

SHORT COMMUNICATIONS

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Fluorescence effects at phase boundaries: petrological implications for Fe-Ti oxides

MATRIX corrections in electron probe micro-analysis, commonly called the ZAF procedure, comprise the atomic number (Z), mass absorption (A) and fluorescence (F) corrections. Both atomic number and mass absorption corrections have recently been improved, in particular with respect to light element analysis (Ugarte *et al.*, 1987; Scott and Love, 1989; Bastin and Heyligers, 1989).

The magnitude of the fluorescence correction is generally far less than the atomic number and mass absorption terms. In the data collection of 430, mainly binary, systems used for the evaluation of correction programs, the characteristic fluorescence factor is less than 1% in 90% of the systems studied and very rarely exceeds 5% (Scott and Love, 1989). It is, therefore, not surprising that the mathematical expression of Reed (1965) is still widely used for the correction of characteristic fluorescence.

The continuum fluorescence term is still of less importance, and is usually not incorporated in on-line ZAF computer programs on commercial WDS and EDS systems because of its cumbersome, lengthy and questionable nature (Heinrich, 1981). Low concentrations of heavy elements in a relatively light silicate matrix (for example: Fe in Mg-rich olivine, pyroxene or garnet), however, give fluorescence correction factors of 0.97 and 0.98 (Sweatman and Long, 1969). Correction factors are highest at low accelerating voltage and high take-off angles.

A special case in which fluorescence corrections must be taken into consideration, concerns the situation at phase boundaries. The influence of fluorescence effects is often underestimated here or even neglected, in particular in the study of Fe-Ti oxides. The composition of coexisting magnetite-ulvöspinel and ilmenite-hematite solid solutions may provide equilibrium temperature and oxygen fugacity estimates (Buddington

and Lindsley, 1964). These phases (Fe_3O_4 - Fe_2TiO_4 and FeTiO_3 - Fe_2O_3 respectively) are frequently intimately intergrown following exsolution accompanied by oxidation. The resultant texture consists of ilmenite lamellae in the (111) planes of magnetite and hematite lamellae in the (0001) planes of ilmenite (Lindsley, 1976).

Accurate microprobe analysis of both phases is normally considered only to be possible when the primary X-ray excitation volume lies well within a single phase. The spatial resolution for quantitative analysis, d-quant, is given by the expression of Reed (1975):

$$\text{d-quant} = 0.231(E_0^{1.5} - E_c^{1.5})/\rho$$

At an accelerating voltage E_0 of 20 keV, with a critical excitation voltage (E_c) for Fe- $K\alpha$ radiation of 7.1 keV and densities (ρ) of 5.2 and 4.72 for magnetite and ilmenite respectively, d-quant values are 3.1 and 3.5 μm . This would imply that quantitative analysis of lamellae with an apparent thickness, at the intersection with the surface, of at least 10 μm may be easily obtained, regardless of whether they are vertical or inclined (up to some 40°) to the surface. The inclination cannot be seen in these opaque phases. Fluorescence effects, however, play an unexpected role, even if these restrictions are obeyed. If the electron beam impinges, for example, on magnetite, well away from the contact with ilmenite, Ti- $K\alpha$ radiation will still be excited within the ilmenite by Fe- $K\alpha$ radiation and continuum radiation from the magnetite, and this leads to an apparent concentration of Ti in the magnetite.

This effect has already been described by Reed and Long (1963) across an artificial boundary between iron and nickel at 20 keV and by Reed (1975) in a zinc-nickel couple at 25 keV. In both cases apparent concentrations of both Fe and Ni of about 1% were found at a distance of 10 μm from the interface.

