Quantitative analyses (II) & Element mapping

- Preparing your analysis
- Peak interferences
- From weight-% to atomic proportion (mineral formula normalization)

And also...
- Image quality and beam resolution
- Common artifacts
- Quantitative element maps

Creating a new analysis setup, some guidelines...

1) **Prepare your sample** (mounting, polishing…) and take pictures of your sample (scans and/or microphotographs).
2) **Coat** (carbon or metal) the sample; use same coating on standards!
3) Determine **domains to be analyzed** and make a list of mineral to be analyzed. You might need more than one analytical setup!
4) Determine **list of elements** that need to be analyzed.
5) Choose **X-ray line** to be analyzed for each element. Try to avoid X-ray line associated with valence electron (additional complications here…). Pay attention to possible peak and background interferences!
6) Determine the **optimum acceleration voltage** based on the higher critical ionization energy of all X-ray lines to be analyzed.
7) Determine **beam current** and **beam size**. No absolute rule, might need…
   - 20 nA and focused ("0 μm") to 5 μm beam size works for most application (good counting rate, good spatial resolution)
   - Lower current and/or larger beam size for beam sensitive minerals
   - Set the beam size adequately in function of the feature you need to analyze, but not too small if your sample is beam sensitive. Might need tests to assess this…
   - Use a higher current for trace element analysis desirable (50 to 200 nA or more!).
Creating a new analysis setup, some guidelines...

8) Determine which *diffraction crystals / monochromators* you will need. For some element more than one crystal might be available, choice will depend on whether you need spectral resolution or higher count rate...

9) Optimize your setting by *minimizing the total analysis time*:
   - Split elements over all available spectrometer / monochromators. Some restrictions can apply (e.g. monochromator only available on 1 or 2 spectrometers).
   - Avoid flipping monochromators if possible.
   - Adjust counting time for peak & background to optimize total analysis time. Use short counting time for major elements (10-20 sec) and longer (100-500 sec) for trace elements (depending on the precision level / detection limit you need to reach). Optimize counting time so all spectrometers finish acquisition at same time.

10) Optimize the PHA setting for each spectrometer / element.

11) Pay attention to *possible complications* (peak & background positions), Perform WDS scan if not sure...

12) Choose *adequate standard* and analyze them. For one element you might want different standard (different mineral to analyze)...

13) Finally *run a secondary standard analysis* to make sure your analysis setup is OK, then *analyze your own sample*.

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### Creating a new analysis setup, some guidelines...\n
<table>
<thead>
<tr>
<th>Feldspar (JEOI-8803)</th>
<th>Plagioclase, K-feldspar</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Min. systematic:</strong></td>
<td>Silicate</td>
</tr>
<tr>
<td><strong>Type:</strong></td>
<td>Oxide-like</td>
</tr>
<tr>
<td><strong>Not analyzed:</strong></td>
<td>0</td>
</tr>
<tr>
<td><strong>Voltage:</strong></td>
<td>15 kV</td>
</tr>
<tr>
<td><strong>Current:</strong></td>
<td>20 nA</td>
</tr>
<tr>
<td><strong>Beam size:</strong></td>
<td>5 μm</td>
</tr>
</tbody>
</table>

#### *** Setup 1 ***

<table>
<thead>
<tr>
<th>Cl. (µm)</th>
<th>Std. name</th>
<th>Line</th>
<th>Spectro. Crystal</th>
<th>Peak</th>
<th>Dkg</th>
<th>Bkg</th>
<th>Bkg std</th>
<th>Dia.</th>
<th>Dia. type</th>
<th>Std Bkg type</th>
<th>Time (min)</th>
<th>Bias (V)</th>
<th>Window size</th>
<th>Mode</th>
<th>Count</th>
<th>Cnt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na (4)</td>
<td>Analyses (04)</td>
<td>Zrka</td>
<td>Zrka</td>
<td>119-135</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>Linear</td>
<td>Linear</td>
<td>2020</td>
<td>17-15</td>
<td>17-15</td>
<td>5 µm</td>
<td>2 µm</td>
<td>1.078</td>
</tr>
<tr>
<td>Mg (11)</td>
<td>Mg-Fe-Fe</td>
<td>Jolka</td>
<td>Zrka</td>
<td>107-151</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>Linear</td>
<td>Linear</td>
<td>2020</td>
<td>17-15</td>
<td>17-15</td>
<td>5 µm</td>
<td>2 µm</td>
<td>1.083</td>
</tr>
<tr>
<td>Fe (10)</td>
<td>Analyses (04)</td>
<td>Zrka</td>
<td>Zrka</td>
<td>118-132</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>Linear</td>
<td>Linear</td>
<td>2020</td>
<td>17-15</td>
<td>17-15</td>
<td>5 µm</td>
<td>2 µm</td>
<td>1.087</td>
</tr>
<tr>
<td>Ca (9)</td>
<td>Analyses (04)</td>
<td>Zrka</td>
<td>Zrka</td>
<td>118-132</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>Linear</td>
<td>Linear</td>
<td>2020</td>
<td>17-15</td>
<td>17-15</td>
<td>5 µm</td>
<td>2 µm</td>
<td>1.087</td>
</tr>
<tr>
<td>Na (4)</td>
<td>Analyses (04)</td>
<td>Zrka</td>
<td>Zrka</td>
<td>118-132</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>Linear</td>
<td>Linear</td>
<td>2020</td>
<td>17-15</td>
<td>17-15</td>
<td>5 µm</td>
<td>2 µm</td>
<td>1.087</td>
</tr>
<tr>
<td>K (5)</td>
<td>Analyses (04)</td>
<td>Zrka</td>
<td>Zrka</td>
<td>118-132</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>Linear</td>
<td>Linear</td>
<td>2020</td>
<td>17-15</td>
<td>17-15</td>
<td>5 µm</td>
<td>2 µm</td>
<td>1.087</td>
</tr>
</tbody>
</table>

