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COMPARISON OF FOUR ELEMENTAL MASS BALANCE METHODS FOR CLAY MINERAL QUANTIFICATION[1]

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Abstract—The quantification of the relative mineralogical composition of clay mixtures by powder X-ray diffraction or chemical mass balance methods has been severely hampered by a lack of representative standards. The recent development of elemental mass balance models that do not require standards for all minerals in the mixture may help circumvent this problem. These methods, which are based on the numerical optimization of systems of non-linear equations using the Marquardt algorithm, show promise for mineral quantification. The objective of this study is to make a preliminary assessment of the accuracy of these methods and to compare them to linear models that require standards for all mineral phases. Methods 1 and 2 are based on weighted average solutions to simultaneous linear equations solved for single samples with known standards. Solutions were achieved by a matrix decomposition algorithm and the Marquardt algorithm, respectively. Methods 3 and 4 are based on a set of simultaneous non-linear equations with reduced non-linearity solved by least squares optimization based on the Marquardt algorithm for multiple samples. Illite and halloysite compositions were fixed in Method 3, only the halloysite composition was fixed in Method 4. All models yielded relative weight fractions of the three mineral components; additionally, Methods 3 and 4 yielded compositions of smectite, and smectite and illite, respectively. Ten clay mixtures with varying proportions of the <0.2 μm size fraction of three different reference clays (Wyoming bentonite, Fithian illite, and New Bedford halloysite) were prepared gravimetrically and analyzed by inductively coupled plasma-atomic emission spectroscopy. Accuracy of the four methods was evaluated by comparing the known mineralogical compositions of the mixtures with those predicted by the models. Relative errors of 5 and 10% (randomly +/−) were imposed on the elemental composition of the smectite standard to simulate errors due to lack of good standards. Not surprisingly, the accuracy of Methods 1 and 2 decreased rapidly with increasing error. Because Methods 3 and 4 optimized for the smectite composition and only used it for an initial guess, they were unaffected by the level of introduced error. They accurately quantified the mineralogical compositions of the mixtures and the elemental compositions of smectite, and smectite and illite, respectively.

Key Words—Elemental mass balance, Marquardt algorithm, Non-linear models, Numerical optimization, Quantification.

INTRODUCTION

Methods of quantification

Quantification of clay minerals by X-ray powder diffraction (XRD) has proven difficult due to a variety of physical problems associated with clay minerals. A number of computer programs have been developed that quantify powder XRD patterns using some function of peak height or peak area (Smith, 1989; Hosterman and Dulong, 1989; Jones, 1989), but difficulties arise when applying these programs to soil clays. Many soil clays, particularly smectites, give broad powder XRD peaks because of interstratification, poor cyrstallinity, and small crystal size common in soil clays. Crystal orientation can also be problematic, as most soil clays have acicular, platy or tabular morphologies that promote non-random orientation, whereas most techniques for quantifying powder XRD patterns require random orientation. Most of these problems directly result from a lack of reference clay standards that can be confidently assumed to have XRD characteristics similar to those of the soil clays present in the sample. Generally, quantitative analysis of clays by powder XRD is considered good if relative errors are $<\pm 10\%$ for major constituents, and $<\pm 20\%$ for minerals constituting $<20\%$ of the sample (Moore and Reynolds, 1989).

A variety of quantification methods have been developed based on XRD and/or compositional data. Four major XRD methods requiring standards have been developed: 1) the method of external standards, 2) the method of internal standards, 3) the method of known additions, and 4) the Rietveld method. Although the Rietveld method doesn't actually require a standard, it does require accurate knowledge of the chemical composition and structural characteristics of the minerals of interest. From a practical standpoint,

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however, all of these methods require calibration with representative standards which are rarely available for soil clays.

