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Automated quantitative phase analysis of bauxites

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Abstract

A BASIC program package has been developed for the quantitative interpretation of digitally recorded X-ray diffractometric data of bauxites. It corrects for background, searches the peaks, and calculates the integrated intensities. Information stored in the phase library permits the identification of the components and thereafter the intensities are corrected for overlapping. Using the data extracted from the diffraction patterns, as well as the analytically determined quantities of the main chemical constituents, the program supplies the results of phase analysis in a tabular arrangement. A conversational mode of execution allows the operator to control, and if deemed necessary, to correct the data processing at all levels.

Introduction

General experience has proved that the phase analysis of multicomponent mineral mixtures, like bauxites, can be accomplished with the highest reliability if several methods (polarization and electron microscopy, X-ray diffraction, IR spectrometry, thermal analysis, *etc.*) are used in a complementary manner (Bárdossy, 1972). However, it seems reasonable to start the mineral phase analysis with X-ray diffraction measurements, because they can detect the widest range of phases, and switch over to another method only if unresolved problems are recognized. Also, in X-ray diffraction, automation of measurements and data processing is fairly advanced (*e.g.* Jenkins *et al.*, 1972; Göbel *et al.*, 1978). However, total automation of bauxite analysis has not yet been achieved. Data acquisition and bookkeeping even in the form of a data bank present no problems in this respect, but the programs can hardly cope with the scarcely known crystallographic variability of these minerals, and extremely careful monitoring of automated interpretation is needed. Thus, the use of interactive computer programs is justified (Johnson, 1978). This paper presents a modular program package for quantitative phase analysis of bauxites, based on X-ray diffraction and chemical data.

Principles

The 40-year history of diffractometric quantitative phase analysis was reviewed by Alexander (1977), and showed that recent efforts have been concentrated essentially on the possibilities of avoiding lengthy calibrations and the need of well-defined standard samples. Some problems, like preferred orientation and particle size distribution in the specimen, overlapping of the diffraction peaks and their shifts, as well as changes in relative intensities due to solid solution effects and mineral individualities, the

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uncertainties of the intensity conversion factors (ICF's), *etc.*, render the quantitative phase analysis difficult in most practical cases. Depending on the materials studied, one or some of these difficulties become dominant and others can be neglected.

In bauxites 160 minerals have been identified so far; however, only 20 of them occur in rock-forming quantities (Bárdossy, 1979). From the latter the following minerals are included in the phase library of the program: boehmite, gibbsite, diaspore, corundum, goethite, hematite, pyrite, siderite, kaolinite, chamosite, anatase, rutile, calcite, dolomite, crandallite, lithiophorite, and quartz. The problem of the compositional variability generally encountered in the phase analysis of clay rocks is not present in the case of bauxites, because usually the only clay mineral component is kaolinite with fixed stoichiometry. During the analysis of a huge number of bauxite samples following the tehniques published by Bárdossy (1966), we found that the main sources of uncertainties in analysis are isomorphous substitution and the variation of ICF's. In order to diminish these effects the following procedure has been adopted for computer implementation.

It is assumed that the set of minerals included in the phase library covers all the components present in the sample and a complete identification is possible. After determining the extent of isomorphous substitution from peak shifts the correct stoichiometry of all phases is regarded as known. Consequently a matrix can be defined with elements

$$Q(i, l) = S(i, l) \cdot r(i, l)/s(i)$$

characterizing the contribution of the l-th chemical constituent (oxide, radical, *etc.*) to the i-th phase $[0 \leq Q(i, l) \leq 1]$. Here

$s(i)$—the molar weight of the i-th phase,
$S(i, l)$—the molar weight of the l-th chemical constituent occuring in the i-th phase,
$r(i, l)$—coefficient related to the thermal decomposition of the i-th phase.

