SIMULTANEOUS MINERALOGICAL QUANTIFICATION AND CHEMICAL CHARACTERIZATION OF SOIL CLAYS

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Abstract—A new chemical mass balance technique has been developed for simultaneous mineralogical quantification and chemical characterization of soil clays. The procedure includes separation of the whole clay (<2 μm fraction) into six particle size fractions (<0.02, <0.06, <0.2, 0.02–0.06, 0.06–0.2, and 0.2–2 μm fractions), chemical analysis of the whole clay and each of the six fractions, and fitting of a non-linear chemical mass balance model to the chemical analyses. As written, the chemical mass balance model is valid only for samples containing mixtures of quartz, kaolinite, illite, and mixed-layered smectite-illite. Samples containing carbonates and free iron compounds may be analyzed using the technique if these phases are chemically removed prior to particle size fractionation. Accuracy of the new technique was tested using synthetic data and found to depend on the quality of the input data; however, clay phase quantification within three percentage points of known values was readily achieved. Precision of the technique was evaluated by independently preparing and analyzing five samples of the same soil clay. Standard deviations for clay phase percentages (w:w) in the <2 μm fraction were all less than one percent. The new technique yields accurate determinations of chemistry for the smectitic and illitic phases in mixed-layered smectite-illite, and qualitative estimates for the chemistry of 10 Å-illite. The elemental compositions of quartz and kaolinite are assumed *a priori* and treated as constants within the non-linear chemical mass balance model.

Key Words—Chemistry, Illite, Mass-balance, Protoillite, Quantify, Smectite.

INTRODUCTION

Quantitative clay mineralogy by most x-ray diffraction (XRD) techniques requires mineral standards with XRD properties similar to those of the mineral phases in unknown samples (Brindley 1980). Unfortunately, the heterogeneous nature of clays in soils and sediments inherently limits the reliability of reference clays (e.g., Wyoming bentonite, Georgia kaolinite, etc.) for use as standards in XRD analyses. The Rietveld technique does not require mineral standards, but does require that the structure factor be constant for a given reflection and that no non-Bragg diffraction effects be exhibited (Bish 1993). For most clay-size layer silicates, the structure factor is not constant and stacking disorders cause two-dimensional diffraction effects; hence applicability of the Rietveld technique for quantification of clays in soils and sediments is severely limited (Bish 1993).

The multi-component approach to quantitative clay mineralogy (Alexiades and Jackson 1966; Johnson *et al* 1985; Engler and Iyengar 1987) integrates a variety of independent measures. For example, illite is quantified based on the K_2O content of an unknown sample after accounting for K associated with feldspars and by assuming a value for the K_2O content of illite in the sample. Vermiculite is quantified by assuming that vermiculite is the only mineral phase capable of "fixing K" (Alexiades and Jackson 1965). Gibbsite and kaolinite are quantified using differential thermal analyses based on the magnitude of specific endotherms (Dixon 1966).

Modern mass balance techniques for quantitative mineralogy incorporate aspects of the multi-component approach, but they typically rely heavily on chemical mass balance. Pearson (1978) considered the range of published chemical compositions to define upper and lower limits for compositions of mineral phases in unknown samples. A graphical solution to sets of simultaneous linear equations depicted regions of self-consistent solutions, and thus defined upper and lower limits for proportions of mineral phases in unknown samples. Other researchers (Gold *et al* 1983; Hodgson and Dudeney 1984; Braun 1986; Slaughter 1989; Calvert *et al* 1989) have developed computer programs for quantitative mineralogy based on constrained chemical mass balance techniques similar to that used by Pearson (1978). Hodgson and Dudeney (1984) considered stoichiometries and water mass balance to constrain solutions to linear chemical mass balance equations. Slaughter (1989) constrained linear chemical mass balance equations using semi-quantitative XRD estimates of mineralogy, measured d-values, as well as stoichiometries and ranges in chemical compositions for mineral phases. Calvert *et al* (1989) used a non-linear mass balance model to quantify clay mineralogy; however, they relied on assumed ranges for chemical

compositions, surface areas, and cation exchange capacities of minerals to constrain the solutions.

