# cationCalc4EPMA: Efficient processing tool for EPMA dataset

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Summary

The cationCalc4EPMA is a freely available MATLAB tool designed to process electron probe microanalysis (EPMA) data by converting oxide weight percentages into cation-based formulas. This conversion is crucial for petrological tasks such as determining structural formulas, estimating Fe^{3+}/Fe^{2+} ratios, recognizing solid-solution series, and performing thermobarometric modeling. The tool features automatic mineral identification using empirical composition thresholds and includes built-in functions for calculating commonly used petrological indices, like the Mg# (Mg / Mg + Fe) for olivine. Additionally, it provides batch averaging based on sample codes to streamline data interpretation. By replacing manual or proprietary workflows, cationCalc4EPMA improves reproducibility, transparency, and accessibility in the geoscientific analysis of EPMA datasets.

Statement of Need

Electron probe microanalysis (EPMA) is a contemporary technique grounded in the physical principles of electron-induced X-ray emission and wavelength-dispersive spectroscopy (WDS), initially developed by Raymond Castaing during his doctoral research in Paris (Castaing, 1951). This method stands out as one of the most effective microanalytical approaches for conducting precise, non-destructive, and quantitative elemental analysis of solid substances, such as minerals, at the micrometer level (Yang, 2022). As a result, EPMA is extensively utilized and has profoundly influenced geoscientific studies (Basch et al., 2024; Kouketsu et al., 2014; Sweatman & Long, 1969; Wiedenbeck et al., 2007).The compositional information derived from EPMA is crucial for interpreting pressure-temperature-time (*P-T-t)* histories (e.g., Ozawa, 2004), reconstructing fluid-rock interaction processes (e.g., Whattam et al., 2022), and assessing geodynamic conditions within the Earth's interior (e.g., Chardelin et al., 2024).

To extract meaningful petrological insights from EPMA data, it is crucial to convert weight percent values into cation-based formulas, which are typically standardized to a specific number of oxygen atoms or cations, depending on the mineral group. This transformation is essential for calculating structural formulas, evaluating Fe^{3+}/Fe^{2+} ratios, identifying solid-solution series, and performing thermobarometric modeling. Ensuring the reproducibility of this conversion method is particularly crucial, as several minerals, including amphibole (Holland & Blundy, 1994; Putirka, 2016; **?**), mica (**?**), and garnet (Grew et al., 2013), are named based on the calculated cation distribution. Despite its importance, many researchers continue to rely on outdated spreadsheet macros, manual calculations, or proprietary software, all of which are prone to human error and difficult to verify or replicate.

To address this issue, we have created cationCalc4EPMA, a cation calculator for EPMA datasets,

₄₂ designed for MATLAB. This tool imports .csv files produced by EPMA and transforms weight
₄₃ percent data into cations, adhering to open science principles to enhance reproducibility and
₄₄ transparency. The calculation procedures in cationCalc4EPMA are primally based on those of
₄₅ Deer et al. (Deer et al., 2013), except for the Fe^{3+} calculation.

₄₆ To estimate Fe^{3+}, the charge balance method or site allocation method is employed. This
₄₇ approach is tailored for specific minerals: pyroxenes (Papike & Baldwin, 1974), spinel and
₄₈ inverse spinel (Droop, 2018), amphibole (Holland & Blundy, 1994), epidote (Masumoto et al.,
₄₉ 2014), and garnet (Enami, 2012). Nonetheless, if verifying the exact amount of Fe^{3+} proves
₅₀ challenging or if its calculated presence might influence the end-member ratio, users have the
₅₁ option to assume $Fe^{3+} = 0$ by activating the commented-out code.

₅₂ A key feature of this calculator is its ability to automatically identify the mineral phase from
₅₃ the measured data using empirical mass percentages and subsequently compute the cations.
₅₄ Additionally, the calculator is composed of one module and one .m file, enabling users to easily
₅₅ modify the code to suit their specific requirements, such as for minerals with an extensive
₅₆ list or for calculations tailored to particular data based on location. This design caters to a
₅₇ broader spectrum of users who rely on EPMA analysis.

