AN INTERACTIVE CODE (NETPATH) FOR MODELING NET GEOCHEMICAL REACTIONS ALONG A FLOW PATH– VERSION 2.0

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ABSTRACT

NETPATH is an interactive Fortran 77 computer program used to interpret net geochemical mass-balance reactions between an initial and final water along a hydrologic flow path. Alternatively, NETPATH computes the mixing proportions of two to five initial waters and net geochemical reactions that can account for the observed composition of a final water. The program utilizes previously defined chemical and isotopic data for waters from a hydrochemical system. For a set of mineral and (or) gas phases hypothesized to be the reactive phases in the system, NETPATH calculates the mass transfers in every possible combination of the selected phases that accounts for the observed changes in the selected chemical and (or) isotopic compositions observed along the flow path. The calculations are of use in interpreting geochemical reactions, mixing proportions, evaporation and (or) dilution of waters, and mineral mass transfer in the chemical and isotopic evolution of natural and environmental waters. Rayleigh distillation calculations are applied to each mass-balance model that satisfies the constraints to predict carbon, sulfur, nitrogen, and strontium isotopic compositions at the end point, including radiocarbon dating. DB is an interactive Fortran 77 computer program used to enter analytical data into NETPATH, and calculate the distribution of species in aqueous solution. This report describes the types of problems that can be solved, the methods used to solve problems, and the features available in the program to facilitate these solutions. Examples are presented to demonstrate most of the applications and features of NETPATH. The codes DB and NETPATH can be executed in the UNIX or DOS[1] environment. This report replaces U.S. Geological Survey Water–Resources Investigations Report 91-4078, by Plummer and others, which described the original release of NETPATH, version 1.0 (dated December, 1991), and documents revisions and enhancements that are included in version 2.0.

[1] The use of trade, brand or product names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

INTRODUCTION

NETPATH is an interactive Fortran 77 computer program used to interpret net geochemical mass-balance reactions between an initial and final water along a hydrologic flow path. The net geochemical mass-balance reaction consists of the masses (per kilogram of water (H_2O)) of plausible minerals and gases that must enter or leave the initial water along the flow path to produce the composition of a selected set of chemical and isotopic observations in the final water. If initial waters mix and subsequently react, NETPATH computes the mixing proportion of two to five initial waters, and net geochemical reactions that can account for the observed composition of a final water. The program uses previously defined chemical and isotopic data for waters from a hydrochemical system. Every possible geochemical mass-balance reaction is examined between selected evolutionary waters for a set of chemical and isotopic constraints, and a set of plausible phases in the system. The calculations are of use in interpreting geochemical reactions, mixing proportions, evaporation and (or) dilution of waters, and mineral mass transfer in the chemical and isotopic evolution of natural and environmental waters. If sufficient isotopic data are available, Rayleigh distillation calculations are applied to each mass-balance model that satisfies the constraints to predict carbon, sulfur, nitrogen, and strontium isotopic compositions at the end-point. Radiocarbon dating is extensively treated in NETPATH. The modeling approach of NETPATH is discussed by Plummer and Back (1980), Parkhurst and others, (1982), Plummer and others, (1983), Plummer (1984), Plummer and others (1990), Plummer and others (1992), and Parkhurst and Plummer (1993). The isotopic evolution equations used and a description of radiocarbon dating may be found in Wigley and others, (1978, 1979), Fontes and Garnier (1979), and Wigley and Muller (1981).

This report describes the concepts of mass-balance reaction modeling included in NETPATH, capabilities of the program, the methods needed for entering and manipulating data, methods for interpreting the results of the program, and limitations of the calculations. Detailed examples are presented that demonstrate most of the features of the code. This report replaces Plummer and others (1991), which described the original release of NETPATH, version 1.0 (dated December, 1991), and documents revisions and enhancements that are included in version 2.0. Attachment A describes an alternative geochemical mass-balance program, BALNINPT. Although NETPATH and BALNINPT produce identical results for overlapping problems, the two codes have unique features and limitations (Attachment A).

NETPATH modeling uses two Fortran 77 codes: DB.FOR and NETPATH.FOR. DB is a database program that allows entering and editing of chemical and isotopic data for a set of water analyses. A generalized aqueous speciation program, based on WATEQ (Truesdell and Jones, 1974), WATEQF (Plummer and others, 1976), and WATEQ4F (Ball and Nordstrom, 1991) is included in DB to calculate mineral saturation indices and create input files to NETPATH. DB accepts a [Filename] which is attached to key files created for the particular set of analyses. The most important of these are the "[Filename].LON" file which contains all the hydrochemical data for the set of water analyses and the "[Filename].PAT" file which contains all the chemical and isotopic data for the water analyses read by NETPATH. Below is a list of the essential and internal files required to enter hydrochemical data through DB and run NETPATH.

Essential Files

The files listed below are required in compiling and running DB and NETPATH. If it is not necessary to recompile DB and NETPATH, only the files DB.EXE, NETPATH.EXE, NETPATH.DAT, and DB.DAT need to be resident in the directory to run the programs DB and NETPATH.

DB.FOR: This is the Fortran 77 source code of the database editing program, DB. The hydrochemical data and field information are entered and saved in the .LON file for later manipulation. DB.FOR also includes the program WATEQFP which is a generalized aqueous ion-association model. WATEQFP is based on WATEQ (Truesdell and Jones, 1974), and WATEQF (Plummer and others, 1976), but is coded generally, with the data base of ion-association equilibria defined in an external data file, DB.DAT. Thermodynamic data in DB.DAT are consistent with current versions of WATEQ4F (Ball and Nordstrom, 1991) and PHREEQE (Parkhurst and others, 1980), and may be edited as needed. Current thermodynamic data used in the WATEQ-generation ion-association models are described by Nordstrom and others (1990). WATEQFP is used to calculate the distribution of aqueous species and mineral saturation indices, and to construct the input file to NETPATH ([Filename].PAT). The batch file FLDB.BAT shows the options used to compile DB using Microsoft Fortran 5.0.

DB.EXE: Executable file for DB. The copy of DB.EXE provided on the distribution diskette was compiled using Microsoft Fortran (rev. 5.0) and is consistent with revisions 4.0 and later. The distributed executable file does not utilize a math co-processor.

DB.DAT: This file contains thermodynamic data and information on the aqueous model used to calculate the distribution of species by WATEQFP. Description of the free-formatted variables listed under the keywords ELEMENTS and SPECIES in the DB.DAT file is given in Parkhurst and others (1980). For further information see Truesdell and Jones (1974), Plummer and others (1976), Nordstrom and others (1990), and Ball and Nordstrom (1991). The DB.DAT file is listed in Attachment B. The file FNAMES.FIL contains the path to DB.DAT. If FNAMES.FIL is omitted, DB prompts for the path and name of the thermodynamic data base when speciating the waters (<S>ave/<S>peciate).

NETPATH.FOR: This is the Fortran 77 source code to the main program. This program allows the input data to be used to create mass-balance models between evolutionary water analyses. The file ALLNP2-0.FOR contains the NETPATH source code in a single file. For compilation using the batch file FLNP.BAT, the source code was subdivided into three segments: NETPATH.FOR, NETPATHA.FOR, and NETPATHB.FOR on the distribution diskette.

NETPATH.EXE: Executable file for NETPATH. The copy of NETPATH.EXE provided with this report was compiled using Microsoft Fortran (rev. 5.0) and is consistent with revisions 4.0 and later. The distributed executable file does not utilize a math-coprocessor.

NETPATH.DAT: This is a file of previously entered phases, their stoichiometries, and default isotopic compositions which is read by NETPATH. These can be used directly or after editing as plausible phases in a reaction model. The NETPATH.DAT file is listed in Attachment C.

Internal Files

Other files are essential but are created and managed internally by DB and NETPATH. These are listed below ([Filename].extension) by extension and name.

Files Created and Managed by Program DB

.LON: This file contains all of the chemical and isotopic data entered through DB for the particular [Filename]. The .LON file is updated through the <S>ave/<S>peciate option of DB.

.PAT: This file contains all chemical and isotopic data needed by NETPATH for the particular [Filename]. The .PAT file is created by DB by selecting the <S>ave/<S>peciate option of DB.

.IN: This is the input file to WATEQFP. The .IN file is deleted by DB after the .PAT file has been written.

.OUT: This is the output file from WATEQFP. The file contains the distribution of species, saturation indices, and other calculations made by WATEQFP (see Truesdell and Jones, 1974; and Plummer and others, 1976 for further details).

DB.FIL: This file contains an updated list of prefix names ([Filename]) to all [Filename].LON files created by DB.

NETPATH.FIL: This file contains an updated list of prefix names ([Filename]) to all [Filename].PAT files created by DB. The file is also read by NETPATH. On initiation of NETPATH the list of .PAT files is displayed for selection. All modeling within NETPATH is performed on water analyses from a single .PAT file, that is, it is not possible to construct models using waters selected from more than one .PAT file.

CHECK: This file contains the percent charge imbalance of each water analysis in the .LON file. CHECK is created from the <P>rint option of DB and is an optional selection.

OUTPUTnn: This file contains a report of the water analysis for well number nn. The report is printed from the <P>rint option of DB. Selecting "99" within the <P>rint option automatically produces an output file for each water in the .LON file.

Files Created and Managed by Program NETPATH

MODEL.FIL: If previous reaction models have been constructed and saved through NETPATH, this file contains a list of the user-defined names of these reaction models associated with the selected .PAT file. Any resident model files are displayed by NETPATH after selection of a new well file (listed in the NETPATH.FIL file). Later, a new model can be chosen in NETPATH through the <E>dit command.

NETPATH.DAT: This file contains stoichiometries of previously defined phases (see Attachment C). Although a preliminary version of NETPATH.DAT is provided with NETPATH, phases in NETPATH.DAT can be added, deleted, and their chemical composition edited with NETPATH. Default dissolution-only or precipitation-only constraints on minerals can also be edited using NETPATH. The file NETPATH.DAT should reside in the directory containing the NETPATH run module. If a copy is not present, an empty NETPATH.DAT file is created by NETPATH. Default isotopic values for phases can be included in NETPATH.DAT using a text editor. The notation used to define isotopic values is as follows: I1 (δ^{13}C in per mil); I2 (^{14}C in percent modern carbon (pmc)), I3 (δ^{34}S in per mil); I4 (^{87}Sr/^{86}Sr isotope ratio); and I5 (δ^{15}N in per mil).

NETPATH.OUT: If Rayleigh isotope simulations are invoked through NETPATH, selected data specific to these isotope fractionation calculations are written to NETPATH.OUT.

Model files: Model files can be saved using the <S>ave option of NETPATH. The user-assigned file name is stored in the file MODEL.FIL for subsequent retrieval and editing and (or) running through NETPATH.

Result files: NETPATH results can be saved to user-defined result files using the <S>ave option.

How to Obtain the Software

The latest DOS and Unix versions of the software described in this report and a Postscript file of this document can be obtained by anonymous ftp from the Internet address: brrcrftp.cr.usgs.GOV. The files reside in directories /geochem/pc/netpath and /geochem/unix. A typical anonymous ftp session follows:

```
% ftp brrcrftp.cr.usgs.GOV
Name: anonymous
Password: userid@machine          (replaced with your userid and machine name)
ftp> cd geochem/pc/netpath        (change directory)
ftp> ls                           (list files in directory)
netpext.exe
read.bat
text1.txt
text2.txt
text3.txt
text4.txt
text5.txt
text6.txt
text7.txt
ftp> mget *.txt read.bat          (transfer multiple files)
ftp> type binary                  (eliminate any ascii translation for binary files)
ftp> get netpext.exe              (transfer single file)
ftp> quit                         (quit ftp)
```

Alternatively, the documentation and DOS or Unix versions of the software can be ordered from the following addresses:

U.S. Geological Survey
NWIS Program Office
437 National Center
Reston, VA 22092

Additional copies of this report are available from:

U.S. Geological Survey
Earth Science Information Center
Open-File Reports Section
Box 25286, MS 517
Denver Federal Center
Denver, CO 80225-0046

For additional information, write to the address on page ii of this report.

Installation and Setup of the DOS Version

The self-extracting file, NETPEXT.EXE, obtained by anonymous ftp or from the distribution diskette, should be copied to a directory on the hard drive of the microcomputer where NETPATH is to be set up and executed. To retain pre-designed sub-directories during extraction, type NETPEXT -D at the DOS prompt for the hard drive. During extraction, the executable files (.EXE files) and essential data files are extracted in the directory, for example,

C:\NETPATH\, where NETPEXT.EXE was copied. The source codes are extracted in the sub-directories C:\NETPATH\SOURCE\DB\ and C:\NETPATH\SOURCE\NETPATH\. The sub-directory C:\NETPATH\EXAMPLES\ contains the .LON, .PAT, NETPATH.FIL, MODEL.FIL, and model files necessary to run the seven examples and test problems of this report. The sub-directory C:\NETPATH\BALN\ contains all files and data pertaining to the BALNINPT software package (Attachment A).

