg	rim Msd#	rim Msd	rim Msd	core Prg	rim Msd	rim Msd
SiO_2	41.1	35.6	36.4	37.1	42.9	37.7	37.9	37.3	42.2	37.4	37.2
TiO_2	1.76	4.02	2.71	2.70	1.19	2.64	2.81	2.88	1.66	2.87	2.88
Al_2O_3	17.2	22.2	22.0	20.9	15.3	19.8	19.7	20.0	15.9	20.9	20.2
Cr_2O_3	0.00	0.00	0.02	0.01	0.05	0.02	0.03	0.00	0.00	0.01	0.00
FeO*	5.27	7.10	8.03	6.76	5.40	6.45	6.85	6.60	4.60	5.98	5.58
MnO	0.19	0.24	0.21	0.18	0.09	0.14	0.12	0.15	0.02	0.18	0.14
MgO	16.2	12.5	12.0	13.4	17.0	14.2	14.3	14.0	17.1	14.3	14.4
CaO	12.5	12.2	12.2	12.5	12.7	12.7	12.5	12.5	13.0	12.5	12.6
Na_2O	3.24	3.48	3.32	3.33	2.89	2.61	2.62	2.67	2.89	2.81	2.81
K_2O	0.24	0.57	0.57	0.49	0.74	1.48	1.37	1.24	0.87	1.28	1.19
F	0.37	0.28	0.27	0.29	0.20	0.16	0.17	0.16	0.34	0.24	0.25
Cl	0.04	0.02	0.02	0.02	0.13	0.14	0.14	0.15	0.17	0.17	0.12
-O=F+Cl	0.17	0.10	0.11	0.12	0.11	0.10	0.10	0.10	0.18	0.14	0.14
Total	97.9	98.1	97.6	97.6	98.5	97.9	98.4	97.6	98.6	98.5	97.2
H_2O**	1.91	1.93	1.92	1.92	1.98	1.96	1.96	1.94	1.90	1.93	1.91
Fe_2O_3***	0.12	0.54	0.09	0.60	0.30	0.95	0.82	0.73	0.21	0.77	0.78
FeO***	5.17	6.61	7.95	6.22	5.13	5.59	6.11	5.94	4.41	5.29	4.88
Total	99.9	100.1	99.6	99.5	100.5	100.0	100.5	99.6	100.5	100.5	99.2
Structural formulae based on 23 O atoms											
Si	5.882	5.173	5.324	5.395	6.105	5.470	5.477	5.435	6.002	5.384	5.416
$^{[4]}Al$	2.118	2.827	2.676	2.605	1.895	2.530	2.523	2.565	1.998	2.616	2.584
ΣT	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000
$^{[6]}Al$	0.783	0.975	1.116	0.977	0.671	0.856	0.832	0.869	0.667	0.930	0.882
Ti	0.189	0.439	0.298	0.295	0.127	0.288	0.305	0.316	0.178	0.311	0.315
Cr	0.000	0.000	0.002	0.001	0.006	0.002	0.003	0.000	0.000	0.001	0.000
Fe^{3+}	0.013	0.060	0.010	0.066	0.032	0.104	0.090	0.080	0.022	0.083	0.085
Fe^{2+}	0.619	0.803	0.972	0.756	0.611	0.680	0.739	0.724	0.525	0.637	0.595
Mn	0.023	0.030	0.026	0.022	0.011	0.017	0.015	0.019	0.002	0.022	0.017
Mg	3.456	2.708	2.616	2.905	3.606	3.071	3.081	3.041	3.625	3.069	3.126
ΣC	5.083	5.015	5.040	5.022	5.064	5.018	5.065	5.049	5.019	5.053	5.020
ΣC-5	0.083	0.015	0.040	0.022	0.064	0.018	0.065	0.049	0.019	0.053	0.020
Ca	1.917	1.899	1.912	1.948	1.936	1.974	1.935	1.951	1.981	1.928	1.966
$^{[B]}Na$	0.000	0.086	0.048	0.030	0.000	0.008	0.000	0.000	0.000	0.019	0.014
ΣB	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
$^{[A]}Na$	0.899	0.894	0.894	0.909	0.797	0.726	0.734	0.754	0.797	0.765	0.779
K	0.044	0.106	0.106	0.091	0.134	0.274	0.253	0.230	0.158	0.235	0.221
ΣA	0.943	1.000	1.000	1.000	0.931	1.000	0.987	0.984	0.955	1.000	1.000
Total cation	15.943	16.000	16.000	16.000	15.931	16.000	15.987	15.984	15.955	16.000	16.000
F	0.167	0.129	0.125	0.133	0.090	0.073	0.078	0.074	0.153	0.109	0.115
Cl	0.010	0.005	0.005	0.005	0.031	0.034	0.034	0.037	0.041	0.041	0.030
OH	1.823	1.866	1.870	1.862	1.879	1.893	1.888	1.889	1.806	1.850	1.855

