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Fe-Ti OXIDE MINERALS IN THE HOROMAN PLUTONIC COMPLEX OF THE HIDAKA METAMORPHIC BELT, HOKKAIDO

by

Yoichi Motoyoshi

(with 5 text-figures and 1 table)

Abstract

Fe-Ti oxide minerals in the Horoman plutonic complex of the Hidaka metamorphic belt are mostly of ilmenite (α -phase: ilmenite-hematite solid solution) and the occurrence of β -phase (magnetite-ulvöspinel solid solution) has not been reported so far. The ilmenite from Horoman are chemically analyzed in order to estimate the crystallization condition of the dioritic host rocks. Although the Mn/Fe²⁺ ratio of the host rocks remains constant during the differentiation, the Mn/Fe²⁺ ratio and R₂O₃ content of the ilmenite increase successively as the differentiation proceeds. This change in composition must be largely attributed to a decrease of temperature and an increase of oxygen activity in the magma from which the ilmenite crystallized. This observation implies that the Horoman diorite was formed under the 'oxidizing' condition, which means that the decreasing rate of f_{O_2} was lower than that of the standard buffer curve and the crystallization might have proceeded along the course intersecting QFM buffer curve.

With these points as background, the crystallization condition of the plutonic rocks in the Hidaka metamorphic belt is briefly discussed with respect to f_{O_2} , referring to the isotopic data presented by Sasaki and Ishihara (1979) and Shibata and Ishihara (1979).

Introduction

Fe-Ti oxide minerals provide valuable information on the generation of rocks containing them, and can be served as a useful indicator to evaluate the temperature and oxygen fugacity (f_{O_2}) in the magma from which they crystallized.

Recently, the importance of f_{O_2} on the formation of igneous rocks has attracted much interest. For example, the existence of two distinct granitic rock series, magnetite-series and ilmenite-series, is explained by the difference of f_{O_2} condition (Ishihara, 1977; Tsusue, 1976a, b) and also the petrogenesis are discussed with respect to the tectonic environment. Although studies on Fe-Ti oxides associated with plutonic rocks have already been performed by many workers, most of which were concerned with granitic rocks (e.g. Czamanske and Mihálik, 1972; Duchesne, 1972; Tsusue, 1973). This paper deals with Fe-Ti oxides occurring in the basic plutonic rocks and there are very few report discussing the f_{O_2} condition by examining the change in composition of the Fe-Ti oxides. As f_{O_2} in a crystallizing magma is closely related to the geological background, this kind of study is very important for considering the tectonic environment of the magma evolution.