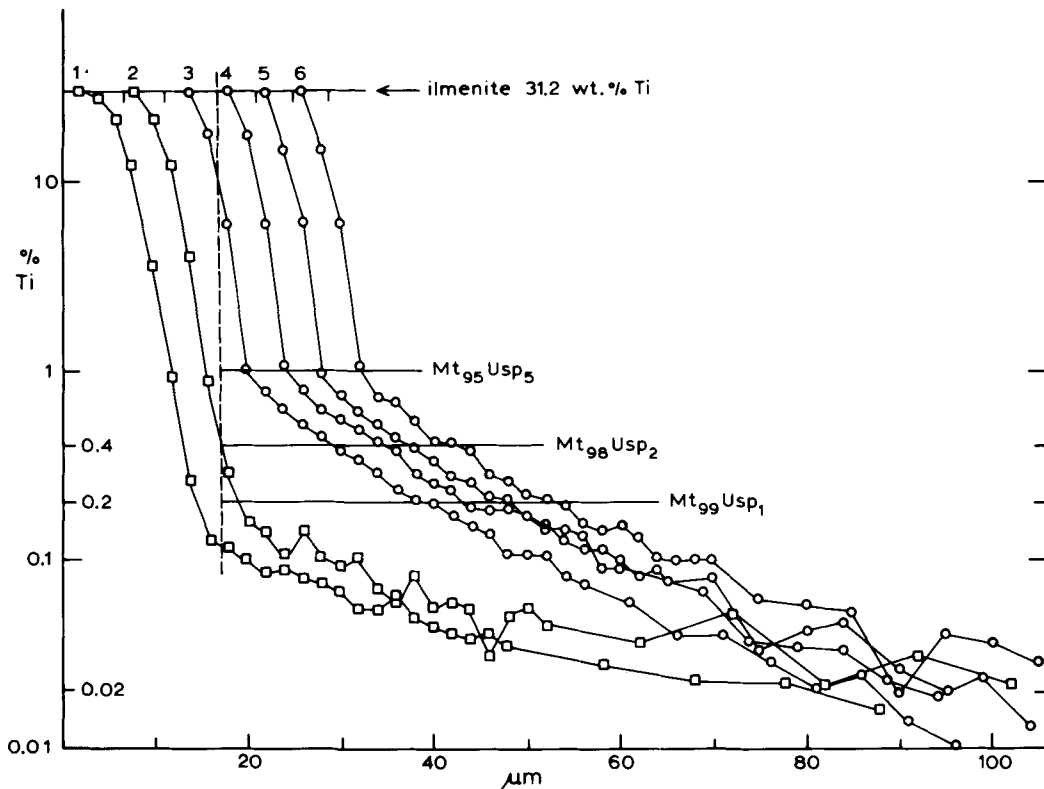


Fig. 1. Step scans for Ti- $K\alpha$ radiation across ilmenite-glass and ilmenite-hematite couples. Scans 1 and 2, marked with squares, represent ilmenite-glass traverses, and scans 3-6, marked with circles, ilmenite-hematite traverses. The vertical dashed line marks the boundary between ilmenite and hematite for scan 3. Interfaces for scans 4, 5 and 6 are offset to the right for clarity, with the contacts marked in each case by a vertical dash; interfaces for scans 1 and 2 are offset to the left. At the 1, 0.4 and 0.2 wt.% Ti level, calculated amounts of magnetite-ulvöspinel solid solution are given. For further explanation see text.

In order to check quantitatively the magnitude of these effects in Fe-Ti oxides, two polished chips of pure hematite and ilmenite were mounted against each other and screwed together between two glass strips, leaving a gap of only $2\ \mu\text{m}$ in between. Electron microprobe analysis was carried out on a Cambridge Instruments Microscan-9, equipped with two spectrometers and a take-off angle of 75° , at the following analytical conditions: 20 keV accelerating voltage, 25 nA probe current and 25 sec counting time. The sample was positioned in the sample holder with the interfaces perpendicular to the Rowland circle, so as to investigate possible differences between the results from both spectrometers.

Step scans of $2\ \mu\text{m}$ and, further away from the contact, of 5 and $10\ \mu\text{m}$ were made across both the ilmenite-hematite and the ilmenite-glass contacts. Ti- $K\alpha$ radiation was recorded on both

spectrometers with PET and LiF-200 diffracting crystals up to $100\ \mu\text{m}$ distance into the hematite or glass chip.

Fig. 1 shows the results of the various traverses on a logarithmic percentage scale: 1 and 2 are step scans across the ilmenite-glass contact, and 3-6 mark step scans across the ilmenite-hematite contact. The odd numbered scans were made on the left spectrometer, with a PET crystal, the even one, simultaneously, on the right spectrometer with a LiF-200 crystal. Scans 5 and 6 were made at $50\ \mu\text{m}$ distance from scans 3 and 4. These four ilmenite-hematite scans show great similarities: starting from the ilmenite level at 31.2 wt.% Ti, the Ti- $K\alpha$ intensity decreases even before the ilmenite-hematite interface has been reached, and follows a slightly curved, steep line until about the 1 wt.% Ti level. Here, a marked inflection occurs and percentages further decrease along almost straight lines towards the

lower limit of detection level (3σ) of about 0.02 wt.% at a 80 μm distance from the interface. The ilmenite-glass traverses show a comparable, steep decrease down to the 1 wt.% level, but continue to fall along a similar line until about the 0.1 wt.% level, from which point a gentle decrease follows until the detection level of 0.02 wt.% Ti.

A physical explanation of these curves is suggested as follows. Where the Ti- $K\alpha$ intensities start to decrease at the starting point of the curves indicates the point where the primary excitation volume is no longer completely within the ilmenite phase. The inflection point in the ilmenite-hematite scans marks the point at which the primary excitation volume no longer touches the ilmenite phase and Ti- $K\alpha$ radiation is only excited by secondary characteristic (Fe- $K\alpha$) fluorescence and, to a minor extent, by continuum fluorescence. The distance between these two points is about 6 μm ; the boundary is situated halfway at 3 μm . This value is in good accordance with the data given above for the spatial resolution. In the ilmenite-glass scans, characteristic fluorescence of Ti- $K\alpha$ by Fe- $K\alpha$ radiation from the hematite is not present, and only a small contribution of continuum fluorescence appears. The difference between the two sets of curves consists almost wholly of the characteristic fluorescence contribution. Due to the heavier mean atomic number of hematite, its continuum spectrum is somewhat higher than that of the glass, resulting in a slightly larger contribution of continuum fluorescence in the hematite. Apparent concentrations may be read from Fig. 1. At 12 and 25 μm from the interface 0.4 and 0.2 wt.% Ti is recorded.

The implications for petrological studies may be judged from this theoretical case. The close spacing of exsolution lamellae, in combination with their unknown inclination and the possible

presence of invisible subsurface lamellae, indicate that the petrological reality easily leads to far higher apparent Ti concentrations above the true values. It is, therefore, highly recommended to analyse these complex phases with utmost accuracy and search for minimum Ti values in the magnetite. Analyses should be carried out at points at least 10 μm and preferably more than 50 μm from observable lamellae.

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