**Analysis order & time (setup 1)**

<table>
<thead>
<tr>
<th>Sp. 1</th>
<th>Sp. 2</th>
<th>Sp. 3</th>
<th>Sp. 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>K</td>
<td>Ca</td>
<td>Fe</td>
</tr>
<tr>
<td>Mg</td>
<td>Zrka</td>
<td>Zrka</td>
<td>Zrka</td>
</tr>
</tbody>
</table>

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*Footnotes for setup 1:*

1. Can use the same setting with another Mg-rich clino-plagioclase (e.g. Plagioclase (04))
2. Use K-rich sample, self-background to −5.5 & +4.5.
3. High background can be set to −1.5 for Ca-poor samples. For K and Ca-rich samples, increase the high background to 7 to avoid Ca and K-blows.
4. Use for Zr-contents (e.g. garnet and garnet) as its −130 to −160 or −180 analytes, while garnet (analyses 04) at −100 to −120 analytes (−10% deviation from standard values).
5. *F* measured on Zr-peak increases the count rate but reduces peak wobble. To improve precision using Zr-peak.
6. *Increase counting time (e.g. 190 to 1180 on peak and background) or beam current.*
Spectral Interferences

We need to accurately measure element A ($\lambda_A$), which is interfered by a minor X-ray line of element B ($\lambda'_B$). Need to correct for peak interferences, i.e. intensity stemming from another peak – not the one we are actually measuring.

First raw correction, using Gilfrich et al. (1978) equation…

$$I_{corrected} = I_{measured} - f I_{Interference}$$

f = interference coefficient (intensity of interfering element in standard that do NOT contain the interfered element, normalized to the concentration of the interfering element)
Spectral Interferences

\[ I_{\text{corrected}} = I_{\text{measured}} - \int I_{\text{Interference}} \]

Eq. 1

\[ C_A^L = C_A^S \frac{[ZAF]^L_A}{[ZAF]^S_A} \frac{I^L(\lambda_A)}{I^S(\lambda_A)} \]

Gilfrich et al. (1978)

What you need to know…

- \( I^L_A(\lambda_A) \): Intensity measured at wavelength of element A (\( \lambda_A \))
- \( I^S_A(\lambda_A) \): Intensity of standard for A at wavelength of element A (\( \lambda_A \))
- \( I^B(\lambda_A) \): Intensity of interfering element B in standard at \( \lambda_A \)
- \( C_B^S \): Concentration of interfering element B in standard
- \( C_B^L \): Concentration of interfering element B in unknown

The rest of the equation remains similar to any other quantitative analysis:

\[ C_A^L = C_A^S \times \left( \frac{ZAF^u}{ZAF^s} \right) \times \left( \frac{I^u}{I^s} \right) \]

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Spectral Interferences

New software offer a fully quantitative matrix correction and iteration method (rigorously accurate even for extreme overlap situations such as “cascade” and “pathological” overlaps situations).

Eq. 2

\[ C_A^L = C_A^S \frac{[ZAF]^L_A}{[ZAF]^S_A} \frac{I^L(\lambda_A)}{I^S(\lambda_A)} \]

Donovan et al. (1993)
Quantitative spectral interference correction

Self-Interfering Analyses

<table>
<thead>
<tr>
<th></th>
<th>wt. % (nominal)</th>
<th>wt. % (uncorrected)</th>
<th>wt. % (% Eq. 1)</th>
<th>wt. % (% Eq. 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba Lx ** Ti Kx</td>
<td>33.13</td>
<td>11.26 ± 0.18</td>
<td>11.59</td>
<td>13.08 ± 0.18</td>
</tr>
<tr>
<td>Fe Lx ** Ti Kx</td>
<td>11.69</td>
<td>11.71 ± 0.08</td>
<td>11.59</td>
<td>11.59 ± 0.08</td>
</tr>
<tr>
<td>Fe Lx ** As Kx</td>
<td>0.01</td>
<td>0.010 ± 0.006</td>
<td>0.010</td>
<td>0.022 ± 0.008</td>
</tr>
<tr>
<td>Ti Kx ** V Kx</td>
<td>0.01</td>
<td>0.216 ± 0.01</td>
<td>0.020</td>
<td>0.021 ± 0.010</td>
</tr>
</tbody>
</table>

1 Benitoite (BaTiSi3O9) is assumed stoichiometric:  Si 20.38, Ba 33.15, Ti 11.69, O 34.90
2 Shultenite (HAsPbO4) is assumed stoichiometric:  Pb 59.69, As 21.58, O 18.44