The programs can be executed from the distribution diskette, but operation is inefficient and the number and size of files generated by DB and NETPATH will soon exceed the available space on the diskette. To run the examples and test problems, the essential files in the top-level directory (.EXE, .DAT, .FIL) should be copied to the C:\NETPATH\EXAMPLES\ sub-directory. For further information about installation, run the READ batch file that is included in the distribution. Either insert the diskette into the A: drive of the microcomputer and type A: READ, or transfer READ.BAT and the six text files by anonymous ftp to the microcomputer and then type READ. The READ batch file sequentially writes the contents of text1.txt through text6.txt to the screen. Two other files that are distributed with NETPATH, INFO and WAISINFO, give additional information about NETPATH.

DB and NETPATH use screen-control commands that are specific to VT100 terminals. For operation on a microcomputer, the CONFIG.SYS file located in the top-level directory should contain the statement DEVICE=ANSI.SYS, or if the ANSI.SYS file is not located in the top-level directory, the CONFIG.SYS file should show the full path name to the ANSI.SYS file, such as, DEVICE=C:\DOS\ANSI.SYS, if the file is located in the DOS directory on the C drive. If DB and NETPATH are transported to mini-computers or mainframes, the results should be viewed on a VT100 terminal, or a terminal configured to emulate a VT100 terminal.

The executable files of DB and NETPATH in the top-level directory were compiled using Microsoft Fortran 5.0 and are consistent with Microsoft Fortran revision 4.0 and greater. The distributed executable files were compiled for microcomputers configured without math co-processors, but will run on microcomputers with math co-processors. The sub-directory C:\NETPATH\LAHEY\ contains executable files of DB and NETPATH that were compiled using a Lahey compiler to produce 32-bit executables with DOS extension (beyond the 640K limitation of DOS). These executable files run on 386SX and higher microcomputers with math co-processor. If execution time becomes a limitation when speciating large .LON files or when a large number of models is being computed, the Lahey executable files will generally run faster than the Microsoft Fortran versions.

Installation and Setup of the Unix Version

The Unix source code differs from the DOS source code only in two variable definitions. The variable Icase = 1 causes the programs to be case sensitive to file names and the variable Tunit = 6 causes output to be directed to the screen. Additional scripts and a makefile are included in the Unix distribution. The following steps should be used to transfer, compile, and install the program on a Unix machine.

(1) Transfer the compressed tar files to your home machine with ftp or obtain the Unix version on diskette as described above. Be sure to use type binary for the transfer. Put the tar file in a directory named "netpath".

(2) Uncompress the compressed tar file and extract the files with tar. The files will automatically extract into subdirectories named bin, data, doc, src, and test.

% **uncompress netpath.x.x.tar.Z**

% **tar -xvof netpath.x.x.tar**

(3) Change directory into src and compile the programs using make. Two executables will be created, ../bin/netpath.exe and ../bin/db.exe.

% **cd src**
% **make**

(4) Install the scripts to run NETPATH and DB. These scripts need to be installed in a directory where executables are stored. The makefile automatically edits the scripts to contain the appropriate pathnames to find the NETPATH and DB data files and executable files. The directory is assumed to be in your PATH, so that the programs will run regardless of the directory from which they are invoked. The default directory in which the scripts are installed is $(HOME)/bin:

This command installs scripts in $(HOME)/bin:

% **make install**

This command installs executables in the specified directory:

% **make install BINDIR=/home/jdoe/local/bin**

After the scripts db and netpath are properly installed, they can be executed with the commands "netpath" and "db" from any directory.

Data Needed to Run DB and NETPATH

Certain analytical data are required in every modeling situation. These include temperature, pH, and a name for each water sample. Major ion concentrations, including calcium, magnesium, sodium, chloride, carbon, and sulfate are typically, but not always, needed for realistic mass-balance calculations. In some cases trace element and isotopic data may be included.

DB accepts two levels of data entry– "All data", and "Data needed to run NETPATH". If "All data" is selected, site-specific information including latitude, longitude, site ID number, name and address of well owner, etc. can be entered into the [Filename].LON file, in addition to the chemical and isotopic data needed to run NETPATH.

IMPORTANT CONCEPTS IN NETPATH

In this section, the key concepts and terminology used in constructing net geochemical mass-balance reactions are reviewed. More extensive discussion is given by Plummer and others (1983) and Plummer (1984). In constructing net geochemical mass-balance reactions, it is necessary to select truly evolutionary initial and final waters, such as waters sampled along a flow path in a confined regional ground-water system, or laboratory waters sampled sequentially from a reactor. In ground-water systems, hydrologic data and hydrogeologic intuition are commonly required in selecting truly evolutionary waters. The danger lies in the fact that regardless of whether waters are truly evolutionary, NETPATH has no means of checking this, and will consequently always report reactions if they can be found. In this report, a net geochemical mass-balance reaction is often referred to as a model. A model is defined as the masses (per kilogram H_2O) of a set of plausible minerals and gases that must enter or leave the initial solution in order to exactly define a set of selected elemental and isotopic constraints observed in a final (evolutionary) water.

Constraints

A constraint is typically a chemical element, but may also be an expression of electron conservation (termed redox state) or conservation of a particular isotope of an element. A constraint is included in the model to constrain the masses of selected phases (minerals and gases) that can enter or leave the aqueous solution. The constraints selected for the model will determine the number and types of phases that need to be selected to solve the modeling problem. The total list of constraints available in NETPATH is

List of constraints

1:	Carbon	2:	Sulfur	3:	Calcium	4:	Aluminum
5:	Magnesium	6:	Sodium	7:	Potassium	8:	Chloride
9:	Fluoride	10:	Silica	11:	Bromide	12:	Boron
13:	Barium	14:	Lithium	15:	Strontium	16:	Iron
17:	Manganese	18:	Nitrogen	19:	Phosphate	20:	Redox
21:	Carbon-13	22:	C-14 (pmc)	23:	Sulfur-34	24:	Strontium-87
25:	Nitrogen-15	26:	Deuterium	27:	Oxygen-18	28:	Tritium

If an element is selected that is not contained in any of the chosen phases, the mass balance can be satisfied only by introduction of mixing, evaporation, or dilution of initial waters. The redox state, RS, (Parkhurst and others, 1980, 1982; Plummer and others, 1983) denoted "Redox" in the above list, provides a means of accounting for electron transfer and must be included for any oxidation-reduction reaction. The isotopic constraints should be included only for true isotope mass-balance problems, such as including deuterium or oxygen-18 to determine the mixing of two water masses, or including carbon-13 when there are only mineral sources along the flow path. Using carbon, sulfur, nitrogen, and strontium isotopes as constraints is realistic only when the elements corresponding to the isotopes (carbon, sulfur, nitrogen, or strontium) are also included as constraints. If both sources and sinks for a particular isotope exist along the flow path, the isotope should not be selected as a constraint.

If sufficient chemical and isotopic data are available, NETPATH can calculate the isotopic composition of the final water for a particular model using the generalized isotope evolution model of Wigley and others (1978). An isotope need not be included as a constraint to be treated in isotopic

evolution calculations. Comparing the observed and calculated isotopic compositions at final wells is a means of eliminating reaction models from further consideration. The isotopes carbon-13, carbon-14, sulfur-34, nitrogen-15, and strontium-87 are often involved in reactions with multiple sources and sinks and are more appropriately treated using the isotope evolution calculations of NETPATH, in which case, they should not be included as constraints.

Although many trace elements could have been included in NETPATH, interpretation of mass-balance results based on trace element concentrations requires more detailed knowledge of the composition of phases than is usually available. Therefore, many trace element constraints have not been included in NETPATH.

Redox State

The redox state is defined for each aqueous solution and phase considered by NETPATH and is computed according to the conventions originally defined in Parkhurst and others (1980, 1982), and Plummer and others (1983). The conventions defining redox state are as follows: (1) an operational valence of zero is assigned to O and H in aqueous species and phases; (2) an operational valence of -2 is assigned to H_2 (aqueous, (aq)) and +4 for O_2 (aq); (3) the formal valence is used for any element or species that can change oxidation state in the chemical system under consideration; (4) an operational valence of zero is assigned to any element or species that does not change oxidation state in the system; (5) the operational valence of phases and aqueous complexes is computed as the sum of the products of the operational valence and the stoichiometric coefficient in the phase or aqueous species; and (6) the redox state of an aqueous solution, RS, is the summation of only the element constraints selected in the model. These redox conventions simplify the accounting of electron transfer in reactions. Examples of operational valence of selected species and phases are listed below.

Species	Operational Valence, ν_i	Phase	Operational Valence, ν_i
Ca^{2+}	0.0	$CaCO_3$	4.0
Mg^{2+}	.0	$CaMg(CO_3)_2$	8.0
Na^+	.0	$Ca_{1.05}Mg_{0.9}Fe_{0.05}(CO_3)_2$	8.1
K^+	.0	NaCl	.0
Fe^{2+}	2.0	$CaSO_4$	6.0
Fe^{3+}	3.0	FeOOH	3.0
Cl^-	.0	Fe_2O_3	6.0
$SO_4{}^{2-}$	6.0	$FeCO_3$	6.0
H_2S(aq)	-2.0	FeS	.0
HS^-	-2.0	FeS_2	.0
$HCO_3{}^-$	4.0	$CaSO_4 \cdot 2H_2O$	6.0
CH_4(aq)	-4.0	"CH_2O"	.0
$CaHCO_3{}^+$	4.0	$KAlSi_3O_8$	.0
H_2CO_3(aq)	4.0	$Al(OH)_3$	.0
N_2(aq)	.0	KOH	.0
$NO_3{}^-$	5.0	H_2S(g)	-2.0
$NH_4{}^+$	-3.0	CH_4(g)	-4.0
$Fe(OH)_2^+$	3.0	CO_2(g)	4.0
$FeSO_4$(aq)	8.0	H_2(g)	-2.0
H^+, OH^-	.0	O_2(g)	4.0
H_2(aq)	-2.0	N_2(g)	.0
O_2(aq)	4.0	NH_3(g)	-3.0
H_2O	.0	CaF_2	.0

The above list is obviously incomplete, but should serve as an example for other species and minerals that might be considered. For example, in natural environments, sodium occurs only in the +1 oxidation state. In NETPATH it is normally not necessary to consider electron-transfer reactions involving sodium, so an operational valence of zero is assigned. If, however, the intent was to interpret waters that had evolved from reaction of sodium metal (Na°) with water, an operational valence of -1 would be assigned to the phase Na°.

It is important to re-state rule 6 (above) for defining the redox state of aqueous solutions. In NETPATH the redox state of an aqueous solution, RS, includes only the constraints selected in the model, and, if entered in DB, dissolved oxygen is always included in calculating RS– that is,

$$\mathrm{RS} = \sum_{i=1}^{I} m_i \nu_i + 4 m_{O_2(aq)} \ ,$$

where m is the concentration in millimoles per kg H_2O (mmols/kg H_2O) of the ith species of operational valence v_i, and I is the total number of analyzed aqueous species necessary to define the total elemental concentrations of the selected constraints. Dissolved concentrations of hydrogen, $H_{2(aq)}$ are insignificant in most natural environmental waters, and are not included in defining RS. The value of RS depends on the actual selection of constraints in the model. For example, if a water contained dissolved inorganic carbon, sulfate and ferrous iron, and the selected constraints for the model were carbon and sulfur (only), the RS would be computed considering the dissolved inorganic carbon and sulfur, but would not include the contribution from ferrous iron. If the model

were subsequently expanded to include iron as a constraint, the RS would automatically be summed for dissolved inorganic carbon, sulfur, and iron species in solution.

Because dissolved organic carbon (DOC) can represent the sum of numerous organic species containing carbon in different oxidation states, DB accepts data for the average redox state of carbon in DOC. The default value is zero, for carbohydrate. The average oxidation state of carbon in DOC can be modified further in NETPATH using <E>dit, and Redox state of DOC (see below). As a general rule, the oxidation state, $\nu_{org.}$ of carbon in organic compounds or species containing carbon, hydrogen, and oxygen is

$$\nu_{org.} = 2\left(\frac{\mathrm{O}}{\mathrm{C}}\right) - \left(\frac{\mathrm{H}}{\mathrm{C}}\right) \ ,$$

where O/C and H/C are the atomic ratios of oxygen to carbon and hydrogen to carbon in the organic compound or species. For example, the formal oxidation state of carbon in lignite having the average composition, $CH_{0.8}O_{0.2}$ is -0.4 and the formal valence for the lignite molecule is 0.0 (see for example, Stumm and Morgan, 1981, p. 420). But by the previously defined redox conventions, an operational valence of -0.4 is assigned to the lignite molecule in NETPATH. Kinetic information for the relative rates of oxidation of organic compounds could be used to define the average oxidation state of carbon reacting when there is more than a single source of dissolved and(or) particulate organic carbon.