In general, constrained mass balance techniques for quantitative clay mineralogy are reasonably accurate if all phases are identified and if the parameters used in the model fall within the assumed ranges (Calvert *et al* 1989; Gold *et al* 1983). However, if model parameters fall outside of the assumed ranges such mass balance techniques are inaccurate. Mixed-layered clays, such as smectite-illite, cause additional problems for constrained mass balance quantification techniques, because such techniques typically lump the illitic phase in the mixed-layered clay with 10 Å-illite (Calvert *et al* 1989). However, Laird *et al* (1991a) recently determined both chemical compositions and mass proportions for smectitic and illitic phases in mixed-layered smectite-illite using a non-linear chemical mass balance model. Unlike previous models, only one constraint was placed directly on the chemical compositions of the mineral phases (the smectitic phase was assumed to be K free). Rather, the model was constrained by assuming mass balance and by assuming that the chemistry of the smectitic and illitic phases was the same in each of six fine-clay particle size fractions (<0.09, <0.06, <0.045, <0.036, <0.026, <0.02 μm) separated from the same agricultural soil. Relative proportions of the smectitic and illitic phases were allowed to vary in the six size fractions. The model used by Laird *et al* (1991a) was designed for a two-phase system. Later, Kolka *et al* (1994) demonstrated that a similar non-linear chemical mass balance model could accurately determine the chemistry of two phases (smectite and illite) and mass proportions for three phases (smectite, illite, and halloysite) in 10 artificial mixtures of reference clays. The model used by Kolka *et al* (1994) was designed to test the accuracy of the non-linear chemical mass balance approach and was not intended for general use with soil or sediment samples. In this manuscript, we describe a similar non-linear chemical mass balance model that is designed for quantification of five clay mineral phases commonly found in temperate region soils. Accuracy and precision of the model are tested, and limitations on the use of the model are discussed.

MATERIALS AND METHODS

QSCM3

QSCM3 (quantitative soil clay mineralogy version 3) is a computer program for simultaneous mineral quantification and chemical characterization of soil clays.[1] At the heart of QSCM3 is a non-linear chemical mass balance model that relates chemical compositions and mass proportions for five mineral phases in soil

clay samples to measured chemical compositions of seven particle size fractions derived from each sample. Independent variables within the non-linear model are optimized relative to measured data using the Marquardt algorithm (Bevington 1969) as modified by Barak *et al* (1990).

Nomenclature

In the authors' experience, many temperate region soils contain both 10 Å-illite and mixed-layered smectite-illite. Fundamental particles of 10 Å-illite consist of multiple (>5), contiguous 2:1 phyllosilicate layers coordinated by dehydrated interlayer cations, usually K. Whereas, quasicrystals of mixed-layered smectite-illite are composed of randomly stacked elementary smectite and elementary illite particles (Nadeau *et al* 1984). Elementary illite particles differ from fundamental 10 Å-illite particles in that they consist of only two tetrahedrally charged dioctahedral 2:1 phyllosilicate layers coordinated by dehydrated interlayer K with hydrated exchangeable cations associated with charge sites on the external surfaces (Laird *et al* 1991a; Laird and Nater 1993). Elementary smectitic particles consist of fully hydrated, individual 2:1 phyllosilicate layers.

The non-linear chemical mass balance model within QSCM3 treats the "smectitic phase associated with mixed-layered smectite-illite," the "illitic phase associated with mixed-layered smectite-illite" and "10 Å-illite" as three separate phases; and within this manuscript it is necessary that these phases be distinguished, therefore hereafter they are referred to as "smectite," "protoillite," and "illite," respectively.

Synthetic data sets used for evaluation of QSCM3

Seven synthetic data sets were used to evaluate the accuracy of QSCM3. The first synthetic data set was obtained by assuming reasonable chemical compositions and weight fractions for each mineral phase and then calculating hypothetical oxide compositions for the seven particle size fractions in accordance with all of the assumptions in QSCM3 (except, K_2O for illite was assumed to be 90 g kg^{-1} while in QSCM3 K_2O for illite was set at 80 g kg^{-1}). The calculated oxide compositions were rounded to six significant figures and stored in an input data file named "Syn(0.0)." The other six synthetic data sets, "Syn(0.5)," "Syn(1.0)," "Syn(1.5)," "Syn(2.0)," "Syn(2.5)," and "Syn(5.0)" were prepared by introducing arbitrary error into the original Syn(0.0) data set at the 0.5%, 1.0%, 1.5%, 2.0%, 2.5%, and 5.0% RSD level, respectively. A cumulative normal distribution curve and a random number generator were used to generate arbitrary error terms for each oxide in units of standard deviation ($+/-$). The same arbitrary error terms were used for each of the corrupted synthetic data sets (e.g., $MgO_{Syn(2.0)} = MgO_{Syn(0.0)} + (MgO_{Syn(0.0)} \times AE_{MgO} \times 0.02)$; where AE_{MgO} is the

