


Electron Probe Microanalysis of Variable Oxidation State Oxides: Protocol and Pitfalls

Shui-Yuan Yang (1)* , Ruo-Xi Zhang (1), Shao-Yong Jiang (1, 2) and Jing Xie (3)

(1) State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan, 430074, China

(2) Faculty of Earth Resources and Collaborative Innovation Centre for Scarce and Strategic Mineral Resources, China University of Geosciences, Wuhan, 430074, China

(3) Key Laboratory of Continental Collision and Plateau Uplift, Institute of Tibetan Plateau Research, Chinese Academy of Sciences, Beijing, 100101, China

* Corresponding author. e-mail: shuiyuanyang@cug.edu.cn

Electron probe microanalysis of geological oxide materials relies on stoichiometric considerations to estimate the content of undetermined oxygen and thus calculate ZAF (atomic number, absorption, fluorescence) matrix correction factors, requiring the valences of cations in the corresponding software to be unambiguously defined. However, stoichiometric ZAF corrections may be problematic in the presence of other undetermined elements or variable valence state cations. Herein, we analyse several oxides containing such cations, that is magnetite (Fe_3O_4), haematite (Fe_2O_3), hausmannite (Mn_3O_4) and cuprite (Cu_2O). We compare data re-calculated for incorrect valence states (Method 1) with reference values, revealing incorrect results, due to an incorrect amount of oxygen used in the matrix correction. Some solid-solution series of haematite and magnetite were also modelled in CalcZAF program to prove the relative errors when the incorrect oxygen is used. To resolve these issues, we describe two accurate methods. Method 2 uses the true valence states of analysed elements. In Method 3, all cations are analysed as metals, with the content of undetermined oxygen determined by difference. As EPMA software does not allow the use of non-integer valences, Method 3 is applicable to cations with non-integer or dubious valences in cases where these non-integer valences cannot be defined.

Keywords: electron probe microanalysis, oxide, variable oxidation state, magnetite, haematite, hausmannite, cuprite.

Received 19 Jun 17 – Accepted 16 Nov 17

Electron probe microanalysis (EPMA) is widely used for determining the contents of most elements in solids (Sweetman and Long 1969, McGee and Keil 2001, Zhao *et al.* 2015). To obtain accurate results, the intensities of characteristic X-rays obtained during the analysis must be corrected for matrix effects for both samples and reference materials. Matrix correction can be performed in a number of ways, for example by constructing calibration curves (Ziebold and Ogilvie 1964), or utilising the Bence-Albee (Bence and Albee 1968, Armstrong 1988), phi-rho-z methods (e.g., Brown 1991, Pouchou and Pichoir 1991, Reed 1993, Armstrong 1995) and ZAF methods (Love 1993, Reed 1993). EPMA of oxides does not explicitly determine the content of oxygen, but rather assumes a certain stoichiometry based on cation valences for including oxygen in the matrix correction. In this method, the content of oxygen was calculated by defining the valences of cations in EPMA

software, which is useful for analysing oxides where the identities and oxidation states of all cations and anions are known. However, the presence of cations with variable valence states (e.g., FeO vs. Fe_2O_3 vs. Fe_3O_4 ; MnO vs. Mn_3O_4) may complicate the determination of stoichiometric oxygen and significantly affect matrix corrections, as the above cations are assigned a fixed oxidation state (e.g., Fe^{2+} for FeO, Fe_2O_3 and Fe_3O_4 , and Mn^{2+} for both MnO and Mn_3O_4), for example Fe oxides have been extensively described as FeO (e.g., Heidarian *et al.* 2016, Ivanyuk *et al.* 2016, Tan *et al.* 2016, Velasco *et al.* 2016, Uenver-Thiele *et al.* 2017, Yin *et al.* 2017), and Mn oxides have been extensively described as MnO (e.g., Gnos and Peters 1995, Bosi *et al.* 2010). Besides, the valence of Fe cation in some solid-solution series of haematite and magnetite is various and cannot be defined before analysis. In this case, the analytical quality is difficult to assess whether the valence

states of cations are not known or incorrectly set (Raudsepp 1995), as the oxygen content determined from the assumed stoichiometry is used for ZAF matrix correction.

