An unusual titanomagnetite replacing spinel

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In a recent investigation of the Fe-Ti-oxides in the Koster dyke swarm, SW Sweden, one of the dykes from sector I (41197) was omitted because the cubic Fe-Ti-oxides in this dyke were found to deviate from those in all the other dykes.

The Fe-Ti-oxides in 41197 consist partly of ilmenite as free grains, and partly of titanomagnetite with sandwich as well as trellis oxyexsolution lamellae of ilmenite. Some of the titanomagnetite grains have a core of grey spinel, and there are also grains consisting mainly of spinel, but with the spinel clearly being replaced by titanomagnetite.

Electron microprobe analyses of these Fe-Ti-oxides have revealed that the ilmenite as free grains has a composition quite similar to that in the other Koster dykes from sector I. Apart from a small content of Cr, the ilmenite lamellae in the titanomagne-tite grains also show good agreement with the other Koster dykes from sector I, but there are small but significant differences between the ilmenite lamellae from grain to grain within the sample.

The titanomagnetite groundmass also shows small but significant differences be-tween different grains. The composition of the titanomagnetite varies from ferrofer-rites to ferrochromferrites.

The grey spinel varies from ferrospinel over ferrochromspinel to ferroferrichromspinel. Except for the spinel grain with only incipient replacement by titanomagne-tite, the spinels have a rim which is richer in Mg, Al and Zn and poorer in Cr and Fe⁺⁺⁺ than the core. Temperature and fO_2 of coexisting pairs of ilmenite and titanomagnetite varies

Temperature and fO_2 of coexisting pairs of ilmenite and titanomagnetite varies from 991°C, $fO_2 \ 10^{-12.9}$, to 1104° C, $fO_2 \ 10^{-11.2}$.

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Introduction

The petrology, geochemistry and structural geology of the Koster dyke swarm, SW Sweden, has been thoroughly dealt with by Hageskov (1984, 1985, 1987). The Fe-Ti-oxides in the Koster dykes were the object of a separate study by Jensen (1990). In this investigation, however, one of the dykes (41197) from sector I (Hageskov 1984) was omitted, because the cubic Fe-Ti-oxides in this dyke were found to deviate from those in all the other dykes. The dyke in question is an olivine-porhyritic dyke; Hageskov (1987) mentions that about 5–10% of the Koster dykes are porphyritic, and he omitted these from his geochemical studies.

The Fe-Ti-oxides in 41197 consist of ilmenite as free grains and titanomagnetite with sandwich as well as trellis oxyexsolution lamellae of ilmenite; the titanomagnetite grains sometimes have a core of grey spinel.

During the investigation by Jensen (1990) electron microprobe analyses of one such spinel core, the ilmenite lamellae and titanomagnetite groundmass in the titanomagnetite surrounding the spinel core, ilmenite lamellae, and titanomagnetite groundmass in neighbouring titanomagnetite grains without spinel cores, and ilmenite as free grains were carried out, but not published. The grain with spinel core is referred to as grain 0.

Further investigation has shown that although only some titanomagnetite grains have a core of spinel, there are also grains having a texture that clearly shows that titanomagnetite has replaced spinel. New electron microprobe analyses have been carried out on the spinel, ilmenite lamellae and titanomagnetite groundmass of four such grains, in the following referred to as grains 1, 2, 3 and 4.

Grain 0 is shown in fig. 1; grain 1 with only incipient replacement of spinel by titanomagnetite is shown in fig. 2, and grain 4 with more advanced replacement of spinel by titanomagnetite is shown in fig. 3.

In grain 1 the spinel seems homogeneous from core to rim, whereas all the other grains have rims that are



Fig. 1. Grain 0. Oil immersion. \times 230. Titanomagnetite grain with spinel core.

more or less darker than the cores. However, only for grains 0 and 2 are the electron microprobe analyses differentiated between core and rim, for the other grains only analyses of cores were carried out.

Analytical results

The electron microprobe analyses (WDS) were carried out with a Jeol Superprobe JCXA 733 with 15.0 kV accelerating voltage and a sample current of 20.0 nA using olivine, corundum, rutile, V₂O₃, Cr₂O₃, MnTiO₃, hematite, Ni and ZnO as standards. Total iron was distributed between ferrous and ferric iron using the method suggested by Finger (1972).

The results for Fe-Ti-oxides are shown in tables 1 to 4 and for olivine in table 5.

Spinel analyses

The results of the electron microprobe analyses of spinel are shown in table 1. It can be seen that the spinel in grain 0, core as well as rim, is significantly poorer in Mg than all the other grains. Grain 0 is lower in Al than grains 1, 3 and 4, and the rim of grain 0 is lower than the rim of grain 2, but the core of grain 2 is not significantly different from the core of grain 0. The rim of grain 2 is low in Ti, but otherwise there are no significant differences in Ti. TiO₂ versus Mg/Mg + Fe⁺⁺ is shown in fig. 4.