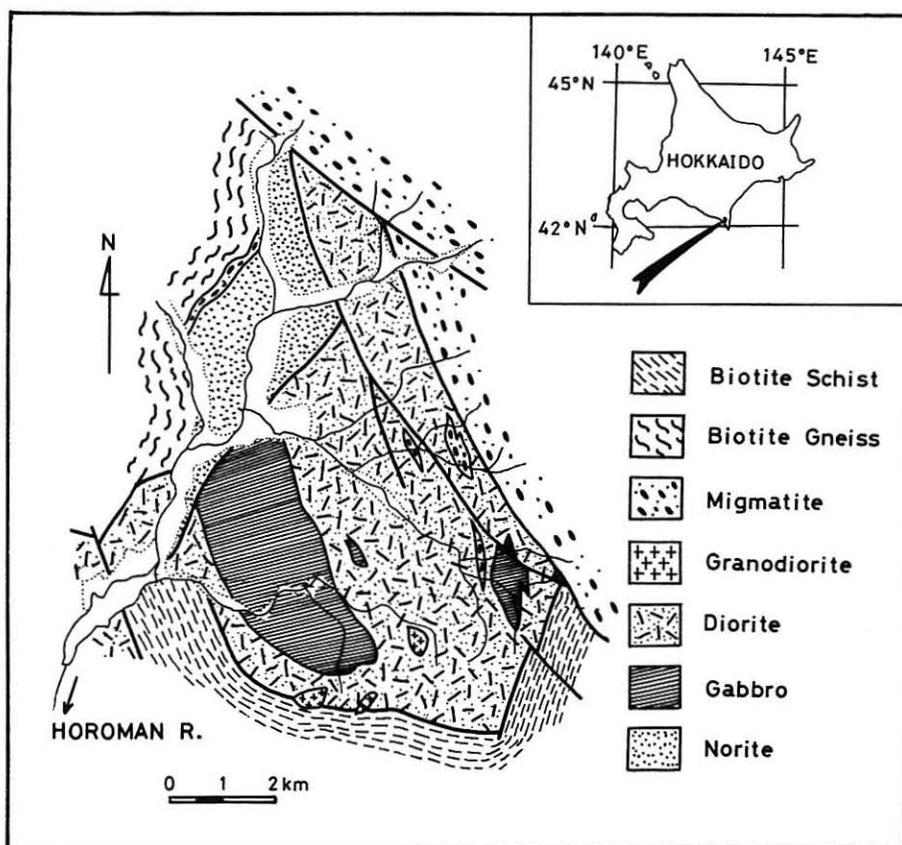
The occurrence of significant amount of basic plutonic rocks is one of the characteristics of the Hidaka metamorphic belt, but the mode of occurrence and chemical composition of Fe-Ti oxide minerals from the plutonic rocks have scarcely been reported. The Fe-Ti oxides here described are from the Horoman plutonic complex, one of the basic

igneous plutons in the Hidaka metamorphic belt, which is mainly composed of gabbro and diorite. Microscopic observations and electron microprobe analyses show that the Fe-Ti oxides from Horoman are of only ilmenite in stead of magnetite (Motoyoshi, 1980), and this observation is a general feature of other plutonic rocks in the Hidaka metamorphic belt (Ishihara, 1977; Sasaki and Ishihara, 1979; Shibata and Ishihara, 1979).

This paper gives the mode of occurrence and chemical composition of the ilmenite from Horoman in order to examine the crystallization condition with respect to temperature and f_{O_2} , and tries to investigate the generation of the basic plutonic rocks in the Hidaka metamorphic belt by applying the theory as discussed in the granitoid genesis. In addition, the geological environment for producing the ilmenite-series plutonic rocks are considered with special reference to the role of crustal materials.

Mode of occurrence and chemical composition of ilmenite

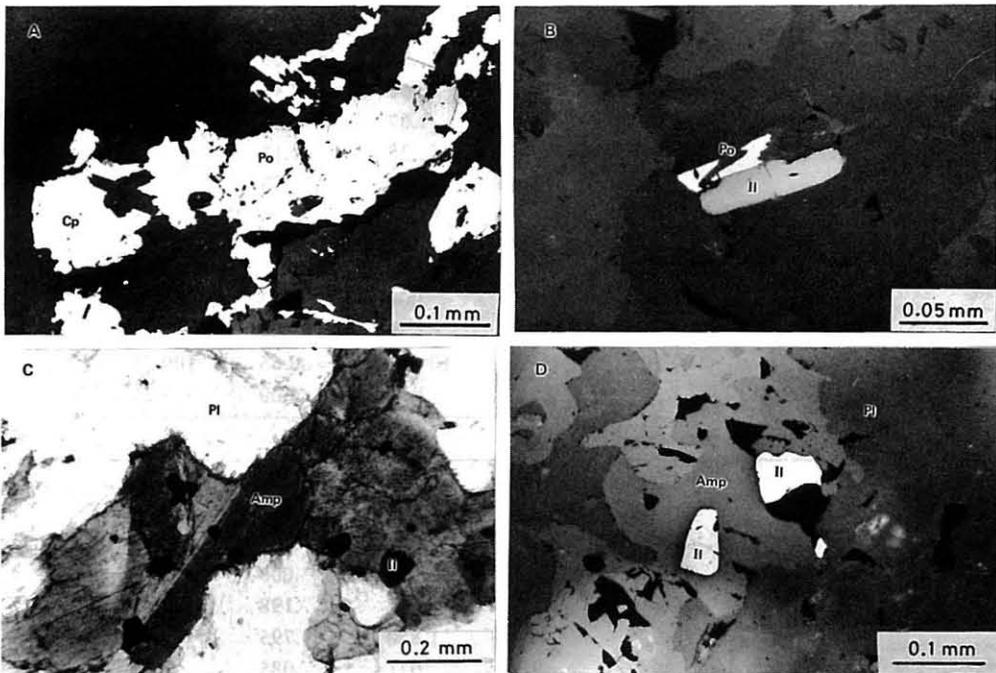
The Horoman plutonic complex crops out along the upper stream of the Horoman