This study aimed to critically assess the existing EPMA analytical technique for oxides with variable valence-state cations, and showing the potential limitations of defining the valences of cations in EPMA software, that is the non-integer valences cannot be defined in JEOL and CAMECA EPMA software packages, which allow only integer values. Finally, we presented two methods providing accurate results for Fe, Mn and Cu oxide minerals (haematite, magnetite, hausmannite and cuprite), and the solid-solution series of haematite and magnetite as examples. These two methods can solve the potential limitations of defining the valences of cations with non-integer or dubious valences in EPMA software.

Materials and methods

Sample preparation

As Fe, Mn and Cu are commonly present in various minerals and exhibit different valence states, magnetite (Fe_3O_4), haematite (Fe_2O_3), hausmannite (Mn_3O_4) and cuprite (Cu_2O) were chosen as targets. These minerals are EPMA reference materials, and their compositions are homogeneous.

Prior to analysis, samples were coated with a thin conductive carbon film using a vacuum evaporator (JEOL JEE-420, JEOL Ltd., Tokyo, Japan) at the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences (CUG) at Wuhan. Measures suggested by Zhang and Yang (2016) were used to minimise carbon film thickness differences between samples and obtain almost uniform ~20-nm-thick coatings.

Electron probe microanalyses

Analyses by electron probe microanalyser were performed at CUG-Wuhan using a JEOL JXA-8100 instrument (JEOL Ltd.) with four wavelength-dispersive spectrometers. Fe ($K\alpha$), Mn ($K\alpha$) and Cu ($K\alpha$) were determined by an LIFH crystal. Accelerating voltages of 20 kV for cuprite and 15 kV for other minerals, a beam current of 20 nA and a defocused 10- μm -diameter electron beam were used. The peak counting time for each determined element equalled 20 s, with the background counting time equalling one half of the peak counting time at high- and low-energy background positions. Fifteen randomly distributed points were selected in mineral crystals for X-ray intensity

determination, and the oxide mass percentage were obtained by the following three matrix correction methods, with results presented in online supporting material Table S1.

Method 1: During matrix correction, iron was treated as Fe^{2+} in both haematite and magnetite, manganese was treated as Mn^{2+} in hausmannite, and copper was treated as Cu^{2+} in cuprite, with the oxygen content determined based on the corresponding stoichiometric considerations used for ZAF matrix correction. After matrix correction, the final results (oxide mass percentage) were re-calculated using relative molecular mass ratios: $m(\text{Fe}_2\text{O}_3) = m(\text{FeO}) \times 1.1113$; $m(\text{Fe}_3\text{O}_4) = m(\text{FeO}) \times 1.0742$; $m(\text{Mn}_3\text{O}_4) = m(\text{MnO}) \times 1.0752$; $m(\text{Cu}_2\text{O}) = m(\text{CuO}) \times 1.1118$. The above technique is commonly used for EPMA of haematite and magnetite.

Method 2: True valence states of determined elements were used in the EPMA procedure, with oxygen content determined from the resulting stoichiometry used for ZAF matrix correction. Haematite was assumed to contain Fe^{3+} , and cuprite was assumed to contain Cu^+ . As magnetite contains both Fe^{2+} and Fe^{3+} , hausmannite contains both Mn^{2+} and Mn^{3+} , an oxidation state of 2.667 was used for Fe and Mn in this case. However, only integer valences can be defined in the JEOL and CAMECA EPMA software packages. Hence, Fe and Mn were determined as metals, and the amount of undetermined oxygen (mol) was calculated as 1.333 times that of Fe and Mn, respectively (as both the O:Fe ratio in magnetite and the O:Mn ratio in hausmannite equal 4:3), and used for ZAF matrix correction.

Method 3: In this method, the content of undetermined O was added by difference and involved in the ZAF matrix correction. Subsequently, the final results (oxide mass percentage) of the oxide were re-calculated based on the measured cations and added oxygen, which were acquired from the formula stoichiometry based on the valence of the cations.