The actual chemical composition of the sample can be determined up to 98–99% by analysis for a definite number (L) of elements. The phase analysis will be consistent with the elemental analysis if the equation

$$\sum_{n=1}^{H} x(n) \cdot Q(n, l) = e(l) \qquad (1)$$

is satisfied, where

$e(l)$—the analyzed quantity of the l-th chemical element,
$x(n)$—the weight percentage of the n-th component in the mixture,
H—the number of identified phases.

Equation 1 will be satisfied if the phase percentages are calculated from the measured diffracted intensities and the chemical analysis data, using the equation

$$x(i) = T(i) \cdot e(l)/\left[Q(i, l) \cdot \sum_{n=1}^{H} T(n)\right], \text{ where} \qquad (2)$$

$$T(i) = C(i, l) \cdot I(i), \text{ and} \qquad (3)$$

$C(i, l)$—the relative intensity conversion factor (RICF), referring to the l-th chemical constituent,
$I(i)$—weighted average intensity of the i-th phase calculated from several measured integrated peak intensities.

The use of C(i, l)'s in Equation 2 through Equation 3 permits the conversion of measured intensities to phase percentages within a group of phases containing the same chemical constituent (*e.g.* gibbsite, diaspore, boehmite, and corundum, all containing aluminum). Within each such group one RICF can be set equal to unity by choosing the relevant phase arbitrarily as reference for that group. By subdividing the phases being analyzed into as many groups as the number of main chemical elements, errors due to the uncertainties of the ICF's are not carried over to the next subgroup and each group is normalized in itself by an elemental analysis.

The self-consistency of the mineral phase analysis accomplished by the proposed method can be checked through three calculated figures:

(1) The sum of the calculated phase percentages should be >99%. Undetected material is deemed to be acceptable up to 1%; however, higher deficiencies give rise to suspicions of serious faults in the identification of phases or the presence of a significant amorphous content.

(2) The total calculated loss on ignition (LOI) should match the measured LOI (determined in air in the temperature range 105–1300°C).[1]

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[1] In some cases the usual LOI value is insufficient and a more detailed chemical analysis is desirable (*e.g.* for reduced bauxites a separate determination of the following components is necessary: H_2O-, H_2O+, S, SO_3, and organic carbon).

(3) The calculated effective ICF's for each phase should fall into the range determined empirically for the main bauxite components (Bárdossy *et al.*, 1977).

As regards the problems of preferred orientation, our investigations of single phases of the main bauxite minerals do not show any significant preferred orientation, except for kaolinite or other clay minerals. Commercial bauxites contain less than 20% clay minerals, and the effect of preferred orientation can be diminished to an appropriate level by the following sample preparation method. The raw bauxite is ground to a 5- to 20-micron grain size. The powder is filled into a common sample holder and the surface to be measured is made rough by pressing it with an abrasive paper of fine grain size. A set of experiments with and without the use of abrasive paper proved useful.

Instrumentation

Diffracted X-ray intensities were collected on punched tapes by a Philips diffractometer equipped with an automatic sample changer. The measurements were made usually in the 2θ range 5–55° with 0.05° sampling. The data processing was made on a 16K byte Hewlett-Packard 9830A desk calculator programmable in BASIC extended with matrix and string-handling features. The peripheries used are as follows: HP 9863A paper tape reader, HP 9866A thermal printer, HP 9865A tape cassette unit, HP 8961A typewriter, and HP 9862A X–Y plotter.

Software

The measured intensity data of a suite of 38 diffraction patterns can be stored on cassettes. The files allocated to the patterns contain all the data necessary to identify the samples and the conditions of the measurements. These files also accommodate the quantities derived in the course of the calculations.

The data processing is completely automatic. A baseline is determined and the intensities are corrected for the background scattering (Appendix A), the data are smoothed, and the location, amplitude, and integrated intensity of each peak is determined (Appendix B).

