

ESTIMATION OF CLAY PROPORTIONS IN MIXTURES BY X-RAY DIFFRACTION AND COMPUTERIZED CHEMICAL MASS BALANCE

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Abstract—As part of a laboratory study of the hydrothermal alteration of kimberlite, a mass balance procedure has been developed for estimating the relative proportions of synthetic phyllosilicate phases—chlorite, vermiculite, smectite, kaolinite and serpentine—present in reaction products. The procedure is based on a combination of X-ray powder diffraction (XRD) measurements (for phase identification), atomic absorption determinations (for total Si, Al, Fe, and Mg) and published analyses of clay minerals (for stoichiometric deductions). It centers on the computer inversion of a 4×4 matrix form of four simultaneous equations representing the mass balance of Si, Al, Fe, and Mg in four chosen minerals and incorporates a systematic routine for selecting from all possible permutations of high and low estimates of the mineral chemical analyses acceptable sets of product stoichiometries and phase proportions consistent with the total metal analyses. To minimize uncertainties and computing time, the program takes account of elemental relationships and water mass balances associated with phyllosilicates. It also accommodates data relevant to poorly crystalline phases for which a range of theoretical type-analyses modeled on aluminum oxyhydroxides and 9–11-Å, 2:1 layered aluminosilicates are employed.

The procedure produces reliable trends in phase proportions consistent with the intensities of characteristic XRD peaks of clay minerals present in the analyzed mixture; for example, increases in estimated kaolinite proportions correspond with larger 7-Å (and other) peaks in analyzed samples. A precision of 7–25% has been routinely achievable.

Key Words—Chemical mass balance, Chlorite, Kaolinite, Quantitative mineralogy, Smectite, Vermiculite, X-ray powder diffraction.

INTRODUCTION

Phase analysis of clay mixtures is seldom straightforward. In particular, uncertainties arise from the variable composition and crystallinity of clay minerals. Many reports (e.g., Carthew, 1955; MacKenzie and Mitchell, 1962; van der Marel, 1966; Cody and Thompson, 1976; Brindley and Brown, 1980) estimated clay mineral proportions by X-ray powder diffraction (XRD), thermal analysis, or infrared (IR) techniques, but most dealt with relatively favorable cases such as the determination of a particular well-crystallized phase, or employed carefully selected synthetic mixtures for calibration. Quantitative phase analysis of clay mixtures based on extraction of reference standards from the test samples was achieved by Gibbs (1967), but the method is not readily applicable to complex mixtures of interlayered phases.

Pearson (1978) adopted a different approach in which predominant phases were identified by XRD and estimated quantitatively by elemental mass balance. He related the chemical compositions of a series of mud-

stones to their mineral constituent compositions by sets of simultaneous equations of the type:

$$a_i x + b_i y + c_i z = 100k_i, \quad (1)$$

where a_i , b_i , c_i , and k_i are the percentages of element i in mineral phases X, Y, Z, and the mudstone, respectively, and x , y , and z are the phase proportions of X, Y, and Z. For the minerals involved—kaolinite, illite, and chlorite—he employed published maximum and minimum analyses for a_i , b_i , and c_i with measured values of k_i to convert the mass balances (as in Eq. (1)) to a series of straight lines drawn as a composite plot of, e.g., % illite vs. % kaolinite. An enclosed central area within the lines was taken to represent self-consistent solutions of the simultaneous equations, which was reduced in size by means of revised calculations and plots assuming certain elemental relationships. From estimates of % illite and % kaolinite, the proportion of chlorite could be obtained by equations of the form of Eq. (1). Pearson developed a computer program for the routine quantitative analysis of a series

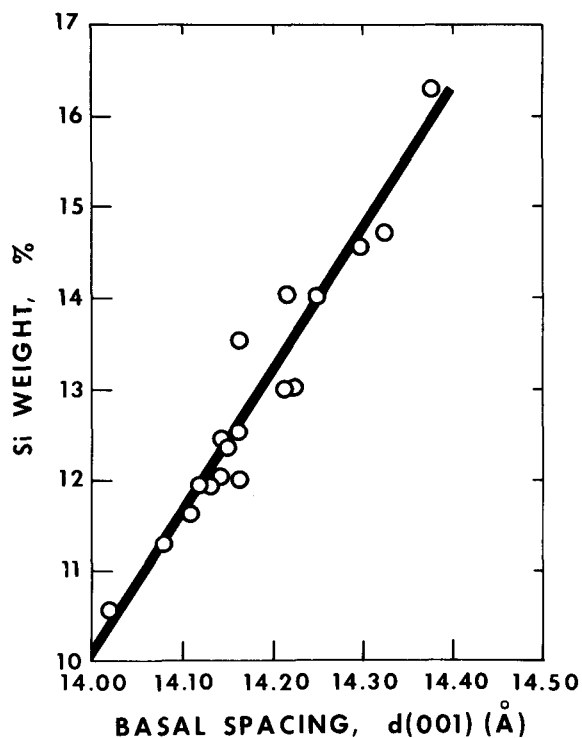


Figure 1. Relation between $d(001)$ and % Si for chlorites.

of related mudstones employing matrix inversion for the solution of the simultaneous mass-balance equations. Uncertainties were minimized by refining the input elemental data of the minerals.

The present work is a modification and extension of Pearson's (1978) approach to include a wider range of minerals, including poorly crystallized phases, some of which are not amenable to Pearson's technique.

THEORY

A mixture of clay minerals consisting predominantly of chlorite (chl), vermiculite (verm), kaolinite (kao), and smectite (sm) provides a convenient example. For this mixture Eq. (2) is the matrix equivalent of Eq. (1), using the elements Si, Al, Fe, and Mg to establish the mass balance.

$$\begin{matrix} \text{Si} \\ \text{Al} \\ \text{Fe} \\ \text{Mg} \end{matrix} \begin{bmatrix} \text{chl} & \text{verm} & \text{kao} & \text{sm} \\ \text{H/L} & K_1 & K_2 & \text{H/L} \\ \text{H/L} & \text{H/L} & K_3 & \text{H/L} \\ \text{H/L} & \text{H/L} & 0 & \text{H/L} \\ \text{H/L} & \text{H/L} & 0 & \text{H/L} \end{bmatrix} \begin{bmatrix} \% \text{ chl} \\ \% \text{ verm} \\ \% \text{ kao} \\ \% \text{ sm} \end{bmatrix} = \begin{bmatrix} \% \text{ Si}_T \\ \% \text{ Al}_T \\ \% \text{ Fe}_T \\ \% \text{ Mg}_T \end{bmatrix} \quad (2)$$