Text-fig. 1. Geological sketch map of the Horoman plutonic complex. The diorite series and the olivine gabbro series in the text are labeled 'Diorite' and 'Gabbro', respectively.

River, the southern part of the Hidaka metamorphic belt. It has been classified by Motoyoshi (1980) that the complex consists of two distinct rock types; the olivine gabbro series and the diorite series. These rocks are considered to be intrusive into the surrounding metamorphic rocks as sheet-like form (Text-figure 1). Although the genetic relationship between the olivine gabbro series and the diorite series are still remained unsolved, the difference in mode of occurrence, textural feature and chemical composition suggests that these two types might have solidified under the different condition to each other. Further detailed discussion on this problem will be given in the near future.

The ilmenite mostly occurs in the diorite series, whereas opaque minerals are scarce in the olivine gabbro series. The diorite series, which is presumed to be comagmatic on the basis of the petrographic, mineralogic and chemical data, usually contains amphibole and plagioclase as main constituents. As SiO_2 increases, amount of biotite and quartz increase together with accessory sphene and apatite. Since distinct cumulus textures are scarcely observed in the diorite series, its bulk chemical composition is close to the magmatic composition at each stage of the differentiation. According to Motoyoshi (1980), the diorite series belongs to the calc-alkaline rock series because of no sign of iron enrichment. Sporadic occurrence of pyrrhotite ore deposit is another characteristic of the diorite series (Text-figure 2A, B).



Text-fig. 2. Photomicrographs of the polished and thin sections illustrating the mode of occurrences of the ore minerals in the Horoman diorite.

A: Mode of occurrence of pyrrhotite in the diorite series. B: Fragmentary pyrrhotite associated with idiomorphic ilmenite. C: Ilmenite grains in amphibole. D: Homogeneous ilmenites with no exsolution lamellae. Po: pyrrhotite. Cp: chalcopyrite. Il: ilmenite. Amp: amphibole. Pl: plagioclase.

The occurrence of these opaque minerals and relatively low oxidation ratio* of their host rocks (less than 23.49) indicate that the Horoman diorite belongs to the ilmenite-series defined by Ishihara (1977).

Ilmenite is the dominant accessory opaque mineral in the diorite series, occurring as small (0.1 - 0.4 mm in size), homogeneous (with neither inclusion nor exsolution lamellae, however the existence of compositional zoning is uninvestigated) anhedral to subhedral grains, or less frequently as tabular idiomorphic grains which are commonly included in and/or contact with mafic silicate mineral, in most cases, amphibole (Text-figure 2C, D).

The ilmenites from the Horoman plutonic complex were analyzed by electron microprobe analyzer using the model JEOL JXA-50A at the Department of Metallurgical Engineering, Hokkaido University. Specimen current was always kept at about 0.02 microampere and accelerating voltage at 15 kv. Synthesized pure oxides and natural minerals were used for standards, with intensity data being adjusted using the correction method of

Table 1. Selected microprobe analyses of ilmenites from the Horoman plutonic complex.

