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QUANTITATIVE ANALYSIS OF MINERAL MIXTURES USING LINEAR PROGRAMMING

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Abstract—The approximate maximum and minimum amounts of any phase in a complex mineral mixture can be determined by solving a linear programming problem involving chemical mass balance and X-ray powder diffraction (XRD) data. The chemical information necessary is the bulk composition of the mixture and an estimation of the compositional range of each of the minerals in the mixture. Stoichiometric constraints for the minerals may be used to reduce their compositional variation. If only a partial chemical analysis for the mixture is available, the maximum amounts of the phases may still be estimated; however, some or all of the stoichiometric constraints may not apply. XRD measurements (scaled using an internal standard) may be incorporated into the linear programming problem using concentration-intensity relations between pairs of minerals. Each XRD constraint added to the linear programming problem, in general, reduces the difference between the calculated maximum and minimum amounts of each phase. Because it is necessary to define weights in the objective function of the linear programming problem, the proposed method must be considered a model. For many mixtures, however, the solution is relatively insensitive to the objective function weights.

An example consisting of a mixture of montmorillonite, plagioclase feldspar, quartz, and opal-cristobalite illustrates the linear programming approach. Chemical information alone was used to estimate the mineral abundances. Because quartz and opal-cristobalite are not chemically distinct, it was only possible to determine the sum, quartz + opal-cristobalite, present in the mixture.

Key Words—Chemical analyses, Linear programming, Mineral analyses, Montmorillonite, Opal C-T, X-ray powder diffraction.

INTRODUCTION

A problem of fundamental importance in earth science is the determination of the mineral composition of a multiphase system. X-ray powder diffraction (XRD) and optical point-counting methods are the principal means of obtaining quantitative information on the phase composition of a mixture. Both of these methods have drawbacks. Mineral analysis based on XRD measurements is sensitive to preferred orientation, crystallite size, crystallinity, and chemical composition of the various phases present in the mixture. Optical point-counting methods are tedious, subject to sampling errors, and difficult to apply to fine-grained mixtures.

Several approaches to the analysis of complex mineral mixtures are available. These include the set of procedures integrating chemical and thermal techniques for the analysis of clay-rich materials outlined by Alexiades and Jackson (1966). The use of multicomponent chemical mass balance was discussed by Wright and Doherty (1970), Reid *et al.* (1973), Albarede and Provost (1977), Pearson (1978), and LeMaitre (1981). Methods which incorporate both chemical mass balance and XRD information have also been presented (Hodgson and Dudney, 1984).

A general linear programming method is herein presented that integrates chemical and XRD data, the emphasis being on the use of chemical information. The method utilizes the bulk chemical composition of the mixture in conjunction with estimates of the compositional variation of each mineral and XRD measurements to determine the approximate maximum and minimum amounts of any mineral in the mixture. If mineral polymorphs are present in the mixture, chemical information must be supplemented by XRD measurements inasmuch as polymorphs are not chemically distinct.

The proposed method is a general one and takes into account compositional variations of the minerals, uncertainties in the XRD data, and information related to the stoichiometry of the minerals.

DEFINITIONS

The abbreviations used in this report are defined below:

- $\vec{b}$ = generalized bulk composition vector of a mixture.
- m = number of phases in mixture.
- n = number of components necessary to describe sufficiently all the phases.
- $\vec{q}_j$ = general phase composition vector with n components; components are weight percentages.
- $(q_i)_j$ = i^{th} component of composition vector $\vec{q}_j$.
- $\vec{q}'_j = \vec{q}_j - [\Delta q]_j \vec{V}_j$.
- $\vec{V}_j$ = a vector of n or fewer elements, all of which

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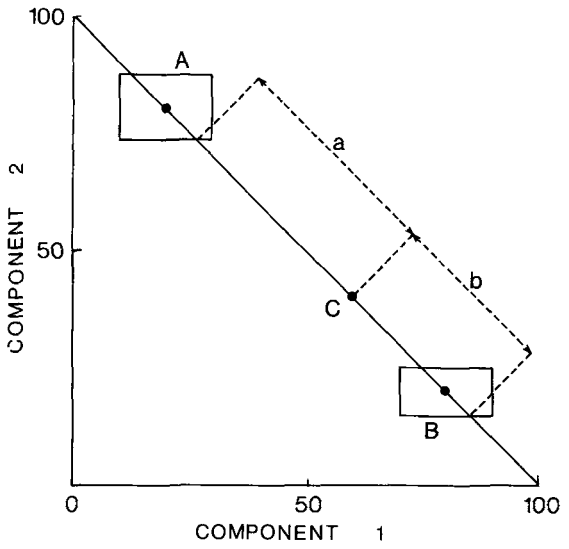


Figure 1. Illustration of chemical mass balance for a two-component system. The maximum amount of phase A in the mixture A + B with bulk composition C is b/(a + b). The total compositional variation of each phase is represented by a rectangle, and the actual composition of each phase is confined to the diagonal line which corresponds to a component sum of 100.

are equal to unity; the number of elements in $\vec{V}_j$ equals that in $\vec{q}_j$.