Grain 0 is higher in V than grains 1, 2 and 4, but is not significantly different from grain 3. It is higher in Cr than grains 1, 3 and 4, and the rim of grain 0 is higher than the rim of grain 2, but core of grain 0 is not significantly different from core of grain 2.

There are no significant differences in Mn.

Grain 0 is higher in Fe^{++} than all the other grains, and higher in Fe^{+++} than grain 3, but is not significantly different from the other grains as regards Fe^{+++} .

There are no significant differences in Ni.

Grain 0 is higher in Zn than grains 1 and 3, but is not significantly different from grains 2 and 4.

The rims in grains 0 and 2 are richer in Mg, Al and Zn and poorer in Cr and Fe^{+++} than the cores.

According to the terminology of Zhelyazkova-Panayotova (1971) grains 1 and 4 and the cores of grains 0 and 2 are ferroferrichromspinels, grain 3 and the rim of grain 0 are ferrochromspinels, and the rim of grain 2 is ferrospinel.

Ilmenite analyses

The results of the electron microprobe analyses of ilmenite are shown in table 2. The table comprises analyses of ilmenite lamellae in grains 1, 2, 3 and 4 as well as analyses of ilmenite as free grains. However, the second column labelled "Lamellae Grain 0" presents averages for ilmenite lamellae both in grain 0 and in neighbouring titanomagnetite grains without a spinel core.

It is clearly seen from the table that there are no significant differences between these ilmenite lamellae ("Grain 0") and ilmenite occurring as free grains. Therefore, in the following, comparisons are made only between the grains 1, 2, 3 and 4 and ilmenite as free grains.

No variations are found for AI, V, Ni and Zn, which if present at all occur only in very small amounts.

Ilmenite lamellae in all four grains are higher in Mg than ilmenite as free grains, and Mg varies from 0.019 in grain 4 to 0.057 in grain 1 (all figures for contents of elements are for cations based on 32 O).

Likewise Cr is higher in the lamellae in all four grains

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Fig. 2. Grain 1. Oil immersion. \times 230. Spinel grain with incipient replacement by titanomagnetite.

than in ilmenite as free grains, and Cr varies from 0.007 in grain 2 to 0.028 in grain 1.

Lamellae in grain 2 are higher in Ti than ilmenite as free grains, whereas lamellae in grain 4, because of the higher standard deviation, are only higher than free grains in the confidence level between 0.975 and 0.99. TiO_2 versus Mg/Mg + Fe⁺⁺ for ilmenite is shown in fig. 5.

Ilmenite lamellae in grain 3 are higher in Mn than ilmenite as free grains, but otherwise there are no significant differences. Mn varies from 0.016 to 0.021.

Ilmenite lamellae in grains 1 and 3 are lower in Fe⁺⁺ than ilmenite as free grains, whereas lamellae in grains 2

Fig. 3. Grain 4. Oil immersion. \times 230. Spinel grain with advanced replacement by titanomagnetite.



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Table 1.	Spinel analyses				-		
	Grain 0 Core	Grain 0 Rim	Grain 1	Grain 2 Core	Grain 2 Rim	Grain 3	Grain 4
Number of analyses	14	8	6	12	4	2	e
MgO	1.13±0.08	1.32±0.15	3.22±0.18	1.73±0.15	3.53±0.49	4.67±0.40	2.10±0.06
Al ₂ O ₃	24.24±0.52	31.11±2.75	26.41±1.01	24.68±1.35	41.94±2.06	30.16±1.48	26.35±0.81
Tio ₂	0.62±0.08	0.49±0.21	0.72±0.29	0.65±0.15	0.19±0.21	0.66±0.16	0.67±0.24
V ₂ 0 ₃	0.80±0.12	<u>,0.77±0.13</u>	0.53±0.08	0.47±0.13	0.35±0.09	0.90±0.07	0.54±0.12
Cr2O3	25.91±0.61	20.97±1.83	24.40±0.72	25.61±1.13	13.88±1.42	23.41±0.98	24.54±0.52
MnO	0.36±0.17	0.40±0.17	0.52±0.27	0.35±0.20	0.42±0.02	0.50±0.18	0.63±0.21
FeO	33.53±0.99	34.01±1.19	30.71±0.49	32.18±0.54	31.25±0.92	28.66±0.40	31.59±1.03
Fe ₂ O ₃	12.48±0.59	9.76±1.95	12.16±0.77	12.35±0.76	5.99±0.76	9.55±0.79	11.71±0.92
Nio	0.02±0.02	0.01±0.01	0.04±0.09	0.01±0.00	0.01±0.00	0.15±0.18	0.01±0.00
ZnO	1.36±0.40	2.11±0.16	0.17±0.26	0.93±0.40	1.51±0.28	0.67±0.32	1.03±0.72
Sum	100.45±0.67	100.95±1.16	98.88±0.48	98.96±0.74	99.07±0.50	99.33±0.72	99.17±0.19
Cations base	4 on 32 0						
Mg	0.446±0.032	0.502±0.057	1.258±0.071	0.688±0.059	1.287±0.179	1.770±0.151	0.825±0.024
A	7.565±0.162	9.372±0.828	8.152±0.312	7.757±0.425	12.078±0.593	9.033±0.443	8.184±0.252
F	0.124±0.016	0.094±0.040	0.142±0.057	0.130±0.030	0.035±0.038	0.127±0.031	0.133±0.048
>	0.170±0.025	0.158±0.026	0.112±0.017	0.101±0.027	0.069±0.018	0.183±0.014	0.114±0.025
ö	5.426±0.127	4.239 <u>+</u> 0.370	5.055±0.150	5.402±0.239	2.682±0.275	4.704±0.197	5.114±0.108
Mn	0.081±0.038	0.086±0.037	0.115±0.060	0.079±0.045	0.087±0.004	0.107±0.038	0.141±0.048
Fe [±]	7.429±0.220	7.272±0.255	6.729±0.107	7.180±0.120	6.387±0.188	6.093±0.086	6.964±0.226
Fe**	2.488±0.118	1.877±0.375	2.398±0.151	2.480±0.152	1.101±0.140	1.827±0.151	2.322±0.182
ïZ	0.005±0.005	0.002±0.002	0.008±0.019	0.002±0.000	0.001±0.000	0.031±0.037	0.002±0.000
ភ	0.266±0.078	0.398±0.031	0.033±0.050	0.183±0.079	0.273±0.050	0.125±0.060	0.201±0,139
Sum	24.000±0.001	24.000 <u>4</u> 0.001	24.002±0.003	24.002±0.003	24.000±0.001	24.000±0.001	24.000±0.001