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Table 1a. Parameters for determining oxide weight fractions of mineral phases in the non-linear chemical mass balance model used in QSCM3.

Size fraction (μm)	Mineral phase					Fractions of size fractions in <2.0 μm sample
	Smectite	Proto-illite	Illite	Kaolinite	Quartz	
<2.0	D[1]	D	D	D	D	
<0.2	D	D	D	D	D	
<0.06	D	D	C	C	C	
<0.02	D	Y3	C	C	C	X1
0.02–0.06	D	Y4	C	C	C	X2
0.06–0.2	Y1	Y5	Y7	Y9	Y11	X3
0.2–2.0	Y2	Y6	Y8	Y10	Y12	X4

[1] X and Y indicate independent variables, D indicates dependent variables, and C indicates constants.

Table 1b. Parameters for determining the chemical composition of mineral phases in the non-linear chemical mass balance model used in QSCM3.

Oxide	Mineral phase				
	Smectite	Protoillite	Illite	Kaolinite	Quartz
SiO_2	Z1[1]	Z9	Z17	C	C
Al_2O_3	Z2	Z10	Z18	C	C
MgO	Z3	Z11	Z19	C	C
CaO	Z4	Z12	Z20	C	C
Fe_2O_3	Z5	Z13	Z21	C	C
MnO	Z6	Z14	Z22	C	C
TiO_2	Z7	Z15	Z23	C	C
ZnO	Z8	Z16	Z24	C	C
K_2O	C	D	C	C	C

[1] Z indicates independent variables, D indicates dependent variables, C indicates constants.

arbitrary error term for MgO and 0.02 sets the level of error at 2%).

Preparation and chemical analyses of soil clay samples

Five measured data sets were used to evaluate the precision of QSCM3. The measured data sets were obtained by independent preparation and chemical analyses of five portions of one soil clay sample. The soil clay (<2 μm particle size fraction) was separated by sedimentation from the Ap horizon of a Kenoma (Vertic Argiudoll) soil collected near Paola, KS. Organic matter and free iron compounds were removed from the clay fraction by treatment with H_2O_2 and dithionite-citrate-bicarbonate (DCB), respectively (Kunze and Dixon 1986). Following the DCB treatment, the clay was washed two times with 2 mol liter^{-1} NaCl, washed once with distilled water, and freeze dried. For each of the five independent sample preparations, eight samples of the freeze dried clay (6.0 g total) were transferred to 50 ml centrifuge tubes and diluted to 30 ml with distilled water. The samples were first stirred (to break up the clay pellets) and then sonicated for 30 seconds at 80 W to produce homogeneous suspensions. The samples were centrifuged using a Sorvall[2] SS-34 angle-head rotor (20 min at 1800 RPM) and decanted. The sediment was redispersed in distilled water, centrifuged, and decanted two more times. Sediment remaining after the third centrifugation was retained as the 0.2–2.0 μm fraction. A portion of the combined supernatant was saved as the <0.2 μm fraction. The remaining supernatant was fractionated (6000 rpm for 20 min) to separate the <0.06 and 0.06–0.2 μm fractions. As before, the sediment (0.06–0.2 μm fraction)

and a portion of the supernatant (<0.06 μm fraction) were saved and the remaining supernatant was fractionated (18,000 rpm for 20 min) to separate the <0.02 and 0.02–0.06 μm fractions.