$\vec{X}$ = vector whose elements are the fractional amounts of the various phases in a mixture; the number of nonzero elements will be less than or equal to m.

$[\Delta q]_j$ = diagonal increment matrix associated with a composition vector $\vec{q}_j$. The iith element of $[\Delta q]_j$ is $(\Delta q_{ii})_j$.

$\Delta\vec{X}_j$ = vector of coefficients which, along with $[\Delta q]_j$, describes the compositional variation of the jth phase; the compositional range of phase j is given by

$$\vec{q}_j \pm [\Delta q]_j\Delta\vec{X}_j, \text{ or } \vec{q}'_j + 2[\Delta q]_j\Delta\vec{X}_j,$$

where $(\Delta X_i)_j$ is an element of $\Delta\vec{X}_j$ and $0 \leqq (\Delta X_i)_j \leqq 1$.

MASS BALANCE CONTRIBUTIONS TO THE LINEAR PROGRAMMING PROBLEM

If the jth phase of a system of m phases is allowed to vary within the following compositional limits:

$$\begin{aligned}(q_1)_j &\pm (\Delta q_1)_j\\ (q_2)_j &\pm (\Delta q_2)_j\\ &\vdots \quad\quad \vdots\\ (q_n)_j &\pm (\Delta q_n)_j,\end{aligned}$$

a specific composition of that phase can be described by

$$\vec{q}_j \pm [\Delta q]_j\Delta\vec{X}_j \quad \text{or} \quad \vec{q}'_j + 2[\Delta q]_j\Delta\vec{X}_j,$$

where $0 \leqq (\Delta X_i)_j \leqq 1$, $1 \leqq i \leqq n$, and $[\Delta q]_j$ is a diagonal matrix whose elements $(\Delta q_{11})_j \ldots (\Delta q_{nn})_j$ are respectively $(\Delta q_1)_j \ldots (\Delta q_n)_j$.

If the measured bulk composition of the system of phases is given by the vector $\vec{b}$, and the jth phase is permitted to have any composition described by $\vec{q}'_j + 2[\Delta q]_j\Delta\vec{X}_j$, the maximum amount of the tth phase can be found by solving the following programming problem:

$$\text{Maximize } X_t \qquad \text{(objective function)}$$

subject to

$$\begin{aligned}&X_1(\vec{q}'_1 + 2[\Delta q]_1\Delta\vec{X}_1) \ldots\\ &+ X_t(\vec{q}'_t + 2[\Delta q]_t\Delta\vec{X}_t) + \ldots = \vec{b}\end{aligned} \qquad (1)$$

with

$$X_j \geqq 0, \quad \sum_{j=1}^{m} X_j = 1, \quad 0 \leqq (\Delta X_i)_j \leqq 1,$$

$$1 \leqq j \leqq m, \quad \text{and} \quad 1 \leqq i \leqq n.$$

Inasmuch as no phase can have a negative composition, the appropriate elements of $[\Delta q]_j$ must be adjusted so that the composition spans the desired range and the components of $\vec{q}'_j$ are positive. A solution to Eq. (1) will exist provided that the point in n component space associated with $\vec{b}$ lies "inside or on" any hypervolume formed by connecting the extremities of the hyperparallelepipeds

$$\begin{aligned}&\vec{q}'j + 2[\Delta q]_j\Delta\vec{X}_j, \qquad 0 \leqq (\Delta X_i)_j \leqq 1,\\ &1 \leqq j \leqq m, \qquad 1 \leqq i \leqq n.\end{aligned}$$

Because all minerals have some type of compositional constraint(s), the very general optimization problem given by Eq. (1) must be modified. An obvious set of constraints that can be added to Eq. (1) results from the fact that the component weight percentages of a phase must sum to 100 (in the ideal case). To account for this dependency between the components of the jth phase, the following constraint must be added to Eq. (1):

$$\vec{V}^T\vec{q}'_j + 2\vec{V}^T[\Delta q]_j\Delta\vec{X}_j = 100, \qquad (2)$$

where $\vec{V}^T$ is the transpose of $\vec{V}$. Constraint (2) is not necessary for phases of fixed composition (e.g., quartz). The application of Eqs. (1) and (2) may be illustrated graphically for a simple two-component system. Figure 1 shows two phases (A and B) and a bulk composition (C) described by two components.

