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Geochemical mole-balance modeling with uncertain data

David L. Parkhurst
U.S. Geological Survey, Lakewood, Colorado

Abstract. Geochemical mole-balance models are sets of chemical reactions that quantitatively account for changes in the chemical and isotopic composition of water along a flow path. A revised mole-balance formulation that includes an uncertainty term for each chemical and isotopic datum is derived. The revised formulation is comprised of mole-balance equations for each element or element redox state, alkalinity, electrons, solvent water, and each isotope; a charge-balance equation and an equation that relates the uncertainty terms for *p*H, alkalinity, and total dissolved inorganic carbon for each aqueous solution; inequality constraints on the size of the uncertainty terms; and inequality constraints on the sign of the mole transfer of reactants. The equations and inequality constraints are solved by a modification of the simplex algorithm combined with an exhaustive search for unique combinations of aqueous solutions and reactants for which the equations and inequality constraints can be solved and the uncertainty terms minimized. Additional algorithms find only the simplest mole-balance models and determine the ranges of mixing fractions for each solution and mole transfers for each reactant that are consistent with specified limits on the uncertainty terms. The revised formulation produces simpler and more robust mole-balance models and allows the significance of mixing fractions and mole transfers to be evaluated. In an example from the central Oklahoma aquifer, inclusion of up to 5% uncertainty in the chemical data can reduce the number of reactants in mole-balance models from seven or more to as few as three, these being cation exchange, dolomite dissolution, and silica precipitation. In another example from the Madison aquifer, inclusion of the charge-balance constraint requires significant increases in the mole transfers of calcite, dolomite, and organic matter, which reduce the estimated maximum carbon 14 age of the sample by about 10,000 years, from 22,700 years to 12,600 years.

Introduction

Quantitative mole-balance modeling was introduced to geochemical literature by *Garrels and Mackenzie* [1967]. They developed a mole-balance model that accounted for the compositional difference between an ephemeral spring and a more chemically evolved perennial spring by the reaction of minerals in Sierra Nevada rocks. A mole-balance model is a set of mixing fractions of initial aqueous solutions and mole transfers of minerals and gases that quantitatively account for the chemical composition of the final solution. Implicit in this approach is the assumption that the final solution did indeed evolve from the initial aqueous solutions by reaction with the proposed minerals and gases. This assumption is frequently applicable in regional aquifer studies, where the flow system and mineralogy are well known and the chemical composition of water in the aquifer can be assumed to be nearly a steady state, that is, invariant at each location with respect to time (see discussion by *Glynn and Brown* [1996]).

In their simplest form the constitutive equations of a mole-balance model are mass conservation equations for each element in the chemical system [*Plummer et al.*, 1983]

$$\sum_{Q-1} \alpha_q T_{j,q} + \sum_{P} c_{j,p}\alpha_p = T_{j,Q}, \qquad (1)$$

where j represents an element, Q is the number of aqueous solutions and the first $Q - 1$ solutions mix to form the last solution Q, α_q is the mixing fraction of solution q, $T_{j,q}$ is the total concentration of element j in solution q, P is the number of reactive phases, $c_{j,p}$ is the stoichiometric coefficient of element j in phase p, and α_p is the mole transfer of phase p. The unknowns in this formulation are the mixing fractions α_q and the mole transfers of the phases α_p. The formulation described by *Parkhurst et al.* [1982] leads to a set of linear mole-balance equations, one equation for each element in the system except for hydrogen and oxygen. The set of equations can be solved by Gaussian elimination, provided the number of unknowns equals the number of equations and the equations are linearly independent. Enhancements of the mole-balance approach have added an equation to conserve electrons, which forces oxidative reactions to balance reductive reactions, and isotope-balance equations [*Plummer and Back*, 1980; *Parkhurst et al.*, 1982; *Plummer et al.*, 1983; *Plummer et al.*, 1990, 1991, 1994]. Another enhancement to the mole-balance approach addresses the problem when the number of reactant phases P exceeds the number of mole-balance equations n. In this case the mole-balance equations are formulated for every combination of n reactant phases. All sets of n phases for which a solution to the equations can be found are potential mole-balance models. These models can then be accepted or rejected by determining whether they are consistent with any dissolution or precipitation constraints that can be deduced from thermodynamic considerations or microscopic evaluation of minerals. The program NETPATH has the capability for

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mole-balance modeling with all of these enhancements [*Plummer et al.*, 1991, 1994].

The present work expands on the previous approaches by including an additional set of unknowns that are uncertainty terms for each chemical and isotopic datum. These uncertainty terms allow each datum to increase or decrease, but the magnitude of the increase or decrease is constrained to vary only within a specified limit. Each limit is specified on the basis of the sources of uncertainty in the datum, which include analytical uncertainty and sampling uncertainty, and may also include uncertainty due to spatial variability. The constraints on the uncertainty terms are formulated as a set of linear inequality constraints. The new formulation uses the same chemical and analytical data as previous approaches to mole-balance modeling but requires the additional specification of the uncertainty limits for all chemical and isotopic data.

In addition, the new formulation expands on the previous approaches by including (1) mole-balance equations for each valence state of an element (in place of one mole-balance equation for the total element), if an element may exist in more than one valence state in aqueous solution (a redox element), (2) a different electron-balance equation, (3) a mole-balance equation on alkalinity, (4) a charge-balance equation for each aqueous solution, (5) a mole-balance equation for solvent water, and (6) an equation relating the uncertainty terms for *p*H, alkalinity, and total dissolved inorganic carbon for each aqueous solution. The combined set of equations and inequality constraints are solved using a modification of the simplex algorithm.

Mole-balance models calculated by using the new formulation are more reliable because charge balance is explicitly included, more robust because small differences in chemical data or mineral composition do not lead to major differences in the mole-balance models, and more consistent because the new formulation provides the means for assessing the significance of mole transfers relative to uncertainties in the chemical data. This work shows that consideration of reasonable uncertainties in field data can entirely eliminate certain reactants and aqueous solutions from mole-balance models and can determine which reactants and aqueous solutions are essential in mole-balance models. The revised formulation of mole-balance modeling provides a method to determine the simplest sets of geochemical reactions that explain the chemical and isotopic data within specified limits of uncertainty.

Equations and Inequality Constraints

Several changes in the set of equations previously used for mole-balance modeling are needed to account for uncertainties in the chemical and isotopic data. The revised set includes mole-balance equations for each element or element valence state, an electron-balance equation, an alkalinity-balance equation, a charge-balance equation for each aqueous solution, a water-balance equation, isotope-balance equations, and equations relating the uncertainty terms for *p*H, alkalinity, and total dissolved inorganic carbon. Inequalities are included to constrain uncertainty terms to be smaller than specified uncertainty limits and to constrain specified phases to dissolve or precipitate.

Mole-Balance Equations

In previous formulations, mole-balance equations were included only for the total concentration of each element (except hydrogen and oxygen) and for the redox state of the aqueous solution [*Parkhurst et al.*, 1982; *Plummer et al.*, 1983, 1991, 1994]. If uncertainties are considered for the total concentration of an element, no simple way exists to consider the uncertainties in individual redox states of elements. Uncertainties in trace redox elements would be effectively neglected in the redox-state equation because of the larger magnitude of the uncertainties for the major redox elements (sulfur and carbon) in the total redox state of the solution.

The new formulation includes a mole-balance equation for each valence state of each redox element in the system. It is assumed that the number of moles of an element or element valence state in the final solution may be derived from the initial aqueous solutions, the reactive phases, and in the case of element valence states, aqueous redox reactions. As an example of an aqueous redox reaction, the following equation would transfer ferrous iron to ferric iron or the reverse, depending on the sign of the mole transfer:

$$Fe^{2+} \Rightarrow Fe^{3+} + e^{-}. \quad (2)$$

The mole-balance equation including uncertainty terms and redox reactions can be written as follows:

$$\sum_{q}^{Q} c_q \alpha_q (T_{m,q} + \delta_{m,q}) + \sum_{p} c_{m,p} \alpha_p + \sum_{r} c_{m,r} \alpha_r = 0, \quad (3)$$

where $T_{m,q}$ is the total number of moles of element or element valence state m in aqueous solution q, $\delta_{m,q}$ is a term for the uncertainty in the number of moles of $T_{m,q}$, $c_{m,p}$ is the stoichiometric coefficient of element or element valence state m in the dissolution reaction for phase p (by convention, all chemical reactions for phases are written as dissolution reactions; precipitation in mole-balance models is indicated by negative mole transfers, $\alpha_p < 0$), and $c_{m,r}$ is the coefficient of the element valence state m in redox reaction r. The last aqueous solution, number Q, is assumed to be formed from mixing the first $Q - 1$ aqueous solutions such that $c_q = 1.0$ for $q < Q$ and $c_Q = -1.0$. The unknowns in the equation are the mixing fractions of the solutions α_q (unitless), the mole transfers of the phases α_p (moles), the extent of redox reactions α_r (moles), and a term for the uncertainty in the number of moles of the element or element valence state in each aqueous solution $\delta_{m,q}$ (moles).

Electron-Balance Equation

In place of the redox-state equation used in previous mole-balance modeling formulations, a mole-balance equation for electrons is used. Electrons may enter or leave the aqueous phase through aqueous redox reactions or through phase dissolution and precipitation reactions. However, the electron-balance equation requires that the sum of all electrons entering and leaving the aqueous phase must be zero,

$$\sum_{r} c_{e^-,r} \alpha_r + \sum_{p} c_{e^-,p} \alpha_p = 0, \quad (4)$$

where $c_{e^-,r}$ represents the number of electrons released or consumed in each aqueous redox reaction and $c_{e^-,p}$ is the number of electrons released or consumed in the phase dissolution reaction.

