

## Fe-Ti oxides in the Malene supracrustals and the occurrence of Nb-rich rutile

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### **Abstract**

Data are presented on Fe-Ti oxide compositions and assemblages in Malene supracrustal rocks from the Godthåb District and surrounding territory, West Greenland. Amphibolite facies samples contain ilmenite ± rutile, in which the ilmenite has a low Fe<sub>2</sub>O<sub>3</sub>-content (< 6 mole %). Granulite facies samples contain ilmenite ± rutile, and ilmenite ± magnetite ± hematite, in which the Fe<sub>2</sub>O<sub>3</sub>-content of ilmenite ranges to ~ 15 mole %. In all cases, ilmenite contains only small quantities of MgO and MnO, and magnetite is virtually pure Fe<sub>3</sub>O<sub>4</sub>.

The above observations suggest that granulite facies samples are more oxidized than amphibolite facies ones, contrary to expectation. Possible causes include (1) re-equilibration during retrograde metamorphism, or (2) H<sub>2</sub>O-dissociation to H<sub>2</sub> and O<sub>2</sub> with subsequent loss of hydrogen producing a more oxidizing local environment during prograde metamorphism.

In amphibolite facies 'cordierite anthophyllite rocks' (CAR), Fe-Ti oxide assemblages are related systematically to silicate mineralogy: rutile occurs in Mg-rich samples, and ilmenite is found in Fe-rich ones, with ilmenite ± rutile present in samples with intermediate Fe/Mg. Rutile is modally abundant (up to ~ 3 vol %), and contains high Nb<sub>2</sub>O<sub>5</sub> (up to ~ 6 wt %), which suggests an absolute Nb-enrichment in CAR by a mechanism not well understood.

### **Introduction**

The Fe-Ti oxides (hematite, magnetite, ilmenite and rutile) are common accessory phases in metamorphic rocks, with the occurrence of each mineral or assemblage of minerals being controlled by several factors including rock composition, oxygen fugacity, temperature and pressure. It is apparent from the literature that Fe-Ti oxides in metamorphic rocks have not received the kind of detailed systematic study carried out on their counterparts in igneous rocks. Nevertheless, the recent summary by Rumble (1976) has established the broad characteristics of oxides in metamorphic rocks which provides a reasonable framework for additional study of these minerals.

This paper describes the occurrence and chemistry of Fe-Ti oxides in the Archaean Malene supracrustal rocks of southern West Greenland, and reports the discovery of Nb-rich rutile in certain 'cordierite-anthophyllite' rocks, which raises intriguing questions concerning the origin of the sedimentary protolith for this rock type.

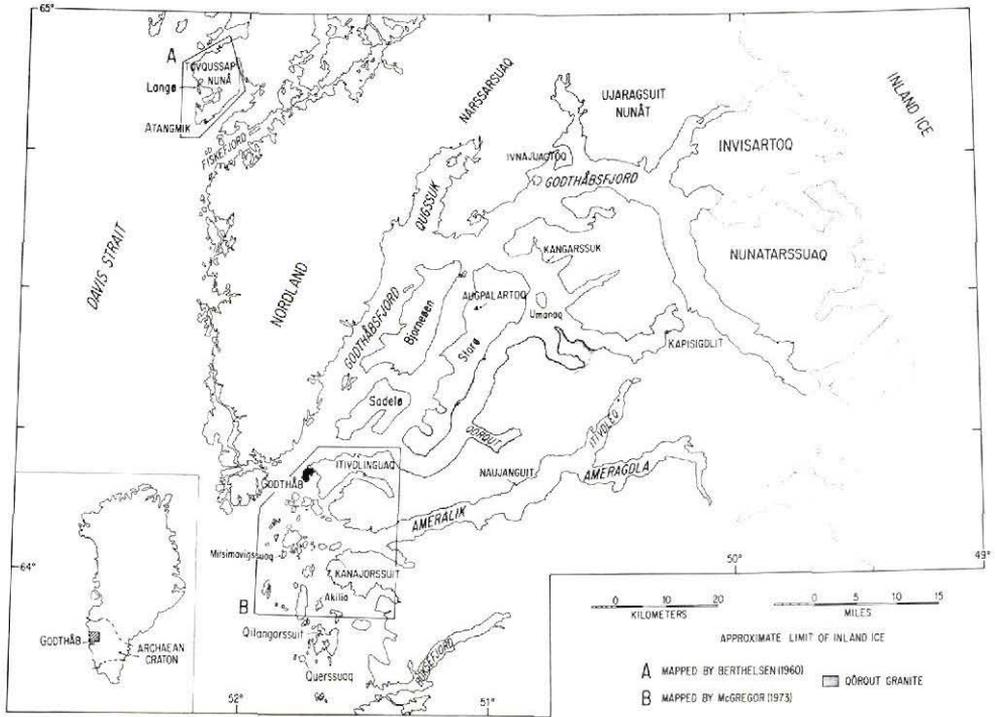


Fig. 1. General map of the Godthåb District and surrounding region of West Greenland illustrating locations referred to in the text. Boundaries of the Oôrqut Granite Complex are adapted from Brown *et al.* (1981).