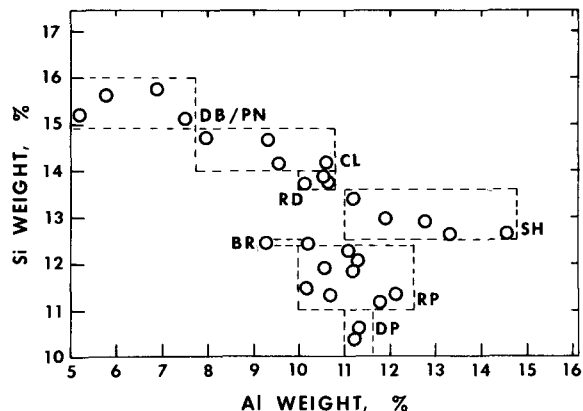


Figure 2. Regressed boundary limits for % Si and % Al for chlorites. BR = brunsvigite; CL = clinocllore; DB = diabante; DP = daphnite; PN = penninite; RD = rodingite; RP = ripidolite; SH = sheridanite.

Of the two 4×1 matrices given in Eq (2), the left hand matrix refers to the required mineral proportions and the right hand matrix to the experimentally determined total elemental content. The 4×4 matrix gives the literature proportions of the four elements in each of the mineral phases. Considering the top left hand entry in this matrix, H/L is the highest (H) or lowest (L) % Si for natural chlorites. It is evident from chlorite structural formulae that this percentage must vary with the extent of substitution of Al for Si in the tetrahedral layers of the chlorite structure. The other H/L terms similarly take the place of the Si, Al, Fe, and Mg compositions in chlorite, vermiculite, and smectite in the remainder of the matrix. Five entries are shown as constant. For example, a small variation exists in literature tabulations (Deer *et al.*, 1962) of % Si in vermiculite; hence a constant value ($K_1 = 16.2 \pm 0.8$) has been used. For kaolinite, % Si ($K_2 = 21.7 \pm 0.5$) and % Al ($K_3 = 20.9 \pm 0.5$) are essentially constant. There is negligible Fe or Mg in this mineral. Solutions to Eq. (2) may be then obtained as follows: (1) The mixed clay sample is analyzed for total Si, Al, Fe, and Mg, and the results are inserted into the right hand matrix as % Si_T , % Al_T , % Fe_T , and % Mg_T ; (2) A choice is made of one of the possible permutations of data in the 4×4 matrix, e.g., the data may be chosen to correspond to all the highest (H) literature values together with the K_1 , K_2 , K_3 , and zero entries; (3) The 4×4 matrix is inverted (Staib, 1969; Imperial College, 1980) in order to solve the simultaneous Eqs. (1) and (2), the calculation yields values of % chl, % verm, % kao, and % sm provided certain conditions are met, and acceptable answers must be numerically positive and sum to $100 \pm 5\%$; (4) Procedures (2) and (3) are repeated with a new choice of permutation; (5) Procedures (2), (3), and (4) are repeated until all possible

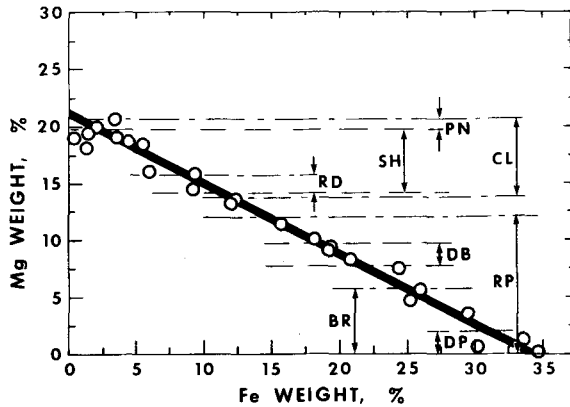


Figure 3. Regressed boundary limits for % Mg and % Fe for chlorites. (Abbreviations as given in Figure 2.)

(2¹¹) permutations have been calculated. The 'acceptable' results for each mineral are averaged and the resulting means taken as the best estimates of the true proportions of the four minerals.

ELEMENTAL RELATIONSHIPS

The number of permutations required and the uncertainty associated with the calculated clay proportions can be reduced by taking account of independent information on elemental distributions within and between clay minerals. For example, $\Sigma(\text{Si} + \text{Al}) = 8/\text{unit cell}$ in the tetrahedral layers of various sheet silicates; hence, % Si and % Al are inter-dependent.

The d(001) spacings of chlorites (Gillery, 1959; Deer *et al.*, 1962) are related to the extent of Al replacement of Si in the tetrahedral layer. Inasmuch as all of the Si, but not all of the Al, resides in this layer, the 001 spacing is an independent measure of the Si content of a chlorite. The direct relationship between the Si proportion and d(001) spacing is shown in Figure 1. Figure 2 shows literature values of % Si vs. % Al for a number of natural chlorites. The rectangular lines outline the estimated compositional limits of different chlorite types. In an 'unknown' mixture, d(001) values should indicate the type and % Si of a contained chlorite phase, and Figure 2 should yield an estimate of the corresponding range of compatible % Al values. A unique value will not be obtained because % Al varies with the extent of octahedral substitution of Fe and Mg by Al. Figure 3 is a similar plot of % Mg vs. % Fe. Here, a linear relationship applies, the presence of other ions (Ti⁴⁺, Mn²⁺, Ca²⁺) having a negligible effect on this relationship.

The elemental relationships described above are applied in the following steps in which d(001) measurements and Figures 1-3 are employed in conjunction with matrix inversion procedures: (1) To avoid uncertainties associated with a single estimated d(001) value

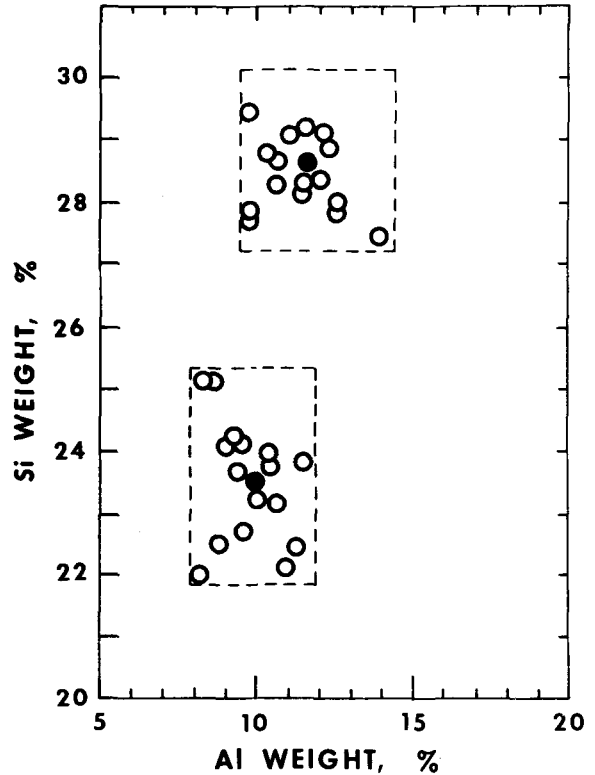


Figure 4. Distribution of % Si and Al for dioctahedral smectites. Averaged values indicated by solid circles.

