

TWO T – f(O₂) PATHS IN THE MYOKEN-ZAN MAGNETITE-BEARING GRANITIC COMPLEX, SAN'YO BELT, SOUTHWESTERN JAPAN

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ABSTRACT

The Myoken-zan igneous complex is a magnetite-series granitoid complex occurring among the ilmenite-series granitoids of the San'yo belt, Japan. The complex is composed of seven rock units that vary in composition from tonalite to monzogranite. Petrographically, the calcic amphiboles and magnetite from the complex can be divided in two groups, conveniently called amphiboles-1 and -2, and magnetite-1 and -2, respectively. With increasing Si contents, Mg/(Mg+Fe+Mn) in amphiboles-1 commonly increases, but that in amphiboles-2 remains unchanged. Magnetite-1 and -2 are characterized by thin (<1 μm) and thick (>3 μm) lamellae of ilmenite, respectively. Three rock units contain a pair of amphiboles-1 + magnetite-1, and the rest (four units) contain a pair of amphiboles-2 + magnetite-2. Exceptions to the rule are rare. Geothermometric and geobarometric calculations for the Fe-Ti oxides and the mafic silicates indicate that two separate T-f(O₂) paths produced the magnetite of the Myoken-zan igneous complex. The first path developed in the late-magmatic to subsolidus stages and led to the production of magnetite-1 over a temperature range of about 750° to 650°C, while oxygen fugacities in the melts remained above those of the Ni-NiO buffer. The second path developed at the subsolidus stage and led to the production of magnetite-2 by a reaction between mafic silicates and the water-rich fluid exsolved from the magmas. Oxygen fugacities in the fluid phase varied from those of the Ni-NiO buffer to those of the FMQ buffer, with falling temperature from about 670° to 570°C.

Keywords: granitic pluton, Fe-Ti oxides, conditions of crystallization, redox path, Myoken-zan, Japan.

SOMMAIRE

Le complexe granitique à magnétite de Myoken-zan a été mis en place parmi les complexes granitiques à ilménite de la ceinture de San'yo, au Japon. Il est fait de sept unités distinctes variant en composition de tonalite à monzogranite. Les amphiboles calciques et la magnétite du complexe forment deux groupes, 1 et 2. A mesure que les teneurs en Si augmentent, le rapport Mg/(Mg + Fe + Mn) dans les amphiboles du groupe 1 augmente, en général, mais il demeure constant dans celles du groupe 2. La magnétite du groupe 1 contient de minces (<1 μm) lamelles d'exsolution d'ilménite, tandis qu'elles sont plus épaisses (>3 μm) dans la magnétite du groupe 2. Dans trois des unités, il y a une coexistence d'amphiboles et de magnétite du groupe 1, tandis que dans les quatre autres, les amphiboles et la magnétite coexistentes sont du groupe 2. Les exceptions sont rares. Les calculs géothermométriques et géobarométriques fondés sur les oxydes Fe-Ti et les silicates mafiques indiquent deux tracés différents responsables de la magnétite en termes de T – f(O₂) dans le complexe de Myoken-zan. Le premier s'est développé aux stades tardi-magmatiques à subsolidus, et a donné la magnétite 1 entre environ 750° et 650°C, à une fugacité d'oxygène magmatique supérieure aux conditions du tampon Ni-NiO. Le second tracé s'est développé au stade subsolidus, et a donné la magnétite 2 par réaction des silicates mafiques et d'une phase aqueuse exsolvée des magmas. La fugacité d'oxygène de la phase fluide a varié entre ceux des tampons Ni-NiO et FMQ, avec les températures allant en diminuant de 670° à 570°C.

Mots-clés: pluton granitique, oxydes Fe-Ti, conditions de cristallisation, tracé redox, Myoken-zan, Japon.

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INTRODUCTION

Granitoid rocks with magnetic susceptibilities greater than 2.7×10^{-3} SI units (or 100×10^{-6} emu/g) are called magnetite-series granitoids, and those having lower values are called ilmenite-series granitoids (Ishihara 1977). The two series tend to form paired terranes, as reported from many regions of the world (Ishihara 1979, Ishihara & Ulriksen 1980, Tainosho *et al.* 1988, Gastil *et al.* 1990).

Many investigators have considered that rocks of the two series of granitoid rocks differ in chemical composition, including isotopic composition, or in physical conditions during cooling of the magmas. It has commonly been accepted that magnetite-series granitoid rocks were formed under a higher fugacity of oxygen than ilmenite-series granitoid rocks (*e.g.*, Czamanske *et al.* 1981). Czamanske & Wones (1973) suggested that the oxygen fugacity of the Finnmåra magma was enhanced by a diffusive loss of H_2 during progressive crystallization of the magma. Haslam (1968) and Murakami (1969) suggested that oxidized granitoid rocks might result from magmas that reacted with oxygen-charged groundwater. Recent studies suggested that the relatively reduced state of magnetite-free rocks probably results from contamination of the original magmas with graphite contained in sedimentary rocks (Shimizu 1983, Ishihara *et al.* 1985, Ague & Brimhall 1987). However, the processes responsible for the division of granitoid rocks into the two series have not yet been clearly explained.

Ilmenite is present in most granitoid rocks, but magnetite is commonly lacking in the ilmenite-series granitoids. Thus, values of magnetic susceptibility are nearly proportional to the modal amount of magnetite (Ishihara 1977). Some ilmenite-series granitoids are found in terranes occupied by magnetite-series granitoid rocks, and some magnetite-series granitoids are found in terranes occupied by ilmenite-series granitoid rocks. The two series of granitoid rocks often occur together in composite bodies and may intrude a single formation. Such field occurrences suggest that progressive changes in the redox states of cooling magmas result from inherent properties of magmas.

Takagi (1992) discussed the origin of the magnetite-series Kayo granite, in the ilmenite-series terrane named the San'yo belt, and showed that magnetite crystallized during the latest magmatic to subsolidus stages of the magma. The Myoken-zan igneous complex, with which we will now be concerned, offers another example of a magnetite-series pluton in the San'yo belt. In this study, we present evidence of two kinds of equilibrium relationships between the mafic silicates and Fe-Ti oxides.

GEOLOGICAL SETTING

In southwestern Japan, paired magnetite-series and

ilmenite-series terranes composed of Cretaceous-Paleogene granitoid rocks are typically developed and juxtaposed in the north-south direction. The northern, San'in belt is predominantly composed of Paleogene granitoid rocks that belong to the magnetite series, whereas granitoid rocks in the southern, San'yo and Ryoke belts are mainly composed of Cretaceous granitoids belonging predominantly to the ilmenite series (Fig. 1; Ishihara 1979, 1990). Most of the granitoid rocks of the San'yo and Ryoke belts are comparable in petrographic characteristics with the I-type granitoids of Chappell & White (1974) (Takahashi *et al.* 1980).

The Myoken-zan complex is situated in a mountainous area to the northeast of Okayama, in the San'yo belt (Fig. 1). This complex is about 5.4 km across in a N-S direction and 2.8 km wide; its northern and southern borders are bounded by E-W faults (Fig. 1). Rhyolitic pyroclastic rocks are distributed to the east and southwest of the complex, and a granite mass, which probably differs in origin from the Myoken-zan complex (Shirakawa 1975), lies to the south; upper Paleozoic shale, gabbroic rocks and basic pyroclastic rocks lie to the west. Wide contact aureoles were developed on the eastern and western sides of the complex, and rocks of the pyroxene-hornfels facies have been reported (Asami & Nureki 1978).

A rock unit (tonalite-2) in the Myoken-zan complex yielded a K-Ar age of 75.7 ± 2.0 Ma (Shibata 1979), which is younger than the Rb-Sr ages of surrounding granitoid masses, dated at about 85 Ma (Kagami *et al.* 1988).

Values of magnetic susceptibility for the Myoken-zan complex were measured on outcrops with a KAPPA Meter KT-5 (Fig. 2). The magnetic susceptibility is generally greater than 3×10^{-3} SI units, which has been taken as a limiting value between magnetite-series and ilmenite-series granitoids (Ishihara 1977). The granitoid rocks central to the Myoken-zan complex tend to have higher values than rocks on the margins. In particular, a rock unit (quartz monzodiorite-1) that forms the summit of Mt. Myoken-zan has high values, above 30×10^{-3} SI unit. As shown in Figure 2, two contours of equivalent magnetic susceptibility (A and B) cross rock-unit boundaries. This suggests that the values of magnetic susceptibility in the Myoken-zan complex are independent of boundaries between the rock units.