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Table 2. Ilmenite	analyses					
	Free grains	Lamellae Grain 0	Lamellae Grain 1	Lamellae Grain 2	Lamellae Grain 3	Lamellae Grain 4
Number of analyses	œ	14	4	9	7	3
MgO	0.12±0.10	0.18±0.04	1.53±0.11	0.64±0.09	1.33±0.34	0.52±0.30
Al ₂ O ₃	0.06±0.10	0.01±0.01	0.07±0.07	0.10±0.10	0.62±0.77	0.01±0.00
TIO2	50.26±0.53	51.11±0.29	52.12±1.23	52.28±0.52	51.61±1.13	52.48 <u>+</u> 2.11
V ₂ O ₃	0.22±0.03	0.23±0.10	0.17±0.10	0.18±0.10	0.18±0.14	0.23±0.09
Cr ₂ O ₃	0.10±0.05	0.27±0.14	1.43±0.26	0.34±0.20	1.12±0.90	0.46±0.16
MnO	0.63±0.05	0.64±0.14	0.81±0.17	0.76±0.21	1.01±0.12	0.81±0.13
FeO	44.34±0.60	44.99±0.30	43.15±1.13	44.82±0.55	42.80±1.49	44.68±0.41
Fe ₂ O ₃	3.37±0.48	2.69±0.57	1.02±0.70	0.64±0.70	1.29±0.92	1.06±1.07
NiO	0.03±0.02	0.03±0.04	0.13±0.14	0.05±0.11	0.07±0.15	0.01±0.00
ZnO	n.a.	n.a.	0.01±0.00	0.01±0.00	0.18±0.29	0.01±0.00
Sum	99.13±0.63	100.15±0.35	100.44±1.31	99.82±0.74	100.21±1.21	100.27±1.50
Cations based on 32 (0					
Mg	0.005±0.004	0.007±0.002	0.057±0.004	0.024±0.003	0.049±0.013	0.019±0.011
AI	0.002±0.003	0.000±0.001	0.002±0.002	0.003±0.003	0.018±0.022	0.000±0.000
Ē	0.964±0.006	0.969±0.005	0.974±0.011	600 ⁻ 0∓066 ⁻ 0	0.966±0.027	0.991±0.023
>	0.005±0.001	0.005±0.002	0.004±0.002	0.004±0.002	0.004±0.002	0.005±0.002
Ċ	0.002±0.001	0.005±0.003	0.028±0.005	0.007±0.004	0.022±0.017	0.009±0.003
Mn	0.013±0.001	0.014±0.003	0.017±0.004	0.016±0.005	0.021±0.003	0.017±0.003
Fe**	0.945±0.009	0.949±0.006	0.897±0.012	0.944±0.008	0.891±0.034	0.939±0.012
Fe***	0.065±0.009	0.051±0.011	0.019±0.013	0.012~0.013	0.024±0.017	0.020±0.021
Ni	0.001±0.001	0.001±0.001	0.003±0.003	0.001±0.002	0.001±0.003	000.0±0000.0
Zn			0.000±0.000	000 ⁻⁰⁰⁰⁰⁻⁰	0.003±0.005	000.0±000.0
Sum	2.002±0.003	2.001±0.002	2.001±0.002	2.001±0.002	1.999±0.002	2.000±0.001
Ti/Fe***	14.83	19.00	51.26	82.50	40.25	49.55
n.a. = not analysed for		,				

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Fig. 4. TiO₂ versus Mg/Mg + Fe⁺⁺ for spinel analyses.

and 4 are similar to free grains. Fe⁺⁺ varies from 0.891 to 0.944.