A standardless XRD method of quantification was developed by Salyn and Drits (1972) and refined by Zevin (1977). This method requires partial separation of phases in two or more fractions, usually accomplished by centrifugation. A rearrangement of terms describing the relationship between weight proportions, mass attenuation coefficients, and peak intensity ratios for the fractions relative to the original sample produces equations that may be solved for the relative quantities of two or more phases in the original mixture, providing concentrations of the components in the mixtures change about 20–30% relative to initial values. This method has been shown to be reasonably accurate, as two-phase mixtures agree within ±2% and three-phase mixtures within about ±5–10%. The generalized version of this method (Zevin, 1977) requires n^2 intensities for n phases as well as mass attenuation coefficients of each phase, a significant drawback for clay mixtures with more than two phases. Additionally, minor and amorphous components cannot be quantified by standardless methods based on powder XRD.

Chemical methods

Most chemical methods are based on an elemental mass balance model that uses least squares optimization or other means to fit the elemental composition of individual phases to that of the mixture. Chemical methods have been used alone or in conjunction with powder XRD data for clay mineral quantification (McNeal and Sansoterra, 1964; Hussey, 1972; Johnson *et al.,* 1985; Calvert *et al.,* 1989; Slaughter, 1989; Hodgson and Dudeney, 1984; Braun, 1986). The majority of these methods have used simultaneous linear equations (SLEs) to solve for the quantities of each phase in a mixture. Such methods require an accurate knowledge of the chemical composition of each phase in the mixture, or at least a knowledge of the compositional range of a particular clay phase.

New techniques using non-linear elemental mass balance models allow simultaneous determination of both the quantity and the chemical composition of two or more clay mineral phases in mixed clay samples (Laird *et al.,* 1991a). The relative accuracy of these new chemical mass balance techniques, however, has not been evaluated using samples whose composition is known a priori. The objective of this study is to provide an initial assessment of the accuracy of these methods and to compare them to linear models that require standards for all mineral phases. To accomplish this objective, artificial mixtures containing known quantities of reference clays of known elemental composition were made and subjected to total elemental analysis, and the results were used to test the different models. Application of these techniques to quantification of mixtures of soil clays will be presented in a subsequent manuscript.

MATERIALS AND METHODS

Sample pretreatment

Three reference clays, Fithian illite No. 35, New Bedford halloysite No. 12 (Wards Natural Science Est. Inc., Rochester, NY), and Wyoming bentonite (Baroid Division of National Lead Co., Houston, TX) were selected for this experiment. Bulk samples were crushed, washed with 1 M NaCl, and mechanically dispersed in 20 liters of distilled H_2O. After settling for 16 hours the supernatant (20 cm) was siphoned off, frozen to promote flocculation, thawed, centrifuged, and decanted to concentrate the <2 μm fraction. Samples of the <2 μm fraction were washed again with 1 M NaCl, dispersed in 200 ml of distilled H_2O, and the <0.2 μm fraction was collected by repeated centrifugations. Carbonates and sesquioxides were removed by treatment with pH 5.0 Na-acetate buffer solution and dithionite-citrate-bicarbonate (DCB), respectively (Kunze and Dixon, 1986). Samples were analyzed by XRD to verify mineralogical composition. Because these methods rely solely on elemental composition, structural information and mineral purity are not necessary for quantification. These methods merely require that there are significant compositional differences between the samples and that the compositions of the aliquots used to make the mixtures are representative of the whole sample (i.e., they are well-mixed).

Preparation of mixtures

The <0.2 μm size fraction of each reference clay sample was saturated with Ca by four washings with 0.5 M $CaCl_2$, then washed eight times with 95% ethanol to remove excess $CaCl_2$. After final decantation with 95% ethanol, 100 ml of deionized water were added to the Ca-saturated reference clays and the clays were dispersed by sonication for 30 seconds at 60 watts. The reference clay suspensions were then heated to 70°C for two hours to volatilize excess ethanol. The suspensions were gravimetrically diluted to 200 g and an aliquot (10 ml) of each suspension was oven dried and weighed to determine clay concentration. The suspensions were gravimetrically combined to prepare ten mixtures with varying proportions of the three Ca-saturated reference clays.