Notes: Prg=pargasite, Msd=magnesiosadanagaite.
Chemical compositions of magnesiosadanagaite for the X-ray study. * Total iron as FeO.
** H_2O calculation based on an assumption of OH+F+Cl=2.0 apfu.
*** Fe^{3+}/Fe^{2+} calculation based on the minimum ferric estimation (Schumacher, 1997).

15 kV and 12 nA on a Faraday cup, respectively. Beam diameter was 10 μm for F and Cl analyses and 2 μm for other element analyses. Synthetic quartz (for Si), rutile (Ti), corundum (Al), Cr_2O_3 (Cr), MnO (Mn), hematite (Fe), periclase (Mg), wollastonite (Ca) and F-phlogopite (F), as well as natural albite (Na), adularia (K) and Cl-rich hastingsite (Cl) were used as standards. The Bence & Albee (1968) method was employed for matrix corrections. Detection limits for F and Cl were about 0.08 and 0.01 wt.% (3σ level), respectively.

Amphibole

Table 1 shows representative analyses of amphiboles. The chemical formulae were calculated on the basis of 23 oxygens. The Fe^{3+}/Fe^{2+} ratios were estimated using the minimum ferric method described by Schumacher (1997).

Amphibole crystal consists of an $^{[4]}Al$-poorer core (< 2.19 apfu) and $^{[4]}Al$-richer rim (< 2.84 apfu). The core has a fairly homogeneous composition within a thin-section scale, *i.e.*, pargasitic with $X_{Fe^{2+}}$ [= $Fe^{2+}/(Fe^{2+}$ + Mg)] = 0.12-0.16 (Fig. 3). Its $^{[4]}Al$ and Ti contents are

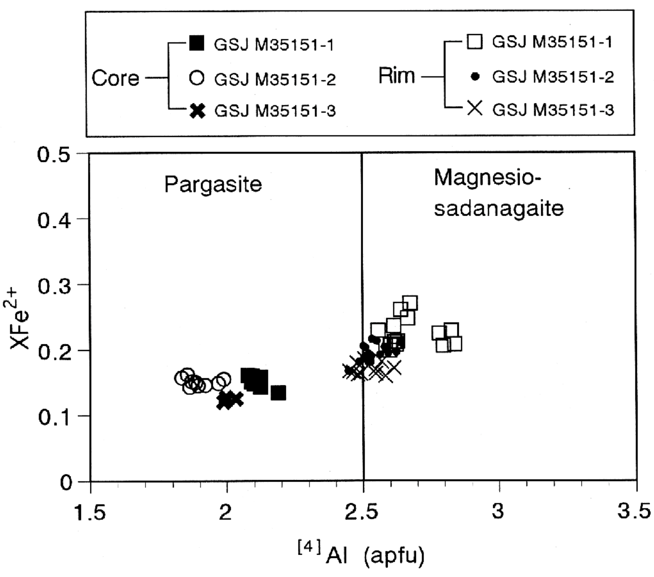

Fig. 3. $^{[4]}Al$ *vs.* $X_{Fe^{2+}}$ plots for amphiboles from the Kasuga-mura area.

