

## PETROLOGY OF DOLOMITIC MARBLES FROM KASUMI ROCK, PRINCE OLAV COAST, EAST ANTARCTICA

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**Abstract:** Dolomitic marble containing primary chlorite, Zn-rich spinel and F-rich clinohumite occurs in the upper amphibolite-facies Kasumi Rock, Prince Olav Coast, East Antarctica. Minerals in the chlorite-bearing dolomitic marble along with another dolomitic marble from the Kasumi Rock were analyzed with an EPMA. Phase relations and vapor phase compositions are discussed in the light of experimentally determined phase equilibria and petrological data from other high-grade metamorphic terrains in East Antarctica and other areas. Mg-Fe partitioning between Ca-amphibole and other minerals is exceptionally irregular, and strongly depends on the Al-content of Ca-amphibole. The low-variance assemblage of the Kasumi Rock dolomitic marble buffered the vapor phase composition at low  $X_{\text{CO}_2}$  in harmony with that in the nearby calcite marbles. Spinel in the high-grade dolomitic marbles may have been produced by chlorite-consuming reactions during prograde metamorphism.

### 1. Introduction

Southwestward progressive metamorphism of intermediate-pressure type from the upper amphibolite to granulite facies has been revealed by the studies of continuous and discontinuous mineral changes in pelitic, basic-intermediate and calc-silicate rocks (HIROI *et al.*, 1983a, b, 1987; SHIRAIISHI *et al.*, 1984), and is characteristic of the Late Proterozoic Lützow-Holm Complex exposed along the Prince Olav and Sôya Coasts, East Antarctica (68–69.5°S, 39–45°E) (Fig. 1). In the complex occur dolomitic marbles in a small amount, which sometimes contain Zn-rich spinel (SUWA and TATSUMI, 1969; MATSUMOTO, 1982; MATSUEDA *et al.*, 1983). Progressive mineral changes in the rocks are important to establish phase equilibria in such a rock type at high metamorphic grades and to characterize the complex. In particular, primary chlorite was newly found with clinohumite, olivine, and Zn-rich spinel in a dolomitic marble from the upper amphibolite-facies Kasumi Rock, Prince Olav Coast. Moreover, dolomitic marbles carrying Zn-rich spinel are known to occur as ceylonite in Sri Lanka, which is considered to have been situated close to East Antarctica before the breaking up of Gondwanaland. The purpose of this paper is to present petrography and mineral chemistry of dolomitic marbles from the Kasumi Rock and to discuss phase relations in the light of recent experimental data as well as petrological data from other localities in East Antarctica, Sri Lanka, *etc.* Mineral abbreviations of KRETZ (1983) are used to represent assemblages and reactions of minerals in this paper.

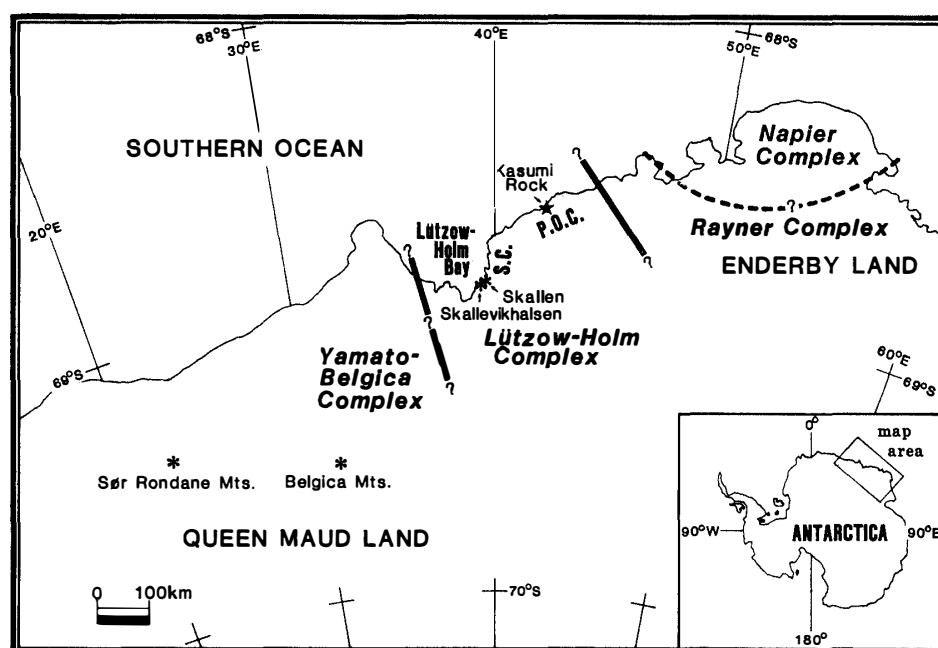


Fig. 1. Map of East Antarctica between 20°E and 60°E, showing localities of dolomitic marbles and boundaries between complexes. P.O.C.=Prince Olav Coast; S.C.=Sôya Coast.