Alkalinity-Balance Equation

Chemical data for aqueous solutions always contain some analytical error. One manifestation of this error is that al-

though all aqueous solutions are physically charge balanced, most chemical analyses have some charge imbalance between analyzed cations and analyzed anions. This charge imbalance should be considered in mole-balance modeling, but to formulate a complete charge-balance equation, it is necessary to include the charge contribution of alkalinity.

For the purposes of mole-balance modeling, the alkalinity of an aqueous solution is defined operationally by a summation

$$\mathrm{Alk}_q = \sum_i c_{\mathrm{Alk},i} m_{i,q}, \tag{5}$$

where Alk_q is the alkalinity of solution q, $c_{\mathrm{Alk},i}$ is the alkalinity contribution of aqueous species i, and $m_{i,q}$ is the number of moles of species i in solution q. If a set of master or basis species is chosen, one for each element or element valence state plus hydrogen ion and water, then chemical equations for all other aqueous complexes can be written in terms of the master species, with no electrons in the reaction. The values of $c_{\mathrm{Alk},m}$ for the master species are chosen such that the reference state ($c_{\mathrm{Alk},i} = 0$) for each element or element valence state is the predominant aqueous species at the approximate pH of the endpoint of a titration; pH 4.5 is used in all the calculations in this paper. The following definitions apply to hydrogen ion, $c_{\mathrm{Alk},\mathrm{H}^+} = -1.0$, and water, $c_{\mathrm{Alk},\mathrm{H_2O}} = 0$. The alkalinity contribution of an aqueous complex is defined to be the sum of the alkalinity contributions of each of the master species in a balanced chemical association reaction that contains only master species and no electrons. By disallowing electrons in the equation, the alkalinity contribution of an aqueous species is defined unequivocally; if electrons were allowed in the equation, then different alkalinity contributions for a single species could be calculated by using association reactions involving different redox states. The unique definition of the alkalinity contribution of an aqueous species allows a unique definition of the calculated alkalinity of a solution, which is determined by (5) from the distribution of aqueous species as calculated by an ion-association speciation model.

Conceptually, the calculated alkalinity for a solution differs from the measured alkalinity. The calculation assumes that all of the aqueous species present at the measured sample pH are converted to species with defined alkalinity contributions of zero in the course of a titration. In an alkalinity titration, however, significant concentrations of the species with defined alkalinity contributions that are nonzero may exist at the end point of the titration. The extent to which these species exist at the end point of the titration causes the measured alkalinity to differ from the calculated alkalinity. (The correct alkalinity should be the calculated alkalinity at the initial pH minus the calculated alkalinity at the end point of the titration, but the end point of the titration is not known a priori.) Species that are especially susceptible to this problem are the hydroxide complexes of iron and aluminum. However, in most solutions the operational definition of alkalinity is adequate because alkalinity is derived predominantly from carbonate species, for which alkalinity contributions can be reliably defined.

The alkalinity contribution of a phase is the sum of the alkalinity contributions of the aqueous species in a balanced chemical reaction for the dissolution of the phase. Phase dissolution reactions can include electrons, and so, the defined alkalinity for a phase can vary, depending on the chemical reaction that is used to define it. However, the reactions for the phases are only used in combination with redox transfer reactions in the complete mole-balance formulation. The combination of the phase mole transfer and the redox mole transfers gives the correct alkalinity contribution to the aqueous solution, provided the same definitions for the alkalinities of the master species are used in all chemical reactions. The alkalinity contribution of the electron is 0, $c_{\mathrm{Alk},e^-} = 0$.

The form of the mole-balance equation for alkalinity is identical to the form of the other mole-balance equations,

$$\sum_q^Q c_q \alpha_q (T_{\mathrm{Alk},q} + \delta_{\mathrm{Alk},q}) + \sum_p c_{\mathrm{Alk},p} \alpha_p + \sum_r c_{\mathrm{Alk},r} \alpha_r = 0, \tag{6}$$

where the coefficients $c_{\mathrm{Alk},p}$ are calculated from balanced chemical reactions for phase dissolution reactions, $c_{\mathrm{Alk},p} = \Sigma_i \mathrm{Alk}_i c_{i,p}$, and $c_{i,p}$ is the stoichiometric coefficient of aqueous species i in the dissolution reaction for phase p; and $c_{\mathrm{Alk},r}$ are calculated from aqueous redox transformations, $c_{\mathrm{Alk},r} = \Sigma_m \mathrm{Alk}_m c_{m,r}$, and $c_{m,r}$ is the stoichiometric coefficient of the master species m in aqueous redox reaction r.

Charge-Balance Equation

A charge-balance equation is included for each of the aqueous solutions. The concentrations of the elements and element valence states are allowed to vary within specified uncertainty limits, but variations in concentrations should not be allowed to generate charge imbalanced solutions. In fact, the variations in the concentrations should correct for the calculated charge imbalance in each aqueous solution. The charge-balance equations constrain the uncertainty terms for the chemical data (δ) to be such that when the δ values are added to the original analytical data, charge balance is produced in each aqueous solution. The revised mole-balance formulation allows any combination of adjustments within the uncertainty limits to obtain charge balance for each aqueous solution. The charge-balance equation for an aqueous solution is as follows:

$$\sum_m \bar{z}_m \delta_{m,q} = -T_{z,q}, \tag{7}$$

where $T_{z,q} = \Sigma_i^{N_{\mathrm{aq}}} z_i n_{i,q}$ is the charge imbalance (in equivalents) in aqueous solution q, which is calculated by summing charge z_i times moles $n_{i,q}$ for all aqueous species in solution q. The summation in (7) ranges over all elements and element valence states and also includes a term for alkalinity. For alkalinity, $\bar{z}_{\mathrm{Alk}}$ is defined to be -1.0. For the master species of an element or valence state m, $\bar{z}_m$ is defined to be the charge on the master species plus the alkalinity assigned to the master species, $\bar{z}_m = z_m + \mathrm{Alk}_m$. Adding the alkalinity to the charge avoids double accounting of the charge contribution of the element or element valence state when the master species is defined to have a nonzero alkalinity contribution. Thus the summation for charge balance can be divided into two parts: a part that is calculated by a summation over the concentrations of each element and element valence state (accounted for by $\bar{z}_m$) and a part that is the alkalinity. This division is most important for inorganic carbon, which is the major source of alkalinity in most natural waters. If CO_3^{2-} is chosen as the master species for carbon (IV), the alkalinity assigned to this species is 2. The value of $\bar{z}_{\mathrm{C(IV)}}$ is the charge plus the alkalinity, which equals zero ($\bar{z}_{\mathrm{C(IV)}} = -2 + 2 = 0$). These definitions imply that no charge contribution for carbon (IV) is included in the first part of the charge-balance summation (the summation over elements and element valence states) and all of the

charge contribution for carbon (IV) is contained in the second part of the charge-balance summation, the measured alkalinity.

Water-Balance Equation

A mole-balance equation is included for water. This equation is a generalization of the constraint that the mixing fractions for the initial aqueous solutions sum to 1.0, which was used in previous mole-balance formulations. The water-balance equation states that the moles of water derived from the initial aqueous solutions plus water produced or consumed in redox reactions plus water produced or consumed in mineral and gas reactions equals the moles of water in the final aqueous solution. The equation is approximate because it does not account for homogeneous hydrolysis reactions that produce or consume water within the aqueous phase, for example, hydrolysis of ferric ion to form ferric hydroxide aqueous complexes. However, homogeneous reactions are expected to produce or consume less than a few millimoles of water out of approximately 55.5 moles in a kilogram of water.

The mole-balance equation for water is as follows:

$$\sum_{q}^{Q} \frac{W_{\mathrm{aq},q}}{\mathrm{GFW}_{\mathrm{H_2O}}} c_q \alpha_q + \sum_{p} c_{\mathrm{H_2O},p} \alpha_p + \sum_{r} c_{\mathrm{H_2O},r} \alpha_r + \delta_{\mathrm{H_2O},Q} = 0, \tag{8}$$

where $\mathrm{GFW}_{\mathrm{H_2O}}$ is the gram formula weight for water (~0.018 kg/mol), $W_{\mathrm{aq},q}$ is the mass of water in solution q, $c_{\mathrm{H_2O},p}$ is the stoichiometric coefficient of water in the dissolution reaction for phase p, $c_{\mathrm{H_2O},r}$ is the stoichiometric coefficient of water in the aqueous redox reaction, and $\delta_{\mathrm{H_2O},Q}$ is an uncertainty term for the number of moles of water in the final aqueous solution. To avoid multiple correlated unknowns, the last term in (8) accounts for all the uncertainty in the moles of water in the system; conceptually, the individual terms for the uncertainty in the moles of water in each aqueous solution are included in this single term.

Isotope-Balance Equations

Geochemical mole-balance models must account for the isotopic composition as well as the chemical composition of the final aqueous solution. In general, isotopic evolution requires solving a differential equation that accounts for fractionation processes for precipitating solids and exsolving gases. In the development presented here, only the simpler case of isotopic mole balance, without explicit fractionation, is considered. This approach is correct if all isotope-bearing phases dissolve but is approximate when isotope-bearing phases precipitate or exsolve.