Results and discussion

In EPMA, the relationship between characteristic X-ray intensity and element content is generally non-linear, with the extent of non-linearity depending on matrix composition (Sweetman and Long 1969). Thus, to convert X-ray intensities of reference material and unknown samples into absolute mass percentages, one needs to apply appropriate matrix corrections, which require complete knowledge of the sample composition. The ZAF correction method determines the mass percentage C_A of an element A as follows (Reed 2005):

$$C_A^{unk} = C_A^{std} \times \frac{I_A^{unk}}{I_A^{std}} \times \frac{ZAF_A^{unk}}{ZAF_A^{std}} \quad (1)$$

where I_A is the X-ray intensity of element A (cps μA^{-1}), *std* indicates reference material specimen, *unk* indicates unknown specimen and ZAF is the matrix correction factor. The ZAF factor includes contributions of atomic number (Z), absorption (A) and fluorescence (F) correction coefficients, which are calculated separately and combined to provide the overall correction factor.

Using the above-mentioned methods, we analysed haematite, magnetite, hausmannite and cuprite, comparing the oxide mass percentage obtained by different matrix correction methods. The fifteen X-ray intensities obtained from each mineral were similar, indicating the homogeneity of the targets (Table S1). The average of oxide mass percentages obtained by different matrix correction methods and their relative error is also shown in Table 1.

For haematite, the oxide mass percentages obtained from different matrix correction methods exhibited some variation (Figure 1). The mass percentages of Fe_2O_3 in haematite (reference value = 100%) calculated by Method 1 (average = 98.40%) were obviously lower than those obtained by Methods 2 and 3 (99.97% and 99.97%, respectively) (Table 1).

Correspondingly, the mass percentages (Figure 2) of Fe_3O_4 in magnetite (reference value = 99.80%) showed trends similar to those of haematite, that is the average of oxide mass percentages obtained by Methods 2 and 3 are 99.88% and 99.83%, respectively, whereas those obtained by Method 1 are 98.83% (Table 1).

In the case of Mn_3O_4 in hausmannite (reference value = 99.75%), the corresponding average of oxide mass percentages exhibited deviations between Method 1 and the other two methods (Figure 3), that is those obtained by Method 1 were 98.43%, lower than those determined by Methods 2 and 3 (99.60% and 99.66%, respectively) (Table 1).

For Cu_2O in cuprite, the average of oxide mass percentage determined by Method 1 equals to 101.96%, exceeding those obtained by Methods 2 and 3 (~ 99.93% and 99.95%, respectively; Figure 4) (Table 1).

In view of the fact that the same X-ray intensities (I_A) of the above cations used in matrix correction, Equation (1) (Reed 2005) leads to the conclusion that the difference of oxide mass percentage obtained by Methods 1 and 2/3 could be ascribed to the corresponding ZAF factors. The ZAF factors of

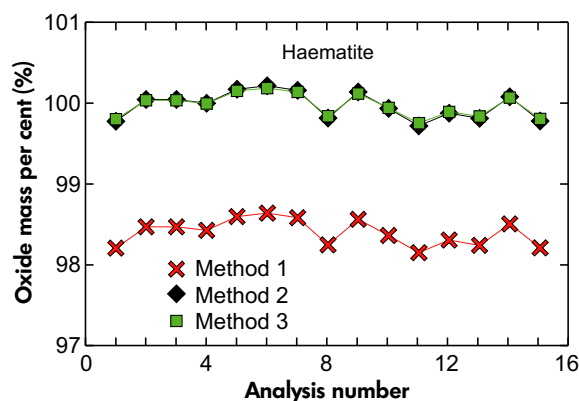


Figure 1. Comparison of oxide mass percentages of Fe_2O_3 in determined by three methods. [Colour figure can be viewed at wileyonlinelibrary.com]

Table 1.
The average of Fe, Mn and Cu oxide mass percentages and their relative error in variable oxidation-state oxide matrices obtained by different matrix correction methods

Oxide	Method 1		Method 2		Method 3	
	Mass (%m/m)	Relative error (%)	Mass (%m/m)	Relative error (%)	Mass (%m/m)	Relative error (%)
Fe_2O_3	Haematite, $m(\text{Fe}_2\text{O}_3) = 100\%$					
	98.40	1.60	99.97	0.03	99.97	0.03
Fe_3O_4	Magnetite, $m(\text{Fe}_3\text{O}_4) = 99.80\%$					
	98.83	0.97	99.88	0.08	99.83	0.03
Mn_3O_4	Hausmannite, $m(\text{Mn}_3\text{O}_4) = 99.75\%$					
	98.43	1.33	99.60	0.15	99.66	0.09
Cu_2O	Cuprite, $m(\text{Cu}_2\text{O}) = 99.57\%$					
	101.96	2.40	99.93	0.36	99.95	0.38

