SOFTWARE NOTICE

MINFILE: A microcomputer program for storage and manipulation of chemical data on minerals*

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ABSTRACT

MINFILE is a menu-driven computer program for the storage and manipulation of chemical data on minerals. The program contains subroutines for rapid normalization of chemical analyses of any chemical compound into a formula on the basis of a specified number of cations or oxygens, for conversion of elements to oxides and of oxides to elements, for performing arithmetic operations, and for plotting binary or ternary diagrams. Several external subprograms are provided to optimize normalizations and distribution of elements among sites for specific mineral groups. These subprograms may be modified to accommodate additional mineral formulas.

INTRODUCTION

The current generation of electron-microprobe analyzers (EMPA) can provide a large throughput of chemical analyses of minerals, usually expressed as weight percentages of elements or their oxides. Such analyses, which do not account for the content of light elements (e.g., H, C, O) or electrical charge of multivalent elements (e.g., Fe, Mn), need to be recast into mineral formulas based on knowledge of crystal chemistry and charge neutrality. MINFILE was initially written for this purpose but has evolved into a general purpose system for the storage and manipulation of chemical data on all mineral groups. The program includes new algorithms as well as graphics subroutines ported and modified from existing programs. The MINFILE package is optimized for the Microsoft QUICKBASIC compiler to run on IBM-PC compatible microcomputers, but can be modified for other compilers and operating systems. Users are encouraged to modify the programs to suit their particular needs and to share useful outcomes from such endeavors with others.

PROGRAM STRUCTURE

The program package consists of a main program, MINFILE.EXE, which performs commonly used operations, and several external subprograms (e.g., PYROXENE.EXE) that can be called from within MINFILE to perform specific calculations. MINFILE.EXE performs the following functions:

1. A file editor allows the user to specify variables (e.g., SiO_2, Cd, $\delta^{18}O$, total); enter sample identifications, descriptions, groupings, and concentrations from the keyboard; edit data; re-order variables or analyses; average a group of analyses (such as several EMPA spot analyses); and add or delete data.

2. Input and output routines transfer data to and from disk files. Data in memory can be displayed in several formats on the screen, printed, or saved as tables in ASCII files for inclusion in manuscripts.

3. Internal subroutines perform common arithmetic manipulations such as calculating sums, ratios, or $\log_{10}$ of specified variables; converting weight percentages of elements to or from weight percentages of oxides; and normalizing element concentrations into formulas on the basis of a specified number of atoms or oxygens. The user can then distribute elements among sites or estimate oxidation states of multivalent elements from the calculated charge balance.

4. The plotting functions generate cartesian, ternary, and frequency plots on systems that emulate IBM 640×200 or 640×350 pixel graphics.

5. The reference menu displays atomic numbers, symbols, and atomic weights used by the program and allows a calculation of weight percentage of an element from a specified formula.

The symbols of all elements and ions from H to U are used by MINFILE to represent the weight percentage concentration of elements or oxides. The valence of monovalent elements, such as Si, is implicit by default; the desired valence of multivalent elements, such S and Mn, may be implicitly specified as part of the element or oxide name (e.g., S+6, SO_3). The variables "Total" and "TOTAL" are used to maintain running totals. Using these conventions, variables specified by the user such as Si, Fe+2, or Bi_2O_3 are identified by comparison with all element symbols, which allows user-transparent identification of elements or oxides, their valence states, and atomic weights. This permits the principal subroutines to perform calculations without requiring that elements or oxides be placed in any particular order, while maintaining maximum flexibility in naming variables.

Data arrays and variables can be shared in memory between MINFILE and several external subprograms. The latter perform specific calculations (such as normalization of weight percentage data to a "complete" amphibole formula) and then pass the results to MINFILE for plotting, display, or permanent storage on disk. In typical operation, normalizations and site assignments are performed on an IBM-PC in less than 1 s per sample. Additional external subprograms may be written or modified from existing programs to perform a wide variety of calculations, such as calculating mole fractions of mineral end members, calculating a site-correlation matrix, or fitting data to functions.

DATA STRUCTURE

Data are permanently stored in sequential (ASCII) files on disk or other media. A total of 260 samples (analyses) and 60 variables (elements or oxides) can be contained in each data file and manipulated within memory at once. Data files can be split into smaller files or merged into larger files. Other programs provided with the package allow conversion of MINFILE data files to or from other formats, such as those used by the GPP and IGPET

program packages. Additional routines were written to allow direct transfer of data files from EMPA units to MINFILE, precluding the need for keyboard input.

In typical operation, several files from each data set are produced. Original element or oxide weight percentages for a given mineral group are stored in a master file. Additional files are then produced that include normalized data, sums, ratios, etc.

EQUATIONS FOR MINERAL NORMALIZATION

Silicate minerals are typically normalized on the basis of a fixed number of anions $(O + Cl + F)$ as described by Deer et al. (1966). Microprobe analyses, however, do not distinguish oxidation states of multivalent elements such as Fe and Mn and cannot detect light elements such as H. A better procedure for such analyses is to normalize on the basis of the maximum number of analyzed elements (usually a subset of cations) that substitute in a known number of sites in the structure.