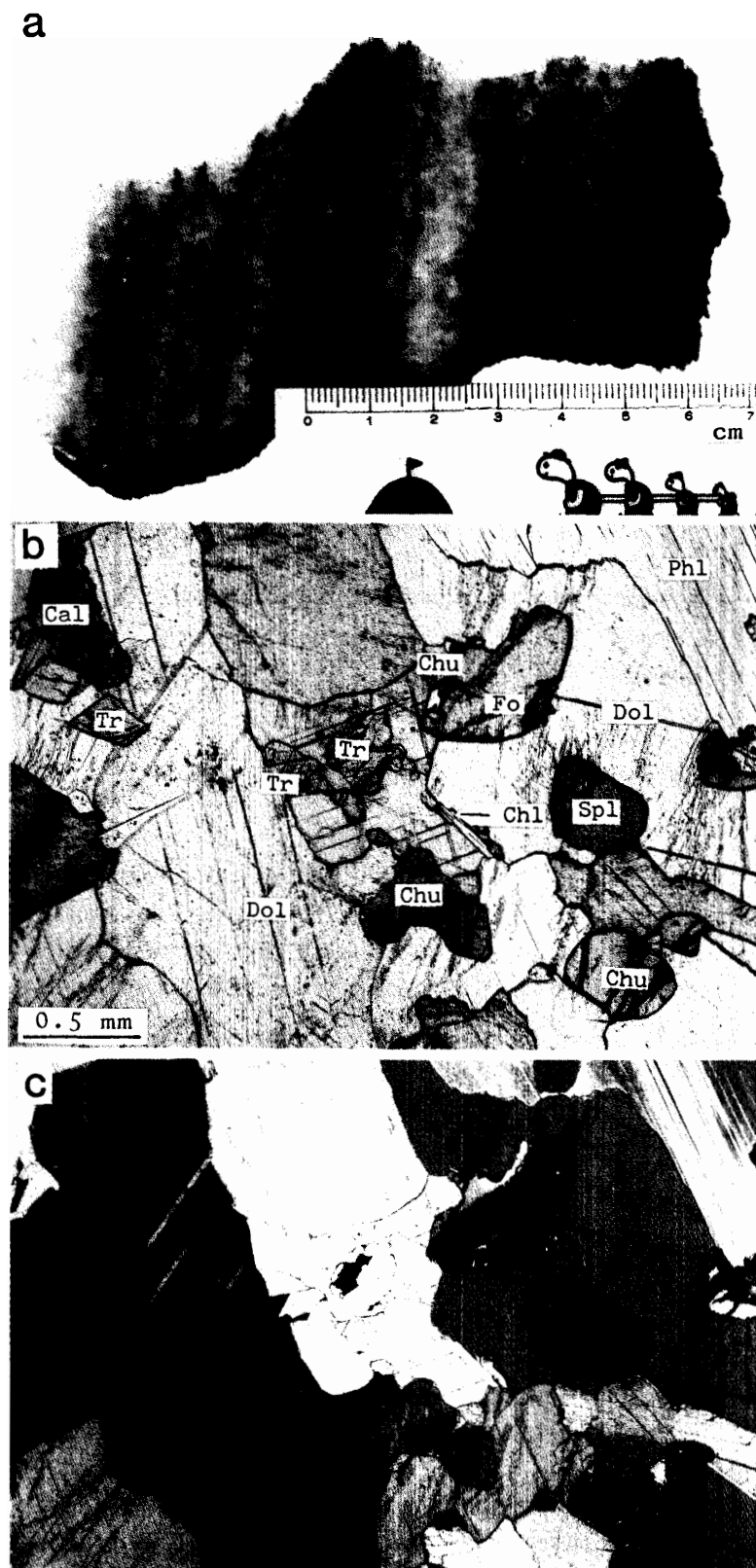
## 2. General Geology and Petrology of Lützow-Holm Complex

The Lützow-Holm Complex consists largely of well-layered pelitic-psammitic and basic-intermediate gneisses with small amounts of metamorphosed calcareous and ultramafic rocks. The calcareous and ultramafic rocks occur as thin layers and isolated blocks up to 10 m in diameter. Migmatitic rocks of granitic to granodioritic compositions are also present mainly in the Prince Olav Coast, that is in the lower-grade part of the complex.

The Lützow-Holm Complex has been deformed, at least twice; the axial planes of earlier isoclinal folds trend N-S to NW-SE and those of later open to close folds NE-SW (SHIRAISHI, 1986; HIROI and SHIRAISHI, 1986). It was extensively intruded by the Early Paleozoic granite and pegmatite.

Many K-Ar and Rb-Sr ages of about 500 Ma obtained from whole rock and mineral separates indicate a heating event coeval with the Early Paleozoic granite and pegmatite activity (YANAI and UEDA, 1974; SHIBATA *et al.*, 1985), which is known over a large portion of East Antarctica (GREW, 1982). The Rb-Sr whole rock method, however, often indicates older ages of 680–1200 Ma (SHIRAHATA, 1983; SHIBATA *et al.*, 1986), which probably date the earlier regional metamorphism of the complex. It is significant that the initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of metasedimentary rocks of the Lützow-Holm Complex are relatively low (0.705–0.706) (SHIBATA *et al.*, 1986). This suggests that most, if not all, metasedimentary rocks of the complex did not have a long pre-metamorphic history. It is in good agreement with the result of Sm-Nd geochronologic study in the region (TANAKA *et al.*, 1985).

The Prince Olav to Sôya Coast region is divided into three terrains of different



a. Polished slab showing fine compositional layering. Reddish mineral is clinohumite.

b. Photomicrograph showing minerals in the specimen. Plane polarized light.

c. Ditto. Crossed nicols.