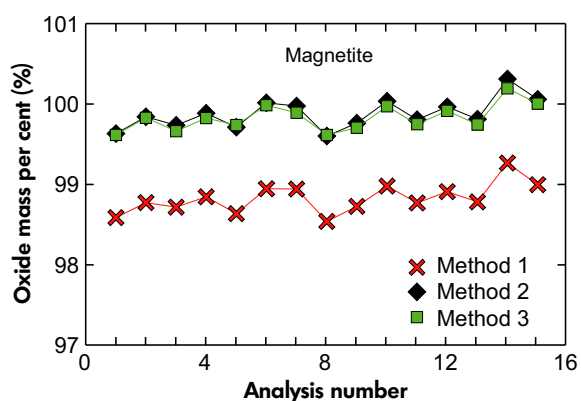


Figure 2. Comparison of oxide mass percentages of Fe_3O_4 in magnetite determined by three methods. [Colour figure can be viewed at wileyonlinelibrary.com]

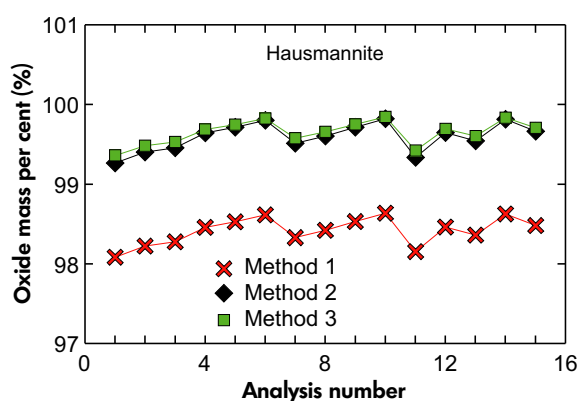


Figure 3. Comparison of oxide mass percentages of Mn_3O_4 in hausmannite determined by three methods. [Colour figure can be viewed at wileyonlinelibrary.com]

Fe, Mn and Cu in different oxidation states calculated using the CalcZAF program (Probe Software Inc., Eugene, OR, USA) are listed in Table 2, which shows that the contributions of fluorescence (F) and absorption (A) effects in different oxidation states are similar, whereas those of the atomic number effect (Z) is subject to significant variation. The atomic number effect correction features two parts, namely electron stopping power and backscattering corrections (Duncumb and Reed 1967, Reed 1993, Joy 1995). In order to evaluate the backscattering factor, the content values for all elements in the sample and reference material need to be present in the correction. Thus, during ZAF matrix correction, the complete composition of the unknown has to be used (Sweetman and Long 1969). Consequently, the failure of

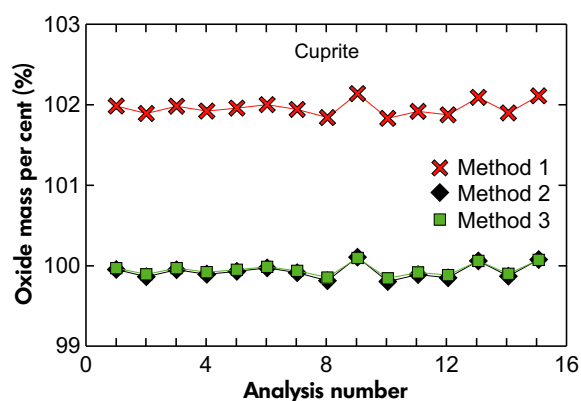


Figure 4. Comparison of oxide mass percentages of Cu_2O in cuprite determined by three methods. [Colour figure can be viewed at wileyonlinelibrary.com]

Table 2. Calculated ZAF factors for Fe, Mn and Cu in variable oxidation-state oxide matrices