In some cases, it may be desirable to relax the set of constraints (2) and substitute the following:

$$\vec{V}^T\vec{q}'_j + 2\vec{V}^T[\Delta q]_j\Delta\vec{X}_j \leqq 100 + \epsilon_1$$

and (2′)

$$\vec{V}^T\vec{q}'_j + 2\vec{V}^T[\Delta q]_j\Delta\vec{X}_j \geqq 100 - \epsilon_1,$$

where ϵ_1 and ϵ_2 are small numbers.

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The optimization problem consisting of Eqs. (1) and (2) or the inequalities (2′) is nonlinear, but may be converted to a linear programming problem by rewriting Eq. (1) as

$$\text{Maximize } (X_t)$$

subject to

$$\begin{aligned} X_1\vec{q}'_1 + 2[\Delta q]_1\Delta\vec{X}_1 + \ldots X_t\vec{q}'_t \\ + 2[\Delta q]_t\Delta\vec{X}_t \ldots = \vec{b} \end{aligned} \qquad (3)$$

$$X_j \geqq 0, \quad \sum X_j = 1, \quad X_j \geqq (\Delta X_i)_j,$$
$$1 \leq i \leq n, \quad 1 \leq j \leq m,$$

where $(\Delta X_i)_j$ is an element of $\Delta\vec{X}_j$. To incorporate Eq. (2) into the linear programming problem, the following relations for each phase of variable composition must be written:

$$X_j(\vec{V}^T\vec{q}'_j) + 2\vec{V}^T[\Delta q]_j\Delta\vec{X}_j - 100A_j = 0, \qquad (2'')$$

where

$$X_j = A_j.$$

If a partial analysis is used for the j^{th} phase, and it is known that the components will not sum to 100, a value less than 100 can be used in Eq. (2″). If one or more phases has been omitted from the problem, the relation

$$\sum_{j=1}^{m} X_j \leqq 1$$

should be substituted for

$$\sum_{j=1}^{m} X_j = 1.$$

If a solution to Eq. (3) does not exist, "free variables" may be incorporated into the linear programming problem. A free variable's presence in the mass balance equations guarantees that a solution exists. Nonzero free variables indicate equality and/or inequality relations that are not exactly satisfied. The free variables are introduced into both the objective function and the mass balance equations. For example, if the maximum amount of phase t present in the mixture is required, the objective function has the form

$$\text{Maximize } X_t + \sum_{e=1}^{n}(-100D_e) + \sum_{e=1}^{n}(-100D'_e),$$

and the mass balance relations have the form

$$\begin{aligned} X_1\vec{q}'_1 + 2[\Delta q]_1\Delta\vec{X}_1 + \ldots \\ X_t\vec{q}'_t + 2[\Delta q]_t\Delta\vec{X}_t + \ldots \end{aligned}$$

$$+ D_1\begin{bmatrix}100\\0\\\cdot\\\cdot\\0\end{bmatrix} - D'_1\begin{bmatrix}100\\0\\\cdot\\\cdot\\0\end{bmatrix} + D_2\begin{bmatrix}0\\100\\\cdot\\\cdot\\0\end{bmatrix}$$

$$- D'_2\begin{bmatrix}0\\100\\\cdot\\\cdot\\0\end{bmatrix} + \ldots = \vec{b}, \qquad (3')$$

where D_e and D'_e are free variables for the mass balance equations. The negative weights for D_e and D'_e in the objective function are to prevent the free variables from being used except if a mass balance cannot be effected by the minerals known to be present. If a phase is also a component (e.g., quartz and SiO_2), it is not necessary to include a free variable with a positive coefficient, D_e, for that particular component.

