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Relations between the spectral reflectance and the chemical composition in the magnetite-ulvöspinel series

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SUMMARY. Spectral reflectances and chemical compositions of twenty-eight different grains of exsolved titanomagnetite were measured. Relations between reflectance and composition were established by calculating best-fit planes (Kummell, 1879) for the reflectance at 499 and at 617 nm. These were then transformed to expressions from which the contents of Ti and Mg can be estimated. Even though these estimates are not as accurate as microprobe values, the method is still a useful tool in the study of chemical variation in exsolved titanomagnetites.

THIS paper is the second report of an investigation of the reflectance of titanomagnetites. In the first paper (Halfen, 1976) it was shown that single-phase and exsolved titanomagnetites of closely identical compositions have significantly different spectral curves.

In the present paper an investigation of the relations between spectral reflectance and chemical composition of exsolved titanomagnetites is reported. The expression 'exsolved titanomagnetite' here refers to a fine intergrowth of a magnetite-rich and a ulvöspinel-rich spinel phase.

Description of the sample. Titanomagnetites from several localities were studied. On the basis of microscopical investigation, which included preliminary reflectance measurements, twenty-eight grains were selected for the final investigation. All grains show a fine intergrowth of two apparently isotropic phases. In addition some grains contain lamellae of ilmenite and sometimes lamellae of a grey mineral which probably is ceylonite. Table I lists the grains and the source localities. Grains nos. 1 to 4 are identical with those with the same numbers in the first paper (Halfen, 1976).

Exsolution of single-phase titanomagnetite takes place at a late stage in the cooling history of a basic magma, but still subsequent oxidation of the ulvöspinel-rich phase may sometimes take place. According to O'Reilly and Banarjee (1967) a rhombohedral phase, with a composition on the $FeTiO_3$-Fe_2O_3 join, and a cation-deficient Fe-Ti-spinel develop during this oxidation process. The spinel phase is unstable and tends to decompose to magnetite and ilmenite. For the purpose of the present work a slightly cation-deficient ulvöspinel can be accepted. Measurements were made on areas of grains devoid of ilmenite.

In order to further confirm the existence of a magnetite and an ulvöspinel phase, X-ray diffraction analysis was carried out on magnetically separated material from the specimens used for the polished sections. The specimens from Smålands Taberg and from La Blache Lake were not X-rayed due to insufficient amounts of material. For all samples analysed except the one from Dopma Mountain double reflections were obtained at the 2θ-positions consistent with the presence of a magnetite-rich and an ulvöspinel-rich phase. The sample from Dopma Mountain showed well-defined reflections only at magnetite positions. Still the second phase observed under the microscope most probably is ulvöspinel, though present in amounts insufficient for detection by X-ray analysis. This assumption is in accordance with the circumstance that the grains from Dopma Mountain have the lowest content of Ti of all grains analysed by electron microprobe. Also, in the polished section as a whole, lamellae of ilmenite are abundant and occur in amounts similar to those of the presumed ulvöspinel. Nevertheless, no ilmenite reflections were detected in the X-ray diffraction analysis.

The exsolution texture. According to Ramdohr (1953) magnetite and ulvöspinel are intergrown along their (100)-faces. Different patterns develop depending on the relative amounts of the two phases and on the crystallographic orientation of the polished surface. In the present material the following patterns were observed: in grains dominated by magnetite ulvöspinel occurs as evenly distributed lamellae aligned in one, two, or three different directions. These lamellae sometimes appear a bit undulating and occasionally there is even a branch-like pattern. The thickness of the lamellae varies from 0·2 to 0·6 microns. The lamellae aligned in one direction often appear coarser than those following another orientation. These differences are either due to a real difference in thickness or a consequence of the sectioning effect on variously orientated lamellae. In grains richer in ulvöspinel there is a different kind of texture, formed by crystallites of magnetite in a matrix of ulvöspinel. The crystallites are either evenly distributed or show clustering tendencies. Depending on the crystallographic orientation these crystallites look like squares, rectangles, or triangles. Their edges are curved and are concave towards the matrix. (Cf. the electron replica micrographs published by Nickel, 1958.) Under a 16/22 interference-contrast objective the investigated grains show perfectly level and unscratched surfaces, but in the more coarsely exsolved grains a faint orange-peel texture was observed.