All seven particle size fractions were washed four times with 0.5 mol liter^{-1} $CaCl_2$ and eight times with 95% ethanol, air dried, and crushed in an agate mortar. The samples were analyzed for nine elements by ICP-AES using suspension nebulization (Laird *et al* 1991b). Portions of each particle size fraction were oriented on glass slides by the paste method (Theissen and Harward 1962) and analyzed by x-ray powder diffraction using $CuK\alpha$ radiation and a Siemens D5000 X-ray diffractometer.

RESULTS

Data required for QSCM3 are relative oxide compositions (SiO_2, Al_2O_3, MgO, CaO, Fe_2O_3, ZnO, MnO, TiO_2, and K_2O) for each of seven particle size fractions (<2.0, <0.2, <0.06, <0.02, 0.2–2.0, 0.06–0.2, and 0.02–0.06 μm fractions) obtained by sequential fractionation of whole clay (<2.00 μm fraction) samples. Output from QSCM3 includes weight fractions for five mineral phases in each of the seven particle size fractions and chemical compositions for smectite, protoillite, and illite. Chemical compositions for two other mineral phases (kaolinite and quartz) are assumed *a priori* and treated as constants within the model.

Model description

The non-linear chemical mass balance model within QSCM3 is based on:

$$O_{ef} = \sum_{j=1}^{j=n} [O_{ej} \times W_{jf}] \qquad (1)$$

where, O_{ef} is the measured oxide composition for element e in size fraction f, O_{ej} is the oxide composition for element e in mineral j, and W_{jf} is the weight fraction of mineral j (expressed as an oxide) in size fraction f.
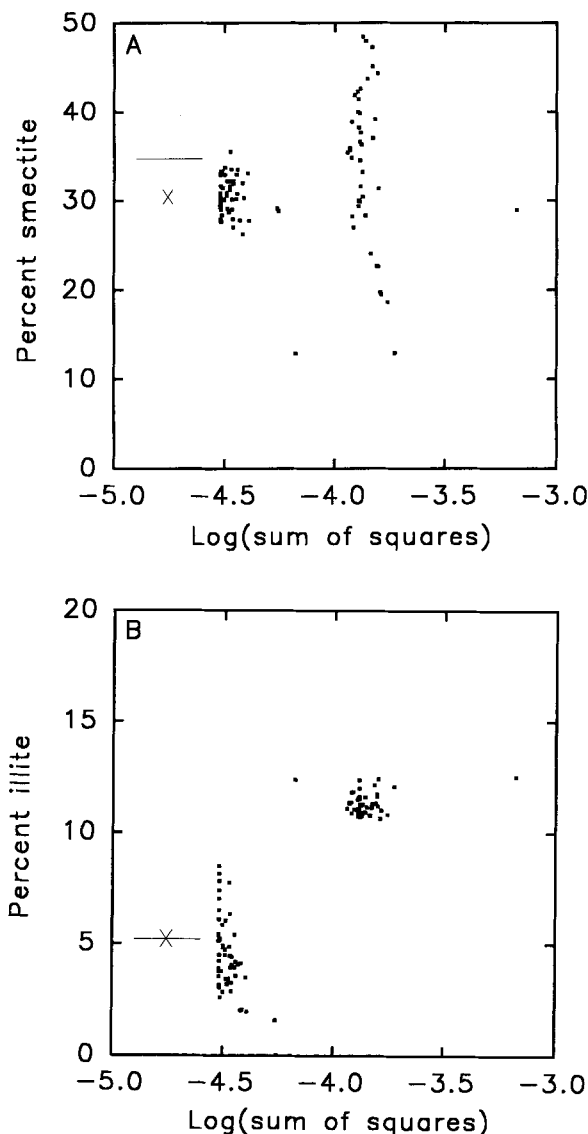
Figure 1. Relationship between the final sum of squares for fit of the non-linear chemical mass balance model to the Syn(1.0) data set and estimates of (a) percent smectite and (b) percent illite in the <2 μm fraction. The horizontal line indicates known percentages for the minerals and the "X" indicates the average of 26 accepted solutions.

The model requires a total of 80 parameters (45 O_{ej} values and 35 W_{jf} values), of which 36 are independent variables, 15 are dependent variables, and 29 are constants (Tables 1a and 1b). Four additional independent variables (oxide weight fractions for the 0.2–2.0, 0.06–0.2, 0.02–0.06 and <0.02 μm particle size fractions in the <2 μm particle size fraction) are needed for evaluation of the dependent variables.