Fig. 2. Sp. K79020411 from Kasumi Rock.

metamorphic facies. The eastern part of the Prince Olav Coast is an amphibolite-facies terrain where Ca-poor amphiboles (anthophyllite and cummingtonite) occur and no orthopyroxene has been found (RAVICH and KAMENEV, 1975; HIROI *et al.*, 1983b). Its western part is a transitional terrain from the amphibolite facies to the granulite facies. In the transitional terrain orthopyroxene occurs sporadically, confined to rocks of appropriate bulk chemical compositions (HIROI *et al.*, 1983b, 1986; SHIRAISHI *et al.*, 1984; SUZUKI, 1984). The Sôya Coast to the southwest is a granulite-facies terrain characterized by the common occurrence of orthopyroxene in basic-intermediate and some psammitic rocks as well as ultramafic rocks (BANNO *et al.*, 1964; KIZAKI, 1964; SUWA, 1968; YOSHIDA, 1978; SUZUKI, 1982; KATSUSHIMA, 1985; MOTOYOSHI, 1986; HIROI *et al.*, 1986). In pelitic rocks the sillimanite + K-feldspar + quartz assemblage without primary muscovite was stable over the entire region (HIROI *et al.*, 1983a, b; MOTOYOSHI *et al.*, 1985). Moreover, the corundum + K-feldspar + muscovite assemblage was stable in the amphibolite-facies terrain (HIROI *et al.*, 1983a, b). These facts indicate that the muscovite + quartz assemblage was not stable throughout the region. It is significant and characteristic of the Lützow-Holm Complex that a small amount of metastable kyanite occurs as relict inclusions within garnet and plagioclase grains in many pelitic gneisses regardless of metamorphic grade (HIROI *et al.*, 1983a, b; MOTOYOSHI *et al.*, 1985). This suggests that rocks of the complex uniformly experienced prograde metamorphism from the kyanite to the sillimanite stability fields. On the other hand, andalusite occurs locally in pelitic rocks intruded extensively by the Early Paleozoic granite and pegmatite, showing contact metamorphism by the granite and pegmatite (HIROI *et al.*, 1983a, b).

The Kasumi Rock is a small bedrock exposure located in the eastern part of the Prince Olav Coast (Fig. 1), that is in the amphibolite-facies terrain. Detailed geology of the Kasumi Rock is given by NISHIDA *et al.* (1982, 1984).

### 3. Petrography of Dolomitic Marbles from Kasumi Rock

Two specimens (*Sp. K79020410* and *Sp. K79020411*) of dolomitic marbles were collected and briefly described by geologists of the 20th Japanese Antarctic Research Expedition (NISHIDA *et al.*, 1982, 1984). The dolomitic marbles, together with calcite marbles, occur as thin layers up to several meters thick intercalated in biotite gneisses. Fine compositional layering reflecting the variation of modal amounts of colored minerals is conspicuous in one of the specimens (Fig. 2a). As for the mineral assemblages of the rocks, some descriptions and corrections are added to the previous reports.

*Sp. K79020410* is composed mainly of dolomite, calcite and olivine with subordinate amounts of phlogopite, Ca-amphibole, clinohumite, ilmenite, apatite and Fe-sulphide. Secondary serpentine minerals with magnetite are also present replacing olivine. Dolomite together with calcite forms the equigranular coarse-grained matrix, in which silicate minerals are scattered. Calcite contains abundant dolomite lamellae. Olivine is present as subhedral to anhedral porphyroblasts up to several mm in length. Phlogopite is also present as euhedral to subhedral porphyroblastic plates. Ca-amphibole occurs in a small amount. Clinohumite is found locally as grains interlocking with olivine.

*Sp. K79020411* consists of dolomite, calcite, olivine, phlogopite, clinohumite,

Ca-amphibole, chlorite, spinel, ilmenite, apatite and Fe-sulphide (Fig. 2b, c). Secondary serpentine minerals with magnetite are present in a small amount, partially replacing olivine. Clinohumite occurs much more abundantly in this specimen than in *Sp. K79020410*, being in direct contact with all other minerals. On the other hand, calcite is present rather sporadically in this specimen. Chlorite flakes usually form aggregates, and are in direct contact with the other minerals. Spinel is pale grayish blue in color and occurs as euhedral to subhedral grains up to several mm in diameter. It is often included in dolomite grains. Small amounts of phlogopite and Ca-amphibole are scattered.

The texturally stable mineral assemblages in the amphibolite-facies dolomitic marbles from the Kasumi Rock are; Dol + Cal + Fo + Chu + Hbl + Phl  $\pm$  Spl  $\pm$  Chl.

#### 4. Mineral Chemistry

Minerals were analyzed with an energy-dispersive instrument (Hitachi S550 + Kevex 7000Q-75) at Chiba University. The analytical method is given by MORI and KANEHIRA (1984). Generally several grains at two or more points per grain of each mineral per specimen were analyzed. Fluoline in hydrous minerals was analyzed semi-quantitatively with a wave-dispersive instrument (JEOL JXA-733) at the National

Table 1. Representative microprobe analyses of minerals in *Sp. K79020410* from Kasumi Rock.

Mineral	Ol	Chu*	Hbl	Phl	Dol	Cal
SiO <sub>2</sub>	41.42	37.26	52.86	41.70	—	—
TiO <sub>2</sub>	—	2.79	0.38	0.64	—	—
Al <sub>2</sub> O <sub>3</sub>	—	—	4.74	13.08	—	—
FeO**	7.79	6.44	1.59	1.59	0.88	0.20
MgO	51.10	50.92	22.78	27.35	20.66	3.06
CaO	—	—	13.23	0.08	29.60	52.74
Na <sub>2</sub> O	—	—	1.49	0.32	—	—
K <sub>2</sub> O	—	—	0.26	10.24	—	—
Total	100.31	97.40	97.32	95.00	51.14	56.01
O	4	(13 cations)	23	22	6	6
Si	1.001	4.015	7.336	6.128	—	—
Ti	—	0.226	0.039	0.070	—	—
Al	—	—	0.775	2.265	—	—
Fe	0.157	0.580	0.185	0.196	0.070	0.017
Mg	1.841	8.178	4.713	5.992	2.921	0.447
Ca	—	—	1.967	0.013	3.009	5.536
Na	—	—	0.401	0.091	—	—
K	—	—	0.046	1.920	—	—
Total	2.999	12.999	15.462	16.675	6.000	6.000
Mg/(Mg + Fe)	0.921	0.934	0.962	0.968	0.977	0.964
Mg/Fe	11.69	14.09	25.52	30.60	41.97	26.76

\* Clinohumite contains considerable F (ca. 1.5 wt%).

