Fe^{2+}/ Fe^{3+} Calculation In Spinels From Oxygen Deficiency Sum

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A typical electron microprobe printout of an oxide analysis shows weight percent concentrations of different elements in terms of their oxides. Fe is usually expressed as FeO. For minerals, it also shows calculated number of cations on the basis of an assumed (theoretical) number of oxygen atoms. For example,in olivines, $(Mg,Fe)_2SiO_4$, the theoretical number of oxygen atoms is four and the sum of cations should add up to three if the analysis is good. However, in case of spinels such as magnetite, Fe_3O_4, which contain significant amounts of Fe_2O_3, the analysis total falls below 100 and the cation sum (based on four oxygens) exceeds the theoretical cation sum. In other words, the formula calculation shows an oxygen deficiency. Geologists use this information to calculate the amount of Fe_2O_3 in the spinel assuming the other cations have only one oxidation state. Following is one way of doing this calculation:

$$\Sigma O = \frac{\Sigma Cat_{THEOR}}{\Sigma Cat} .(2Si + 2Ti + 1.5Al + 1.5Cr + Fe^{*} + Mn + Mg + Ca + Ni)$$

If $\Sigma O_{THEOR} > \Sigma O$,

$$Fe^{3+} = 2(\Sigma O_{THEOR} - \Sigma O);\quad Fe^{2+} = Fe^{*}. \frac{\Sigma Cat_{THEOR}}{\Sigma Cat} - Fe^{3+};$$

$$FeO(wt\%) = FeO^{*}. \frac{Fe^{2+}}{Fe^{2+} + Fe^{3+}}\ ;\ Fe_2O_3(wt\%) = FeO^{*}. \frac{M_{Fe_2O_3}}{2M_{FeO}} \cdot \frac{Fe^{3+}}{Fe^{2+} + Fe^{3+}}\ ;$$

$$NewTotal(wt\%) = Total - FeO^{*} + FeO + Fe_2O_3;$$

$$New\ \Sigma Cat = \Sigma Cat - Fe^{*} + Fe^{2+} + Fe^{3+}$$

$$New\ \Sigma O = \frac{\Sigma Cat_{THEOR}}{New\ \Sigma Cat} .(2Si+2Ti+1.5Al+.5Cr+1.5Fe^{3+}+Fe^{2+}+Mn+Mg+Ca+Ni)$$

where,

ΣCat and ΣO are calculated sum of cations based on a theoretical sum of oxygen, ΣO_{THEOR}; and the calculated sum of oxygen based on a theoretical sum of cations, ΣCat_{THEOR} respectively;

Si, Ti, Al, Cr, Mn, Mg, Ca and *Ni* are the calculated numbers of these cations based on ΣO_{THEOR}; Fe^{*} is the calculated total number of Fe atoms based on ΣO_{THEOR};

Fe^{2+} and Fe^{3+} and calculated number of divalent and trivalent Fe atoms;

FeO^{*} is measured wt% concentration of total Fe expressed as FeO; *FeO* and Fe_2O_3 are calculated wt% concentrations of FeO and Fe_2O_3 respectively;

M_{FeO} and $M_{Fe_2O_3}$ are molecular weights of FeO and Fe_2O_3 respectively;

Total and *New Total* are the oxide wt% totals before and after the Fe^{2+}/Fe^{3+} calculation;

and,
$New\Sigma Cat$ and $New\Sigma O$ are the calculated sum of cations and oxygen after the Fe^{2+}/Fe^{3+} calculation. ■

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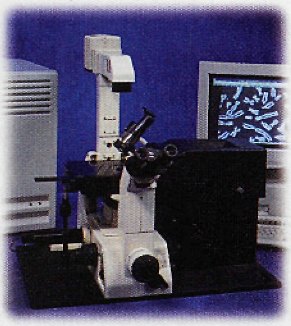

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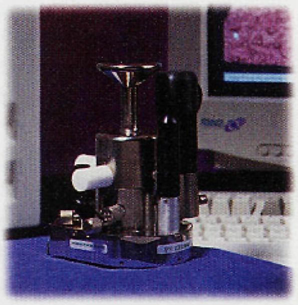

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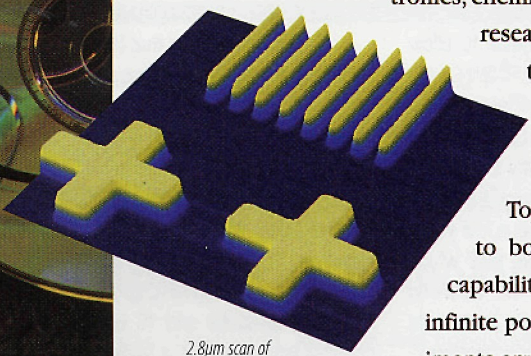

2.8µm scan of NIST Standard SRM-209A with 200nm pitch.

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