Element	Matrix	Z	A	F	ZAF
Fe	FeO	1.0530	0.9974	1.0000	1.0503
Fe	Fe_3O_4	1.0660	0.9969	1.0000	1.0626
Fe	Fe_2O_3	1.0718	0.9966	1.0000	1.0682
Mn	MnO	1.0578	0.9973	1.0000	1.0549
Mn	Mn_3O_4	1.0719	0.9966	1.0000	1.0683
Cu	CuO	1.0616	0.9982	1.0000	1.0596
Cu	Cu_2O	1.0341	0.9990	1.0000	1.0330

Method 1 to obtain correct oxide mass percentages can be ascribed to the incorrect amount of oxygen used in the iterative ZAF correction algorithm, that is an underestimated amount of oxygen was employed in the ZAF correction for haematite, magnetite and hausmannite, and an overestimated amount of oxygen was employed in the case of cuprite. These deviations are caused by the incorrect cation valences, which introduce errors in the amounts of oxygen determined based on stoichiometry.

The variable oxidation-state oxides in nature often contain other elements. For example, titanohaematite, TiO_2 represent as allomerism in haematite. In this case, the incorrect amount of oxygen used in the iterative ZAF correction algorithm (Method 1) would also lead to incorrect results of TiO_2 . To show the relative errors of TiO_2 and Fe_2O_3 contents in titanohaematite when the incorrect oxygen is used, we set a series of 'samples' which contain different content of TiO_2 (1–20% *m/m*, in integral number) in haematite. Each sample was treated as a reference material and also an unknown. The same X-ray intensity of element in each reference material and unknown for Ti and Fe was