Mole balance for an isotope can be written as follows:

$$\sum_{q}^{Q} \left[c_q \alpha_q \sum_{M_e} (R^{\prime}_{m,q} + \delta_{R^{\prime}_{m,q}})(T_m + \delta_{m,q}) \right] + \sum_{p} c_{e,p}(R^{\prime}_{e,p} + \delta_{R^{\prime}_{e,p}})\alpha_p = 0, \tag{9}$$

where M_e ranges over all valence states of element e, $R^{\prime}_{m,q}$ is the isotopic ratio (which may be delta notation (for example, $\delta^{13}C$ or $\delta^{34}S$), ^{14}C activity in percent modern carbon, or any units that allow linear mixing) for isotope i for valence state m in aqueous solution q, $\delta_{R^{\prime}_{m,q}}$ is an uncertainty term for the isotopic ratio for a valence state in the aqueous solution, $R^{\prime}_{e,p}$ is the isotopic ratio of element e in phase p, and $\delta_{R^{\prime}_{e,p}}$ is an uncertainty term for the isotopic ratio of the element in the phase.

Expanding (9) and neglecting the products of δ values gives the following approximation:

$$\sum_{q}^{Q} \sum_{M_e} (c_q R^{\prime}_{m,q} T_m \alpha_q + c_q R^{\prime}_{m,q} \alpha_q \delta_{m,q} + c_q T_m \alpha_q \delta_{R^{\prime}_{m,q}}) + \sum_{p} (c_{e,p} R^{\prime}_{e,p} \alpha_p + c_{e,p} \alpha_p \delta_{R^{\prime}_{e,p}}) \approx 0. \tag{10}$$

Commonly, the uncertainty limit for the valence state will be small relative to the concentration of the valence state or the uncertainty limit for the isotopic ratio will be small relative to the isotopic ratio itself. In either case the products of δ values that are neglected will be small relative to the other terms and (10) will be a good approximation. The approximation in (10) will be poor only if the concentration of the valence state and the isotopic ratio have large calculated δ values. In this case the overall effect is that the true values of the uncertainty terms will be larger than the specified uncertainty limits. The neglected terms can be made smaller by decreasing the uncertainty limits on either the valence-state concentrations or the isotopic ratios for each aqueous solution. In the future, nonlinear programming may provide a better approach to avoid neglecting terms as well as to allow for isotopic fractionation and evaluation of the uncertainties in carbon 14 ages.

Relation Among *p*H, Alkalinity, and Total Dissolved Inorganic Carbon Uncertainty Terms

In general, the uncertainty terms associated with the chemical data (δ) are assumed to be unrelated, except for the charge-balance relation for ions. However, the uncertainty terms for some sets of data can be related, including (1) *pe* (by convention, *pe* is the negative log of the activity of the electron) and the concentrations of the valence states of a redox element and (2) *p*H, alkalinity, and total dissolved inorganic carbon. In the current mole-balance formulation, uncertainty terms are included for each valence state of each redox element. However, no relation has been included between the uncertainty in *pe* and the uncertainty terms for the concentrations of the individual valence states of an element, and uncertainty in the *pe* is not included in the formulation at all. The lack of a relation with *pe* is potentially a problem only when the total concentration of a redox element is specified and *pe* is used to distribute this element among its valence states. Usually, *pe* is not used to distribute the major redox elements (carbon, sulfur, dissolved oxygen, and nitrogen) into their individual valence states. Other redox elements tend to have trace concentrations. Usually, these trace redox elements are either conserved in the solid phases (for example iron), which makes the aqueous concentrations relatively unimportant, or the stoichiometries of the sources of these elements are not well defined, which indicates that mole-balance modeling is not applicable for these elements.

If inorganic carbon is included in the model, one additional equation is added for each aqueous solution. This equation is needed because the combination of alkalinity, charge-balance, electron-balance, and element mole-balance equations overdetermine the chemical system. The uncertainty terms for *p*H, alkalinity, and total dissolved inorganic carbon are not independent, and the revised mole-balance formulation uses the following equation to account for the interdependency:

$$\delta_{C(IV)_q} = \frac{\partial C(IV)_q}{\partial Alk_q} \delta_{Alk,q} + \frac{\partial C(IV)_q}{\partial pH_q} \delta_{pH,q}. \quad (11)$$

The partial derivatives for this equation can be evaluated numerically for each aqueous solution. Inequality constraints (see (12)) are included for carbon (IV), alkalinity, and pH for each aqueous solution.

Inequality Constraints

The revised formulation for mole-balance modeling makes sense only if the values of δ are small, which means that the adjusted aqueous solution compositions (original data plus δ values) do not deviate much from the original data. A set of inequality constraints ensures that the values of δ are small. The absolute value of the uncertainty term for each chemical datum $\delta_{m,q}$, is constrained to be smaller than a specified uncertainty limit $u_{m,q}$,

$$|\delta_{m,q}| \le u_{m,q}. \quad (12)$$

Likewise, the absolute value of the uncertainty term for each isotope ratio for each aqueous solution $\delta_{R'_{m,q}}$, is constrained to be smaller than a specified uncertainty limit $u_{R'_{m,q}}$,

$$|\delta_{R'_{m,q}}| \le u_{R'_{m,q}}, \quad (13)$$

and the absolute value of the uncertainty term for each isotope ratio for each phase is constrained to be less than a specified uncertainty limit $u_{R'_{e,p}}$,

$$|\delta_{R'_{e,p}}| \le u_{R'_{e,p}}. \quad (14)$$

In addition, the mixing fractions for the initial aqueous solutions ($q < Q$) are constrained to be nonnegative,

$$\alpha_q \ge 0. \quad (15)$$

If phases are known only to dissolve, or only to precipitate, the mole transfer of the phases may be constrained to be nonnegative,

$$\alpha_p \ge 0 \text{ (dissolution)}, \quad (16)$$

or nonpositive,

$$\alpha_p \le 0 \text{ (precipitation)}. \quad (17)$$

Change of Variables

The unknowns in the system of equations and inequality constraints for mole-balance modeling (equations (3), (4), (6)–(8), (10)–(17)) are denoted α and δ. The equations, as presented, are nonlinear because they include the product of unknowns of the forms $\alpha_q\delta_{m,q}$, $\alpha_q\delta_{R'_{m,q}}$, and $\alpha_p\delta_{R'_{e,p}}$. However, if the following substitutions are made,

$$\varepsilon_{m,q} = \alpha_q\delta_{m,q}, \quad (18)$$

$$\varepsilon_{R'_{m,q}} = \alpha_q\delta_{R'_{m,q}}, \quad (19)$$

$$\varepsilon_{R'_{e,p}} = \alpha_p\delta_{R'_{e,p}}, \quad (20)$$

the system can be linearized.

The mole-balance equations (3) are written as

$$\sum_q^Q c_q T_{m,q}\alpha_q + \sum_q^Q c_q\varepsilon_{m,q} + \sum_p c_{m,p}\alpha_p + \sum_r c_{m,r}\alpha_r = 0. \quad (21)$$

The electron-balance equation (4) is unchanged. The alkalinity-balance equation (6) is written as

$$\sum_q^Q c_q T_{Alk,q}\alpha_q + \sum_q^Q c_q\varepsilon_{Alk,q} + \sum_p c_{Alk,p}\alpha_p + \sum_r c_{Alk,r}\alpha_r = 0. \quad (22)$$

By multiplying through by α_q the charge-balance equation (7) is written as

$$T_{z,q}\alpha_q + \sum_m \bar{z}_m\varepsilon_{m,q} = 0. \quad (23)$$

The mole-balance equation for water (8) is unchanged. The isotope-balance equation (10) is written as

$$\sum_q^Q \sum_{M_e} (c_q R'_{m,q} T_m\alpha_q + c_q R'_{m,q}\varepsilon_{m,q} + c_q T_m\varepsilon_{R'_{m,q}}) + \sum_p (c_{e,p}R'_{e,p}\alpha_p + c_{e,p}\varepsilon_{R'_{e,p}}) \approx 0. \quad (24)$$

By multiplying through by α_q, the pH-alkalinity-carbon relation (11) is written as

$$\varepsilon_{C(IV)_q} = \frac{\partial C(IV)_q}{\partial Alk_q} \varepsilon_{Alk,q} + \frac{\partial C(IV)_q}{\partial pH_q} \varepsilon_{pH,q}. \quad (25)$$

The inequality constraints must also be modified to be consistent with the new unknowns. Each inequality for the chemical data (12) is multiplied by α_q to change variables and then converted into two inequalities to remove the absolute value function,

$$-u_{m,q}\alpha_q \le \varepsilon_{m,q} \le u_{m,q}\alpha_q. \quad (26)$$

These two inequalities can be written because both α_q and $u_{m,q}$ are required to be nonnegative. Putting these inequalities into a standard form gives

$$\varepsilon_{m,q} - u_{m,q}\alpha_q \le 0 \quad (27)$$

$$-\varepsilon_{m,q} - u_{m,q}\alpha_q \le 0. \quad (28)$$

Similarly, each inequality for the isotopic composition of an element or valence state in an aqueous solution (13) is transformed to the following two inequality constraints:

$$\varepsilon_{R'_{m,q}} - u_{R'_{m,q}}\alpha_q \le 0 \quad (29)$$

$$-\varepsilon_{R'_{m,q}} - u_{R'_{m,q}}\alpha_q \le 0. \quad (30)$$

To use the same approach to constrain the uncertainty term for the isotopic composition of a phase (14), the sign of the mole transfer of the phase must be known. Thus, to use purely linear programming, all reactant phases containing isotopes must be constrained either to dissolve or precipitate. If a phase is constrained to dissolve, $\alpha_p \ge 0$, the following two inequality

constraints are used for the uncertainty term for the isotopic composition of the phase:

$$\varepsilon_{R'_{c,p}} - u_{R'_{c,p}}\alpha_p \leq 0 \quad (31)$$

$$-\varepsilon_{R'_{c,p}} - u_{R'_{c,p}}\alpha_p \leq 0. \quad (32)$$

If a phase is constrained to precipitate, $\alpha_p \leq 0$, then the following two inequality constraints are used:

$$\varepsilon_{R'_{c,p}} + u_{R'_{c,p}}\alpha_p \leq 0 \quad (33)$$

$$-\varepsilon_{R'_{c,p}} + u_{R'_{c,p}}\alpha_p \leq 0. \quad (34)$$

The equations (4), (8), and (21)–(25) and inequalities (15)–(17) and (27)–(34) constitute the complete formulation for mole-balance modeling. All of the equations and inequality constraints are linear in the unknowns α and ε, and once the values of all of the α and ε are known, the values of δ can be easily determined from (18)–(20).