and to make fuller use of the H/L computational procedure, two measurements are taken of the d(001) spacing (in the range 14.0-14.4 Å). These two values give two extreme estimates of % Si from Figure 1. Thus, if the extreme d(001) values happen to be 14.15 and

Table 1. Major phases in mineral systems investigated.

System code	Major phases ¹
10	chl-verm-kaot-9-11-Å phase
11	chl-verm-kaot-(Al,Fe)OOH
12	chl-verm-kaot-9-11-Å phase/AlOOH
20	kaol-serp/MgCO ₃ -9-11-Å phase-(Al,Fe)OOH
30	verm-kaot-sm-9-11-Å phase
31	verm-kaot-sm-(Al,Fe)OOH
32	verm-kaot-sm-9-11-Å phase/AlOOH
40	chl-verm-kaot-sm
42	chl-verm-kaot-sm-AlOOH

¹ In the table the symbol "/" indicates compositionally linked minerals interchangeable in the same column in the 4 × 4 matrix. In system 42 the phase AlOOH is in great excess and acts as a "sink" for aluminum not assignable to the four clay phases, the latter being entered in the 4 × 4 matrix. (chl = chlorite; kao = kaolinite; kaot = kaolin group mineral, serp = serpentine; sm = dioctahedral smectite; verm = vermiculite.)

Table 2. Constants A–I ($\times 10^2$) calculated for chlorite (chl), vermiculite (verm), dioctahedral smectite (sm), and kaolin group (kaot) mineral coefficient estimations.¹

	A	B	C	D	E	F	G	H	I
chl,Si	153.0	11.20	1.32	-1.51	-1.48	0.23	-0.21	0.02	-0.07
chl,Al	256.0	-26.10	25.5	-0.66	-3.10	0.79	-0.34	—	0.02
chl,Fe	38.8	5.10	-6.41	10.3	-2.69	-0.28	0.25	0.04	0.09
chl,Mg	277.0	-27.4	2.97	-2.21	27.6	0.76	-0.40	0.02	-0.27
verm,Si	297.0	7.17	-7.78	-3.66	-4.14	—	—	—	—
verm,Al	156.0	-5.41	13.9	-1.99	-2.02	—	—	—	—
verm,Fe	51.3	-1.43	-1.53	7.97	-0.96	—	—	—	—
verm,Mg	327.0	-6.96	-12.1	-5.96	10.6	—	—	—	—
sm,Si	358.0	9.17	-13.9	-6.53	-9.54	-0.20	-0.24	0.47 ²	—
sm,Al	163.0	-2.35	7.56	1.63	-1.64	-0.04	0.16	-0.66 ²	-0.42
sm,Fe	136.0	-10.9	3.26	7.51	-1.08	0.20	-0.18	-0.50 ²	0.09
sm,Mg	-72.0	7.52	-0.97	0.27	13.7	-0.16	—	-0.15 ²	0.33
kaot,Si	-301.0	47.4	-3.69	-0.96	-3.2	-0.93	-0.03	0.52	0.01
kaot,Al	-73.0	8.42	14.5	3.15	-2.66	-0.25	-0.21	-2.69	0.11
kaot,Fe	-291.0	23.0	4.32	4.68	0.50	-0.53	-0.11	-0.48	0.05
kaot,Mg	-453.0	56.9	-14.9	1.77	4.29	-1.34	0.37	-0.57	0.06

¹ — indicates that the data had insignificant magnitude.

² The constant H for Sm,Si is the product of the % Si and % Al assays, as this variable produced an improved regression.

14.25 Å, indicated values of % Si are 12.3 and 14.0%, respectively. (2) With the aid of Figure 2 the % Si values are associated with two 'end-members' chlorites and corresponding ranges of % Al. The end members are sheridanite and clinochlore in the example above, for which % Al is 11.0–15.0 and 7.8–10.8, respectively. (3) The mass balance is computed as above, first evaluating solutions for one end-member and then the other. For this purpose the left hand column of the 4×4 matrix (Eq. (2)) is modified so that the upper H/L entry takes the options of % Si dictated by the two d(001) spacings. In the example given, H = 14.0 (clinochlore) and L = 12.3 (sheridanite). With H = 14.0, the H/L entry for % Al has the options H = 10.8 or L = 7.8 (with H = 12.3, the corresponding options are H = 15.0 or L = 11.0). The other two H/L entries (% Fe and % Mg) have similar options, but Figure 3 shows that when % Fe is high, % Mg is low and vice versa: for example, for sheridanite, acceptable options are H (% Fe) = 12.0 → Mg = 14.0 or L (% Fe) = 2.5 → Mg = 20.0.

For natural dioctahedral smectites, a plot of % Si vs. % Al yields concentrations of points in two distinct areas (Figure 4). By taking the mean for the % Si and % Al values in each area, two corresponding 'average'

compositions (the large circles in the figure) may be deduced. These compositions are taken to represent two distinct types of dioctahedral smectite in the 4×4 matrix (Eq. (2)). Thus, in the right hand column of this matrix the options become H = 28.3 (Si) and H = 12.0 (Al) or L = 23.5 (Si) and L = 10.3 (Al). The 4×4 matrix may now be written

$$\begin{matrix} \text{Si} \\ \text{Al} \\ \text{Fe} \\ \text{Mg} \end{matrix} \begin{bmatrix} \text{chl} & \text{verm} & \text{kao} & \text{sm} \\ \text{(H/L)}_d & K_1 & K_2 & \text{(H/L)}_{t,\text{Al}} \\ \text{(H/L)}_{\text{Si}} & \text{H/L} & K_3 & \text{(H/L)}_{t,\text{Si}} \\ \text{(H/L)}_{t,\text{Mg}} & \text{H/L} & 0 & \text{H/L} \\ \text{(H/L)}_{t,\text{Fe}} & \text{H/L} & 0 & \text{H/L} \end{bmatrix},$$

where subscripts d, t, Si, Al, Mg, and Fe denote dependence upon d spacing, clay type, % Si, % Al, % Mg, and % Fe respectively, and other terms are as in Eq. (2). The number of permutations required now becomes 2⁹. As a result, the uncertainty in computed clay proportions (expressed in terms of the standard deviation of the averaged results) is decreased when elemental relationships are included, because the ranges of values standing for H/L are reduced.