STOICHIOMETRIC CONSTRAINTS

If a particular mineral is variable in composition, its compositional variation can commonly be approximated by a small number of components. For example, it is only necessary to specify the weight percent SiO_2 in a particular member of the plagioclase series to approximate the weight percentages of Al_2O_3, CaO, and Na_2O. This approximation is simply a reflection of the plagioclase stoichiometry:

$$Na_VCa_{1-V}Al_{2-V}Si_{2+V}O_8 \quad (0 \leqq V \leqq 1).$$

Substitutional information can be incorporated directly into Eq. (3). Using the plagioclase series as an example, the following equations may be written which relate the oxide components:

$$\begin{aligned} \Delta Al_2O_3 &= -0.67\ \Delta SiO_2 \\ \Delta CaO &= -0.80\ \Delta SiO_2 \\ \Delta Na_2O &= 0.46\ \Delta SiO_2, \end{aligned}$$

where ΔAl_2O_3, ΔCaO, ΔNa_2O, and ΔSiO_2 represent changes in the oxide weight percentages. If $\vec{q}'_{pl}$ is the composition of a specific plagioclase, the plagioclase contribution to the mass balance in Eq. (3) will be

$$X_{pl}\vec{q}'_{pl} + \begin{bmatrix}1.00\ \Delta SiO_2\\-0.67\ \Delta SiO_2\\-0.80\ \Delta SiO_2\\0.46\ \Delta SiO_2\end{bmatrix}\Delta\vec{X}_{pl}$$

subject to

$$X_{pl} \geqq \Delta X_{pl},$$

where the array in brackets represents the matrix $[\Delta q]_{pl}$. In this example, where stoichiometry is incorporated directly into the mass balance relations, the matrix $[\Delta q]_{pl}$ is not diagonal. The composition vector $\vec{q}'_{pl}$ is some extreme point (minimum SiO_2) of the compo-

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sitional region (here, a line), and ΔSiO_2 is the maximum increment to be considered. For this simplified compositional region, the vector $\Delta\vec{X}_{pl}$ has only a single element. A more complicated example of the use of stoichiometry is presented below.

It is not necessary to use stoichiometric rules in the manner outlined above. A series of composition vectors may be used to describe the compositional variation of a mineral. For example, if the p compositions $(\vec{q}_j)_1$, $(\vec{q}_j)_2 \ldots (\vec{q}_j)_p$, approximately span the compositional range of the j^{th} mineral, the contribution of the j^{th} mineral to the mass balance equations is

$$(X_j)_1(\vec{q}_j)_1 + (X_j)_2(\vec{q}_j)_2 + \ldots (X_j)_p(\vec{q}_j)_p \qquad (4)$$

and the amount of the j^{th} mineral in the mixture is

$$\sum_{i=1}^{p} (X_j)_i.$$

It is usually simpler to use an approach based on stoichiometric rules, except where the compositional variation of a mineral is very restricted (e.g., a mineral described by two components). Where only a partial bulk chemical analysis ($\vec{b}$) is available, the complete set of stoichiometric rules may not apply.

INCLUSION OF X-RAY POWDER DIFFRACTION INFORMATION

Except for certain restricted situations (e.g., Zevin, 1977), standards are necessary to utilize XRD for quantitative mineral analysis. The standards should be the same compositionally and structurally as the minerals in the unknown mixture. Preferred orientation and crystallite size differences between standards and unknowns also complicate the analysis. For complex minerals, the XRD method is difficult to apply on a routine basis; however, XRD data can be used to add constraints to the linear programming problem for determining the maximum and minimum amounts of the phases in a mixture.

The weight fraction of the j^{th} phase in a mixture can be related to the weight fraction of the r^{th} phase by the equation

$$X_j = X_r \frac{K_r I_j}{K_j I_r}, \qquad (5)$$

where I_j and I_r are the intensities diffracted from selected (*hlk*) planes of phase j and phase r, respectively, and

$$\frac{K_j}{K_r} = \left[\frac{I_j}{I_r}\right]_{50/50}$$

(Chung, 1974a and 1974b). $(I_j/I_r)_{50/50}$ represents the intensity ratio from a 50/50 mixture of phases j and r. The parameter K can be measured or, in some cases, approximated using the list given by McClune (1981). Eq. (5) is linear in X_j and X_r and can be incorporated directly into the optimization problem. Each Eq. (5) that is added is independent of the mass balance equations of Eq. (3). Because of problems discussed above, K for a specific phase will generally not be known exactly, but usually an upper and lower bound can be given. Thus, for some mixtures, it may be better to use two inequalities to relate the j^{th} and r^{th} phases which are of the form

$$X_j - \frac{(K_r - \Delta_r)I_j}{(K_j + \Delta_j)I_r} X_r \geqq 0, \qquad (6)$$