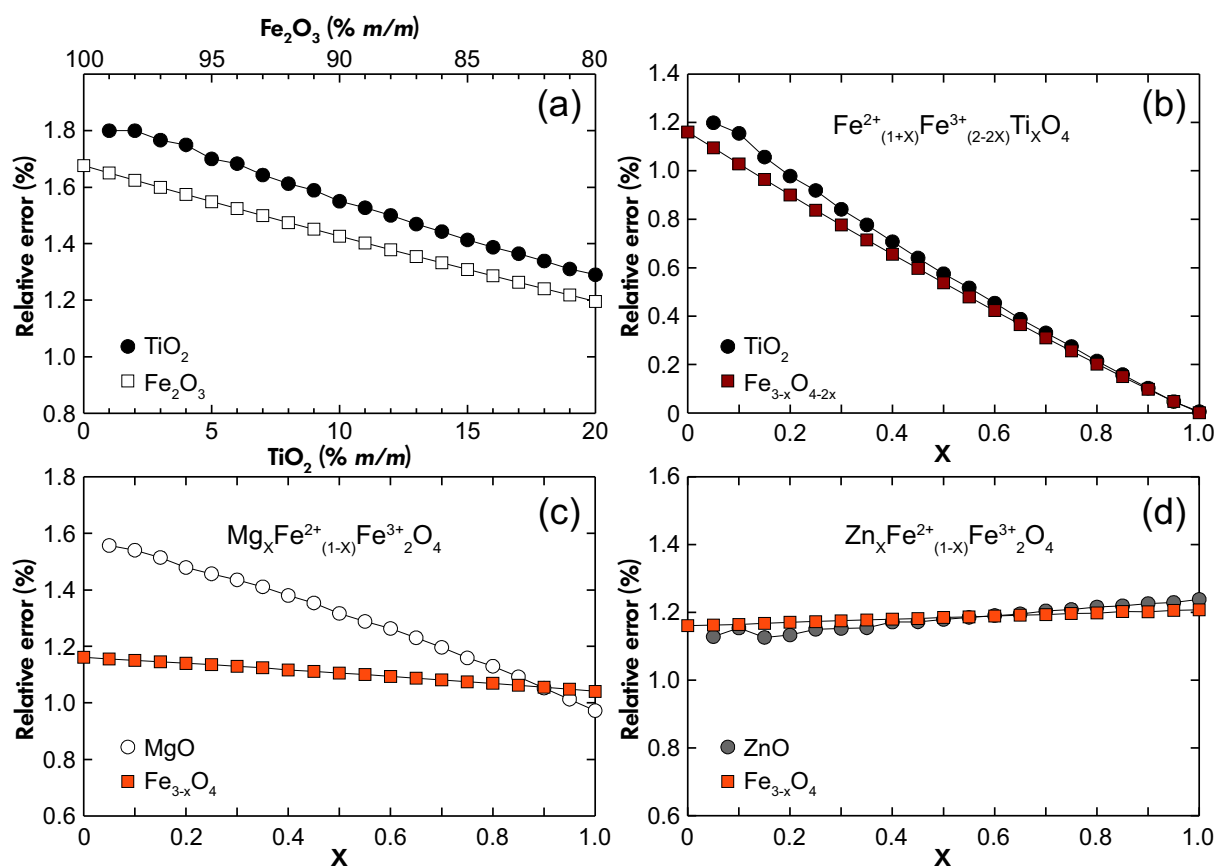


Figure 5. The relative errors of Fe oxide and other elements in solid-solution series of haematite and magnetite when Fe was treated as Fe^{2+} (Method 1) and the incorrect oxygen were used during EPMA. (a) TiO_2 represent allomerism in haematite; (b) $\text{Fe}^{2+}_{(1+X)}\text{Fe}^{3+}_{(2-2X)}\text{Ti}_X\text{O}_4$ solid solution, (c) $\text{Mg}_X\text{Fe}^{2+}_{(1-X)}\text{Fe}^{3+}_2\text{O}_4$ solid solution and (d) $\text{Zn}_X\text{Fe}^{2+}_{(1-X)}\text{Fe}^{3+}_2\text{O}_4$ solid solution. [Colour figure can be viewed at wileyonlinelibrary.com]

supposed while Fe was treated as Fe^{2+} in the unknown (Method 1) and as Fe^{3+} in the reference material. The results (oxide mass percentage) of the unknowns were obtained from the CalcZAF program (Probe Software Inc). The relative errors for TiO_2 and Fe_2O_3 in each unknown were calculated and are shown in Figure 5a. Both TiO_2 and Fe_2O_3 have large relative error when the content of TiO_2 is low (up to 1.8% and 1.65%, respectively). The relative errors for TiO_2 and Fe_2O_3 decrease with increasing the content of TiO_2 .

Another case is that some other elements present in variable oxidation-state oxides can lead to the ratio variation of polyvalency cations (such as $\text{Fe}^{2+}/\text{Fe}^{3+}$) due to their substitution. In magnetite, some elements can replace Fe to form a series of solid solution, such as $\text{Fe}^{2+}_{(1+X)}\text{Fe}^{3+}_{(2-2X)}\text{Ti}_X\text{O}_4$, $\text{Mg}_X\text{Fe}^{2+}_{(1-X)}\text{Fe}^{3+}_2\text{O}_4$ and $\text{Zn}_X\text{Fe}^{2+}_{(1-X)}\text{Fe}^{3+}_2\text{O}_4$. The ratio of $\text{Fe}^{2+}/\text{Fe}^{3+}$ in these solid solutions is variable based on the content of substitutional element ($X = 0-1$). The relative errors of the oxide of substitutional element and Fe oxide content in these magnetites when the incorrect oxygen

is used (Method 1) were also obtained from CalcZAF program as described above. In $\text{Fe}^{2+}_{(1+X)}\text{Fe}^{3+}_{(2-2X)}\text{Ti}_X\text{O}_4$, the relative errors of TiO_2 and Fe oxide decrease from about 1.2% to 0% with increasing X , and equal to 0 when $X = 1$ (in this situation all the valence of Fe is +2) (Figure 5b). In $\text{Mg}_X\text{Fe}^{2+}_{(1-X)}\text{Fe}^{3+}_2\text{O}_4$, with increasing X , the relative errors of MgO decrease from about 1.6% to 1.0%, and Fe oxide decrease slowly (from 1.2% to 1.0%) (Figure 5c). However, in $\text{Zn}_X\text{Fe}^{2+}_{(1-X)}\text{Fe}^{3+}_2\text{O}_4$, the relative errors of TiO_2 and Fe oxide were nearly constant between 1.1% and 1.2% (Figure 5d).