Cascade Interference Analyses

<table>
<thead>
<tr>
<th></th>
<th>wt. % (nominal)</th>
<th>wt. % (uncorrected)</th>
<th>wt. % (% Eq. 1)</th>
<th>wt. % (% Eq. 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni Kx → Fe Kx</td>
<td>Cu 0.022</td>
<td>0.019 ± 0.006</td>
<td>0.010</td>
<td>0.022 ± 0.008</td>
</tr>
<tr>
<td>Fe Kx → Co Kx</td>
<td>Cu 0.025</td>
<td>0.216 ± 0.01</td>
<td>0.020</td>
<td>0.021 ± 0.010</td>
</tr>
<tr>
<td>Ti Kx → V Kx</td>
<td>Cu 0.023</td>
<td>0.019 ± 0.006</td>
<td>0.010</td>
<td>0.022 ± 0.008</td>
</tr>
</tbody>
</table>

3 SRM 1159 includes:  Ni 48.2, Fe 51.0, C 0.007, Mn 0.30, P 0.003, S 0.003, Si 0.32, Cu 0.038, Cr 0.06, Mo 0.01
4 SRM 654b includes:  Ti 88.974, Al 6.34, V 4.31, Fe 0.23, Si 0.045, Ni 0.028, Sn 0.023, Cu 0.004, Mo 0.013, Zr 0.008

Iterated correction!

Constructing mineral formulas

From chemical analyses to balanced equations
Basic terminology

Atomic weight \((A_w, \text{dimensionless})\): ratio of average mass of an atom relative to 1/12 the mass of one atom of \(^{12}\text{C}\) in its neutral and electronic ground state (= atomic mass constant, \(m_u \sim 1.66\times10^{-24} \text{ g}\)).

Molecular weight (dimensionless): weight of all atoms in a given molecule.

Example: 1 mole \(H_2O = 2H + 1O = (2\times1.008) + (1\times15.999) = 18.015 \text{ g}\)

Mole: ratio of number of entities \(N\) (atoms or molecules) to amount of substance \(n \Rightarrow 1\) mole of a substance = \(6.022 \times 10^{23}\) atoms = \(N_A\).

Avogadro’s Number = \(N_A\) = \(N/n\)

\[= 1 \text{ gram per mole}\]
\[= 1 \text{ gram-molecule}\]

1 gram-molecule = equivalent number of atom in 12 g of \(^{12}\text{C}\)
Basic terminology (2)

Every crystalline substance can be expressed as a mineral formula reflecting the atomic proportion (e.g. SiO₂, FeTiO₃, etc.). To obtain a mineral formula, we need to convert a chemical analysis (amount of substance: weight-percent, ppm, gram…) in a number of atoms that will fit our expected mineral formula. This process is called normalization or mineral formula recalculation, which aims to normalize a quantity to a fixed (constrained) value. This is commonly done assuming a fixed total of oxygen, cation and/or one or more atom(s):

- 2 oxygens, 1 cation in quartz: SiO₂
- 8 oxygens, 5 cations in feldspar: (Na,K)AlSi₃O₈
- 3 atoms in pyrite: FeS₂

Atoms per formula units (a.p.f.u. or p.f.u.): numbers of atoms in a chemical (mineral) formula.

O-Factor (oxygen-factor): the a.p.f.u.’ value scaled to a standard chosen number of oxygens based on the simplified mineral formula for a given mineral species.

4 ways of expressing mineral composition

Talc: sheet silicate usually formed from metamorphosed ultramafics.

Ideal chemical formula: Mg₃[Si₄O₁₀](OH)₂

In terms of weight percent oxides (wt%) and molecular proportion:

<table>
<thead>
<tr>
<th></th>
<th>MgO</th>
<th>SiO₂</th>
<th>H₂O</th>
<th></th>
<th>MgO</th>
<th>SiO₂</th>
<th>H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>31.88</td>
<td>63.37</td>
<td>4.75</td>
<td></td>
<td>3</td>
<td>4</td>
<td>1</td>
</tr>
</tbody>
</table>

In terms of weight percent elements and a.p.f.u.:

<table>
<thead>
<tr>
<th></th>
<th>Mg</th>
<th>Si</th>
<th>O</th>
<th>H</th>
<th>Mg</th>
<th>Si</th>
<th>O</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>19.23</td>
<td>29.62</td>
<td>50.62</td>
<td>0.53</td>
<td>3</td>
<td>4</td>
<td>12</td>
<td>2</td>
</tr>
</tbody>
</table>
Mineral formula 1 – all elements analyzed

Example: oxygen-free mineral, metal alloy…

1) Determine the mineral formula you expect from the chemical analysis (i.e. determine the proportion of each element and the total number of cation and anion).

2) Divide each weight-% value by its atomic weight to obtain an atomic proportion.

3) Total up the number of atom proportions and divide each atomic proportion by this value. You obtain the ratio of the number of each element present in the formula. The sum of these equal 1 (or 100%).

4) Multiply these results by the total number of elements expected in your mineral formula. You should obtain a fraction of each element, and thus the mineral formula!