PETROGRAPHY

Description of the Myoken-zan igneous complex

The Myoken-zan complex is a massif composed of five rock types: tonalite, quartz monzodiorite, quartz monzonite, granodiorite, and monzogranite, in terms of the IUGS nomenclature (Le Bas & Streckeisen 1991). All of these granitoids contain magnetite and

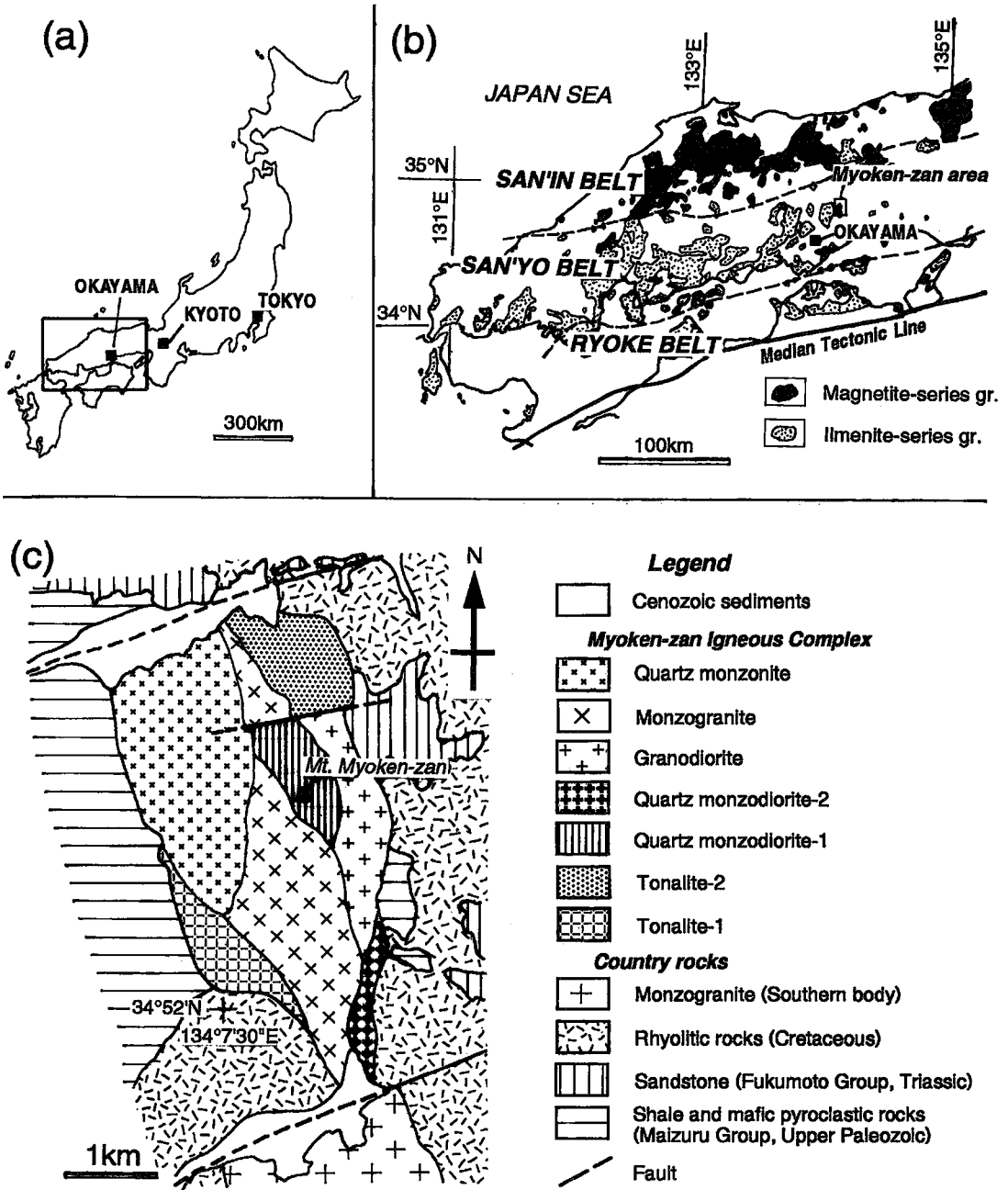


FIG. 1. Geological map of the Myoken-zan igneous complex. Geology outside the Myoken-zan complex is based on a map from Asami & Nureki (1978).

calcic amphiboles, which are grouped in two types or trends (as shown below in Figs. 5 and 6). One type of magnetite, or one trend of amphiboles, commonly characterizes one rock body. In particular, magnetite is

indicative of the grouping of the granitoids rocks.

We differentiate the two types of Myoken-zan magnetite by calling them "magnetite-1" and "magnetite-2". Magnetite-1 is characterized by thin

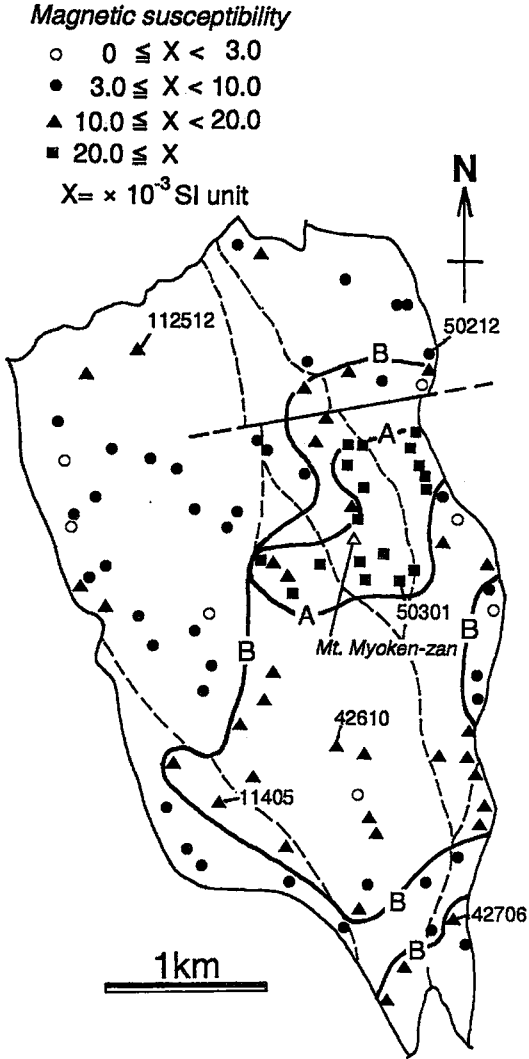


FIG. 2. Map showing values of magnetic susceptibility for the Myoken-zan complex, and sample localities for chemical analyses of minerals. Broken lines, rock-unit boundaries. Bold lines, contours for magnetic susceptibility values; A: >20 , and B: $>10 \times 10^{-3}$ SI unit.

(<1 μm) and short lamellae of ilmenite, which develop at regular intervals of 1 μm or less (Fig. 3a). Magnetite-2 contains two kinds of ilmenite lamellae; one type is 3 μm or more in thickness, occurs at intervals of 10 μm or more, and crosses another lamella at a high angle (Fig. 3b), whereas the other is commonly

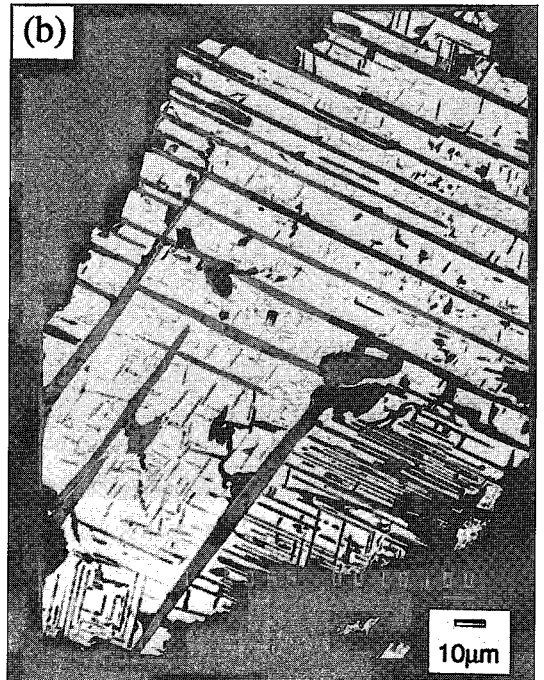


FIG. 3. Back-scattered electron images of magnetite-1 (a) and magnetite-2 (b). Both images are at the same scale.

thinner than 1 μm and develops at intervals of several μm or less. The thin lamellae are parallel to the thick lamellae (Fig. 3b). Thin sections or hand specimens of the Myoken-zan granitoid rocks contain either magnetite-1 or magnetite-2, and the two types of magnetite are very rarely mixed (seen in only a few hand specimens).

We call the tonalite that contains magnetite-1 "tonalite-1", and the tonalite that contains magnetite-2, "tonalite-2"; in the same manner, we divided quartz monzodiorite into "quartz monzodiorite-1" and "quartz monzodiorite-2". The monzogranite contains magnetite-1, and the quartz monzonite and granodiorite contain magnetite-2. Thus, the five rock types of the Myoken-zan complex were defined as seven rock units in association with magnetite-1 or -2 (Fig. 1). However, contacts between the different rock units have generally not been clearly observed. The three rock units accompanied by magnetite-1 are located in the central to southern part, and the four other units, accompanied by magnetite-2, are at the eastern and western margins of the Myoken-zan massif.

Tonalite-1, located at the southwest corner of the massif, is a two-pyroxene – hornblende – biotite tonalite; it is medium grained, equigranular and massive. Orthopyroxene and augite occur commonly as euhedral grains, 1–3 mm long, but are commonly largely altered to fine-grained actinolite and biotite. Green to pale green hornblende [$\text{Mg}^\# = \text{Mg}/(\text{Mg}+\text{Fe}+\text{Mn})$ between 0.55 and 0.50] occurs as anhedral to subhedral grains; its margins are typically altered to actinolitic hornblende or fibrous actinolite ($0.70 < \text{Mg}^\# < 0.55$). Biotite ($\text{Mg}^\#$ in the range 0.49–0.40) occurs as fine flakes and usually encloses hornblende. Plagioclase is normally zoned, from An_{74} to An_{23} . Ilmenite is commonly associated with two pyroxenes, amphiboles and biotite; magnetite is associated with amphiboles and biotite, but not with pyroxenes. Apatite and zircon occur as accessory minerals.