Table 3. X-ray powder diffraction data for magnesiosadanagaite.

h	k	l	GSJ M35151-1 I	d (Å)obs.	d (Å)calc.	GSJ M35151-2 I	d (Å)obs.	d (Å)calc.
0	2	0	50	8.98	8.96	50	8.97	9.00
1	1	0	100	8.38	8.40	70	8.47	8.43
-1	1	1	30	4.92	4.92	30	4.92	4.93
0	4	0	30	4.49	4.48	20	4.50	4.50
1	1	1	20	3.97	3.97	10	3.97	3.99
-1	3	1				20	3.91	3.90
1	3	1	60	3.37	3.37	60	3.38	3.38
2	4	0	50	3.26	3.26	50	3.27	3.27
3	1	0	80	3.11*	3.12	70	3.13*	3.13
-3	1	1	10	3.06	3.05	10	3.04	3.05
2	2	1	40	2.93	2.93	50	2.94	2.94
3	3	0	25	2.81	2.80	30	2.82	2.81
-3	3	1	45	2.75	2.75	40	2.76	2.75
1	5	1	80	2.70	2.69	100	2.70	2.70
0	6	1	75	2.58	2.58	70	2.59	2.59
-2	0	2	90	2.56	2.56	100	2.57	2.56
-2	6	1				20	2.42	2.42
3	5	0	20	2.38	2.37	30	2.39	2.38
-3	5	1	80	2.34	2.34	90	2.35	2.35
-4	2	1			2.34			2.34
-3	1	2	40	2.30	2.30	40	2.30	2.30
-1	7	1			2.29			2.30
-2	4	2	25	2.24	2.22	20	2.23	2.23
2	6	1	55	2.16	2.15	60	2.16	2.16
2	0	2	35	2.04	2.04	40	2.04	2.04
-4	0	2			2.04			2.04
3	5	1	60	2.00	2.01	20	2.02	2.01
1	9	0				10	1.957	1.958
-3	5	2	10	1.951	1.947			
5	1	0				10	1.901	1.899
-1	9	1	35	1.854	1.855	20	1.863	1.863
-1	7	2	10	1.833	1.843			
0	10	0				10	1.801	1.800
-1	3	3	40	1.683	1.692	20	1.694	1.695
-2	8	2			1.685	10	1.680	1.691
4	6	1	50	1.645	1.642	30	1.650	1.648
1	11	0	50	1.609	1.606	30	1.614	1.613
6	0	0			1.586			1.591
-1	5	3	70	1.587	1.583	30	1.591	1.586
4	0	2	40	1.549	1.548	30	1.552	1.553
-2	6	3	45	1.520	1.519	40	1.525	1.522
5	5	1			1.495	30	1.502	1.501
0	12	0	20	1.501	1.493			
-6	6	1	35	1.442	1.440	60	1.447	1.445
-5	5	3	20	1.371	1.371	20	1.373	1.373
1	11	2	40	1.333	1.333	30	1.337	1.339
-7	5	1	30	1.313	1.313	30	1.318	1.317
-2	12	2	20	1.291	1.290	20	1.301	1.295
-1	3	4			1.285			
-4	0	4	20	1.285	1.279			
-5	11	2	20	1.200	1.199	20	1.204	1.203
			a = 9.875(9) Å			a = 9.905(9) Å		
			b =17.92(1) Å			b =18.00(1) Å		
			c = 5.314(6) Å			c = 5.322(5) Å		
			β=105.55(7)°			β=105.47(7)°		

* Estimated from data with the external Si-standard, beacause of overlap by the 111 diffraction of Si-standard.