Elemental analysis

Portions (0.1 g) of the reference clays and each mixture were sonicated for 2 min at 60 watts in 100 ml of 0.1 M NaCl prior to elemental analysis. Elemental analyses (Si, Al, Fe, Ca, Mg, K, Mn, Zn, and Ti) were performed on the prepared clay suspensions using suspension nebulization (Laird *et al.,* 1991b) with analysis by inductively coupled plasma atomic-emission spec-

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trometer (ICP-AES) (Applied Research Laboratories Model 3560, Fisons Instruments, Inc., Valencia, CA). The spectrometer was calibrated with multi-element solution standards prepared with 0.1 M NaCl + 0.5 M HNO_3 matrix solutions. All samples and standards contained 10 mg Co liter^{-1} as an internal standard.

Quantification models

The models are based on the elemental mass balance equation:

$$E_i = \sum_{j=1}^{n} W_j E_{ij} \quad (1)$$

where E_i is the mass ratio of element oxide i to the sum of all oxides in the mixture, E_{ij} is the mass ratio of oxide i in phase j to the sum of all oxides in phase j, and W_j is the mass ratio of the sum of all oxides in phase j to the sum of all oxides in the sample. In the final step of each model, W_j values are multiplied by the sum of oxides for mineral j and divided by the formula unit weight for mineral j, and then normalized to sum to one for each sample. Where all E_{ij} values are known (i.e., reference standards exist), the non-linear model reduces to a set of SLEs; these can be solved by a variety of methods. If reference standards do not exist for one or more minerals, however, then the E_{ij} values are not known and the model becomes a set of simultaneous non-linear equations; these are much more difficult to solve. In this study, E_i values are based on ICP-AES analyses of the various clay mixtures; where treated as knowns, E_{ij} are based on analyses of the reference clay standards. Four models having different inputs and/or methods of solution were constructed and compared.

Method 1: Simultaneous linear equations. In this model, E_{ij} values for all three minerals were treated as knowns, thus producing a set of SLEs. Solutions were independently obtained for each mixture for all possible combinations of mass balance equations for Si, Al, Mg, Ca, Fe, Ti, and K using a matrix decomposition algorithm. Weighted average W_j values were determined by weighting each solution by the sum of oxides for elements included in the solution relative to the total oxides for the sample.

The Marquardt Algorithm. Models 2 through 4 were solved by non-linear optimization using the Marquardt algorithm (Bevington, 1969, as modified by Barak *et al.*, 1990). A fully non-linear model would determine both the relative proportions of three mineral phases as well as their compositions, and would require optimization of the following parameters: 1) the relative weight fractions of three minerals in 10 mixtures; and 2) nine element fractions for each of three minerals, for a total of 47 parameters. The number of parameters can be reduced, and the likelihood of success increased, by constraining the model by application of a priori knowledge. For example, the K contents of smectite and halloysite are, by definition, assumed to be zero. The model can be further constrained by fixing the elemental composition of one or more phases if accurately known. The composition of soil smectites is more variable than that of the other clays, and it differs most from that of available reference standards. Halloysite composition is probably best represented by available reference standards, and illite falls somewhere between the other two. Consequently, we were most interested in enhancing the ability of the model to optimize for the smectite composition. The halloysite composition remained fixed (the reference clay composition) in all three models.

Required data inputs for all of these models include 1) the composition of all fixed mineral phases; 2) initial guesses for the composition of all mineral phases to be optimized; 3) initial guesses for the weight fractions of each of the three phases; and 4) a sensitivity value. Optimization was terminated when reduction in the sum of squares relative to the previous iteration was less than the sensitivity value (0.05% unless otherwise stated).

Method 2: Linear model, Marquardt solution. This model is similar to that used in Method 1 in that the composition of all three mineral phases was fixed. The main difference is that the system of SLEs was solved using the Marquardt algorithm (Bevington, 1969, as modified by Barak *et al.*, 1990) instead of the matrix decomposition algorithm used in Method 1. The least squares best fit between measured and predicted elemental compositions of mixed clay samples was determined on an individual mixture basis. When all three phases were optimized, the number of data points was 9 (each element) leaving 5 degrees of freedom (9 − 3 − 1) for fit of the model. When only two phases were present, the number of data points was again 9 but there were 6 degrees of freedom (9 − 2 − 1). Required inputs for Method 2 include the composition of all three clay phases (their E_i values).