### Geological overview

The Malene supracrustal rocks were defined by McGregor (1973) to include various types of amphibolite and metasediment in the vicinity of Godthåb which are intruded by ~ 3000 Ma Nûk orthogneiss and are largely in tectonic contact with ~ 3750 Ma Amitsoq orthogneiss. This name has subsequently been applied throughout the Archaean gneiss complex of West Greenland to all supracrustal rocks with lithological characteristics and stratigraphic position similar to the ones originally described by McGregor (cf. Bridgwater *et al.*, 1976). This convention is adopted here, and Fe-Ti oxides from two associations of Malene supracrustal rocks are described: granulite-grade occurrences from Langø, and amphibolite-grade occurrences from the Godthåbsfjord–Ameralik region.

Langø is a small island ~ 75 km north of Godthåb (lat. 64°52'N, long. 52°12'W) (fig. 1). It occurs on the western flank of the Tovqussaq dome, the structure of which was described in detail by Berthelsen (1960). Dymek & Albee (1976) and Dymek (1977a) have reported on the petrology of the rocks on Langø, and noted petrographic and mineral-chemical evidence for a prograde granulite facies metamorphism and a retrograde amphibolite facies metamorphism.

The Godthåbsfjord–Ameralik region includes the area mapped by McGregor (1973), and

the country to the northeast, west and southeast. Metamorphism of the Malene supracrustals in this region has been described by Dymek (1977b, 1978). A prograde amphibolite facies metamorphism was followed locally by retrogression to greenschist facies.

## Results and sample description

### Godthåbsfjord–Ameralik region

*Amphibolites.* Hornblende-plagioclase-quartz amphibolites represent the dominant supracrustal lithology. Types that contain garnet, cummingtonite, anthophyllite or diopside in addition to hornblende are also present, and may be quite abundant locally. Biotite is a common accessory phase in all amphibolites, and minor amounts of apatite, tourmaline, allanite, zircon and sulfide minerals ( $\text{Py} \pm \text{Po} \pm \text{Ccp}$ ) may also occur.

Ilmenite is the only Fe-Ti oxide found in the amphibolites, where it typically forms

Table 1. Microprobe analyses of ilmenite (Godthåbsfjord–Ameralik region)

	1	2	3	4	5
SiO <sub>2</sub>	0.09	0.03	0.11	0.14	0.08
TiO <sub>2</sub>	50.85	51.65	50.00	50.69	49.76
Al <sub>2</sub> O <sub>3</sub>	0.00	0.00	0.00	0.00	0.00
Cr <sub>2</sub> O <sub>3</sub>	0.01	0.18	0.00	0.04	0.00
Fe <sub>2</sub> O <sub>3</sub> *	3.02	1.28	5.01	3.66	5.77
FeO	43.61	43.98	42.74	44.59	42.89
MgO	0.10	0.46	1.09	0.40	0.91
ZnO	0.12	0.00	0.00	0.00	0.00
MnO	1.82	1.63	0.28	0.28	0.25
ZrO <sub>2</sub>	0.00	0.00	0.05	0.00	0.00
Nb <sub>2</sub> O <sub>5</sub>	0.00	0.07	0.12	0.19	0.18
Total	99.62	99.28	99.40	99.99	99.84
<b>FORMULA PROPORTIONS BASED ON 2 CATIONS AND 3 OXYGENS</b>					
Si	0.002	0.001	0.003	0.004	0.002
Ti	0.970	0.985	0.947	0.962	0.943
Al	0.000	0.000	0.000	0.000	0.000
Cr	0.000	0.004	0.000	0.001	0.000
Fe <sup>3+</sup>	0.058	0.024	0.095	0.070	0.110
Fe <sup>2+</sup>	0.924	0.933	0.900	0.940	0.903
Mg	0.004	0.017	0.041	0.015	0.034
Zn	0.002	0.000	0.000	0.000	0.000
Mn	0.039	0.035	0.006	0.006	0.005
Zr	0.000	0.000	0.007	0.000	0.000
Nb	0.000	0.001	0.001	0.002	0.002
% Hem	3.0	1.3	5.1	3.6	5.7
% Ilm	97.0	98.7	94.9	96.4	94.3

