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

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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 (Fe₃O₄), haematite (Fe₂O₃), hausmannite (Mn₃O₄) and cuprite (Cu₂O). 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.

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Electron probe microanalysis (EPMA) is widely used for determining the contents of most elements in solids (Sweatman 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 Albbee 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. Fe₂O₃ vs. Fe₃O₄; MnO vs. Mn₃O₄) may complicate the determination of stoichiometric oxygen and significantly affect matrix corrections, as the above cations are assigned a fixed oxidation state (e.g., Fe²⁺ for FeO, Fe₂O₃ and Fe₃O₄ and Mn²⁺ for both MnO and Mn₃O₄, for example Fe oxides have been extensively described as FeO (e.g., Heidarian et al. 2016, Ivanuk 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 (Fe₃O₄), haematite (Fe₂O₃), hausmannite (Mn₃O₄) and cuprite (Cu₂O) 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 (Kα), Mn (Kα) and Cu (Kα) 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 Fe³⁺ in both haematite and magnetite, manganese was treated as Mn²⁺ in hausmannite, and copper was treated as Cu²⁺ 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 Fe³⁺, and cuprite was assumed to contain Cu⁺. As magnetite contains both Fe²⁺ and Fe³⁺, hausmannite contains both Mn²⁺ and Mn³⁺, 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 (Sweatman 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):
\[ C_{n}^{\text{unk}} = C_{n}^{\text{std}} \times \frac{I_{n}^{\text{unk}}}{I_{n}^{\text{std}}} \times ZAF_{n}^{\text{unk}} \quad ZAF_{n}^{\text{std}} \]

where \( I_{n} \) is the X-ray intensity of element \( n \) (cps mm\(^{-1}\)), \( \text{std} \) indicates reference material specimen, \( \text{unk} \) 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\(_2\)O\(_3\) 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\(_3\)O\(_4\) 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\(_3\)O\(_4\) 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\(_2\)O 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 (\( I_{n} \)) 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

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Method 1</th>
<th>Method 2</th>
<th>Method 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mass (%m/m)</td>
<td>Relative error (%)</td>
<td>Mass (%m/m)</td>
</tr>
<tr>
<td>Fe(_2)O(_3)</td>
<td>Haematite, ( m(Fe_2O_3) = 100% )</td>
<td>98.40</td>
<td>1.60</td>
</tr>
<tr>
<td>Fe(_3)O(_4)</td>
<td>Magnetite, ( m(Fe_3O_4) = 99.80% )</td>
<td>98.83</td>
<td>0.97</td>
</tr>
<tr>
<td>Mn(_3)O(_4)</td>
<td>Hausmannite, ( m(Mn_3O_4) = 99.75% )</td>
<td>98.43</td>
<td>1.33</td>
</tr>
<tr>
<td>Cu(_2)O</td>
<td>Cuprite, ( m(Cu_2O) = 99.57% )</td>
<td>101.96</td>
<td>2.40</td>
</tr>
</tbody>
</table>

Figure 1. Comparison of oxide mass percentages of Fe\(_2\)O\(_3\) in 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 (Sweatman and Long 1969). Consequently, the failure of 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 allomericism 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$_2$O$_3$ 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

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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\(^{2+}\)O\(_3\) in each unknown were calculated and are shown in Figure 5a. Both TiO\(_2\) and Fe\(^{2+}\)O\(_3\) 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\(^{2+}\)O\(_3\) 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 Fe\(^{2+}/Fe^{3+}\)) due to their substitution. In magnetite, some elements can replace Fe to form a series of solid solution, such as Fe\(^{2+}\)(1\(+X\))Fe\(^{3+}\)(2\(-2X\))\(Ti_XO_4\). The ratio of Fe\(^{2+}/Fe^{3+}\) 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 Fe\(^{2+}\)(1\(+X\))Fe\(^{3+}\)(2\(-2X\))\(Ti_XO_4\), 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 Mg\(_X\)Fe\(^{2+}\)(1\(-X\))Fe\(^{3+}\)2\(O_4\) 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 Zn\(_X\)Fe\(^{2+}\)(1\(-X\))Fe\(^{3+}\)2\(O_4\), 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 \(^{2+}\). However, the non-integer Fe and Mn valences of 2.667 cannot be used in JEOL and CAMECA EPMA software.

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) Fe\(^{2+}\)(1\(+X\))Fe\(^{3+}\)(2\(-2X\))\(Ti_XO_4\) solid solution, (c) Mg\(_X\)Fe\(^{2+}\)(1\(-X\))Fe\(^{3+}\)2\(O_4\) solid solution and (d) Zn\(_X\)Fe\(^{2+}\)(1\(-X\))Fe\(^{3+}\)2\(O_4\) solid solution. [Colour figure can be viewed at wileyonlinelibrary.com]
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 Fe₂O₃ in magnetite and 3:4 for Mn₃O₄ 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 (Fe₂O₃), 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

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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).