The first step in QSCM3 is the input of assumed values for constants and measured values for the oxide compositions in each of the seven particle size frac-

tions. A random number generator is used to obtain unbiased initial guesses for all independent variables. The independent variables are then optimized using three separate submodels relative to a test statistic (chi-square) for fit of each submodel to the measured data. Following optimization, the solution set is stored in an output file along with the final sum of squares for fit of the whole model to the measured data, and then the program loops back to the random number generator. The procedure is repeated an arbitrary number of times (typically 100). Solution sets with final sum of squares substantially larger than the minimum sum of squares (typically 5%, determined by analysis of the sum of squares distribution, see Figures 1a and 1b) for all sets are rejected. Parameter means and standard deviations for the accepted solution sets are calculated. To account for structural water, the oxide weight fractions are multiplied by a ratio (formula unit weight : oxide formula weight) and normalized to make the sum equal to 1.00.

A computationally intensive Monte-Carlo approach is utilized within QSCM3 to increase accuracy of the results and to avoid bias imposed by selection of initial guesses for independent variables in the model. Figures 1a and 1b illustrate the distribution of solutions for two parameters (% smectite and % illite in the <2.00 μm particle size fraction) relative to the final sum of squares for fit of the model to the Syn(1.0) data set. Of 100 solutions, 26 have final sum of squares ranging from 3.03×10^{-5} to 3.18×10^{-5}, these 26 solutions were assumed to closely approach the global minimum, and were utilized for calculating means and standard deviations of each parameter. The other 74 solutions were assumed to represent local minima and were rejected.

Accuracy of QSCM3

Results obtained for analysis of the synthetic data sets using QSCM3 are presented in Tables 2 and 3. The predicted clay phase percentages (w:w) for the Syn(0.0) data set are within ±2 percentage points of the known values (Table 2), and the predicted chemistries of the smectite and protoillite are accurate to four significant figures (Table 3). With increasing levels of arbitrary error in the input data (results for Syn(0.5) through Syn(5.0), Table 2), the predicted amount of smectite is increasingly underestimated and the predicted amount of quartz is increasingly overestimated. Predicted amounts of protoillite, illite and kaolinite are within 3% of known values regardless of the level of arbitrary error in the input data. The systematic trends in the smectite and quartz results primarily reflect increasing levels of SiO_2 and decreasing levels of Al_2O_3 in the corrupted synthetic data for the <2 μm particle size fraction. The final sum of squares for fit of the model to the synthetic data sets increases rapidly with even a small amount of error in the input data, but levels off with greater error (Table 2). Thus, the

Table 2. Known and determined mineral phase distributions and final sum of squares for synthetic data sets with increasing levels of introduced error. Data given for the <2 μm fraction only.

| Data set | Mineral phase | | | | | Final sum of squares |
	Smectite	Protoillite	Illite	Kaolinite	Quartz	
			%			
Known	34.7	29.9	5.2	11.6	18.5	
Syn(0.0)[1]	33.0 (1.8)[2]	30.6 (3.7)	5.7 (1.4)	11.8 (2.2)	18.9 (2.1)	6.89×10^{-12}
Syn(0.5)	31.4 (2.0)	32.3 (3.1)	5.0 (1.2)	11.9 (1.7)	19.5 (1.6)	7.72×10^{-6}
Syn(1.0)	30.5 (1.9)	31.6 (4.6)	5.2 (1.7)	12.4 (1.9)	20.3 (2.4)	3.07×10^{-5}
Syn(1.5)	30.4 (3.2)	30.4 (4.7)	5.6 (1.7)	12.8 (1.7)	20.7 (2.0)	6.80×10^{-5}
Syn(2.0)	30.6 (2.7)	32.2 (5.7)	4.9 (2.2)	11.9 (2.5)	20.5 (1.9)	1.20×10^{-4}
Syn(2.5)	28.9 (2.4)	29.2 (5.5)	6.0 (2.0)	13.5 (2.4)	22.4 (2.4)	1.83×10^{-4}
Syn(5.0)	28.0 (3.1)	31.6 (5.3)	4.8 (2.0)	11.7 (2.1)	23.9 (2.2)	6.87×10^{-4}

[1] Values in parentheses indicate the level of introduced error in % RSD.