1. OGA-48A, Amphibolite, Itivdliunguaq
2. 163211, Diopside amphibolite, Bjørneøen
3. OGA-48J, Garnet-Biotite schist, Itivdliunguaq
4. 163246, Cord-Anth-Garn gneiss (with rutile), S. Shore
5. OGA-48L, Garn-Anth gneiss, Itivdliunguaq Ameragdla

\* Total iron analyzed as FeO; Fe<sub>2</sub>O<sub>3</sub> recalculated from stoichiometry and end-member assignment.

subequant to lath-shaped grains up to 500  $\mu\text{m}$  long. Sphene may occur with ilmenite, and is particularly abundant in diopside amphibolites, where two generations may be present: in those samples in which retrogressive metamorphism has caused the breakdown of diopside + hornblende to actinolite + epidote  $\pm$  chlorite, secondary sphene coronas have formed on ilmenite.

As shown by the analyses listed in Table 1 (Nos 1 & 2), ilmenite in amphibolites is characterized by moderate MnO ( $\sim 1.3\text{--}2.0$  wt %) and low MgO ( $< 0.5$  wt %), and little to no ZnO,  $\text{Al}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{ZrO}_2$  and  $\text{Nb}_2\text{O}_5$ . The hematite-content of the ilmenite, based on calculated  $\text{Fe}_2\text{O}_3$ , is low and ranges from 1–5 mole %.

*Pelitic and semi-pelitic schists.* The most abundant Malene metasedimentary rock type is a semi-pelitic biotite + quartz + plagioclase  $\pm$  sillimanite schist containing garnet and cordierite. Locally, pelitic to subarkosic lithologies with abundant muscovite  $\pm$  alkali feldspar are also present. Garnet and cordierite occur in Fe- and Mg-rich muscovite schists respectively, although cordierite is exceedingly rare in rocks that contain muscovite. Both the pelitic

Table 2. Microprobe analyses of rutile

	1	2	3	4	5	6
$\text{SiO}_2$	0.04	0.04	0.00	0.05	0.00	0.03
$\text{TiO}_2$	98.19	93.17	90.72	98.17	99.34	98.01
$\text{Al}_2\text{O}_3$	0.00	0.06	0.10	0.00	0.02	0.04
$\text{Cr}_2\text{O}_3$	0.58	0.00	0.11	0.09	0.43	0.10
$\text{Fe}_2\text{O}_3^*$	0.00	2.18	3.06	0.38	0.05	0.36
MgO	0.00	0.00	0.01	0.00	0.00	0.00
ZnO	0.00	0.01	0.00	0.17	0.09	0.00
MnO	0.00	0.00	0.00	0.00	0.00	0.00
$\text{ZrO}_2$	0.16	0.12	0.07	0.01	0.03	0.00
$\text{Nb}_2\text{O}_5$	0.12	3.08	5.03	0.63	0.00	0.80
Total	99.09	98.66	99.10	99.50	99.96	99.34

FORMULA PROPORTIONS BASED ON 1 CATION AND 2 OXYGENS

Si	0.001	0.001	0.000	0.001	0.000	0.000
Ti	0.982	0.949	0.930	0.988	0.992	0.989
Al	0.000	0.001	0.002	0.000	0.000	0.001
Cr	0.006	0.000	0.001	0.001	0.004	0.001
Fe	0.000	0.022	0.031	0.004	0.001	0.004
Mg	0.000	0.000	0.000	0.000	0.000	0.000
Zn	0.000	0.000	0.000	0.002	0.001	0.000
Mn	0.000	0.000	0.000	0.000	0.000	0.000
Zr	0.010	0.008	0.004	0.001	0.002	0.000
Nb	0.001	0.019	0.031	0.004	0.000	0.005

GODTHÅBSFJORD-AMERALIK REGION

1. OGA-16, green mica quartzite; N. Shore Ameragdla
2. OGA-12B, Cord-Anth gneiss; S. Coast Mitsimavigssuag
3. 163246, Cord-Anth-Garn gneiss (with Rutile); S. Shore Ameragdla

LANGØ

4. OGA-28B, Orthopyroxene gneiss
5. OGA-35B, Pyriboleite
6. OGA-28I-2, Bitotite-rich Pyriboleite

\* Total iron analyzed as  $\text{FeO}$ ; recalculated as  $\text{Fe}_2\text{O}_3$

and semi-pelitic schists are typically rusty-weathering due to the presence of abundant sulfide minerals. Zircon, apatite, tourmaline and graphite are common accessory phases.