Total Dissolved Carbon

For each element selected as a constraint, NETPATH considers the total concentration of that element in each aqueous solution. Even though data are entered separately for selected oxidation states of sulfur, nitrogen, and carbon in DB, total concentrations of each oxidation state of an element are summed to define the total concentration of the element in solution in NETPATH. This definition has some special consequences as regards total dissolved carbon (TDC), which is defined, in millimoles per kilogram H_2O, as the sum of total dissolved inorganic carbon (TDIC), dissolved methane, and dissolved organic carbon (DOC):

$$m_{TDC} = m_{TDIC} + m_{CH_4} + m_{DOC} \ .$$

In selecting carbon as a constraint, all mass-balance calculations are constrained by the total dissolved carbon concentrations and the redox states of the aqueous solutions include contributions from all three carbon oxidation states (if appropriate analytical data are given). The definition of TDC allows NETPATH to treat combined reactions involving both inorganic and organic species. Applications include (1) the inorganic carbonate system, if only TDIC is entered in DB, (2) organic carbon systems, if DOC and (or) dissolved methane are entered in DB, and (3) mixed inorganic and organic systems if TDIC and (or) DOC and (or) dissolved methane are entered in DB. It is, therefore, possible to consider in NETPATH the degradation of both natural and anthropogenic organic species in mineral-water systems. If no data are available for DOC and dissolved methane, zero values of their concentrations are assumed in NETPATH and TDC is equal to TDIC. Reactions involving organic compounds included as phases can always be considered regardless of the nature of the original analytical data defining the TDC. However, the user should evaluate the appropriateness of reaction models if potentially important analytical data are missing.

The above definition of total dissolved carbon has further consequences to the definition and interpretation of carbon isotope data, particularly as applied to defining (1) the carbon-13 and carbon-14 content of TDC, (2) carbon–isotope fractionation factors which are computed relative to

the average isotopic composition of TDC in solution, and (3) the initial ^{14}C content, A_0, of TDC used in radiocarbon dating. In NETPATH, DOC represents the sum of the moles (expressed in millimoles of carbon per kilogram H_2O) of all dissolved organic species. It is usually not possible to identify all the individual dissolved organic carbon species that make up DOC. Similarly it is difficult to determine the carbon-13 and carbon-14 content, and RS of all individual organic species in solution. Considering these uncertainties, NETPATH accepts an average carbon-13, carbon-14, and RS content for the total DOC. If it is known, for example, from laboratory experiments that one or several of the dissolved organic species which make up the total DOC are reactive, more realistic models would be obtained using data specific to the reactive species. See Example 7 for a test problem using the full definition of TDC.

Phases

A phase is any mineral or gas that can enter or leave the aqueous solution along the evolutionary path. Selected phases should be known to occur in the system, even if in trace amounts. Reaction modeling can usually be refined by more detailed knowledge of the chemical and isotopic composition of phases in the system. For example, reaction models in a carbonate system constrained by carbon, sulfur, iron and sodium could be refined by knowledge of the amounts of iron, sulfate and sodium substituted in carbonate minerals occurring there. Reaction models could be further checked using data for the carbon-13 composition of carbonates in the system.

In defining the stoichiometry of phases it is important to include its redox state. If omitted, a zero redox state is assumed for the phase. If the redox state of a phase is not zero, it must be defined whenever RS is included as a constraint.

Some of the phases under consideration can realistically only be precipitated or dissolved, but not both along the flow path. For example, organic matter can only dissolve. NETPATH allows phases to be marked for "precipitation only" or "dissolution only". If this is done, only models in which the particular phase precipitates or dissolves will be displayed. Examination of the saturation index data from WATEQFP (listed in the generated file, [Filename].OUT) and geochemical intuition are often useful in assigning precipitation only or dissolution only attributes to phases. For example, if the WATEQFP calculations showed that gypsum was undersaturated throughout the system under consideration, there would be little reason to see models requiring gypsum precipitation. Therefore, in this case, it would be meaningful to mark gypsum for dissolution only and the total number of models considered by NETPATH could be reduced.

If a phase is known to always react in the system, it is possible to "force" the phase to be included in every model. This way, more realistic models can be selected for further study and the total number of models may possibly be reduced.

A list of phase stoichiometries is stored in the NETPATH.DAT file and phases can be retrieved from this list in running NETPATH. The NETPATH.DAT file contains two phases that have special meaning. These are "EXCHANGE" and "CO2-CH4". The "EXCHANGE" phase is used to define different fractions of Ca^{2+} and Mg^{2+} that exchange for Na^+, [Ca^{2+} + Mg^{2+}] / Na^+.

There are four choices available for "EXCHANGE": "Computed" calculates the Ca^{2+}/Mg^{2+} ratio in the exchange from the molar ratio of calcium to magnesium in the final well. Selecting "50/50" results in equal amounts of calcium and magnesium being assumed in the exchange. "Ca/Na" results in pure calcium/sodium ion exchange. The last choice, "Var. Ca/Mg", allows the user to enter any fraction of Ca in the exchange. This option can be used in place of "50/50" or "Ca/Na" with the value 0.5 or 1.0, respectively.

Selected ion exchange reactions are included in NETPATH.DAT and in Examples 3, 5, 6, and 7 (see Examples and Test Problems). Example 3 assumes ferrous iron exchanges for sodium on an exchanger according to the reaction

$$Na_2X + Fe^{2+} \rightarrow FeX + 2Na^+ \ .$$

The file NETPATH.DAT defines the above reaction as Fe: -1.0, Na: +2.0, and RS: -2.0; written to release Na^+ to the aqueous solution. The sign of RS is then determined according to the previously stated conventions. If, alternatively, the reaction were written in reverse, adding Fe(II) to the aqueous solution, the sign of RS and the stoichiometric coefficients would be reversed. The results would be unchanged, however, because the sign of the computed mass transfer for the reaction would also be reversed. The direction the reaction actually proceeds depends on the sign of the computed mass transfer and the direction the reaction was written in assigning the sign of RS and the stoichiometric coefficients. In the above example of Fe(II)/Na exchange, a positive mass transfer for the phase "FeII-Na" (see Example 3-3a) would indicate the reaction proceeded in the direction given above in which Fe(II) was transferred to the exchanger releasing Na^+ to solution.

Examples 3 and 5 consider the possibility of calcium exchanging for both sodium and protons on an exchanger. In general, reactions involving exchange or release/uptake of protons are implicitly included whenever the stoichiometry of a phase does not balance in charge. As an example, Problems 3 and 5 consider the reaction

$$Na^+_{1.6}H^+_{0.4}X + Ca^{2+} \rightarrow CaX + 1.6Na^+ + 0.4H^+ \ .$$

The reaction stoichiometry is defined as Na: +1.6, and Ca^{2+}: -1.0 in Examples 3 and 5. Notice that RS in this case is zero and the reaction coefficients do not balance in charge. Because NETPATH works with implicitly charge-balanced waters and charge-balanced reactions, charge imbalances in reaction coefficients are interpreted as addition (or removal) of protons to (from) the aqueous solution. In the above example, the exchanger is assumed to be occupied by Na^+ and H^+ in the fixed ratio of 1.6:0.4, respectively. Although there is some evidence for the occurrence of proton exchange reactions (Appelo, 1994), experimental data may be required to define the composition of the exchanger in a specific application. In some cases it may not be valid to assume that cation ratios in exchange reactions remain constant along a flow path.

As another example of an exchange reaction, consider the possibility of NH_4^+ exchange for Ca^{2+}. In assigning the stoichiometry, NH_4^+: +2.0, Ca^{2+}: -1.0, and RS: -6.0, the reaction is written as

$$(NH_4)_2\,X + Ca^{2+} \rightarrow CaX + 2NH_4{}^+ \ ,$$

where RS is again assigned by the previously stated conventions. In this case a positive mass transfer would indicate that NH_4^+ was released from the exchanger to solution and calcium taken up by the exchanger in the mole proportion NH_4:Ca of 2:1. Many other ion exchange reactions can be considered in NETPATH, for which the above should serve as examples.

If mixtures of phases are known to react in fixed proportions, such mixtures can be combined and defined as a single phase in mass-balance models. This allows more phases to be included in the model than are separately allowed for the selected constraints. NETPATH.DAT contains one such phase, a CO_2-CH_4 gas mixture, with the added option of defining the fraction of CO_2 in the gas mixture. When the CO_2-CH_4 phase is included and the CO_2 fraction in the mixture defined, all computed mass transfer for this gas mixture always enters or leaves the aqueous solution in the defined CO_2/CH_4 proportion. Incoming and outgassing of methane-carbon dioxide gas mixtures can be important in some geochemical environments undergoing methanogenesis. The fraction of

CO_2 in the CO_2-CH_4 gas mixture will define the average redox state for the gas mixture. By combining these two gases into one phase, the number of phases under consideration is effectively increased by one. Note that isotopic values for CO_2 and CH_4 are entered, edited, and stored separately. They are combined linearly according to the CO_2/CH_4 ratio for the purpose of isotope computation. Other phase mixtures could be defined in NETPATH.DAT and used in mass-balance models, but there are no general features for editing their mixing proportions without defining a separate phase mixture.

Models

Many more phases can be selected than there are constraints. NETPATH finds every subset of the selected phases that satisfies the chosen constraints. A model is a subset of the selected phases (and the computed mass transfer) that satisfies all the selected constraints. The model is of the form

$$\text{Initial water} + \text{“Reactant Phases”} \rightarrow \text{Final water} + \text{“Product Phases”} .$$

In some cases, it becomes necessary to assume that mixing of initial waters, with or without further reaction, results in the observed final water. NETPATH (version 2.0) allows mixing of as many as five initial waters. The initial waters are named INIT1 - INIT5. The modeling assumes that the selected initial waters mix in some proportion, with or without further mineral-water reactions. The fraction of each initial water mixed to produce the final water is displayed, in a mixing case. Negative mixing fractions are not allowed (that is, models giving negative mixing fractions are not reported). Although NETPATH allows mixtures of as many as five initial waters, there are probably few realistic situations where chemical and isotopic data are sufficient to demonstrate mixing of more than 2-3 waters.

Because of the additional dependent variables (mixing fractions) when considering mixing, one less phase can be included in a model for every additional initial water in the mixture. Therefore, mixing models will run with one fewer phase than constraints for each additional initial water, whereas nonmixing cases require at least as many phases as constraints. If two initial waters are mixed and one constraint is not contained in any of the selected phases, a message is displayed at the main screen informing the user that the mixing ratio will be determined by the amount of the constraint in the initial and final wells. If n initial waters are mixed, $n-1$ constraints may be included that are not contained in any of the selected phases. Mixing fractions can also be found when all selected constraints are contained in the stoichiometry of one or more selected phases in the model. If n initial waters are mixed, no models can be found if the number of constraints not contained in any phase is $> (n-1)$.

For a given set of initial waters and the final water, NETPATH is not capable of determining where along the overall flow path that mixing (and mineral-water reaction) actually takes place. Although the net mineral-water reactions and mixing proportions are unaffected, Rayleigh distillation calculation of the isotopic composition of the final water is sensitive to the extent of reaction/mixing progress. For mixing cases in which Rayleigh distillation calculations are allowed, NETPATH assumes that all mixing occurs at the initial condition, followed by subsequent mineral-water reaction. This is a limitation that needs to be considered when mixing and Rayleigh distillation calculations are considered in the same problem. Reliable isotopic results cannot be obtained from NETPATH if mixing occurs at some point in reaction progress other than at the initial condition. However, such problems could be solved in NETPATH by considering additional (intermediate) waters along the flow path.

NETPATH also considers the possibility of evaporation or dilution (with pure water). The treatment is similar to that of mixing, but with the second initial water, INIT2, defined to be pure water. Both the evaporation factor and dilution factor are computed as positive numbers (≥ 1) and identified as either dilution or evaporation (NETPATH version 2.0). The Dilution Factor indicates that initial concentrations were decreased (divided) by the "Dilution Factor". In evaporation, all initial concentrations were increased (multiplied) by the "Evaporation Factor". NETPATH (version 2.0) also displays the grams of water remaining in the final solution, which is >1000 in cases of dilution and <1000 if evaporation is modeled. The number of remaining grams of water is, for dilution, 1000x"Dilution Factor", and for evaporation, 1000/"Evaporation Factor". All computed mineral (and gas) mass transfers are computed relative to an initial 1000 grams of water (and associated initial masses of solutes). The total number of phases that can be included in a model is reduced by one when the Evaporation/Dilution option is selected. Mixing and Evaporation/Dilution may both be selected for a particular model.

