Rule-Based Mineral Sequences in Geochemical Flow Processes

The infiltration of an aqueous solution into a permeable medium generally results in the dissolution of some of the minerals initially present and the possible precipitation of others. When the infiltration velocities are small, as is the case for many natural processes, conditions of local equilibrium apply and the dissolution and precipitation processes exhibit a wave-type behavior reminiscent of chromatographic fronts. Zones of constant composition (state) will be separated by narrow regions within which the aqueous and solid phase concentrations exhibit sharp changes. Because of this wave-like structure, an algebraic solution of the coupled material balance equations exists, but in a form that involves a trial and error solution procedure which has heretofore discouraged its application. This paper describes the essence of a scheme which uses a combination of graph theory and heuristics to minimize trials and thereby render the algebraic solution practical. The scheme offers an alternative to time-sequencing solutions (e.g., finite difference) of the set of partial differential equations.

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Introduction

Metasomatic processes are those which cause the replacement of one or more minerals initially present in a permeable medium by other minerals which precipitate as fluids infiltrate the medium (Korzhinskii, 1970). There are a number of such processes of practical interest, such as the formation of ore bodies (Lichtner, 1985; Walsh, 1983; Lichtner and Helgeson, 1982), the recovery of valuable minerals by *in-situ* leaching (Kabir et al., 1982; Nguyen et al., 1982), the migration of inorganic pollutants in soils (Stohs, 1986), and the injection of caustic for enhanced oil recovery (Walsh, 1983; Walsh et al., 1982; Hekim and Fogler, 1980).

Such precipitation and dissolution processes occurring during reactive flow in permeable media lead to the formation of waves that closely resemble chromatographic phenomena. However, the theories describing the two processes are different because the thermodynamic constraints that apply to dissolution and precipitation are inequalities and the conditions for equilibrium do not include the quantity of solids present (Walsh, 1983). Indeed, only the presence or absence of a particular solid, not the total amount of the solid, is relevant in formulating the equations describing the aqueous phase compositions (Bryant et al., 1987).

One-dimensional problems with constant injection and initial boundary conditions, called Riemann problems, can be solved by fixing the total number of waves present and assuming the identities of the solids included across each wave. Using an algebraic calculation scheme, it is possible to determine whether or not the assumed mineral sequence is the physical solution (Bryant et al., 1987; Bryant, 1986; Walsh et al., 1984). When a physical contradiction occurs during calculation of an assumed sequence, the sequence is rejected and a new one assumed. Testing continues in this fashion until the solution is found.

The set of mathematically possible solid progressions is infinite; thus, an unstructured generate-and-test algorithm is impossible. In order to conduct a systematic, efficient search, we develop rules that permit a significant reduction in the number of candidate solutions to be tested. Some of the rules are exact and subject to mathematical proof. Others are generally true without known contradictions, but not yet proved. Finally, some of the rules are most often true, but admit exceptions. The "expert system" consisting of these rules is implemented using elementary techniques from graph theory. This method for solving precipitation/dissolution problems is unique and represents one significant contribution of this work.

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The calculating procedure we present may be thought to possess a degree of intelligence because the process of calculating and rejecting candidate sequences that are invalid frequently allows rejection of other candidate sequences without their being tested. Thus, data gathered from sequence rejection helps to narrow the list of candidate solutions to be tested in the search for the correct mineral sequence.

Algebraic Calculation Scheme

The algebraic calculation scheme is discussed in detail elsewhere (Bryant et al., 1987; Bryant, 1986; Walsh et al., 1984). We summarize the important points and extensions here.

Previous development

In geochemical processes where precipitation/dissolution reactions dominate (i.e., sorption is negligible), perturbation of a field (with constant initial condition) with an injection fluid of constant composition causes a series of abrupt composition changes, or waves, separating regions of constant composition, Figure 1. The waves propagate with a constant velocity and thus appear as rays emanating from the origin on the distance-time diagram. The number of waves and the mineral identities in each constant-state region (zone), along with initial and injection conditions, completely quantify all compositions and wave velocities. Systems with nonconstant initial or injection conditions, i.e., non-Riemann problems, can be resolved into a series of Riemann problems (Dria, 1988).

The algebraic procedure is derived from an analytical solution of the material balance partial differential equations, with explicit dispersion, which govern the flow. The compositions in each zone are calculated using local equilibrium and rules derived from an analytical solution in the limit of zero dispersion. Two of these rules are the Coherence Condition, and the Downstream Equilibrium Condition (Bryant, 1986).