Tonalite-2, located at the northeastern corner of the massif, is a medium- to fine-grained, augite – hornblende – biotite tonalite. Augite commonly occurs as a relict mineral in hornblende. The hornblende ($0.56 < \text{Mg}^\# < 0.45$) locally shows zoning from a green core to a bluish green rim. Both the augite and hornblende are commonly altered in part to fibrous actinolite ($0.45 < \text{Mg}^\# < 0.25$). Plagioclase is normally zoned, from An_{79} to An_{17} . Ilmenite is associated with augite, hornblende, actinolite, and biotite; magnetite is commonly associated with actinolite, biotite ($0.41 < \text{Mg}^\# < 0.32$) and, locally, with hornblende, but not with augite. Apatite, zircon, and titanite are found as accessory minerals.

Quartz monzodiorite-1, located at the top of Mt. Myoken-zan, has a medium- to fine-grained, equigranular texture; locally, K-feldspar and quartz show a

micrographic texture. The mafic phases are orthopyroxene, augite, hornblende, and biotite. The pyroxenes are partly replaced by actinolitic hornblende ($\text{Mg}^\# = 0.65$), biotite ($0.62 < \text{Mg}^\# < 0.59$), and Fe–Ti oxides. Green to pale green hornblende ($0.67 < \text{Mg}^\# < 0.57$) occurs as tabular crystals, and biotite commonly forms aggregates and encloses hornblende. Plagioclase shows normal zoning, from An_{79} to An_{17} , and rarely includes small grains of augite and magnetite. Magnetite and ilmenite commonly occur in association with hornblende and biotite, but ilmenite is also associated with the pyroxenes. Apatite and zircon occur as accessory minerals.

Quartz monzodiorite-2, found at the southeastern corner of the massif, is medium grained and contains two pyroxenes, hornblende and biotite. Orthopyroxene occurs either as euhedral to subhedral grains or as very thin lamellae in augite. The pyroxenes may be partly replaced by fibrous actinolite ($0.59 < \text{Mg}^\# < 0.54$) or, rarely, cummingtonite ($\text{Mg}^\# = 0.42$). Hornblende ($0.59 < \text{Mg}^\# < 0.53$) is green to pale green and rarely includes brown tschermakitic hornblende ($\text{Mg}^\# = 0.64$) as a relic. Plagioclase is normally zoned, from An_{85} to An_{24} , and rarely includes small grains of augite and magnetite. Perthitic K-feldspar and quartz occur interstitially. Ilmenite is associated with all mafic silicates, but magnetite is associated only with biotite, actinolite, cummingtonite and, rarely, actinolitic hornblende.

The granodiorite, situated on the eastern border of the massif, is an equigranular, medium-grained rock containing clinopyroxene, hornblende and biotite; the former two minerals are commonly altered to actinolite, and generally, the rock is deeply weathered.

The monzogranite is elongated north–south in the center of the Myoken-zan complex. It is a medium-grained, and rather porphyritic, biotite–hornblende granite with rare clinopyroxene that is largely altered to green hornblende and actinolite. Hornblende ($0.65 < \text{Mg}^\# < 0.61$) occurs as subhedral grains or fibrous aggregates. Biotite ($0.55 < \text{Mg}^\# < 0.45$) occurs as subhedral flakes and occasionally shows "worm-eaten" forms. Plagioclase occurs as a phenocrystic mineral and shows normal zoning, from An_{38} to An_{18} ; K-feldspar and quartz occur interstitially. Magnetite and ilmenite are generally associated with hornblende and biotite. Apatite and zircon are accessory minerals.

Quartz monzonite, situated in the northwestern part of the massif, is a medium-grained massive rock that is slightly porphyritic in appearance; augite and hornblende are common, but biotite is rare. The augite contains thin exsolution-lamellae of orthopyroxene and commonly includes ilmenite but not magnetite. Hornblende ($0.56 < \text{Mg}^\# < 0.37$) is generally zoned from a dark green core to a colorless or bluish green rim. Plagioclase shows normal zoning, from An_{78} to An_{17} , and rarely includes small grains of augite and magnetite. K-feldspar and quartz form a micrographic texture. Magnetite and ilmenite commonly occur in

TABLE 1. WHOLE-ROCK CHEMISTRY OF REPRESENTATIVE SAMPLES OF THE MYOKEN-ZAN COMPLEX

Rock type	TO1	QMD1	MG	TO2	QMD2	GRD	QMZ
No. *	2	2	4	2	1	1	3
SiO ₂ (wt%)	61.02	63.16	67.28	58.25	61.60	62.06	66.24
TiO ₂	0.76	0.75	0.54	0.95	0.80	0.85	0.57
Al ₂ O ₃	16.60	16.17	14.52	16.77	15.55	15.86	15.38
Fe ₂ O ₃	0.86	1.28	1.01	1.29	0.71	1.34	0.54
FeO	5.14	3.92	3.59	5.93	5.33	4.87	3.78
MnO	0.10	0.10	0.10	0.14	0.08	0.12	0.09
MgO	3.06	1.71	1.80	3.15	3.15	2.04	1.56
CaO	6.33	5.39	3.83	7.30	6.08	5.71	4.35
Na ₂ O	3.08	3.43	3.20	3.04	2.92	3.14	3.19
K ₂ O	1.96	2.33	3.07	1.39	2.18	2.11	2.80
F ₂ O	0.16	0.18	0.12	0.20	0.16	0.21	0.12
H ₂ O	1.31	0.89	1.03	1.51	1.39	1.53	1.62
H ₂ O ⁺	0.20	0.20	0.18	0.25	0.20	0.24	0.21
Total	100.53	99.49	100.25	99.76	100.15	100.08	100.45
Fe#	0.87	0.77	0.80	0.83	0.89	0.80	0.89

*: Number of analyses. Fe#; Fe²⁺/(Fe²⁺+Fe³⁺) (mol.). Abbreviations: TO1 tonalite-1; QMD1 quartz monzodiorite-1; MG monzogranite; TO2 tonalite-2; QMD2 quartz monzodiorite-2; GRD granodiorite; QMZ quartz monzonite.

Analyzed with X-ray fluorescence (JEOL JSX-60S7 at Shimane University; Kobayashi *et al.* 1981). Ferrous iron contents were determined by the Wilson method (Jeffery and Hutchison 1981), which was improved in part by Uchida *et al.* (1986).

association with chlorite and colorless amphibole (0.45 < Mg# < 0.30). Titanite, apatite, and zircon occur as accessory minerals.

Whole-rock chemistry

Whole-rock compositions of fifteen rock samples from the Myoken-zan complex are reported in Table 1. The Myoken-zan complex compares favor-

ably with the I-type granitoid rocks of Chappell & White (1974).

The SiO₂ content of Myoken-zan granitoids varies from 58 (tonalite-2) to 67 wt.% (monzogranite). Comparing the whole-rock compositions of the Myoken-zan granitoids with the average compositions of Japanese granitoids (Aramaki *et al.* 1972), the former are richer in FeO and CaO by 1.1 and 0.7 wt.% on average, but poorer in Al₂O₃ and Fe₂O₃ by 0.9 and 0.7 wt.% on average, respectively. The CaO contents of the Myoken-zan granitoids probably reflect the higher modal proportion of plagioclase, which varies from 40 in granodiorite to 55 in tonalite-2. The plagioclase in the Myoken-zan granitoids commonly has an unusually calcic core, except in the monzogranite.

The Fe²⁺/(Fe³⁺+Fe²⁺) ratio in the Myoken-zan granitoids is in the range 0.87–0.77 for rocks with magnetite-1, and 0.89–0.80 for rocks with magnetite-2 (Table 1). These values are equivalent to those in the range 0.90–0.82 for the Ukan granodiorite, which is an ilmenite-series granitoid in the San'yo belt (Takagi 1992).

MINERAL CHEMISTRY

Pyroxenes, amphiboles, biotite, and Fe–Ti oxides, and plagioclase in the Myoken-zan granitoids have been analyzed for major elements with an electron microprobe (JEOL JXA-733 at Okayama University),