	1	2	3	4	5
SiO ₂	.11	.12	.05	.16	.09
TiO ₂	52.11	51.35	51.14	50.14	49.43
Al ₂ O ₃	.05	.02	.02	.04	.00
Cr ₂ O ₃	.10	.06	.00	.00	.06
FeO*	46.72	46.49	46.66	47.49	47.12
MnO	1.17	1.45	1.67	2.00	2.96
MgO	.22	.15	.26	.17	.15
CaO	.03	.01	.00	.13	.04
Total	100.51	99.65	99.80	100.13	99.85
Recalculated analyses**					
Fe ₂ O ₃	1.50	2.13	3.08	5.23	6.54
FeO	45.37	44.57	43.89	42.78	41.24
Total	100.66	99.86	100.11	100.65	100.51
R ₂ O ₃ Mol%	1.58	2.12	2.95	5.00	6.25
On the basis of 6 oxygens					
Si	.006	.006	.003	.008	.005
Ti	1.963	1.952	1.939	1.892	1.871
Al	.003	.001	.001	.002	.000
Cr	.004	.002	.000	.000	.002
Fe ³⁺	.056	.081	.117	.198	.247
Fe ²⁺	1.901	1.884	1.850	1.795	1.735
Mn	.050	.062	.071	.085	.126
Mg	.016	.011	.020	.013	.011
Ca	.002	.001	.000	.007	.002

(Analyst: Y. Motoyoshi)

* Total Fe as FeO ** After Carmichael (1967)

*Oxidation ratio is defined as $100 \times 2\text{Fe}_2\text{O}_3 / (2\text{Fe}_2\text{O}_3 + \text{FeO})$ in mole ratio (Chinner, 1960).

Bence and Albee (1968).

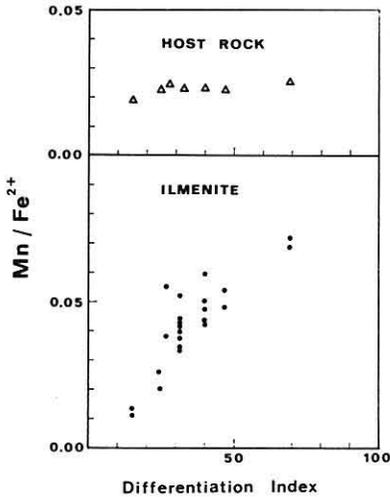
Selected analyses of the Horoman ilmenites are listed in Table 1, in which the Fe_2O_3 and R_2O_3 component are recalculated values after Carmichael (1967). Generally, chemical composition of ilmenite is expressed as a first approximation in terms of ilmenite (RTiO_3) and hematite (R_2O_3) which are well known to form an extensive solid solution at high temperature (Carmichael, 1961). The Horoman ilmenites contain the hematite component ranging from 1.50 to 6.56 wt. %.

In general, Fe-Ti oxide minerals are very sensitive to the change of physico-chemical condition and easily cause exsolution at subsolidus temperature. In the α -phase whose composition is close to FeTiO_3 end-member, however, considerable low temperature is required for exsolution (Nakada, 1980). Since the Horoman ilmenite is probably an early crystalline phase unaccompanied by β -phase, and no exsolution lamellae is observed in the phase, it can be served as a useful indicator to evaluate the temperature and f_{O_2} in the magma from which they crystallized. The following discussions stand on this assumption.

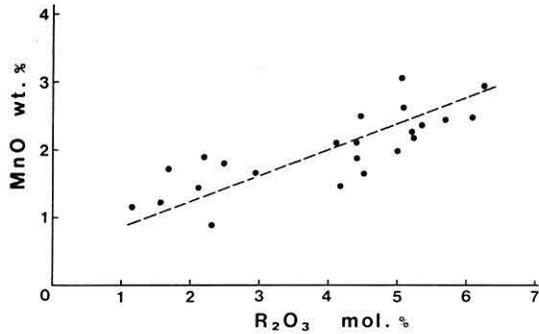
Discussion

Among some previous works on ilmenite composition, much attention has been paid on the process of Mn enrichment. In general, the Mn/Fe^{2+} ratio in ilmenite is presumed to be governed by three factors as follows: (1) the Mn/Fe^{2+} ratio in the source magma (Tsusue, 1973), (2) the temperature of the formation of ilmenite (Buddington and Lindsley, 1964; Duchesne, 1972; Neumann, 1974), (3) the f_{O_2} in the magma (Anderson, 1968; Czamanske and Mihálik, 1972).