Ilmenite is by far the predominant Fe-Ti oxide in these rocks, although rutile occurs in several samples. Ilmenite ranges from stubby laths to blocky grains (up to 250  $\mu\text{m}$  across), and is a common inclusion in garnet porphyroblasts. Rutile forms subequant to elongated grains ranging from 25–100  $\mu\text{m}$  long.

The ilmenite analysis listed in Table 1 (No. 3) is typical of the compositions found, which are characterized by low MnO (0.2–0.4 wt %), low to moderate MgO (0.3–1.3 wt %), and small amounts of  $\text{Nb}_2\text{O}_5$  (0.1–0.2 wt %). The contents of ZnO,  $\text{Al}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$  and  $\text{ZrO}_2$  are at or near their detection limits ( $< \sim 0.05$  wt %). Calculated hematite-contents of the ilmenite are small, and range from 3–6 mole per cent. The few analyses carried out on rutile indicate that it is pure  $\text{TiO}_2$ .

*Green Mica Rocks.* Perhaps the most striking, albeit least abundant, Malene metasedimentary rock type is a series of green mica schists that are referred to in the field as 'fuchsite quartzites'. The details of mica chemistry are reported by Dymek *et al.* (1983), who note that the green micas range in composition from nearly pure muscovite to types with up to  $\sim 17$  wt %  $\text{Cr}_2\text{O}_3$  and  $\sim 8$  wt % BaO.

Rutile is the only oxide present in green mica *quartzites*, and occurs as subequant, euhedral grains 50–100  $\mu\text{m}$  across dispersed throughout each sample, and less commonly as irregularly shaped 5–10  $\mu\text{m}$  wide inclusion in the mica. A typical analysis of rutile from this lithology is listed in Table 2 (No. 1), which shows that it is nearly pure  $\text{TiO}_2$ , but contains some  $\text{Cr}_2\text{O}_3$ ,  $\text{ZrO}_2$ , and  $\text{Nb}_2\text{O}_5$ . Although there are exceptions, the  $\text{Cr}_2\text{O}_3$ -content of rutile in green mica rocks is higher than that found in other lithologies.

*'Cordierite-Anthophyllite' rocks\* (CAR).* These constitute a widespread and characteristic metasedimentary lithology in the Malene supracrustals. The phase petrology of this rock type is quite complex, and involves various combinations of the minerals: Sill-Ky-Stl-Cord-Garn-Anth-Talc. Other minerals in CAR include abundant quartz, plagioclase and biotite, together with minor to trace quantities of apatite, corundum, monazite, sulfide, tourmaline and zircon.

Both ilmenite and rutile occur in CAR, the latter forming up to  $\sim 3$  volume % in some samples. Ilmenite typically occurs as stubby plates up to  $\sim 250$   $\mu\text{m}$  long that are distributed uniformly throughout most samples, and as inclusions in garnet and anthophyllite. Rutile forms euhedral equant grains 50–100  $\mu\text{m}$  across that also tend to be distributed evenly throughout a sample. However, in certain cases, rutile is found only as inclusions in garnet, whereas ilmenite occurs in the sample matrix. This petrographic feature suggests that the spatial distribution of Fe-Ti oxides in CAR is partly related to localized equilibration established during prograde continuous reactions.

In general, however, the occurrence of rutile and ilmenite is related to the nature of the coexisting silicate phase assemblage. As illustrated schematically in figure 2, rutile is restricted to Mg-rich assemblages, and it is superseded by ilmenite in Fe-rich assemblages. The

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\* Anthophyllite is the name applied here to all orthorhombic amphiboles including types rich in Na and Al, which could be called gedrite. There is no apparent compositional gap in the orthorhombic amphibole series in the Malene supracrustals, but rather a continuum of compositions (cf. Spear, 1980).