TABLE 2. CHEMISTRY OF PYROXENES, MYOKEN-ZAN COMPLEX

Rock type	TO1		QMD1		QMD1		TO2		QMD2		QMD2		QMZ
Sample No.	11405		50301		50301		112512		42706		42706		112512
Mineral	OPX	CPX	OPX—CPX		OPX—CPX		CPX	OPX—CPX		OPX—CPX		CPX	
SiO ₂ (wt%)	51.8	50.5	50.9	51.8	50.8	50.5	52.5	50.5	52.5	51.9	51.8	51.4	
TiO ₂	0.29	0.54	0.28	0.27	0.24	0.35	0.30	0.18	0.08	0.24	0.34	0.50	
Al ₂ O ₃	0.73	1.44	0.56	0.88	0.71	1.60	0.78	0.44	0.28	0.73	1.01	1.50	
FeO*	24.9	12.6	28.6	13.8	29.2	13.3	13.8	28.4	13.1	22.4	9.34	12.7	
MnO	0.64	0.31	1.01	0.47	0.85	0.39	0.42	0.71	0.38	0.43	0.22	0.35	
MgO	19.7	13.2	16.0	11.7	15.8	11.2	10.7	17.1	11.8	22.1	14.6	12.5	
CaO	1.60	21.1	1.62	20.6	1.43	20.8	20.9	1.30	21.7	1.24	21.7	20.8	
Na ₂ O	n.d.	0.23	n.d.	0.38	0.01	0.39	0.22	0.01	0.31	n.d.	0.22	0.24	
K ₂ O	0.03	n.d.	0.02	0.01	0.03	0.02	0.05	0.01	0.02	n.d.	0.01	0.01	
Total	98.69	99.92	98.91	99.91	99.07	98.55	99.67	98.65	100.17	99.04	99.24	100.00	
Cations normalized to 6 oxygens													
Si	1.970	1.922	1.988	1.975	1.986	1.953	2.002	1.976	1.993	1.961	1.953	1.948	
Ti	0.008	0.015	0.008	0.008	0.007	0.010	0.009	0.005	0.002	0.007	0.010	0.014	
Al	0.033	0.065	0.026	0.040	0.033	0.073	0.035	0.020	0.013	0.033	0.045	0.067	
Fe	0.792	0.401	0.934	0.440	0.955	0.430	0.440	0.930	0.416	0.708	0.295	0.403	
Mn	0.021	0.010	0.033	0.015	0.028	0.013	0.014	0.024	0.012	0.014	0.007	0.011	
Mg	1.117	0.749	0.932	0.665	0.921	0.646	0.608	0.998	0.668	1.245	0.821	0.766	
Ca	0.065	0.860	0.068	0.841	0.060	0.862	0.854	0.055	0.883	0.050	0.877	0.845	
Na	—	0.017	—	0.028	0.001	0.029	0.016	0.001	0.023	—	0.016	0.018	
K	0.001	—	0.001	0.000	0.001	0.001	0.002	0.000	0.001	—	0.000	0.000	
Total	4.006	4.039	3.991	4.012	3.992	4.016	3.981	4.009	4.010	4.016	4.023	4.013	
Mg#	0.58	0.65	0.49	0.59	0.48	0.59	0.57	0.51	0.61	0.63	0.73	0.63	
Eq. T(°C)	1062				1051				1067				1151

*: Fe as totally FeO. — : coexisting pairs. Mg# : Mg/(Fe+Mg+Mn).

Eq.T equilibration temperatures from the Wood & Banno geothermometer (1973);

OPX orthopyroxene; CPX clinopyroxene; n.d. not detected. Abbreviations of rock types as in Table 1.

using an accelerating voltage of 15 kV and a sample current of 2×10^{-8} A. The mafic silicates of the granodiorite were not analyzed because they are extensively altered. The data were reduced by the method of Bence & Albee (1968), with alpha-factors of Nakamura & Kushiro (1970).

Pyroxenes

Orthopyroxene was analyzed in quartz monzodiorite-1 and -2 and tonalite-1, whereas clinopyroxene was analyzed in all rock units except the monzogranite (Table 2, Fig. 4). Orthopyroxene from the Myoken-zan granitoids is mostly enstatite and generally zoned with increasing Fs-content from core to rim. The difference in Fs-content within grains of orthopyroxene is largest in quartz monzodiorite-1 ($En_{71}Fs_{26}Wo_3$ to $En_{47}Fs_{50}Wo_3$) and smallest in tonalite-1 ($En_{63}Fs_{34}Wo_3$ to $En_{49}Fs_{48}Wo_3$). The clinopyroxene is predominantly augite; the grains are homogeneous. The Al and Na contents are relatively low, 0.07–0.01 and 0.03–0.02 atoms per formula unit (apfu) respectively, compared to those in common augite (Table 2). Herzberg (1978) suggested that clinopyroxene with low Al and Na contents possibly crystallized under low-pressure conditions.

The ferrous iron – magnesium distribution coefficient K_D (Kretz 1963) for the two pyroxenes is 0.67 on average (Table 2); pyroxenes in tonalite-1 give the

highest value, 0.74, which is very close to the value proposed by Kretz (1963), 0.73, as being typical of an igneous differentiation series (Skaergaard intrusion). Figure 4 also suggests equilibrium relations among the pairs of pyroxenes.

Amphiboles

Amphiboles are the most common mafic silicate of the Myoken-zan granitoids. Chemical compositions of the calcic amphiboles are shown and projected on Leake's diagram (Leake 1978) (Table 3, Fig. 5), except for those from the granodiorite. The Si contents of the calcic amphiboles increase systematically from green hornblende (6.8–7.2 apfu) to colorless amphibole (>7.5 apfu). Calcic amphibole grains from tonalite-2 and the quartz monzonite are zoned from a ferro-hornblende core to a ferro-actinolite rim; rarely, a cummingtonite zone occurs between the zones. Calcic amphibole grains from tonalite-1, quartz monzodiorite-1 and -2 also may be zoned, with a composition ranging from a magnesio-hornblende core to an actinolite rim. Brown tschermakitic hornblende is found only as a xenocryst in magnesio-hornblende cores from quartz monzodiorite-2. Actinolite occurs as aggregates commonly enclosing hornblende and pyroxenes. An outermost rim of hornblende is invariably green close to plagioclase, but colorless or bluish green close to quartz or K-feldspar.

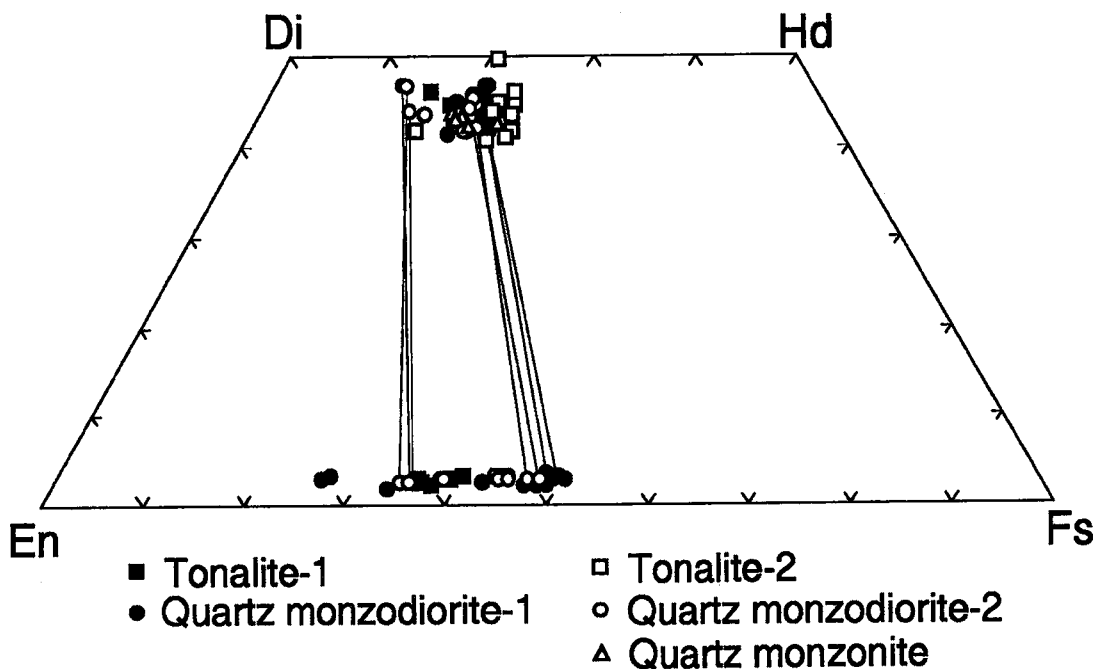


FIG. 4. Compositional ranges of Ca-rich and Ca-poor pyroxenes from the Myoken-zan igneous complex.

TABLE 3. CHEMISTRY OF AMPHIBOLE, MYOKEN-ZAN COMPLEX

Rock type	TO1		QMD1		MG		QMD2		TO2		QMZ
Sample No.	11405		50301		42610		42706		50301		112512
Mineral	Hbl — Hbl#		Hbl — Hbl#		Hbl — Hbl#		Hbl — Hbl#		Hbl — Hbl#		Act
SiO ₂ (wt%)	45.9	46.1	46.1	47.0	49.4	51.2	46.6	47.4	45.9	48.8	47.8
TiO ₂	1.49	1.40	1.66	1.58	1.10	0.78	1.35	1.17	1.09	0.05	0.03
Al ₂ O ₃	6.14	6.09	6.25	6.20	4.26	3.20	6.08	5.54	6.06	4.50	2.66
FeO*	17.5	17.2	15.3	14.5	14.6	14.0	15.4	16.9	20.8	24.2	32.9
MnO	0.24	0.26	0.29	0.25	0.43	0.44	0.20	0.34	0.41	0.63	1.63
MgO	11.8	12.0	13.1	13.7	14.0	15.3	13.1	12.7	9.76	7.03	2.53
CaO	11.1	11.0	11.1	11.3	10.9	11.0	11.3	10.7	10.7	11.8	10.2
Na ₂ O	1.53	1.44	1.71	1.70	1.25	1.00	1.48	1.46	1.40	0.21	0.46
K ₂ O	0.61	0.55	1.02	0.93	0.44	0.35	0.90	0.65	0.76	0.16	0.19
Total	96.31	96.04	96.53	97.16	96.38	97.27	96.41	96.86	96.88	97.38	98.40
Cations normalized to 23 oxygens											
Si	6.987	7.017	6.952	6.999	7.349	7.496	7.020	7.125	7.050	7.491	7.608
Ti	0.171	0.160	0.188	0.177	0.123	0.086	0.153	0.132	0.126	0.006	0.004
Al	1.102	1.093	1.111	1.088	0.747	0.552	1.080	0.982	1.097	0.814	0.499
Fe	2.228	2.190	1.930	1.806	1.816	1.714	1.940	2.125	2.672	3.107	4.379
Mn	0.031	0.034	0.037	0.032	0.054	0.055	0.026	0.043	0.053	0.082	0.220
Mg	2.678	2.723	2.945	3.041	3.105	3.339	2.942	2.846	2.235	1.609	0.600
Ca	1.810	1.794	1.793	1.803	1.737	1.725	1.824	1.723	1.761	1.941	1.739
Na	0.452	0.425	0.500	0.491	0.361	0.284	0.432	0.426	0.417	0.063	0.142
K	0.118	0.107	0.196	0.177	0.084	0.065	0.173	0.125	0.149	0.031	0.039
Total	15.576	15.542	15.652	15.614	15.376	15.317	15.590	15.527	15.559	15.143	15.229
Mg#	0.542	0.551	0.600	0.623	0.624	0.654	0.599	0.568	0.451	0.335	0.115
Pl (An%)	38.7		20.9		21.3		24.1		17.3		
Eq. T (°C)	723		687		571		660		564		