1) In some cases, you further need to perform a site repartition, i.e., placing each atoms to a specific crystallographic site. Some mineral can have the same atom at different site!

---

Mineral formula 1 – Example “sulfide”

A chemical analysis of an unknown mineral is given below:

<table>
<thead>
<tr>
<th>Element</th>
<th>Fe</th>
<th>Cu</th>
<th>S</th>
<th>Sum</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30.41</td>
<td>34.53</td>
<td>34.87</td>
<td>99.81</td>
</tr>
</tbody>
</table>

From the amount of Fe, Cu and S we can guess this has to be a sulfide of copper and iron, this can be (among other solutions…):

– Chalcopyrite \( \text{CuFeS}_2 \) => total 4 atoms per formula
– Cubanite \( \text{CuFe}_5\text{S}_3 \) => total 6 atoms per formula
– Bornite \( \text{Cu}_5\text{FeS}_4 \) => total 10 atoms per formula
– Haycockite \( \text{Cu}_4\text{Fe}_2\text{S}_8 \) => total 17 atoms per formula

Calculation (normalization) based on one of these 4 minerals yields…

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Fe</th>
<th>Cu</th>
<th>S</th>
<th>Sum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chalcopyrite</td>
<td>1.001</td>
<td>0.999</td>
<td>2.000</td>
<td>4.000</td>
</tr>
<tr>
<td>Cubanite</td>
<td>1.502</td>
<td>1.499</td>
<td>2.999</td>
<td>6.000</td>
</tr>
<tr>
<td>Bornite</td>
<td>2.503</td>
<td>2.498</td>
<td>4.999</td>
<td>10.000</td>
</tr>
<tr>
<td>Haycockite</td>
<td>4.256</td>
<td>4.246</td>
<td>8.498</td>
<td>17.000</td>
</tr>
</tbody>
</table>

The unknown mineral is thus Chalcopyrite: \( \text{Fe}_{1.001}\text{Cu}_{0.999}\text{S}_{2.000} \)
1) Chalcopyrite (CuFeS₂)

<table>
<thead>
<tr>
<th>Element</th>
<th>wt% charge</th>
<th>wt% element</th>
<th>Atomic weight</th>
<th>Atomic proportion</th>
<th># of elements</th>
<th>Atomic proportion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>2</td>
<td>30.41</td>
<td>55.845</td>
<td>0.5445</td>
<td>0.2503</td>
<td>1.0013</td>
</tr>
<tr>
<td>Cu</td>
<td>2</td>
<td>34.53</td>
<td>63.546</td>
<td>0.5434</td>
<td>0.2498</td>
<td>0.9992</td>
</tr>
<tr>
<td>S</td>
<td>-2</td>
<td>34.87</td>
<td>32.066</td>
<td>1.0874</td>
<td>0.4999</td>
<td>1.9996</td>
</tr>
<tr>
<td>SUM</td>
<td>E7</td>
<td>2.1754</td>
<td>1.0000</td>
<td>4.0000</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1) Determine the mineral formula you expect from the chemical analysis (i.e. determine the proportion of each element and the total number of cation [Fe, Cu] and anion [2 * S]).
2) Divide each weight-% value (column C) by its atomic weight (column D) to obtain an atomic proportion (column E).
3) Total up the number of atom proportions (cell E7) and divide each atomic proportion by this value (column F) ➔ ratio of the number of each element present in the formula. The sum of these equal 1.
4) Multiply these results by the total number of atoms expected in your mineral formula (here, 4 atoms). You should obtain a clear fraction of each element, and thus the mineral formula!

Mineral formula 2 – Oxides (fixed oxidation state)

Example: anhydrous silicates, phosphates… ➔ All but one element not analyzed (oxygen)

Key point: you need to know (or assume) the oxidation state of each analyzed cations…

Example: olivine is a solid solution series between an Mg and Fe rich set of end-members: **Forsterite** (Mg₂SiO₄) and **Fayalite** (Fe₂SiO₄)
➔ ideal formula (Mg, Fe, ±Ca, ±Mn)₂ SiO₄

Chemical analysis (adapted from Floran & Papke, 1973)

<table>
<thead>
<tr>
<th>SiO₂</th>
<th>FeO</th>
<th>MnO</th>
<th>MgO</th>
<th>CaO</th>
</tr>
</thead>
<tbody>
<tr>
<td>30.09</td>
<td>70.10</td>
<td>0.28</td>
<td>0.91</td>
<td>0.08</td>
</tr>
</tbody>
</table>

Comment: oxygen not analyzed, but all element weight-percent is converted in oxide weight-percent.

QUESTIONS…
– Which olivine is this an analysis of?
– In this case, we did not analyze all elements, especially oxygen. How can we smartly calculate the formula in apfu?
– How many oxygen atoms will we need to base the calculation on?
Mineral formula 2 – Oxygen normalization, solution I
Based on weight-% element & total positive charges balanced by oxygen

1) Convert from weight-% oxide to weight-% element using tabulated conversion factors and the appropriate atomic weight.

2) Calculate the a.p.f.u.' values by dividing the weight-% element by the atomic weight.

3) Determine the total positive charge by multiplying the stated charge and the a.p.f.u. value for each element.