The interpretation and correction of the patterns are carried out in an interactive mode. The processed diffractogram is drawn by the X–Y plotter on a preprinted form containing some information useful for the evaluation of bauxite patterns. This includes bars positioned on the 2θ scale corresponding to the most important reflections of bauxite minerals and proportional in length to the relative intensities. Special labels mark the reflections calibrated for isomorphous substitution(↑) as well as the reference lines (*) (see Fig. 1). The position of the pattern can be shifted with respect to the 2θ scale in such a way that a peak selected by the operator should match the ideal position of a specified mineral's reflection. Usually the 101 reflection of anatase is used for this purpose, because the structure of anatase is the least variable among all bauxite minerals. The intensities are scaled to fill the full height of the form. The peaks are numbered and the integration limits are marked (Fig. 1). The user-definable keys of the HP calculator are programmed to permit the operator a wide variety of easy corrections (recalibration of the 2θ scale, deleting parasitic peaks, defining new ones, reintegration of the peaks, *etc.*).

Next the calculator searches for the phases present and comes up with a printed proposal of preliminary identification. Again, this can be corrected. Once the preliminary qualitative analysis has been accepted by the operator, the program looks for complete matching between the observed reflections and the data of the phase library (Appendix C). From the results of the final identification the intensities are corrected for overlapping, and a weighted average intensity is calculated for each phase from several reflections (Appendix D).

In the last subroutine the phase percentages are computed (Appendix E). In the general case the input of the elemental analysis data is needed for the main chemical constituents expressed in oxide percentages (*e.g.* Al_2O_3, Fe_2O_3, TiO_2, *etc.*). The final printed table summarizes the results of quantitative phase analysis, listing the input data, indicating the relation between oxide and phase percentages, and giving control figures mentioned in the description of principles (Fig. 2). All these quantities are subsequently stored in a data bank.

Discussion

Much labor could be saved by carrying out the quantitative interpretation of long suites of bauxite X-ray patterns with the capabilities of a programmable calculator. Provided the significant components are among the mineral phases included in the phase library,[2] the data processing, phase identifi-

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[2] According to the evaluation of world bauxite resources (Bárdossy, 1979), about 70–80% of all bauxites fit these requirements. The amorphous content of recent bauxites might exceed 20%, so their analysis requires a special procedure.