and

$$X_j - \frac{(K_r + \Delta_r)I_j}{(K_j - \Delta_j)I_r} X_r \leqq 0,$$

where Δ_j and Δ_r are positive numbers. If the inequalities (6) are such that a solution to the entire set of linear constraints [Eqs. (3′) and (2″) and inequalities (6)] is not possible, "free variables" may be added to inequalities (6). These free variables have a heavy negative weight in the objective function to prevent them from being used except when the constraints of inequalities (6) prevent a feasible solution from existing. Free variables are incorporated into inequalities (6) in the following way:

$$X_j - \frac{(K_r - \Delta_r)I_j}{(K_j + \Delta_j)I_r} X_r + F_{rj} \geqq 0 \qquad (6')$$

$$X_j - \frac{(K_r + \Delta_r)I_j}{(K_j - \Delta_j)I_r} X_r - F'_{rj} \leqq 0.$$

The set of constraints of inequalities (6) or (6′) will be necessary for each XRD relationship between two phases.

If the XRD constraint applies to a phase whose stoichiometry is being described by a set of fixed compositions, the constraints of inequalities (6′) must be modified. For example, if phase j is being described by p discrete compositions [as in Eq. (4)], the inequality relations of inequalities (6′) have the forms:

$$\sum_{i=1}^{p} (X_j)_i - \frac{(K_r - \Delta_r)I_j}{(K_j + \Delta_j)I_r} X_r + F_{rj} \geqq 0$$

$$\sum_{i=1}^{p} (X_j)_i - \frac{(K_r + \Delta_r)I_j}{(K_j - \Delta_j)I_r} X_r - F'_{rj} \leqq 0.$$

COMPUTATIONAL METHOD

The equalities and inequalities given by Eqs. (3′) and (2″) and inequalities (6) or (6′) are linear and may be solved using the methods of linear programming. A linear programming problem is one in which a function (the objective function) is either maximized or minimized. In the objective function each variable has a constant weight (either positive or negative). The variables, X_j ($1 \leqq j \leqq m$), are constrained by linear equality

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and/or inequality relations. The constraint, $X_j \geqq 0$, is implicit in linear programming. Any linear programming problem (at least in theory) can be solved using the simplex method or one of its variants. If a solution to a specific linear programming problem does not exist or the solution is unbounded, the simplex computational procedure is still applicable and indicates which of the above conditions is present. For details of linear programming, readers are referred to Gass (1975) or Spivey and Thrall (1970). One need not necessarily be thoroughly familiar with the methods used to solve the programming problem, because any large computing facility will have some linear programming routines available. For a system consisting of 5 or 6 phases, the total number of unknowns can easily reach 40 or 50. This, however, is not an unreasonable number of unknowns, because the solution would require only a few seconds of computer time.

For each system of m phases, the optimization must be carried out m times; that is, the same linear constraints apply, but the objective function (maximize X_t) changes m times. As the amount of each phase is maximized, the X values for the other m − 1 phases should be recorded. The minimum amount of a particular phase determined during any of the m maximization steps can serve as an approximation to the minimum amount of that phase possible in the mixture.

To be certain that a feasible solution to the linear programming problem exists, it is best, as mentioned above, to add free variables to the objective function and mass balance relations. The final form of the linear programming problem to maximize the amount of phases t is

$$\text{Max } X_t + \sum_{i=1}^{n} (-100D_i) + \sum_{i=1}^{n} (-100D'_i) + \sum (-100F_{rj}) + \sum (-100F'_{rj}),$$

subject to

$$\text{mass balance } X_1\vec{q}'_1 + 2[\Delta q]_1\Delta\vec{X}_1 + \ldots + X_t\vec{q}'_t + 2[\Delta q]_t\Delta\vec{X}_t + \ldots + D_1\begin{bmatrix}100\\0\\\cdot\\\cdot\\0\end{bmatrix} - D'_1\begin{bmatrix}100\\0\\\cdot\\\cdot\\0\end{bmatrix} + D_2\begin{bmatrix}0\\100\\\cdot\\\cdot\\0\end{bmatrix} - D'_2\begin{bmatrix}0\\100\\\cdot\\\cdot\\0\end{bmatrix} + \ldots = \vec{b},$$

XRD constraints

$$X_j - \frac{(K_r - \Delta_r)I_j}{(K_r + \Delta_j)I_r}X_r + F_{rj} \geqq 0$$

$$X_j - \frac{(K_r + \Delta_r)I_j}{(K_r - \Delta_j)I_r}X_r - F'_{rj} \leqq 0,$$

with

$$\sum X_j = 1, \quad X_j \geqq 0, \quad X_j \geqq (\Delta X_i)_j, \quad 1 \leqq i \leqq n, \quad 1 \leqq j \leqq m.$$

The limits have purposely been left off the summations in the objective function for the XRD free variables. The sums are to be taken over all XRD constraints. In general, the sum $\sum X_j$ is taken over more than m values if stoichiometric constraints for any phase are to be represented by several fixed compositions. The constraints necessary to incorporate stoichiometric rules in the general case have been omitted from the above relations.