Local equilibrium stipulates that all species exist in equilibrium concentrations at each point in the medium. This means especially that the aqueous phase is in equilibrium with the solid(s) present at each point in space. The Coherence Condition is a statement of the weak (integral) flux-matching conditions across each precipitation/dissolution shock wave. The Coherence Condition states that each chemical component of the shock travels with the same specific velocity v_n given by

$$v_n = \frac{1}{1 + D_n} \tag{1}$$

where D_n is a delay factor given by

$$D_n = \frac{\Delta_n \bar{E}_i}{\Delta_n E_i} \tag{2}$$

In Eq. 2, $\Delta_n \bar{E}_i$ is the change in total solid phase concentration of element i across the nth wave and $\Delta_n E_i$ is the change in total aqueous phase concentration of element i across the nth wave. The Downstream Equilibrium Condition (DEC) states that the aqueous phase downstream of the nth wave is in equilibrium with (all) the solids in the region immediately upstream of the nth wave. The DEC is a direct consequence of concentration matching conditions at the wave front (with explicit dispersion) and the fact that the aqueous compositions are constant downstream of each wave.

The algebraic method is a two-pass procedure in which all aqueous compositions are calculated before any solid compositions are calculated. The identity of solid(s) in each zone must

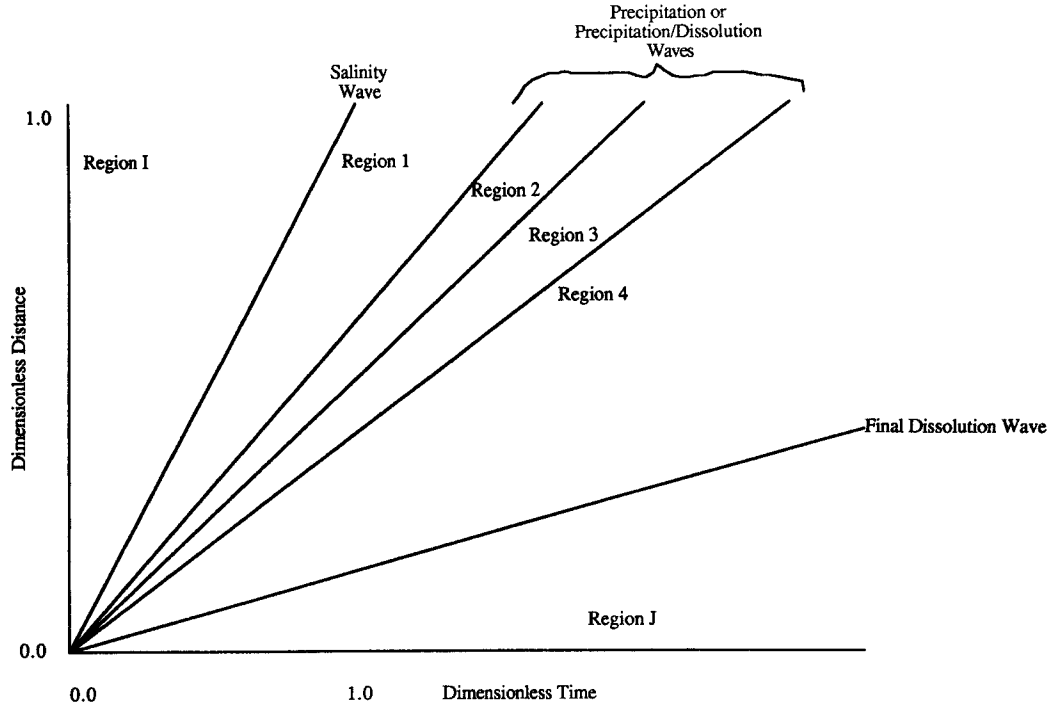

Figure 1. Distance-time diagram.

be known before any calculation can be performed. For example, in Figure 1, we must know which solids are in Regions 2, 3, and 4 before applying the algebraic method. (The solids in Region 1 are present in the same concentration as in Region I; these zones are separated by a salinity wave.)

Since, in general, the initial and injection conditions and equilibrium data are known, the number of waves and the minerals present between each wave are the only unknowns. Such specification allows a straightforward algebraic calculation of the aqueous composition in each of the constant-state regions, followed by an algebraic determination of the solid concentrations and wave velocities (Bryant, 1986; Walsh et al., 1984).

Extension

We have extended this theory to include intraaqueous reactions following the Mass Action model. While adding only superficial numerical complexity, this extension broadens the "sibling" relationship of solids previously associated with this theory. It was previously asserted that, in a precipitation/dissolution wave, the precipitating solid(s) and the dissolving solid must have a common ion, the so-called sibling relationship. This constraint must be relaxed, however, because most anions and cations that form ionic solids are weak acids or conjugate bases of weak acids and thus the concentration of essentially all aqueous species are interrelated through the solution pH. Analogous arguments hold for redox equilibria where relationships through water and redox chemistry lead to the conclusion that, in general, any solid may precipitate when another dissolves. The interaction of ions liberated by a dissolving solid may therefore cause an increase in the concentration of apparently unrelated ions resulting in the precipitation of another solid.