Method 3: Non-linear model with known illite and halloysite compositions. In this model, non-linearity was reduced by fixing the composition of illite ($E_{i,illite}$) and halloysite ($E_{i,halloysite}$). Both the W_j and $E_{i,smectite}$ values were determined by iterative parameter fitting, yielding the smectite composition and clay phase weight percentages. The least squares best fit was determined between measured and predicted elemental compositions for all 10 clay mixtures simultaneously. Method 3 optimizes nine elements in 10 mixtures allowing for 90 data points. All clay phase weight percentages are variables (27) as well as the major five elements (Si, Al, Ca, Mg, and Fe) in smectite for a total of 32 variables,

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leaving 57 degrees of freedom (90 − 32 − 1) for fit of the model.

Method 4: Non-linear model with known illite composition. Method 4 is similar to Method 3 except that it also optimizes for the elemental composition of illite ($E_{i,illite}$), thus yielding the composition of the illite and smectite and the relative proportions of all three phases. The only fixed composition is that of halloysite. Method 4 optimizes 9 elements in 10 mixtures allowing for 90 data points. All clay phase percentages are variables (27) as well as five major elements (Si, Al, Ca, Mg, and Fe) in the smectite standard and six major elements in the illite standard (Si, Al, Ca, Mg, Fe, and K) for a total of 38 variables. This leaves 51 degrees of freedom (90 − 38 − 1) for fit of the model.

Model evaluation

If the composition of reference clay standards reflects the composition of soil clays, each of these methods should accurately estimate the relative quantity of each phase in each mixture. As discussed previously, however, this is not necessarily the case in soils because the chemical composition of reference clays often differs markedly from that of soil clays, particularly for smectites. In order to approximate this situation, two levels of errors were introduced into the chemical composition of the smectite standard: the oxide fractions for each element were randomly increased or decreased by 0%, 5%, and 10%. The models were run using $E_{i,smectite}$ values that contained three levels of introduced error: 0%, 5%, and 10%; the E_{ij} values for the other two phases were not modified by introduced errors.

The four methods were evaluated by comparing the known gravimetrically-determined percentages of each mineral phase in the mixtures with that predicted by each method and, in the case of Methods 3 and 4, by comparing the predicted smectite and/or illitic phase compositions with those measured by ICP-AES analyses of the reference clay standards.

RESULTS AND DISCUSSION

The elemental compositions of the <0.2 μm size fractions of the reference clays (Table 1) are consistent with their presumed mineralogy. Small amounts of K were found in both the halloysite and smectite samples, indicating the presence of small amounts of an illitic material or potassium feldspar. Minor amounts of Ti were found in all three samples. This may be structural Ti, or may result from the presence of small amounts of rutile or anatase, or possibly contamination from the sonicator tip.

Weight fraction percentages predicted by each model from the elemental compositions of the mixtures are presented in Table 2 along with standard errors (SE; Eq. 2) and average errors (AE; Eq. 3) for each method:

Table 1. Elemental compositions of the <0.2 μm fraction of the reference clays (g kg^{-1}).

Element	Halloysite	Illite	Smectite
Si	248.68	261.63	307.47
Al	242.46	141.06	125.15
Mg	0.29	15.07	17.02
Ca	1.79	7.06	24.27
Fe	2.24	48.08	30.65
Mn	0.01	0.15	0.02
Ti	0.28	2.58	0.82
Zn	0.10	0.21	0.10
K	2.57	54.30	0.22

$$SE = \left[\sum \frac{(X_m - X_p)^2}{(n - 2)}\right]^{1/2} \quad (2)$$

$$AE = \sum \frac{(X_m - X_p)}{n} \quad (3)$$

where X_m is the measured weight percentage, X_p is the predicted weight percentage, and n is the number of analyses.