\*\* Total Fe as FeO.

Table 2. Representative microprobe analyses of minerals in Sp. K79020411 from Kasumi Rock.

Mineral	Ol	Chu	Chl	Spl	Hbl	Phl	Dol	Cal
SiO <sub>2</sub>	42.08	37.83	31.68	—	53.51	40.69	—	—
TiO <sub>2</sub>	—	2.37	—	—	0.11	0.46	—	—
Al <sub>2</sub> O <sub>3</sub>	—	—	16.46	65.33	4.90	14.87	—	—
FeO	5.59	4.42	1.82	5.01	1.16	1.37	0.55	0.18
MgO	53.36	53.52	35.59	18.96	22.76	27.34	21.13	2.20
ZnO	—	—	tr	10.74	—	—	—	—
CaO	—	—	—	—	13.30	—	29.93	53.74
Na <sub>2</sub> O	—	—	—	—	1.04	0.72	—	—
K <sub>2</sub> O	—	—	—	—	0.34	10.05	—	—
F**	—	2.1	tr	—	0.5	1.2	—	—
Total	101.03	100.24	85.56	100.04	97.63	96.70	51.61	56.10
O	4	(13 cations)		4	23	22	6	6
Si	1.000	3.996	6.033	—	7.404	5.689	—	—
Ti	—	0.188	—	—	0.012	0.048	—	—
Al	—	—	3.694	1.976	0.799	2.451	—	—
Fe	0.111	0.391	0.290	0.108	0.135	0.160	0.043	0.015
Mg	1.889	8.426	10.102	0.725	4.694	5.697	2.951	0.322
Zn	—	—	tr	0.204	—	—	—	—
Ca	—	—	—	—	1.971	—	3.006	5.663
Na	—	—	—	—	0.279	0.195	—	—
K	—	—	—	—	0.060	1.793	—	—
Total	3.000	13.001	20.119	3.013	15.354	16.033	6.000	6.000
Mg/(Mg+Fe)	0.944	0.956	0.972	0.871	0.972	0.969	0.986	0.957
Mg/Fe	16.99	21.58	34.81	6.747	34.82	31.47	68.96	22.23

\* Total Fe as FeO.

\*\* Semi-quantitative analysis.

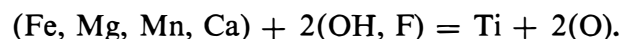
Institute of Polar Research. Representative analyses of minerals in the Kasumi Rock specimens are listed in Tables 1 and 2.

#### 4.1. Olivine

Olivines in Sp. K79020410 and Sp. K79020411 are forsterite, having 8 and 6% fayalite molecule respectively. Mn, Ni, Zn and Cr were not detected.

#### 4.2. Clinohumite

Clinohumites are relatively rich in both F and Ti around 0.2 per 13 cations. Their  $X_F$  (F/OH + F) are estimated to be around 0.6. Ti in the clinohumites is well-explained by the following substitution (Fig. 3):



#### 4.3. Ca-amphibole

Ca-amphiboles in the Kasumi Rock specimens are hornblende, containing Al up to 0.8 per 23 oxygens. They are slightly richer in Al and alkalis than the tremolite from the amphibolite-facies Belgica Mountains, but poorer in these elements than the

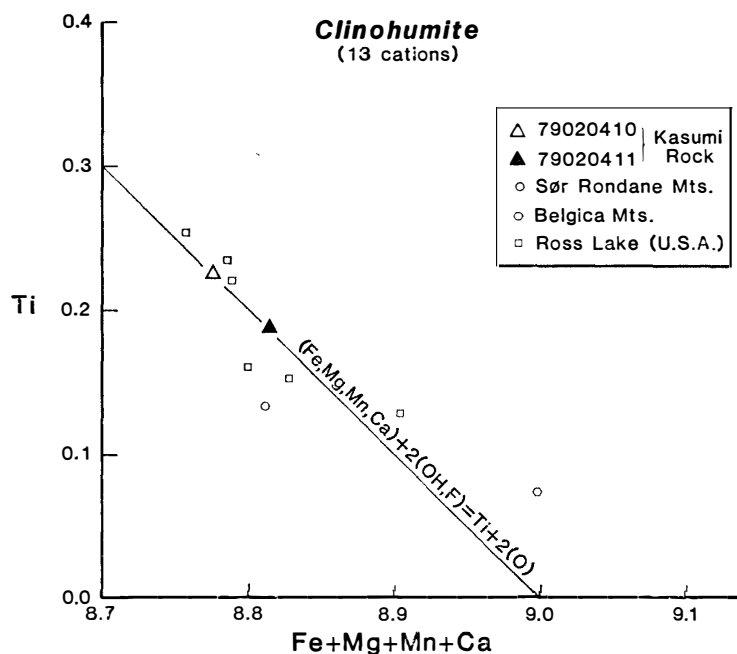


Fig. 3. Plot of Ti vs. Fe + Mg + Mn + Ca in clinohumites. Data sources: Sør Rondane Mts. = OSANAI (1986); Belgica Mts. = ASAMI et al., 1986; Ross Lake (U.S.A.) = RICE (1980). Loss Lake clinohumites contain variable F.