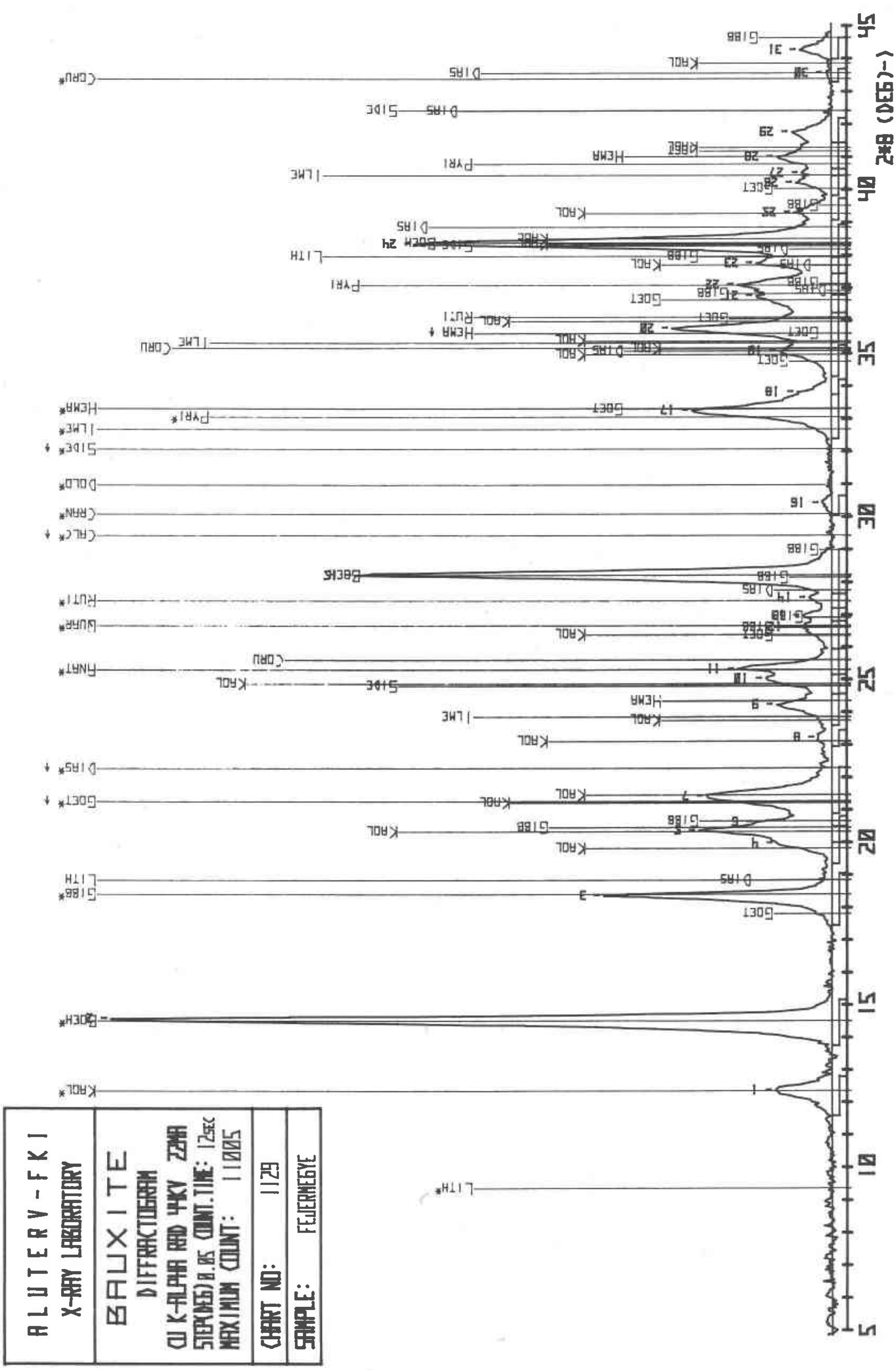
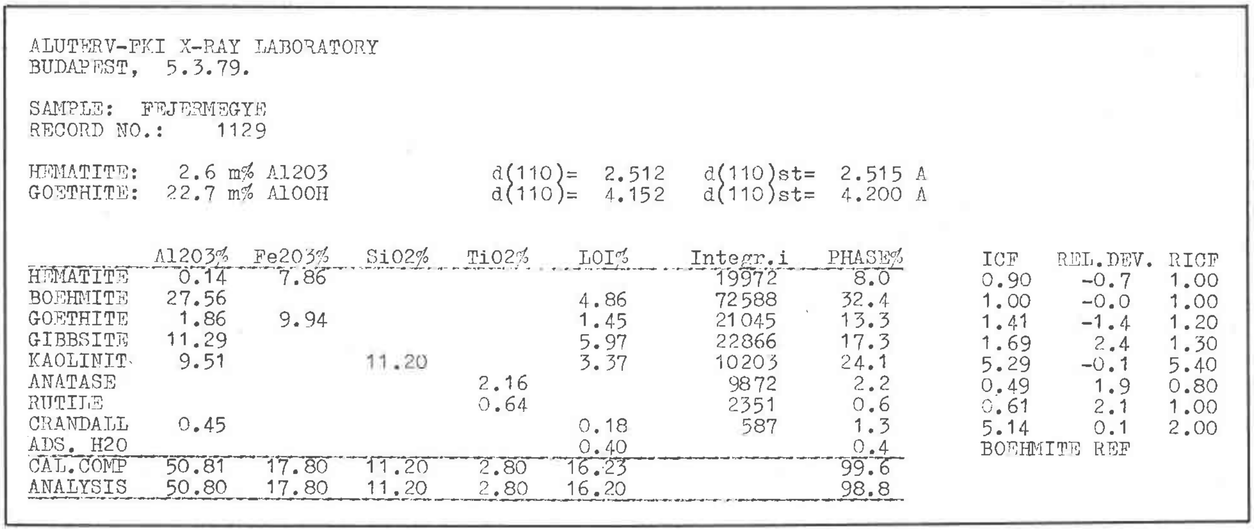


Fig. 1. Bauxite diffractogram in an intermediate state of data processing.