By way of illustration, it might appear that the dissolution of $MgCO_{3(s)}$ should not cause $CaSO_4 \cdot 2H_2O_{(s)}$ to precipitate. However, intra-aqueous reactions connect the behavior of the four primary ions involved. The representative reactions

$$MgCO_{3(s)} = Mg^{++} + CO_3^-$$
$$CO_3^- + HSO_4^- = HCO_3^- + SO_4^-$$
$$Mg^{++} + CaOH^+ = MgOH^+ + Ca^{++}$$
$$Ca^{++} + SO_4^- + 2H_2O = CaSO_4 \cdot 2H_2O_{(s)}$$

demonstrate that dissolution of $MgCO_{3(s)}$ may increase the concentration of Ca^{++} and SO_4^- and cause $CaSO_4 \cdot 2H_2O_{(s)}$ to precipitate. Other factors, such as the buffering capacity of a particular system, the solution pH, and the total aqueous calcium concentration control the extent to which the calcium cation and sulfate anion concentrations increase. Nevertheless, $MgCO_{3(s)}$ must be considered to be related to $CaSO_4 \cdot 2H_2O_{(s)}$ despite the fact that a cursory examination may not reveal the connections between the two.

Outline of Solution Scheme

The solution procedure based on these results is outlined as follows.

1. Assume the number of constant state zones.
2. Assume identities of the solids that appear in each zone.
3. Calculate the aqueous phase composition in each region, starting at the known injected aqueous composition (Bryant, 1986).
4. Calculate the solid phase concentrations across each wave, given all aqueous phase concentrations, starting with the known initial solid compositions (Bryant, 1986).
5. Examine the solution for physical reality and discard if nonphysical. Criteria for physical acceptability include: all concentrations must be nonnegative; the wave velocities must decrease monotonically with the fastest wave furthest downstream; all solubility product expressions must be satisfied in every region; and at least one element must change in total concentration across each wave (a consequence of Riemann problems).
6. If the correct answer has not been found, assume a new mineral sequence and return to step 2.

As stated earlier, determining the proper solid sequence is the remaining difficulty in this approach. In a sense it appears that one must know the answer before it can be calculated. The purpose of this paper is to define a workable procedure whereby the correct solid sequence can be selected from the infinite set of possible solid sequences.

Identifying Candidate Solid Sequences

To make the procedure more concrete and understandable, a simple system composed of the three solids calcite ($CaCO_3$), magnesite ($MgCO_3$), and gypsum ($CaSO_4 \cdot 2H_2O$) will illustrate the process.

Random search

One possible approach to finding the correct mineral sequence is a random search. This involves generating and testing sequences in an arbitrary manner. Such a procedure is not feasible since the set of all possible solid sequences is unbounded even though the number of solids which may appear is finite. It is essential to reduce the set of solid sequences to be tested to a manageable number that will include the correct solution.

Rule-based search

Heuristic rules and graph theory allow efficient generation of a list of solid sequences, which becomes progressively smaller as more rules are included. Application of various rules allows reduction of set size, depicted schematically in Figure 2. The progressive reduction is based on rules that

1. provide a bounded search space,
2. eliminate nonphysical sequences,
3. eliminate sequences with incorrect initial and injected conditions, and
4. allow an "intelligent" search of the remaining sequences.

These reductions correspond to the sets of Figure 2, from largest to smallest, respectively. For the calcite-magnesite-gypsum example problem, the number of sequences in each set are (∞, 109,600, 93, 18, 18, and 1).

The heuristically-guided search tests sequences one at a time. When a sequence is rejected, other sequences that have a parallel structure are also rejected, without algebraic calculation. This search is depicted as a dashed circle in Figure 2 to emphasize that the number of candidate sequences remaining to be tested shrinks as the search proceeds, both because of numerical calculation and heuristic elimination of sequences. The heuristically-guided search is performed at run time and is highly dependent upon equilibrium data and the injected condition of each problem.

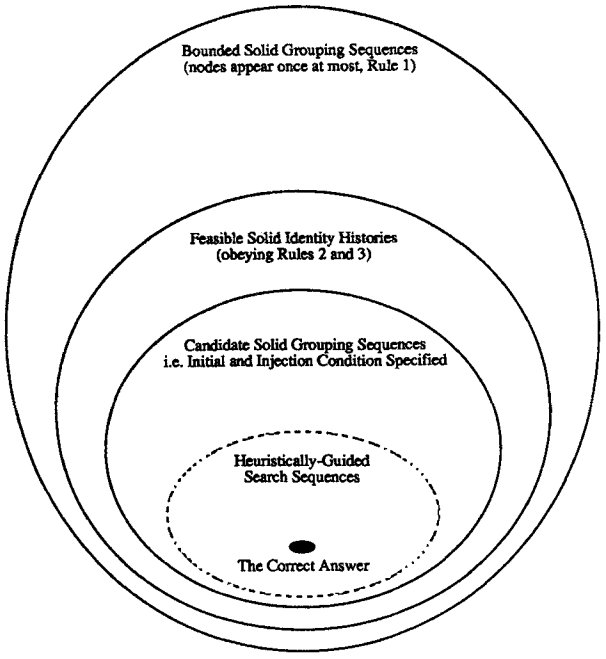

Figure 2. Subsets of unbounded solid grouping sequence space.