EXAMPLE

To illustrate the method presented above, a relatively simple example involving a Wyoming bentonite will be described. The bentonite consists of dioctahedral montmorillonite, opal-cristobalite (opal-CT), plagioclase, and quartz. Chemical information alone will be used to determine the amounts of the phases in the mixture. The bulk composition of the mixture (weight percentages) is as follows: $SiO_2 = 67.8$, $Al_2O_3 = 17.8$, $Fe_2O_3 = 2.5$, $CaO = 2.2$, $Na_2O = 1.7$, $MgO = 1.5$, and $H_2O = 5.4$. Quartz and opal-CT are assumed to consist entirely of SiO_2. This latter assumption is valid for quartz, but not necessarily for opal-CT (primarily because of the presence of H_2O). Because the two silica materials are assumed to have the same composition, it will only be possible to compute the sum, opal-CT + quartz, present in the mixture.

The following stoichiometric rules may be used to restrict the montmorillonite composition (Ross and Hendricks, 1945):

(1) Charge balance requirements are given by

$$k(Si\cdot 4 + Fe\cdot 3 + Al\cdot 3 + Mg\cdot 2 + X) = 22,$$

where k is a scaling constant, and the element symbols refer to atomic proportions. The number 22 is the total charge due to the anions $O_{10}(OH)_2$. The symbol X refers to the total number of equivalents of exchangeable cations (Ca^{2+} and Na^+ in this example).

(2) The tetrahedral occupancy constraint is given by

$$k(Si + Y) = 4.$$

(3) The constraint for octahedral occupancy can be written

$$k(Al - Y + Fe + Mg) = 2,$$

where Y represents the amount of Fe + Al occupying a tetrahedral site. In the strictest sense, a

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constraint should be used which prevents Mg^{2+} from occupying a tetrahedral site. Because in this example there will always be sufficient octahedral (Al + Fe) such that

$$Al + Fe \geqq Y,$$

this added restriction is not necessary.

(4) Two constraints to require the number of equivalents of exchangeable cations per 100 g to be between 0.08 and 0.15 are also included.

$$Na + 2\,Ca \geqq 0.08 \qquad Na + 2\,Ca \leqq 0.15.$$

The final constraint for montmorillonite, which forces the oxide sum to equal 1, is

$$\sum \text{oxide wt. \%} = 1.$$

The four stoichiometric constraints and the closure constraint listed above will have to be modified slightly to be included in the linear programming problem.

Before the stoichiometry of montmorillonite can be incorporated into the linear programming problem, the compositional range of interest must first be defined. The following ranges essentially span the compositional variation of the montmorillonites given in Ross and Hendricks (1945) and Weaver and Pollard (1973):

	$(q_i)'_{mont}$	$2(\Delta q_{ii})_{mont}$
SiO_2	57.6	7.2
Al_2O_3	17.0	10.3
Fe_2O_3	0.0	7.3
CaO	0.0	3.5
Na_2O	0.0	3.4
MgO	1.4	6.0
H_2O	6.2	4.2,

where the compositional variation for montmorillonite is given by the relation

$$\vec{q}'_{mont} + 2[\Delta q]_{mont}\Delta\vec{X}_{mont}.$$

The matrix $[\Delta q]_{mont}$ is a 7 × 7 diagonal matrix with diagonal elements, $2(\Delta q_{ii})_{mont}$, listed above. The compositional ranges represent materials dried at 105°C. Minor components (e.g., TiO_2, K_2O) have been omitted. The omission of these components should not significantly affect the final solution.

