Dear Sir:

I have recently come across the Canadian Mineralogist for 1958 containing the following paper (6, pt. 2, pp. 191–199):


Having seen no comment on the paper in the 1959 issue, I should like to review it in the light of other workers' results in this field, to which the author may not have had access.

The following discussion is based on the premise that the intergrowth described is a member of the binary Fe₂O₄-Fe₂TiO₄ solid solution series (in the FeO-Fe₂O₃-TiO₂ system), in which Fe²⁺ + Ti⁴⁺ substitute for 2Fe³⁺ in all proportions.

Nickel proposes that the ulvöspinel in the sample examined contains aluminium; which is unlikely, for the following reasons: Transparent spinels must come out of solid solutions in this system at much higher temperatures than those at which magnetite-ulvöspinel exsolution commences, as was shown by heating experiments described in Vincent et al. (1957), where transparent spinels re-dissolved only at high temperatures, long after the intergrowths themselves were homogenized. This contention is supported by the much greater size of the spinel lamellae, relative to the main intergrowth, indicating a higher temperature of separation, when ionic diffusion processes are more rapid, and encourage the growth of large lamellae. Indeed, early exsolution of aluminous spinels is inevitable, in view of their much smaller cell dimensions (hercynite and pleonaste have cube sides of about 8.1 Å), relative to magnetite (8.4 Å) and ulvöspinel (8.5 Å). It is therefore concluded that the spinel residue which Nickel obtained after refluxing the ore concentrate for many hours in concentrated sulphuric acid, did not include all the spinels—most of them may well have been dissolved away earlier. Furthermore, the amount of spinels visible in the microphotograph (Fig. 2, Nickel) suggests that their amount is greater than the 1.8% quoted in the text.

Following the method proposed by Chevallier and described in Vincent et al. (op. cit., p. 628), I have calculated a normative composition for the intergrowth, using the partial analysis given by Nickel in Table 1, column b, of his paper—in which the high Al₂O₃ figure presumably represents a considerable proportion of transparent spinels.
Partial analysis | Wt. % oxides | Molecular % norm
---|---|---
Fe* | 54.3 | FeO † | 44.6 | FeO. Fe₂O₃ | 27.4 | \{33.3% Magnetite
Ti | 10.8 | MgO | 5.3 | MgO. Fe₂O₃ | 5.9 | \{7.6% Spinel
Al₂O₃ | 4.1 | Fe₂O₃ † | 28.0 | Fe₂O₃.Al₂O₃ | 6.3 | \{42.7% Ulvöspinell
MgO | 5.3 | Al₂O₃ | 4.1 | MgO.Al₂O₃ | 1.3 | 
O (by difference) | 25.5 | TiO₂ | 18.0 | 2FeO.TiO₂ | 35.2 | 100.0 | 2MgO.TiO₂ | 7.5 |

Excess FeO | 13.5 | Excess MgO | 2.9 | 100.0

*Understood to include 0.5% Mn, to be included (following Nickel) with the Fe in all subsequent calculations, owing to the similarity of atomic weights.
† Figures arrived at by a simultaneous equation using known Fe and calculated O available after forming TiO₂.

There are 16.4 mol. % of excess MO oxides in this norm, implying either greatly reduced conditions during consolidation, or (more probably) slight inaccuracies in the analysis. In any case, the calculation of large oxygen contents by difference in an analysis is always of dubious validity, particularly when, as in this instance, it is not certain that there are no other constituents in the sample.

Recalculated to 100%, the normative molecular percentages of magnetite and ulvöspinell are 44 and 56 respectively (the normative weight percentages are 45 and 55 respectively). Using the figure of 8.438 Å obtained by Nickel for the cell edge of the homogenized intergrowth, the calculated composition falls somewhat below the "Végard line" between magnetite and ulvöspinell, as shown in Fig. 1 of this letter (after Vincent et al., op. cit., Fig. 3). The discrepancy is no doubt partly due to the inadequate norm based on insufficiently precise data, but may also be partly attributed to re-entry of at least some aluminous spinel into the solid solution, on homogenization (Vincent et al., p. 632); both aluminium and magnesium have the effect of lowering the cell size of magnetite (Nicholls, 1955, Figs. 16, 17).

The cell edge of the ulvöspinell in this intergrowth was determined by Nickel to be 8.460 Å, as against the average of 8.490 Å obtained by Vincent et al. (Fig. 3), from nearly pure ulvöspinell. Nickel's value for the cube edge corresponds to a composition of about 65 mol. % ulvöspinell, when plotted on the Végard line (Fig. 1, this letter). The magnetite in the intergrowth, on the other hand, has a cell dimension close to that of pure Fe₃O₄.
According to the magnetite-ulvöspinel solvus determined by Vincent et al. (Fig. 4), two such phases, one of nearly pure magnetite, the other of impure ulvöspinel, could be produced in an intergrowth, in which exsolution was halted by rapid cooling from about 400°C (Fig. 2, this letter).

Chilling of the intergrowth in this way would account for the difference between the approximate weight percentages of magnetite and ulvöspinel as calculated above (46 and 55 respectively), and the amounts determined modally by Nickel (36 and 64 respectively): the presence of some magnetite dissolved in the ulvöspinel phase, would increase the proportion by volume of the latter in the intergrowth.

The validity of these arguments can only be checked:

(a) By full chemical analysis, in terms of oxide constituents, of the purified intergrowth freed from silicates and granular ilmenite. Such an analysis would enable a more reliable norm to be calculated.

(b) If necessary, by re-measurement of the cube edge of the ulvöspinel component ulvöspinel; tends to reflect x-rays poorly.

(c) By magnetic measurements, using methods developed by Chevallier, which would assist in confirming whether or not the ulvöspinel phase does in fact hold some magnetite in solid solution.
(d) By investigating as to whether or not there are any signs of late-stage, relatively rapid cooling in the original ore-body or its host rock.

In conclusion, I would like to remark on the excellence of the photographs illustrating the details of the exsolution textures, particularly the electron micrographs.

REFERENCES


These two works cite practically all the important literature on the subject of titaniferous iron ores.

J. B. WRIGHT