All four methods accurately predicted clay phase weight percentages in the mixtures when the smectite standard had no introduced error. As errors were introduced into the smectite standard, however, the accuracy of Methods 1 and 2 decreased rapidly, indicating the need for very accurate standards, which are usually nonexistent for soil minerals. Because $E_{i,smectite}$ values are dependent variables in Methods 3 and 4, those methods should be essentially independent of the level of error introduced into the smectite composition. However, the smectite composition does provide an initial guess, or starting point, for the optimization routines used in these models, and if the starting point is sufficiently in error, the algorithms may converge on a local minimum rather than the global minimum that represents the true solution of the chemical mass balance model.

Method 3 was virtually unaffected by the choice of starting point, whereas Method 4 was affected to some degree (Table 2) due to the looser constrictions given the algorithm (no assumed illite composition). Method 4 was slightly more accurate with 5 and 10% introduced error in the smectite standard than it was with no introduced error. This is interesting considering that no smectite composition was assumed for any of the error levels. Methods 3 and 4 both accurately predicted the elemental composition of the smectitic, and the smectitic and illitic phases, respectively (Tables 3 and 4).

Mixture #5 was problematic throughout this investigation. Mixture #5 was apparently contaminated by Fe and various trace metals prior to elemental analysis (Table 5). Significantly greater error is apparent in the results for mixture #5 than for any other mixture (Tables 2 and 5). The error in mixture #5 illustrates an-

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Table 2. Clay phase quantification using four elemental mass balance models.

Mixture #	Minerals	Measured	Predicted mineralogical composition (%)											
			0% introduced error				5% introduced error				10% introduced error			
			Method #											
			1	2	3	4	1	2	3	4	1	2	3	4
1	Halloysite	50.9	50.7	50.4	50.6	51.6	50.7	50.6	50.6	50.5	50.7	50.6	50.6	50.3
	Illite	49.1	49.3	49.6	49.4	48.4	49.3	49.4	49.4	49.5	49.3	49.4	49.4	49.7
2	Halloysite	48.9	45.6	49.4	49.2	48.2	43.8	44.5	49.2	49.3	42.1	38.3	49.2	49.4
	Smectite	51.1	54.4	50.6	50.8	51.8	56.2	55.5	50.8	50.7	57.9	61.7	50.8	50.6
3	Illite	49.6	49.7	49.6	48.6	48.6	45.7	47.0	48.6	49.6	53.0	45.3	48.6	49.6
	Smectite	50.4	50.3	50.4	51.4	51.4	54.3	53.0	51.4	50.4	47.0	54.7	51.4	50.4
4	Halloysite	42.8	42.3	43.0	43.0	44.0	42.1	42.5	43.0	42.9	41.9	41.8	43.0	42.7
	Illite	51.6	52.8	51.9	51.8	51.9	52.9	51.9	51.8	53.0	52.5	52.0	51.8	53.2
	Smectite	5.6	4.9	5.1	5.3	4.1	5.0	5.7	5.3	4.1	5.6	6.2	5.3	4.1
5*	Halloysite	41.5	36.9	38.5	38.7	37.9	34.3	33.5	38.7	38.9	31.2	27.2	38.7	39.0
	Illite	4.9	14.1	11.0	9.3	8.7	18.4	10.7	9.3	8.8	19.8	11.2	9.3	8.9
	Smectite	53.6	49.0	50.5	52.0	53.5	47.3	55.8	52.0	52.3	49.0	61.6	52.0	52.1
6	Halloysite	4.5	4.7	4.4	4.6	4.5	4.4	0.0	4.5	4.6	6.5	0.0	4.5	4.6
	Illite	45.7	45.7	46.2	45.0	45.0	45.1	46.1	45.1	46.0	47.1	48.4	45.1	46.1
	Smectite	49.8	49.6	49.4	50.4	50.5	50.5	53.9	50.4	49.4	46.4	51.6	50.4	49.3
7	Halloysite	31.3	30.5	31.7	31.8	32.0	29.3	28.5	31.8	31.9	27.6	24.5	31.8	31.9
	Illite	35.6	37.1	35.5	34.7	34.6	37.3	35.5	34.7	35.4	39.2	36.0	34.7	35.5
	Smectite	33.1	32.4	32.8	33.5	33.5	33.4	35.9	33.5	32.8	33.2	39.5	33.5	32.7
8	Halloysite	50.0	50.1	50.5	50.6	50.6	49.1	48.0	50.6	50.6	47.9	44.8	50.6	50.6
	Illite	24.0	24.1	23.4	22.7	22.7	24.3	23.4	22.7	23.2	25.7	23.8	22.7	23.3
	Smectite	26.0	25.8	26.1	26.7	26.7	26.6	28.6	26.7	26.2	26.5	31.4	26.7	26.1
9	Halloysite	21.1	20.7	21.1	21.2	21.8	19.7	18.5	21.2	21.1	18.4	15.0	21.2	21.0
	Illite	51.2	51.8	51.3	50.6	50.6	52.0	51.3	50.6	51.8	50.6	51.8	50.6	51.9
	Smectite	27.7	27.5	27.6	28.1	27.6	28.3	30.2	28.1	27.1	31.1	33.1	28.1	27.1
10	Halloysite	20.6	19.5	20.2	20.3	19.9	17.4	14.9	20.3	20.5	15.0	8.3	20.3	20.5
	Illite	25.1	29.4	26.1	24.8	24.5	32.0	26.2	24.8	25.0	33.5	27.0	24.8	25.1
	Smectite	54.3	51.1	53.8	54.9	55.6	50.6	58.9	54.9	54.5	51.6	64.7	54.9	54.4
Average error with #5			1.5	0.8	0.8	0.9	2.7	2.5	0.8	0.7	3.5	4.9	0.8	0.7
Average error without #5			1.0	0.3	0.5	0.8	1.9	2.2	0.5	0.4	2.7	4.3	0.5	0.4
Standard error with #5			2.7	1.5	1.2	1.3	4.2	3.4	1.2	1.0	5.1	6.6	1.2	1.2
Standard error without #5			1.6	0.4	0.6	0.9	2.8	2.9	0.6	0.6	3.7	5.9	0.6	0.6