The initial step is to convert oxide weight percentages to element weight percentages and then calculate the atomic proportions of each element (P_i) from its concentration in weight percent (W_i) and its atomic weight (A_i):

$$P_i = W_i/A_i. \tag{1}$$

When normalizing to C cations or atoms, the number of atoms in the formula (N_i) of each element i is given by

$$N_i = P_i C(\Sigma \ P_b)^{-1}, \tag{2}$$

where P_b denotes atomic proportions of elements on which the normalization is based, usually excluding cations that substitute in sites with vacancies. When normalizing to O oxygen atoms, the equation becomes

$$N_i = P_i O(\tfrac{1}{2} \ \Sigma \ P_i C_i)^{-1}, \tag{3}$$

where C_i is the charge for each cation. A special case is rendered by minerals in which anions include OH^-, F^-, or Cl^-, in which case Equation 3 becomes

$$N_i = P_i O(\tfrac{1}{2} \ \Sigma \ P_i C_i + \tfrac{1}{2}P_{Cl} + \tfrac{1}{2}P_F)^{-1}, \tag{4}$$

where the summation includes all cations (including H^+) necessary to balance the O anions, and $P_{Cl,F}$ denotes the atomic proportions of the halogens. If H_2O has not been determined, normalization may be based on equivalent oxygen anions [= total anions $- \tfrac{1}{2}(OH,F,Cl)$ in the formula] using Equation 3.

As a check on the normalization, a charge balance is calculated:

$$charge = \Sigma \ N_i C_i, \tag{5}$$

where the summation includes all cations and anions. This charge balance may be used to evaluate the basis for normalization and/or the quality of each analysis. For microprobe analyses of minerals in which Fe is the only multivalent element, any charge imbalance produced when normalizing to cations may further be used to estimate the proportions of Fe^{3+} and Fe^{2+}.

The program package offers two options for mineral normalization. Equations 1 to 3 are included in subroutines within the main program (MINFILE) in order to calculate formulas from any combination of elements in any compound based on user-selected subsets of elements or anions. The numbers of atoms of each element in each sample and a charge balance are calculated and added to the data array, thus freeing the user from the most tedious aspects of such calculations. The user is left to perform site assignments and to calculate mole fractions of chemical components. Equations 1 to 5 are also included in external sub-

TABLE 1. Biotite analysis showing the effect of various normalization schemes on the calculated formula

	A	B	C	D	E	F
SiO$_2$	37.17	37.17	37.17	37.17	37.17	37.17
TiO$_2$	3.14	3.14	3.14	3.14	3.14	3.14
Al$_2$O$_3$	14.60	14.60	14.60	14.60	14.60	14.60
Fe$_2$O$_3$	3.75	—	33.59*	—	0.33*	3.75
FeO	26.85	30.22*	0	30.22*	29.92*	26.85
MnO	0.06	0.06	0.06	0.06	0.06	0.06
MgO	4.23	4.23	4.23	4.23	4.23	4.23
CaO	0.17	0.17	0.17	0.17	0.17	0.17
Na$_2$O	0.15	0.15	0.15	0.15	0.15	0.15
K$_2$O	8.25	8.25	8.25	8.25	8.25	8.25
H$_2$O	1.35	3.47*	3.81*	3.38*	3.47*	1.35
F	0.85	0.85	0.85	0.85	0.85	0.85
O≡F	0.36	0.36	0.36	0.36	0.36	0.36
Total	100.21	101.97	105.67	101.87	101.99	100.21
^{IV}Si	5.97	5.75	5.28	5.89	5.75	5.70
^{IV}Al	2.03	2.25	2.45	2.11	2.25	2.30
^{IV}Fe	0	0	0.27	0	0	0
Z site	8.00	8.00	8.00	8.00	8.00	8.00
^{VI}Al	0.74	0.42	0	0.61	0.41	0.34
^{VI}Ti	0.38	0.37	0.34	0.37	0.37	0.36
Fe^{3+}	0.45	0	3.33	0	0.04	0.43
Fe^{2+}	3.61	3.91	0	4.00	3.87	3.44
Mn^{2+}	0.01	0.01	0.01	0.01	0.01	0.01
Mg	1.01	0.98	0.90	1.00	0.98	0.97
Y site	6.20	5.68	4.56	6.00	5.67	5.55
Ca	0.03	0.03	0.03	0.03	0.03	0.03
Na	0.05	0.05	0.04	0.05	0.04	0.04
K	1.69	1.63	1.50	1.67	1.63	1.61
X site	1.77	1.70	1.56	1.74	1.70	1.69
O	20.00	20.00	20.00	20.00	20.00	20.00
O	2.12	0	0	0	0	0
OH	1.45	3.58	3.62	3.57	3.59	3.59
F	0.43	0.42	0.38	0.43	0.41	0.41
Charge	0	0	0	1.02	0	0

Note: Columns are (A) complete data, on the basis of 24 (O,OH,F); (B) partial data, all iron as Fe^{2+}, on the basis of 24 (O,OH,F); (C) partial data, all iron as Fe^{3+}, on the basis of 24 (O,OH,F); (D) partial data, on the basis of 14 tetrahedral and octahedral cations; (E) partial data, on the basis of 13.67 tetrahedral and octahedral cations; (F) complete data, on the basis of 13.55 tetrahedral and octahedral cations. Data from analysis no. 6, Deer et al. (1966, p. 199).
* Calculated.

programs that optimize normalizations, valence, and site assignments for specific mineral groups such as amphiboles, epidotes, and spinels. The site assignments are based, to various degrees, on assumptions that become obvious from the results.