[2] Values in parentheses are standard deviations.

final sum of squares is a sensitive index of accuracy for QSCM3 results.

Precision of QSCM3

X-ray diffraction patterns for five particle size fractions separated from the Kenoma soil clay are illustrated in Figure 2, and quantitative phase analyses obtained using QSCM3 for the soil clay are presented in Table 4. True clay phase percentages for the soil clay are not known; however, relative XRD peak intensities qualitatively support the QSCM3 results. Furthermore, the final sums of squares for fit of the model to the five measured data sets ranged from 2.9×10^{-6} to 4.8×10^{-6}, indicating that the accuracy of the analysis for the soil clay samples is slightly better than that achieved with the Syn(0.5) data set (Table 2). Standard deviations for the five independent determinations of clay phase percentages in the <2.00 μm fraction are all less than one percentage point (Table 4), indicating that results obtained using QSCM3 are highly reproducible.

Results for the chemistry of smectite, protoillite, and illite in the soil clay are presented in Table 5. Again, true values for the chemistry of these minerals are not known, however the standard deviations indicate that the smectite and protoillite results are highly reproducible. Standard deviations for the chemistry of the illite indicate considerably more variability in the results.

DISCUSSION

The illite chemistry determinations for the synthetic data sets were both less accurate and less precise than the chemistry determinations for smectite and protoillite. Within QSCM3, the chemistry of illite is constrained only by restricting illite to particle size fractions greater than 0.06 μm and by assuming a value for the K_2O content of illite. In an attempt to offer a fair test of QSCM3, the K_2O content of illite was assumed to be 90 g kg^{-1} in the synthetic data sets, while

within QSCM3 illite was assigned 80 g kg^{-1} K_2O. This discrepancy accounts for some of the inaccuracy in determinations of the illite chemistry for the synthetic data sets (Table 3). Further problems are caused by the similarity in the chemistry of illite, protoillite, and smectite. Because of this similarity, small changes in estimated proportions for smectite and protoillite in size fractions larger than 0.06 μm are balanced by large changes in the estimated chemistry for illite.

The assumption that chemical composition is independent of particle size is reasonable for quartz, kaolinite, and smectite, however, this assumption is not valid for the illitic materials in soils. In effect, QSCM3 quantifies endmembers of an illite continuum (e.g., illite and protoillite). The approach ought to be more accurate than lumping all illitic materials together as is commonly done in other chemical mass balance models. Arbitrary division of the illite continuum undoubtedly causes some error in the illite chemistry determinations for the Kenoma soil clay. Furthermore, the coarse clay fraction (0.2–2.0 μm) of the Kenoma soil contains trace amounts of feldspar (small XRD peaks between 27 and 28 °2Θ, Figure 2) and may well contain rutile or anatase (note high TiO_2 values for illite in Table 5). Such phases are not considered within QSCM3, but any chemical contribution of these phases is lumped with the reported chemistry of illite. Thus, the reported chemistry for illite in the soil clay (Table 5) should be regarded as qualitative.

Three assumptions within QSCM3 tightly constrain possible solutions for the chemistry of smectite and protoillite: (1) the three finest particle size fractions (0.02–0.06, <0.06, and <0.02 μm) are assumed to contain only smectite and protoillite; (2) smectite is assumed to contain no K; and (3) Ca and K equivalents in protoillite are assumed to be equal (actually the Ca:K equivalent ratio = 1.0267, which allows for a small contribution of edge charge). The first assumption is supported by XRD analyses of the Kenoma soil clay (Figure 2). The second and third assumptions are in-

Table 3. Chemical composition of mineral phases in synthetic data sets, with introduced error at the 0% [Syn(0.0)], 0.5% [Syn(0.5)], and 5.0% [Syn(5.0)] RSD level.