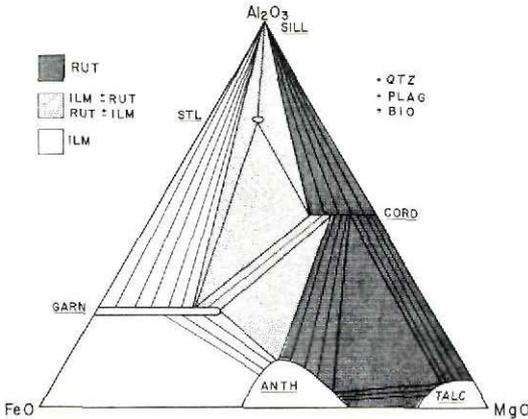
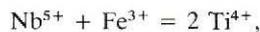


Fig. 2. Schematic representation of phase relationships in Malene 'cordierite-anthophyllite' rocks (CAR) from the Godthåbsfjord–Ameralik region for middle amphibolite metamorphic grade (~ 550°C). At higher grade, staurolite is absent, and talc and anthophyllite are replaced by orthopyroxene. At lower grade, staurolite coexists with anthophyllite, and kyanite may occur instead of sillimanite. Fields where rutile, ilmenite or both occur are indicated by the different patterns.

area of 'overlap' (i.e. ilmenite + rutile) varies from locality to locality, and is related not only to bulk composition, but also to metamorphic history, as indicated above. In addition, the presence of abundant sulfide minerals in some samples may affect a bulk composition shift to higher Mg/(Mg + Fe) for the silicates and oxides, which could control the appearance of rutile vs. ilmenite.

The composition of ilmenite in CAR is not unlike that found in semi-pelitic schists, except that the concentration of Nb<sub>2</sub>O<sub>5</sub> is commonly higher (~ 0.2 wt %; Table 1, Nos 4 and 5). The composition of rutile is unusual, and is characterized by large amounts of Nb, reaching values as high as 6 wt % Nb<sub>2</sub>O<sub>5</sub> (Table 2, Nos 2 and 3).

Substitution of niobium into rutile cannot occur directly for titanium due to differences in ionic charge. However, iron is also enriched in the rutile (cf. Table 2), which could provide a means of charge compensation. Nb- and Fe-contents of several analyzed rutile grains are illustrated in figure 3. The fact that the data points lie almost exactly on a 1:1 line suggests a coupled substitution of the following type:



and all iron has been recalculated to Fe<sub>2</sub>O<sub>3</sub> accordingly.

Analytical totals for several rutile analyses are low (98–99 wt %), even with iron recalculated to Fe<sub>2</sub>O<sub>3</sub>. Qualitative energy dispersive analyses indicate the presence of small amounts of tantalum (<~ 0.5 wt %) which could account for this deficiency.

### Langø

*Pyriboles*. The term 'pyribole' was introduced by Berthelsen (1960) to describe mafic rocks metamorphosed at high-grade to the assemblage orthopyroxene + clinopyroxene + hornblende. On Langø, a variety of pyriboles are present, ranging from those containing Cpx + Opx + Hbl to types with abundant biotite or garnet. Plagioclase is abundant in all types, but quartz is typically absent, except in biotite-rich pyriboles where it may constitute up to 15 volume per cent of a given sample. Accessory apatite, sulfide and zircon occur in most samples, and green pleonaste spinel is found in garnet pyriboles.

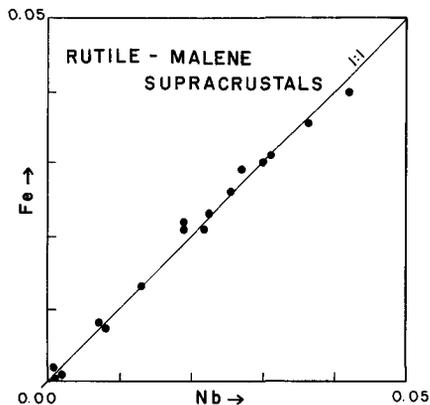


Fig. 3. Formula proportions Nb and Fe (based on 1 cation and 2 oxygens) in rutile from Malene 'cordierite-anthophyllite' rocks (CAR).

Various combinations of homogenous ilmenite, lamellar ilmenite-hematite intergrowths, and magnetite occur in pyriboites. These typically form polygonal grains up to  $\sim 1$  mm across, which occur interstitial to mafic minerals and plagioclase, and as inclusions in the mafic minerals. Rutile is a rare mineral in pyriboites, and where it does occur, the mafic silicates tend to be Mg-rich. Ilmenite + rutile were noted in one sample.

The composition of ilmenite in pyriboites is highly variable. MgO- and MnO-contents range from  $\sim 0.5$ – $1.2$  and  $\sim 0.4$ – $3.3$  wt % respectively. The concentrations of  $\text{Al}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ , ZnO,  $\text{ZrO}_2$  and  $\text{Nb}_2\text{O}_5$  are typically very low. Calculated hematite contents range from  $\sim 2$ – $11$  mole per cent, with the highest amounts found in ilmenite containing hematite lamellae.