* : Fe as totally FeO. — : Single grain

Abbreviations: Hbl hornblende (core); Hbl# hornblende (outermost rim); Act actinolite; Mg#

Mg/(Fe+Mg+Mn); Pl (An%) anorthite contents of coexisting plagioclase; Eq. T equilibration temperature from the Blundy and Holland geothermometer (1990) at 2kbar. Abbreviations of rock types as in Table 1.

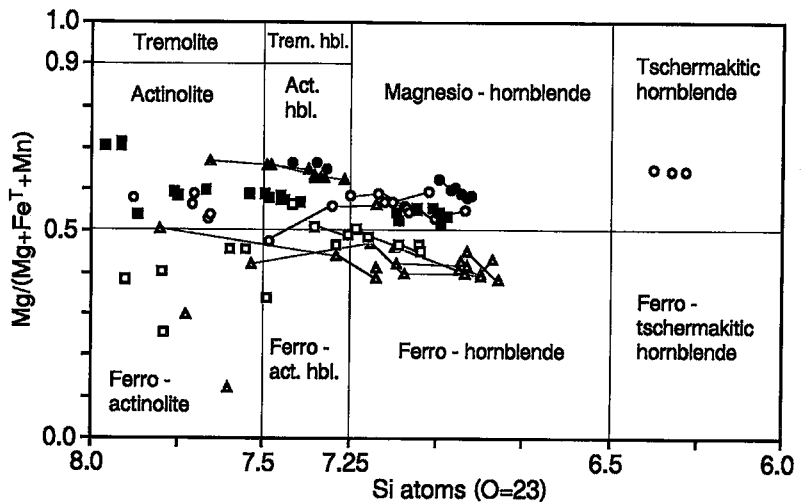


Fig. 5. Amphibole compositions plotted on Leake's diagram (Leake 1978). Tie lines connect core and rim of individual grains, with the composition of the rim invariably plotting to the left of that of the core.

Amphiboles-1

● Quartz monzodiorite-1

■ Tonalite-1

▲ Monzogranite

Amphiboles-2

○ Quartz monzodiorite-2

□ Tonalite-2

▲ Quartz monzonite

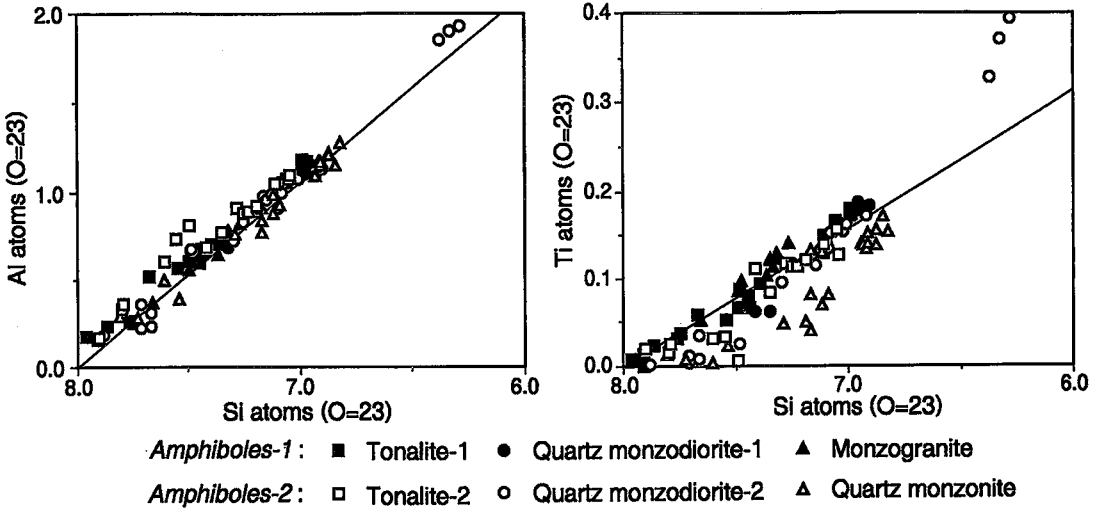


Fig. 6. Al-Si and Ti-Si diagrams for amphiboles in the Myoken-zan suite.

In Figure 5, two compositional trends for the calcic amphiboles can be recognized: (1) Mg[#] in calcic amphiboles from tonalite-1, quartz monzodiorite-1, and monzogranite increases with increasing Si content, and (2) Mg[#] in calcic amphiboles from tonalite-2, quartz monzodiorite-2, and quartz monzonite remains unchanged or decreases with increasing Si contents. We refer to the former as trend-1 amphiboles (= amphiboles-1) and the latter as trend-2 amphiboles (= amphiboles-2). Each rock unit is characterized by a distinct trend. Thus, amphiboles-1 are usually accompanied by magnetite-1, and amphiboles-2, usually by magnetite-2. Amphiboles-1 tend to be richer in Mg content than amphiboles-2; however, amphiboles-2 in quartz monzodiorite-2 are exceptionally rich in Mg content compared to common amphiboles-2 (Fig. 5). The Al^T and Ti contents of amphiboles-1 decrease systematically with increasing Si contents, but the correlation of Ti and Si is much poorer in amphiboles-2 than in amphiboles-1 (Fig. 6).

Biotite

Biotite is common in all Myoken-zan granitoids, except in the quartz monzonite. In general, Mg[#] in biotite associated with amphiboles-1 increases with increasing Si content (Table 4, Fig. 7). In contrast, Mg[#] in biotite associated with amphiboles-2 remains nearly constant as Si content increases, and is generally lower than biotite associated with amphiboles-1, with some exceptions for quartz monzodiorite-2. For some biotite flakes in quartz monzodiorite-2, however, Mg[#] increases with increasing Si content, just as for biotite associated with amphiboles-1. Thus, quartz

monzodiorite-2 contains two populations of biotite: one may be similar in origin to biotite associated with amphiboles-1, but the other seems to be distinct.

Fe-Ti oxides

Representative compositions of magnetite and ilmenite, recalculated according to Stormer (1983), are presented in Table 5. Ilmenite occurs commonly as discrete inclusions in all mafic silicates, and locally occurs as composite grains with magnetite in biotite, amphibole, and chlorite.

TABLE 4. CHEMISTRY OF BIOTITE, MYOKEN-ZAN COMPLEX

Rock type	TO1		QMD1		MG	TO2		QMD2	
Sample No.	11405		50301		42610	50212		42706	
Mineral	Bt	Bt	Bt	Bt	Bt	Bt	Bt	Bt	Bt
SiO ₂ (wt%)	36.3	36.1	38.3	39.0	36.9	35.8	35.6	37.7	36.4
TiO ₂	4.79	4.83	4.34	3.84	5.11	4.23	4.70	3.46	5.14
Al ₂ O ₃	12.8	12.8	11.9	11.7	13.0	12.6	12.6	11.4	12.5
FeO*	23.0	23.6	17.3	16.3	19.0	24.9	24.3	24.3	21.2
MnO	0.28	0.27	0.11	0.07	0.21	0.14	0.28	0.13	0.14
MgO	9.35	8.79	14.1	15.5	12.4	7.94	8.35	9.71	10.7
CaO	0.04	0.11	0.01	0.07	0.01	0.21	0.12	0.02	0.02
Na ₂ O	0.11	0.08	0.18	0.14	0.20	0.06	0.09	0.04	0.11
K ₂ O	9.17	9.01	9.05	9.05	8.92	8.98	9.09	9.03	8.80
Total	95.84	95.59	95.29	95.67	95.75	94.86	95.13	95.79	95.01
Cations normalized to 22 oxygens									
Si	5.630	5.628	5.783	5.827	5.602	5.665	5.612	5.862	5.633
Ti	0.559	0.556	0.493	0.431	0.583	0.503	0.557	0.405	0.598
Al	2.340	2.352	2.118	2.060	2.326	2.350	2.341	2.089	2.280
Fe	2.983	3.077	2.185	2.037	2.412	3.295	3.203	3.160	2.744
Mn	0.037	0.036	0.014	0.009	0.027	0.019	0.037	0.017	0.018
Mg	2.162	2.043	3.174	3.453	2.806	1.873	1.962	2.251	2.468
Ca	0.007	0.018	0.002	0.011	0.002	0.036	0.020	0.003	0.003
K	0.033	0.024	0.053	0.041	0.059	0.018	0.028	0.012	0.033
Na	1.814	1.792	1.743	1.725	1.727	1.813	1.828	1.791	1.737
Total	15.565	15.537	15.563	15.594	15.545	15.372	15.588	15.590	15.514
Mg [#]	0.417	0.396	0.591	0.628	0.535	0.361	0.377	0.415	0.472

*: Fe as totally FeO. Bt Biotite; Mg[#] Mg/(Mg+Fe+Mn). Abbreviations of rock types as in Table 1.