Numerical Method

The algebraic constraints for the mole-balance problem can be posed with the following matrix equalities and inequalities:

$$\begin{aligned} CX &= D \\ EX &\leq F. \end{aligned} \quad (35)$$

Previous mole-balance formulations contained only a set of the equalities in which the number of unknowns equaled the number of equations and could be solved by simple Gaussian elimination. A more complicated algorithm developed by *Barrodale and Roberts* [1980] is used to solve the revised formulation, which includes inequality constraints and has more equations and inequality constraints than unknowns. Their algorithm performs an L1 minimization (minimize the sum of the absolute values) on a set of linear equations,

$$AX = B, \quad (36)$$

subject to equality and inequality constraints. The matrix equation $AX = B$ is minimized such that $\Sigma_i |b_i - \Sigma_j a_{i,j}x_j|$ is a minimum, where i is the row index and j is the column index. Thus, if (35) is the set of equations and inequality constraints for a mole-balance problem, any set of equalities (36) may be chosen as the objective functions. The algorithm will find a solution that minimizes the objective functions ($AX = B$) or will determine that no model exists subject to the constraints (equation (35)).

Initially, $AX = B$ is set to minimize $\Sigma_i^{N_\varepsilon} |\varepsilon_i|/u_i$, where N_ε is the total number of unknowns labeled ε, regardless of subscripts. This is accomplished with N_ε equations of the form $\varepsilon_i/u_i = 0$. Because $\varepsilon = \alpha\delta$, these objective functions minimize the sum of the absolute values of the deviations from the original chemical and isotopic data (δ values), standardized by the specified uncertainty limits u and weighted by the mixing fraction α_q or mole transfer α_p (for isotopes only). The weighting is an artifact of the change of variables to maintain linearity and is necessary to maintain the use of the linear programming technique. The weighting affects the values of the uncertainty terms, but the values of the uncertainty terms are not necessarily uniquely defined anyway. In practice, the actual values of the uncertainty terms are not as significant as the fact that uncertainty terms can be found that allow a mole-balance model to be valid within the specified uncertainty limits. Standardizing by the uncertainty limits produces mole-balance models with mole transfers that have central values relative to the range of mole transfers that are possible within the constraints of the uncertainty limits.

The equality constraints ($CX = D$) include all mole-balance, electron-balance, alkalinity-balance, charge-balance, water-balance, isotope-balance, and pH-alkalinity-carbon equations. The inequality constraints ($EX \leq F$) include two inequalities for each of the ε values for the chemical data, an inequality for each mixing fraction for an aqueous solution, an inequality for each phase that is specified only to dissolve or only to precipitate, two inequalities for each isotope of each valence state in each aqueous solution, and two inequalities for each isotope in each phase.

Application of the optimization technique will determine whether a mole-balance model exists that is consistent with the constraints, that is, if there is at least one set of mixing fractions and phase mole transfers (plus associated ε values) that satisfy the constraints. But could other sets of aqueous solutions and phases also produce feasible mole-balance models? An additional algorithm is used to find unique mole-balance models.

Ignoring the values of ε and redox mole transfers (α_r), let the set of nonzero α_q and α_p (mixing fractions and phase mole transfers) uniquely identify a mole-balance model. A binary sequence of zeros and ones is constructed to define the model, a one for each aqueous solution and phase that is included in the model and a zero for each aqueous solution and phase that is not included. The magnitudes of α are not considered in the identity of an mole-balance model, only the fact that a set of the α values are nonzero.

Assuming P reactant phases and Q aqueous solutions, we proceed as follows: If no feasible model is found when all Q aqueous solutions and P phases are included in the formulation, the job is done because no feasible model exists. If a feasible model is found, then a procedure is used to identify a "minimal" model; a minimal model is defined to be a model for which no feasible model can be found with any proper subset (that is, any subset smaller than the whole set) of the solutions and phases of the model. To find a minimal model, a revised model is derived from the original model by using the optimization method to test the necessity of including each aqueous solution or phase in the model. Initially, all of the aqueous solutions and phases of the original model are included in the revised model. The first aqueous solution or phase in the revised model is removed, and the remaining set of aqueous solutions and phases is tested for the existence of a feasible model. If a feasible model is found when excluding the aqueous solution or phase, then that aqueous solution or phase is not essential and is removed from the revised model; if no feasible model is found, then the aqueous solution or phase is essential and is retained in the revised model. Next the second aqueous solution or phase is removed from the revised model, and the existence of a feasible solution is tested. After each aqueous solution and phase has been tested, the aqueous solutions and phases that remain in the revised model constitute a minimal model. Three lists of binary sequences that represent feasible and infeasible models are kept during this process, one list for each feasible model, another list for each infeasible model, and a third list for each minimal model. The minimal models are the simplest models that account for the data within the uncertainty limits. It is sometimes useful to find only the minimal models, both because they are the simplest

and because the algorithm is computationally faster when looking only for these models.

Next each combination of $P - 1$ phases is tested for feasible models as follows: If the set of aqueous solutions and phases is a subset of an infeasible model or a subset of a minimal model, the model is automatically infeasible or equal to the minimal model, so the model is not tested with the optimization method. If only minimal models are to be found, the model is not tested if it is a superset of a minimal model, because any new minimal model must not contain at least one of the phases of any other minimal model. If a model is not eliminated because of these comparisons, the optimization problem is formulated and solved by using the set of aqueous solutions and the $P - 1$ phases in the same way as described above, maintaining the three lists during the process. Once all sets of $P - 1$ phases have been tested, the process continues with sets of $P - 2$ phases, and so on until the set containing no phases is tested or until, for a given number of phases, $P - n$, every set of phases tested is either a subset of an infeasible model or a subset of a minimal model.

At this point the entire process is repeated using each possible combination of one or more of the $Q - 1$ initial aqueous solutions. Although the process at first appears extremely computer intensive, most sets of phases are eliminated by the subset and superset comparisons on the binary sequences, which are very fast binary comparisons. The number of models that are formulated and solved by the optimization procedure are relatively few (commonly less than 200). The process has the useful feature that it determines immediately whether any feasible model exists with the first invocation of the optimization procedure.

Not every feasible model is found by this search procedure. The relevant criterion is that every feasible model that minimizes the objective function is found by the algorithm. It is almost always possible to include a tiny amount of a new phase in a mole-balance model and with minor adjustments in the mole-transfers of the other phases or the uncertainty terms, still satisfy all of the equality and inequality constraints. However, this augmented model will be identified by the algorithm only if it reduces the objective function. Also, only end-member models are found by the algorithm. Additional mole-balance models can be constructed by taking linear combinations of the end-member models. Each linear combination produces a new mole-balance model that satisfies all the constraints, provided the coefficients of the linear combination are positive and sum to 1.

An alternative formulation of the objective functions can be used to determine the ranges of mixing fractions for each aqueous solution and mole transfers for each phase that are consistent with the specified uncertainty limits. For this "range" calculation the equality and inequality constraints for a given model are solved twice for each aqueous solution and phase in the model, once to determine the maximum value and once to determine the minimum value of the mixing fraction or mole transfer. In these calculations the sums of ε/u are not minimized; instead, the single objective function for maximization is simply

$$\alpha = M, \tag{37}$$

and for minimization,

$$\alpha = -M, \tag{38}$$

where α refers to either α_q or α_p, and M is a positive number larger than the absolute value of any mixing fraction or mole transfer. The optimization algorithm will minimize the difference between α and M and $-M$, thus calculating maximum and minimum mixing fractions or mole transfers that are consistent with the constraints.

Examples

Two examples are presented that are taken from regional groundwater studies that contained mole-balance modeling results. The examples demonstrate some of the features of the revised mole-balance formulation and contrast mole-balance results derived with and without consideration of uncertainties. The program NETPATH [*Plummer et al.*, 1994] is a computer program for calculating mole-balance models. It does not have any capabilities for directly including uncertainty in the mole-balance calculations but does have the capability to calculate isotopic evolution and carbon 14 ages by including fractionation effects. For the examples in this report, NETPATH was used to make the mole-balance calculations that do not include consideration of uncertainty, and it was used for all carbon 14 age calculations. Mole-balance models calculated without uncertainty will be referred to as "NETPATH models."

PHREEQC [*Parkhurst*, 1995] is a computer program that has the capability to calculate mole-balance models by using the revised formulation described in this report, except that isotope mole-balance equations are not included. A modified version of PHREEQC was developed that has the added capability to model isotope mole balance with the associated uncertainty terms. Other minor enhancements in the modified version include the incorporation of an uncertainty term for the moles of water in the system and the capability to include any selected phase in the range calculation. These modifications explicitly implement the complete revised mole-balance formulation described in this report. For the examples in this report, mole-balance calculations that consider uncertainty in the chemical and isotopic data were made with the modified version of PHREEQC, and mole-balance models calculated with uncertainty will be referred to as "PHREEQC models."