Other elemental relationships can be developed. For

Table 3. Example of computer output: phase proportions estimated for a kimberlite alteration product.

Mineral	Mass (%)	Modeled composition (%)				Modeled coefficients				Water (%)
		Si	Al	Fe	Mg	Si	Al	Fe	Mg	
chl	20.1 ± 1.2	12.7	13.4	2.9	20.0	2.51	2.77	0.30	4.57	11.8
verm	48.2 ± 4.7	16.3	5.7	8.3	16.4	2.72	0.97	0.70	2.70	20.1
kaot	24.8 ± 6.7	19.8	3.2	7.2	15.0	2.00	0.34	0.39	1.80	13.6
9–11-Å phase	6.9 ± 3.9	12.7	6.5	5.4	5.6	3.02	1.62	1.66	1.56	43.5

example, the kaolin-group minerals (denoted kaot)—assumed here to be solid solutions of kaolinite and serpentine—can be represented as a 4×1 set of linked H/L entries within the 4×4 matrix. Groups of % Si, % Al, % Fe, and % Mg values are entered according to the permutation procedure. Thus, one calculation may involve a 'kaolin set' of assays and a second one a 'serpentine set'.

POORLY CRYSTALLINE PHASES

Alteration reactions can give rise to poorly crystallized phases which do not give sharply defined XRD patterns and defy positive identification. A high proportion of such a phase can be accommodated in the matrix inversion procedure by assigning the phase a modeled structural formula based on a major clay type. In this work, peaks noted in the 9–11-Å region were assumed to belong to partly formed pyrophyllite-like 2:1 layered silicates (cf. Bauer and Sclar, 1981) having the formula:



No literature analyses of such a phase exist, but suitable compositional data can be generated if the following assumptions are made: (1) The relative proportions of Mg, Fe, and Al in the formula are the same as those for % Mg_T , % Fe_T , and % Al_T (as defined in Eq. (2)); and (2) the terms t and n range from 0 to 2 (for Al replacement of Si) and 0 to 30, respectively. The latter range accounts for the possibility of extensively hydrated clays. The above formula can be rewritten as:



where $\text{RMg} = a/y = 1 - \text{RAI} - \text{RFe}$; $\text{RFe} = b/y = \% \text{Fe}_T / (\% \text{Mg}_T + \% \text{Fe}_T + \% \text{Al}_T)$; and $\text{RAI} = c/y = \% \text{Al}_T / (\% \text{Mg}_T + \% \text{Fe}_T + \% \text{Al}_T)$. From electroneutrality:

$$6 + t = 2a + 3(b + c), \quad (3)$$

hence, from atomic weight data the molecular weight, M , of the clay is given by:

$$M = 24.3y\text{RMg} + 55.9y\text{RFe} + 27.0(y\text{RAI} + t) + 28.1(4 - t) + 194.0 + 18.0n, \quad (4)$$

such that the metal proportions are given by: % $\text{Mg} = 2430y\text{RMg}/M$; % $\text{Fe} = 5590y\text{RFe}/M$; % $\text{Al} = 2700(y\text{RAI} + t)/M$; % $\text{Si} = 2810(4 - t)/M$.

Values of % Si, % Al, % Fe, and % Mg can thus be calculated for the extremes of t and n dictated by assumption (2) and Eqs. (3) and (4). The resulting theoretical analyses should be compatible with the H/L matrix inversion procedure if both the model structure and the accompanying assumptions are correct.

Other poorly crystalline alteration products encountered in the present work were Al and Fe oxyhydroxides, for which the metal ion content can be varied between suitable stoichiometric extremes in the matrix

Table 4. Effect of chemical analysis error on computed phase proportions.¹

Assay variation	Calculated phase proportion (%)			
	chl	verm	kaot	AlOOH
HLHH	17.0	53.3	20.3	9.4
LHLL	15.6	49.6	17.6	17.2
LHHH	17.4	49.9	15.6	16.1
HHHL	14.7	53.1	19.7	12.5
HLLH	15.5	55.4	19.6	9.5
LHHL	16.6	48.5	17.8	17.1
LLL	13.9	53.7	16.4	15.0
HHHH	17.7	49.0	20.4	12.9
Mean	16.1	51.6	18.4	13.9
Coeff of var. (%)	8.3	5.0	9.6	23.8
Exp. values	16.3	51.4	18.9	13.3

¹ The sequence HLHH refers to high (H) or low (L) levels of elemental assays taken in the order % Si, % Al, % Fe, % Mg. Thus, from left to right an element of 5% was added to % Si experimentally determined, subtracted from % Al, added to % Fe and added to % Mg. A similar procedure was employed for the other sequences. The experimental data were % Si, 14.5; % Al, 12.6; % Fe, 2.6; % Mg, 10.8; % H_2O , 14.79; $d(001)$, 14.3 and 14.2 Å.

procedure. Thus, for Al, $H = 44$ (equivalent to AlOOH) and $L = 34$ (equivalent to Al(OH)₃).

COMPUTER PROCEDURES

The laborious calculations were carried out using a Fortran IV computer program written for use with CDC 4120 equipment. This program has six sections: input or $d(001)$ assay data and system code (Table 1); assignments in Eq. (2) modified as necessary to take account of elemental relationships; solution of the simultaneous equations by matrix inversion; testing and storing 'acceptable' values; testing and continuation of permutations as necessary; and output of averaged phase proportions.