Definitions

Solid groupings

A grouping is a set of solid identities. Each region of constant state consists of one such grouping. All possible groupings can be determined with combinatorics. Including the empty set, there are

$$N = \sum_{i=0}^{K} \frac{K!}{(K-i)!\,i!} = 2^K \tag{3}$$

groupings for a problem in which K solids may appear. These are generated by taking K solids 0 at a time, K solids 1 at a time, etc. The example problem has $K = 3$ solids and $N = 2^3 = 8$ groupings. These eight groupings are shown in Table 1.

Grouping sequences

A grouping sequence is an ordered collection of solid groupings. Such sequences are listed here as histories, thus the grouping furthest downstream (i.e., initial grouping) is leftmost. For example, G6-G7-G4-G1, Table 1, represents a history in which magnesite and gypsum (G6) precede calcite and gypsum (G7), followed by gypsum (G4) and the null set (G1).

Table 1. Solid Groupings for the Calcite-Magnesite-Gypsum Problem

Character Symbol	Solid Identities		
1	—	—	—
2	Magnesite	—	—
3	—	Calcite	—
4	—	—	Gypsum
5	Magnesite	Calcite	—
6	Magnesite	—	Gypsum
7	—	Calcite	Gypsum
8	Magnesite	Calcite	Gypsum

The set of grouping sequences contains all such progressions and is unbounded (e.g., sequences such as {C}-{M}-{C}-{M}- . . . are not excluded). A bounded list of sequences can be generated by allowing each solid grouping to appear once at most (see Rule 1 below). The bounded list containing all possible grouping arrangements could be determined with combinatorics. Disallowing repeated groupings, there are

$$N_S = \sum_{i=1}^{N} \binom{N}{i} \times i! = \sum_{i=1}^{N} \frac{N!}{(N-i)!} \tag{4}$$

grouping sequences for an N-grouping problem. For a three-solid problem, $N = 8$, and

$$N_S = 8 + 8 \times 7 + 8 \times 7 \times 6 + \ldots + 8! = 109{,}600 \tag{5}$$

The $N_S = 109{,}600$ grouping sequences for a three-solid problem would all be generated with a strictly combinatoric approach and all would need to be examined until the correct answer is found. Solid grouping sequences are generated without considering initial and injected conditions.

Feasible solid histories

Feasible histories are a rule-based subset of solid grouping sequences that represent all potential solutions to the problem of interest. Solid histories are generated without specification of initial conditions, injected conditions, or equilibrium data. Thus, the set of feasible histories contains every grouping sequence that obeys the rules developed below. This set can be considered to represent all problems that contain the specified chemical species and elements.

Rules for Identification of Feasible Histories

The following rules, which are based on both precise physical laws and intuitive arguments, reduce the set of grouping sequences to the set of feasible solid histories.

Rule 1. A solid grouping may not appear more than once in the same sequence.

Rule 2. One and only one solid must dissolve completely across each wave but any number (including zero) solids may precipitate.

Rule 3. If the solids present in region $i - 2$ are a subset of the union of the solids in regions i and $i - 1$, no change in aqueous composition will occur between the i-1th and i-2th regions and thus the sequence is invalid. Mathematically, this invalidating relationship can be expressed as

$$\{S_{i-2}\} \in \{S_i \cup S_{i-1}\} \tag{6}$$

Rule 1 is empirical at present. We have found no contradiction to this rule but have been unable to prove it. This rule imposes a maximum on the number of solid sequences by limiting the number of groupings possible in a sequence. This heuristic rule states that a solid sequence can have up to, but not more than, N groupings, defined in Eq. 3. Note that this does not prevent a particular solid from dissolving completely at one wave and precipitating at another wave further upstream.

Rule 2, while not susceptible to rigorous mathematical proof,

does have a sound physical basis. If a solid partially dissolves (region i) and any number of solids precipitate (region $i + 1$) the solids in region i are a subset of the solids in region $i + 1$ and thus no change in aqueous concentration can occur. Since there must be a change in the aqueous concentration of at least one element at each wave, one solid must dissolve completely. It is possible for two solids to dissolve at a single wave, but this is improbable because the solids must be present in a mathematically precise ratio for this to happen. At ratios infinitesimally different, the solids must dissolve in distinct waves.