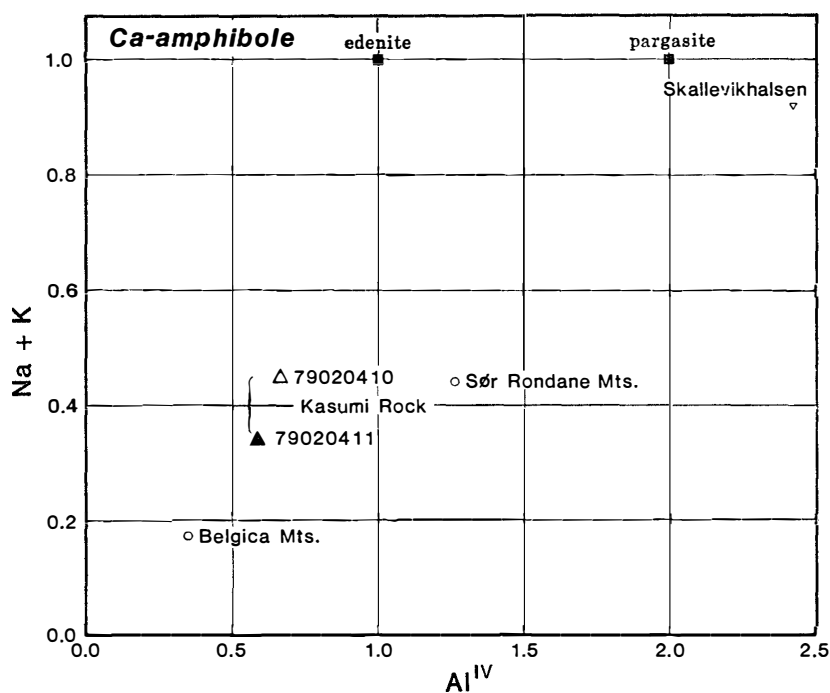
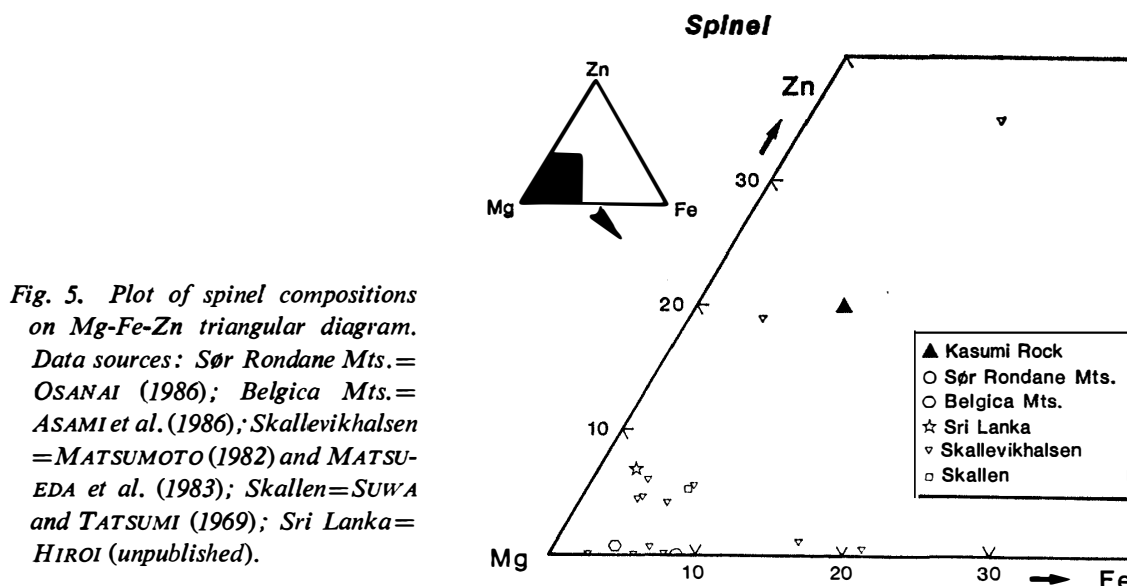


Fig. 4. Plot of tetrahedral aluminium vs. total alkalis in Ca-amphiboles. Data sources: Sør Rondane Mts. = OSANAI (1986); Belgica Mts. = ASAMI et al. (1986); Skallevikhalsen = MATSUEDA et al. (1983).

Ca-amphiboles from the granulite-facies Skallevikhalsen and the Sør Rondane Mountains (Fig. 4).

#### 4.4. Phlogopite

Phlogopites have Mg/(Mg + Fe) of around 0.97 and are poor in Ti (up to 0.07 per



22 oxygens). Phlogopite in *Sp. K79020411* contains slightly higher Al than that in *Sp. K79020410*, probably reflecting the difference in bulk chemical composition.

#### 4.5. Spinel

Spinel occurs only in *Sp. K79020411*. It has  $Mg/(Mg+Fe)$  of 0.87 and is considerably rich in Zn with gahnite molecule about 20% (Fig. 5).

#### 4.6. Chlorite

Primary chlorite occurs only in *Sp. K79020411*, and is clinochlore in composition. Its  $Mg/(Mg+Fe)$  is 0.97. Fluoline is present only in a trace amount.