Each acceptable permutation was associated with particular high, low, or fixed/zero values of % Si, % Al, % Fe, and % Mg. The values were averaged for each element, for all acceptable permutations, and printed out as averaged elemental analyses. When smectite and poorly crystalline phases were considered, a water mass balance was calculated and similarly modeled. Stoichiometric coefficients were calculated from the averaged analyses to that an empirical formula, consistent with the calculated phase proportions, could be written for each major phase. For this purpose the following empirical equation was employed.

$$\alpha_i(P) = A + B\% \text{Si}(P) + C\% \text{Al}(P) + D\% \text{Fe}(P) + E\% \text{Mg}(P) + F(\% \text{Si}(P))^2 + G(\% \text{Al}(P))^2 + H(\% \text{Fe}(P))^2 + I(\% \text{Mg}(P))^2. \quad (5)$$

In Eq. (5) the term $\alpha_i(P)$ is the stoichiometric coefficient for element i (Si, Al, Fe, or Mg) in mineral P ; % Si(P), % Al(P), % Fe, % (P), and % Mg(P) are the respective

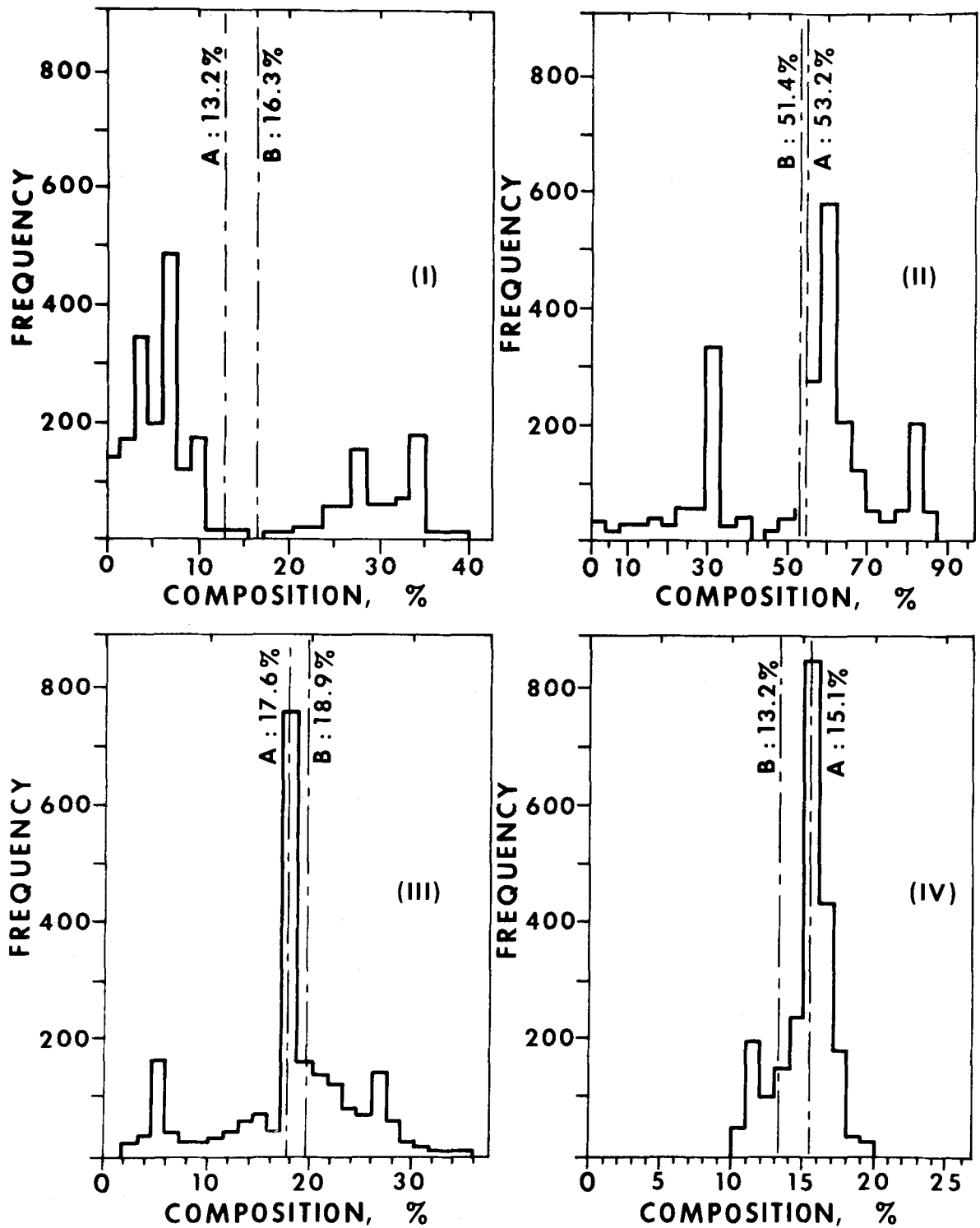


Figure 5. Frequency distributions for computed phase proportions (327, 678 test permutations): (I) = chl, (II) = verm, (III) = kaot, (IV) = AlOOH.