Some problems include waves that may superficially violate Rule 2 (double-discontinuity waves). Fortunately, such cases have a degenerate wave structure, which is simply obtainable from sequences that follow Rule 2. Though infrequent, these double-discontinuity waves may prove to be important in physical processes and are discussed elsewhere (Bryant, 1986; Dria, 1988).

Rule 3 is a mathematically-provable consequence of Riemann boundary conditions. It represents the only "nonlocal" rule; that is, it is a rule that applies not to adjacent groupings but to collections of three groupings. We demonstrate Rule 3 in the Appendix for a simple problem and apply this to all cases using induction and analogy.

Graph Representation

Solid groupings and the allowed transitions between groupings can be conveniently represented in a graph, as shown in Figure 3, for the calcite-magnesite-gypsum example. Each node (circle) stands for a solid grouping and each directed line segment (arrow) connects the nodes as dictated by Rule 2. Rules 1 and 3 cannot be incorporated in such graphs.

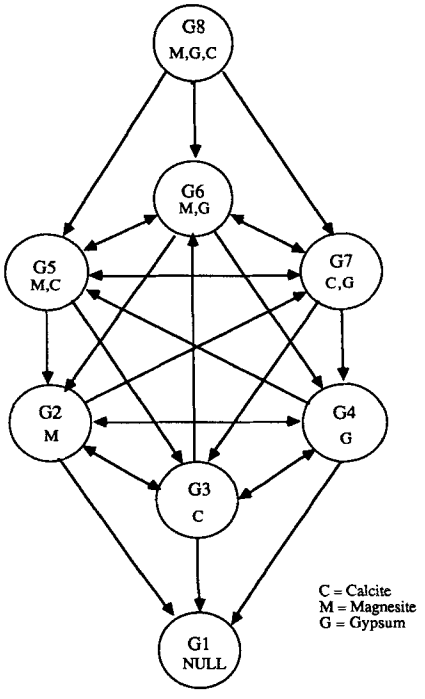

Figure 3. Representation of adjacency for the calcite-magnesite-gypsum problem.

Graph for the calcite-magnesite-gypsum problem

The graph for the calcite-magnesite-gypsum (C-M-G) system, Figure 3, is interpreted as follows. Each permitted transition from grouping to grouping is represented by an arrow; a double-headed arrow indicates that transition is permitted in both directions. For example, the arrow pointing from G5 to G6 indicates that the order {M, C}-{M, G}, with calcite dissolving and gypsum precipitating, is allowed. (This is a history; flow is toward the left.) Since the arrow also points in the opposite direction, the reverse transition is also allowed. Rule 2 is satisfied in either case since only one solid dissolves. There is no directed line segment from node G7 to node G1 because the progression {C, G}-{ } designates a case in which two solids dissolve at one wave, a situation precluded by Rule 2. An arrow does point from G5 to G2 because, for {M, C}-{M}, one solid dissolves. However, no arrow points from G2 to G5 ({M}-{M, C}) because a solid would precipitate when no solid dissolves.

Adjacency Matrix

The adjacency matrix is a mathematical description of a graph. As such, it embodies all the rule-permitted single-wave histories (histories with two groupings) of the graph. Manipulation of this matrix using well-defined mathematics yields the set of all feasible solid histories, i.e. all sequences that follow the Rules.

Character adjacency matrix

The character adjacency matrix (CAM) for the C-M-G problem, Table 2, mathematically expresses the adjacency, or connectivity, of the groupings from the graph representation (Bellman et al., 1970). For our purposes, two groupings are adjacent when it is possible to go directly from the first to the second grouping, following rule 2, or, equivalently, following an arrow in Figure 3. This matrix explicitly shows which groupings can appear immediately upstream of another grouping. A nonnull element in row i, column j indicates that node i and node j are adjacent, i.e., that node i is connected by a directed line segment to node j, or equivalently that rules permit transitions from node i to node j.

Each nonnull element in the CAM stands for a permitted transition; disallowed transitions contain the empty set, designated by '--' or '0'. The ordered pair in each non-null element of the CAM is mapped to the corresponding row and column indices of the matrix, which in turn designate groupings. The adjacency matrix is asymmetric due to the direction-specific nature of the rule 2.

Table 2. Character Adjacency Matrix for the Calcite-Magnesite-Gypsum Problem

	1	2	3	4	5	6	7	8
1	—	—	—	—	—	—	—	—
2	21	—	23	24	—	—	27	—
3	31	32	—	34	—	36	—	—
4	41	42	43	—	45	—	—	—
5	—	52	53	—	—	56	57	—
6	—	62	—	64	65	—	67	—
7	—	—	73	74	75	76	—	—
8	—	—	—	—	85	86	87	—

Illustration of connectivity in the CAM

For the example considered here, each non-null element in Table 2 contains a character label which represents one of the directed line segments of Figure 3. The character symbol representing a pair of groupings is the same as the pair of grouping numbers in Table 1.