Geochemical mass-balance models can be no better than the data on which they are based. Because of a failure to analyze for all dissolved species and (or) analytical error, water analyses rarely are exactly charged balanced. Mass-balance reaction models combine positive and negative charges in water analyses to compute masses of uncharged phases. As a consequence of this process, charge-balance errors in the analysis contribute to the computed masses of one-component phases, such as CO_2 gas, CH_2O, N_2 gas, etc. The problem can be particularly acute with brines and other high-salinity waters, where even a small percent of charge imbalance can cause tens of millimoles of organic matter or CO_2 to be computed erroneously. As discussed below, DB offers one option for balancing the charge on water analyses in constructing the .PAT file. It is recommended that as a part of the modeling exercise, this option be selected temporarily for comparison to the unadjusted original analyses. When the charge-balancing option of DB is selected, the original data stored in the .LON file remain unchanged. Only the .PAT file is adjusted. However, the charge-balancing option will modify all constituents in the analysis, in proportion to their total equivalents in solution. This may not be desirable, as some constituents may be less certain than others. Alternatively, the user can adjust the analysis more appropriately and reenter the adjusted analysis into DB.

Errors in analytical data, even for charge-balanced waters, will be distributed through the calculated mass transfers of all phases containing that element, which will, in turn, likely affect the mass transfers of other phases. Obviously, great care should be taken in selecting reliable chemical, mineralogic, and isotopic data. The charge imbalance in water analyses can be checked in DB by selecting the <P>rint option, and selecting "99" to check the data. The charge imbalances are written to the file CHECK within the working directory. Charge imbalances and percent charge imbalance are also written in the output from the speciation calculation, [Filename].OUT, and may be viewed interactively after selecting the <S>ave/<S>peciate option of DB.

The validity of the mass-balance models depends significantly on the geochemical insight of the modeler in selecting appropriate phases in the model. Generally, only phases that occur in the system should be considered in modeling. The results can be improved significantly as more reliable mineral compositional data are used in the modeling, such as the actual anorthite composition of plagioclase feldspars, the iron content of dolomite, the sulfur isotopic composition of sulfate in substitution in calcite, the ^{14}C content of carbon in calcite of the unsaturated zone, and so forth. Geochemical modeling should not be separated from an aggressive effort to study the mineralogy and petrology of the system.

As discussed by Plummer and others (1983), Plummer (1984), and Parkhurst and Plummer (1993), geochemical modeling rarely leads to unique solutions. The modeling process is best suited for eliminating reaction models from further consideration. For example, a mass-balance model

could be eliminated if it requires the net precipitation of a phase that is known to be undersaturated in the system. Similarly, a mass-balance model could be eliminated if the predicted isotopic composition of the final water differs significantly from the observed. Although the final results are rarely unique, the elimination process is useful in limiting the number of reaction possibilities, identifying additional data that could help resolve modeling uncertainties, and in guiding reasoning in the modeling process.

The effects of hydrodynamic dispersion are not explicitly accounted for in mass-balance modeling. In solving the net mass balance for waters along a flow path, the compositional mixing effects due to hydrodynamic dispersion cannot be separated from the analytical data and become incorporated into the implied phase mass transfer. Although this effect is thought to be negligible in applications to regional flow systems (see Appendix A of Wigley and others, 1978), mass-balance interpretations of localized hydrochemical problems, such as associated with point-source injection, could be in serious error without proper evaluation of the effects of hydrodynamic dispersion. It may be possible to test mass-balance models for uncertainties caused by hydrodynamic dispersion by application of the net mass transfer results in solute-transport models.

The user needs also to evaluate the appropriateness of the steady-state assumption that is implicit in mass-balance modeling. Some systems may be in a dynamic state, where water entering the aquifer today differs significantly in chemical and (or) isotopic composition from the recharge-water that has evolved chemically to the presently observed final water. Or perhaps a chemical front, or chromatographic effect has not even reached the final point along the flow path. These cases would lead to misleading results. The mass-balance modeling of NETPATH applies strictly to the case of chemical steady state along the flow path.

NETPATH does not currently consider the uncertainty in the analytical data, and how this uncertainty affects modeling results. Parkhurst (1994) shows that by combining analytical uncertainties in the set of linear equations which now contain inequalities, "minimal models" can be found. A "minimal model" contains only the phases and mass transfers that must be considered to account for the water chemistry within the analytical uncertainties. Because this capability has not yet been implemented in NETPATH, some models may not be displayed, and others displayed may contain mass transfers of phases that are small and within the analytical uncertainty of the constituent in solution. If, for example, a phase is marked for dissolution only, any model requiring precipitation of the phase will not be displayed, even if the amount of the phase precipitated is very small and within the uncertainties of the analytical data. To avoid this problem, it is recommended that initially, relatively few dissolution/precipitation constraints be assigned to phases. The dissolution/precipitation constraints can be added later to refine the modeling exercise. Pearson (1989, 1992) considered uncertainty analysis in modeling the isotopic evolution of ^{13}C and ^{14}C in ground water. Future developments in mass-balance reaction modeling will likely consider uncertainties in the analytical data.

ISOTOPIC CALCULATIONS

NETPATH considers two types of isotopic calculations: (1) isotope mass balance and (2) Rayleigh distillation calculations. Isotope mass balance is included by selecting any of the following as constraints: Carbon-13 [2] , C-14 (pmc), Sulfur-34, Nitrogen-15, Deuterium, Oxygen-18, Tritium, and Strontium-87. The user needs to be careful to specify the sulfur, carbon, nitrogen, and (or) strontium stoichiometry and isotopic compositions of appropriate phases in a model. If phases are included that contain C, S, N, or Sr, these elements should also be included as constraints. Alternatively, if the isotope is not contained in any phase, any one of the isotope constraints could be used to determine a mixing fraction. In general, Carbon-13, Carbon-14 (pmc), Sulfur-34, Nitrogen-15, and Strontium-87 should be selected as constraints only for processes (reactions) involving the constraint as a source, such as (1) the mixing of two waters, (2) mineral dissolution (without precipitation), or (3) ingassing (without outgassing). An isotope can also be included as a constraint for the special case of precipitation (without dissolution) if, and only if, the fractionation factor, α, is unity. In such a case, the isotopic composition of the precipitate would be identical to that of solution regardless of extent of reaction. Of the isotopes available in NETPATH, this latter case would apply only to precipitation of a strontium-bearing phase from an initial Sr-bearing water, since the $^{87}Sr/^{86}Sr$ fractionation factor, and similarly for other heavy isotopes, is essentially unity.

When there is both a source and sink for a particular isotope in the reaction, regardless of the value of the fractionation factor, it is usually not valid to include the isotope as a constraint in the mass balance, since the problem must be treated as a Rayleigh distillation problem (see for example Wigley, and others, 1978). The Rayleigh calculations are solved in NETPATH using the general case of N non-fractionating inputs and M fractionating outputs considered by Wigley and others (1978, 1979).

After each mass-balance model is calculated, NETPATH computes the $\delta^{13}C$, ^{14}C (pmc), $\delta^{34}S$, $\delta^{15}N$, and $^{87}Sr/^{86}Sr$ ratio of the final water as a Rayleigh distillation problem for the modeled mass transfer. If $\delta^{13}C$, ^{14}C (pmc), $\delta^{34}S$, $\delta^{15}N$, and (or) $^{87}Sr/^{86}Sr$ are selected as constraints, the isotopic composition of the final water calculated by the Rayleigh model can be compared with the observed to examine differences between the fractionating differential problem of isotopic evolution and the mass-balance result. For the special valid cases mentioned above where isotopic data are correctly treated as isotope mass-balance problems, the final modeled isotopic composition will always equal the final observed value. But for the general case of isotope evolution, the calculations usually involve comparing sensitivity of isotopic values computed at the final well to uncertainties in isotopic and compositional data of the selected phases.

The user should be aware of some of the assumptions in applying the Wigley and others (1978, 1979) Rayleigh distillation equations to net mass-balance results in isotope evolution problems. The equations of Wigley and others (1978, 1979) are analytical solutions to the general differential

[2] Throughout this report the abundances of isotopes of carbon-13, sulfur-34, nitrogen-15, oxygen-18, and deuterium are given in delta notation, denoted δ, and expressed in units of parts per thousand (per mil, $‰$). The delta value is expressed as

$$\delta_i = \left(\frac{R_i}{R_{Std.}} - 1 \right) 1000 \, ,$$

where R is the $^{13}C/^{12}C$, $^{34}S/^{32}S$, $^{15}N/^{14}N$, $^{18}O/^{16}O$, or the $^{2}H/^{1}H$ ratio in the ith species or phase, or in the standard, denoted "*Std.*". Carbon-14 is expressed in percent modern carbon (pmc). Strontium-87 abundance is expressed as the ratio, $^{87}Sr/^{86}Sr$. Tritium concentration is expressed in tritium units (TU); 1 TU is one atom of tritium in 10^{18} atoms of hydrogen.

problem of chemical mass balance and isotope mass balance with fractionating output. The two basic equations solved (for carbon as an example) are:

Carbon mass balance

$$d\left(m_C\right) = \sum_{i=1}^{N} dI_i - \sum_{i=1}^{M} dO_i \ .$$

Isotope mass balance

$$d\left(Rm_C\right) = \sum_{i=1}^{N} R_i^* dI_i - \sum_{i=1}^{M} R_i \alpha_{is} dO_i \ ,$$

where R refers to the isotope ratio, m_C is the total concentration of the element, I and O refer to incoming and outgoing masses of the element, such as through dissolution and precipitation, N and M are the total number of incoming and outgoing phases, the superscript $*$ refers to the incoming phases, and α_{is} is the fractionation factor between the ith phase and the solution. The analytical solution to the isotope evolution problem assumes constant relative rates of reaction along the flow path. Thus the ratio of incoming to outgoing mass of an element is assumed constant along the flow path, and equal to that calculated for the net mass-balance problem. Though the net mass transfer can be determined by NETPATH, the relative rates of reactions may vary along the flow path. It is also assumed that a single value of the additive fractionation factor (relative to the solution) applies over the entire length of the flow path. Test calculations (Wigley and others, 1978; Plummer and others, 1983) have shown that, in selected carbonate cases considered, the modeled isotopic outcome is not usually sensitive to uncertainties in relative rates of reaction and variations in additive fractionation factors. This conclusion is tentative and may not be valid for yet untested reactions. One means of testing the validity of isotopic-evolution results was demonstrated by Plummer and others (1983) in simulating the final isotopic composition of a net mass-balance model over a wide range of possible reaction paths. Such calculations require use of a forward reaction simulation code such as PHREEQE[3] (Parkhurst and others, 1980).

Fractionation Factors for the Inorganic Carbon-13 System

Two sets of fractionation factors for the inorganic carbon-13 system are available in NETPATH through the Edit menu. The default set, identified as Mook, is a selection of equilibrium fractionation factors for carbonate species and calcite from Thode and others (1965), Vogel and others (1970), Mook and others (1974), Mook (1980), and Mook (1986). All fractionation factors in the "Mook set" are based on experimental measurements, except for values relating to CO_3^{2-}, which were derived theoretically by Thode and others (1965). The second set of carbonate fractionation factors is identified as Deines, and taken from Deines and others, (1974). The Mook set is given as additive fractionation factors, $\epsilon_{i\text{-}j}$, (in per mil), and the Deines and others set is given as the fractionation factor α_{i-j}, as in the original sources. The carbon–isotope fractionation factors given in the Mook and Deines sets are provided for ease of calculations, but in general, the user should evaluate fractionation factors carefully. NETPATH allows editing of all fractionation factors (provided they are computed relative to the average isotopic composition of total dissolved carbon in solution) through the Edit and Isotope Data menus. Changes to the expressions for individual fractionation factors can only be made by changing the source code which then must be

[3] **PH**-**RE**dox-**EQ**uilibrium-**E**quations

re-compiled. For additional data on carbon–isotope fractionation factors, the reader is referred to Turner (1982), Inoue and Sugimura (1985), Mook (1986), Leśniak and Sakai (1989), and Romanek and others (1992).