Electron microprobe analysis. The analyses were carried out on a Hitachi XMA-5B Electron Microanalyser. Stoichiometric oxides and metals were used as standards. The correction program used was EMSKOR, which is a modified version of a program made by Springer (1967). The modifications, made by J. G. Rönsbo, are in accordance with suggestions by Sweatman and Long (1969). The analytical conditions were: acceleration voltage 20·0 kV, sample current on a Faraday cage 20·0 mμA, defocused beam approximately 20 microns in diameter, counting time 10 seconds. Shifting the target area three to four times did not render significant changes in the counting rates. The analysed elements were: Fe, Ti, Mg, Al, Mn, V, and Cr. The analyses were recalculated to a basis of 100 atoms (including oxygen), assuming the ideal formula R_3O_4 (Table I). The data are presented as atomic percentages because reflectance is more straightforwardly related to these parameters than to the weight percentages of the constituents. To indicate the probable accuracy of the analyses the total weight percentages of the oxides (assuming ideal stoichiometry) are included.

Reflectance measurements. A detailed description of the method used was given by Halfen (1976) and thus only some features specific to the present material will be considered here.

The titanomagnetite grains examined often showed bireflectance of the order of 0·1 % R and occasionally 0·2 % R. In some the R maxima were coincident with the vibration direction of the polarizer when this was parallel to the lamellae of the lamellar intergrowths. Klemm (1962) made a careful study of optical anisotropy in twenty-one different cubic minerals. He found frequent anisotropy in most of the minerals investigated. For example, 44 out of 73 grains of magnetite showed weak anisotropy. In the present material the observed anisotropy is not necessarily a feature specific to exsolved grains, but rather a phenomenon common in cubic minerals.

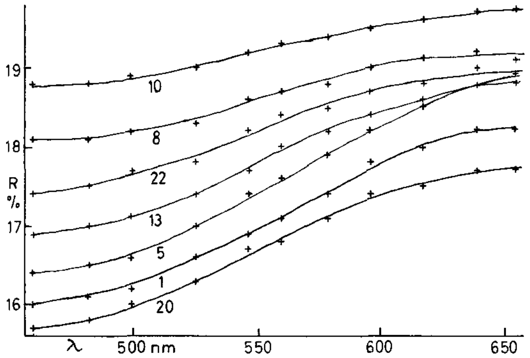

FIG. 1. Spectral reflectance curves of some grains in the studied sample illustrating the variation in level and slope.

Results. All reflectance values are summarized in Table II. Fig. 1 shows some representative spectral reflectance curves. All curves have a positive slope and they converge at the red end of the spectrum. The largest variation in reflectance is consequently found in the blue part of the spectrum, where R varies from 15·8 to 18·8 %, a relative variation of 17 %. In Halfen (1976) the relative accuracy of the reflectance measurements was estimated at ±1 %. The measured reflectances are thus rather sensitive in distinguishing the different titanomagnetites in the present material.

Relations between the measured reflectances and the microprobe analyses. The spectral reflectance curves in fig. 1 show two characteristics that may be related to the chemical composition: variation in level (R at a given wavelength) and variation in slope (convergence towards the red end of the spectrum). As the variation in R between different grains was greatest in the blue part of the spectrum, and since the photomultiplier used was most sensitive at 499 nm, this wavelength was chosen to illustrate variation in R. Reflectances at a second wavelength, 617 nm, were chosen to illustrate the differences in slope.