Consider row 6 for the CAM for the calcite-magnesite-gypsum problem, Table 2. The non-null elements are '62', '64', '65', and '67'. (The single quotes mean that these are characters, not numbers.) Row 6 lists the possible progression from grouping 6 (G6) as G6-G2, G6-G4, G6-G5, and G6-G7. These correspond to arrows from G6 in the graph representation for the calcite-magnesite-gypsum problem, Figure 3.

Procedure for Identifying Permissible Multiwave Histories

Multiwave histories, or histories with more than two solid groupings, can be determined by operating on the character adjacency matrix. This matrix is concatenated with itself in a manner similar to matrix multiplication,

$$A \otimes A = A^2 = B \tag{7}$$

defined as

$$b_{ij} = \{a_{i1}a_{1j}, a_{i2}a_{2j}, \ldots a_{iN}a_{Nj}\} \tag{8}$$

where $a_{ik}a_{kj}$ indicates a concatenation, that is, the placing next to each other of the characters a_{ik} and a_{kj}. If either of these characters is zero, the result of the concatenation is null by definition. In addition, if a character is repeated in a sequence, the pair is reduced to a single character.

For the calcite-magnesite-gypsum example,

$$\begin{aligned} b_{11} &= \{0, 021, 031, 041, 0, 0, 0, 0\} \\ &= \{0, 0, 0, 0, 0, 0, 0, 0\} \\ b_{21} &= \{210, 021, 2331, 2441, 0, 0, 270, 0\} \\ &= \{0, 0, 231, 241, 0, 0, 0, 0\} \\ b_{31} &= \{0, 321, 0, 341, 0, 0, 0, 0\} \end{aligned} \tag{9a}$$

Recalling that '0' represents a null transition, and interpreting a '0' to be the absence of sets, the above elements reduce to

$$\begin{aligned} b_{11} &= \{0\} \\ b_{21} &= \{231, 241\} \\ b_{31} &= \{321, 341\} \end{aligned} \tag{9b}$$

The complete A^2 matrix is formed in an analogous manner. Each element of A^2, of which three are shown above, may contain any number of sequences.

The authors believe that this character matrix representation and the concatenation operation are unique, since we have found no mention of these in the literature.

Application of rules 1 and 3

Although Rule 2 is embodied in the adjacency matrix and thus applied implicitly, Rules 1 and 3 have to be applied explicitly. This requires examining each nonnull sequence resulting from concatenation and discarding it if it does not comply. Rule 1 is applied simply by searching each string for a character label that appears more than once. For example, the string '231' contains three unique characters which represent three unique groupings. The string '232' is invalid by Rule 1 because it contains two "2's," which indicate a repeated grouping.

The application of Rule 3 is straightforward using the set-theory description, Eq. 6.

Interpreting the Powers of the Character Adjacency Matrix

The interpretation of the A^2 $(= B)$ array is analogous to that of the character adjacency matrix. Just as the adjacency matrix represents the set of all permitted paths leading from one node to another following a single line segment, the A^2 matrix represents the set of all permitted paths with two such line segments. In general, the A^m matrix represents the set of all permitted paths with m line segments, where

$$A^m = A^{m-1} \otimes A, \quad m = 1, 2, \ldots N - 1 \tag{10}$$

Terminating sequence generation

The process of concatentation and application of Rules 1 and 3 is repeated until all the elements of the matrix are null. This will require at most $N - 2$ concatenations, because every sequence with $N + 1$ nodes must contain a repeated node and this would violate Rule 1.

Creating the Set of Candidate Grouping Sequences

The search space can be contracted to form the set of candidate grouping sequences by specifying the identities of the solids initially present and the solids present after all possible (or practical) dissolutions have occurred. The initial solids are known and the final solid grouping is generally the empty set, although it may contain solids if the injected solution is saturated with respect to one or more of the initial solids. In the latter case, these solids constitute the final grouping. This does not prevent minerals not in these two groupings from forming, it merely directs consideration to the node of A^m which represents the initial and final mineral groupings for the problem of interest. The set of candidate solid grouping sequences is the smallest subset of unbounded solid grouping sequences obtainable without recourse to algebraic calculation for the particular problem.