* See Table 5 and text for discussion of mixture #5.

other advantage of Methods 3 and 4 as these models minimize errors due to sample contamination in part because they average compositional errors over all ten mixtures at the same time. This "averaging advantage" may also mean, however, that the results for the other 9 mixtures may have increased errors because the averaged smectite composition was slightly incorrect. For mixture #5, total standard errors were 12.0, 11.5, 3.6, and 3.3% for Methods 1, 2, 3, and 4 respectively.

Table 3. Elemental composition of the smectite (g kg^{-1}) as predicted by Method 3 and the percent error for the predicted values relative to the measured elemental composition of the smectite (Table 1).

Element	Predicted value (g kg^{-1})	Absolute error (g kg^{-1})	Relative error (%)
Si	304.64	2.83	−0.92
Al	125.26	0.11	+0.09
Mg	16.73	0.29	−1.70
Ca	24.08	0.19	−0.78
Fe	33.59	2.94	+9.59
Mn	0.03	0.01	+50.00
Ti	0.98	0.16	+19.51
Zn	0.14	0.04	+40.00
K	0.27	0.05	+22.73

Methods 2, 3, and 4 require initial guesses of the relative percentage of each phase prior to computation. Initial guess errors of up to 30% (absolute) gave identical results when compared to guesses without errors for Methods 2 and 3 (data not shown), but Method 4 was more sensitive to initial guesses (Table 6). Average phase percentage estimation errors for Method 4 increased by about 8× when initial guesses were (on average) 8.8% in error, indicating that the model was finding local minima and not solving for the best fit of the model, probably due to the larger number of variables in the model. Although average errors increased by approximately 8× when more erroneous guesses

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Table 4. Elemental compositions of the smectite and illite as predicted by Method 4 and percent errors for the predicted values relative to their measured compositions (Table 1).

Element	Smectite		Illite	
	Predicted value (g kg^{-1})	Relative error (%)	Predicted value (g kg^{-1})	Relative error (%)
Si	299.56	−2.57	264.82	+1.22
Al	134.85	+7.75	130.38	−7.57
Mg	15.35	−9.99	16.58	+10.02
Ca	22.28	−8.20	7.79	+10.34
Fe	31.88	+4.01	50.67	+5.39
Mn	0.03	+50.00	0.18	+20.00
Ti	0.97	+18.29	2.98	+15.50
Zn	0.14	+40.00	0.25	+19.05
K	0.27	+22.73	58.76	+8.21

were input, relative errors were 3–4%, still quite accurate for quantification of clay mixtures.