In order to examine these factors, differentiation index of the host rocks vs. Mn/Fe^{2+} in



Text-fig. 3. The Mn/Fe^{2+} ratio vs. differentiation index for host rock and ilmenite.



Text-fig. 4. Positive relation between MnO and R_2O_3 in ilmenite from Horoman.

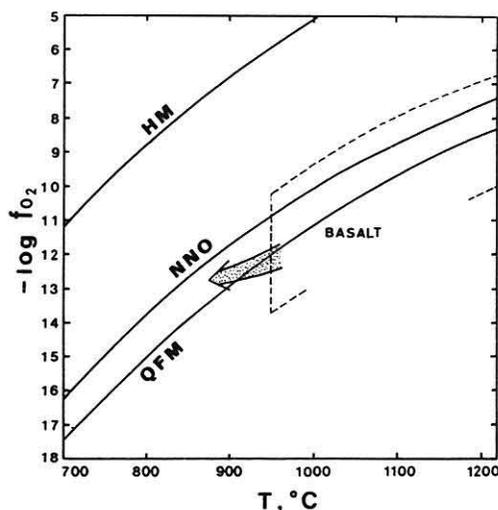
the ilmenite and in the host rocks is presented in Text-figure 3. The Mn/Fe²⁺ ratio in the ilmenite increases successively with an increase of the differentiation index of the host rocks. On the other hand, the Mn/Fe²⁺ ratio in the host rocks is almost constant during the period of differentiation. This contrast suggests that, in the case of the Horoman plutonic complex, the effect of bulk composition of the source rock on the Mn enrichment in the ilmenite can be negligible.

The proceeding of the differentiation of the Horoman diorite coincides with the fall of temperature inferred from decreasing Ti content in amphibole (Verhoogen, 1962; Ernst, 1968; Helz, 1973), hence the observation mentioned above is consistent with the proposal that the preference of Mn²⁺ to Fe²⁺ in ilmenite structure increase with decreasing temperature as stated in Neumann (1974).

On the other hand, Czamanske and Mihálik (1972) explained the effect of f_{O_2} on the process of Mn enrichment as follows; Fe²⁺ is more readily oxidized out of the ilmenite structure than Mn²⁺, and under the condition of increasing f_{O_2} , oxidation and the consequent extraction of Fe²⁺ from ilmenite will result in Mn enrichment. To estimate the f_{O_2} effect, MnO vs. R₂O₃ in the ilmenite is examined in Text-figure 4. In general, as Fe³⁺/Fe²⁺ ratio in a Fe-bearing phase is a reflection of the oxidizing/reducing condition, the positive relation between MnO and R₂O₃ in the Horoman ilmenite suggests that Mn enrichment is controlled both by temperature and f_{O_2} . This estimation is consistent with the result of Buddington and Lindsley (1964).

Under the natural magmatic circumstances, it is commonly observed that f_{O_2} decreases with falling temperature and follows a path subparallel to the standard oxide buffer curve, such as NNO or QFM. In the case of the Horoman diorite, however, the solidification of the rocks took place under the 'oxidizing' condition, which means that the oxygen activity was increased in the Horoman magma as the crystallization proceeded. This condition, however, does not always require the absolute uprise of f_{O_2} , that is, even if the f_{O_2} is decreased with falling temperature, the 'oxidizing' condition may be attained in the magma if only the decreasing rate of f_{O_2} is lower than that of standard buffer curve. This situation must be the case for the Horoman diorite.