1.84-2.19 and 0.11-0.20 apfu, respectively. Chemical variation in the rim is relatively small in a single rock specimen. The rim of amphibole ranges in composition from pargasite to magnesiosadanagaite (Fig. 3), and its $^{[4]}$Al and Ti contents are 2.45-2.84 and 0.22-0.44 apfu, respectively. The rim shows slightly higher $X_{Fe^{2+}}$ values (0.16-0.27) than the core (0.12-0.16) (Fig. 3). Both the core and rim have relatively high $^{[A]}$Na (0.67-0.96 apfu) and low K contents of < 0.29 apfu. The K+$^{[A]}$Na contents of the core and rim are 0.90-1.00 and 0.93-1.00 apfu, respectively, and Ca contents are over 1.85 apfu. Chlorine content is less than 0.19 wt.% for both the core and rim. The core possess a slightly higher amount of F (0.20-0.42 wt.%) than the rim (0.13-0.31 wt.%).

Other minerals

Chemical compositions of some minerals coexisting with the amphibole are shown in Table 2 (It can be obtained from the authors or through the E.J.M. Editorial Office - Paris). Phlogopite shows highly variable Na_2O contents, and its Na content is 0.19-1.59 apfu (O = 22) for GSJ M35151-1 and less than 0.24 apfu for the two other samples (Banno *et al.*, in prep.). The $X_{Fe^{2+}}$ values of phlogopite and chlorite are 0.09-0.14 and 0.11-0.29, respectively.

Spinel belongs to the spinel-hercynite series with $X_{Fe^{2+}}$ about 0.35 and contains ZnO up to 4.69 wt.%. Ilmenite contains minor geikielite (7-11 %) and pyrophanite (4 %) components. The meionite component in scapolite ranges from 51 to 53 %. Up to 1.58 wt.% Al_2O_3 is present in titanite.

Physical and optical properties of magnesiosadanagaite

Physical and optical properties of magnesiosadanagaite were examined for sample GSJ M35151-2. Magnesiosadanagaite is brownish black in the hand specimen, and brown with reddish tint in powdered form. It is brittle with an uneven fracture, has perfect {110} cleavage. The Vickers microhardness is 665-792 kg/mm^2 (100 g load). It corresponds to 5.5-6 on Mohs' hardness scale. Magnesiosadanagaite is optically biaxial positive with α 1.674(2), β (calc.) 1.683 for 2*V* of 85°, γ 1.694(2), 2*V*(meas.) > 80° and < 90°; *Z* ^ c 20° and *Y* = b. It is pleochroic with *X* = pale yellow, *Y* = yellowish brown and *Z* = reddish brown.

X-ray crystallography of magnesiosadanagaite

Single crystal fragments of magnesiosadanagaite carefully handpicked from thin sections of GSJ M35151-1 and M35151-2 were used for X-ray study. Chemical compositions of the magnesiosadanagaite are presented in Table 1.

X-ray powder study

The X-ray powder diffraction data obtained with a 114.6 mm Gandolfi camera (at the National Science Museum) using Cu/Ni radiation are given in Table 3. Observed *d*-values were corrected by the method proposed by Toraya (1993). Peaks were indexed by reference to the data of hornblende (Borg & Smith, 1969) and potassic-magnesiosadanagaite (Shimazaki *et al.*, 1984). The unit cell parameters obtained from the present data are *a* = 9.875(9), *b* = 17.92(1), *c* = 5.314(6) Å, ß = 105.55(7)° and V = 906(1) Å^3 for GSJ M35151-1 and *a* = 9.905(9), *b* = 18.00(1), *c* = 5.322(5) Å, ß = 105.47(7)° and V = 915(1) Å^3 for GSJ M35151-2. Due to the lower Fe^{2+} and K contents, cell volumes for both samples are distinctly smaller than that (926 Å^3) measured for potassic-magnesiosadanagaite (K = 0.75 apfu: $X_{Fe^{2+}}$ = 0.43, Shimazaki *et al.*, 1984).

Table 4. Crystallographic data and experimental details of single crystal studies on magnesiosadanagaite.