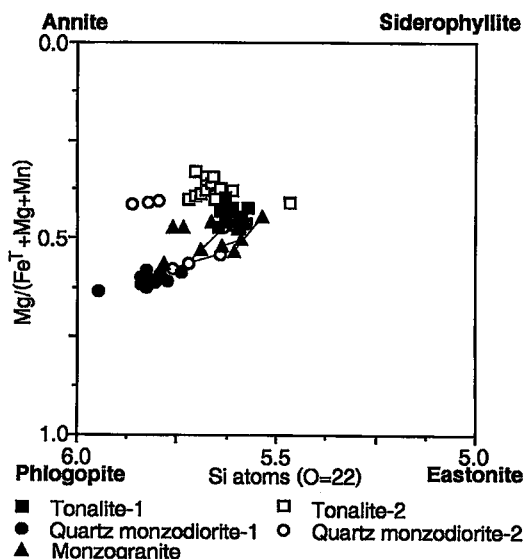


Fig. 7. $Mg/(Fe^T+Mg+Mn)$ -Si diagram for biotite in the Myoken-zan suite.

TABLE 5. CHEMISTRY OF MAGNETITE AND ILMENITE, MYOKEN-ZAN COMPLEX

Rock type	QMD1		TO1		QMD2		TO2	
Sample No.	50301		11405		42706		50212	
Mineral	mt1	ilm	mt1	ilm	mt2	ilm	mt2	ilm
SiO ₂ (wt%)	0.11	0.02	0.09	0.18	0.14	0.04	0.15	0.06
TiO ₂	6.47	48.6	6.39	48.2	1.11	49.7	0.68	49.7
Al ₂ O ₃	0.80	0.02	0.92	n.d.	0.37	0.01	0.24	n.d.
Cr ₂ O ₃	0.07	0.06	0.31	0.39	0.58	0.10	0.12	0.04
Fe ₂ O ₃	55.2	8.19	53.8	7.32	65.7	6.61	65.8	6.00
FeO	36.9	41.5	36.1	39.9	32.4	42.9	30.7	41.1
MnO	0.32	1.97	0.57	3.40	0.04	1.48	0.47	3.50
MgO	0.02	0.14	0.05	0.08	0.01	0.21	0.10	0.06
CaO	0.01	0.01	n.d.	n.d.	n.d.	0.01	n.d.	0.03
Total	99.90	100.51	98.23	99.47	100.35	101.06	98.26	100.49
Cations*								
Si	0.034	0.001	0.028	0.009	0.043	0.002	0.047	0.003
Ti	1.484	1.841	1.489	1.844	0.255	1.871	0.160	1.882
Al	0.288	0.001	0.336	-	0.133	0.001	0.088	-
Cr	0.017	0.002	0.076	0.016	0.140	0.004	0.030	0.002
Fe ³⁺	12.668	0.311	12.546	0.280	15.126	0.249	15.476	0.227
Fe ²⁺	9.411	1.749	9.356	1.697	8.290	1.796	8.025	1.731
Mn	0.083	0.084	0.150	0.146	0.010	0.063	0.124	0.149
Mg	0.009	0.011	0.023	0.006	0.005	0.016	0.047	0.005
Ca	0.003	0.001	-	-	-	0.001	-	0.002
Total	23.996	4.000	24.004	3.999	24.002	4.001	23.996	4.000
X _{mp}	0.192	-	0.194	-	0.033	-	0.020	-
X _{im}	-	0.920	-	0.927	-	0.936	-	0.941

*: Cations normalized to 32 atoms of oxygen for magnetite and 6 atoms of oxygen for ilmenite. X_{mp} and X_{im} calculated using the method of Stormer (1983). - : coexisting pairs. Abbreviations: mt1 magnetite-1; mt2 magnetite-2; ilm ilmenite; usp ulvöspinel; n.d. not detected. Abbreviations of rock types as in Table 1.

Magnetite-1 was analyzed with a wide beam (10 μ m in diameter) because of the fine intergrowth of ilmenite lamellae and magnetite. The compositions are believed to approach those of the unexsolved, primary magnetite-1. The magnetite host in magnetite-2 can generally be analyzed with a narrow microprobe beam to approach its last re-equilibrated compositions, but ilmenite lamellae of magnetite-2 are commonly altered. The ulvöspinel content of magnetite-1 varies from 10.8 to 24.0 mol.%, and that of magnetite-2 varies from 0.7 to 11.3 mol.%.

Ilmenite in the Myoken-zan granitoids is usually lacking in exsolution lamellae and chemically homogeneous. Hematite contents in ilmenite occurring as composite grains with magnetite-1 are generally higher than those in ilmenite occurring as composite grains with magnetite-2, averaging 8.7 and 6.5 mol.%, respectively. The pyrophanite (MnTiO₃) content in ilmenite in the Myoken-zan granitoids varies from 0.1 to 9.1 mol.%, equivalent to that in magnetite-series granitoid rocks (0.3-9.8 mol.%) in the San'in belt (*cf.* Tainosho 1982). The pyrophanite content of ilmenite included in biotite is generally higher than that of ilmenite included in the pyroxenes. These chemical characteristics are comparable to those reported for the ilmenite-series Ukan complex (Takagi 1992).

Plots of Mn/Fe (molar ratio) of ilmenite inclusions versus that in the host biotite and amphiboles-1 (Fig. 8) yield linear regressions, which give $K_{ilm-bi} = 9.53$ ($r = 0.84$) and $K_{ilm-amp} = 2.98$ ($r = 0.83$).

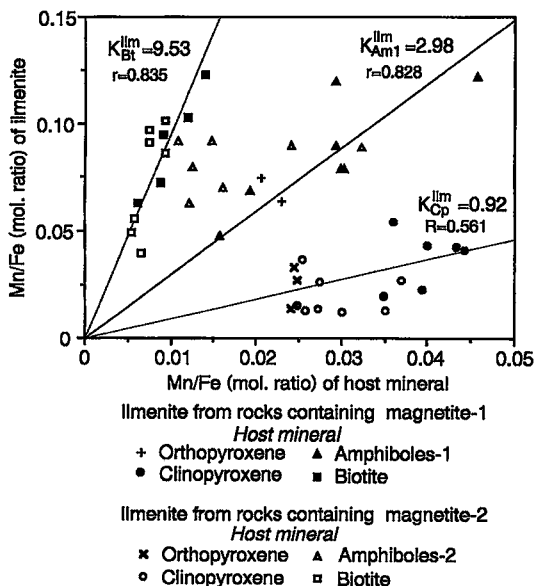


Fig. 8. Mn/Fe molar ratio of ilmenite and coexisting mafic silicates.

However, most of the plots for amphiboles-2 are not correlated in the case of the regression line $K_{ilm-amp}$. Similar plots of Mn/Fe in ilmenite *versus* that in the host clinopyroxene tend to show a linear regression with a lower correlation-coefficient ($r = 0.56$). Orthopyroxene and amphiboles-2 of the Myoken-zan granitoids show no correlations with ilmenite composition.

Plagioclase

Plagioclase from the Myoken-zan granitoids is generally characterized by normal zoning, with a wider range of An% than that of zoned plagioclase in common rocks of the same category. Shirakawa (1975) found that the zoning of plagioclase in these rocks is not gradual, but abrupt. The core of plagioclase is commonly characterized by oscillatory zoning with small compositional differences, less than 20% An, and forms 60 to 70% of a grain's volume. Marginal parts of plagioclase grains show normal zoning, but the An content of the marginal zones drops abruptly by 20 to 30% from the amount in the outermost core.

Referring to a diagram of Burri *et al.* (1967), Shirakawa (1975) noticed as a result of optical measurements that the plagioclase in the monzogranite, porphyritic adamellite in her terminology, belongs to a low-temperature type at the core but to a high-temperature type at the rim of a grain.

GEOTHERMOMETRY AND GEOBAROMETRY

Temperature of crystallization of pyroxene pairs and ilmenite-pyroxene pairs

The equilibration temperatures of pyroxene pairs from quartz monzodiorite-1 and -2 were calculated on the basis of the geothermometry of Wood & Banno (1973). The temperatures calculated for quartz monzodiorite-1 and -2 are very close, 1051°–1062°C and 1067°–1151°C, respectively (Table 2); the temperature of crystallization is the same for the two rock units, considering the analytical uncertainty.

Equilibration temperatures of ilmenite-pyroxene pairs from the Myoken-zan complex also were calculated by means of the geothermometer proposed by Bishop (1980). The temperatures calculated for the ilmenite-orthopyroxene pairs generally range from 300 to 600°C, too low if one proposes that the two minerals crystallized together. It seems probable that no ilmenite-orthopyroxene pairs crystallized together from magma, as suggested in Figure 8. Temperatures calculated for some ilmenite-clinopyroxene pairs in the quartz monzonite are in a range of 964°–1043°C, sufficiently high to consider a magmatic origin of these pairs. However, many ilmenite-clinopyroxene pairs yield very low temperatures, ranging from 255° to 843°C. These results suggest that ilmenite in the

Myoken-zan granitoids did not invariably crystallize in equilibrium with clinopyroxene.