The experiments by Holloway and Burnham (1972) and Helz (1973) showed that in 1921 Kilauea olivine tholeiite, magnetite appeared at the f_{O_2} above NNO buffer and only ilmenite crystallized as Fe-Ti oxide at QFM buffer. The initial magma that derived the Horoman diorite is presumed to have the composition of the fine-grained gabbro, which has a fine-grained mosaic texture with mineral assemblage of olivine, two pyroxene, plagioclase and ilmenite and has a less-differentiated chemical composition corresponding to olivine tholeiite of Yoder and Tilley (1962). Therefore, it is possible to estimate the course of crystallization of the Horoman diorite in the f_{O_2} - temperature diagram presented in Text-figure 5. As the two pyroxene equilibrium temperature of the fine-grained gabbro is calculated to be about 950°C after the method of Wood and Banno (1973), the crystallization might have proceeded along the course shown by the arrow in Text-figure 5, and intersected QFM buffer curve, but never crossed NNO buffer curve until the last product had solidified because of the absence of magnetite in it.



Text-fig. 5. Estimated course of crystallization of the Horoman diorite series. Field of basalt bounded by dashed lines is from Carmichael and Nicholls (1967). See the text in detail.

This estimation is compatible with the proposal by Ishihara (1977) that ilmenite-series plutonic rocks are formed under the condition of lower fO_2 domain below the NNO buffer, but, further detailed examination, such as Fe^{3+}/Fe^{2+} ratio in biotite (Wones and Eugster, 1965), is necessary to confirm this problem.

As already stated in the preceding introduction, the plutonic rocks of the Hidaka metamorphic belt mostly belong to the ilmenite-series (*e.g.* Ishihara, 1977). This developed idea implies that these rocks were formed under the relatively low fO_2 condition. Sasaki and Ishihara (1979) and Shibata and Ishihara (1979) suggested on the basis of the sulfur and strontium isotopic data, that the crustal sulfur and sedimentary graphite were concerned in the generation of the Hidaka plutonic rocks. This effect is probably due to the contamination of crustal materials into basic magmas when they intrude upwards. During this process, sedimentary graphite might have been incorporated with the magma and buffered the fO_2 in relatively low. The occurrence of graphite deposit in the gabbroic rocks in Horoman and the neighbouring Oshirabetsu regions (Bamba and Takahashi, 1980; Bamba, in press) may have a connection with the contamination of pre-existing sediments.