	GSJ M35151-1	GSJ M35151-2
a (Å)	9.869(3)	9.906(2)
b (Å)	17.933(7)	17.971(5)
c (Å)	5.322(2)	5.3190(10)
β (°)	105.29(3)	105.48(2)
V (Å^3)	908.6(6)	912.5(4)
Space group	*C2/m*	*C2/m*
Z	2	2
D_{calc} (g/cm^3)	3.179	3.171
μ (cm^{-1})	2.191	2.194
Crystal dimension (mm)	0.12 x 0.12 x 0.05	0.17 x 0.17 x 0.07
Diffractometer	Rigaku AFC-7R	Rigaku AFC-7R
Radiation	Mo*K* α (graphite)	Mo*K* α (graphite)
Scan mode, rate (°/ min in ω)	2θ-ω, 16	2θ-ω, 8
2θ range	7.9 — 60.0	7.9 — 55.0
Reflection range	-13 ≤ h ≤ 13, 0 ≤ k ≤ 25, -7 ≤ l ≤ 3,	-12 ≤ h ≤ 7, 0 ≤ k ≤ 23, -6 ≤ l ≤ 6,
No. of measured reflections	1653	1307
No. unique reflections	1374	1082
No. of observed reflections [$F^2 > 2\sigma(F^2)$]	1009	962
R_{int}	3.3 %	1.7 %
Variable parameters	103	102
$R1$ [$F^2 > 2\sigma(F^2)$], $R1$ (all reflections)	4.2 %, 7.1 %	2.8 %, 3.3 %
w$R2$ (all reflections)	14.0 %	12.8 %
Weghting parameters, a, b	0.1, 0	0.1, 0
Goodness of Fit	0.947	1.109
Final $\Delta\rho_{max}$ (e/Å^3)	0.780	0.472
Final $\Delta\rho_{min}$ (e/Å^3)	-0.895	-0.828

$R1 = \Sigma\,||F_o| - |F_c||\,/\,\Sigma|F_o|$

$wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]\,/\,\Sigma[w(F_o^2)^2]\}^{0.5}$

$w = 1\,/\,[\sigma^2(F_o^2) + (aP)^2 + bP]$

$P = [2F_c^2 + F_o^2]\,/\,3$

Structure refinement

Single-crystal diffraction data were collected and refined for two samples, GSJ M35151-1 and M35151-2. Experimental details pertaining to the collection are given in Table 4. The data reductions to Fo^2 with corrections for Lorentz, polarization and absorption (ψ-scan procedure) were made with a computer program written by Dr. Kazumasa Sugiyama of the University of Tokyo. The crystal structures were refined with SHELXL-97 (Sheldrick, 1997) based on Fo^2 against all reflections with the weighting function shown in Table 4. Scattering factors for neutral atoms were taken from the International Tables for X-ray Crystallography Volume C (1992). The numbers of equivalent reflections collected from the samples GSJ M35151-1 and M35151-2 are 279 and 225, respectively. The refinements for GSJ M35151-1 and M35151-2 converged with $R1$ [$F^2 > 2\sigma(F^2)$] = 0.0422 and 0.0277, respectively and $R1$ (all reflections) = 0.0710 and 0.0329, respectively. The results of the refinements were summarized in Table 4. The final atomic coordinates, cation occupancies, equivalent isotropic and anisotropic displacement parameters are given in Table 5. Selected interatomic distances and angles are in Table 6 (It can be obtained from the authors or through the E.J.M. Editorial Office - Paris).

The occupancy factors of Al in the T(2) site, $^{T(2)}$Al(apfu), were calculated for both samples using equation (5) in Oberti *et al.* (1995), which was corrected as follows; $^{T(2)}$Al = [<T(2)-O>-<T(2)-O>$_c$] x 35.2592 (Sokolova *et al.*, 2000; Oberti, pers. comm.). The results, $^{T(2)}$Al (apfu) = 0.47 and 0.35, are both smaller than the values calculated from the differences between tetrahedral Al and Al in the T(1) site, $^{[4]}$Al (apfu)-$^{T(1)}$Al (apfu) = 0.58 and 0.62 for GSJ M35151-1 and M35151-2, respectively. Equation (1) reported in Oberti *et al.* (1995) to calculate <T(2)-O>$_c$ was obtained from a regression of lower-Al amphiboles and may not be applicable for these higher Al-amphiboles.