4) Calculate how much oxygen is needed to balance the charge by taking the sum of the a.p.f.u. charges and dividing by -2.

5) Calculate the O-factor based on the idealized chemical formula.

6) Multiply the O-factor by the a.p.f.u. values.

Once these steps are complete, an analysis based on the oxides can be converted to a balanced formula.

Mineral formula 2 – Oxides (fixed oxidation state)
Example: anhydrous silicates, phosphates...
⇒ All but one element not analyzed (oxygen)

Olivine is a solid solution series between an Mg and Fe rich set of end-members: Forsterite and Fayalite.

Olivine general formula: \[M2 \text{ M1 SiO}_4\] (atom radii: \(M2 > M1\))

\[\begin{align*}
M2 &= \text{Ca}^{2+}, \text{Mg}^{2+}, \text{Fe}^{2+/3+}, \text{Mn}^{2+} \\
M1 &= \text{Mg}^{2+}, \text{Fe}^{2+/3+}, \text{Mn}^{2+}
\end{align*}\]

Based on the general formula \((\text{Mg,Fe})_2\text{SiO}_4\), we can now assign a new formula to this specific species of Olivine:

\[
(\text{Mg}_{0.0450} \text{Fe}_{1.9464} \text{Mn}_{0.0079} \text{Ca}_{0.0028}) \text{Si}_{0.9989} \text{O}_4
\]

Sum of M1 and M2 cations: \(0.0450 + 1.9464 + 0.0079 + 0.0028 = 2.0021\ (-2)

What does the difference to 2.000 (= +0.0021) in \(M1+M2\) site mean?
• Missing element or extra element (e.g. from inclusion)
• Void / vacancy
• Most likely reflect your analysis error!
### Olivine

<table>
<thead>
<tr>
<th>Oxide</th>
<th>El. charge</th>
<th>wt% oxide</th>
<th>wt% conversion factor</th>
<th>wt% atomic element</th>
<th>wt. apfu</th>
<th>apfu charge</th>
<th>apfu</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>Si⁺⁺</td>
<td>4</td>
<td>30.09</td>
<td>0.4674</td>
<td>14.06</td>
<td>28.086</td>
<td>0.5008</td>
</tr>
<tr>
<td>FeO</td>
<td>Fe⁺⁺</td>
<td>2</td>
<td>70.10</td>
<td>0.7773</td>
<td>54.49</td>
<td>55.845</td>
<td>0.9757</td>
</tr>
<tr>
<td>MnO</td>
<td>Mn⁺⁺</td>
<td>2</td>
<td>0.28</td>
<td>0.7745</td>
<td>0.22</td>
<td>54.938</td>
<td>0.0039</td>
</tr>
<tr>
<td>MgO</td>
<td>Mg⁺⁺</td>
<td>2</td>
<td>0.91</td>
<td>0.6030</td>
<td>0.55</td>
<td>24.305</td>
<td>0.0226</td>
</tr>
<tr>
<td>CaO</td>
<td>Ca⁺⁺</td>
<td>2</td>
<td>0.08</td>
<td>0.7147</td>
<td>0.06</td>
<td>40.078</td>
<td>0.0014</td>
</tr>
</tbody>
</table>

1) Convert from wt% oxide to wt% element using tabulated conversion factors and the appropriate atomic weight (columns C to F).

2) Calculate the apfu values by dividing the wt% element by the atomic weight (column G and H).

3) Determine the total positive charge by multiplying the stated charge and the apfu value for each element (column I).

4) Calculate how much oxygen is needed to balance the charge by taking the sum of the apfu charges and dividing by 2 (O = 2 negative charges; cell I₁₂ = I₁₁ / 2).

5) Calculate the O-factor based on the idealized chemical formula (cell I₁₄ = I₁₃ / I₁₂).

6) Multiply the O-factor by the apfu values (column J).

---

**Note on the oxide to element conversion**

Calculation of conversion is done following this logic (example Al₂O₃):

- Get the molecular weight of Al₂O₃: \( W_{\text{Al}_2\text{O}_3} = 101.96 \)
- Get the atomic weight of Al: \( W_{\text{Al}} = 26.98 \)
- Determine # of mole of element in oxide: \( n_{\text{Al}} = 2 \text{ mole} / 1 \text{ mole Al}_2\text{O}_3 \)
- Use the following calculation to convert you oxide to element weight-%:

\[
(\text{Element} \%) = \text{Oxide} \% \times \frac{\text{W}_{\text{Al}}n_{\text{Al}}}{\text{W}_{\text{Al}_2\text{O}_3}} = \frac{\text{Oxide} \%}{0.5292}
\]
Mineral formula 2 – Oxygen normalization, solution II
Based on weight-% oxide & total number of oxygen

1) Divide each oxide value by its molecular weight to obtain a molecular proportion.

2) Calculate the atomic proportion by multiplying the molecular proportion of each oxide by the number of oxygen in the oxide formula (e.g. 2 for SiO₂, 3 for Al₂O₃).

3) Sum all atomic proportions and divide it by the expected number of O (“total O”) in mineral formula = O-factor.

4) Multiply each atomic proportion by the O-factor. You obtain the number of O for each oxides based on the “total O”.