Application to the Central Oklahoma Aquifer

This example calculation incorporates uncertainties in mole-balance modeling to evaluate geochemical reactions in the central Oklahoma aquifer. Two types of water predominate in the aquifer: a calcium magnesium bicarbonate water in the unconfined part of the aquifer with *p*H in the range from 7.0 to 7.5 and a sodium bicarbonate water in the deep and confined parts of the aquifer with *p*H in the range from 8.5 to 9.2 [*Parkhurst et al.*, 1996]. In addition, marine-derived sodium chloride brines exist below the aquifer and presumably in fluid inclusions and in dead-end pore spaces within the aquifer. The conceptual model for the evolution of the water in the aquifer is that the calcium magnesium bicarbonate water, which is produced during or soon after recharge, evolves to the sodium bicarbonate water that is present at the distal ends of flow paths by chemical reactions and by mixing with brines. The modeling attempts to identify and quantify the geochemical reactions that cause this chemical evolution of water along the flow path.

Water compositions and reactants. The two initial waters used in this example are calcium magnesium bicarbonate waters representative of the unconfined part of the aquifer.

Table 1. Analytical Data for Solutions Used in the Central Oklahoma Aquifer Example

Analyte	Solution 1	Solution 2	Brine	Solution 3
*p*H	7.38	7.21	5.5	9.07
Ca	1.34	1.65	430	0.03
Mg	1.32	1.62	190	0.02
Na	0.06	0.06	4990	8.27
K	0.01	0.01	0	0.01
Si	0.30	0.30	0	0.16
TDIC	5.54	7.16	0	7.22
SO_4	0.13	0.13	0	0.14
Cl	0.07	0.07	6230	0.31
Al	0	0	0	0
$\delta^{13}C$	−14 ± 3	−14 ± 3	···	−10.7 ± 1

All data are in millimoles per kilogram of water, except *p*H and $\delta^{13}C$. TDIC, total dissolved inorganic carbon; $\delta^{13}C$, carbon 13 composition of TDIC in per mil relative to Pee Dee belemnite (PDB); ±, uncertainty limit assigned in inverse modeling. Uncertainty limit for *p*H was 0.05, uncertainty limit for all other data was 5% of value.

Parkhurst et al. [1996] demonstrated that the range in chemical composition of the calcium magnesium bicarbonate waters is primarily the result of evaporation of rainwater, influx of varying amounts of carbon dioxide in the soil zone, and reaction of calcite and dolomite. The most important factor determining the chemical composition of the waters is the amount of carbon dioxide that enters the aqueous solution as it passes through the unsaturated zone. The two calcium magnesium bicarbonate solutions used in this example (Table 1, solutions 1 and 2) were generated by *Parkhurst et al.* [1996, Table 10] by using the program PHREEQE [*Parkhurst et al.*, 1980] to simulate the addition of 3.0 and 4.0 mmol of carbon dioxide to evaporated rainwater, followed by equilibration with calcite and dolomite. The concentration of silica in the two simulated waters is the mean of silica concentrations in recharge-water samples from the aquifer. The concentrations of chloride, sodium, and sulfate are 10 times rainwater values and are based on the estimated range of evapotranspiration factors for the aquifer [*Parkhurst et al.*, 1996]. Isotopic values for solutions 1 and 2 are based on isotopic data from recharge-water samples.

A simplified brine composition (Table 1) that is typical of the most concentrated brines found in deep formations in central Oklahoma is used as a source of chloride in the aquifer. Even though fluid flow should have been sufficient to remove brines from the active flow system in the aquifer, it is assumed that water similar to this brine is available in fluid inclusions and very impermeable siltstones in the parts of the aquifer in which the sodium bicarbonate water evolves. A typical sodium bicarbonate water from the aquifer [*Parkhurst et al.*, 1996, sample number 34, Table 8] was selected to represent the net result of geochemical reactions in the aquifer (Table 1, solution 3).

Optical and scanning electron microscope evidence and cation exchange measurements [*Breit et al.*, 1990; *Parkhurst et al.*, 1996] suggest that the primary reactants in the aquifer are calcite, dolomite, silica, kaolinite, chlorite, potassium feldspar, plagioclase, cation-exchanging clays, and gypsum. The stoichiometries and dissolution constraints that were used for these minerals are listed in Table 2. The constraints were determined on the basis of mineral textures and saturation indices for the minerals. As a simplification, the cation exchange reaction was assumed to exchange sodium for calcium and magnesium, with a calcium to magnesium ratio of 1:1. The calcium to magnesium ratio is consistent with the exchangeable cation data for clays from the aquifer [*Parkhurst et al.*, 1996], which show ratios of approximately 1:1 to 2:1.

The uncertainty limits assigned to the chemical and isotopic data include contributions from analytical, sampling, and spatial uncertainties. Replicate samples from the central Oklahoma aquifer indicate that the combination of analytical uncertainty and sampling uncertainty is relatively small, plus or minus 1 to 2%. Spatial uncertainty was estimated from five pairs of deep wells; each pair was from the same well field, of similar depth, and separated by less than a kilometer horizontally. The median fractional uncertainty ($|(\nu_1 - \nu_2)/(\nu_1 + \nu_2)|$, where ν represents the sample values for the two wells) for eight major constituents of water (Ca, Mg, Na, K, alkalinity, Cl, SO_4, SiO_2) from these five pairs of wells was 0.05. In three separate calculations the effect of increasing uncertainty was investigated by assigning uncertainty limits of plus or minus 1, 2, and 5% to all chemical data. Aluminum concentrations are below detection limits in almost all samples from central Oklahoma, so aluminum concentrations were assumed to be essentially zero. For all calculations the uncertainty limit for *p*H was arbitrarily set to 0.05 units, which is approximately the measurement uncertainty. On the basis of the range of $\delta^{13}C$ measurements in recharge waters, sodium-bicarbonate waters, and in calcite and dolomite [*Parkhurst et al.*, 1996] the uncertainty limits for $\delta^{13}C$ were specified to be 3‰ for the initial solutions, 1‰ for the final solution, and 1‰ for dolomite and calcite (Tables 1 and 2). PHREEQC was used to determine only the simplest, or minimal models for each of the three levels of uncertainty in the chemical data (1, 2, and 5%).

Results and discussion. The mole-balance modeling calculations allowed the two calcium bicarbonate waters to mix with the brine and react with the specified phases to produce the sodium bicarbonate water. Concentrations of bicarbonate, which is the dominant anion in the system, are roughly the same in initial waters and the final water. Thus the main effect of the reactions is to vary the cation composition. Calcite, dolomite, chlorite, plagioclase, and cation-exchange mole transfers all interact to produce the calcium, magnesium, and sodium concentrations in the final water. Because dissolved aluminum concentrations are negligible, any aluminum produced by the dissolution of feldspars and chlorite must precipitate as kaolinite. Similarly, any silicon produced by dissolution reactions (and some dissolved silica from the initial solutions) must precipitate in kaolinite and the silica phase. The mixing

Table 2. Chemical Formula for Each Reactant in the Central Oklahoma Aquifer Example

Reactant	Formula	Constraint	$\delta^{13}C$
Calcite	$CaCO_3$	dissolve	−8.0 ± 1
Dolomite	$CaMg(CO_3)_2$	dissolve	−9.0 ± 1
Silica	SiO_2	none	
Kaolinite	$Al_2Si_2O_5(OH)_4$	none	
Chlorite	$Mg_5Al_2Si_3O_{10}(OH)_8$	dissolve	
K feldspar	$KAlSi_3O_8$	dissolve	
Plagioclase	$Ca_{0.4}Na_{0.6}Al_{1.4}Si_{2.6}O_8$	dissolve	
Cation exchange	$Ca_{0.5}Mg_{0.5}/Na_2$	dissolve	
Gypsum	$CaSO_4 \cdot 2H_2O$	none	

Formula for plagioclase corresponds to An40. Positive mole transfer for exchange causes calcium and magnesium to decrease and sodium to increase in solution. Here $\delta^{13}C$, carbon 13 composition in per mil relative to PDB; ±, uncertainty assigned in inverse modeling.

Table 3. Mole-Balance Results for the Central Oklahoma Aquifer Example

Calculation	Mixing Fraction			Mole Transfer, mmol/kg H_2O								
	Solution 1	Solution 2	Brine	Calcite	Dolomite	SiO_2	Kaolinite	Chlorite	K Feldspar	Plagioclase	$Ca_{0.5}Mg_{0.5}/Na_2$ Exchange	Gypsum
						Group 1						
NETPATH A	0.66	0.34	0.00004	···	0.57	−0.14	−0.006	0.006	0.0002	···	4.01	0.005
1% uncertainty	0.63	0.37	0.00004	···	0.55	−0.14	−0.0001	···	0.0002	···	3.97	0.004
2% uncertainty	0.63	0.37	0.00004	···	0.54	−0.14	···	···	···	···	3.95	0.005
5% uncertainty	0.63	0.37	0.00004	···	0.54	−0.14	···	···	···	···	3.95	···
						Group 2						
NETPATH B	0.23	0.77	0.00004	0.43	···	−0.23	−0.09	0.09	0.0002	···	4.01	0.005
1% uncertainty	0.20	0.80	0.00004	0.40	···	−0.23	−0.09	0.09	0.0002	···	3.97	0.005
2% uncertainty	···	1.0	0.00004	0.34	···	−0.22	−0.08	0.08	···	···	4.01	0.005
5% uncertainty	···	1.0	0.00004	0.36	···	−0.23	−0.09	0.09	···	···	4.01	···
						Group 3						
NETPATH C	···	1.0	0.00004	0.06	···	−0.87	−0.45	0.06	0.0002	0.55	3.84	0.005
NETPATH D	···	1.0	0.00004	···	0.03	−0.92	−0.48	0.06	0.0002	0.60	3.83	0.005
1% uncertainty	···	1.0	0.00004	···	···	−0.94	−0.49	0.06	0.0002	0.62	3.78	0.005
2% uncertainty	···	1.0	0.00004	···	···	−0.89	−0.46	0.06	···	0.58	3.78	0.005
5% uncertainty	···	1.0	0.00004	···	···	−0.86	−0.44	0.05	···	0.56	3.75	···

Positive numbers for mineral mass transfer indicate dissolution; negative numbers indicate precipitation. For $Ca_{0.5}Mg_{0.5}/Na_2$ exchange, positive mole transfer causes calcium and magnesium to decrease and sodium to increase in solution.

fraction of brine is determined solely by the chloride concentration in the final water, which is relatively small. The mole transfer of gypsum is determined solely by the sulfate concentration in the final water, which also is relatively small.