The stoichiometric constraints written to be consistent with the compositional ranges and a linear programming model have the following form:

(1′) Charge balance:

$$X(4.84) + \Delta X_{SiO_2}(0.479) + \Delta X_{Al_2O_3}(0.606) + \Delta X_{Fe_2O_3}(0.275) + \Delta X_{CaO}(0.123) + \Delta X_{Na_2O}(0.110) + \Delta X_{MgO}(0.297) - 22k' = 0,$$

where X is the amount of montmorillonite in the mixture; ΔX_{SiO_2}, $\Delta X_{Al_2O_3}$ . . . describe the variation in the weight percentages of SiO_2, Al_2O_3 . . . , k′ is a constant (k′ = 1/k), and the numbers in parentheses are moles of the oxide multiplied by ionic charge of the cation.

(2′) The constraint limiting the number of tetrahedral cations takes the form:

$$X(0.959) + \Delta X_{SiO_2}(0.120) + Y - 4k' = 0,$$

where Y is the amount of tetrahedral cations other than Si and the numbers in parentheses are moles of Si.

(3′) Two constraints will be used to confine the number of octahedral cations between 1.98 and 2.10.

$$X(0.370) + \Delta X_{Al_2O_3}(0.202) + \Delta X_{Fe_2O_3}(0.092) + \Delta X_{MgO}(0.148) - Y - k'(1.98) \geqq 0$$

$$X(0.370) + \Delta X_{Al_2O_3}(0.202) + \Delta X_{Fe_2O_3}(0.092) + \Delta X_{MgO}(0.148) - Y - k'(2.10) \leqq 0,$$

where the numbers in parentheses are moles of a given cation.

(4′) The exchangeable cation constraints are written:

$$\Delta X_{Na_2O}(0.110) + \Delta X_{CaO}(0.123) - A(0.08) \geqq 0$$

$$\Delta X_{Na_2O}(0.110) - \Delta X_{CaO}(0.123) - A(0.15) \leqq 0,$$

where A is defined below.

The final two constraints force the sum of the oxide weight percentages to equal 100.

$$X(82.3) + \Delta X_{SiO_2}(7.2) + \Delta X_{Al_2O_3}(10.3) + \Delta X_{Fe_2O_3}(7.3) + \Delta X_{CaO}(3.5) + \Delta X_{Na_2O}(3.4) + \Delta X_{MgO}(6.0) + \Delta X_{H_2O}(4.2) - A \cdot 100 = 0$$

and

$$X - A = 0.$$

In this problem, plagioclase is considered to be ideal and lies in the range An_{30} to An_{40}. The compositional variation for plagioclase is given by the following (see previous discussion regarding plagioclase compositional variation):

	q'_{pl}	$2[\Delta q]_{pl}$
SiO_2	61.1	−2.6
Al_2O_3	24.6	1.7
CaO	6.0	2.1
Na_2O	8.4	−1.2.

The complete linear programming problem is given in Tables 1 and 2. The top line in both tables is the linear programming objective function to maximize the amount of montmorillonite. An objective function weight between 5 and 10 for the phase to be maximized, 0 for the other phases present, and −100 for the free variables generally results in a reasonable approximation to the maximum value for a specific phase. If the weight for the phase to be maximized is increased

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Table 1. Partial linear programming array to maximize the amount of montmorillonite.[1]

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1				10	·	·	·	·	·	·	·	·	·	·
2	1	1		1	·	·	·	·	·	·	·	·	·	·
3	100	61.1	−2.6	57.6	7.2									
4		24.6	1.7	17.0		10.3	·	·	·	·	·	·	·	·
5				0.1			7.3							
6		6.0	2.1					3.5						
7		8.4	−1.2	·	·	·	·	·	3.4					
8				1.4						6.0			·	·
9				6.2	·	·	·	·	·	·	4.2			
10				1	−1									
11				1		−1						·		
12				1			−1							
13				1				−1						
14				1					−1					
15				1						−1				
16				1							−1			
17				82.3	7.2	10.3	7.3	3.5	3.4	6.0	4.2	−100		
18				1								−1		
19				4.84	0.479	0.606	0.275	0.123	0.110	0.297			−22	
20				0.959	0.120								−4	1
21				0.37		0.202	0.092			0.148			−2.10	−1
22				0.37		0.202	0.092			0.148			−1.98	−1
23								0.123	0.110			−0.08		
24								0.123	0.110			−0.15		