In all four grains ilmenite lamellae are lower in Fe^{+++} than ilmenite as free grains. Fe^{+++} varies from 0.012 to 0.024.

Analyses of the titanomagnetite groundmass

The results of the electron microprobe analyses of titanomagnetite groundmass are shown in table 3. The first column labelled "Grain 0" is the average of the groundmass in Grain 0 and groundmass of neighbouring titanomagnetite grains without a spinel core.

Mg varies between 0.029 and 0.399; grains 1, 3 and 4 are higher in Mg than "Grain 0", whereas grain 2 is not significantly different from "Grain 0".

Al varies between 1.023 and 1.834; grain 3 is higher and grain 2 is lower in Al than "Grain 0", whereas grains 1 and 4 are not significantly different from "Grain 0".



Fig. 5. TiO₂ versus $Mg/Mg + Fe^{++}$ for ilmenite analyses.

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Fig. 6. TiO₂ versus Mg/Mg + Fe⁺⁺ for analyses of titanomagnetite groundmass.

Ti varies between 0.457 and 1.354; grain 3 is higher in Ti than "Grain 0", whereas grains 1, 2 and 4 are not significantly different from "Grain 0". TiO₂ versus Mg/Mg + Fe⁺⁺ for the titanomagnetite groundmass is shown in fig. 6.

V varies between 0.286 and 0.607; grains 1, 2 and 4 are lower in V than "Grain 0", but grain 3 is not significantly different.

Cr varies between 1.824 and 4.007; grains 1, 3 and 4 are higher and grain 2 is lower in Cr than "Grain 0".

Mn varies between 0.041 and 0.148; grains 1, 3 and 4 are higher in Mn than "Grain 0", whereas grain 2 is not significantly different.

 Fe^{++} varies between 8.038 and 8.778; grain 3 is higher and grain 1 is lower in Fe^{++} than "Grain 0", whereas grains 2 and 4 are not significantly different.

Fe⁺⁺⁺ varies between 6.858 and 11.782; grains 1, 3 and 4 are lower and grain 2 is higher in Fe⁺⁺⁺ than "Grain 0".

There are no significant differences in Ni and Zn.

According to the terminology of Zhelyazkova-Panayotova (1971) grains 1, 3 and 4 are ferrochromferrites, whereas grains 0 and 2 are ferroferrites.



Fig. 7. TiO₂ versus $Mg/Mg + Fe^{++}$ for the calculated composition of the original titanomagnetite.

Table 3. Analyse:	s of titanomagnetite	groundmass			
	Grain 0	Grain 1	Grain 2	Grain 3	Grain 4
Number of analyses	21	Ø	Ø	9	3
MgO	0.0±0.0	0.59±0.15	0.06±0.10	0.91±0.12	0.36±0.05
Al ₂ O ₃	4.35±0.36	4.56±0.73	2.86±0.36	5.30±0.31	4.64±0.30
TIO2	2.07±0.51	2.22±0.71	2.25±0.73	6.13±0.90	2.90±1.07
V ₂ O ₃	2.32±0.26	1.20±0.12	1.42±0.10	2.58±0.27	1.49±0.09
Cr ₂ O ₃	11.12±0.58	17.03±0.89	7.60±0.33	17.20±0.49	13.85±0.06
MnO	0.16±0.06	0.59±0.17	0.34±0.34	0.50±0.20	0.35±0.11
FeO	34.19±0.56	32.30±0.63	32.94±0.54	35.74±1.15	33.93±1.55
Fe ₂ O ₃	47.29±1.11	40.71±1.47	51.58±1.52	31.03±0.96	42.66±0.88
NiO	0.04±0.07	0.12±0.18	0.13±0.18	0.07±0.14	0.01±0.00
ZnO	n.a.	0.09±0.17	0.01±0.00	0.17±0.27	0.01±0.00
Sum	101.63±0.68	99.41±0.75	99.19±0.76	99.63±1.08	100.20 <u>+</u> 2.20
Cations based on 32	0				
Mg	0.039±0.039	0.261±0.066	0.029±0.046	0.399±0.053	0.158±0.021
AI	1.504±0.125	1.599±0.248	1.023±0.129	1.834±0.108	1.618±0.105
Τi	0.457±0.113	0.497±0.159	0.514±0.166	1.354±0.192	0.645±0.224
٧	0.546±0.062	0.286±0.029	0.345±0.024	0.607±0.064	0.354±0.021
ŗ	2.579±0.134	4.007±0.209	1.824±0.078	3.994±0.113	3.239±0.014
Mn	0.041±0.014	0.148±0.043	0.088±0.088	0.124±0.049	0.087±0.024
Fe⁺⁺	8.388±0.137	8.038±0.152	8.362±0.137	8.778±0.216	8.395±0.200
Fe***	10.438±0.247	9.116±0.320	11.782±0.347	6.858±0.212	9.499±0.196
ïZ	0.009±0.016	0.029±0.043	0.031±0.044	0.016±0.034	0.002±0.000
Zn		0.020±0.038	0.002±0.000	0.037±0.058	0.002±0.000
Sum	24.001±0.002	24.001±0.002	24.000±0.001	24.001±0.002	23.999±0.002
Ti/Fe***	0.044	0.055	0.044	0.197	0.068
n.a. = not analysed for					

