LETTER IN REPLY TO COMMENTS BY J. B. WRIGHT ON:

*The Composition and Microtexture of an Ulvöspinel-Magnetite Intergrowth**

Mines Branch,
Department of Mines and Technical Surveys,
Ottawa.

Editor,
Canadian Mineralogist.

DEAR SIR:

I appreciate Mr. Wright's comments concerning my ulvöspinel paper (Nickel, 1958). Unfortunately my manuscript was in the hands of the publisher when the excellent paper by Vincent *et al.* (1957) appeared, and I was therefore unable to make use of their data.

The gist of Mr. Wright's argument appears to be as follows: (1) The intergrowth can be regarded as a member of the Fe_3O_4-Fe_2TiO_4 solid solution series, that is, there is no magnesium or aluminum in solid solution; (2) The normative magnetite and ulvöspinel calculated from the chemical analysis, when compared with the modal analysis obtained from grain counting, provides an approximate measure of the ulvöspinel composition in terms of the Fe_3O_4-Fe_2TiO_4 solid solution series; (3) The composition of the ulvöspinel indicates the temperature at which exsolution ceased.

Mr. Wright, in his contention that all the aluminum in the original solid solution exsolved as a magnesium-aluminum spinel, leaving none in the ulvöspinel, appears to suggest that the solid solution exsolved immediately into its end-members. However, unmixing generally proceeds with a progressive change in composition of the unmixing components toward the end-members, and the pure end-members do not necessarily result. Mr. Wright supports his contention by pointing to the coarser exsolution forms of the spinel, to which I also drew attention in my original submission. However, this indicates only that the ulvöspinel began to exsolve first, and has little bearing on the question as to whether any aluminum or magnesium remains in the ulvöspinel. Mr. Wright's further observation that the amount of spinel in my photomicrograph, Fig. 2, is much greater than 1.8% is also open to question. Although the photomicrograph was not necessarily intended to be representative, the spinel percentage can be estimated by measuring the area underlain by spinel in the photomicrograph. The sum of the lengths of the lamellae is 220 mm. If the average width is taken as 1 mm., the

*Published by permission of the Director, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

total area of the exposed spinel is 2.2 sq. cm. in a photograph area of 87 sq. cm., which is equivalent to 2.5%. Converting this to weight percentages, we obtain 1.9% spinel, which is very close indeed to the percentage originally proposed. If the average width of the lamellae is taken as 1.5 mm., the percentage of spinel is still only 2.9%, which is much less than the 7.6% given by Mr. Wright's normative calculations.

The validity of Mr. Wright's normative calculations is also open to doubt in view of the considerable excess of FeO and MgO. In my opinion, a more reasonable normative composition is that given in Table 1 (this letter). These values require only slightly less iron and slightly more oxygen than given in the analysis, but leave no excess oxides.

Further, in connection with Mr. Wright's distribution of the oxides among magnetite, spinels, and ulvöspinel, it is interesting to note that he includes significant amounts of the $MgFe_2O_4$ component with the magnetite, and Mg_2TiO_4 with the ulvöspinel. This is at variance with his initial premise that the intergrowth is strictly a member of the binary Fe_3O_4-Fe_2TiO_4 solid solution series.

TABLE 1. NORMATIVE COMPOSITION OF ULVÖSPINEL-MAGNETITE INTERGROWTH

I End members	II Molecular % norm	Analysis in wt. %		
			Calc. from column II	Used by Wright
$MgO.Al_2O_3$	8.7	Fe	54.0	54.3
$2MgO.TiO_2$	9.6	Ti	10.8	10.8
$2FeO.TiO_2$	38.3	Al_2O_3	4.1	4.1
$FeO.Fe_2O_3$	43.4	MgO	5.3	5.3
		O	25.8	25.5
	100.0			
			100.0	100.0

Both in his criticism and in his paper with Vincent and co-workers (1957), Mr. Wright uses a cell edge for Fe_2TiO_4 of 8.495 Å. However, Pouillard (1950) reported a value of 8.534 Å for this compound—a value which has been substantiated by recent experimental work in the Mines Branch on the Fe_3O_4-Fe_2TiO_4 system (A. H. Webster, personal communication). Therefore in my further discussion I shall use the latter value.

The modally determined ratio of magnetite to ulvöspinel in the intergrowth was given in my original paper as 35.6·64.4. Since this ratio is different from that calculated by Mr. Wright (45·55, respectively), he suggests that some magnetite dissolved in the ulvöspinel phase would increase the proportion of the ulvöspinel in the intergrowth. Using Mr. Wright's values, we arrive at an ulvöspinel composition of 86 mole

% Fe_2TiO_4 and 14 mole % Fe_3O_4. Such an ulvöspinel, according to a Végard plot, should have a cell edge of 8.514 Å. This, however, does not conform to the measured cell edge of the ulvöspinel (8.460 Å).