With the limited number of phases and the multiple constraints for dissolution of phases (Table 2) that were identified by scanning electron and optical microscopy, it is possible to find only four unique models with NETPATH. In two of the models (A and B) the two initial solutions mix with the brine and react with additional phases to produce the final solution. In the other two models (C and D) only the second initial solution mixes with the brine and reacts with additional phases. Calculations with the modified version of PHREEQC produce three sets of minimal mole-balance models, and the results in Table 3 are separated into three groups corresponding to PHREEQC models. The phases in NETPATH models in each group are supersets of the phases in the PHREEQC models for that group.

The first group of models contains NETPATH model A and three PHREEQC models, one for each of the specified uncertainty levels for chemical data, 1, 2, and 5%. The distinguishing feature of these models is a relatively large mole transfer of dolomite. All these models indicate a mixture of approximately two-thirds initial solution 1, one-third initial solution 2, and a small fraction (0.00004) of the concentrated brine. In NETPATH model A, dolomite dissolves (0.57 mmol/kg H_2O), and calcium and magnesium exchange for sodium (4.01 eq/kg H_2O). In addition, small amounts of chlorite, K feldspar, and gypsum dissolve (0.006, 0.0002, and 0.005 mmol/kg H_2O) while silica and kaolinite precipitate (−0.14 and −0.006 mmol/kg H_2O).

The PHREEQC results are very similar for the mixing fractions and for the phases that have large mole transfers, including dolomite. However, the small mole transfers have varying degrees of significance. With a 1% uncertainty limit (adjustments to the chemical data must be 1% or less), chlorite can be eliminated, and the kaolinite mole transfer can be reduced almost to zero. With a 2% uncertainty limit, kaolinite, chlorite, and K feldspar can be eliminated. With a 5% uncertainty limit, kaolinite, chlorite, K feldspar, and gypsum can be eliminated. Thus, with uncertainties of plus or minus 5%, which are within the range of spatial uncertainty estimated for the aquifer, the simplest dolomite-containing model requires a mixture of solution 1, solution 2, and the brine plus only three additional reactions: cation exchange, dissolution of dolomite, and precipitation of silica.

The second group of results (Table 3) is similar to the first group, except that calcite is a major reactant in place of dolomite. The PHREEQC results with a 1% uncertainty limit are very similar to the results of NETPATH model B. The minor differences are due to the charge-balance constraints included in the PHREEQC formulation. With a 2% uncertainty limit, solution 1 and K feldspar can be eliminated. With a 5% uncertainty limit, gypsum also can be eliminated. Thus, with a 5% uncertainty limit the simplest calcite-containing model requires a mixture of solution 2 and the brine plus cation exchange, dissolution of calcite and chlorite, and precipitation of silica and kaolinite.

In the third group of results (Table 3), NETPATH models C and D mix only solution 2 with the brine and have a relatively large mole transfer of plagioclase. Even with as little as a 1% uncertainty limit the small mole transfers of calcite or dolomite included in the NETPATH models are eliminated in the PHREEQC model. With a 2% uncertainty limit, K feldspar can be eliminated, and with a 5% uncertainty limit, gypsum also can be eliminated. Thus, with a 5% uncertainty limit the simplest plagioclase-containing model requires a mixture of solution 2 and the brine plus cation exchange, dissolution of chlorite and plagioclase, and precipitation of silica and kaolinite.

The NETPATH or PHREEQC models in each group account for the aqueous $\delta^{13}C$ data if the $\delta^{13}C$ values of the initial solutions are approximately −11‰, which is within the range observed in recharge samples from the aquifer. The mole transfer of carbon-bearing minerals is not large enough in any of the models to affect significantly the isotopic composition of the aqueous solution. Any of the models of either NETPATH or PHREEQC are plausible reactions for the central Okla-

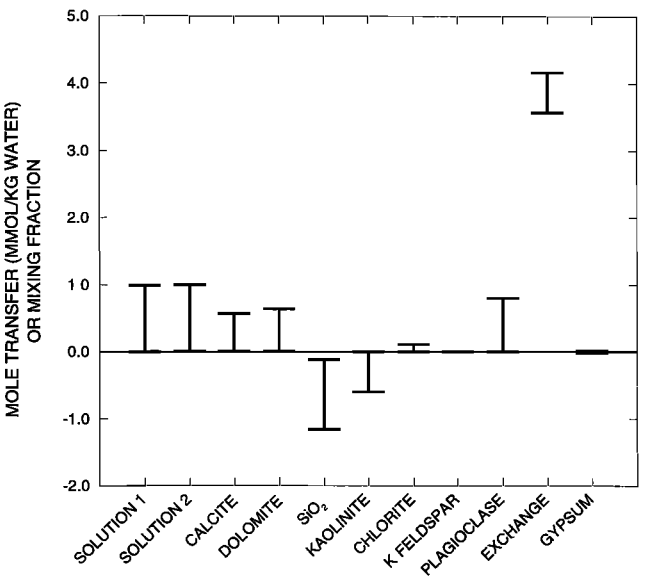

Figure 1. Maximum range of mixing fractions of aqueous solutions and mole transfers of phases for example 1, the central Oklahoma aquifer. Ranges are calculated with 5% uncertainty limits for chemical data. Other uncertainty limits and dissolution/precipitation constraints on the phases are noted in Tables 1 and 2.

homa aquifer, because they are consistent with the chemical, isotopic, and microscopic data for the aquifer. The models that include dolomite are preferred because of the prevalence of dolomite relative to calcite [*Parkhurst et al.*, 1996] and the greater reactivity of dolomite relative to silicates. However, linear combinations of each of the end-member models are plausible; a new model containing dolomite, calcite, and (or) plagioclase may be constructed by summing fractions of the end-member models, provided the sum of the fractions is equal to 1.0.

The revised mole-balance formulation can be used to determine the maximum and minimum values of mixing fractions and mole transfers that can be attained within specified uncertainty limits. The calculated range of values provides additional information about the significance of mixing fractions and mole transfers. The maximum and minimum values for example 1 were calculated by using an uncertainty limit of 5% for all chemical data (other uncertainty limits are those given in Tables 1 and 2) and allowing the reaction of all solutions and phases simultaneously (Figure 1). The NETPATH and minimal model PHREEQC results alone indicate that the mixing fraction of solution 2 could range from 0.34 to 1.0 (Table 3); however, the range calculation indicates that it is possible to find models with a very small mixing fraction for solution 2 (less than 0.01) with adjustments to the chemical data of 5% or less. Thus, in this problem it is not possible to determine the mixing fractions of solutions 1 and 2 with assurance if an uncertainty limit of 5% in the chemical data is accepted.

In contrast, the mixing fraction of brine and the mole transfers of some of the phases are well constrained within the specified uncertainty limits. The mixing fraction of brine is too small to show on Figure 1 but is approximately 0.00004. This mixing fraction can vary by only about 10% because of the uncertainty limits that were specified for chloride (plus or minus 5%). The only reactions that are required in all models are cation exchange and precipitation of silica. Cation exchange is approximately 4 mmol/kg H_2O, regardless of other reactions. Silica precipitation is at least 0.1 mmol/kg H_2O but may be greater if chlorite or plagioclase dissolve to a significant extent. Similarly, kaolinite precipitation may vary from 0 to 0.6 mmol/kg H_2O, depending on the extent of chlorite and plagioclase dissolution. Dissolution of up to 0.57 mmol of calcite or 0.64 mmol of dolomite dissolution is consistent with the uncertainty limits and with the microscopic data, but neither are essential reactants in all mole-balance models. Gypsum and K feldspar dissolution are negligible.

The primary use of the range calculation of the revised mole-balance formulation is to assess the significance of mixing fractions and mole transfers. Some apparently small mole transfers (silica in group 1; silica, kaolinite, and chlorite in group 2; chlorite in group 3) are found to be essential reactants within the specified uncertainty limit of 5%. However, the range calculation shows that the mixing fractions of solutions 1 and 2 can not be determined with assurance, and many of the mole transfers of phases required in the NETPATH models (kaolinite, chlorite, K feldspar, and gypsum in NETPATH A; K feldspar and gypsum in NETPATH B; and calcite, dolomite, K feldspar, and gypsum in NETPATH C and D (Table 3) can be shown to be insignificant by the PHREEQC calculations. For all three groups of models the revised formulation leads to simpler models that require fewer phases to explain the predominant geochemical reactions. The simplest model requires a mixture of solutions 1 and 2 with the brine plus only three additional reactions: cation exchange, dolomite dissolution, and silica precipitation. The simple models do not rule out the possibility of more complex reactions; for example, the NETPATH models are more complicated but are still reasonable geochemical reactions. Furthermore, the simpler the model calculated by PHREEQC, the greater the deviation from the original analytical data. However, if the principle of Occam's razor is accepted, that the simplest explanations are the best, then the revised formulation of mole-balance modeling, with a search for minimal models, provides a method to determine objectively the simplest geochemical reactions that explain the chemical and isotopic data within specified limits of uncertainty.