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ALUTERV-FKI X-RAY LABORATORY
BUDAPEST,  5.3.79.

SAMPLE:  FEJERMEGYE
RECORD NO.:     1129

HEMATITE:   2.6 m% Al203                d(110)=  2.512   d(110)st=  2.515 A
GOETHITE:  22.7 m% AlOOH                d(110)=  4.152   d(110)st=  4.200 A

           Al203%  Fe203%   Si02%   Ti02%    LOI%  Integr.i  PHASE%      ICF  REL.DEV.    RICF
HEMATITE     0.14    7.86                             19972     8.0     0.90      -0.7    1.00
BOEHMITE    27.56                            4.86     72588    32.4     1.00      -0.0    1.00
GOETHITE     1.86    9.94                    1.45     21045    13.3     1.41      -1.4    1.20
GIBBSITE    11.29                            5.97     22866    17.3     1.69       2.4    1.30
KAOLINIT     9.51           11.20            3.37     10203    24.1     5.29      -0.1    5.40
ANATASE                             2.16               9872     2.2     0.49       1.9    0.80
RUTILE                              0.64               2351     0.6     0.61       2.1    1.00
CRANDALL     0.45                            0.18       587     1.3     5.14       0.1    2.00
ADS. H20                                     0.40               0.4     BOEHMITE REF
CAL.COMP    50.81   17.80   11.20    2.80   16.23              99.6
ANALYSIS    50.80   17.80   11.20    2.80   16.20              98.8
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Fig. 2. Final results of the quantitative phase analysis. ADS · H20 is the estimated value of non-crystalline water present after drying the sample at 130° C, thus contributing to the measured LOI value. CAL · COMP is the sum of chemical constituents allocated to the different phases as described in Appendix E. The difference between the totals of PHASE% (99.6) and ANALYSIS (98.8) is due to the P_2O_5 content of crandallite, which was not determined.

cation, and quantitative analysis become straightforward routines accomplished by well-defined algorithms. Reproducibility is enhanced thereby, and subjectivity is eliminated. However, an interactive human control seems necessary at certain stages of the automatic operations. A trained technician can do this in a few minutes per sample. Using the same principles, efficiency could be advanced by faster and more sophisticated hardware (*e.g.* on-line data collection, disc storage, CRT-display, *etc.*). The accuracy, which is about 5% (rel) at present, could be improved if independent data on other phase-analytical methods (IR spectroscopy, thermal analysis, *etc.*) were appropriately correlated with the X-ray results within the computer program. This has been done manually before (Bárdossy, 1972). Research along these lines is current in our laboratories.

Appendix A

Calculation of the baseline

Several algorithms have been published for this purpose (Blessing *et al.*, 1974; Lehman, 1975; Sonneveld and Visser, 1975; Göbel *et al.*, 1978; Johnson, 1978). Experience showed that a smooth monotonously decreasing baseline is the most adequate one for bauxites. This is determined in three consecutive steps: (a) the measured counts are gathered into groups of tens, and then the average value within each subgroup is assigned to the first point; (b) a set of averages monotonously decreasing with the scattering angle is selected; and (c) the final baseline is fitted to those points of this set which can be connected by straight lines with monotonously decreasing slopes.

Appendix B

Determination of the positions and integrated intensities of the peaks

From consideration of some publications on peak search (Taupin, 1973; Wilson, 1965; King and Smith, 1974; Heck *et al.*, 1975) the spacing of sampling of 0.05° (2θ) was chosen, in order to obtain measured *d* values accurate enough for phase identification.

The following conditions have to be fulfilled for a peak position: (i) $I(i-1) < I(i) > I(i+1)$, where the argument denotes the peak position minus or plus a single step of 0.05° (2θ); (ii) either three monotonously decreasing counts follow I(i) in both directions, or there are at least four monotonously decreasing counts in one direction; and (iii) the peak localized this way is statistically significant [*i.e.* $I(i) > 3\sqrt{B(i)}$], where B(i) is the background intensity.