5) Finally, divide each of these previous values by the ratio of number of oxygen to the number of cation in oxide (e.g. 2 for Si⁴⁺O₂⁻, 1.5 in Al³⁺O₃²⁻, 0.5 in K⁺O²⁻...).

Result (olivine): (Mg₀.0450Fe₁.948₄Mn₀.0079Ca₀.0028)Si₀.9989O₄
The valance state problem

Valance state of some species can vary from specimen to specimen and sometimes within single minerals.

While Cr (2+,3+), Ti (3+,4+), and V (2+ to 5+) are not very common, others are, most notably Fe and Mn:
- \( \text{Fe}^{2+} \) (FeO) & \( \text{Fe}^{3+} \) (\( \text{Fe}_2\text{O}_3 \))
- \( \text{Mn}^{2+} \) (MnO) & \( \text{Mn}^{3+} \) (\( \text{Mn}_2\text{O}_3 \))

For accurate mineral formula, percentages of each valance state must be determined; EPMA* and SEM (EDS) are not accurate enough to do this, and other techniques are required (e.g. Mössbauer spectroscopy, wet chemistry…).

* EMPA can only giving you an idea based on the “charge balance”: fixing the amount of cation during normalization and assuming a determined number of oxygen, we can deduce the charge deficiency of excess. Charge deficiency can to some extent be balanced with variable amount of +2/-3 cations (either Fe or Mn or another, but only one of these…).

One technique involving the measurement of X-ray related to valence electron (Fe Lα/Lβ) can estimate \( \text{Fe}^{2+}/\text{Fe}^{3+} \) proportion. However: less precise + need specific calibration for each mineral type!

Mineral formula 3 – Cation normalization

Based on total number of cation AND oxygen

1) Divide each oxide value by its molecular weight and multiply by the number of cation in the oxide to obtain the number of cation.

2) Sum the number of cation and divide the ideal number of cation by this sum. Multiply each number of cation by this ratio.

3) We obtain here the apfu of the mineral formula by forcing a fixed amount of cation. The total charge of these cations is calculated and compared to the number of O in the formula. Any discrepancy between the charge of cation and the number of O (excess charge + or deficiency −) may reflect:
   a) Error in the analysis (missing element, too high/low wt-% of element)
   b) Charge deficiency (may be balanced, e.g. between \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \))
   c) Presence of additional anion, excess of oxygen (\( \text{F}^- \), \( \text{Cl}^- \), \( \text{O}^{2-} \)).

Result (olivine): \( (\text{Mg}_{0.0459}\text{Fe}^{2+}_{1.9425}\text{Fe}^{3+}_{0.0028}\text{Mn}_{0.0079}\text{Ca}_{0.0028})\,\text{Si}_{0.9988}\text{O}_4 \)
OLIVINE | C | D | E | F | G | H | I | J
| oxide | El. | Cation | charge | wt% molecular weight | Nbr Cation | Nbr cation norm. | Charge balance | wt% oxide |
| SiO2 | Si4+ | 1 | 4 | 30.09 | 60.0843 | 0.5008 | 0.9986 | 0.9986 |
| FeO | Fe2+ | 1 | 2 | 70.10 | 71.8444 | 0.9757 | 1.9456 | 1.9429 | 70.0004 |
| Fe2O3 | Fe3+ | 2 | 3 | 159.6900 | - | - | 0.0028 | 0.2213 |
| MnO | Mn2+ | 1 | 2 | 0.28 | 70.9374 | 0.0039 | 0.0079 | 0.0079 |
| MgO | Mg2+ | 1 | 2 | 0.91 | 40.3044 | 0.0226 | 0.0450 | 0.0450 |
| CaO | Ca2+ | 1 | 2 | 0.08 | 56.0774 | 0.0014 | 0.0028 | 0.0028 |

1) Divide each oxide value by its molecular weight and multiply by the number of cation in the oxide to obtain the number of cation.

2) Sum the number of cation and divide the fixed number of cation by this sum. Multiply each number of cation by this ratio.

3) We obtain apfu of mineral formula by forcing a fixed amount of cation AND oxygen. The total charge of these cations is calculated and compared to the number of O in the formula. Any discrepancy between the number of cation and the number of O (excess charge + or deficiency −) may reflect:
   a) Error in the analysis (missing element, too high/low weight-% of element)
   b) Charge deficiency (may be balanced, e.g. between Fe2+ and Fe3+)
   c) Presence of additional anion, excess of oxygen (F−, Cl−, O2−)
   d) Etc.

Recalculation of FeO and Fe2O3 wt-%

Charge balance with Fe3+

Taking back example of olivine, let’s check the charge balance:

a) OXYGEN normalization…

(Mg0.046Fe1.946Mn0.008Ca0.003)Σ=2.002 Si0.999 O4

b) CATION AND OXYGEN normalization…

(Mg0.046Fe2+1.946Fe3+0.003Mn0.008Ca0.003)Σ=2.002 Si0.998 O4

a) Charge balanced is respected by fixing amount of oxygen, but the total number of cation may or may not be exactly 3.

b) Charge balanced is achieved by converting a little amount of Fe2+ in Fe3+, and the total amount of cation AND oxygen reaches exactly the expected values (4 oxygens, 3 cations)
Example from the amphibole

Idealized (or general or ideal) formula:

\[ \text{A}_{0.1} \text{B}_2 \text{C}_5 \text{T}_8 \text{O}_{22} (\text{OH})_2 \]

Na Ca₂ (Mg,Fe²⁺)₄Ti (Si₆Al₂) O₂₂ (OH)₂

\[ O^{2-} + (OH)^- + F^- + Cl^- = \approx 24 \text{ oxygen / anion units} \]

How to fill each site in amphibole?