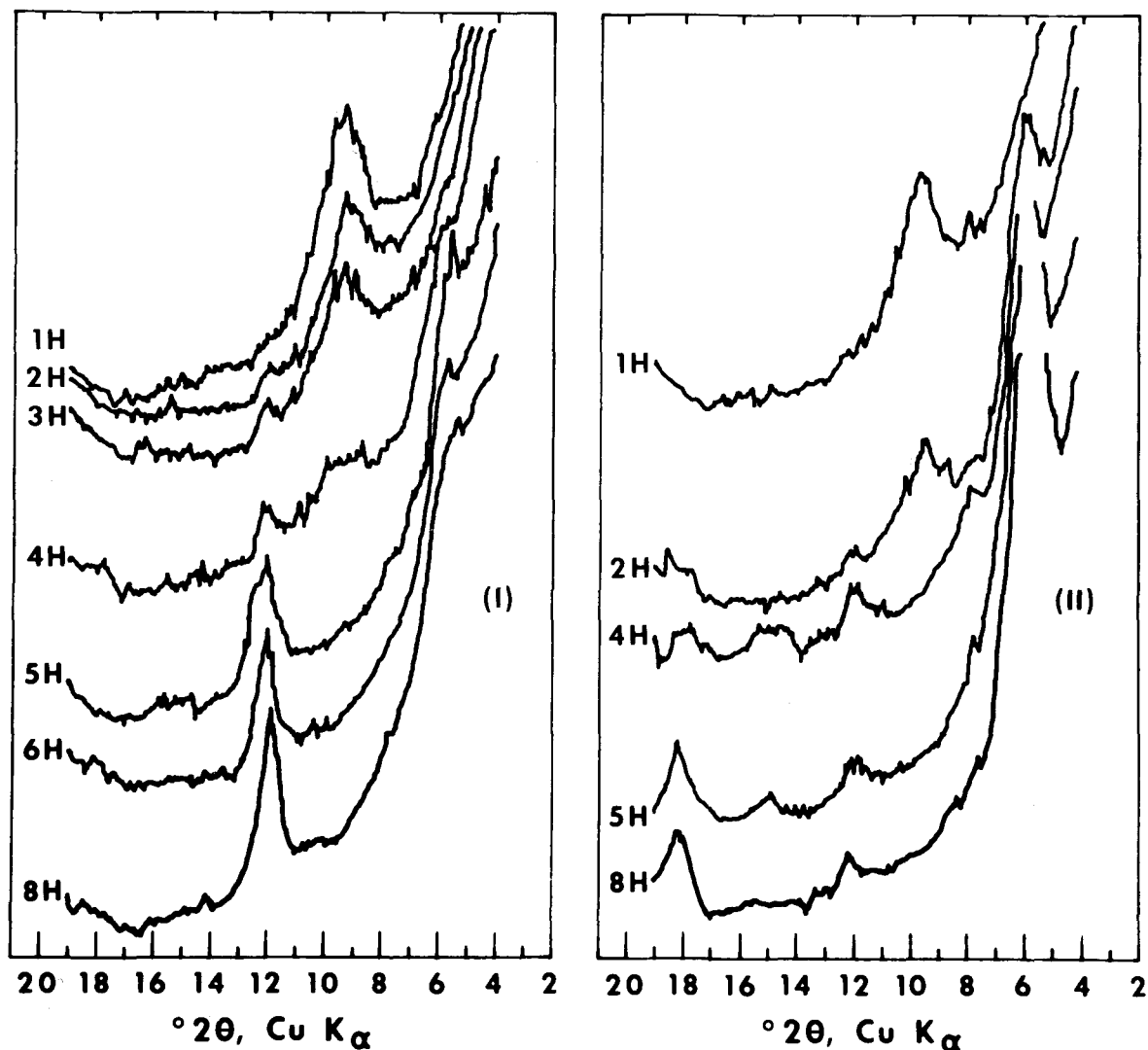


Figure 6. X-ray powder diffractograms of kimberlite alteration products after various reaction times (H = hours): (I) = 260°C (II) = 300°C.

metal percentages in P; A–I are constants regressed from natural phases for which $\alpha_i(P)$ and corresponding elemental assay data are known.

Table 2 shows values of the constants calculated for chlorites, vermiculites, kaolinite-serpentines, and dioctahedral smectites. The required data (Deer *et al.*, 1962) were employed in conjunction with a MINITAB II (Ryan *et al.*, 1978) computer regression routine. Correlation coefficients exceeded 0.95.

In one alteration experiment (Hodgson, 1981), a reaction product was shown by XRD techniques to contain chlorite, vermiculite, a kaolin mineral, and a poorly crystalline, 2:1 aluminosilicate. The $d(001)$ values for the chlorite were 14.0–14.3 Å. Analysis of a fused and dissolved sample by atomic absorption spectrometry showed 16.6% Si, 6.8% Al, 6.9% Fe, and 16.5%

Mg. System 10 (Table 1) was selected and the resulting computer output is shown in Table 3. This product was taken to contain about 20% of a chlorite phase of empirical formula $Mg_{4.57}Fe_{0.30}Al_{2.77}Si_{2.51}O_{10}(OH)_8$; the estimated structural formulae and proportions of the other components are given in Table 3.

ESTIMATION OF ERRORS

Owing to the lack of a complete set of representative 'standard' minerals, absolute checks on the accuracy of the method were not possible. Only kaolinite and vermiculite were obtained in a sufficiently pure form (>99%), whereas samples of chlorite, montmorillonite, and serpentine available contained major impurities. The alteration products (obtained from other testwork) were too complex and finely divided for effective sep-

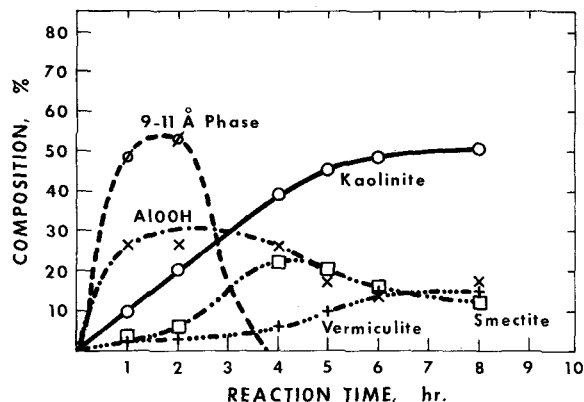


Figure 7. Computed proportions of phases in kimberlite alteration products produced at 260°C.

eration. The precision and internal consistency of the method are considered below.

Qualitative phase analysis

The assumption is made that four phases sufficiently describe the composition of an alteration product; any other phases present contribute insignificantly to the total mass. The method could be developed to account reliably for a mixture of five phases only if a fifth element or other intrinsic property is present for analysis so that a 5×5 matrix can be set up. Two possible sources of error thus arise: four phases are considered when five or more could be significant, and one or more phases could be misidentified. If the assay data employed, however, are not consistent with the system selected for computation (Table 1), acceptable solutions of matrix inversion are likely to be few in number or nil. Trial and error soon determines which system gives the largest number of acceptable solutions with the minimum standard deviation. If this system is consistent with the XRD trace, as is common with alteration products, all should be well. For example in one sample, the 9–11 Å peak was modeled as pyrophyllite, and no acceptable solutions were obtained because the water mass balance was not satisfied. When remodeled as the 9–11 Å phase mentioned above, the results were satisfactory.

Where mixed-layer clays were suspected, the program (as written) considered them in terms of their constituent minerals, e.g., corrensite was treated as a mixture of two separate species: chlorite and smectite. The technique, however, allows a mineral mixture system to be used in which one phase could be corrensite, to which would be allocated the relevant compositional ranges for % Si, % Al, % Fe, and % Mg.

Quantitative elemental analysis

A relative error of $\pm 5\%$ was associated with the atomic adsorption method employed. To judge the

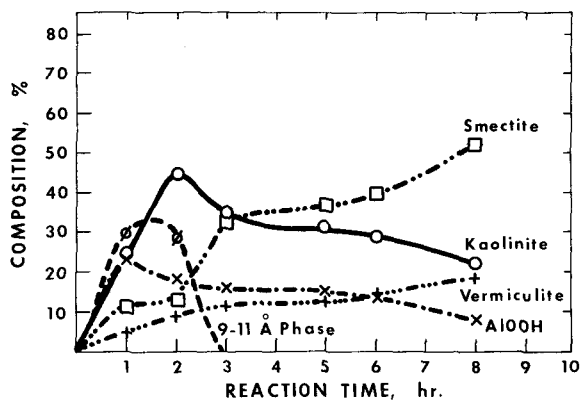


Figure 8. Computed proportions of phases in kimberlite alteration products produced at 300°C.

sensitivity of computed results to variations in the input data, calculations were carried out with assay values set at high or low extremes as shown (for the system chl-verm-kaot-AlOOH) in Table 4. The variations are $< 10\%$ for the clay minerals, indicating that the results were unlikely to be ambiguous due to assay errors.