Integrated intensities are calculated for single peaks by summation of counts from background to background in both directions, where the observed count is regarded as background if $I(i) < 3\sqrt{B(i)}$. Overlapping peaks are separated at the local minimum points.

Appendix C

Identification, phase library

In contrast to general identification programs (Johnson and Vand, 1968; Frevel, 1977; VanTrump and Hauff, 1977; Dismore, 1977), our system handles bauxite data only. The necessary information stored on magnetic tape cassettes is compiled for each mineral phase as follows:

Mineral name, *d*(*hkl*) and I(rel) values according to the JCPDS–PDF cards (1975), tolerance parameters for identification of *d* values, stoichiometric percentages, parameters characterizing the isomorphous substitution, the ICF together with its expected range and the RICF, the reference line of the phase.

The identification is accomplished in two steps. First a search compares the measured peaks to two interplanar spacings and the corresponding relative intensities for each phase included in the library, and a preliminary identification is obtained. This should be controlled by the analyst.

The program allocates a peak to a previously identified phase if *d*(meas) corresponding to its position matches with one of the filed *d*(f) values of this phase within the specified tolerance. The magnitude of the tolerance parameter depends on the *d*(f) value, the phase and the sign of the difference. A maximum of 18 reflections can be allocated to each phase.

Appendix D

The separation of overlapping peak intensities

Let the measured integrated intensity of the reference line for the i-th phase be I(i, REF) and its relative intensity R(i, REF), then the calculated integrated intensity of the j-th line with R(i, j) relative intensity can be written as

$$I(i, j) = I(i, REF) \cdot R(i, j)/R(i, REF)$$

Using this relation the measured total intensity (I) of any peak having K (<5) overlapping components has to be distributed among the contributing phases by K − 1 successive subtractions. The residue

$$I(RES) = I - \sum_{k=1}^{K-1} I(k, REF) \cdot R(k, m)/R(k, REF)$$

will be allocated to the phase identified last. The difference between the residue and its calculated counterpart yields a figure of merit for this procedure. When for the j-th reflection of the last (K-th) phase

$$|I(K, j) - I(RES)| \gg 0$$

one or more of the following problems must be faced:

(1) there is a large error in the intensity measurement; (2) a serious fault occurred in the identification; (3) the phases contributing to the I total intensity deviate substantially from those included in the library with respect to real structure.

A weighted average is calculated from the separated intensities belonging to the same phase. The average is used for each phase in calculating the phase percentages.

Appendix E

Calculation of the percentages of crystalline components

The calculation of phase quantities is performed in four steps:

(1) The Q(i, l) matrix of Equation 1 is modified according to the substitutions determined from peak shifts.

(2) Input of the results of chemical analyses. It is appropriate to analyze bauxites for Al, Fe, Si, Ti, Ca, Mg, S, P, Mn, C, and LOI. Because of the interference of certain peaks it is recommended in some cases to determine chemically the non-reactive silica, which can be taken as quartz. Similarly it can be very useful to know separately the respective amounts of Fe^{2+} and Fe^{3+}.

If a chemical analysis is not available the program proceeds, using the ICF's from the library and a $\Sigma x(i) = 100\%$ normalization. In this case step 3 is omitted but consequently larger errors are likely.

(3) The calculation of phase percentages starts with the column of the Q(i, l) matrix containing least non-zero terms. (The corresponding chemical element occurs in the smallest number of phases.) The quantity of this element is distributed among the relevant phases according to Equation 2 in order to yield the percentages of the mineral components. On the other hand the amounts of other elements required stoichiometrically for the phases already fixed are subtracted from the terms of the remaining columns. This procedure is repeated until all chemical constituents are handled in turn. The LOI is not tackled, but as already mentioned, used for control in the same way as the sum of the phase percentages and the calculated ICF's, which are all derived in this step.

(4) The final table of results is printed (Fig. 2).

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