Application to the Madison Aquifer

In this example the revised mole-balance formulation, including isotope mole balance, is applied to the evolution of a water sample in the Madison aquifer in Montana. *Plummer et al.* [1990] used mole-balance modeling to quantify the extent of dedolomitization at locations throughout the aquifer. In the dedolomitization process, anhydrite dissolution causes the precipitation of calcite and dissolution of dolomite. Additional reactions identified by mole-balance modeling include sulfate reduction, cation exchange, and halite and sylvite dissolution [*Plummer et al.*, 1990]. The $\delta^{13}C$ and $\delta^{34}S$ data were used to corroborate the mole-balance models, and carbon 14 was used to estimate groundwater ages [*Plummer et al.*, 1990]. Initial and final water samples were selected from a flow path that extends from north central Wyoming northeast across Montana [*Plummer et al.*, 1990, flow path 3]. This pair of water samples was selected specifically because it was one of the few pairs that showed a relatively large discrepancy between previous mole-balance approaches and the revised mole-balance approach; results for most sample pairs were not significantly different between the two approaches. In addition, this pair of samples

Table 4. Analytical Data for Solutions Used in the Madison Aquifer Example

Analyte	Solution 1	Solution 2
Temperature, °C	9.9	63.0
*p*H	7.55	6.61
Ca	1.20	11.28
Mg	1.01	4.54
Na	0.02	31.89
K	0.02	2.54
Fe(II)	0.001	0.0004
TDIC	4.30	6.87
SO_4	0.16	19.86
H_2S	0	0.26
Cl	0.02	17.85
$\delta^{13}C$	-7.0 ± 1.4	-2.3 ± 0.2
$\delta^{34}S$(VI)	9.7 ± 0.9	16.3 ± 1.5
$\delta^{34}S$(-II)	...	-22.1 ± 7.0
^{14}C	52.3	0.8
Charge balance	+0.11	+3.24

Charge balance is milliequivalents per kilogram of water. All other data are in millimoles per kilogram of water, except *p*H, $\delta^{13}C$, $\delta^{34}S$, and ^{14}C. TDIC, total dissolved inorganic carbon, $\delta^{13}C$, carbon 13 composition of TDIC in per mil relative to PDB; $\delta^{34}S$(VI), sulfur 34 composition of sulfate in per mil relative to Cañon Diablo Troilite (CDT); $\delta^{34}S$(-II), sulfur 34 composition of total sulfide in per mil relative to CDT; ^{14}C, carbon 14 composition in percent modern carbon; ±, uncertainty assigned in inverse modeling. Uncertainty limit for *p*H was 0.1, uncertainty limit for all other data was 5% of value, except iron, which was 100%.

was selected because it was modeled in detail in *Plummer et al.* [1990] to determine the sensitivity of mole-balance results to various model assumptions and because it was used as an example in the NETPATH manual [*Plummer et al.*, 1994, example 6].

Water compositions and reactants. The initial water for mole-balance modeling (solution 1, Table 4) is the water identified as the recharge water for flow path 3 [*Plummer et al.*, 1990]. This calcium magnesium bicarbonate water is typical of recharge water in a terrane containing calcite and dolomite. The final water (solution 2, Table 4) is a sodium calcium sulfate water (with significant chloride concentration) (see *Plummer et al.* [1990, Table 1] for Mysse Flowing Well), which has a charge imbalance of +3.2 meq/kg H_2O. The final water also contains measurable sulfide. An uncertainty limit of 5% was assigned to all chemical data, except iron, for the initial water and final water. This uncertainty limit was chosen for the initial water because of spatial uncertainty in the location of a recharge water that is on the same flow path as the final water, and this limit was chosen for the final water because it was near the minimum uncertainty limit necessary to obtain charge balance. Iron was assigned an uncertainty limit of 100% because of the small concentrations. An uncertainty limit of 0.1 unit was assigned to *p*H, which is conservative because of the potential for CO_2 degassing at this sampling site (L. N. Plummer, U.S. Geological Survey, written communication, 1996). The $\delta^{13}C$ values become heavier from the initial water to the final water (−7.0 to −2.3‰), as do $\delta^{34}S$ values (9.7 to 16.3‰). Uncertainty limits for isotopic values of the initial solution were set to half the range in isotopic composition in the four recharge waters from flow paths 3 and 4 [*Plummer et al.*, 1990] (Table 4). Uncertainty limits for isotopic values of the final water were set to half the range in isotopic composition in samples from the distal end of flow path 3 [*Plummer et al.*, 1990] (Table 4).

Reactants considered by *Plummer et al.* [1990] were dolomite, calcite, anhydrite, organic matter (CH_2O), goethite, pyrite, Ca/Na_2 cation exchange, halite, sylvite, and CO_2 gas. In sensitivity calculations, Mg/Na_2 cation exchange and methane were considered as potential reactants. The aquifer was considered to be a closed system with respect to CO_2, and methane gain or loss was considered to be unlikely [*Plummer et al.*, 1990]; therefore, CO_2 and methane were not included as reactants in mole-balance modeling with uncertainty. The uncertainty limits for the isotopic compositions of dissolving phases were taken from data presented by *Plummer et al.* [1990] with slight modifications as follows: $\delta^{13}C$ of dolomite, 1 to 5‰; $\delta^{13}C$ of organic carbon, −30 to −20‰; and $\delta^{34}S$ of anhydrite, 11.5 to 15.5‰. The $\delta^{13}C$ of precipitating calcite depends on the isotopic evolution of the solution and is affected by isotopic fractionation. The fractionation equations are not included in PHREEQC, so it is necessary to assume a compositional range of calcite that represents the average isotopic composition of the precipitating calcite. The average isotopic composition of precipitating calcite from NETPATH calculations was about −1.5‰ [*Plummer et al.*, 1994], and an uncertainty limit of 1.0‰ was selected to account for uncertainties in fractionation factors. The $\delta^{34}S$ of precipitating pyrite was estimated to be −22‰ [*Plummer et al.*, 1990] with an uncertainty limit of 2‰; sensitivity analysis indicated that the isotopic value for the precipitating pyrite had little affect on mole transfers.

Mole-balance calculations included equations for all elements in the reactive phases and an equation for $\delta^{34}S$. NETPATH calculations included isotopic fractionation equations to calculate the $\delta^{13}C$ of the final water, while PHREEQC calculations included a mole-balance equation on $\delta^{13}C$. The adjusted concentrations (original data plus calculated δ values) from the PHREEQC results were rerun with NETPATH to obtain carbon 14 ages and to consider the fractionation effects of calcite precipitation. One NETPATH calculation used the charge-balancing option to identify the effects of charge-balance errors. The charge-balance option adjusts the concentrations of all cationic elements by a fraction f and of all anionic elements by a fraction $1/f$ to achieve charge balance for the solution. (The charge-balance option of NETPATH was improved in version 2.13 to produce an exact charge balance; previous versions produced only an approximate charge balance.)

For all NETPATH calculations (including calculations that used PHREEQC-adjusted concentrations), carbon dioxide was included as a potentially reactive phase, but the $\delta^{34}S$ of anhydrite was adjusted to produce zero mole transfer of carbon dioxide. The $\delta^{13}C$ values of dolomite and organic matter were adjusted within their uncertainty limits to reproduce the $\delta^{13}C$ of the final solution as nearly as possible.

Results and discussion. The predominant reactions determined by mole-balance modeling are dedolomitization, ion exchange, halite dissolution, and sulfate reduction (Table 5). The driving force for dedolomitization is dissolution of anhydrite (about 20 mmol/kg H_2O, Table 5), which causes dolomite dissolution and calcite precipitation. Some of the calcium from anhydrite dissolution and (or) magnesium from dolomite dissolution is taken up by ion-exchange sites, which release sodium to solution. About 15 mmol/kg H_2O of halite dissolves. Oxidation of organic matter by sulfate reduction leads to dissolution of iron oxyhydroxides and precipitation of pyrite.