Oxide	Known	Synethtic data sets		
		Syn(0.0)	Syn(0.5)	Syn(5.0)
		mg kg^{-1}		
Smectite				
SiO_2	616.047	616.045 (1.1×10^{-16})[1]	616.091 (5.8×10^{-4})	617.092 (0.030)
Al_2O_3	191.714	191.717 (0.0)	192.591 (0.0017)	199.962 (0.038)
MgO	23.482	23.481 (1.7×10^{-18})	23.734 (3.0×10^{-4})	26.216 (0.014)
CaO	36.673	36.673 (1.0×10^{-17})	36.418 (7.6×10^{-4})	34.376 (0.020)
Fe_2O_3	130.177	130.175 (2.7×10^{-17})	129.242 (0.0018)	120.244 (0.037)
MnO	0.251	0.25 (2.7×10^{-20})	0.246 (5.3×10^{-20})	0.209 (2.2×10^{-4})
TiO_2	1.200	1.200 (0.0)	1.221 (1.1×10^{-19})	1.425 (0.0027)
ZnO	0.456	0.456 (5.3×10^{-20})	0.459 (5.3×10^{-20})	0.476 (1.6×10^{-4})
K_2O	—[2]	—	—	—
Protoillite				
SiO_2	591.177	591.180 (2.0×10^{-4})	592.884 (6.1×10^{-4})	607.254 (0.062)
Al_2O_3	269.090	269.088 (2.7×10^{-17})	268.653 (0.0012)	264.507 (0.021)
MgO	25.499	25.501 (6.8×10^{-18})	25.037 (3.1×10^{-4})	20.168 (0.027)
CaO	18.399	18.400 (5.1×10^{-18})	18.389 (8.2×10^{-4})	18.038 (0.025)
Fe_2O_3	56.584	56.584 (3.4×10^{-18})	55.834 (0.0017)	51.879 (0.16)
MnO	0.279	0.280 (0.0)	0.287 (5.3×10^{-20})	0.356 (0.0)
TiO_2	8.600	8.600 (2.5×10^{-18})	8.562 (3.0×10^{-4})	8.067 (0.012)
ZnO	0.271	0.272 (0.0)	0.265 (5.3×10^{-20})	0.220 (6.3×10^{-4})
K_2O	30.101	30.102 (8.5×10^{-18})	30.084 (0.0013)	29.510 (0.041)
Illite				
SiO_2	567.500	559.225 (120)	543.121 (130)	442.070 (150)
Al_2O_3	258.263	245.877 (110)	230.114 (110)	255.443 (120)
MgO	24.396	24.533 (9.8)	25.659 (9.6)	41.811 (17)
CaO	1.545	8.575 (11)	12.554 (12)	16.083 (19)
Fe_2O_3	49.090	75.268 (37)	103.511 (46)	153.409 (88)
MnO	0.187	0.189 (0.12)	0.155 (0.12)	0.428 (0.46)
TiO_2	8.200	6.035 (3.6)	4.552 (3.4)	10.294 (4.3)
ZnO	0.214	0.282 (0.14)	0.320 (0.17)	0.447 (0.34)
K_2O	90.605	80.016[3] —	80.016 —	80.016 —

[1] Values in parentheses are standard deviations.
[2] Assumed to be zero.
[3] Assumed to be 80.016 mg kg^{-1}.

herent to the definitions of smectite and protoillite as used in this manuscript (see Materials and Methods—Nomenclature). The validity of these assumptions is further supported by previous work with the Webster soil (Laird *et al* 1991a; Laird and Nater 1993), and by the fact that the sum of squares for fit of the model to the Kenoma data was reduced by nearly six orders of magnitude during optimization (average sums of squares before and after optimization were 1.59 and 3.69 $\times$ 10^{-6}, respectively).

Table 4. Averages for five independent determinations for clay mineral distribution in particle size fractions of the Kenoma soil clay.

Size fraction	Mineral phase				
	Smectite	Protoillite	Illite	Kaolinite	Quartz
μm	%				
<2.0	33 (0.9)[1]	41 (0.6)	11 (0.3)	4 (0.4)	12 (0.3)
<0.2	42 (0.9)	53 (1.0)	4 (0.3)	0 (0.2)	1 (0.1)
<0.06	54 (1.2)	46 (1.2)	—[2]	—	—
<0.02	72 (2.0)	28 (2.0)	—	—	—
0.02–0.06	32 (1.0)	68 (1.0)	—	—	—
0.06–0.2	1 (1.3)	78 (3.8)	17 (1.5)	2 (1.0)	2 (0.5)
0.2–2.0	6 (1.9)	8 (2.5)	30 (0.8)	13 (1.7)	43 (1.4)