Ti substituting for Fe is the major chemical variation in the titanomagnetites studied. In fig. 2 the R_{499} values are plotted against Ti; a good correlation exists, but some variation still remains unexplained; the R_{617} values show a similar pattern. A possible method of analysing the dependence of R_{499} and R_{617} on chemical composition is

TABLE I. *Electron-probe analyses of titanomagnetites, expressed in atomic percentages, assuming the ideal formula* R_3O_4

No.	Fe*	Ti	Mg	Al	Mn	Cr	V	Fe^{3+}	Sum†
1	30·43	7·52	2·08	1·92	0·12	0·07	0·72	10·81	99·43
2	29·86	7·93	2·28	1·69	0·22	0·15	0·73	10·13	100·28
3	30·54	7·38	2·08	1·93	0·14	0·09	0·70	11·08	99·27
4	30·25	7·66	2·14	1·84	0·12	0·14	0·71	10·55	100·10
5	32·02	7·89	0·67	1·51	0·21	0·03	0·53	10·71	100·01
6	31·80	8·06	0·81	1·43	0·20	—	0·56	10·45	99·42
7	35·34	4·00	2·19	0·63	0·48	—	0·22	19·71	101·03
8	34·94	3·90	2·62	0·71	0·47	—	0·22	19·83	99·62
9	37·82	2·46	0·58	1·59	0·06	—	0·35	21·70	99·51
10	38·27	2·27	0·55	1·37	0·04	—	0·36	22·29	98·34
11	37·52	2·58	0·60	1·72	0·06	—	0·38	21·30	100·67
12	32·54	6·35	2·00	1·19	0·14	—	0·64	14·03	99·77
13	32·20	6·43	2·22	1·24	0·12	—	0·65	13·81	99·26
14	31·73	6·98	2·21	1·15	0·19	0·04	0·56	12·85	100·59
15	32·39	6·67	1·94	1·12	0·17	0·05	0·52	13·56	100·44
16	29·58	6·85	3·77	2·02	0·17	—	0·47	12·37	99·05
17	29·30	6·85	3·85	2·23	0·16	—	0·47	12·16	98·76
18	31·28	6·04	3·17	1·85	0·12	—	0·40	14·23	99·27
19	31·80	5·53	3·35	1·63	0·32	—	0·23	15·64	100·37
20	28·57	7·66	4·06	1·98	0·08	—	0·51	10·75	101·34
21	29·04	7·26	3·87	2·11	0·14	—	0·44	11·49	99·00
22	33·68	5·13	2·03	1·52	0·12	—	0·38	16·40	100·62
23	35·30	3·78	1·94	1·26	0·20	—	0·38	19·36	100·90
24	34·98	4·35	0·96	1·90	0·14	0·18	0·35	17·43	99·89
25	34·86	4·43	0·95	1·96	0·14	0·18	0·34	17·22	100·27
26	31·96	7·29	0·87	2·07	0·16	0·09	0·42	11·40	99·83
27	31·92	7·21	0·91	2·17	0·17	0·08	0·40	11·49	99·68
28	29·88	8·52	2·17	1·55	0·17	0·11	0·46	9·40	99·18

* Total iron.

† Sum of oxides.

Grains 1 to 4 were from an ore concentration in the Ulvö dolerite, a flat-lying layered intrusion in the eastern part of central Sweden.

Grains 5 and 6 were from normal Ulvö dolerite.

Grains 7 and 8 were from a magnetite-olivinite from Alnö Island, eastern part of central Sweden.

Grains 9 to 11 were from an ore concentration in a small gabbro intrusion, Dopma Mountain, north of Trondheim, Norway.

Grains 12 to 15 were from a small dyke of coarse-grained magnetite-olivinite in a larger body of magnetite-olivinite, Smålands Taberg, southern Sweden.

Grains 16 to 23 were from the Peter Prezunka ore, Yamaska Mountain, Quebec, Canada.