#### 4.7. Dolomite and calcite

Dolomite has the highest  $Mg/(Mg+Fe)$  among coexisting minerals, and  $Mg/(Mg+Fe)$  of calcite is slightly lower than that of coexisting dolomite.

### 5. Discussion

#### 5.1. Phase equilibria

The texturally stable mineral assemblages in the amphibolite-facies dolomitic marbles from the Kasumi Rock are;  $Dol + Cal + Fo + Chu + Hbl + Phl \pm Spl \pm Chl$ . In Fig. 6 atomic Mg/Fe ratios of minerals are plotted on a logarithmic basis to examine the Mg-Fe exchange equilibrium among the coexisting minerals. Mg and Fe are partitioned consistently between the coexisting phases except for Ca-amphibole, suggesting that exchange equilibrium was generally attained. The order of preference for Mg relative to Fe is; dolomite > phlogopite > chlorite > clinohumite > olivine > spinel. The Mg-Fe partitioning between Ca-amphibole and other minerals is apparently irregular, but it is well-explained by the effect of Al in Ca-amphibole, as shown in Fig. 7. This suggests strong non-ideality of Ca-amphibole solid solutions (tremolite-pargasite join in



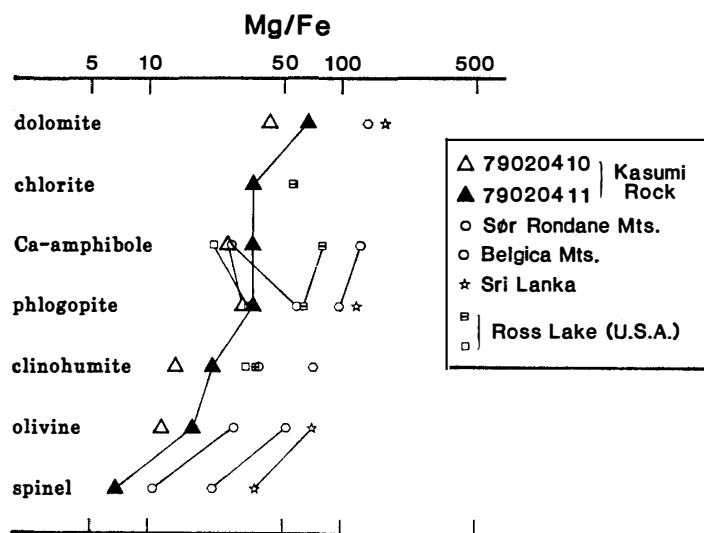


Fig. 6. Plot of atomic ratios of  $Mg/Fe$  on logarithmic basis. All  $Fe$  as  $FeO$ . Data sources: Sør Rondane Mts.=OSANAI (1986); Belgica Mts.=ASAMI et al. (1986); Ross Lake (U.S.A.)=RICE (1980); Sri Lanka=HIROI (unpublished).