The fractionation factor, $\alpha_{i\text{-}j}$, between the ith and j^{th} species (phases) is defined as

$$\alpha_{i\text{-}j} = \frac{R_i}{R_j} = \frac{1000 + \delta_i}{1000 + \delta_j} ,$$

where R is the isotope ratio, and δ is the isotopic composition in per mil relative to a standard. That is,

$$\delta_i = \left(\frac{R_i}{R_{std.}} - 1 \right) 1000 ,$$

where R_i and $R_{std.}$ are, for carbon-13, the ratio $^{13}C/^{12}C$ in species (phase) i and in the standard.

The additive fractionation factor, ϵ, is related to the fractionation factor, α, by the equation

$$\epsilon_{i\text{-}j} = 1000 \, (\alpha_{i\text{-}j} - 1) .$$

Friedman and O'Neil (1977) give an extensive review of literature values of α. The fractionation factors of the Mook and Deines and others sets are from various sources. Generally, they are based on experimental data between 0 and 50 °C (degrees Celsius), but can be applied to temperatures approaching 100 °C. The two sets of fractionation factors are as follows–

Mook (1980, 1986)

$$\epsilon_{CO_{2aq}\text{-}HCO_3^-} = 24.12 - \frac{9866}{T} \approx \delta^{13}C_{CO_{2aq}} - \delta^{13}C_{HCO_3^-}$$

$$\epsilon_{CO_3^{2-}\text{-}HCO_3^-} = 2.52 - \frac{867}{T} \approx \delta^{13}C_{CO_3^{2-}} - \delta^{13}C_{HCO_3^-}$$

$$\epsilon_{calcite\text{-}HCO_3^-} = 15.10 - \frac{4232}{T} \approx \delta^{13}C_{calcite} - \delta^{13}C_{HCO_3^-}$$

$$\epsilon_{CO_{2aq}\text{-}CO_{2gas}} = 0.19 - \frac{373}{T} \approx \delta^{13}C_{CO_{2aq}} - \delta^{13}C_{CO_{2gas}}$$

and

$$\epsilon_{CO_{2gas}\text{-}HCO_3^-} = 23.89 - \frac{9483}{T} \approx \delta^{13}C_{CO_{2gas}} - \delta^{13}C_{HCO_3^-} ,$$

where T is temperature in kelvins. The Mook set contains a redundancy in fractionation factors. For example, inclusion of an expression for $\epsilon_{CO_{2aq}\text{-}CO_{2gas}}$ introduces an small inconsistency in the Mook set of fractionation factors (above), because $\epsilon_{CO_{2aq}\text{-}CO_{2gas}}$ can be determined from combination of $\epsilon_{CO_{2aq}\text{-}HCO_3^-}$ and $\epsilon_{CO_{2gas}\text{-}HCO_3^-}$. However, the expression for $\epsilon_{CO_{2aq}\text{-}CO_{2gas}}$ is retained in the Mook set because it is based on experimental data (Vogel and others, 1970; Mook and others, 1974; Mook, 1980; Mook, 1986).

Deines and others (1974)

$$1000ln\ \alpha_{CO_{2aq}\text{-}CO_{2(g)}} = -0.91 + \frac{6300}{T^2}$$

$$1000ln\ \alpha_{CO_3^{2-}\text{-}CO_{2(g)}} = -3.4 + \frac{870000}{T^2}$$

$$1000ln\ \alpha_{calcite\text{-}CO_{2(g)}} = -3.63 + \frac{1194000}{T^2}$$

and

$$1000ln\ \alpha_{HCO_3^-\text{-}CO_{2(g)}} = -4.54 + \frac{1099000}{T^2}\ ,$$

where T is temperature in kelvins. Within NETPATH the $\alpha_{i\text{-}CO_{2(g)}}$ values from Deines and others (1974) are converted to $\epsilon_{i\text{-}HCO_3}$. Values of $\epsilon_{CO_{2aq}\text{-}CO_{2g}}$ and $\epsilon_{CO_{2aq}\text{-}calcite}$ are used in the A_o model of Eichinger (1983) (See Radiocarbon Dating section).

The most significant difference between the Mook and Deines and others sets of fractionation factors occurs in the fractionation between calcite and HCO_3^-. At 25° C the Deines and others (1974) value for $\epsilon_{calcite-HCO_3}$ is 1.98 per mil and the Mook (1980, 1986) value is 0.91 per mil. Experimental values of the calcite-HCO_3^- fractionation factor determined by Turner (1982) at very low rates of calcite crystal growth are in closer agreement with the calcite-HCO_3^- expression of Deines and others (1974) than that given by Mook (1980, 1986). The expression of Mook (1980, 1986) for the calcite-HCO_3^- fractionation factor is derived from the relatively rapid calcite precipitation experiments of Rubinson and Clayton (1969). However, Romanek and others (1992) found the calcite-HCO_3^- fractionation factor is nearly independent of growth rate and consistent with the results of Rubinson and Clayton (1969). Mook (1986) and Romanek and others (1992) also give values of the aragonite-HCO_3^- fractionation factor which are about 1.8 per mil (Mook, 1986) or 1.7 per mil (Romanek and others, 1992) larger than that for calcite between 10 and 40° C. The CO_3^{2-}-HCO_3^- fractionation factors also differ by about 1 per mil between the two sets, but the difference has little effect in most groundwaters because HCO_3^- is usually the predominant inorganic carbon species.

Carbon-Isotope Fractionation Factors

In NETPATH, all fractionation factors are defined relative to the average isotopic composition of the element in the aqueous solution, rather than to an individual aqueous species. Within a single oxidation state, such as for the dissolved inorganic carbon, the additive fractionation factors for calcite and CO_2(g) relative to the average isotopic composition of the dissolved inorganic carbon in solution are functions of temperature and pH (Wigley and others, 1978, 1979).

NETPATH also accepts several oxidation states of carbon, sulfur, and nitrogen. If more than one oxidation state of the element is present in solution, NETPATH computes additive fractionation factors relative to the average isotopic composition of the element in solution. For example, NETPATH defines total dissolved carbon as the sum of dissolved inorganic carbon, methane, and dissolved organic carbon–that is,

$$m_{TDC} = m_{TDIC} + m_{CH_4} + m_{DOC}\ ,$$

where m is millimoles per kilogram H_2O, and the subscripts TDC, TDIC, CH_4, and DOC refer to total dissolved carbon, total dissolved inorganic carbon, dissolved methane, and dissolved organic carbon, respectively. According to this definition, the average δ^{13}C isotopic composition of TDC is

$$\delta^{13}\mathrm{C}_{TDC} = \frac{m_{TDIC}\delta^{13}\mathrm{C}_{TDIC} + m_{CH_4}\delta^{13}\mathrm{C}_{CH_4} + m_{DOC}\delta^{13}\mathrm{C}_{DOC}}{m_{TDIC} + m_{CH_4} + m_{DOC}} .$$

The fractionation factors, α, for carbonates calculated relative to the average δ^{13}C isotopic composition of the aqueous solution depend on (1) the distribution of carbonate species computed by WATEQFP, (2) the δ^{13}C of TDIC, (3) the mmol/kg H_2O of methane and mmol/kg H_2O of carbon from DOC, and (4) the δ^{13}C composition of dissolved methane and DOC which is user defined within NETPATH (see the <E>dit, Isotope Data option). The default values of the equilibrium carbon isotope fractionation factors for calcite, and CO_2 gas are calculated relative to the average isotopic composition of the solution using the formal relations:

$$\alpha_{Cal.-Soln.} = \frac{\alpha_{Cal.-HCO_3^-}}{N_{CO_{2aq}}\alpha_{CO_{2aq}\text{-}HCO_3} + N_{HCO_3} + N_{CO_3}\alpha_{CO_3\text{-}HCO_3} + N_{CH_4}\alpha_{CH_4\text{-}HCO_3} + N_{DOC}\alpha_{DOC\text{-}HCO_3}}$$

and

$$\alpha_{CO_2(g)\text{-}Soln.} = \frac{\alpha_{CO_2(g)\text{-}HCO_3^-}}{N_{CO_{2aq}}\alpha_{CO_{2aq}\text{-}HCO_3} + N_{HCO_3} + N_{CO_3}\alpha_{CO_3\text{-}HCO_3} + N_{CH_4}\alpha_{CH_4\text{-}HCO_3} + N_{DOC}\alpha_{DOC\text{-}HCO_3}} ,$$

where N_i is the mole fraction of the subscripted carbon species (relative to TDC), and $\alpha_{CH_4\text{-}HCO_3}$ and $\alpha_{DOC\text{-}HCO_3}$ are treated as empirical kinetic isotope fractionation factors and defined from the analytical data, if available–that is,

$$\alpha_{CH_4\text{-}HCO_3} = \frac{1000 + \delta^{13}C_{CH_4}}{1000 + \delta^{13}C_{HCO_3}}$$

$$\alpha_{DOC\text{-}HCO_3} = \frac{1000 + \delta^{13}C_{DOC}}{1000 + \delta^{13}C_{HCO_3}}$$

and

$$\delta^{13}C_{HCO_3} = \frac{1000 + \delta^{13}C_{TDIC}}{N_{CO_{2aq}}\alpha_{CO_{2aq}\text{-}HCO_3} + N_{HCO_3} + N_{CO_3}\alpha_{CO_3\text{-}HCO_3}} - 1000 .$$

The default equilibrium carbon–isotope fractionation factors for all carbonate minerals are initially defined as that for calcite. The section below on <E>dit, Isotope Data shows how user-defined fractionation factors can be entered into NETPATH. The default equilibrium fractionation factor for methane gas relative to solution is undefined and must be entered by the user.

Inspection of the above equations shows that if dissolved methane and DOC have zero concentrations in the .PAT file, all calculations in the carbon system of NETPATH reduce to the usual definitions for the inorganic carbon system. The user should be aware of the consequences of entering data for DOC and (or) dissolved methane in DB, as these data fully impact the definition of total dissolved carbon, the redox state of the solution, and the treatment of the isotopic evolution of the carbon system. In running isotope-evolution problems in NETPATH with analytical data that include DOC and (or) dissolved methane, NETPATH prints the modeled $\delta^{13}C$ of both the dissolved inorganic carbon (for direct comparison with known analytical data) and the $\delta^{13}C$ of total dissolved carbon (which is usually not measured directly, but can be computed from the analytical

data). Comparison of modeled δ^{13}C isotopic compositions with analytical data at the final well is of considerable value in testing model sensitivity to uncertainties in data and, in some cases, eliminating models from further consideration.

If the carbon-14 content is also modeled in fractionating processes, NETPATH initially assigns default values of the additive fractionation factors for carbon-14 that are twice those for carbon-13 (Craig, 1954). There is some experimental and theoretical evidence that additive fractionation factors for carbon-14 may be approximately 2.3 times greater than those for carbon-13 (Saliege and Fontes, 1984). Uncertainties in isotopic fractionation factors may be tested in NETPATH through the <E>dit, Isotope data screens (see later discussion).

Sulfur-Isotope Fractionation Factors

As with the carbonate phases, the fractionation factor for sulfur-bearing phases is defined relative to the average isotopic composition of sulfur in the solution. However, NETPATH does not include dissolved organic sulfur. The average isotopic composition of sulfur in solution is calculated in NETPATH using the total concentrations of SO_4 and H_2S and their individual isotopic values specified in DB–that is,

$$\delta^{34}S_T = \frac{m_{SO_4}\delta^{34}S_{SO_4} + m_{H_2S}\delta^{34}S_{H_2S}}{m_{SO_4} + m_{H_2S}} \ .$$

where SO_4 and H_2S refer to total dissolved quantities.

Only one default isotope fractionation factor is calculated for the sulfur system. This applies to precipitation of sulfide phases from solution, and is specifically intended to describe kinetic, microbial fractionation of sulfur accompanying sulfate reduction and precipitation of iron sulfide phases. It is initially assumed that the sulfur isotopic composition of sulfide phases is that of the dissolved hydrogen sulfide in solution. The additive fractionation factor for sulfur-34 between, for example, pyrite (pyr.) and solution (soln.) is then

$$\epsilon_{pyr.\text{-}soln.} = 1000\,(\alpha_{pyr.\text{-}soln.} - 1) = \delta^{34}S_{H_2S} + \epsilon_{pyr.\text{-}H_2S} - \delta^{34}S_T \ .$$

The additive fractionation factor between pyrite and hydrogen sulfide, $\epsilon_{pyr.\text{-}H_2S}$, is small (Price and Shieh, 1979) and is initially assumed to be zero in NETPATH, but may be changed by selecting the appropriate phase number on the fractionation factor screen. Several calculations are possible in defining the default sulfur isotope fractionation factor depending on the available data in DB: (1) If both sulfate and sulfide and their isotopic values are defined for the water analysis in DB, the default sulfur isotope fractionation factor for sulfide phases will be calculated directly from the analyzed data as given above; (2) if no value of the sulfur isotopic composition of dissolved hydrogen sulfide is available, the correlation introduced by Plummer and others (1990) is used to estimate $\delta^{34}S_{H_2S}$ based on the observed sulfur isotopic composition of dissolved sulfate and water temperature,

$$\delta^{34}S_{H_2S} = \delta^{34}S_{SO_4} - 54. + 0.40t \ ,$$

where t is water temperature in ° C; and, (3) if no data are available for the sulfur isotopic composition of dissolved sulfate, the default fractionation factor is undefined. The default fractionation factors may be changed by selecting the appropriate phase number appearing on the screen displaying fractionation factors.