Hematite lamellae in ilmenite contain 7–11 wt %  $\text{TiO}_2$ , but are otherwise relatively pure. No separate hematite grains were observed. Magnetite contains small amounts of  $\text{Al}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  ( $< 0.50$  wt % each), and is exceedingly Ti-poor. Recalculated magnetite compositions yield  $< 1$  mole per cent ulvospinel in all cases. Rutile is typically pure  $\text{TiO}_2$ , but may contain up to  $\sim 0.4$  wt % each  $\text{Cr}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ , and up to  $\sim 0.8$  wt %  $\text{Nb}_2\text{O}_5$ . Representative analyses of Fe-Ti oxides in pyriboites are listed in Table 2 (Nos 4 and 5) and Table 3 (Nos 1–4).

*Orthopyroxene gneiss.* These are probably the higher-grade equivalents of CAR, and contain various combinations of the minerals  $\text{Opx} \pm \text{Cord} \pm \text{Garn} \pm \text{Sill}$ , together with abundant quartz, plagioclase and biotite. Accessory apatite, sulfide and zircon occur in most samples.

Ilmenite is the most abundant Fe-Ti oxide, and has compositions similar to those in CAR. Rutile also occurs in some samples, with the highest measured  $\text{Nb}_2\text{O}_5$ -content being  $\sim 0.6$  wt % (Table 2, No. 4).

*Biotite Gneiss.* A series of leucocratic gneisses containing the assemblage  $\text{Bio} + \text{Qtz} + \text{Plag} + \text{Kfsp} \pm \text{Garn} \pm \text{Cord} \pm \text{Sill}$  are probably the high-grade equivalents of the semipelitic to pelitic schists described above for the Godthåbsfjord–Ameralik region. Types with cordierite-garnet-sillimanite only contain ilmenite, whereas those without aluminous minerals (i.e. biotite gneiss *sensu stricto*) contain ilmenite or ilmenite + hematite.

Table 3. Microprobe analyses of ilmenite, hematite and magnetite (Langø)

	1	2	3	4	5	6	7
SiO <sub>2</sub>	0.00	0.00	0.06	0.02	0.01	0.05	0.03
TiO <sub>2</sub>	48.51	8.55	0.14	50.28	49.43	12.45	49.43
Al <sub>2</sub> O <sub>3</sub>	0.00	0.00	0.11	0.00	0.00	0.02	0.00
Cr <sub>2</sub> O <sub>3</sub>	0.04	0.24	0.49	0.07	0.05	0.05	0.49
Fe <sub>2</sub> O <sub>3</sub> *	8.61	83.75	67.80	4.70	6.24	77.07	6.36
FeO	40.58	7.58	30.84	41.15	43.04	10.79	40.69
MgO	1.14	0.04	0.05	0.50	0.31	0.08	0.97
ZnO	0.00	0.00	0.16	0.04	0.00	0.00	0.22
MnO	1.01	0.04	0.00	3.09	0.87	0.26	1.82
ZrO <sub>2</sub>	0.03	0.06	0.03	0.01	0.00	0.05	0.00
Nb <sub>2</sub> O <sub>5</sub>	0.06	0.00	0.00	0.00	0.00	0.00	0.00
Total	99.98	100.26	99.68	99.86	99.95	100.82	100.01
FORMULA PROPORTIONS BASED ON	2 CATIONS AND 3 OXYGENS (Ilmenite-Hematite)		3 CATIONS AND 4 OXYGENS (Magnetite)				
Si	0.000	0.000	0.002	0.000	0.000	0.001	0.001
Ti	0.916	0.168	0.004	0.954	0.940	0.243	0.935
Al	0.000	0.000	0.005	0.000	0.000	0.001	0.000
Cr	0.001	0.005	0.015	0.001	0.001	0.001	0.000
Fe <sup>3+</sup>	0.157	1.642	0.994	0.088	0.120	1.498	0.120
Fe <sup>2+</sup>	0.857	0.166	1.967	0.869	0.909	0.241	0.856
Mg	0.043	0.001	0.003	0.019	0.012	0.003	0.036
Zn	0.000	0.000	0.005	0.001	0.000	0.000	0.004
Mn	0.022	0.001	0.000	0.066	0.019	0.006	0.039
Zr	0.004	0.008	0.005	0.002	0.000	0.006	0.000
Nb	0.001	0.000	0.000	0.000	0.000	0.000	0.000
% Hem	8.7	83.2	99.6†	4.9	6.1	76.3	6.6
% Ilm	91.3	16.8	0.4†	95.1	93.9	23.7	93.4
1. Ilmenite } 2. Hematite } 3. Magnetite } 4. Ilmenite, OGA-25D, Pyriboleite	OGA-24E, Pyriboleite		5. Ilmenite } 6. Hematite } 7. Ilmenite, OGA-33A-1, Calc-silicate				
† % Magnetite (Fe <sub>3</sub> O <sub>4</sub> ) and ulvospinel (Fe <sub>2</sub> TiO <sub>4</sub> )	* Total iron analyzed as FeO; Fe <sub>2</sub> O <sub>3</sub> recalculated from stoichiometry and end-member assignments.						