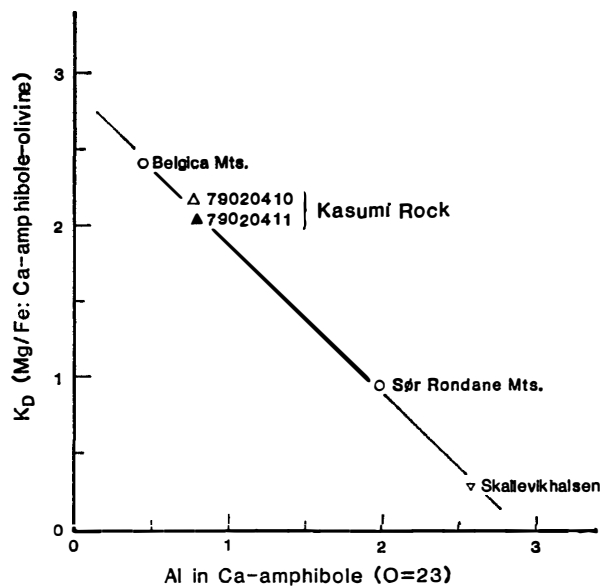
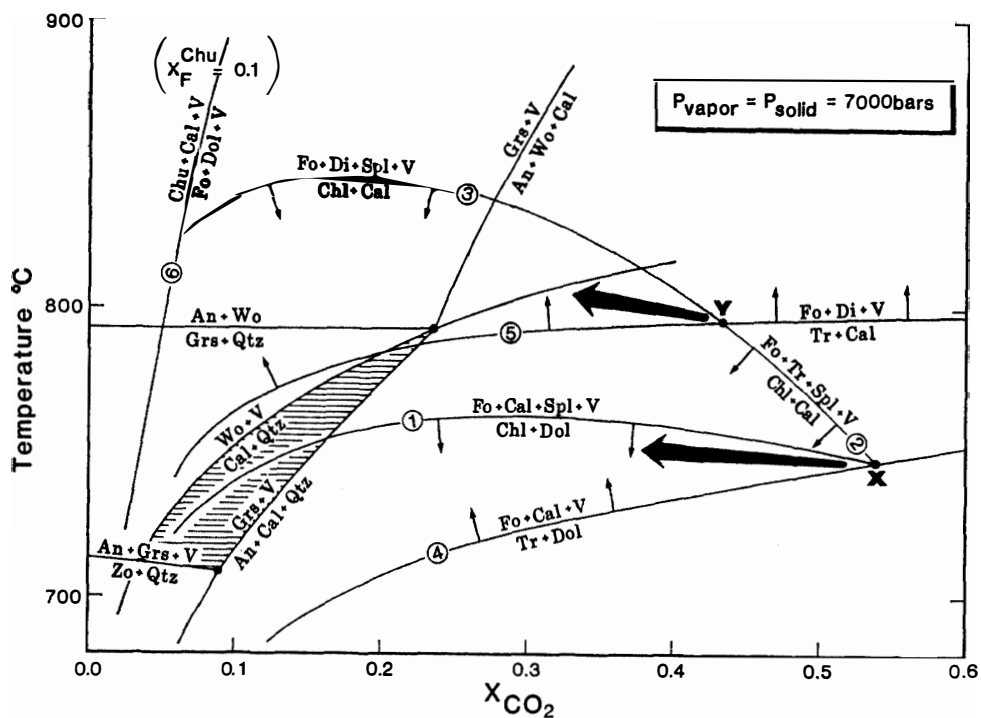
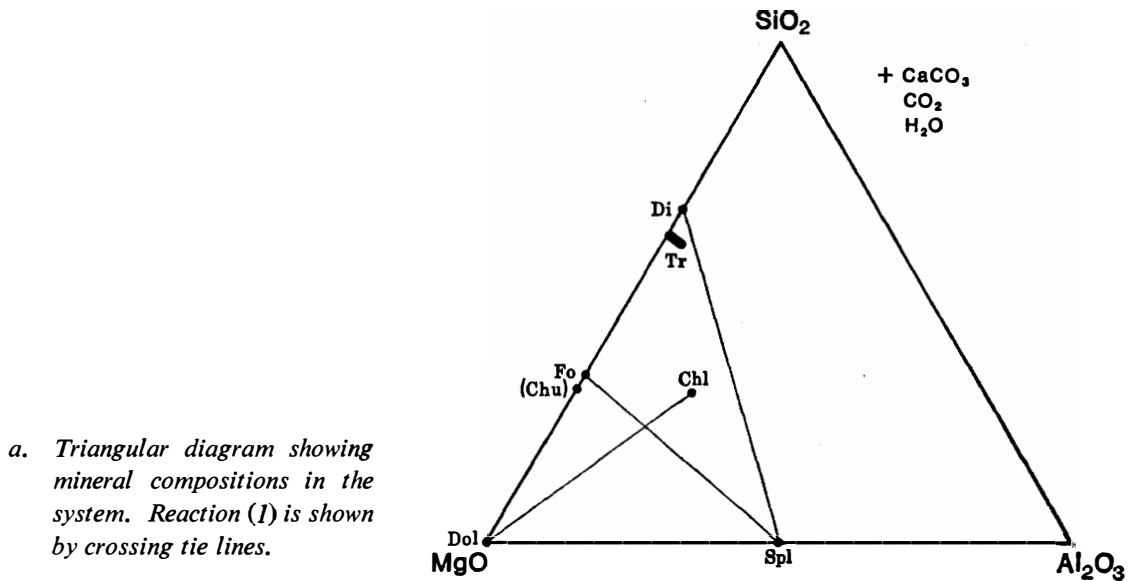


Fig. 7. Plot of  $K_D$  ( $Mg/Fe$ : Ca-amphibole-olivine) vs. Al in Ca-amphibole. Line is for reference only. Data sources as in Fig. 4.

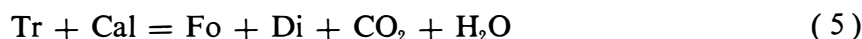
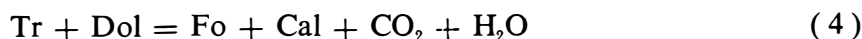
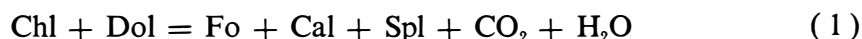
this case) even at the high metamorphic grades. Temperatures evaluated by the calcite-dolomite thermometer of ANOVITZ and ESSENE (1987) are below  $600^{\circ}C$ , probably owing to retrograde resetting.

SUWA and TATSUMI (1969) reported the following mineral assemblages in the granulite-facies dolomitic marbles from Skallen;  $Dol + Cal + Fo + Di + Spl + Phl \pm Hbl$ . Therefore, it is suggested that chlorite-, clinohumite- and hornblende-consuming and diopside- and spinel-producing reactions took place during prograde metamorphism of the dolomitic marbles. Mineral reactions in dolomitic marbles are analyzed, for the first approximation, in the system  $CaO-MgO-Al_2O_3-SiO_2-CO_2-H_2O$  (Fig. 8a). The following reactions are relevant to the upper amphibolite to granulite-facies rocks:



b. Schematic isobaric  $T$ - $X_{\text{CO}_2}$  diagram at  $P_{\text{vapor}} = P_{\text{solid}} = 7000$  bars, showing mineral reactions in the system. Some reactions in the nearby calcite marbles and the estimated  $T$ - $X_{\text{CO}_2}$  for them in the amphibolite-facies to lower-grade granulite-facies terrains are also shown (striped region) after HIROI et al. (1987). Small and large arrows show the direction of movement of univariant reaction boundaries and invariant points, respectively, in the presence of additional components such as Zn in spinel and Al and alkalis in Ca-amphibole. Reaction (1) after WIDMARK (1980); reaction (4) after KÄSE and METZ (1980); reaction (6) after RICE (1980).

Fig. 8. Reaction relations of minerals in the system  $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-CO}_2\text{-H}_2\text{O}$ .