Titanium is usually considered as an octahedral cation in most amphiboles, and most structural studies of amphiboles with low Ti contents (< 0.20 apfu) have assigned Ti to the M(2) site. Recently, Oberti *et al.* (1992) and Hawthorne *et al.* (1998) studied the behavior of Ti in sodic-calcic and sodic amphiboles. They showed that in these minerals the entry of Ti occurs primarily in the substitution, $^{M(1)}Ti^{4+} + 2^{O(3)}O^{2-} \rightarrow {}^{M(1)}(Mg, Fe)^{2+} + 2^{O(3)}OH^-$, and that the M(1)-O(3) distance decreases markedly with increasing Ti content in the structure. Sokolova *et al.* (2000) pointed out that dehydroxylated amphiboles with OH + F < 2 apfu and significant Ti^{4+} and Fe^{3+} at M(1) [and M(3)] show M(1)-O(3) << <M(1)-O>. The magnesiosadanagaite in this study shows that M(1)-O(3) is not less than <M(1)-O> (Table 6), indicating that the magnesiosadanagaite is not dehydroxylated and has no Ti^{4+} at the M(1) site.

The O(5)-O(6)-O(5) angles for GSJ M35151-1 and M35151-2 are 160.4° and 161.8°, respectively. The studied samples have the lowest values of the O(5)-O(6)-O(5) angle ever reported in *C2/m* amphibole (*cf.* Fig. 3 in Sokolova *et al.*, 2000), indicating maximal kinking of the double-chain of tetrahedra.

Discussion

Potassicsadanagaite and potassic-magnesiosadanagaite, described initially as "sadanagaite" and "magnesiosadana-

Table 5. Final atomic coordinates, cation occupancies and displacement parameters (Å^2) for magnesiosadanagaite.

GSJ M35151-1

Site	Occupancy (apfu)	x	y	z	U$_{eq}$
T(1)	1.97Si+2.03Al	0.27999(10)	0.08616(5)	0.30473(19)	0.0077(2)
T(2)	3.43Si+0.57Al	0.29136(10)	0.17386(5)	0.81769(18)	0.0080(2)
M(1)	1.62Mg+0.38Fe	0.0000	0.08999(7)	0.5000	0.0079(3)
M(2)	0.53Mg+0.19Fe+0.98Al+0.30Ti	0.0000	0.17726(7)	0.0000	0.0104(3)
M(3)	0.75Mg+0.25Fe	0.0000	0.0000	0.0000	0.0080(3)
M(4)	1.95Ca+0.02Mn+0.03Na	0.0000	0.28122(5)	0.5000	0.0109(2)
A (2)	0.91Na+0.09K	0.0000	0.4776(4)	0.0000	0.068(3)
O(1)	4O	0.1050(3)	0.09056(15)	0.2122(5)	0.0132(5)
O(2)	4O	0.1182(3)	0.17486(13)	0.7402(5)	0.0108(5)
O(3)	1.87O+0.13F	0.1083(4)	0.0000	0.7139(7)	0.0112(7)
O(4)	4O	0.3700(3)	0.25190(14)	0.7921(5)	0.0126(5)
O(5)	4O	0.3522(3)	0.14168(14)	0.1176(5)	0.0130(5)
O(6)	4O	0.3425(3)	0.11659(15)	0.6141(5)	0.0143(5)
O(7)	2O	0.3368(4)	0.0000	0.2715(7)	0.0154(7)
H	1.87H	0.173(15)	0.0000	0.85(3)	0.15(7) *

