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CALCMIN – an EXCEL^{TM} Visual Basic application for calculating mineral structural formulae from electron microprobe analyses ☆

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ABSTRACT

CALCMIN, an open source Visual Basic program, was implemented in EXCEL^{TM}. The program was primarily developed to support geoscientists in their routine task of calculating structural formulae of minerals on the basis of chemical analysis mainly obtained by electron microprobe (EMP) techniques. Calculation programs for various minerals are already included in the form of sub-routines. These routines are arranged in separate modules containing a minimum of code. The architecture of CALCMIN allows the user to easily develop new calculation routines or modify existing routines with little knowledge of programming techniques. By means of a simple mouse-click, the program automatically generates a rudimentary framework of code using the object model of the Visual Basic Editor (VBE). Within this framework simple commands and functions, which are provided by the program, can be used, for example, to perform various normalization procedures or to output the results of the computations. For the clarity of the code, element symbols are used as variables initialized by the program automatically. CALCMIN does not set any boundaries in complexity of the code used, resulting in a wide range of possible applications. Thus, matrix and optimization methods can be included, for instance, to determine end member contents for subsequent thermodynamic calculations.

Diverse input procedures are provided, such as the automated read-in of output files created by the EMP. Furthermore, a subsequent filter routine enables the user to extract specific analyses in order to use them for a corresponding calculation routine. An event-driven, interactive operating mode was selected for easy application of the program. CALCMIN leads the user from the beginning to the end of the calculation process.

1. Introduction

Perhaps the most widely used instrument for full chemical analyses (except H, Li, and noble gases) of minerals and solid inorganic compounds is the electron microprobe (EMP). In contrast to other analytical techniques, the EMP allows one to obtain reliable non-destructive analyses of solid phases in the micrometer range with a high degree of accuracy. After analytical work, often producing a large amount of data, the geoscientist is confronted with the task of recalculating the analyses arranged in data files into cationic formula units of minerals that can occasionally have a complex composition. Such structural formulae are needed, for instance, for thermobarometric calculations or simply for classification purposes and mineralogical characterization of a rock sample. Most published computer programs for calculating a mineral structural formula using EMP data are aimed at specific minerals. Many such programs are designed for amphiboles (e.g., Rock and Leake, 1984; Spear and Kimball, 1984; Rock, 1987; Mogessie et al., 1990; Richard and Clarke, 1990; Tindle and Webb, 1994; Rao and Rao, 1996; Yavuz, 1996, 1999; Mogessie, 2001; Esawi, 2004). Programs for the structural recalculation of other rock-forming minerals (e.g., garnets, Knowles, 1987; micas, Yavuz, 2003; pyroxenes, Sturm, 2002) from EMP data are less frequent. In contrast to such "specific mineral calculators", only a small number of general mineral formulae calculation programs are presented in the literature which are, for instance, PASFORM (De Bjerg et al., 1995), HYPER-FORM (De Bjerg et al., 1992), MINTAB (Rock and Caroll, 1990), and MINFILE (Afifi and Essene, 1988). Furthermore, sub-routines exist, such as COMP.EXE and AX, which are associated with or included in programs for calculating phase equilibria (TWQ: Berman, 1991; Thermocalc: Holland and Powell, 1998, respectively). These sub-routines are mainly designed to create composition files compatible with subsequent phase equilibria computations.

Except for the latter computer programs, there are only a few citations in the literature of the programs mentioned above. On the author's experience, many scientists use unpublished software solutions for recalculating mineral formulae. In many cases, these programs are internal software developments of the corresponding scientific departments or individually coded solutions. The main reason for using such individual software solutions is that

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☆ Code available from server at http://www.iamg.org/CGEditor/index.htm.

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the flexibility of the above programs is insufficient. Most of the published programs deal, for example, with a limited number of elements and ignore the possible input of minor or trace elements, or determine end members not suitable for subsequent thermodynamic calculations. In addition, the flexibility of the aforementioned programs is also limited due to the difficulty or even impossibility of achieving modifications in the original algorithms of the authors, especially for sequentially coded programs. The high degree of flexibility required is predominantly caused by the fact that only some aspects of the calculation procedure to determine mineral structural formulae are straightforward. In many cases, the final structural formula can only be approximated because of analytical uncertainties. In addition to possible measurement errors, such uncertainties can arise from the fact that the lightest elements ($Z<5$) cannot be analyzed. Furthermore, elements with Z between 5 and 10, among the most abundant element in silicates, namely oxygen, are rarely analyzed, because not all EMPs in service today are featured with synthetic multi-layer diffraction devices enabling analyses of light elements. An additional problem is the inability of EMP techniques to determine the oxidation and coordination states of elements, such as Fe. Vacancies are also not analyzable, although these kinds of point defects are probably frequent. Thus, in many cases the final structural formula of a mineral can only be approximated by means of assumptions primarily based on mineral-specific knowledge about crystal chemistry. From the above restrictions, it follows that an algorithm for calculating a mineral structural formula must be mineral-specific and in some respect variable. A number of specific algorithms have been described for the estimation of ferrous–ferric iron in minerals (Stout, 1972; Lindsley, 1983; Droop, 1987; Jacobson, 1989; Schumacher, 1991; Holland and Blundy, 1994).