In Fig. 8b, reactions (1) to (6) are schematically shown on a  $T$ - $X_{\text{CO}_2}$  diagram at  $P_{\text{vapor}} = P_{\text{solid}} = 7000$  bars.  $P_{\text{solid}}$  of 7000 bars is an average of the estimated values for the Lützow-Holm Complex (see HIROI *et al.*, 1987). One of the mineral assemblages in the amphibolite-facies Kasumi Rock specimens corresponds to invariant point X in Fig. 8b, whereas one of those from the granulite-facies Skallen area indicates  $T$ - $X_{\text{CO}_2}$  conditions along the univariant boundary of reaction (5) and  $X_{\text{CO}_2}$  higher than invariant point Y in Fig. 8b. Spinels in the Skallen dolomitic marbles, as well as other high-grade dolomitic marbles (RICE, 1977), may have been produced by reactions (1), (2) and/or (3) during prograde metamorphism.  $X_{\text{CO}_2}$  of vapor phases in the dolomitic marbles seems relatively high around 0.5 or higher. The compositions of vapor phases in the dolomitic marbles will be discussed below in comparison with those in the nearby calcite marbles and in the light of effects of additional components such as Zn in spinel, Al and alkalis in hornblende and F in clinohumite.

### 5.2. Vapor phase composition and effects of additional components

HIROI *et al.* (1987) estimated the vapor phase compositions in the nearby calcite marbles to be low (striped region in Fig. 8b). One of the mineral assemblages of the amphibolite-facies dolomitic marbles from the Kasumi Rock indicates that  $T$ - $X_{\text{CO}_2}$  values were buffered close to invariant point X ( $X_{\text{CO}_2} > 0.5$ ) in Fig. 8b. One of the mineral assemblages of the granulite-facies dolomitic marbles from Skallen also indicates  $X_{\text{CO}_2}$  higher than invariant point Y ( $X_{\text{CO}_2} > 0.4$ ). These follow that  $X_{\text{CO}_2}$  of vapor phases in the dolomitic marble was much higher than that in the nearby calcite marbles.

However, we must examine the effects of additional components on the univariant reaction boundaries and therefore invariants points. The spinel in *Sp. K79020411* contains gahnite and hercynite molecules around 20% and 10%, respectively (Fig. 5). The strong concentration of Zn in spinel relative to other minerals would expand the stability fields of spinel-bearing mineral assemblages. The partitioning of Mg and Fe between the spinels and the olivines, however, is regular regardless of Zn-content of the spinels (Fig. 6). This suggests that Mg-Fe-Zn spinel solid solution is nearly ideal and that the effects of Zn and Fe in the spinel on reactions (1), (2), and (3) are small, as  $X_{\text{Mg}}$  of spinel  $> 0.7$ .

The hornblendes in *Sp. K79020410* and *Sp. K79020411* contain considerable Al about 0.8 per 23 oxygens and alkalis (Tables 1 and 2). The effect of these elements on reactions involving hornblende may be large because of the non-ideality of the tremolite-

pargasite solid solution which is suggested by the remarkable dependence of Mg-Fe partitioning between Ca-amphibole and other minerals on the Al-content of Ca-amphibole (Fig. 7). The enrichment of pargasite molecule in Ca-amphibole would expand the stability fields of mineral assemblages including hornblende. In Fig. 8b, small arrows show the direction of movement of reaction boundaries by the effect of these additional components. Consequently, invariant points X and Y would move toward low  $X_{\text{CO}_2}$  in the presence of these additional components, as shown by large arrows. However, it is not clear whether  $X_{\text{CO}_2}$  of the vapor phases in the dolomitic marbles was as low as that in the nearby calcite marbles.

The clinohumite in the Kasumi Rock specimens are rich in F ( $X_F$  around 0.6). This is in good agreement with the coexistence of clinohumite with dolomite, calcite, forsterite, tremolite, chlorite and spinel, which suggests intersection of the boundary of reaction (6) and invariant point X (see Fig. 8b). Reactions (7) and (8) are significant in the presence of such F-rich clinohumite. However, fluoline may not appreciably affect phase equilibria excluding clinohumite and  $X_{\text{CO}_2}$  of the vapor phases, because the order of preference of F relative to OH is; clinohumite  $\gg$  phlogopite  $>$  tremolite  $\gg$  chlorite, as suggested by RICE (1980).

## 6. Conclusion

Dolomitic marble containing primary chlorite, Zn-rich spinel and F-rich clinohumite was newly found in the upper amphibolite-facies Kasumi Rock, Prince Olav Coast, East Antarctica. Compositions of coexisting minerals in the rock as well as another dolomitic marble from the Kasumi Rock indicate general attainment of Mg-Fe exchange equilibrium. The Mg-Fe partitioning between Ca-amphibole and other minerals is apparently irregular, but is well-explained by the effect of Al in Ca-amphibole. The chlorite-bearing low-variance assemblage of the Kasumi Rock dolomitic marble suggests buffering of the vapor phase composition at relatively low  $X_{\text{CO}_2}$  in agreement with the estimate for  $X_{\text{CO}_2}$  in the nearby calcite marbles by HIROI *et al.* (1987). Spinel in the high-grade dolomitic marbles may have been produced by chlorite-consuming reactions during prograde metamorphism.

## Acknowledgments

We would like to express our sincere thanks to Dr. K. YANAI of the National Institute of Polar Research and Dr. T. NISHIDA of Saga University for information on the field occurrence of the Kasumi Rock specimens. We also thank Dr. K. SHIRAISHI of the National Institute of Polar Research for the EPMA analysis of fluoline in hydrous minerals.

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(Received March 14, 1988; Revised manuscript received April 18, 1988)