Site	U$_{11}$	U$_{22}$	U$_{33}$	U$_{23}$	U$_{13}$	U$_{12}$
T(1)	0.0092(5)	0.0056(4)	0.0089(5)	0.0002(3)	0.0036(4)	-0.0008(3)
T(2)	0.0098(4)	0.0060(4)	0.0096(4)	0.0002(3)	0.0050(3)	0.0003(3)
M(1)	0.0111(6)	0.0064(6)	0.0078(6)	0.000	0.0053(5)	0.000
M(2)	0.0121(6)	0.0090(6)	0.0109(6)	0.000	0.0047(5)	0.000
M(3)	0.0106(8)	0.0061(7)	0.0081(8)	0.000	0.0039(6)	0.000
M(4)	0.0152(5)	0.0076(4)	0.0124(5)	0.000	0.0078(4)	0.000
A	0.058(4)	0.080(7)	0.087(5)	0.000	0.057(4)	0.000
O(1)	0.0123(11)	0.0173(12)	0.0113(12)	-0.0011(9)	0.0054(10)	-0.0040(9)
O(2)	0.0115(11)	0.0087(11)	0.0128(11)	0.0010(8)	0.0039(9)	0.0010(9)
O(3)	0.0104(15)	0.0088(15)	0.0149(17)	0.000	0.0042(14)	0.000
O(4)	0.0171(11)	0.0083(11)	0.0147(12)	0.0007(9)	0.0081(10)	-0.0011(9)
O(5)	0.0136(12)	0.0110(11)	0.0154(12)	0.0021(9)	0.0056(10)	-0.0008(9)
O(6)	0.0125(12)	0.0136(12)	0.0172(13)	-0.0039(10)	0.0044(10)	0.0009(9)
O(7)	0.0164(18)	0.0122(16)	0.0188(18)	0.000	0.0068(15)	0.000

GSJ M35151-2

Site	Occupancy (apfu)	x	y	z	U$_{eq}$
T(1)	2.10Si+1.90Al	0.27942(7)	0.08595(4)	0.30443(14)	0.0066(3)
T(2)	3.37Si+0.63Al	0.29054(7)	0.17353(4)	0.81600(13)	0.0068(3)
M(1)	1.66Mg+0.34Fe	0.0000	0.08973(5)	0.5000	0.0074(3)
M(2)	0.60Mg+0.25Fe+0.86Al+0.29Ti	0.0000	0.17709(5)	0.0000	0.0113(3)
M(3)	0.81Mg+0.19Fe	0.0000	0.0000	0.0000	0.0056(3)
M(4)	1.97Ca+0.01Na+0.02Mn	0.0000	0.28089(4)	0.5000	0.0096(3)
A (2/*m*)	0.73Na+0.27K	0.0000	0.5000	0.0000	0.111(2)
O(1)	4O	0.10562(19)	0.08934(11)	0.2147(4)	0.0119(4)
O(2)	4O	0.11888(19)	0.17438(10)	0.7371(4)	0.0101(4)
O(3)	1.90O+0.07F+0.03Cl	0.1088(3)	0.0000	0.7157(5)	0.0140(6)
O(4)	4O	0.36869(19)	0.25114(10)	0.7914(4)	0.0112(4)
O(5)	4O	0.35101(18)	0.14053(11)	0.1155(3)	0.0122(4)
O(6)	4O	0.34361(18)	0.11710(11)	0.6125(3)	0.0131(4)
O(7)	2O	0.3372(3)	0.0000	0.2766(5)	0.0159(6)
H	1.90H	0.189(5)	0.0000	0.750(8)	0.000(10)*

Site	U$_{11}$	U$_{22}$	U$_{33}$	U$_{23}$	U$_{13}$	U$_{12}$
T(1)	0.0062(4)	0.0069(4)	0.0069(4)	0.0000(2)	0.0022(3)	-0.0008(2)
T(2)	0.0072(4)	0.0069(4)	0.0070(4)	0.0003(2)	0.0032(3)	0.0000(2)
M(1)	0.0085(5)	0.0085(5)	0.0062(6)	0.000	0.0040(4)	0.000
M(2)	0.0119(5)	0.0113(5)	0.0117(6)	0.000	0.0047(4)	0.000
M(3)	0.0075(7)	0.0050(6)	0.0042(6)	0.000	0.0011(5)	0.000
M(4)	0.0109(4)	0.0089(4)	0.0109(4)	0.000	0.0062(3)	0.000
A	0.063(2)	0.205(6)	0.089(3)	0.000	0.062(2)	0.000
O(1)	0.0095(10)	0.0165(10)	0.0099(9)	-0.0007(7)	0.0030(7)	-0.0025(7)
O(2)	0.0076(9)	0.0124(9)	0.0099(9)	0.0014(7)	0.0013(7)	0.0004(7)
O(3)	0.0162(15)	0.0119(13)	0.0141(13)	0.000	0.0044(10)	0.000
O(4)	0.0135(9)	0.0094(9)	0.0125(9)	0.0001(7)	0.0066(7)	-0.0009(7)
O(5)	0.0115(9)	0.0141(10)	0.0114(9)	0.0049(7)	0.0036(7)	0.0003(7)
O(6)	0.0102(9)	0.0150(10)	0.0142(9)	-0.0043(7)	0.0036(7)	0.0012(7)
O(7)	0.0115(13)	0.0149(14)	0.0192(14)	0.000	0.0006(10)	0.000