Plummer et al. [1990] realized that the stoichiometry of the exchange reaction was not well defined and considered two variations on these reactions in the sensitivity analysis of the

Table 5. Mole-Balance Results for the Madison Aquifer Example

Result	Ca/Na_2	Mg/Na_2		$Ca_{0.75}Mg_{0.25}/Na_2$		
	NETPATH A	NETPATH B	PHREEQC B	NETPATH C	NETPATH C' Charge balanced	PHREEQC C
Ca/Na_2 exchange	8.3	...	...	...	...	...
$Ca_{0.75}Mg_{0.25}/Na_2$ exchange	...	...	...	8.3	7.6	8.2
Mg/Na_2 exchange	...	8.3	7.7	...	...	...
Dolomite ($CaMg(CO_3)_2$)	3.5	11.8	11.2	5.6	5.3	5.6
Calcite ($CaCO_3$)	−5.3	−21.8	−23.9	−9.5	−12.3	−12.3
Anhydrite ($CaSO_4$)	20.1	20.1	22.9	20.1	22.5	22.4
CH_2O	0.8	0.8	4.1	0.9	4.3	3.3
Goethite (FeOOH)	0.1	1.0	1.0	0.1	1.0	0.7
Pyrite (FeS_2)	−0.1	−0.1	−1.0	−0.1	−1.0	−0.7
Halite (NaCl)	15.3	15.3	15.3	15.3	15.8	15.3
Sylvite (KCl)	2.5	2.5	2.5	2.5	2.5	2.5
Carbon dioxide (CO_2)	0.0	0.0	...	0.0	0.0	...
^{14}C reaction adjusted	12.3	0.6	0.4	5.7	3.6	3.9
Apparent age, years	22,700	−2,400	−5,400	16,400	12,500	12,600
$\delta^{34}S$ anhydrite	15.6	15.6	12.9	15.6	12.5	13.5
$\delta^{13}C$ dolomite	3.6	1.0	3.5	1.9	5.0	5.0
$\delta^{13}C$, CH_2O	−25.0	−30.0	−20.0	−25.0	−20.0	−20.0
Calculated $\delta^{13}C$, final water	−2.3	−2.2	−2.3	−2.3	−4.3	−2.9
Calculated $\delta^{34}S$, final water	15.8	15.8	16.1	15.8	15.9	16.0

Results are in millimoles per kilogram of water, unless otherwise noted. Here, ^{14}C, carbon 14 in percent modern carbon (pmc); $\delta^{13}C$, carbon 13 in per mil PDB; $\delta^{34}S$, sulfur 34 in per mil CDT; CH_2O, organic matter. Positive numbers for mineral mass transfer indicate dissolution; negative numbers indicate precipitation. For exchange reactions, positive numbers indicate a decrease in calcium and (or) magnesium and an increase in sodium in solution. The $\delta^{34}S$ of pyrite was approximately −22 permil in all models. For comparison to calculated isotopic values, measured $\delta^{13}C$, −2.3‰; measured $\delta^{34}S$ (total), 15.8‰ measured ^{14}C, 0.8 pmc.

mole-balance model. Pure Ca/Na_2 exchange and pure Mg/Na_2 exchange were considered as potential reactants (NETPATH A and B, Table 5). When PHREEQC was run with these two reactants, a model was found with Mg/Na_2 (PHREEQC B), but no model was found with pure Ca/Na_2 exchange. This difference between NETPATH and PHREEQC results is attributed to the charge imbalance of the solutions. Solution 2 (Table 4) has a charge imbalance of 3.2 meq/kg H_2O, which is more than 3% relative to the sum of cation and anion equivalents. This is not an exceptionally large percentage error, but the absolute magnitude in milliequivalents is large relative to some of the mole transfers of the mole-balance models. When the charge-balance constraint is included in the revised mole-balance calculation with pure Ca/Na_2 exchange as the only exchange reaction, it is not possible simultaneously to attain mole-balance on elements and isotopes, produce charge balance for each solution, and keep uncertainty terms within the specified uncertainty limits. The exchange reaction with the largest calcium component for which a model could be found was about $Ca_{0.75}Mg_{0.25}/Na_2$ (PHREEQC C). This exchange reaction was then used in NETPATH to find NETPATH C. NETPATH C' was calculated by using the charge-balance option of NETPATH with all phases and constraints the same as in NETPATH C.

One consistent difference between the NETPATH models without the charge-balance option (NETPATH A, B, and C) and the PHREEQC models is that the amount of organic matter oxidation and the mole transfers of goethite and pyrite are larger in the PHREEQC models. These differences are attributed to the effects of charge balance on the mole transfers. It has been noted that charge-balance errors frequently manifest themselves as erroneous mole transfers of single component reactants, such as carbon dioxide or organic matter [*Plummer et al.*, 1994]. Except for differences in mole transfers in organic matter, goethite, and pyrite, the Mg/Na_2 models are similar (NETPATH B and PHREEQC B). However, both models imply a negative carbon 14 age, which is physically impossible, as noted by *Plummer et al.* [1990].

The PHREEQC model most similar to the pure Ca/Na_2 exchange model (NETPATH A) is the $Ca_{0.75}Mg_{0.25}/Na_2$ model (PHREEQC C). This model has larger mole transfers of carbonate minerals and organic matter than the Ca/Na_2 model, which decreases the reaction-adjusted carbon 14 activity and produces a younger groundwater age, 12,600 (PHREEQC C) compared to 22,700 (NETPATH A) years. This large change in the calculated age can be attributed to the charge-balance error and can be divided into two effects: the change in the exchange reaction and the adjustments for charge-balance errors. The effect of the change in exchange reaction is estimated by the differences between NETPATH A, which contains pure Ca/Na_2 exchange, and NETPATH C, which contains $Ca_{0.75}Mg_{0.25}/Na_2$ exchange, but neither model includes corrections for charge imbalances in the solution compositions. The increase in Mg in the exchange reaction causes larger mole transfers of calcite and dolomite and decreases the calculated age from 22,700 to 16,400 years. The effects of charge-balance errors are estimated by the differences between NETPATH C and C', which differ only in that the NETPATH charge-balance option was used in NETPATH C'. Charge balancing the solutions produces larger mole transfers of organic matter and calcite and decreases the calculated age from 16,400 to 12,500 years. The mole transfers and calculated age for NETPATH C' are similar to PHREEQC C but differ slightly because the uncertainty terms in the PHREEQC model have been distributed to achieve not only charge balance but also to reproduce more closely the observed $\delta^{13}C$ of the final solution.

One advantage of the revised mole-balance formulation is that much of the sensitivity analysis that was formerly done by setting up and running multiple models can now be done by including uncertainty limits for all chemical and isotopic data

simultaneously. For example, one run of the revised mole-balance formulation determines that no pure Ca/Na_2 model can be found even if any or all of the chemical data were adjusted by as much as plus or minus 10%. This kind of information would be very difficult and time-consuming to establish with previous mole-balance formulations. Another improvement in the revised formulation is the explicit inclusion of charge-balance constraints. In this example, including the charge-balance constraint requires a change in the exchange reaction and adjustments to solution composition, which have the combined effect of lowering the estimated maximum age of the groundwater by about 10,000 years. If Mg/Na_2 exchange is a possible reactant, the estimated minimum age may be essentially modern. Thus the estimated range in age is still large, 0 to 12,600 years. However, on the basis of the large calcium to magnesium ratio in solution (2.5:1) and approximately equal cation-exchange constants for calcium and magnesium [*Appelo and Postma*, 1993], a calcium-dominated exchange reaction is more plausible, which is consistent with ages at the older end of the range. Furthermore, comparison with other carbon 14 ages in the aquifer and with groundwater flow model ages also indicates an older age is most reasonable.

Summary and Conclusions

Geochemical mole-balance models describe balanced chemical reactions that account for changes in the chemical and isotopic composition of water along a flow path. A revised mole-balance formulation has been derived that includes an additional uncertainty term for each chemical and isotopic datum. The revised formulation includes the following equations and inequality constraints: mole-balance equations for each element or element redox state, alkalinity, electrons, solvent water, and each isotope; a charge-balance equation and an equation that relates the uncertainty terms for *p*H, alkalinity, and total dissolved inorganic carbon for each aqueous solution; inequality constraints that limit the magnitude of the uncertainty terms; and inequality constraints on the sign of the mole transfer of reactants. The set of equations and inequality constraints is solved by an optimization algorithm that effectively minimizes a weighted sum of the absolute values of the uncertainty terms. Alternatively, the optimization algorithm can be used to determine the ranges of mixing fractions for each aqueous solution and mole transfers for each reactant that are consistent with the specified uncertainty limits. An exhaustive search procedure is employed to find all unique combinations of aqueous solutions and reactants for which the equations and inequality constraints can be solved and the uncertainty terms minimized. A modified search procedure finds only minimal models, which are models such that no model can be found if any one of the aqueous solutions or phases of the model is removed. The mole-balance models that are found with either search procedure are a set of end-members; additional models may be found by linear combinations of these end-members, provided that the coefficients in the linear combination are positive and sum to 1.

By allowing for uncertainty the revised formulation ensures that mole-balance models are robust; that is, small changes to chemical and isotopic data do not cause large changes in the results. The range and minimal model calculations allow systematic evaluation of the significance of mole transfers. In addition, the revised formulation provides an objective means to determine the simplest set of reactions that explain the data within the specified uncertainty limits. In the central Oklahoma aquifer example, if uncertainty is not included, each mole-balance model has seven or more reactants. However, if uncertainty limits for the chemical data are specified to be plus or minus 5%, then the number of reactions can be reduced to as few as three: cation exchange, dolomite dissolution, and silica precipitation.

Inclusion of charge-balance constraints eliminates potentially misleading results due to charge-balance errors in aqueous solution compositions. In the Madison aquifer example, when no corrections are made for charge-balance errors, the mole-balance calculation for one sample that has a large charge imbalance produces a model that includes pure Ca/Na_2 exchange. When charge-balance corrections are made, no model that contains pure Ca/Na_2 exchange is possible; some Mg/Na_2 exchange is necessary. The change in reactant and the correction for the charge imbalance cause significant changes in mole transfers of calcite, dolomite, and organic carbon, which reduce the maximum estimated carbon 14 age for groundwater at this site by about 10,000 years from 22,700 to 12,600 years.

DOS and Unix versions including documentation of the programs PHREEQC (version 1.5) and NETPATH (version 2.13) are available by anonymous ftp from the site brrcrftp.cr.usgs.gov in the directory /geochem or from the World Wide Web site water.usgs.gov. The current version of PHREEQC (1.5) has all the equations of the revised mole-balance formulation described in this report except the isotope mole-balance equations.

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D. L. Parkhurst, U.S. Geological Survey, Box 25046, MS 413, Denver Federal Center, Lakewood, CO 80225. (e-mail: dlpark@usgs.gov)

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