A sensitivity value is also a required input for Methods 2, 3, and 4. Iterations were halted when the reduction in sum of the squares relative to the previous iteration was less than the sensitivity value. The effect of choice of sensitivity value was evaluated for Methods 3 and 4. For both models, increasing the sensitivity values from 0.05% to 0.075 and 0.100% had no effect on the results. Smaller sensitivity values (0.005%) increased computation times and, interestingly, increased errors in the estimated clay phase percentages. This effect was most pronounced in Method 4 (Table 7).

A major disadvantage of Methods 3 and 4 is that they cannot be used with a single sample because a large number of data points are required to provide sufficient degrees of freedom for fit of the models. If, however, one is assured that the compositions of individual clay species in different clay mixtures are identical, then one can solve several mixtures simultaneously using these methods. For example, if sufficient compositional similarity exists among clay species in samples from the same geological provenance, then Method 3 or 4 could be used with samples taken from that provenance. A more practical approach may be to produce several size fractions from a single mixed clay sample by differential centrifugation. Elemental analysis of all the subsamples will produce sufficient data points for the model, as shown by Laird *et al.* (1991a).

Table 5. Elemental analysis of mixture #5 and predicted elemental analysis calculated from standards and gravimetric fractions.

Element	Measured (g kg^{-1})	Predicted (g kg^{-1})	Error (%)
Si	247.87	255.16	+2.94
Al	151.03	154.32	+2.18
Mg	8.99	9.45	+5.17
Ca	12.95	13.42	+3.63
Fe	25.58	18.41	−28.03
Mn	0.11	0.02	−80.69
Ti	2.52	0.62	−75.45
Zn	0.13	0.09	−28.18
K	3.46	3.05	−11.85

Table 6. Effect of initial guess of smectite composition on clay phase percentages estimated by Method 4. Analyses performed without data for mixture #5.

Error in smectite std. (%)	Average error in initial guess (%)	Average error (%)
0%	2.0	0.75
	8.8	3.71
5%	2.0	0.40
	8.8	4.01
10%	2.0	0.44
	8.8	3.43

It is not surprising that Methods 3 and 4 produced accurate results at all levels of introduced error in the smectite standard because they optimize for the Si, Al, Fe, Mg, and Ca content of the smectite as dependent variables. Because Methods 1 and 2 treat these parameters as constants, they are affected much more strongly by errors in these values.

CONCLUSIONS

All four chemical mass balance models accurately predicted clay phase percentages when the composition of the reference standard matched that of the clays in the mixtures, but methods requiring reference standards (Methods 1 and 2) faltered when arbitrary errors were introduced into the composition of the reference smectite. Results for Methods 3 and 4, however, were unaffected by the introduction of errors in the smectite standard because smectite elemental concentrations are dependent variables in these models. Methods 3 and 4 accurately predicted the chemical composition of the smectite, and smectite and illite phases, respectively,

Table 7. Effect of sensitivity value on clay phase percentages predicted by Methods 3 and 4. Analyses performed without data for mixture #5.

Introduced error	Sensitivity	Average error (%)	
		Method 3	Method 4
0%	0.100	0.50	0.75
	0.075	0.50	0.75
	0.050	0.50	0.75
	0.005	0.51	0.99
5%	0.100	0.50	0.40
	0.075	0.50	0.40
	0.050	0.50	0.40
	0.005	0.51	0.68
10%	0.100	0.49	0.44
	0.075	0.49	0.44
	0.050	0.49	0.44
	0.005	0.50	0.60

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as well as the relative weight fraction of all three phases in the system. Method 4 was somewhat less accurate than Method 3, but still within acceptable limits for clay mineral quantification. The use of non-linear chemical mass balance models that can simultaneously determine the compositions of one or more mineral phases and the relative weight fractions of several phases demonstrates a new and promising approach to quantitative clay mineralogy.

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