Grains 24 to 28 were from the La Blache Lake titaniferous magnetite deposit, Quebec, Canada.

to calculate the best-fitting planes (Kummell, 1879). This is a good method provided the experimental errors can be estimated to a fair approximation and provided other factors (such as departure from the ideal R_3O_4) are of minor importance. These requirements can be checked, since if they are fulfilled and the true relation is closely linear the root-mean-square standardized residual should approximate to unity.

It will be seen from fig. 1 that the spectral reflectance curves all show a slight S-shaped curvature. Statistical analysis showed that while the departure from linearity is not significant for any one curve, when all twenty-three are considered together it does appear significant, and therefore a set of cubics were fitted to the curves; although these gave excellent fits, the degree of curvature is too slight to be of any service in seeking relations of dependence on the chemical composition. However, adjusted values of R_{499} and R_{617} were adopted for the further calculations, derived from the cubic curves; in no case do these adjusted values

TABLE II. *Reflectances* (R %) *of titanomagnetites at different wavelengths*

No.	458 nm	481	499	525	546	559	578	596	617	640	655
1	16·0	16·1	16·2	16·6	16·9	17·1	17·4	17·8	18·0	18·2	18·2
2	15·8	15·9	16·1	16·3	16·8	17·0	17·2	17·6	17·8	18·0	18·1
3	16·0	16·0	16·2	16·4	16·9	17·1	17·3	17·7	17·9	18·1	18·2
4	15·9	16·0	16·2	16·5	17·0	17·2	17·4	17·7	18·0	18·2	18·3
5	16·4	16·5	16·6	17·0	17·4	17·6	17·9	18·2	18·5	18·8	18·8
6	16·3	16·4	16·5	16·9	17·3	17·5	17·8	18·1	18·4	18·7	18·7
7	18·2	18·2	18·3	18·4	18·7	18·8	18·9	19·0	19·1	19·2	19·1
8	18·1	18·1	18·2	18·3	18·6	18·7	18·8	19·0	19·1	19·2	19·1
9	18·6	18·6	18·7	18·7	19·0	19·1	19·2	19·3	19·5	19·5	19·5
10	18·8	18·8	18·9	19·0	19·2	19·3	19·4	19·5	19·6	19·7	19·7
11	18·5	18·5	18·6	18·7	19·0	19·0	19·2	19·3	19·5	19·5	19·5
12	16·8	16·7	17·0	17·1	17·6	17·7	18·0	18·2	18·5	18·6	18·7
13	16·9	17·0	17·1	17·4	17·7	18·0	18·2	18·4	18·6	18·8	18·8
14	17·2	17·2	17·3	17·5	17·8	18·0	18·2	18·4	18·6	18·8	18·8
15	17·1	17·1	17·2	17·4	17·7	17·9	18·1	18·3	18·5	18·7	18·8
16	16·3	16·4	16·5	16·8	17·1	17·3	17·5	17·8	18·0	18·1	18·1
17	16·0	16·1	16·3	16·6	16·9	17·1	17·3	17·6	17·8	17·9	17·9
18	16·5	16·5	16·7	17·0	17·3	17·5	17·7	17·9	18·1	18·2	18·2
19	17·0	17·3	17·3	17·5	17·9	18·0	18·2	18·4	18·5	18·7	18·6
20	15·7	15·8	16·0	16·3	16·7	16·8	17·1	17·4	17·5	17·7	17·7
21	15·9	15·9	16·1	16·3	16·7	16·9	17·1	17·3	17·5	17·7	17·7
22	17·4	17·5	17·7	17·8	18·2	18·4	18·5	18·7	18·8	19·0	18·9
23	17·8	18·0	18·2	18·3	18·6	18·8	18·9	19·0	19·1	19·1	19·1
24	—	—	17·8	—	18·4	—	—	—	19·0	—	—
25	—	—	17·9	—	18·4	—	—	—	19·1	—	—
26	—	—	16·8	—	17·5	—	—	—	18·5	—	—
27	—	—	16·5	—	17·2	—	—	—	18·3	—	—
28	—	—	16·3	—	17·1	—	—	—	18·1	—	—

differ from the observed by as much as 0·05. The relative accuracy of the original observations was estimated at 1 %; in calculating the best-fit planes, the relative accuracy of the adjusted values was taken as $\frac{1}{2}$%, and the relative accuracy of the microprobe data at 1 % of the observed mean percentage for each element.