Based on the above discussion, we conclude that defining true valence states for variable oxidation-state cations is critical to obtain correct ZAF factors during EPMA, implying that oxides containing the above cations should be analysed using Methods 2 or 3. During analysis, the content of oxygen was determined assuming the valence of Fe in haematite to equal +3, and that of Cu in cuprite to equal +1. However, the non-integer Fe and Mn valences of 2.667 cannot be used in JEOL and CAMECA EPMA software

packages, which allow only integer values. In this case, Fe in magnetite and Mn in hausmannite was analysed as metal, and the undetermined oxygen content was determined by assuming a 1.333:1 O:Fe molar ratio and a 1.333:1 O:Mn molar ratio, respectively, and used for ZAF matrix correction. Unfortunately this approach is only applicable to pure magnetite and pure hausmannite. Natural magnetite and hausmannite are not always pure, containing TiO₂, SiO₂ and other oxides and thus not allowing Method 2 to be used. Probe EPMA software (Probe Software Inc., Eugene, USA) defines the valence of cations based on cation:oxygen molar ratios (e.g., 3:4 for Fe:O in magnetite and 3:4 for Mn:O in hausmannite), allowing non-integer valences to be used. However, when the valence of the variable oxidation-state cations is various due to element substitution, the cation:oxygen molar ratios cannot be defined. In these cases, Method 3 can be used for cations with non-integer or dubious valences.

Conclusions

Herein, three matrix correction methods were compared to determine the protocol and pitfalls of EPMA of variable oxidation-state oxides. Reference materials of magnetite (Fe₃O₄), haematite (Fe₂O₃), hausmannite (Mn₃O₄) and cuprite (Cu₂O) were selected as examples. Although similar X-ray intensities were obtained for each cation used, the oxide mass percentages determined by Method 1 differed from those calculated by reference values and the two other methods. These errors reveal the pitfalls of Method 1, that is the underestimated oxygen amount in haematite, magnetite and hausmannite used for ZAF correction, and the overestimated amount of oxygen in cuprite used for ZAF correction, which was caused by the usage of incorrect cation valences. Some solid-solution series of haematite and magnetite were also modelled in CalcZAF program to prove the relative errors when the incorrect oxygen is used. Conversely, Methods 2 and 3 use correct oxygen amounts for ZAF matrix correction, obtaining accurate results. This study implies that defining true valence states for variable oxidation-state cations is critical to obtain correct ZAF factors during EPMA, implying that variable oxidation-state oxides should be analysed using Methods 2 or 3. Most of all this study put forward that in cases when non-integer cation valences cannot be defined, Method 3 can be used for cations with non-integer or dubious valences.

Acknowledgements

This work was supported by National Key R&D Plan of China (Grant No. 2017YFC0601404) and Natural Science

Foundation of China (No. 41403022, 41773040) and the Fundamental Research Funds for the Central Universities, China University of Geosciences (Wuhan) (No. CUGL150401). We are grateful to Dr. Christophe Quéfé, and two anonymous reviewers for providing valuable comments and suggestions, which helped improve this manuscript significantly.

References

Armstrong J.T. (1988)

Bence-Albee after 20 years: Review of the accuracy of α -factor correction procedures for oxide and silicate minerals. In: Newbury D.E. (ed.), *Microbeam analysis*. San Francisco Press Incorporated (San Francisco, USA), 469–476.

Armstrong J.T. (1995)

CITZAF: A package of correction programs for the quantitative electron microbeam X-ray-analysis of thick polished materials, thin films, and particles. *Microbeam Analysis*, 4, 177–200.

Bence A.E. and Albee A.L. (1968)

Empirical correction factors for the electron microanalysis of silicates and oxides. *The Journal of Geology*, 76, 382–403.

Bosi F., Hälenius U. and Skogby H. (2010)

Crystal chemistry of the MgAl₂O₄–MgMn₂O₄–MnMn₂O₄ system: Analysis of structural distortion in spinel- and hausmannite-type structures. *American Mineralogist*, 95, 602–607.

Brown J.D. (1991)

$\phi(\rho z)$ equations for quantitative analysis. In: Heinrich K.F.J. and Newbury D.E. (eds), *Electron probe quantitation*. Plenum Press (New York, USA), 77–81.

Duncumb P. and Reed S.J.B. (1967)

The calculation of stopping power and backscatter effects in electron probe microscopy. *Journal of the American Chemical Society*, 62, 1420–1423.

Gnos E. and Peters T. (1995)

Tephroite-hausmannite-galaxite from a granulite-facies manganese rock of the United Arab Emirates. *Contributions to Mineralogy and Petrology*, 120, 372–377.