Temperature of crystallization of hornblende-plagioclase pairs

Equilibration temperatures of hornblende-plagioclase pairs from the Myoken-zan complex (Table 3) were calculated with the method proposed by Blundy & Holland (1990). The total pressure was deduced to be around 2 kbar on the basis of thickness of roof rocks atop the Myoken-zan complex. We are concerned only with temperatures of equilibration for rims, but not for cores, of composite grains of hornblende and plagioclase, because we cannot decide which composition of plagioclase crystallized in equilibrium with which hornblende in the magma.

The hornblende-plagioclase pairs yield temperatures in the range 539°–723°C; a pair from tonalite-1 gives the highest temperature. The calculated temperatures vary by less than 50°C within a thin section. According to Blundy & Holland (1990), the thermometer should yield temperatures of equilibration with uncertainties of about $\pm 75^\circ\text{C}$ for rocks equilibrated at temperatures in the range 500°–1100°C.

Temperature of crystallization of magnetite-ilmenite pairs

There are problems in estimating the primary composition of magnetite in granitoid rocks, because magnetite generally has re-equilibrated during subsolidus processes (Buddington & Lindsley 1964, Wones 1989). However, we have presented a reasonable argument that our magnetite-1 approaches primary compositions. The primary compositions of magnetite-2 are difficult to determine directly but may possibly be inferred.

Temperatures of equilibration of composite magnetite-ilmenite pairs were estimated using the $\Delta\log(\text{O}_2)$ (FMQ) – temperature diagram proposed by Andersen & Lindsley (1988). In Figure 9, plots of magnetite-1 + ilmenite pairs are sharply separated from those of magnetite-2 + ilmenite pairs. The former indicate a temperature range of 650°–750°C, and the latter indicate a temperature range of 510°–630°C. These temperature ranges seem to be consistent with those calculated for hornblende-plagioclase pairs (Table 3).

Oxygen fugacities suggested by the Fe-Ti oxides

In Figure 9, magnetite-1 + ilmenite pairs lie above the Ni-NiO buffer curve at temperatures between 650° and 750°C. Indicated oxygen fugacities are 10^{-17} – 10^{-14} atm, about 1 to 2 log units above the FMQ buffer. These oxygen fugacities for magnetite-1 + ilmenite pairs are near those estimated for

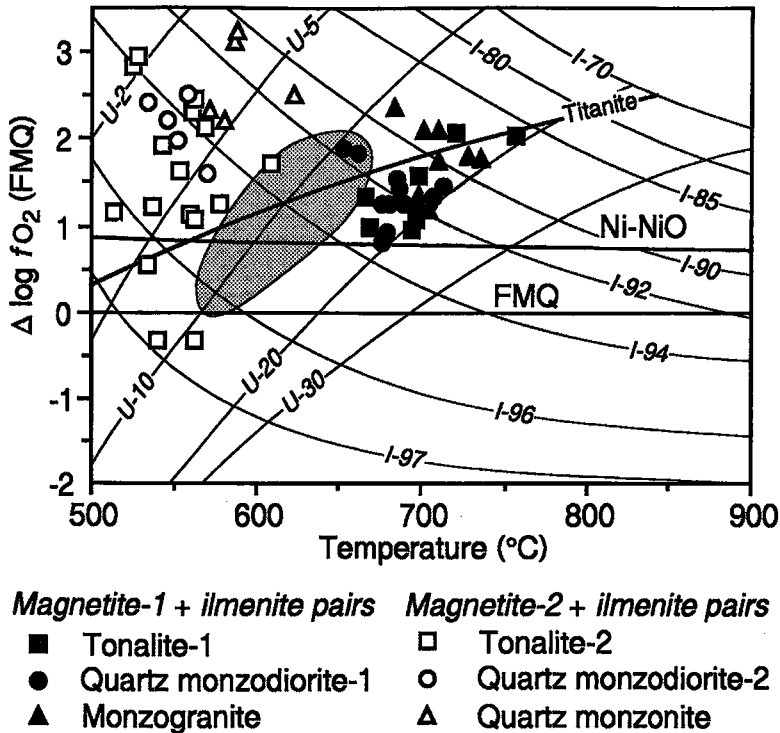
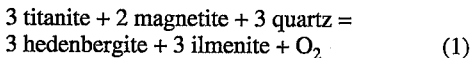


Fig. 9. Diagram showing $\Delta \log f(\text{O}_2)$ – temperature (Andersen & Lindsley 1988) for the Myoken-zan Fe–Ti oxides. Dotted area: distribution of plots for primary magnetite-2 – ilmenite pairs (proposed).

magnetite–ilmenite pairs in magnetite-series granitoids from the San’in belt (*i.e.*, Czamanske *et al.* 1981).

The majority of magnetite-2 + ilmenite pairs also lie above the Ni–NiO buffer curve, but two points are well below the FMQ buffer curve. Indicated oxygen fugacities for magnetite-2 + ilmenite pairs are 10^{-21} – 10^{-17} atm, about 0.5 to 3 log units above the FMQ buffer at temperatures of 510°–630°C.

The heavy line labeled “Titanite” in Figure 9 is an equilibrium-reaction curve defined by Wones (1989, Fig. 1) for an activity of hedenbergite equal to 0.3, based on the following equation:



According to reaction (1), increasing oxygen fugacity will drive the reaction to the left, consuming hedenbergite and ilmenite (Wones 1989). The more magnesian the pyroxene (or amphibole) occurring in a rock, the more oxidized was the magma (Wones 1989). The value of Fe/(Mg+Fe) in clinopyroxene and amphibole of the Myoken-zan granitoids varies from 0.20 to 0.45 and 0.30 to 0.67, respectively (Figs. 4, 5).

A large number of magnetite-1 + ilmenite pairs plot

on the titanite-unstable [lower $f(\text{O}_2)$] side of the “Titanite” curve, whereas a large number of magnetite-2 + ilmenite pairs plot on the titanite-stable [higher $f(\text{O}_2)$] side of the curve. However, titanite appears only in the quartz monzonite and tonalite-2, in association with magnetite-2: no titanite has been found in the other units of the complex.

DISCUSSION

Temperatures at which ilmenite crystallized

Geothermometry for the ilmenite–clinopyroxene pairs yields temperatures of 964°–1043°C; these are quite consistent with the results of two-pyroxene geothermometry, which yields 1067°–1151°C. Considering also the Mn/Fe correlations discussed previously (Fig. 8), we suggest that the ilmenite probably began to crystallize with clinopyroxene and continued crystallizing together with amphibole and biotite.

Discrete grains of ilmenite are commonly fresh in appearance under the microscope, but in rare cases the ilmenite from the quartz monzonite is entirely replaced by titanite. A similar replacement of ilmenite

from Finnmarka was explained by an increase in oxygen fugacity at the subsolidus stage (Czamaszka & Mihálik 1972). The scarcity of biotite in the quartz monzonite of the Myoken-zan complex may be an indication of its decomposition under relatively increased oxygen fugacities at subsolidus temperatures.

Constraints on the crystallization of magnetite-ilmenite pairs

Bacon & Hirschmann (1988) found that for 213 pairs of homogeneous oxide minerals from fresh volcanic rocks, a regression line, $\log(\text{Mg}/\text{Mn})_{\text{mt}} = 0.9317 \log(\text{Mg}/\text{Mn})_{\text{ilm}} - 0.0909$ ($r = 0.990$) represents equilibrium crystallization of the two oxides. They noted that this test may not be applicable to oxides in metamorphic and plutonic rocks, which have commonly exsolved at subsolidus temperatures.

Data for 26 magnetite-1 + ilmenite pairs from the Myoken-zan complex are plotted in Figure 10a. Our data tend to deviate from the equilibrium line of Bacon & Hirschmann (1988) and yield a new regression line, $\log(\text{Mg}/\text{Mn})_{\text{mt}} = 0.8317 \log(\text{Mg}/\text{Mn})_{\text{ilm}} + 0.1838$, for which $r = 0.893$. Although the slope and intercept of the new regression line differ slightly from those given by Bacon & Hirschmann (1988), we interpret the new regression line as suggesting equilibrium crystallization of the magnetite-1 + ilmenite pairs.

Figure 10b suggests that magnetite-2 is not in equilibrium with the ilmenite. We must infer the primary compositions of magnetite-2 in order to discuss the

origin of magnetite-2 + ilmenite pairs. On the basis of the mean modal content of ilmenite lamellae in magnetite-2 grains (4.5–20.7 vol.%), and inferring the compositions of these lamellae to be the same as those of the composite grains of ilmenite, the ulvöspinel contents in primary magnetite-2 were probably 6 mol.% richer on average than the analyzed contents (2–11.3 mol.%, Fig. 9). Thus we infer that the ulvöspinel content of primary, homogeneous magnetite-2 was between 8 and 15 mol.%.

On the assumption that the composition of the ilmenite grains remains fixed, the temperatures at which magnetite-2 + ilmenite pairs are presumed to have crystallized range between 570° and 670°C under oxygen fugacities about 0–2 log units above that of the FMQ buffer, corresponding to 10^{-22} – 10^{-17} atm (Fig. 9).