[1] Rows are continued in Table 2 and row explanations apply to both Table 1 and Table 2. Numbers along perimeter are row and column numbers. Row 1 is the linear programming objective function. Row 2 is the constraint $\sum X_j = 1$; rows 3–9 represent mass balance constraints. Rows 10–16 are the contraints $X_{mont} \geqq (\Delta X_i)_{mont}$; rows 17–24 are the stoichiometric constraints for montmorillonite. Column 1 corresponds to quartz + opal-CT, columns 2 and 3 to plagioclase, and columns 4–14 represent montmorillonite. The vector $\vec{q}'_{pl}$ is given by column 2, rows 3–9, and $[\Delta q]_{pl}$ is given by rows 3–9, column 3. The vector $\vec{q}'_{mont}$ corresponds to rows 3–9, column 4, and $[\Delta q]_{mont}$ is given by rows 3–9, columns 5–11. Blanks and dots represent zeros.

too much beyond 10, free variables are more likely to be incorporated into the solution when they may not be necessary to effect a solution. The solution to the linear programming problem shown in Tables 1 and 2 and the solutions for maximization of quartz + opal-CT and maximization of plagioclase are given in Table 3. Also shown are the minimum values for each phase that were computed in the three maximization calculations.

The relatively large range (difference between maximum and minimum weight fractions) for the amounts of montmorillonite and plagioclase is primarily the result of considering a very large compositional variation for montmorillonite. If XRD information is incorporated into the problem, the calculated range will, in general, decrease. As mentioned above, the objective function weights for the various phases affect the final solutions. To determine how sensitive the solution is to changes in the objective function, a parameter may be calculated that indicates the range over which the objective function of one variable may be changed (all others remain constant) without changing the solution

Table 2. Partial linear programming array to maximize the amount of montmorillonite (continued from Table 1).[1]

	15	16	17	18	19	20	21	22	23	24	25	26	27	28
1	−100	−100	−100	−100	−100	−100	−100	−100	−100	−100	−100	−100	−100	
2	·	·	·	·	·	·	·	·	·	·	·	·	·	1
3	−100	·	·	·	·	·	·	·	·	·	·	·	·	67.8
4	·	100	−100	·	·	·	·	·	·	·	·	·	·	17.8
5				100	−100	·	·	·	·	·	·	·	·	2.5
6						100	−100	·	·	·	·	·	·	2.2
7								100	−100	·	·	·	·	1.7
8										100	−100	·	·	1.5
9	·	·	·	·	·	·	·	·	·	·	·	100	−100	5.4

Refer to Table 1 for row explanations. Columns 15–27 correspond to free variables. The bulk composition vector is represented by column 28. Blanks and dots represent zeros.

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Table 3. Results of linear programming calculations.

	Weight fraction maximum	Weight fraction minimum	Objective function weight	Objective function range
Montmorillonite	0.700	0.572	10	0–10.5
Quartz + opal-CT	0.247	0.235	10	0–47.1
Plagioclase	0.178	0.057	10	0–12.1

The first column is the calculated maximum weight fraction of each phase. Column 2 is the minimum weight fraction of a particular phase(s) calculated for any maximization calculation. Column 3 is the objective function weight of the phase being maximized, and column 4 lists the objective function weight range over which the solution does not change from that calculated using the respective weight listed in column 3.

to the linear programming problem. In linear programming, this type of calculation is included under the general category of sensitivity analysis. The range over which a single objective function may change with no change in the solution can be calculated using the optimal solution. This information is useful because the model is concerned essentially with an objective function consisting of a single, positive weight parameter (excluding free variables). The objective function ranges over which a given optimal solution does not change from that calculated using a weight factor of 10 are given in Table 2.

SUMMARY

A method has been presented which allows the estimation of the maximum and minimum amounts of phases in a mixture by solving a linear programming problem. The information necessary to produce the estimation is the bulk composition of the mixture and compositional constraints for the phases. XRD constraints can be added to restrict further the calculated maxima and minima.

In the method described here, the emphasis is on the utilization of compositional information primarily because it is more readily interpretable than XRD intensity data. Compositional constraints for a given mineral may be approximated using a set of plus or minus increments for the chemical components, with or without stoichiometric restrictions, or a series of discrete phase compositions. Once compositional constraints are available, a series of mass balance equations and inequalities can be generated. XRD intensity-concentration equations (or inequalities) relating pairs of phases are added to the mass balance relations, and the system of equations and inequalities can be solved using linear programming methods. A set of free variables is added to the linear programming problem so that a solution always exists. These free variables are heavily weighted so that they are used only when a feasible solution cannot otherwise be obtained. The maximum and minimum amounts of each phase can be found by making appropriate changes to the linear programming objective function. In general, the more constraints that are available, the smaller the difference will be between the calculated maximum and minimum for each of the phases. Although this discussion has been restricted to the utilization of chemical and XRD constraints, any linear relationship(s) between the phases can be used.

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