**Amphiboles:**

\[ \text{A}_{0.1} \text{M}_4 \text{M}_3 \text{M}_2 \text{M}_1 \text{Si}_8 \text{O}_{22} (\text{OH})_2 \]

\[ \text{A}_{0.1} \text{B}_2 \text{C}_5 \text{T}_8 \text{O}_{22} (\text{OH})_2 \]

(site size: A > B > C > T)

- **A** = K⁺, Na⁺¹
- **B** = Na⁺¹, Ca²⁺, Mg²⁺, Fe²⁺, Mn²⁺
- **C** = Mg²⁺, Fe²⁺/³⁺, Mn²⁺, Al³⁺, Cr³⁺
- **T** = Si⁴⁺, Al³⁺, Fe³⁺
- **OH** = (OH)⁻, F⁻, Cl⁻, O²⁻

**Fill each cation site in this order:** from smaller to larger site.
Example from the amphibole

**Final formula:**

\[
\begin{align*}
N_{a,7650} & \quad K_{0.3201} & \quad Ca_{1.7849} \\
Fe^{2+}_{0.9962} & \quad Mn_{0.0218} & \quad Mg_{2.7402} \\
Fe^{3+}_{0.5096} & \quad Ti_{0.5504} & \quad Cr_{0.0036} \\
Si_{5.8616} & \quad Al_{2.6086} & \quad O_{22.8335} \\
(F_{0.1052} & \quad Cl_{0.0026} & \quad (OH)_{0.10588})
\end{align*}
\]

During calculation, make sure to take into account of F\(^{-}\) and Cl\(^{-}\) as additional anions:

1) They reduce the total charge on a.p.f.u.
2) The O-factor is equal to the number of oxygen divided by the sum of charges of oxygen (O\(^{2-}\)), fluorine (F\(^{-}\)), and chlorine (Cl\(^{-}\)).

Because of the structure of the amphiboles, it is very common to have isomorphous replacements in the A, B and C sites.

**Thumb rule for determining site occupancy:** fill smaller site before filling the largest site (i.e. fill T, then C, then B, and finally A).

---

The problem of OH\(^{-}\) or (CO\(_3\))\(^{2-}\) groups

Normally, for oxides, only one element is not analyzed, and we simply assume a fixed oxidation state / total number of oxygen.

However, for hydrous or carbonate phases, both H (or C) and O are NOT analyzed! Another method is often required and rarely applied unless really necessary (time and money consuming). Without H (or C) analysis, the analysis result of hydrous phases by EMP analysis is often below 100% (i.e. missing x.xx% H\(_2\)O or x.xx% CO\(_2\)). However, adding a second condition during the normalization process permit an estimate of the H\(_2\)O or CO\(_2\) content... Also, it ensures a proper matrix correction (more accurate if we include ALL elements present).

Key principle is to fix the amount of OH-group expected in mineral formula, and recalculate the expected H\(_2\)O content. Once the expected H\(_2\)O content is estimated, a new analysis total can be computed, and if the analysis is correct, this new total should be close to 100%.

**WARNING:** do not forget that F\(^{-}\), Cl\(^{-}\) and sometimes O\(^{2-}\) are also part of this "hydrous-group", and should therefore be deduced from the calculated H\(_2\)O content. One should also calculate an "equivalent oxygen" correction for the presence of extra anion (F, Cl).
Steps to estimate H$_2$O-content based on mineral formula

AFTER the mineral normalization (oxygen- or cation- based)...

a) Determine the theoretical amount of (OH) group per mineral formula $\Rightarrow X_{OH}$

b) Deduce from $X_{OH}$ the a.p.f.u. of F and Cl measured (determined during the mineral normalization process) $\Rightarrow X_{(OH+[F+Cl])}$

c) Multiply $X_{(OH+[F+Cl])}$ by the molecular weight of H$_2$O

d) Divide this value by the oxygen or cation factor used during normalization. The result represent the equivalent H$_2$O weight-% expected assuming the fixed amount of (OH)-group.

Similar calculation applies for (CO$_3$) groups (carbonate!). Point (d) can also be used to recalculate FeO and Fe$_3$O$_4$ from new atomic proportions...

To determine oxygen equivalent from F+Cl anions (O = F,Cl)...

- Multiply the a.p.f.u. of F (or Cl) by the atomic weight-% of oxygen
- Divide the result by (2 * atomic weight of F [or Cl]). The “2” factor stem from the fact that... 2 F$^-$ (or 2 Cl$^-$) = 1 O$^{2-}$ (charge balance!).
- This result should be deduced from the calculated oxygen wt-%...