Literature data selection

To assess the effect on computed results of selecting only two choices of literature assay (H or L) for each element (Si, Al, Fe, or Mg), the computer program was modified to accommodate intermediate values between the extremes of H and L. Preferably the whole range of intermediate literature values would have been included, but this would have led to an unacceptable increase in computing time. As an alternative, 10–15 arbitrary intermediate values were incorporated as equal incremental steps between H and L for each element. Employing this procedure for the system chl-verm-kaot-AlOOH (cf. Table 4) increased the number of permutations from 1280 to 327,678. Figure 5 gives the results obtained in terms of the frequency distributions of 'acceptable' calculated phase proportions for each of the phases: (I) chl, (II) verm, (III) kaot, and (IV) AlOOH. The lines marked A in the plots represent weighted mean properties and provide the best estimate of phase proportions: chl = 13.2%, verm = 53.2%; kaot = 17.6%; and AlOOH = 15.1%. Except for chlorite, for which classification according to the d(001) spacings causes two distinct frequency groupings (Figure 5I), the lines are close to the highest peaks of the distributions. The lines marked B are corresponding means calculated from the unmodified program: chl, 16.3%; verm, 51.4%; kaot, 18.9% and AlOOH, 13.2%. The positions of the lines A and B are not greatly different despite the fact that the former are based on 255 times as many calculations as the latter. The restriction to the simple choice H or L seemed therefore to be justified, and a great deal of computing time could be saved.

Overall random error

The overall error, e_t (Chatfield, 1970), for a particular phase proportion was assumed to be:

$$e_t^2 = e_a^2 + e_b^2 + e_c^2 \quad (6)$$

where e_a is the error due to elemental analysis (from Table 4), e_b the error in averaging acceptable matrix inversions, and e_c the error incurred in restricting computing time. The term e_b was deduced from the uncertainty in calculated mass percentage, as shown, e.g., in column 2 in Table 3. The term e_c was related to the fractional difference between the lines A and B in plots of the type shown in Figure 5. Values of e_t were in the range 7–25%, the error decreasing with an increasing estimate of mineral proportion.

DISCUSSION AND CONCLUSION

The mass balance technique described here has been developed for complex clay mixtures for which well-established methods of separation and appraisal are not available. Although the method contains uncertainties when applied to complex mixtures, answers can be routinely obtained. Such answers are probably qualitatively correct if the computer procedure leads to a large number of acceptable matrix inversions, and semi-quantitatively correct if the results of these inversions cluster around a particular set of phase proportions. The probability of obtaining reliable answers will become less, the less abundant and/or less well-defined is (are) the phase(s) involved. In this context, calculated standard deviations provide a numerical indicator of reliability.

The method relies on finding a set of 'modeled' phases consistent with qualitative XRD analyses, quantitative elemental assays, and the literature of clay composition and structure. Confidence in the results is improved if the 'modeled' phases are also consistent with other independent information. In one group of experiments (Hodgson, 1981), hydrothermal alteration reactions were carried out for varying lengths of time. Figure 6 shows diffractograms of products obtained at 260° and 300°C. Careful examination of the diffractograms (some involving the use of glycolation and potassium saturation techniques (Thorez, 1975)) clearly indicated the presence in some of the products of vermiculite, a dioctahedral smectite, kaolinite, boehmite (AlOOH), and 9–11-Å phases. The phase identifications were supported by separate thermogravimetric and infrared analyses (not described in detail here) which indicated the presence of highly hydrated material other than the principal clay minerals. The former technique gave a quantitative measure of the water content.

Examination of trends in peak heights in the diffractograms with time suggested initial rapid formation of metastable poorly crystalline alteration products which decomposed progressively with time to yield crystalline products. This process was evidently more

rapid at 300°C. At 260°C the main crystalline product was eventually kaolinite, whereas at 300°C it was smectite. As will be discussed elsewhere, such trends were mechanistically plausible; the 'modeled' phases and chemically likely sequences of alteration reactions were mutually supportive, particularly with respect to those components poorly defined by X-ray powder diffraction.

The XRD technique has often been employed for the semi-quantitative estimation of clay minerals (e.g., Gibbs, 1967). Peak heights or areas are measured in comparison with 'standard' clay samples. Although the complex nature of the mixtures considered in this contribution normally precluded reliable comparisons of peak areas, such comparisons were occasionally feasible for isolated, well-defined diffractions forming part of a more complex spectrum. For these reflections the relative peak areas were invariably in accord with the computed phase proportions (cf. Figure 6(I) and 6(II) with Figures 7 and 8).

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REFERENCES

- Bauer, J. F. and Sclar C. B. (1981) The '10 Å phase' in the system MgO–SiO₂–H₂O: *Amer. Mineral.* **66**, 576–585.
- Brindley, G. W. and Brown, G. (1980) *Crystal Structures of Clay Minerals and their X-ray Identification*: Mineralogical Society, London, 495 pp.
- Carthew, A. R. (1955) The quantitative estimation of kaolinite by differential thermal analysis: *Amer. Mineral.* **40**, 107–117.
- Chatfield, C. (1970) *Statistics for Technology*: Chapman and Hall, London, 358 pp.
- Cody, R. D. and Thompson G. L. (1976) Quantitative X-ray powder diffraction analysis of clays using an orientating internal standard and pressed discs of bulk shale samples: *Clays & Clay Minerals* **24**, 224–231.
- Deer, W. A., Howie, R. A., and Zussman, J. (1962) *Rock Forming Minerals*: **3**, Longmans, London, 270 pp.
- Gibbs, R. J. (1967) Quantitative X-ray diffraction analysis using clay mineral standards extracted from the samples to be analyzed: *Clay Miner.* **7**, 79–90.
- Gillery, F. H. (1959) The X-ray study of synthetic Mg-Al serpentines and chlorites: *Amer. Mineral.* **44**, 143–152.
- Hodgson, M. (1981) *The Hydrothermal Alteration of Kimbertite*: Ph.D. thesis, Imperial College, University of London, 449 pp.
- Imperial College (1980) NAGFILE Routines: Computer Centre, Imperial College, London.
- MacKenzie, R. C. and Mitchell, B. D. (1962). Differential thermal analysis. A review: *Analyst* **87**, 420–434.
- van der Marel, M. R. (1966) Quantitative analysis of clay minerals and their admixtures: *Contrib. Miner. Petrol.* **12**, 96–132.
- Pearson, M. J. (1978) Quantitative clay mineralogical analyses from the bulk chemistry of sedimentary rocks: *Clays & Clay Minerals* **26**, 423–433.
- Ryan, T. A., Jr., Joiner, B. L., and Ryan, B. F. (1978) *Minitab II: Reference manual*: Duxbury Press, North Scituate, Massachusetts, 100 pp.