Genetic relations between magnetite and mafic silicates

On the basis of the geothermometry of magnetite-1 + ilmenite pairs (Fig. 9) and of the equilibrium relations between ilmenite and amphiboles-1 or biotite (Fig. 8), we consider that a decrease in Fe and Ti (apfu) contents with increasing Si contents of these mafic silicates probably results from the concomitant crystallization of these silicates with the Fe–Ti oxides (Figs. 5, 6 and 7).

The pairs defined by the rims of amphiboles-1 and plagioclase yield temperatures of 571°–723°C (Table 3), which are roughly equivalent to those

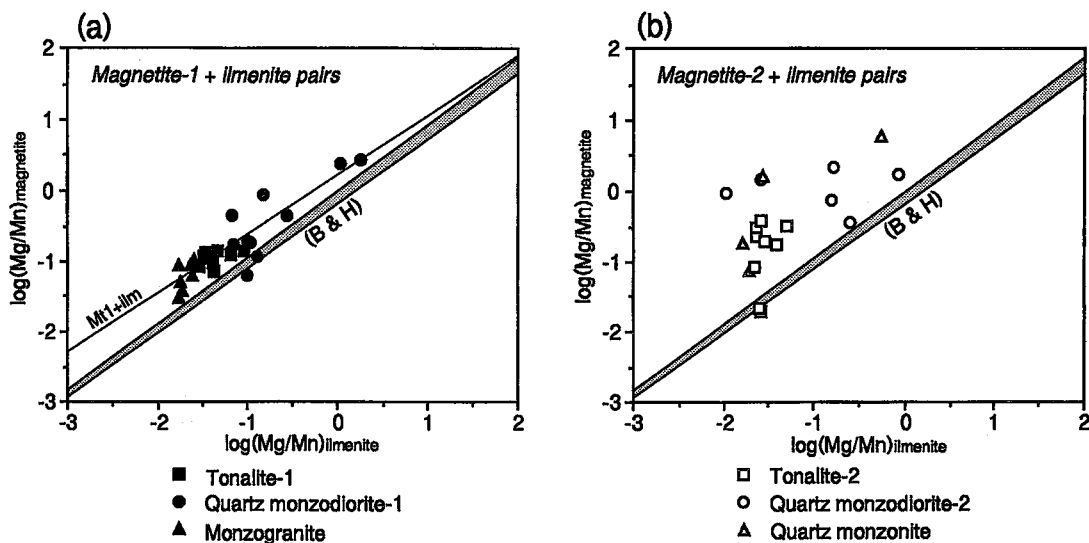


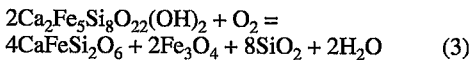
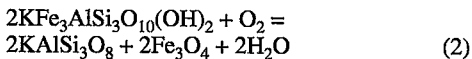
FIG. 10. $\log(\text{Mg}/\text{Mn})_{\text{magnetite}} - \log(\text{Mg}/\text{Mn})_{\text{ilmenite}}$ diagrams for the Myoken-zan granitoids. B & H: Equilibrium line, with the analytical precision (dotted area), from Bacon & Hirschmann (1988). Mt1 + ilm: equilibrium line for the magnetite-1 + ilmenite pairs at Myoken-zan.

obtained from magnetite-1 + ilmenite pairs, *i.e.*, 650°–750°C (Fig. 9), in light of uncertainties of the thermometer (Blundy & Holland 1990).

Equilibrium studies on synthetic granite systems and natural granites (*i.e.*, Tuttle & Bowen 1958, Robertson & Wyllie 1971, Whitney 1988) show that the minimum melting temperatures of granitoids are in a range of 680°–740°C under 2 kbar confining pressure with H₂O. The more Ca the rock contains, the higher the melting temperature (Whitney 1988). The equilibrium temperatures of 650°–750°C yielded by the magnetite-1 + ilmenite pairs may closely approach late magmatic temperatures, considering the high Ca contents, 6.33–3.83 wt.% CaO, of the Myoken-zan granitoids (Table 1).

Magnetite-2 + ilmenite pairs are inferred to have been in equilibrium at temperatures of 570°–670°C under oxygen fugacities of 10⁻²² – 10⁻¹⁷ atm (Fig. 9). This temperature range suggests that magnetite-2 + ilmenite pairs were probably formed under subsolidus conditions. Some reactions between silicates and exsolved water must be inferred for the formation of magnetite-2 + ilmenite pairs.

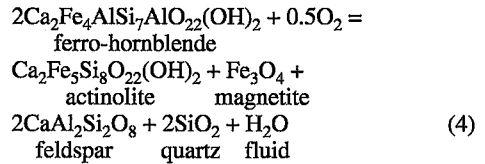
We have no evidence proving the stable coexistence of magnetite with pyroxenes in the Myoken-zan magmas. However, we cannot preclude the possibility that magnetite crystallized stably or metastably with pyroxenes. If a small amount of magnetite was associated with clinopyroxene or feldspar, reactions (2) and (3) would have developed:



Reaction (2) was evaluated experimentally (with sanidine) by Eugster & Wones (1962), Rutherford (1969), and Hewitt & Wones (1984). Reaction (3) has not been experimentally studied, but has been estimated by Frost & Lindsley (1991).

Reactions (2) and (3) indicate that an increase in the activity of H₂O will drive these equilibria to the left, and consequently the magma will tend to undergo relative oxidation at it cools (Frost & Lindsley 1991). The melt will stop crystallizing biotite (or hornblende) once magnetite is consumed. With falling temperature, a relatively oxidized water-rich fluid is expected to exsolve from the oxidized melt and to move along grain boundaries. A relative increase in oxygen fugacity of the fluid will drive reaction (2) to the right, and magnetite will begin crystallizing again together with feldspars under subsolidus conditions. However, reaction (3) will not reverse in the new environment because of the low temperature. Equation (4) is proposed on the basis of an actual assemblage of actinolite + magnetite, but we have not carried out any

thermodynamic calculations.



Oxygen fugacities of the fluid will be kept about 0 – 2 log units above that of the FMQ buffer during the crystallization of magnetite (Fig. 9).

Frost & Lindsley (1991, p. 449) proposed the corresponding ilmenite-bearing reactions, KUIIB and QUAHII, and inferred from thermodynamic calculations that these equilibrium reactions will proceed under physical conditions similar to those of reaction (2) and (3), respectively.

Two T - f(O₂) paths producing magnetite

Shirakawa (1975) and Asami & Nureki (1978) pointed out that the Myoken-zan magnetite-series and associated ilmenite-series (southern monzogranite, Fig. 1) magmas were emplaced in a single formation composed of igneous and sedimentary rocks of Paleozoic–Cretaceous age. One rock unit of the Myoken-zan complex is commonly in contact with two or more different rocks. We have not found, however, a disturbance of magnetic susceptibility values along the boundaries between a rock unit and different rocks. We have no evidence to show that the oxygen fugacity of a magmatic system was controlled by reactions between a magma and supracrustal rocks.

In discussing oxidation in the Finnmarka magmas, Czamanske & Wones (1973) suggested that “only after separation from the melt can H₂O act as an oxidizing medium through dissociation and loss of H₂ (p. 378)”. The loss of H₂ may oxidize the water-rich fluids in magmas. However, we are more inclined to believe that increases in the activity of H₂O during the evolution of a magma system will produce biotite or hornblende with liberation of oxygen, and consequently the production of biotite or hornblende should increase the oxygen fugacity of the melt system (Frost 1990, Frost & Lindsley 1991).

We suggest that two T - f(O₂) paths produced magnetite in the Myoken-zan magmas (Fig. 11). Path A was favorable for the production of magnetite-1. Magnetite began to crystallize together with hornblende and biotite in the magma, when the oxygen fugacity in the melt increased above that of the Ni–NiO buffer, at a temperature of about 750°C (Figs. 9, 11). Magnetite-1 continued to crystallize during the late magmatic (to subsolidus) stages, until the temperature of the melt decreased to about 650°C, under oxygen fugacities remaining above those of the Ni–NiO buffer (Fig. 11).

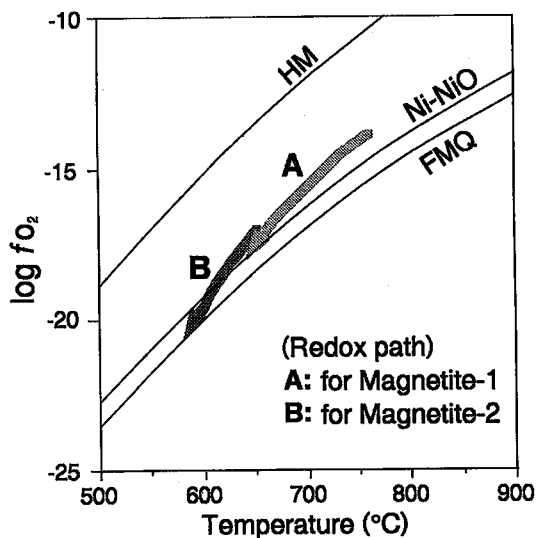


FIG. 11. Schematic diagram showing two T - $f(\text{O}_2)$ paths to produce the Myoken-zan magnetite.

Path B was favorable for the formation of magnetite-2, which began to crystallize by reactions between mafic silicates and the water-rich fluid released by the magmas, once the oxygen fugacity of the fluid increased above that of the Ni-NiO buffer at a temperature of about 670°C (Fig. 9). The reactions along path B were important mainly at the subsolidus stage, until the temperature decreased to about 570°C, whereas the oxygen fugacity of the fluids remained above that of the FMQ buffer (Fig. 11).

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