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References

- Anderson, A.T., 1968. Oxidation of the LaBlache Lake titaniferous magnetite deposit, Quebec. *Jour. Geol.*, 76: 528-547.
- Bamba, T., in press. Nickeliferous pyrrhotite deposits and ores from the Oshirabetsu mine, Tokachi Province, Hokkaido. *Jour. Fac. Sci., Hokkaido Univ.*, Ser. IV.
- Bamba, T. and Takahashi, T., 1980. Nickeliferous pyrrhotite deposits of the Oshirabetsu mine with special reference to the ore. *Mining Geol.*, 30: 37 (in Japanese).
- Bence, A.E. and Albee, A.C., 1968. Empirical correction factors for the electron microanalysis of silicates and oxides. *Jour. Geol.*, 76: 382-403.
- Buddington, A.F. and Lindsley, D.H., 1964. Iron-titanium oxide minerals and synthetic equivalents. *Jour. Petrol.*, 5: 310-357.
- Carmichael, C.M., 1961. The magnetic properties of ilmenite-hematite crystals. *Proc. Roy. Soc. London*, Ser. A., 263: 508-530.
- Carmichael, I.S.E., 1967. The iron-titanium oxides of salic volcanic rocks and their associated ferromagnesian silicates. *Contr. Mineral. Petrol.*, 14: 36-64.
- Carmichael, I.S.E. and Nicholls, J., 1967. Iron-titanium oxides and oxygen fugacity in volcanic rocks. *Jour. Geophys. Res.*, 72: 4665-4687.
- Chinner, G.A., 1960. Pelitic gneiss with varying ferrous/ferric ratios from Glen Clova, Angus, Scotland. *Jour. Petrol.*, 1: 178-217.
- Czamanske, G.K. and Mihálik, P., 1972. Oxidation during magmatic differentiation, Finnmarka complex, Oslo area, Norway: Part 1, The opaque oxides. *Jour. Petrol.*, 13: 493-509.
- Duchesne, J.C., 1972. Iron-titanium oxide minerals in the Bjerkrem-Songdal massif, South-western Norway. *Jour. Petrol.*, 13: 57-81.
- Ernst, W.G., 1968. *Amphiboles*. Springer-Verlag, Berlin. Heiderberg. New York, 229pp.
- Helz, R.T., 1973. Phase relations of basalts in their melting range at $P_{H_2O} = 5$ kb as a function of oxygen fugacity. *Jour. Petrol.*, 14: 249-302.
- Holloway, J.R. and Burnham, E.W., 1972. Melting relations of basalt with equilibrium water pressure less than total pressure. *Jour. Petrol.*, 13: 1-29.
- Ishihara, S., 1975. Acid magmatism and mineralization – Oxidation status of granitic magma and its relation to mineralization –. *Marine Sci. Monthly*, 7: 756-759. (in Japanese with English abstract).
- Ishihara, S., 1977. The magnetite-series and ilmenite-series granitic rocks. *Mining Geol.*, 27: 293-305.
- Motoyoshi, Y., 1980. Petrology of the Horoman plutonic complex of the Hidaka metamorphic belt. *Master Thesis of Hokkaido Univ.*, 108pp. (manuscript).
- Nakada, S., 1980. Chemical variation of ilmenites from the ilmenites-series volcanics – the case of the Osuzuyama acid rocks –. *Magma*, 59: 1-6 (in Japanese).
- Neumann, E.R., 1974. The distribution of Mn^{2+} and Fe^{2+} between ilmenites and magnetites in igneous rocks. *Amer. Jour. Sci.*, 274: 1074-1088.
- Sasaki, A. and Ishihara, S., 1979. Sulfur isotope composition of the magnetite-series and ilmenite-series granitoids in Japan. *Contr. Mineral. Petrol.*, 68: 107-115.
- Shibata, K. and Ishihara, S., 1979. Initial $^{87}Sr/^{86}Sr$ ratios of plutonic rocks from Japan. *Contr. Mineral. Petrol.*, 70: 381-390.
- Tsuse, A., 1973. The distribution of manganese and iron between ilmenite and granitic magma in the Ōsumi Peninsula, Japan. *Contr. Mineral. Petrol.*, 40: 305-314.
- Tsuse, A., 1976a. Granitic magmas and ore deposits, (1) Especially those of Southwest Japan. *Mining Geol. Spec. Issue*, 7: 15-24 (in Japanese with English abstract).
- Tsuse, A., 1976b. Occurrence and chemical composition of iron-titanium oxides. *Jour. Japan. Assoc. Mineral. Petrol. Econ. Geol. Spec. Issue*, 1: 251-259 (in Japanese).
- Verhoogen, J., 1962. Distribution of titanium between silicates and oxides in igneous rocks. *Amer. Jour. Sci.*, 260: 211-220.
- Wones, D.R. and Eugster, H.P., 1965. Stability of biotite: Experiment, theory, and application. *Amer. Mineral.*, 50: 1228-1272.
- Wood, D.R. and Banno, S., 1973. Garnet-orthopyroxene and orthopyroxene-clinopyroxene relationships in simple and complex systems. *Contr. Mineral. Petrol.*, 42: 109-124.
- Yoder, H.S., Jr. and Tilley, C.E., 1962. Origin of basalt magmas: An experimental study of natural and synthetic rock systems., *Jour. Petrol.*, 3: 342-532.