Staib, J. M. (1969) *An Introduction to Matrices and Linear Equations*: Addison-Wesley, Reading, Massachusetts, 336 pp.

Thorez, J. (1975) *Phyllosilicates and Clay Minerals: A Lab-*

oratory Handbook for Their X-ray Diffraction Analysis: Editions G. Lelotte Dison, Belgium, 579 pp.

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Резюме—Как часть лабораторных исследований гидротермического изменения кимберлита, разработан метод для определения относительных пропорции фаз синтетических филлосиликатов—хлорита, вермикулита, смектита, каолинита и серпентина—присутствующих в продуктах реакции. метод основан на комбинации измерений порошковой рентгеновской дифракции (для идентификации фаз), определения атомной абсорбции (для суммарного содержания Si, Al, Fe, и Mg) и опубликованных данных по химическому анализу глинистых минералов (для стехиометрических вычитаний). Этот метод основан на численной инверсии 4×4 матрицы определяемой системой четырех уравнений, определяющих баланс массы Si, Al, Fe, и Mg в четырех выбранных минералах, а также включает процедуру систематического отбора (их всех возможных пермутации высоких и низких оценок минеральных химических анализов) допускаемых групп стехиометрий продуктов и пропорции фаз, совместимых с полным анализом металлов. Для минимизации неопределенности и времени вычислений, программа включает элементарные взаимодействия и баланс массы воды, связанные с филлосиликатами. Эта програма также включает данные относящиеся к слабо кристаллическим фазом, для которых используется диапазон анализа теоретического типа, моделированного на оксигидроокисях алюминия и 9–11 Å, 2:1 слоистых алюмосиликатах.

Этот метод является устойчивым для определения тенденции в пропорции фаз, согласных с интенсивностями линий порошковой рентгеновской дифракции, характерных для глинистых минералов, находящихся в анализируемой смеси; например увеличение пропорции каолинита соответствует увеличению линии 7 Å (и других) в анализируемом образце. Обычно достигались уровни точности порядка 7–25%. [E.G.]

Resümee—Als Teil einer Laboruntersuchung der hydrothermalen Umwandlung von Kimberlit wurde ein Massenbilanzverfahren zur Abschätzung der relativen Anteile von synthetischen Schichtsilikaten—Chlorit, Vermiculit, Smektit, Kaolinit, und Serpentin—die in den Reaktionsprodukten vorkommen, entwickelt. Das Verfahren basiert auf einer Kombination aus Röntgendiffraktionsmessungen (zur Phasenidentifizierung), Atomadsorptionsbestimmungen (für die Bestimmung des Gesamtgehaltes an Si, Al, Fe, und Mg) und publizierten chemischen Tonmineralanalysen (zu stöchiometrischen Ableitungen). Es konzentriert sich auf die Computerinversion einer 4×4 Matrix für 4 simultane Gleichungen, die die Massenbilanz für Si, Al, Fe, und Mg in den 4 ausgewählten Mineralen darstellen. Außerdem schließt es eine systematische Routine zur Auswahl (aus allen möglichen Permutationen von hohen und niedrigen Möglichkeiten einer chemischen Mineralanalyse) möglicher Kombinationen von stöchiometrischen Zusammensetzungen der Produkte und von Phasenverhältnissen ein, die mit der Gesamtmetallanalyse übereinstimmen. Um Unsicherheiten und die Rechenzeit möglichst klein zu halten, berücksichtigt das Programm Elementbeziehungen und die Wasserbilanz, die im Zusammenhang mit den Phyllosilikaten steht. Es bezieht auch Daten mit ein, die im Hinblick auf schlecht kristallisierte Phasen wichtig sind, für die ein Bereich von theoretischen Typanalysen eingesetzt wird, die auf Aluminium-Oxidhydroxiden und Å 9–11 Å 2:1 Alumoschichtsilikaten beruhen.

Diese Vorgangsweise liefert reproduzierbare Trends bei Phasenverhältnissen, die mit den Intensitäten der charakteristischen XRD-Peaks der Tonminerale, die in den analysierten Mischungen vorhanden sind, übereinstimmen; z.B., entsprechen Zunahmen bei den geschätzten Kaolinitanteilen größeren 7 Å (und anderen) Peaks in den analysierten Proben. Genauigkeiten von 7–25% waren routinemäßig zu erreichen. [U.W.]

Résumé—En tant que partie d'une étude de laboratoire de l'altération hydrothermique de la kimberlite, un procédé d'équilibre de masse a été développé pour estimer les proportions relatives de phases phyllosilicates synthétiques—chlorite, vermiculite, smectite, kaolinite, et serpentine—présentes dans les produits de réaction. Le procédé est une combinaison de mesures de diffraction des rayons-X (pour l'identification de phases), de déterminations d'adsorption atomique (pour le contenu total en Si, Al, Fe, et Mg) et d'analyses chimiques de minéraux argileux publiées (pour les déductions stœchiométriques). Il centre sur l'inverse à l'ordinateur d'une forme de matrice 4×4 de quatre équations simultanées représentant l'équilibre de masse de Si, Al, Fe, et Mg dans quatre minéraux choisis, et incorpore une routine systématique pour la sélection (à partir de toutes les permutations possibles d'estimations élevées et basses des analyses chimiques de minéraux) d'ensembles acceptables de stœchiométries produites et de proportions de phases consistantes avec les analyses de métaux totaux. Pour minimiser les incertitudes et le temps à l'ordinateur, le programme tient compte de relations d'éléments et des équilibres de masse d'eau associées avec des phyllosilicates. Il accomode aussi les données ayant rapport aux phases pauvrement cristallines pour lesquelles on emploie une gamme d'analyses-type théoriques modelées sur des oxyhydroxides d'aluminium et sur des aluminosilicates à couches 9–11 Å 2:1.

Le procédé est sûr pour la production de tendances de proportions de phases consistantes avec les intensités de sommets XRD caractéristiques de minéraux argileux présents dans le mélange analysé; par exemple des augmentations de proportions estimées de kaolinite correspondent à de plus hauts sommets 7 Å (et autres) des échantillons analysés. Il était commun d'obtenir des niveaux de précision de 7–25%.