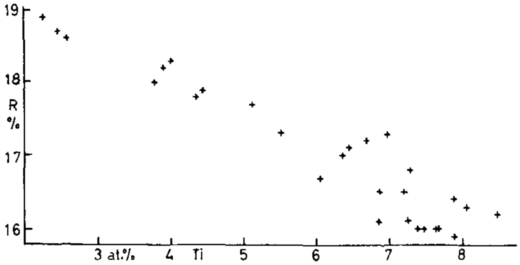

FIG. 2. Reflectance at 499 nm plotted against the content of Ti.

The amounts of Mn and V in the samples studied are small, and the variation in both is restricted; this leads to large standard errors in the coefficients derived for these elements in the best-fit planes, but because the derived coefficients are even larger than that for Al (otherwise the largest), it is preferable to use the atomic sum (Al+Mn+V) rather than to exclude Mn and V from the analysis.

Accordingly, best-fit planes were recalculated using Fe, Ti, Mg, and (Al+Mn+V) as chemical components (Cr was determined in too few grains to be taken into account). The three-flat derived (in six-dimensional space) had a root-mean-square standardized residual of 2·1, suggesting either that the experimental errors were slightly underestimated or that oxidation with consequent cation deficiency could be just appreciable (ideally this residual should be 1).

The resulting equations are (standard errors of the coefficients in parentheses):

$$R_{499} = 20{\cdot}877 - 0{\cdot}353(86)\mathrm{Ti} - 0{\cdot}141(123)\mathrm{Mg} - 0{\cdot}596(365)(\mathrm{Al}+\mathrm{Mn}+\mathrm{V})$$
$$R_{617} = 20{\cdot}966 - 0{\cdot}176(71)\mathrm{Ti} - 0{\cdot}223(102)\mathrm{Mg} - 0{\cdot}420(301)(\mathrm{Al}+\mathrm{Mn}+\mathrm{V}).$$

Setting Al, Mn, and V equal to their sample means gives:

$$R_{499} = 19{\cdot}530 - 0{\cdot}353\mathrm{Ti} - 0{\cdot}141\mathrm{Mg}$$
$$R_{617} = 20{\cdot}017 - 0{\cdot}176\mathrm{Ti} - 0{\cdot}223\mathrm{Mg}$$

for a titanomagnetite with approximately 2·25% Al+Mn+V, and for such material we derive:

$$\mathrm{Ti} = 28{\cdot}108 - 4{\cdot}146R_{499} + 2{\cdot}642R_{617}$$
$$\mathrm{Mg} = 67{\cdot}348 + 3{\cdot}275R_{499} - 6{\cdot}560R_{617}.$$

These equations reproduce the microprobe determinations for the twenty-eight grains studied with a standard deviation of 0·64 atom% in Ti and 0·54 atom% in Mg.

Conclusions. The usefulness of the established relations depends on the degree to which the compositions of exsolved titanomagnetites fall into or close to the compositional range defined by the present material. A large number of chemical analyses of titanomagnetites (including ulvöspinel occurring as separate grains) have now been published. The great majority of samples from plutonic rocks and dykes falls within or close to the mentioned range. However, titanomagnetites with notably different compositions, mostly from volcanic rocks, have been reported. These deviations include high contents of Mg, Al, Mn, and Cr (Agrell *et al.*, 1970; Medenbach, 1972; Prévot and Mergoil, 1973). None of these examples refer to exsolved titanomagnetites, but they indicate that 'abnormal' compositions may occasionally be expected in such grains too. In all probability we can thus conclude that normally the established relations are useful tools in studying the chemical variations in exsolved titanomagnetites.

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