Mineral groups with complex substitutions and multivalent elements such as amphiboles may require repeated normalizations to different numbers of cations in order to satisfy crystal-chemical limits and charge balance (Robinson et al., 1982). These calculations can be rapidly and accurately performed by MINFILE, but as for all computerized procedures, it is up to the user to critically evaluate the validity of the results.

EXAMPLE: BIOTITE

Micas—$X_2Y_{4-6}Z_8O_{20}(OH,O,F,Cl)_4$—typify problems encountered when normalizating microprobe analyses of hydrous Fe-bearing silicates and illustrate the flexibility offered by MINFILE in selecting the basis for normalization. Nine complete analyses of micas from Deer et al. (1966, p. 198–199) were entered in MINFILE and saved in a data file. Oxide weight percentages were

converted to element weight percentages, Fe^{2+} and Fe^{3+} were combined as Fe*, and water contents were changed to zero in order to simulate EMPA analyses. Both complete and partial data sets were repeatedly normalized using the external subprogram MICA.EXE, which allows the user to normalize on the basis of selected subsets of cations or anions. MICA.EXE assumes a full complement of 24 anions and attempts to produce a charge balance in each sample by changing the oxidation state of Fe (if not specified). The program also estimates H_2O weight percentages in each sample from calculated OH (if not specified), and performs the simple task (in micas) of site assignments.

Table 1 is a summary of MICA output for a single Fe-rich biotite (analysis no. 6 of Deer et al., 1966) using both the complete and partial (simulated microprobe) data sets. Column A is a normalization of complete data (H, Fe^{3+}, and Fe^{2+} specified) on the basis of 24 (O + OH + F). The calculated formula is identical to that of Deer et al. (1966). The calculated number of octahedral cations, however, exceeds the maximum of six octahedral sites in mica, which may be due to an erroneously low analyzed amount of H_2O.

Columns B and C are normalizations of two partial sets of simulated microprobe data on the basis of 24 anions generated by specifying all Fe as Fe^{2+} and Fe^{3+}, respectively. These two columns bracket the two extremes of the mineral formula, and the high total in column C suggests that most of the Fe is actually in the divalent state. The total number of octahedral sites in both columns B and C is less than six, representing a significant dioctahedral component.

Column D was obtained by normalizing the simulated microprobe data on the basis of 14 tetrahedral and octahedral cations. The residual positive charge cannot be compensated without either loss of protons (e.g., OH = 2.55, O = 1.02) and/or decrease of the specified number of octahedral sites.

Column E shows the effect of decreasing the specified number of octahedral sites to 13.67, which is within the range of Fe^{3+}/Fe^{2+} where charge imbalance is eliminated. Further decrease in octahedral-site occupancy requires progressively more Fe to occur as Fe^{3+} in order to maintain charge balance. In micas that contain both dioctahedral and trioctahedral layers, a unique estimate of Fe^{3+}/Fe^{2+} is not possible from microprobe data alone.

Column F shows a normalization of the complete data (Fe^{3+}, Fe^{2+}, and H specified) on the basis of 13.548 tetrahedral and octahedral cations, which is the number required to maintain charge balance with a full complement of anions. This normalization is equivalent to normalizing all cations except H on the basis of 22 equivalent oxygens.

The principal benefit of MINFILE is that these normalizations were produced within a few minutes.

ACKNOWLEDGMENTS

REFERENCES CITED

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NOTICES

MEETING OF THE CLAY MINERALS SOCIETY

The 25th annual meeting of the Clay Minerals Society will be held September 18–21, 1988, in Grand Rapids, Michigan. Symposia of interest to researchers in applied clay mineralogy will be featured, including:

1. Chemistry and Physics of Clays: Fundamental Properties
2. Clays, Pillared Clays, and Their Catalytic Properties
3. Composites and Materials Applications of Clay Minerals

General sessions and poster sessions will be devoted to clays in the petroleum industry, diagenesis and weathering, colloid chemistry, soil clays, and environmental and engineering applications. A premeeting workshop on Magnetic Resonance Methods in Clay Science, and a postmeeting field trip, will also be offered.

Additional information can be obtained from Professor Thomas J. Pinnavaia, Department of Chemistry, Michigan State University, East Lansing, Michigan 48824, U.S.A. (517-353-4511).

SELECTION AND DUTIES OF MINERAL CURATORS

The IMA Commission on Museums has published a statement on "Mineral Curators, Their Appointment and Duties." The statement appears in the November-December issue of *Mineralogical Record,* volume 18, pages 389–390, and in *Rocks and Minerals,* volume 63, pages 70–72.