Similar calculations can be made using the normative percentages given in Table 1. Table 2 of this letter shows the molecular proportions recalculated to weight percentages to permit the modal percentage of magnetite to be subtracted. The resultant values, calculated to 100%, can be taken as the normative composition of the ulvöspinel itself (final column of Table 2).

TABLE 2. SUGGESTED NORMATIVE COMPOSITION OF ULVÖSPINEL

	Modal Wt. %	End member components	Wt. % norm of intergrowth	Molecular % norm of ulvöspinel
Ulvöspinel	64.4	$MgAl_2O_4$	5.8	13.0
		Mg_2TiO_4	7.2	14.3
		Fe_2TiO_4	40.0	57.0
		$FeFe_2O_4$	11.4	15.7
Magnetite	35.6	$FeFe_2O_4$	35.6	—
	100.0		100.0	100.0

Cell edges can now be calculated from the normative percentages shown in Table 2, assuming a linear relationship between mole per cent and cell edge of the end-members. This assumption is probably not strictly valid, but may nevertheless serve as an approximation. Table 3 of this letter shows these calculations for the ulvöspinel containing all four end-members, and for the same ulvöspinel without the normative $MgAl_2O_4$. The cell edges (totals of columns 4 and 6, respectively) are 8.441 Å for the ulvöspinel containing all the normative $MgAl_2O_4$, and 8.496 Å for the ulvöspinel containing no $MgAl_2O_4$. The actual measured cell edge of the ulvöspinel (8.460 Å) lies between the two, although closer to the lower one. From this it may be concluded that there probably is some aluminous spinel in solid solution with the ulvöspinel, although perhaps not quite as much as suggested in my original paper.

The measured cell edge of the ulvöspinel is considered to be a reliable one, since a large Debye-Scherrer *x*-ray powder camera (114.6 mm. diameter) was used, and the resulting back reflection lines were sufficiently sharp for consistent measurements to be made. The films were corrected for shrinkage, and the measured back reflection lines were used to determine the cell edge by the Lipson-Wilson graphical extrapolation method. Unfortunately, equally great accuracy cannot be claimed for the norm calculations because of our inability to produce a pure sample of the intergrowth, free of contaminating minerals, and because of the possibility

TABLE 3. CALCULATED CELL EDGES OF ULVÖSPINEL WITH AND WITHOUT $MgAl_2O_4$

		Ulvöspinel with $MgAl_2O_4$		Ulvöspinel without $MgAl_2O_4$	
End member components	Cell edges (Å)	Mol. % norm	Cell edge "fraction"	Mol. % norm	Cell edge "fraction"
$MgAl_2O_4$	8.080 (1)	13.0	1.050	—	—
Mg_2TiO_4	8.456 (2)	14.3	1.209	16.6	1.404
Fe_2TiO_4	8.534 (3)	57.0	4.864	66.0	5.632
$FeFe_2O_4$	8.396 (4)	15.7	1.318	17.4	1.460
		100.0	8.441	100.0	8.496

(1) From Swanson & Fuyat (1953).
(2) From Holgersson & Herrlin (1931) (converted from kX to Å).
(3) From Pouillard (1950).
(4) From Basta (1957).

of some of the spinels being dissolved by the refluxing procedure, as suggested by Mr. Wright.

In conclusion, it is my opinion that this problem cannot be unequivocally resolved without a chemical analysis of a pure concentrate of the ulvöspinel, although the experimental evidence strongly favours the retention of some aluminum and magnesium in the ulvöspinel solid solution. In general, however, if it can be proved satisfactorily than any given ulvöspinel is composed only of the Fe_3O_4-Fe_2TiO_4 end-members, then its composition, as determined by cell edge measurements, might be used as a geological thermometer, according to the data provided by Vincent *et al.*

REFERENCES

BASTA, E. Z. (1957): Accurate determination of the cell dimensions of magnetite, *Min. Mag.*, **31**, 431–442.

HOLGERSSON, S., & HERRLIN, A. (1931): Röntgenographische Untersuchungen von Orthotitanaten, *Zts. f. anorg. u. allg. Chemie*, **198**, 69–78.

NICKEL, E. H. (1958): The composition and microtexture of an ulvöspinel-magnetite intergrowth, *Can. Mineral.*, **6**, 191–199.

POUILLARD, E. (1950): Sur le comportement de l'alumine et de l'oxyde de titane vis-à-vis oxydes de fer. II. Etude du system TiO_2-Fe_2O_3-FeO, *Ann. de Chimie*, **5**, 190–214.

SWANSON, H. E., & FUYAT, R. E. (1953): Standard x-ray diffraction powder patterns, *Nat. Bur. Standards Circ.* 539, **2**, 35–38.

VINCENT, E. A., WRIGHT, J. B., CHEVALLIER, R., & MATHIEU, S. (1957): Heating ex periments on some natural titaniferous magnetites, *Min. Mag.*, **31**, 624–655.

E. H. NICKEL*

*Senior Scientific Officer, Mineral Sciences Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.