Ilmenite in the biotite gneisses contain ~ 0.7–0.9 wt % MnO and ~ 0.3–0.7 wt % MgO, but only trace quantities of Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, ZnO, ZrO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub>. Calculated hematite contents range from 6–9 mole per cent.

Hematite contains from 11–13 wt % TiO<sub>2</sub> and small amounts of MnO (< 0.4 wt %). Compositions of an ilmenite-hematite pair are listed in Table 3 (Nos 5 & 6).

*Calc-silicate gneiss.* A rare lithology on Langø contains the assemblage quartz + plagioclase + scapolite + diopside ± hornblende + sphene ± grossular. Ilmenite is the only Fe-Ti oxide in these rocks, and forms elongated to stubby plates up to ~ 1 mm long. The analysis listed in Table 3 (No. 7) is typical of the compositions found, and show that ilmenite contains high MnO (1.5–5.1 wt %), low MgO (0.5–1.0 wt %), ZnO (0.2–0.3 wt %) and Cr<sub>2</sub>O<sub>3</sub> (0.4–0.6 wt %), but no detectable ZrO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub>. Calculated hematite contents range from 3–6 mole per cent.

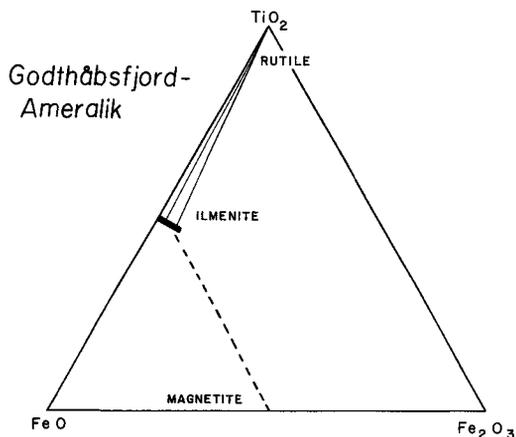


Fig. 4. Summary of Fe-Ti oxide assemblages in Malene supracrustal rocks from the Godthåbsfjord–Ameralik region.

## Discussion

### *Fe-Ti oxide assemblages*

Prograde regional metamorphism of the Malene supracrustals at *c.* 2800 Ma ranged from middle amphibolite to granulite grade, and was followed by retrogressive metamorphism ranging from amphibolite to greenschist grade. Despite complexities associated with such polymetamorphism, the observed Fe-Ti oxide assemblages can be ascribed with some certainty to the main stage prograde metamorphic event. This conclusion is based on petrographic study of over three thousand samples.

Fe-Ti oxide assemblages in Malene supracrustals from the Godthåbsfjord–Ameralik region are summarized in figure 4, which shows the limited compositional range for ilmenite, and tie-lines connecting coexisting ilmenite-rutile pairs. In Malene amphibolites, only ilmenites is found (with or without sphene), whereas in metasedimentary lithologies, ilmenite, rutile or both are present. These observations suggest that variations in rock composition, rather than variable  $f_{O_2}$ , provided the dominant control on oxide parageneses during regional metamorphism of the supracrustal rocks. Moreover,  $f_{O_2}$  appears to have been uniformly 'low' ( $< \sim N-NO$ ), otherwise more oxidized assemblages containing hematite or rutile + magnetite would have formed. The low  $Fe_2O_3$ -content of the ilmenite (1–6 mole per cent) is also consistent with this conclusion.

Note that on figure 4, a dashed line has been drawn between ilmenite and magnetite. On Simiútat, a small island group west of Buksefjorden, magnetite has been identified in complex garnet corona structures in certain CAR. This occurrence has not been studied in detail, but the texture of the samples suggests that this magnetite formed during the development of the coronas, and is probably a result of retrograde metamorphism. However, as pointed out by Rumble (1976), a slight increase in Fe/Ti could convert an ilmenite  $\pm$  rutile assemblage to one containing ilmenite + magnetite, so that the conclusions reached here regarding low  $f_{O_2}$  need not be modified.