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Table 4. Calcula	ted composition of orig	inal titanomagnetite				
	Grain 0	Grain 1	Grain 2	Grain 3	Grain 4	
Number of	21	6	8	9	3	_
MgO	0.15	1.10	0.38	1.09	0.44	_
Al ₂ O ₃	2.16	2.37	1.51	2.87	2.33	
TIO2	27.20	27.70	27.83	28.32	28.39	_
V ₂ O ₃	1.28	0.68	0.81	1.37	0.88	
Cr ₂ O ₃	5.65	9.38	4.07	8.85	7.20	_
MnO	0.42	0.71	0.54	0.75	0.58	_
FeO	56.23	54.79	55.94	55.37	56.65	
Fe ₂ O ₃	6.88	3.09	8.80	1.09	3.51	-
NiO	0.03	0.14	0.10	0.11	0.01	
ZnO	n.a.	0.04	0.01	0.19	0.01	_
Sum	100.00	100.00	99.99	100.01	100.00	_
Cations based on 32	0				в	
Mg	0.064	0.480	0.168	0.472	0.192	
AI	0.752	0.816	0.528	0.984	0.808	
Ti	6.038	6.088	6.193	6.208	6.273	
٧	0.304	0.160	0.192	0.320	0.208	
Ċ	1.320	2.168	0.952	2.040	1.672	
Mn	0.104	0.176	0.136	0.184	0.144	
Fe**	13.883	13.392	13.843	13.496	13.922	
Fe***	1.527	0.680	1.960	0.240	0.776	
ïZ	0.008	0.032	0.024	0.016	0.002	_
Zn		0.008	0.002	0.040	0.002	_
Sum	24.000	24.000	23.998	24.000	23.999	_
n.a. = not analysed for			-			2

Table 5.Olivine analyses

Column I:	Large olivine phenocrysts
Column II:	Small olivine phenocrysts
Column III:	Olivine groundmass grains

	1	11	111
Number of analyses	5	4	5
SiO ₂	38.78±0.11	37.29±0.50	36.00±0.42
TiO ₂	0.01±0.00	0.01±0.00	0.08±0.10
FeO	20.38±0.71	30.24 <u>+</u> 2.62	36.49±0.43
MnO	0.20±0.13	0.26±0.10	0.37±0.08
MgO	40.26±0.57	32.63±2.12	27.31±0.30
CaO	0.06±0.07	0.07±0.12	0.08±0.11
Cr ₂ O ₃	0.04±0.05	0.01±0.00	0.03±0.05
NiO	0.21±0.19	0.14±0.15	0.06±0.10
Sum	99.94±0.28	100.65±0.84	100.42±0.48
Cations based on sum	of 3:	······	
Si	1.000±0.002	1.002±0.005	1.002±0.009
Ti	0.000±0.000	0.000±0.000	0.002±0.002
Fe ⁺⁺	0.440±0.016	0.680±0.066	0.850±0.015
Mn	0.004±0.003	0.006±0.003	0.009±0.002
Mg	1.548±0.020	1.307±0.072	1.133±0.007
Са	0.001±0.002	0.002±0.003	0.002±0.003
Cr	0.001±0.001	0.000±0.000	0.001±0.001
Ni	0.004±0.004	0.003±0.003	0.001±0.003
Oxygen	4.001±0.002	4.002±0.005	4.004±0.010
Mg/Mg+Fe	0.779±0.008	0.657±0.034	0.572±0.005

Comparisons between analyses of spinel, ilmenite and titanomagnetite

There is a positive correlation between spinel and titanomagnetite groundmass for Mg, V and Fe⁺⁺⁺, and a negative correlation for Cr. There is also a positive correlation between spinel, ilmenite lamellae and titanomagnetite groundmass for total Fe.

There is a positive correlation between spinel and ilmenite lamellae for Mg, Al and Fe⁺⁺, and possibly a negative correlation for Cr.

There is a positive correlation between titanomagnetite groundmass and ilmenite lamellae for Mg and Cr.