Some considerations about element maps...
Element mapping – Introduction

Element mapping is easily obtained, and requires a flat, horizontal surface. Can be performed using EDS or WDS, but WDS is preferred as…

- EDS requires a LONG acquisition time (>0.5 to 1 second per point for high resolution image, especially with minor / trace element)
- EDS suffers of peak overlaps. Unless EDS peak is clean, this won’t work properly!

**Acquisition time:** For optimum mapping, you will usually use a longer dwell time than for BSE/SE images. Typical counting time is in the order of 10s to 100s of milliseconds per step, depending on area to map (size) and the time available.

**Example:** 1 mm² area, 2 µm/step resolution, at 50 msec/step = ~3.5 hours.

Element mapping are usually qualitative. Newer software offers options for quantification, using the following procedure:

- Need to remove the background (bremsstrahlung)
- Need to quantify each pixels (counts → weight-%):
  - Most programs will simply use a single standard; so basically it calculates the k-ratio and multiply value by concentration of the element in standard
  - More “evolved” software will permit you a full quantification with matrix correction (ZAF or f(pz)). However, for this to work properly, you NEED TO MAP ALL ELEMENTS (at least the major) or constrain the composition by fixing values for each non-analyzed element. It can also offer a correction for peak interference...

Element mapping – How it works

As for a quantitative analysis using WD spectrometers, we need to set spectrometer position to wavelength of X-ray line (element) to analyze, and choose between two scanning modes:

- **Rastering (beam) mode:** Deflecting beam over a certain area (stage fixed)
- **Stage mode:** Leave beam in “spot mode” (fixed) and move stage over area to map.

Stage mode is preferred for large area to map (> 50-100 µm; see next).

# element to map at once ≠ # of spectrometer (…duh!)

For full quantification, need a second pass to map same area at a background position (or at two background positions – then proceed to correction as you would do for quantitative analyses).

One software offers MAN correction (“mean atomic number” – remember that background value for an element is function of average atomic number…).

**WATCH OUT FOR ARTIFACTS due to geometrical factor** (i.e. Bragg’s law is not fully respected…).
**Element mapping – Artifacts due to z-focus (stage focus)**

A first artifacts occurs when sample is not perfectly flat and you do not correct for changes in z-focus (at the microscope).

Only the area with perfect z-focus will yield an optimum count rate, whereas unfocused area will yield lower count rate.

Effect is stronger for sharp peaks…

**Similar artifacts are produced with non-flat or non-horizontal surface (so cannot map “3D sample”)!**

---

**Element mapping – Artifacts due to beam rastering**

Other common artifact occurs when using beam rastering mode over a large area (> 50-100 μm).

Due to defocussing from the Rowland circle, Bragg’s law is not anymore respected, and counts are lost.

The two images aside where obtained in the same area, using two different spectrometer…

This effect is depending on which spectrometer you use (see next).
**Element mapping – Artifacts due to beam rastering**

![Diagram showing element mapping with artifacts due to beam rastering.]

**Element mapping – EDS vs. WDS**

Both element maps are of K Kα and are acquired at the same time.

EDS map has a higher geometric efficiency as the number of photons per pixel is larger, but the WDS map shows the much better sensitivity of the WDS acquisition and can discern the trace element variation easily.
**Element mapping** – *Mosaic mapping*

Instead of acquiring a stage map for large area, it is often faster to acquire a mosaic image, i.e. acquire several beam maps in rastering mode and stitch them together at the end…

This is called *mosaic mapping (or mosaic imaging)* and it is available on most EMP softwares. Stitching can be imperfect (e.g. problem of blurring or defocussing effect on the side of each picture), so for optimum resolution, stage rastering might be preferred. Still, mosaic image works great with BSE or SE detectors, which are less sensitive to defocussing effect…

---

**Element mapping** – *Improving resolution with multiple pass*

Multiple pass can improve resolution and prevent beam damage due to long and continuous exposure (better than using a single longer counting time).
Element mapping – Example (1)

Very high pressure metamorphism (>25kb, 600° C = Mg-rich core) and uplift of coesite-bearing metasediments from the Zermatt-Saas zone, Western Alps.

Matrix assemblage includes quartz (after coesite), phengite (Si ~ 3.4 apfu), Mn-rich phlogopite, piemontite, and Mn-rich calcite.

Inclusions in garnet are piemontite and quartz.

Note the angular unconformity between core and overgrowth.

Element mapping – Example (2)

Athabasca Granulite Terrane, Saskatchewan

Monazite dating and P-T calculation
Element mapping – Example (3)

Quantitative element map in pyroxene with exsolution lamellae.

The maps have been corrected for background using the MAN background correction. A full matrix correction is applied to each pixel.

The total image serve as a check that all is OK (should be 100%).

FOV: 180 x 165 µm (Mag. 200x)
Conditions: 15 keV; 100 nA, focused beam; 0.3 µm/px; 40 msec/px; Total 4 hr.

Element mapping – Example (4)

Mapping in rhyolite (glass & feldspars)

Quantitative cross-section across WDS element map

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<th>X-Section</th>
<th>SiO₂</th>
<th>TiO₂</th>
<th>Al₂O₃</th>
<th>K₂O</th>
<th>Na₂O</th>
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Glass

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Total | 100.00 | 100.91 | 101.72 | 100.95 | 97.26 |