Heidarian H., Lentz D., Alirezaei S., Peighambari S. and Hall D. (2016)

Using the chemical analysis of magnetite to constrain various stages in the formation and genesis of the Kiruna-type chadormalu magnetite-apatite deposit, Bafq district, Central Iran. *Mineralogy and Petrology*, 110, 927–942.

Ivanyuk G.Y., Kalashnikov A.O., Pakhomovskiy Y.A., Mikhailova J.A., Yakovenchuk V.N., Konopleva N.G., Sokharev V.A. and Bazai A.V. (2016)

Economic minerals of the Kovdor baddeleyite-apatite-magnetite deposit, Russia: Mineralogy, spatial distribution and ore processing optimization. *Ore Geology Reviews*, 77, 279–311.

references

Joy D.C. (1995)

Monte Carlo modelling for electron microscopy and microanalysis. Oxford University Press (New York, USA), 224pp.

Love G. (1993)

X-ray absorption correction. In: Scott V.D. and Love G. (eds), *Quantitative electron-probe microanalysis*. Ellis Horwood Ltd Press (Chichester, UK), 163–192.

McGee J.J. and Keil K. (2001)

Application of electron probe microanalysis to the study of geological and planetary materials. *Microscopy and Microanalysis*, 7, 200–210.

Pouchou J.L. and Pichoir F. (1991)

Quantitative analysis of homogeneous or stratified microvolumes applying the model "PAP". In: Heinrich K.F.J. and Newbury D.E. (eds), *Electron probe quantitation*. Plenum Press (New York, USA), 31–75.

Raudsepp M. (1995)

Recent advances in the electron-probe micro-analysis of minerals for the light elements. *The Canadian Mineralogist*, 33, 203–218.

Reed S.J.B. (1993)

Electron microprobe analysis. Cambridge University Press (Cambridge, UK), 260pp.

Reed S.J.B. (2005)

Electron microprobe analysis and scanning electron microscopy in geology. Cambridge University Press (Cambridge, UK), 189pp.

Sweatman T.R. and Long J.V.P. (1969)

Quantitative electron-probe microanalysis of rock-forming minerals. *Journal of Petrology*, 10, 332–379.

Tan W., Liu P., He H., Wang C.Y. and Liang X. (2016)

Mineralogy and origin of exsolution in Ti-rich magnetite from different magmatic Fe-Ti oxide-bearing intrusions. *The Canadian Mineralogist*, 54, 539–553.

Uenver-Thiele L., Woodland A.B., Ballaran T.B., Miyajima N. and Frost D.J. (2017)

Phase relations of $MgFe_2O_4$ at conditions of the deep upper mantle and transition zone. *American Mineralogist*, 102, 632–642.

Velasco F., Tornos F. and Hanchar J.M. (2016)

Immiscible iron- and silica-rich melts and magnetite geochemistry at the El Laco volcano (northern Chile): Evidence for a magmatic origin for the magnetite deposits. *Ore Geology Reviews*, 79, 346–366.

Yin S., Ma C. and Robinson P.T. (2017)

Textures and high field-strength elements in hydrothermal magnetite from a skarn system: Implications for coupled dissolution–reprecipitation reactions. *American Mineralogist*, 102, 1045–1056.

Zhang R.X. and Yang S.Y. (2016)

A mathematical model for determining carbon coating thickness and its application in electron probe microanalysis. *Microscopy and Microanalysis*, 22, 1374–1380.

Zhao D., Zhang Y. and Essene E.J. (2015)

Electron probe microanalysis and microscopy: Principles and applications in characterization of mineral inclusions in chromite from diamond deposit. *Ore Geology Reviews*, 65, 733–748.

Ziebold T.O. and Ogilvie R.E. (1964)

An empirical method for electron microanalysis. *Analytical Chemistry*, 36, 322–327.

Supporting information

The following supporting information may be found in the online version of this article:

Table S1. EPMA results for magnetite, haematite, manganese dioxide and cuprite performed using three different methods.

This material is available as part of the online article from: <http://onlinelibrary.wiley.com/doi/10.1111/ggr.12199/abstract> (This link will take you to the article abstract).