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Table	6.
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	41	197	L Differ Kost	east entiated er Dyke ctor I	Mean Dy Sec	Koster /ke tor I
SiO ₂		46.770		47.85	4	8.11±0.40
TiO2		1.723		1.97		2.52±0.41
Al ₂ O ₃		14.140		15.63	14	4.41±0.99
Fe ₂ O ₃	·	1.917		1.51	:	2.46±0.57
FeO		11.620		11.57	1:	2.17±0.76
MnO		0.202		0.19		0.21±0.02
MgO	· .	10.770		8.01		6.88±0.75
CaO		9.240		10.06	<u> </u>	9.76±0.33
Na ₂ O		2.110		2.31	2	2.27±0.44
K₂O		0.495	 	0.56		0.74±0.15
H₂O	ļ	1.133		0.76		0.85±0.35
P ₂ O ₅		0.382		0.36		0.47±0.09
Sum		100.502	 	100.78		100.85
FeO	 	13.34		12.93	14	1.39±1.03
FeO'/MgO	ļ	1.24		1.61	2	2.13±0.40
Fe ₂ O ₃ /FeO	[0.16		0.13		0.20±0.05
C.I.P.W. we	ight nor	ns	·	<u> </u>		· .
Q .	0.00	0.00	0.00	0.00	0.00	0.00
or	3.10	3.10	3.35	3.35	4.55	4.55
ab	19.10	19.10	21.10	21.10	20.75	20.75
. an	27.75	27.75	30.79	30.79	27.55	27.55
wo	6.48	6.48	6.86	6.86	7.40	7.40
en di	4.35	4.31	4.17	4.21	4.28	4,14
fs	2.13	2.17	2.69	2.65	3.12	3.26
en	8.63	8.34	8.28	8.55	12.52	11.44
fs	4.23	4.18	5.34	5.39	9.12	9.02
fo	12.74	12.98	7.44	7.21	1.96	2.88
fa OI	6.25	6.52	4.80	4.55	1.43	2.28
mt	2.03	1.85	1.61	1.77	2.64	2.04
11	2.46	2.46	2.82	2.82	3.64	3.64
ар	0.75	0.75	0.75	0.75	1.07	1.07

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Determination of the composition of the original titanomagnetite

Microscopic investigation has revealed that in all the grains the ratio of the volume of ilmenite lamellae to titanomagnetite groundmass is very close to 1:1. No visible deviation from this ratio can be detected, so the following calculation is based on the assumption that oxyexsolved ilmenite and titanomagnetite groundmass are present in equal amounts.

The cations from the electron microprobe analyses of the ilmenite lamellae have been recalculated from sum of cations 2 to sum of cations 3. Then the average of this and the cations from the microprobe analyses of the titanomagnetite groundmass was calculated. The result was calibrated to 4 oxygens with corresponding movement of Fe⁺⁺⁺ to Fe⁺⁺. The ratio of ulvöspinel to magnetite was then determined from this result.

Grain 3 is low in Fe in both ilmenite lamellae and titanomagnetite groundmass, and when calculating the original titanomagnetite of grain 3 there is not enough Fe to make Fe₂TiO₄, FeCr₂O₄, FeAl₂O₄ and FeV₂O₄ from the amounts of Ti, Cr, Al and V present. However, the deficiency is within the standard deviation of Fe⁺⁺ and Fe⁺⁺⁺. The determination of the composition of the original titanomagnetite in grain 3 is therefore based on the average values of Fe⁺⁺ and Fe⁺⁺⁺ increased with the standard deviation.

The calculated composition of the original titanomagnetite is shown in table 4, and TiO_2 versus Mg/Mg + Fe⁺⁺ in fig. 7.

Temperature and fO_2 determinations from coexisting pairs of ilmenite and titanomagnetite

Temperature and fO_2 values are based on the curve for the Akimoto model of Andersen & Lindsley (1988).

The percentage of FeTiO₃ present in the ilmenite is based on the percentage of Fe⁺⁺ present in the electron microprobe analyses of ilmenite as free grains. The percentage of Fe₂TiO₄ in the titanomagnetite is based on the percentage of Ti in the calculated composition of the original titanomagnetite.

Prior to the work of Ghiorso & Sack (1991) there existed no investigations that told how to handle Cr, Al and V when determining the ratio between Fe_2TiO_4 and Fe_3O_4 for use in determining temperature and fO_2 of coexisting pairs of ilmenite and titanomagnetite.

In the previous study (Jensen 1990) the amount of Fe_2TiO_4 was determined as 100 minus the percentage of Fe_3O_4 , which means that Cr, Al and V were calculated as equivalent to Ti.

This was done in the belief that the presence of Cr, Al and V indicates high temperature, and the higher the percentage of Fe_2TiO_4 , the higher the values for temperature obtained.

However, if the same procedure (100 minus the percentage of Fe₃O₄) is used with the Cr-, Al- and V-rich titanomagnetites analysed in this study, the corresponding values of FeTiO₃ and Fe₂TiO₄ fall outside the curves of Andersen & Lindsley (1988). Therefore in this study the percentage of Fe₂TiO₄ is based only on the percentage of Ti in the original titanomagnetite.

The result is a range in temperature from 1042°C to 1096°C and in fO₂ from $10^{-11.5}$ to $10^{-10.7}$.