Candidate sequences are mathematically determined by considering only the row of the CAM which represents the initial solid grouping. All other rows of the higher powers can be ignored in generating the list of candidate solid grouping sequences, although the complete CAM (A^1) is necessary for the row-by-matrix concatenation. And, although this entire row is mathematically necessary, all candidate sequences appear in only one matrix element of this row, that which corresponds to the final grouping. To illustrate, if the initial condition in the example problem is calcite and magnesite (G5), only row 5, representing this grouping, need be generated in the powers of the CAM. If the null set (G1) is the final grouping, then all candidate grouping sequences will appear in the elements $a_{51}, a_{51}^2, \ldots, a_{51}^{N-1}$.

Heuristically-Guided Search

As indicated by the size of the sets depicted by Figure 2, the number of candidate grouping sequences is substantially smaller than the bounded set of grouping sequences. This reduction results from application of the rules given above. The search for a solution to a particular problem then requires that candidate sequences be tested one at a time to find the one that satisfies the conditions of the algebraic model. The set of candidate sequences can be divided into subsets corresponding to a single element of the matrices $A, A^2, A^3, \ldots, A^{N-1}$. The simplest solution to a practical problem corresponds to a series of dissolution-only waves and may be thought to be the most likely. If a problem has K_n initial reactive solids, then K_n simple dissolution waves are required to completely dissolve these solids. Thus the subset of candidate sequences corresponding to the appropriate row of A^{K_n} are tested first, followed by A^{K_n+1} and so forth.

A grouping sequence is tested by starting with the given injected solution compositions and proceeding downstream wave by wave, calculating the aqueous composition in each constant-state region. The calculation is terminated immediately upon encountering a solubility product violation, a negative aqueous concentration, or an overdetermined or underdetermined system of equations for the aqueous concentrations in a region. Any sequence that produces a physical violation in the aqueous phase is called a SePAV, a sequence that produces an aqueous violation. This name was selected to emphasize that terminating the calculation involved only the aqueous concentrations, independent of the solid phase.

SePAV's are important because any other grouping sequence that contains such a sequence (from injected condition through the region in which the violation occurred) as a final subset will experience the same aqueous violation. Once a SePAV is found, all candidate grouping sequences that contain this same grouping sequence as a final subset can be eliminated without testing. ({C, M}-{M}-{ } is a final subset of {M, G}-{G, C}-{C, M}-{M}-{ }.) This narrows the search space using information generated by rejected sequences.

The heuristically-guided search identifies and catalogs those candidate sequences that produce aqueous violations. Each new sequence is then compared with the catalog of SePAV's to determine whether this sequence can be rejected without calculation, based on previous experience.

To illustrate, assume the calculation for sequence 1, Table 3, gives an aqueous violation for the final subsequence {C}-{ }. Any other sequence ending in this subsequence will also produce the same violation. In this case, the guided search would eliminate sequences 8, 12, 13, 14, and 18, due to the result obtained from the calculations for sequence 1.

Based on experience in solving practical problems, the most common aqueous violation seems to be that of exceeding one or more of the solubility products. Overconstrained systems occur rarely and no underconstrained systems have been encountered.

Violations such as a negative solid concentration or nondecreasing wave velocities may occur when calculating the solid phase, but these yield no information useful in eliminating other sequences.

Final Remarks

Our graph theory approach to mineral sequence determination makes the algebraic solution for metasomatic processes efficient and practical. The rules incorporated in sequence generation provide insight into mineral relationships across sharp waves and may lead to source detection for ionic contaminants. The mathematical technique of concatenation is believed unique in the literature and may be useful in other networking applications.

The algebraic solution is an efficient tool for solving precipitation/dissolution problems. It provides information about the wave structure and constant state nature of the solution often obscured in finite-difference solvers.

The small fraction of precipitation/dissolution problems with the degenerate double-discontinuity wave structure have been solved successfully using the algebraic scheme. Only one such problem has proved insolvable by this technique (Dria, 1988).

Table 3. Candidate Solid Grouping Sequences for the C-M-G Problem with an Initial Condition of Calcite and Magnesite

Sequences with Two Regions
1. {C,M}-{C}-{ }
2. {C,M}-{M}-{ }

Sequences with Three Regions
3. {C,M}-{C}-{G}-{ }
4. {C,M}-{M}-{G}-{ }
5. {C,M}-{C,G}-{G}-{ }
6. {C,M}-{M,G}-{G}-{ }
7. {C,M}-{M,G}-{M}-{ }
8. {C,M}-{C,G}-{C}-{ }

Sequences with Four Regions
9. {C,M}-{C,G}-{C}-{M}-{ }
10. {C,M}-{C,G}-{G}-{M}-{ }
11. {C,M}-{C}-{G}-{M}-{ }
12. {C,M}-{M,G}-{M}-{C}-{ }
13. {C,M}-{M,G}-{G}-{C}-{ }
14. {C,M}-{M}-{G}-{C}-{ }