The additive fractionation factor for a sulfate-bearing phase, such as gypsum (gyp.), is also defined relative to the average isotopic composition of sulfur in solution,

$$\epsilon_{gyp.\text{-}soln.} = \delta^{34}S_{SO_4} + \epsilon_{gyp.\text{-}SO_4} - \delta^{34}S_T \ .$$

The default additive fractionation factor between gypsum and sulfate, $\epsilon_{gyp.\text{-}SO_4}$, is defined to be zero, and may be edited by selecting the appropriate phase number under <E>dit, Isotope Data (see below). Inspection of the above equations shows that if no hydrogen sulfide is present in solution, the sulfur-system fractionation factors are the same as for the sulfate system. In deriving the above fractionation factors for sulfur-bearing phases relative to the average isotopic composition of sulfur in solution, use is made of the approximation, $\epsilon_{i\text{-}j} \approx \delta_i - \delta_j$.

Nitrogen-Isotope Fractionation Factors

The nitrogen system in NETPATH includes dissolved NO_3^-, N_2(aq), and NH_4^+. As with the carbon and sulfur phases, fractionation factors for nitrogen-bearing phases are defined relative to the average isotopic composition of nitrogen in solution. Dissolved N_2(aq) is almost always present in ground water, but is not often determined analytically. However, if nitrogen reactions are to be examined with NETPATH, it is necessary to include analytical data for N_2(aq) in DB as well as analytical data for dissolved NO_3^- and NH_4^+, if present. If isotope calculations are being made in the nitrogen system, it is necessary to enter values for the isotopic composition of NO_3^-, N_2(aq), and NH_4^+ in DB. (Note: N_2(aq) is entered in DB as N). The average isotopic composition of nitrogen in solution is calculated in NETPATH using the total concentrations of NO_3^-, N_2(aq), and NH_4^+, and their respective isotopic values specified in DB–that is,

$$\delta^{15}N_T = \frac{m_{NO_3^-}\delta^{15}N_{NO_3^-} + 2m_{N_2(aq)}\delta^{15}N_{N_2(aq)} + m_{NH_4^+}\delta^{15}N_{NH_4^+}}{m_{NO_3^-} + 2m_{N_2(aq)} + m_{NH_4^+}} .$$

where NO_3^- and NH_4^+ refer to total dissolved quantities. There are no default values for fractionation factors in the nitrogen system in NETPATH. In order to make isotopic calculations in the nitrogen system in NETPATH, all necessary nitrogen isotopic compositions of aqueous nitrogen species must be defined in DB, and all nitrogen isotopic compositions of phases and nitrogen isotope fractionation factors must be defined through the <E>dit, Isotope Data menus of NETPATH.

RADIOCARBON DATING

The problem of radiocarbon-dating of ground water can be divided into two parts: (1) definition of the ^{14}C activity at an initial point in the system (A_0), such as in the recharge zone where the water becomes isolated from the modern ^{14}C reservoir; and (2) adjustment of this initial ^{14}C activity for chemical reactions occurring along the flow path to the final well where the ^{14}C activity (A) has been measured (Wigley and others, 1978). Traditionally, radiocarbon dating of ground water has combined these two problems to develop an adjustment model that can be applied to a single water analysis at some point in the flow system. In this case, water chemistry, $\delta^{13}C$, and A of TDIC are measured for a single water analysis. An adjustment model accounting for inorganic reactions affecting the inorganic carbon reservoir is applied to the single water analysis to define the ^{14}C activity expected in the observed water if there were no radioactive decay of ^{14}C. The adjusted ^{14}C activity is compared to the measured ^{14}C activity through the radioactive decay equation to determine the radiocarbon age of the water.

Application of many of the adjustment models requires definition of the ^{14}C activity and $\delta^{13}C$ of soil-gas CO_2 and carbonate minerals dissolving in the aquifer. The ^{14}C activity of soil gas CO_2 is usually assumed to be 100 pmc. Some of the better-known inorganic carbon adjustment models are those of Tamers (1975), Ingerson and Pearson (1964), Mook (1972), Fontes and Garnier (1979), and Eichinger (1983). These models consider, to varying degrees, processes including exchange of dissolved inorganic carbon with soil-zone CO_2 (systems open and closed to soil gas CO_2), dilution of inorganic carbon by carbonate-mineral dissolution, and in some cases, adjustments for other simple mineral-water reactions such as cation exchange which can effect the carbonate-mineral mass transfer, and isotopic exchange with carbonate minerals during recharge. The traditional adjustment-model approach to radiocarbon-dating of ground water is often well suited for many limestone ground waters where carbonate mineral dissolution is the predominant reaction affecting the carbon-isotopic evolution of the water. However, a more detailed modeling approach is necessary in radiocarbon dating of ground water where processes such as oxidation of organic matter, incongruent dissolution and carbonate-mineral recrystallization are occurring. And in general, more reliable radiocarbon dating of ground water depends on quantitatively accounting for all carbon sources and sinks affecting the ^{14}C activity of the water.

The approach to radiocarbon dating of ground water taken in NETPATH differs from the traditional adjustment model approach by treating separately the problems of definition of the initial ^{14}C activity, A_0, and adjustment of A_0 for reactions along the flow path. In NETPATH, two water analyses must be identified for radiocarbon dating: an initial water and a final water along an evolutionary flow path. If the initial and final waters are defined identically, no mass transfer is calculated, regardless of the selected phases and constraints in the reaction model, and radiocarbon dating then resorts to that of the traditional approach where an adjustment model is applied to a single water. However, if the initial water is defined separately from the final water, the traditional adjustment models are applied only to the initial water along a flow path. It is expected that the adjustment models will generally be more applicable to the initial waters because of less complex geochemical evolution in, for example, recharge areas of aquifers. Having solved for the mass transfer of phases between the initial water and a final water downgradient along the flow path, NETPATH uses this mass transfer to adjust the initial ^{14}C composition, A_0, for all sources and sinks of carbon that affect the carbon mass transfer between initial and final wells along the flow path. This procedure calculates the ^{14}C composition at the final well, adjusted for chemical reaction but not radioactive decay, denoted A_{nd}. Radiocarbon dating is then applied to the final well on the flow path using A_{nd} and the observed value, A. This approach to radiocarbon dating of ground water taken in NETPATH, in effect, allows construction of a separate adjustment model

tailored for each pair of initial and final water analyses along a flow path. It is then possible to develop adjustment models for geochemically complex reaction systems.

The reaction path between the initial and final waters may be open or closed to carbon phases such as CO_2 gas, organic matter, and carbonate minerals. All carbon-mass transfer found to leave the aqueous solution between the initial and final waters, such as through carbonate mineral precipitation, or outgassing of CO_2 or methane gas (negative mass-transfer coefficients) is assumed to leave by a Rayleigh-distillation process which uses the previously defined isotopic fractionation factors. All carbon-mass transfer computed for minerals or gases that enter the aqueous phase between the initial and final waters (positive mass-transfer coefficients) is assumed to enter the aqueous solution without isotopic fractionation, and to have $\delta^{13}C$ and ^{14}C (pmc) compositions as defined for the phases (see <E>dit, Isotopic data).

The initial water may represent any point on the flow path. For example, the initial water may be located in the unsaturated zone of the recharge area where it may be in exchange equilibrium with the soil atmosphere; or it could be just downgradient of the recharge zone and isolated from the soil atmosphere; or it could be a water farther downgradient of the recharge zone, but still upgradient of the final water. Selection of an appropriate value for the initial ^{14}C activity requires careful consideration. For example, in calculating the travel time between two waters along a deep confined flow path, the initial ^{14}C value might be best defined as the measured ^{14}C composition of the upgradient well. The modeled ^{14}C "age" of the final water would, in this case, represent only the travel time between the initial and final well. To find the actual age of the final water, it would be necessary to add to this travel time the actual age of the initial water. The age of the initial water is the sum of the residence time of the water in the recharge zone before isolation from the modern reservoir, and the travel time of the water from the first point of isolation from the modern reservoir to the initial well. It is not possible to use ^{14}C data to calculate the residence time of the water in the open-system recharge zone because the carbon isotopic composition of this zone may be continually buffered by the modern soil reservoir. Recent studies of dissolved gases in shallow ground water suggest that open-system isotopic evolution may be limited primarily to the unsaturated zone waters (Dunkle and others, 1993). Once water enters the water table, it appears to be rapidly isolated from the unsaturated zone air, as in a closed system.

Radiocarbon dating then begins at the point in the aquifer where the water is first isolated from the soil reservoir (see for example Wigley and others, 1978) and here the initial ^{14}C composition, A_0, is referenced. NETPATH considers nine options (adjustment models) for definition of A_0 or the initial ^{14}C content along the flow path (see below). Caution needs to be exercised in using these options because each model has been developed for specific reaction conditions. It may not be appropriate, or desirable to apply these models to waters that have experienced extensive chemical evolution at points downgradient from the recharge environment.

If appropriate ^{14}C data are available, NETPATH will attempt radiocarbon dating of the final water. The age-dating procedure depends on three values of ^{14}C activity: (1) the initial ^{14}C value for the initial well, A_0 (such as the estimated prenuclear-detonation ^{14}C content of the recharge water at the moment the water became isolated from a modern source); (2) the adjusted ^{14}C value calculated at the final well by accounting for reaction effects to the initial ^{14}C, A_{nd}; and (3) the measured ^{14}C content in the final water, A, entered in DB. In ^{14}C age-dating, NETPATH computes values of A_{nd} for each reaction model using the defined value of A_0, defined ^{14}C isotopic content of carbon sources, defined ^{14}C fractionation factors, and the computed carbon-mass transfer. The calculated A_{nd} is displayed and used to calculate an adjusted ^{14}C age, according to the equation:

$$\Delta t\,(\text{years}) = \frac{5730}{ln\,2} ln\left(\frac{A_{nd}}{A}\right) \ .$$

The ^{14}C age is the travel time, in years, between the initial and final well.

This approach to radiocarbon dating is more generalized than that of Reardon and Fritz (1978) and Fontes and Garnier (1979) because an unlimited number of reaction possibilities can be considered. The NETPATH modeling approach to radiocarbon dating also differs conceptually from that of Cheng and Long (1984) who treated the reaction corrections as a forward simulation in the subroutine CSOTOP adapted to the reaction simulation code PHREEQE (Parkhurst and others, 1980). NETPATH uses the inverse modeling approach (Plummer, 1984). Each model found by NETPATH is constrained by the analytical data and if treated in a forward simulation, the mass transfer results would reproduce identically the final water composition. PHREEQE simulations assume arbitrary reaction models and are not constrained by the analytical data at the end-point. Forward simulations such as computed with PHREEQE-CSOTOP are useful in investigating possible trends in isotope evolution in response to hypothetical reactions. In complex hydrochemical systems it is very difficult to use forward simulation methods to find reaction models that reproduce the final water chemistry. When analytical data are available at the initial and final points along a flow path, the inverse modeling approach, such as used by NETPATH, will find all possible reaction models consistent with the available data.

Initial ^{14}C Activity Models

Several models have been proposed in the hydrochemical literature for estimation of A_0. NETPATH considers 9 possible means of defining the initial ^{14}C. These are termed: (1) original data, (2) mass balance, (3) Vogel, (4) Tamers, (5) Ingerson and Pearson, (6) Mook, (7) Fontes and Garnier, (8) Eichinger, and (9) user-defined. Several of these cases 3-8 are summarized and evaluated by Fontes and Garnier (1979) and Fontes (1992).