Ghiorso & Sack (1991) have made a programme which in determining temperature and fO_2 of coexisting pairs of ilmenite and titanomagnetite takes Si, Ti, Al, V, Cr, Fe, Mn, Mg, Ca, Zn and Ni into consideration. Using this programme ranges of 991°C-1104°C and $10^{-12.9}$ - $10^{-11.2}$ for temperature and fO_2 respectively were obtained.

If the percentages of Fe_2TiO_4 based on the results of Jensen (1990) are also based only on the percentage of Ti, the values $1100^{\circ}C-1280^{\circ}C$ and $10^{-10}-10^{-8}$ given by Jensen (1990) are changed to $980^{\circ}C-1210^{\circ}C$ and $10^{-11}-10^{-9}$ respectively, whereas the programme of Ghiorso & Sack (1991) gives $746^{\circ}C-1021^{\circ}C$ and fO_2 $10^{-18.2}-10^{-11.5}$.

Olivine analyses

Table 5 shows electron microprobe analyses of olivine, somewhat arbitrarily classed as large phenocrysts, small phenocrysts and groundmass grains respectively.

It can be clearly seen that FeO increases and MgO decreases with decreasing grain size of the olivine. Unfortunately, however, the low content of MgO in the spinels prevents the use of the olivine-spinel geothermometer.

Whole rock analyses

Major elements

41197 has been analysed in the laboratory of the Geological Survey of Greenland by Ib Sørensen. H_2O^+ was determined by the Penfield method and Fe⁺⁺ by wet chemistry. Mg was determined by complexometric titration, Na by flame photometry, and the remaining elements were analysed by XRF on glass discs.

The results are shown in table 6 together with the

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	41197	Least Differentiated Koster Dyke Sector I	Mean Koster Dyke Sector I
Rb	15	15	24 ± 8.6
Ba	168	. 280	303 ± 116.8
Sr	139	171	162 ± 19.7
La	14	8	13 ± 4.9
Υ	35	39	51 ± 9.0
Zr	167	169	. 224 ± 40.7
Nb	10	9.6	11.6 ± 2.2
Ni	197	114	83 ± 22.2
V	242	282	331 ± 44.6
Cr	440	287	206 ± 59.7
	Zr/Nb	Zr/Y	Y/Nb
41197	16.7	4.8	3.5
Least Differentiated Koster Dyke Sector I	17.6	4.33	4.06
Mean Koster Dyke Sector I	19.3	4.4	4.4
Koster dykes Range	17-52	2.8-4.8	3.5-18.3
N-type MORB AAR	17-78	2.2-4.2	4.6-23
N-type MORB SWIR	17-64	1.8-3.6	8-22
T-type MORB AAR	8.8-15.5	3.1-4.7	1.9-4.3
T-type MORB SWIR	7.7-11.8	3.3-7.1	1.3-3.0

Table 7

AAR: American Antarctic Ridge

SWIR: Southwest Indian Ridge (le Roex et al. 1985)

values for Least Differentiated Koster Dyke and Mean Koster Dyke, Sector I, taken from Hageskov (1987). The CIPW weight norms are calculated with the ratio of Fe_2O_3/FeO found by analysis (first column) as well as with this ratio adjusted to 0.15 (second column).

41197 is considerably higher than Mean Koster Dyke in MgO and somewhat lower in SiO₂, TiO₂, CaO and K_2O .

41197 contains 8.5% olivine phenocrysts, and if the composition of these phenocrysts is deducted from the analysis of 41197, complete agreement is obtained with Least Differentiated Koster Dyke (personal information B. Hageskov). Least Differentiated Koster Dyke is the average of 41155 and 41166 (Hageskov 1987).

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Trace elements

Trace elements were analysed directly on pressed powder pellets by J. Bailey, Department of Petrology, University of Copenhagen, by X-ray fluorescence using a Phillips PW 1400 (funded by the Danish Natural Science Research Council) and the techniques of Norrish & Chappel (1977).

The results are shown in table 7 together with the values for Least Differentiated Koster Dyke and Mean Koster Dyke from Hageskov (1987). Zr/Nb, Zr/Y and Y/Nb ratios are shown not only for these dykes, but also for both N-type and T-type MORB from the American

Antarctic Ridge and the Southwest Indian Ridge (le Roex et. al. 1985).

It is seen that the differences in trace elements are less between 41197 and Least Differentiated Koster Dyke than between 41197 and Mean Koster Dyke.

Cr and Ni in 41197 are more than twice as high as in Mean Koster Dyke, whereas the value for V is only 70% of that in Mean Koster Dyke. Also Ba, Sr, Y and Zr are somewhat lower in 41197 than in Mean Koster Dyke.

Based on the ratios Zr/Nb, Zr/Y and Y/Nb, Hageskov (1987) suggested that the Koster dykes are N-type MORB. As regards 41197 however, Zr/Y and Y/Nb are in better agreement with T-type MORB than with Ntype MORB.