Sequences with Five Regions
15. {C,M}-{M,G}-{M}-{C}-{G}-{ }
16. {C,M}-{C,G}-{C}-{M}-{G}-{ }
17. {C,M}-{M,G}-{G}-{C}-{M}-{ }
18. {C,M}-{C,G}-{G}-{M}-{C}-{ }

C = calcite ($CaCO_3$)
M = magnesite ($MgCO_3$)
G = gypsum ($CaSO_4 \cdot 2H_2O$)

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Notation

a_{ij} = element in the ith row and jth column of the character adjacency matrix
a_{ij}^m = element in the ith row and jth column of the mth power of the character adjacency matrix
A = character adjacency matrix
A^m = mth power of the character adjacency matrix
b_{ij} = element in the ith row and jth column of the second power of the character adjacency matrix
B = second power of the character adjacency matrix

$C_p^{(i)}$ = concentration of the pth aqueous species in the ith region
D_n = delay factor of the nth wave
$\bar{E}_i^{(j)}$ = total solid phase concentration of element i in region j
$E_i^{(j)}$ = total aqueous phase concentration of element i in region j
Eh = oxidation potential
K = number of solids
K_q^{sp} = solubility product for the qth solid
N = number of solid groupings
N_S = number of grouping sequences
$\{S_i\}$ = the set of the identities of solids in the ith region
v_n = specific velocity of the nth wave

Greek letters

Δ_n = change across the nth wave

Appendix: Demonstration of Rule 3

Consider the simple problem, where for brevity we let AB = $CaCO_{3(s)}$, etc.

Initial	Region 1	Region 2	Region 3	Injected
AB	AB	AB	—	—
AC	AC	—	AC	—

← downstream

The aqueous compositions in region 2 are subject to the constraints

$$C_A^{(2)} C_B^{(2)} = K_{AB}^{sp} \quad \text{(Local Equilibrium)}$$

$C_A^{(2)} C_C^{(2)} = K_{AC}^{sp}$ (Downstream Equilibrium Condition; Bryant, 1986)

The aqueous compositions in region 1 are determined by the equations

$$C_A^{(1)} C_B^{(1)} = K_{AB}^{sp} \quad \text{(Local Equilibrium)}$$

$$C_A^{(1)} C_C^{(1)} = K_{AC}^{sp} \quad \text{(Local Equilibrium)}$$

$$[C_A^{(1)} - C_A^{(2)}] = [C_B^{(1)} - C_B^{(2)}] + [C_C^{(1)} - C_C^{(2)}] \quad \text{(Charge Balance)}$$

By combining these equations we prove by contradiction that $C_A^{(1)} - C_A^{(2)} = 0$, and thus there is no aqueous concentration change between regions 1 and 2. (If C_A doesn't change, then C_B and C_C, which are constrained by identical solubility products in both regions, cannot change.) Substituting expressions in terms of C_A for the concentrations of B and C in the charge balance,

$$[C_A^{(1)} - C_A^{(2)}] = \frac{K_{AB}^{sp}}{C_A^{(1)}} - \frac{K_{AB}^{sp}}{C_A^{(2)}} + \frac{K_{AC}^{sp}}{C_A^{(1)}} - \frac{K_{AC}^{sp}}{C_A^{(2)}}$$

or

$$[C_A^{(1)} - C_A^{(2)}] = [K_{AB}^{sp} + K_{AC}^{sp}] \left[\frac{1}{C_A^{(1)}} - \frac{1}{C_A^{(2)}} \right]$$

or

$$[C_A^{(1)} - C_A^{(2)}] = [K_{AB}^{sp} + K_{AC}^{sp}] \frac{C_A^{(2)} - C_A^{(1)}}{C_A^{(1)} C_A^{(2)}}$$

Dividing by the negative of the left-hand-side, we obtain the nonphysical result

$$-1 = [K_{AB}^{sp} + K_{AC}^{sp}] \frac{1}{C_A^{(1)} C_A^{(2)}}$$

which indicates that the product $C_A^{(1)} C_A^{(2)}$ is less than zero. This contradiction is caused by the division by zero, i.e., $C_A^{(1)} - C_A^{(2)}$.

This procedure can be generalized as follows. The aqueous phase is forced to change to equilibrate with new solids encountered, solids with which it is not in equilibrium. If the flowing phase enters a region which contains only solids with which it is already in equilibrium, there is no driving force for change. Since the solids in region $i - 2$ and $i - 1$ determine the aqueous phase in region $i - 1$, the aqueous phase in region $i - 1$ is in equilibrium with the solids in regions $i - 2$ and $i - 1$. If the solids in region i are a subset of the solids in regions $i - 2$ and $i - 1$, i.e., Eq. 6, then the aqueous phase in region i is already in equilibrium with the solid phase in region i and no aqueous concentration change occurs.

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