For consistency with the definition of total dissolved carbon in NETPATH (see above), it is necessary to modify the values of A_0 calculated from the literature models which consider only the dissolved inorganic carbon. The modification is as follows:

$$A_{0\,TDC} = \frac{A_{0\,TDIC} m_{TDIC} + {}^{14}C_{CH_4} m_{CH_4} + {}^{14}C_{DOC} m_{DOC}}{m_{TDC}} ,$$

where the subscripts TDC, TDIC, and DOC refer to total dissolved carbon, total dissolved inorganic carbon, and dissolved organic carbon, respectively, and m is molal concentration of the subscripted quantity in the initial water. If DOC and dissolved methane concentrations are zero in the initial water, the initial ^{14}C is defined identically to that for the inorganic carbon system. In calculating $A_{0\,TDC}$, $A_{0\,TDIC}$ is first calculated considering only the inorganic carbon system and using fractionation factors defined for the inorganic carbon system, as in the original references and (or) as summarized in Fontes and Garnier (1979) and Fontes (1992). These values of $A_{0\,TDIC}$ are then adjusted for the DOC and dissolved methane (if present) according to the above equation. If DOC and (or) dissolved methane are entered in DB for the initial water and radiocarbon age-dating is attempted, their ^{14}C contents must be specified (see <E>dit Isotope Data) for proper definition of A_0.

NETPATH lists the various A_0 models, allows selection of a model, and editing of data used in the $A_{0\,TDIC}$ model. An example of the $A_{0\,TDC}$ is as follows:

```
      Initial Carbon-14, A0, (percent modern)
           for Total Dissolved Carbon

       Model              Initial well

 1 : Original Data       :     33.05
 2 : Mass Balance        :     52.33
 3 : Vogel               :     85.00
 4 : Tamers              :     53.46
 5 : Ingerson and Pearson:     52.33
 6 : Mook                :     65.91
 7 : Fontes and Garnier  :     52.31
 8 : Eichinger           :     47.57
 9 : User-defined        :    100.00

Enter number of model to use (<Enter> for 'Mass Balance')
```

Note that the initial ^{14}C value for the Vogel model is given in the above example as 85.00. Because this is the value proposed by Vogel for the inorganic carbon system, it can be assumed that in the above example the concentrations of DOC and dissolved methane were zero in the initial water, or if present, had an average Carbon-14 content of 85 pmc.

For each case of defining A_0 (in pmc), NETPATH has pre-defined default values of parameters associated with the model. Once a particular case for definition of A_0 is selected, opportunity is given for altering the default values used in the particular case, or if desired, default values for all A_0 models may be edited.

Case (1) uses as a value of $A_{0\,TDIC}$, the ^{14}C content of dissolved inorganic carbon defined for the initial water in DB. The "mass balance" model, case (2), was used by Plummer and others (1990) and is similar to Tamers model (Tamers, 1967, 1975; Tamers and Scharpenseel, 1970). A chemical mass balance is made on the initial water composition assuming reaction of pure water with calcite, dolomite, gypsum and CO_2 gas. The default ^{14}C content of the CO_2 gas is assumed to be 100 pmc, and that of carbonate sources 0 pmc. Case (3) refers to the Vogel model (Vogel, 1967; Vogel and others, 1970; and Vogel and Ehhalt, 1963) which assigns $A_{0\,TDIC}$ to be 85 percent modern. The "Tamers model", case (4), is similar to the "Mass Balance" model described above, except that the mass balance is performed only on carbonates and CO_2 gas. The default ^{14}C values are carbonates, 0 percent modern, and CO_2 gas, 100 pmc.

The model of Ingerson and Pearson (1964), case (5), assumes a carbonate dissolution model to estimate $A_{0\,TDIC}$ based on ^{13}C data for the inorganic carbon system (for further discussion see Wigley and others, 1978; Fontes and Garnier, 1979). The initial ^{14}C content is estimated according to

$$A_{0\,TDIC} = \frac{\delta^{13}C - \delta^{13}C_c}{\delta^{13}C_{CO_2} - \delta^{13}C_c}\,(A_{CO_2} - A_c) + A_c\ ,$$

where δ^{13}C is the ^{13}C composition of total dissolved inorganic carbon in the initial water, $\delta^{13}C_c$ is the ^{13}C content of dissolving carbonate (default 0 per mil), $\delta^{13}C_{CO_2}$ is the ^{13}C content of soil gas CO_2 (default -25 per mil), A_{CO_2} is the ^{14}C content of soil gas CO_2 (default 100 pmc), and A_c is the ^{14}C content of soil carbonate minerals (default 0 pmc).

More complex models for the initial ^{14}C content, A_0, of total dissolved inorganic carbon have been proposed by Mook (1972, 1976, 1980), Fontes and Garnier (1979), and Eichinger (1983). All assume that carbon isotopic equilibrium occurs in one or more steps in the evolution of the recharge water. Mook assumes isotopic equilibrium between soil gas and aqueous species in an

open system. Accordingly, Mook obtains from a chemical mass balance (Fontes and Garnier, 1979)

$$A_{0\,TDIC} = N_{CO_{2\,aq}} A_{CO_{2\,aq(0)}} + 0.5\left(1 - N_{CO_{2\,aq}}\right)\left(A_{CO_{2\,aq(0)}} + A_{ls(0)}\right)$$

$$+ \left(A_{CO_{2\,gas(0)}}\left(1 - 2\times 10^{-3}\epsilon_{CO_{2\,gas}\text{-}HCO_3^-}\right) - 0.5\left(A_{CO_{2\,aq(0)}} + A_{ls(0)}\right)\right)$$

$$\cdot \frac{\delta^{13}C - N_{CO_{2\,aq}}\delta^{13}C_{CO_{2\,aq(0)}} - 0.5\left(1 - N_{CO_{2\,aq}}\right)\left(\delta^{13}C_{CO_{2\,aq(0)}} + \delta^{13}C_{ls(0)}\right)}{\delta_{CO_{2\,gas(0)}} - \epsilon_{CO_{2\,gas}\text{-}HCO_3^-}\left(1 + 10^{-3}\delta^{13}C_{CO_{2\,gas(0)}}\right) - 0.5\left(\delta^{13}C_{CO_{2\,aq(0)}} + \delta^{13}C_{ls(0)}\right)} ,$$

where N refers to the fraction of the total dissolved inorganic carbon represented by the subscripted species, the subscript "(0)" refers to the initial condition before isotope exchange reaction, and the subscript "ls" refers to the limestone. See Mook (1972, 1976, 1980) for further details.

Fontes and Garnier (1979) (see also Fontes, 1992) consider a two-stage evolution of recharge waters accounting for dissolution and isotopic exchange of carbonate minerals with CO_2 in the unsaturated zone and isotopic exchange with the carbonate rocks in the saturated zone. A chemical mass balance is performed similar to that of Tamers, with provision for base exchange, to define the mass of carbon dissolved from inorganic sources, C_M. Fontes (1992) shows that the Mook and Fontes and Garnier models reduce to a Tamer's model, if there is no isotopic exchange. Fontes and Garnier (1979) obtain the following relation for $A_{0\,TDIC}$

$$A_{0\,TDIC} = \left(1 - \frac{C_M}{C_T}\right) A_{CO_{2\,gas}} + \frac{C_M}{C_T} A_M + \left(A_{CO_{2\,gas}} - 0.2\epsilon_{CO_{2\,gas}\text{-}calcite} - A_M\right)$$

$$\cdot \frac{\delta^{13}C - \left(C_M/C_T\right)\delta^{13}C_M - \left(1 - \left(C_M/C_T\right)\right)\delta^{13}C_{CO_{2\,gas}}}{\delta^{13}C_{CO_{2\,gas}} - \epsilon_{CO_{2\,gas}\text{-}calcite} - \delta^{13}C_M} .$$

where C_T is the total millimoles of dissolved inorganic carbon in the recharge water with ^{13}C content of $\delta^{13}C$, A refers to the ^{14}C content of the subscripted carbonate minerals, M, and soil CO_2 gas, and ϵ refers to the additive fractionation factor between CO_2 gas and calcite. Fontes and Garnier (1979) discuss some of the possible limitations of their model.

Eichinger (1983) developed an isotope-exchange/mass-balance model accounting for equilibrium isotopic exchange for introduction of soil CO_2 into the water and equilibrium exchange between dissolved inorganic carbon and the carbonate rock. The model is similar to that of Ingerson and Pearson with modification for equilibrium isotopic exchange. Eichinger's equation for A_0 is

$$A_{0\,TDIC} = \frac{\delta^{13}C - \delta^{13}C_{s,eq}}{\delta^{13}C_{b,ex} - \delta^{13}C_{s,eq}} \cdot \left(N_{CO_{2\,aq}} + 0.5 N_{HCO_3^-}\right) A_{CO_{2\,gas}} ,$$

where

$$\delta^{13}C_{b,ex} = N_{CO_{2\,aq}}\left(\delta^{13}C_{CO_{2\,gas}} - \epsilon_{CO_{2\,gas}\text{-}CO_{2\,aq}}\right) + 0.5 N_{HCO_3^-}\left(\delta^{13}C_{CO_{2\,gas}} - \epsilon_{CO_{2\,gas}\text{-}CO_{2\,aq}} + \delta^{13}C_s\right)$$

and

$$\delta^{13}C_{s,eq} = N_{CO_{2\,aq}}\left(\epsilon_{CO_{2\,aq}\text{-}calcite}\right) + N_{HCO_3^-}\left(\epsilon_{HCO_3^-\text{-}calcite}\right) + \delta^{13}C_s .$$

In the Eichinger model, the subscript "s" refers to the solid, the subscript "s, eq" refers to the solid at isotopic equilibrium with the dissolved inorganic carbon of the solution, and the subscript "b, ex"

refers to the state before isotope exchange. N refers to the fraction of total inorganic carbon as CO_2 (aq) and as HCO_3^-. The equation for $\delta^{13}C_{s,eq}$ has been corrected for a misprint in the original Eqn. (6) of Eichinger (1983), (Fontes, J.-Ch., written communication, 1991; Fontes, 1992).

Carbon-13 Composition of Soil Gas Carbon Dioxide

The Models of Ingerson and Pearson, Mook, Fontes and Garnier, and Eichinger all require definition of $\delta^{13}C$ of soil gas CO_2. In the absence of measurement, NETPATH allows four options in defining this value. They are–

```
Choices for delta C-13 (per mil) in soil gas CO2
 0 : User-defined Value
 1 : Mass Balance - no fractionation
 2 : Mass Balance - with fractionation
 3 : Open System (gas-solution equilibrium)
```

Choice 0 is simply user-defined. Choices 1 and 2 each perform an isotope mass balance assuming the initial water evolved by reaction of soil CO_2 with calcite, dolomite and gypsum according to the reaction

$$CO_2(g) + H_2O + CaCO_3 + CaMg(CO_3)_2 + CaSO_4 = \text{Initial Water} .$$

An isotope mass balance defines the ^{13}C content of the CO_2 gas that entered the solution prior to reaction with the carbonate, $\delta^{13}C_{CO_{2,aq(0)}}$,

$$\delta^{13}C_{CO_{2\,aq(0)}} = \frac{\delta^{13}C_{TDIC}C_{TDIC} - \Delta_{calcite}\delta^{13}C_{calcite} - 2\Delta_{dolomite}\delta^{13}C_{dolomite}}{\Delta_{CO_{2\,gas}}} ,$$

where Δ refers to the mmoles of calcite, dolomite, or CO_2 dissolved in forming the initial water, and C_{TDIC} is the total concentration of inorganic carbon in the initial water (mmoles). Option (1) assumes that the $CO_{2\,aq(0)}$ entered without fractionation, such as from complete injection of soil gas CO_2, and therefore the ^{13}C content of the soil gas is defined directly from the mass balance. Option (2) assumes that the $CO_{2\,aq(0)}$ dissolved into the initial water maintaining isotopic equilibrium with the soil gas prior to dissolution of calcite, dolomite and gypsum, that is, gas exchange is assumed to be rapid relative to mineral dissolution. The $\delta^{13}C$ of soil gas is then calculated for option (2) from the $\delta^{13}C$ of $CO_{2\,aq(0)}$ calculated from the mass balance and the equilibrium isotopic fractionation between CO_2(aq) and CO_2 gas—that is, for option (2),

$$\delta^{13}C_{CO_{2\,gas}} = \delta^{13}C_{CO_{2\,aq(0)}} + \epsilon_{CO_{2\,g}\text{-}CO_{2\,aq}} .$$

For option (2), it is assumed that calcite, dolomite, and gypsum subsequently dissolve under closed system conditions. Option (3) assumes a completely open system in which $\delta^{13}C$ of soil gas is defined from $\delta^{13}C$ of the initial water and the $CO_{2\,g-soln}$ equilibrium fractionation defined earlier.