Conclusions

Ilmenite as free grains in 41197 has a composition quite similar to that in other Koster dykes from sector I. Apart from their small content of Cr, the ilmenite lamellae in 41197 also show good agreement with those in the other Koster dykes from sector I, but there are small but significant differences between the ilmenite lamellae in different grains within 41197.

The titanomagnetite groundmass in 41197 is strikingly richer in Cr, Al and Mn than in the other Koster dykes from sector I and generally somewhat richer in Mg and V. In the titanomagnetite groundmass there also are small but significant differences between the different grains.

Spinel rims are clearly poorer in Cr and richer in Al, Mg and Zn than spinel cores.

Haggerty (1976) describes spinel from Icelandic lavas where Cr as well as Al decrease from core to rim. This is in contrast to 41197 where Cr decreases from core to rim but Al increases. The behaviour of 41197, however, is in agreement with what Sigurdsson (1977) calls "normal" zoning involving decrease in Cr/Cr + Al from core to rim.

The zoning in 41197 seems not to be continuous but involves only an outer rim. This fact and the fact that no such rim is found in grain 1 with only incipient replacement might indicate that the rims are a result of replacement, because elements not wanted by the replacing titanomagnetite are being concentrated at the border between spinel and titanomagnetite.

Ilmenite and titanomagnetite crystallised in equilibrium at between 991°C and 1104°C and at fO_2 between $10^{-12.9}$ and $10^{-11.2}$, which is very close to the WM buffer curve. There does not seem to be any correlation between temperature and degree of replacement.

As regards whole rock analyses the deviations in major element contents and the content of Ni are obviously due to the olivine phenocrysts, and the richness in Cr is caused by the Cr-spinels.

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Dansk sammendrag

I afhandlingen om udviklingen af Fe-Ti-oxiderne i Koster dyke sværmen under amfibolitfacies metamorfose (Jensen 1990) blev en af Koster gangene fra sektor I, 41197, udeladt fordi de kubiske Fe-Ti-oxider afveg fra alle de øvrige gange. Denne gang er olivinporfyrisk, og i dette arbejde er såvel Fe-Ti-oxiderne som olivinen undersøgt ved hjælp af mikrosondeanalyser.

Fe-Ti-oxiderne i 41197 består dels af ilmenit i frie korn og dels af titanomagnetit med afblandingslameller af ilmenit. Nogle af titanomagnetitkornene har en kerne af grå spinel med en lidt mørkere rand ud mod titanomagnetiten (fig. 1), andre korn består overvejende af spinel, men det ses tydeligt at spinellen replaceres af titanomagnetit (fig. 2). Der ses også spinelkorn med mere fremskreden replacering af titanomagnetit (fig. 3).

Spinelanalyserne er vist i tabel 1. Sammensætningen varierer fra ferrospinel over ferrochromspinel til ferroferrichromspinel (Zhelyazkova-Panayotova 1971). Med undtagelse af det korn der viser den svageste replacering (fig. 2) har spinelkornene en ydre rand der er rigere på Mg, Al og Zn og fattigere på Cr og Fe⁺⁺⁺ end spinelkernen.

Ilmenitanalyserne er vist i tabel 2. De frie korn har en sammensætning der svarer fuldstændigt til ilmeniten i de øvrige Koster gange fra sektor I. Bortset fra et lille indhold af Cr viser ilmenitlamellerne også god overensstemmelse med ilmenitlamellerne i de øvrige Koster gange fra sektor I, men der er små, men signifikante forskelle mellem ilmenitlamellerne i de forskellige korn.

Analyser af titanomagnetitgrundmassen er vist i tabel 3. Her er også små, men signifikante forskelle mellem de enkelte korn. Sammensætningen af titanomagnetiten varierer fra ferroferrit til ferrochromferrit (Zhelyazkova-Panayotova 1971).

Tabel 4 viser den beregnede sammensætning af den oprindelige titanomagnetit, inden ilmenitlamellerne dannedes ved oxidation af ulvöspinel.

Tabel 5 viser olivinanalyser opdelt i store og små strøkorn samt grundmassekorn.

Tabel 6 og 7 viser bjergartsanalyser af henholdsvis

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hoved- og sporelementer. Til sammenligning er også anført værdierne for mindst differentierede Koster dyke og gennemsnitlige Koster dyke fra sektor I fra Hageskov (1987). 41197 indeholder 8,5% olivinstrøkorn, og hvis sammensætningen af disse strøkorn fratrækkes analysen af 41197 fremkommer der fuldstændig overensstemmelse med mindst differentierede Koster dyke for hovedelementerne. Den afvigende sammensætning af 41197 skyldes således olivinstrøkornene. Det høje sporelementindhold af Ni og Cr skyldes formentlig henholdsvis olivinstrøkornene og chromspinellerne.

Temperatur og ilttryk for den samtidige krystallisation af ilmenit og titanomagnetit er bestemt til 991°C-1104°C og $10^{-12.9}$ - $10^{-11.2}$.

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