Oxide assemblages observed on Langø are summarized in figure 5. Ilmenite occurs in all lithologies, whereas magnetite is largely restricted to pyriboites. Hematite, commonly as lamellae in ilmenite, is found in pyriboites and in a few biotite gneisses. These relationships

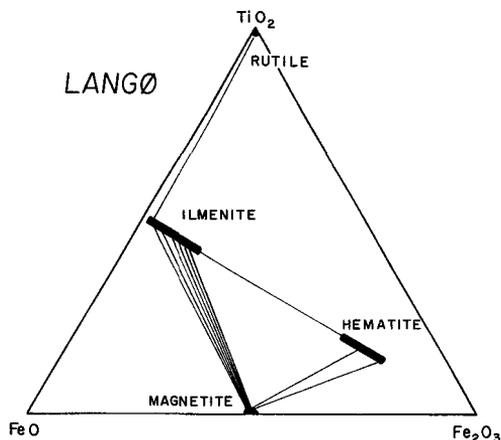


Fig. 5. Summary of Fe-Ti oxide assemblages in supracrustal gneisses on Langø.

suggest that bulk composition in part controlled oxide parageneses. The relatively large compositional range of ilmenite, and the occurrence of ilmenite-magnetite, hematite-magnetite, and ilmenite-hematite pairs suggest equilibration over a modest range of  $f_{O_2}$ . However, the regular orientations of tie lines indicates equilibration at similar T- $f_{O_2}$  conditions for all oxides.

It is important to emphasize that the granulite-grade gneisses on Langø contain hematite and magnetite, and ilmenite with a higher  $Fe_2O_3$ -content than found in samples from amphibolite-grade supracrustals from the Godthåbsfjord–Ameralik region. This suggests slightly higher  $f_{O_2}$  during granulite-grade vs. amphibolite-grade metamorphism. A general discussion of the various mechanisms that could control or buffer  $f_{O_2}$  during metamorphism is clearly beyond the scope of this report. However, it is possible that high temperature dissociation of  $H_2O$  in the fluid phase to  $H_2$  and  $O_2$ , with subsequent preferential diffusive loss of hydrogen, could result in a more oxidizing environment under granulite grade conditions. Nevertheless, the principal point here is that the results of this study do not support the contention that granulite-grade metamorphism occurs under more reducing conditions than amphibolite-grade metamorphism. Additional study is needed to investigate this problem, particularly in regard to any uncertainties related to polymetamorphism and the role of fluids in high-grade metamorphism.

### *Niobian rutile*

The occurrence of Nb-rich rutile in CAR is interesting and merits further discussion. One possible explanation is that the high Nb-content is simply a consequence of the fact that during metamorphism rutile concentrates that element in the same way that staurolite concentrates Zn or garnet Mn. Although such an effect is probably important in some samples, petrographic study indicates no correlation between modal abundance of rutile and Nb-content. In addition, CAR contain an inordinately large amount of zircon, up to ~ 1 modal per cent. These observations point towards an absolute enrichment of Nb and Zr in CAR, but the exact magnitude of this enrichment must await detailed geochemical study.

CAR have been interpreted as 'restites' from partial melting processes (e.g. Grant, 1968;

Lal & Moorhouse, 1969; Gribble, 1970). Although an enrichment in refractory elements such as Nb and Zr would be consistent with this hypothesis, the inferred conditions of metamorphism and absence of field evidence for melting in CAR throughout the Godthåbsfjord–Ameralik region would preclude the partial melting model (cf. Dymek, 1978).

Vallance (1967) has suggested that the protolith of CAR represents the residue from hydrothermal alteration of mafic volcanic rock. In West Greenland, CAR are commonly associated with amphibolites, and it is possible that some type of alteration process prior to metamorphism caused enrichment in Nb and Zr, which was followed by reworking in a sedimentary environment. This hypothesis is not inconsistent with the field occurrence, and may be the most plausible explanation.

An alternative to models involving alteration is that the protolith of CAR was actually a sediment of unusual composition, and the rutile and zircon constitute part of a reworked detrital component, with the composition of the rutile inherited from its source material. Natural examples of Nb-rich rutile are rare, but are known to occur in alkalic igneous rocks and kimberlites (cf. Deans, 1966; Clark & Mitchell, 1975; Dawson & Smith, 1977). Although it is premature to suggest that rutile and zircon in CAR constitute evidence for alkalic igneous activity in the Archaean craton of West Greenland, it will be interesting to determine whether high Nb and Zr are unique to the CAR in the Godthåbsfjord–Ameralik region, or are characteristic of CAR in general.

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