[1] Values in parentheses are standard deviations.
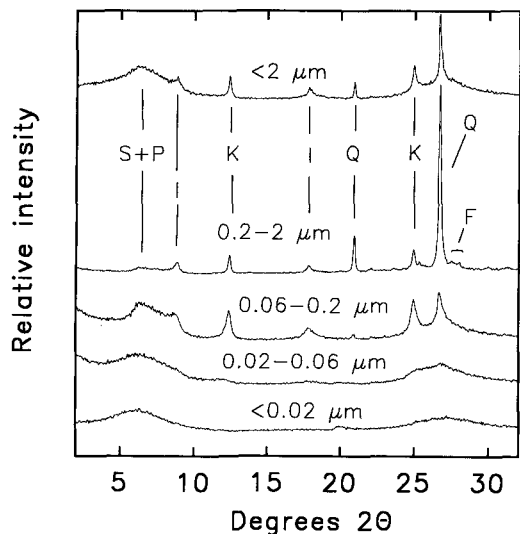[2] Assumed to be zero.

Figure 2. X-ray diffraction patterns for Ca-saturated samples of the <2, 0.2–2, 0.06–0.2, 0.02–0.06, and <0.02 μm particle size fractions separated from the Kenoma soil. Peaks associated with smectite (S), protoillite (P), illite (I), kaolinite (K), quartz (Q), and feldspars (F) are indicated.

Table 5. Average of five independent determinations of the chemical composition for mineral phases in the Kenoma soil clay.

Oxide	Mineral phase		
	Smectite	Protoillite	Illite
	mg kg^{-1}		
SiO$_2$	603.4 (1.6)[1]	571.8 (1.2)	618.7 (15.4)
Al$_2$O$_3$	241.0 (2.1)	303.2 (1.3)	166.7 (11.9)
MgO	15.6 (0.1)	18.1 (0.1)	21.9 (0.7)
CaO	32.3 (1.2)	15.3 (0.4)	7.1 (1.5)
Fe$_2$O$_3$	106.1 (1.5)	60.6 (0.5)	35.2 (4.8)
MnO	0.3 (0.003)	0.2 (0.004)	0.5 (0.01)
TiO$_2$	1.0 (0.3)	5.7 (0.5)	69.7 (2.3)
ZnO	0.4 (0.01)	0.2 (0.01)	0.2 (0.04)
K$_2$O	0.0[2] —	25.0 (0.7)	80.0[3] —

[1] Values in parentheses are standard deviations.
[2] Assumed to be zero.
[3] Assumed to be 80.016 mg kg^{-1}.

In addition to smectite, protoillite, illite, kaolinite, and quartz, temperate region soils commonly contain carbonates, metal oxyhydroxides, feldspars, and various accessory minerals in the clay fraction. Many of these samples can be analyzed with QSCM3 if carbonates and metal oxyhydroxides are chemically removed and independently quantified prior to particle size fractionation, and if the feldspars and accessory minerals represent only a small proportion (<1%) of the sample mass. Soil clay samples containing significant amounts of accessory minerals or well developed hydroxy interlayer materials not removed during DCB treatments, should not be analyzed using QSCM3.

The QSCM3 technique has three advantages over other techniques for quantification of soil clays; (i) no reference standards are required, (ii) the chemistry of smectite and protoillite are simultaneously determined, and (iii) protoillite and illite are independently quantified rather than lumped as a single phase. A major disadvantage of the QSCM3 technique is the large amount of labor required for sample preparation, hence use of QSCM3 for analyses of large numbers of samples is not anticipated. In studies involving large numbers of samples the QSCM3 technique can be used to calibrate XRD or spectroscopic quantification techniques.

Interpretation of results obtained using QSCM3 must be tempered with qualitative (e.g., XRD) analyses of the mineral phases present in a sample and with a thorough understanding of the assumptions inherent to the non-linear chemical mass balance model within QSCM3. However, with caution QSCM3 can be used

to accurately quantify proportions of clay mineral phases in many temperate region soils and simultaneously determine the chemical composition of the smectitic and illitic phases in mixed-layered smectite-illite in those soils.

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