In addition to the lack of flexibility of the computer programs mentioned above, another important point is the user's confrontation with the task of extracting data manually from an output file and preparing these data for a specific input format before running the calculation routines. Only the sequential program MINFILE (Afifi and Essene, 1988) enables an automated read-in of output files of EMP data. MINFILE is thus, in this regard, more user-friendly than others.

The aim of this work was to develop both a user-friendly and a flexible software tool supporting primarily geoscientists in their routine task of calculating mineral structural formulae on the basis of chemical analysis obtained by EMP. An event-driven, interactive operating mode is coded to automatically read-in output files of the CAMECA SX, a widely used EMP, via network. The program can also be used with other EMP data (e.g., JOEL). In this case, the data have to be transferred into the worksheet MANUAL INPUT (see Section 4.1.2). Moreover, a complete dialogue and event-driven filter routine allows users to easily extract specific analyses in order to use them for a corresponding calculation routine. Furthermore, the presented program CALCMIN provides a high-performance Editor and allows the development of individual calculation procedures with a minimum of knowledge of programming techniques. In contrast to previously published programs, CALCMIN allows the assignment of additional quantitative data to each analysis (e.g., ferric/ferrous iron ratios determined by Mössbauer spectroscopy or estimates of cation site occupancy determined by X-ray techniques) which can very easily be addressed in the freely programmable module used for subsequent calculation. This extends the functionality of the program far beyond pure mineral structural formulae calculations. Using site fractions of components in associated minerals as additional data, for instance, a variety of thermobarometric computations can be simultaneously carried out for the entered analyses.

CALCMIN was also designed to simplify the input procedure of the thermodynamic phase equilibrium calculation program PTGIBBS (Brandelik and Massonne, 2004). In contrast to other published mineral structural formulae calculation programs, the calculation modules already included in CALCMIN provide, for the first time, consistent site and mole fractions for the solution models integrated into PTGIBBS.

2. Calculation procedure

In general, the recast of an analysis into a mineral formula is based upon charge neutrality and knowledge of crystal chemistry of the phase to be calculated and proceeds in the following three steps.

Due to the fact that microprobe analyses are usually reported in mass units, the first step is to determine the atomic proportions of the measured elements by conversion from wt% to molar proportions.

The second step is the normalization of the atomic proportions, to calculate the respective number of measured elements ${n_i}^m$ in the structural formula. This can be done in several ways.

For instance, the maximum number of analyzed atoms substituting in a known number of sites in the mineral structure can be taken for normalization (Afifi and Essene, 1988). Atoms that are found at substituting structural sites or associated with hydrogen atoms (often related to OH^- anions) as well as vacancies should therefore be excluded from the normalization procedure. Both calculation steps, the conversion from wt% to molar proportions and the normalization procedure to a specific number of atoms N^n, can be expressed by the equation

$$n_i^m = \frac{w_i^m N^n}{m_i^m \sum_{j=1}^{z} (w_j^n / m_j^n)} \tag{1}$$

with $n_i^m =$ number of measured element i in formula, $w_i^m =$ concentration of element i in wt%, $m_i^m =$ corresponding the atomic weight, $z =$ number of elements used for normalization, $w_j^n =$ concentration in wt%, and $m_j^n =$ atomic weight of element j on which normalization is based. Another method of normalization is based on the charges of elements in the mineral structure and is, for instance, done on the basis of the number of oxygen anions in the formula, which determines the necessary number of positive charges to achieve charge neutrality. When normalizing to a number of oxygen atoms N_{oxygen}, the two first calculation steps in allocating the formula can be summarized by the equation

$$n_i^m = \frac{w_i^m (2N_{oxygen})}{m_i^m \sum_{j=1}^{z} (w_j^n c_j^n / m_i^n)} \tag{2}$$

with $c_j^n =$ charge of cation j. In this equation, the summation includes all measured cations and requires a predefinition of oxidation states of the considered elements.

For full analyses of hydrous minerals (including anions such as OH^-, F^-, and Cl^-), N_{oxygen} can be expressed by

$$N_{oxygen} = O_{anhydrous} + \frac{a_{tot}}{2}\left(\frac{(w_H^m/m_H^m)}{(w_H^m/m_H^m) + (w_F^m/m_F^m) + (w_{Cl}^m/m_{Cl}^m)} + 1\right) \tag{3}$$

with $a_{tot} =$ total number of anions in the hydrous structural site. If the H_2O content is unknown, normalization may be based on equivalent oxygen anions by

$$N_{oxygen} = O_{anhydrous} + \frac{a_{tot}}{2} \tag{4}$$

The third and final step, which has to be undertaken to determine the desired structural formula, is the eventual