*Isotropic displacement parameter.

gaite” by Shimazaki *et al.* (1984), were characterized by their extremely high $^{[4]}$Al (2.76-3.39 apfu) and K contents (0.62-0.75 apfu). Shimazaki *et al.* (1984) suggested that substantial replacement of Si by Al in the tetrahedral site might be crystallochemically necessary for the entry of K into the A site. However, relatively high $^{[A]}$Na (0.70-0.92 apfu) and low K (0.09-0.28 apfu) contents in magnesiosadanagaite from the Kasuga-mura area are not consistent with their view. Figure 4 summarizes the relationships among K, $X_{Fe^{2+}}$ [= $Fe^{2+}/(Fe^{2+} + Mg)$] and $^{[4]}$Al of calcic amphiboles with $^{[4]}$Al > 2.5 apfu in this study and from the literature. The amphiboles with $X_{Fe^{2+}} > 0.4$ show high K contents (0.30-0.84 apfu), whereas those with lower $X_{Fe^{2+}}$ [< 0.3; this study, Mogessie *et al.* (1986) and Wang (1997)] do not show high K content (0.00-0.39 apfu) (Fig. 4). These chemical data indicate that high K substitution in the A site is not an essential feature for the Si-poor member of calcic amphiboles with low $X_{Fe^{2+}}$.

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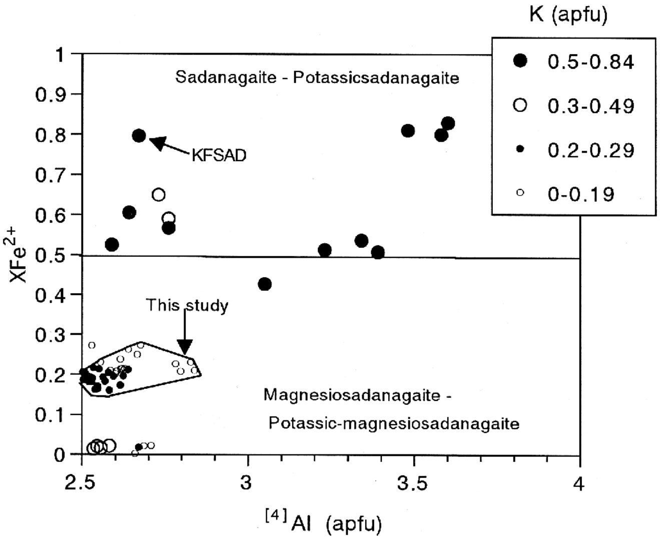

Fig. 4. Relationship between K, [4]Al and $X_{Fe^{2+}}$ contents of sadanagaite, potassicsadanagaite, magnesiosadanagaite, potassic-magnesiosadanagaite and potassic-ferrisadanagaite. The chemical data are from Banno *et al.* (this study), Hawthorne & Grundy (1977), Mogessie *et al.* (1986), Savel'eva & Korikovskii (1998), Sawaki (1989), Shimazaki *et al.* (1984), Sokolova *et al.* (2000), van Marcke de Lumen & Verkaeren (1985) and Wang *et al.* (1997). KFSAD, potassic-ferrisadanagaite.

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