₅₈ Methods

₅₉ cationCalc4EPMA processes EPMA datasets using the following steps:

₆₀ 1. Importing Excel files:

₆₁ Users choose a raw data file (.csv or .xlsx) from a list dialog. The module Cation_moduli.xlsx,
₆₂ which works alongside the main script, is loaded automatically. This module includes two
₆₃ sheets: one that holds the molar weights, cation numbers, oxygen atom counts, and names of
₆₄ oxides/anions; and another that contains stoichiometric details for target minerals. To add
₆₅ more minerals to the list, users need to update this module accordingly.

₆₆ 2. Creating a mineral list:

₆₇ Users select the mineral phases anticipated to be present in the raw dataset to create a
₆₈ list of a list of these mineral phases. The potential candidates for this list can be found
₆₉ in the Cation_moduli.xlsx module. This initial list comprises olivine, orthopyroxene (Opx),
₇₀ clinopyroxene (Cpx), spinel, plagioclase, ilmenite, magnetite, quartz, amphibole, chlorite,
₇₁ epidote, biotite, garnet, and apatite, which are typically found in metamorphic and ultramafic
₇₂ rocks. This list plays a crucial role later in the process for automatic mineral identification
₇₃ (Step 9), so it is essential to include the minerals that have been measured.

₇₄ 3. Pre-processing Excel files:

₇₅ The script is designed to work directly with the EPMA output files. Initial processing steps
₇₆ address any missing data and ready the information for further analysis.

₇₇ 4. Selecting data for cation calculation:

₇₈ Users have the option to choose which elements to factor into the calculation. The script
₇₉ presumes that the sum of the selected columns (wt%) will be close to 100%. If there are any
₈₀ repeated element names, the process stops, and an error is displayed.

₈₁ 5. Filtering by Detection Limit (DL):

₈₂ If the file contains DL values, any measurements that fall below the DL are automatically
₈₃ omitted.

₈₄ 6. Renaming dataset variables:

₈₅ Column (variable) names are renamed to improve readability.

₈₆ 7. Handling missing elements:

87 For elements (e.g., P, V, S) that may not be included in every analysis, NaN-filled dummy
88 columns are added to prevent errors during calculation.

89 8. Creating a total wt% column:

90 The total of the selected wt% columns is calculated for each row.

91 9. Identifying mineral phases:

92 Mineral phases are determined automatically based on empirical composition thresholds.
93 Calculations are then performed for each identified phase. Users must ensure that this
94 classification matches the actual mineral assemblage. Furthermore, since this function is
95 constructed using the if statement, the sequence in which identification is executed is crucial.
96 In the initial script, minerals with distinct compositions are given precedence, followed by the
97 evaluation of silicates. When users introduce new mineral phases, it is advisable for them to
98 determine the "identification" sequence by consulting the commented-out sections within the
99 script.

100 10. Splitting data by mineral phase:

101 The dataset is split into separate tables by assigned mineral names.

102 11. Calculating elemental cation numbers:

103 The cation (or anion) numbers for each element are calculated by dividing the measured data
104 (wt%) by the molar weight.

105 12. Calculating oxygen molar amounts:

106 Oxygen molar quantities are determined using oxide weight percentages and module data. The
107 results are compiled into a single Excel file, organized by mineral.

108 13. Normalizing elemental cation numbers:

109 By utilizing the oxygen molar values and module data, the cation numbers for each element
110 are determined according to the mineral's theoretical formula. Additionally, petrologically
111 significant indices, such as Mg# for olivine and Almandine% for garnet, are computed.

112 14. Outputting cation calculation results:

113 Results are exported to an Excel file, with separate sheets for each mineral phase.

114 15. Averaging values by sample code:

115 EPMA data often uses sample identifiers like EPMA01_01, EPMA01_02, and so forth, which
116 consist of the rock sample name (sample code) followed by a serial number. The script identifies
117 common prefixes and calculates average values for each mineral associated with each sample
118 code. This approach provides a useful estimate of typical compositions, though users should
119 be aware that zoning or variations in composition within grains could affect interpretation.

Package Summary

121 cationCalc4EPMA enables:

122 1. Processing of EPMA data:

123 Facilitates conversion of raw wt% data to cation/anion molar values.

124 2. Automatic mineral identification:

125 Classifies mineral phases based on empirical mass% composition thresholds. These criteria can
126 be modified by the user. The results are output in separate sheets per mineral.

127 3. Calculation of common petrological indices:

128 Calculates commonly used indices, such as Mg# and almandine%, directly from cation data.

129 4. Sample-based averaging:

130 Automatically averages values by mineral phase and sample code prefix.

Acknowledgement

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