Isotopic Exchange

In addition to allowing phases to be marked for dissolution only, or precipitation only, NETPATH allows a phase to be considered to dissolve and precipitate in a single specified amount, a process similar to isotopic exchange. In NETPATH isotope exchange is analogous to the process of recrystallization or ripening of a pure phase. Although this does not affect the mass balance, isotopic

computations will be affected. Isotope exchange may be necessary to model observed isotopic values without disturbing a realistic mass-balance model. During isotopic exchange, the indicated mass of the solid is dissolved at its defined isotopic value and precipitated with an equilibrium fractionation step using the Rayleigh-distillation equations. In the case of carbonates, extensive isotopic exchange can have a profound effect on the modeled ^{13}C and ^{14}C content. This option should not be selected without valid evidence for the occurrence of isotopic exchange in the system. Any phase marked for isotopic exchange may be included in the model and can have net mass transfer (precipitation or dissolution) in addition to the specified amount (in millimoles) exchanged per kilogram of water. The amount exchanged is also displayed if the phase has zero net mass transfer but a specified amount of isotopic exchange. See Example 5 (below) for further information.

RUNNING DB

The first step in using NETPATH is to enter the data into a database. DB is a simple database program that accepts data in various units, allows editing of the data, stores the data in a .LON file and produces a modified WATEQF (Truesdell and Jones, 1974; Plummer and others, 1976) input file which may then be converted into a .PAT file for use in NETPATH.

To start DB, Type: DB [Filename], where [Filename] is optional on the command line. [Filename] is the basic file name to which a suffix will be added for each type of data file produced from the data. If a file name is not entered on the command line, the user is prompted for the file name.

The main screen will now be displayed. If the file contains previously entered data, the names of the wells (or the first 30, if there are more than 30 wells) will be displayed on the screen. DB accepts a total of 50 water analyses per file. An example of the main screen to DB is listed below:

```
 #  Well Name                          | #  Well Name
======================================|======================================
 1) Nashville #4                      | 2) Glynn Co. Casino
 3) FAA Hilliard                      | 4) Landings #1 (Skidaway Is.)
 5) Fernandina Beach Softball Park    | 6) Metter '75
 7) McRae #3                          | 8) Glynn Co. Recreation (Blythe Is)
 9) Blackshear                        |10) Hazelhurst #3
11) Becker                            |12) Stephen Foster Park
13) Homerville #2                     |14) Alma #3
15) Robinson - KOA                    |16) Twin City #2
17) Richmond Hill                     |18) Savannah #23
19) J. Stanfield                      |20) Savannah Beach (Tybee Is.)
21) Avera #2                          |22) Kent Canning
23) Wadley #2                         |24) Midville Exp Sta TW 1
25) City of Swainsboro #3             |26) Hopeulikit TW 2
27) Town of Cadwell #1 (1976)         |28) DNR Laurens Co. #3
29) Albert S. Mercer (1977)           |30) Laurens Park Mill #3
================================================================================
<A>dd, <D>elete, <E>dit, <M>ove, <N>ext page, <P>rint, <S>ave/<S>peciate, or <Q>uit?
```

A list of the available options is displayed at the bottom of this screen. These are accessed by typing the first letter of the desired option. Descriptions of these options follow.

Add

This selection allows data for a water analysis to be entered into the database. After a position is selected where the new analysis should be added, the user is asked whether all data are to be entered or just the data used in NETPATH. Some of the data stored by DB (in the .LON file) do not affect the results of NETPATH modeling, and these need not be entered. This applies to information such as site ID, well depth, well elevation, length of casing, and aquifer name.

Next, the units to be used for the given water analysis must be selected. DB accepts analytical data in units of millimoles per liter (mmol/L), milliequivalents per liter (meq/L), milligrams per liter (mg/L), parts per million (ppm), or millimoles per kilogram of water (mmol/kg H_2O). If the analytical data are to be used in NETPATH without conversion, units of mmol/kg H_2O (option 4) should be selected. For example, if the analytical data were speciated using an aqueous model that differed from that of DB and it was necessary to retain this speciation for definition of total dissolved inorganic carbon, the data should be entered in units of mmol/kg H_2O. Example 2 uses

this feature for a brine analysis that was speciated using the Pitzer aqueous model of PHRQPITZ (Plummer and others, 1988) to define total dissolved inorganic carbon from alkalinity and pH.

A change in version 2.0 of NETPATH now requires all analytical data for both solutes and dissolved gases to be entered into DB with the same analytical units. Other units are as follows, temperature in °C; density in grams per cubic centimeter (g/cm^3) (default is 1.0); Eh in volts; tritium in tritium units (TU); ^{14}C of TDIC in percent modern carbon (pmc); $^{87}Sr/^{86}Sr$ as the mole ratio; and all other stable-isotope data in per mil.

DB also allows selection of one of two options in calculating individual ion activity coefficients (Extended Debye-Hückel and Davies equations; see Plummer and others, 1976), and one of four options in selecting the way TDIC is to be specified. These are (1) the usual field titration alkalinity (as HCO_3^-), uncorrected for non-carbonate alkalinity species, (2) the carbonate alkalinity (as HCO_3^-), in which alkalinity contributions from non-carbonate species have already been subtracted, (3) total dissolved inorganic carbon, TDIC, and (4) the usual field titration alkalinity expressed as $CaCO_3$, rather than as HCO_3^-. Plummer and others (1976) give more information on input data to WATEQF.

For each remaining value to be entered, a prompt is displayed which includes the name of the value and, if applicable, the units in which it is to be entered. A special routine is used to receive and store data. <Enter> causes a missing value condition to be stored for the datum. If an integer value is to be entered, a decimal point is optional in the input.

After all the requested values have been entered, a screen is displayed with the analytical data for the water analysis for the current well. This screen is identical to that obtained with the <E>dit function of the program. See the section on Edit for details. This is an example of the display screen of DB for a particular water analysis:

```
42) Stephen Foster Park              27E003   304943082214701  85/08/14 @ 1000

    1)Temp.       2)pH          3)Diss. O2    4)Field Alk.  5)Tritium
         21.7          7.31           0.0          322.7           0.2
    6)H2S         7)Ca2+        8)Eh          9)Mg2+       10)Na+
          3.4           68.4    SO4/H2S             34.4          59.2
   11)K+         12)Cl-        13)SO42-      14)F-         15)SiO2
          3.6           72.1          61.6           1.0           36.
   16)Br-        17)B          18)Ba2+       19)Li+        20)Sr2+
        0.22          0.060         0.044         0.025         0.620
   21)Fe         22)Mn         23)NO3-N      24)NH4-N      25)PO4-P
        0.059         0.002    <    0.010          1.4          0.001
   26)DOC        27)Sp. Cond.  28)Density    29)13C TDIC   30)14C TDIC
          6.8           786.          1.0        -12.80          1.63
   31)34SSO4     32)34SH2S     33)D          34)18O        35)Diss CH4
         31.5          -30.7         -7.5          -2.15    **********
   36)Sr 87/86   37)Al3+       38)N2-N       39)15N N2     40)15N NO3
      0.70849           0.0    **********    **********    **********
   41)15N NH4
         113.
Enter # of value to change, 42 to edit other data, <Enter> to exit :
```

Less than values, denoted "<", may be stored with DB (see for example NO_3^- above) in the .LON file. In making the .PAT file, less than values are written as zero. Several choices in defining Eh are also available in DB, as originally defined in Plummer and others (1976). In the above example, Eh will be calculated in WATEQFP using an equilibrium relation between dissolved sulfate and dissolved hydrogen sulfide.

Data entered with <A>dd are permanently stored in the .LON file only after a <S>ave/<S>peciate (see Save/Speciate function below).

Delete

With this selection, a well can be removed from the database. This change will only be permanent if the .LON file is subsequently saved (See Save/Speciate function below).

Edit

When the edit screen appears, either upon completion of adding a well or selection of <E>dit, the data for the well are displayed on the screen (see above). Missing, that is, undefined values are displayed as **********. To edit a value, enter the number next to the corresponding label. To edit the well name, as well as the owner's address, date, time, and other data related to the physical characteristics of the well, enter 42. Edit option 42 also allows changing units of concentration and choice of activity coefficient option. The first 4 integers of the first line of information for each water analysis of the .LON file contain the WATEQF flags IUNITS, PECALC, CORALK, and IDAVES (See Plummer and others, 1976 for definition). NOTE: Data changed with <E>dit are permanently stored in the .LON file only after selection of <S>ave/<S>peciate and selecting option (1) "Save raw data", or option (3) "both" (see Save/Speciate function below).

Move

The order in which the wells are displayed can be changed using this command. The number of the well to be moved and the well number after which it is to be inserted are entered, and the move is carried out.

Next Page

Only 30 wells will be displayed on the screen at once. If there are more than thirty wells in the database, <N>ext Page displays the remaining wells on the screen. This command will not be listed if there are fewer than 30 wells in the database. The maximum number of wells that can be stored in a single [Filename] well file is 50.

Print

This option has two functions: (1) to print a report (to a file) of the data for a well, and (2) to perform a preliminary check of cation-anion balance. Printed reports can be generated for a single well or for all wells in the file. Resulting files are named OUTPUTxx, where xx is the number of the well that is printed. Checking cation-anion balance produces a file named CHECK, which lists the percent error (plus or minus) of the charge balance calculation for each well. The percent charge imbalance is calculated from the relation

$$\text{Percent Charge Imbalance} = \frac{\sum meq_{cations} - \sum meq_{anions}}{\sum meq_{cations} + \sum meq_{anions}} \times 100 \ ,$$

where meq is milliequivalents per kilogram H_2O. Note that this calculation of charge imbalance should be used only as a rough guide, because it is based on single, assumed, predominant species for each element. WATEQFP performs a complete charge balance analysis based on the temperature, pH, and chemical speciation. The complete charge balance appears in the .OUT file which is produced in making the .PAT file and may be viewed interactively from DB after the analyses have been speciated in WATEQFP.

Save/Speciate

It is important to save entered data before quitting DB. Three choices are presented when using the <S>ave/<S>peciate command: (1) save raw data (to the .LON file), (2) create a .PAT file, or (3) both (1) and (2). Choice 3, make both the .LON and .PAT file, is default. The .LON file for a system contains all the data entered for all of the wells considered. In creating the .PAT file, a special WATEQFP input file, .IN, is created to be read by WATEQFP to produce the .PAT file.

When making the .PAT file, the user is prompted as to whether the .PAT file is to be adjusted for charge imbalance in the input data. Because of missing data and (or) analytical errors, chemical analyses of waters are rarely electrically charge balanced. As a first attempt to address this problem, DB allows the .PAT file to be constructed in two ways: (1) using the original unaltered analytical data which may or may not be electrically balanced (default), and (2) modifying the original analytical data to attain approximate charge balance. In this latter case the electrical imbalance of each water analysis is distributed proportionally on the basis of equivalents among all the species except H^+, which is retained in the reported pH. When charge balancing is selected, all original analytical data for the analysis are modified in the .PAT file, creating altered water analyses that are approximately charge balanced. The charge-balancing procedure is imprecise because analytical errors in minor element concentrations are ignored and the adjustments do not take into account the full speciation/complexation of the aqueous model. There must be analytical data for at least one major cation and one major anion in the analysis for the charge balancing option to be invoked. If greater accuracy in charge balancing of analytical data is required, or other options are to be considered in obtaining charge-balanced waters, this should be carried out by the user prior to entering data in DB.

Caution should be exercised when selecting the charge balancing option because all the original analytical data will be modified in the .PAT file. However, none of the original data in the .LON file are altered when the charge-balance option is selected. Ideally, geochemical modeling should be conducted using perfectly analyzed, electrically balanced waters, but in practice, this is rarely the case. As discussed earlier, errors in calculated mass transfers can result from mass-balance models based on charge-imbalanced waters. It is advised that as a part of the modeling process, the previously defined and saved models from NETPATH should be examined using charge-balanced waters.

After selecting the appropriate charge-balance option, the user is prompted for the name of the thermodynamic data file to be read by WATEQFP (default is DB.DAT). DB then displays the message "Running aqueous model – please wait". During this operation, Redox Ignored warnings may appear. These indicate that any iron (Fe) and manganese (Mn) results may be incorrect. Without redox information, iron and manganese can not be speciated among the possible redox

states. If Fe or Mn data are given, but Eh data are not available, a default Eh of zero volts is assumed. The default value for solution density is 1.0, if not entered.

WATEQFP was entirely re-written in version 2.0 of DB to produce a generalized aqueous model with all equilibria and thermodynamic data read from an external file, DB.DAT. It is now possible to modify the thermodynamic data base of the WATEQFP aqueous model by editing the DB.DAT file. WATEQFP retains the activity coefficient expressions defined by Truesdell and Jones (1974) and uses the ion association model of WATEQ4F (Ball and Nordstrom, 1991) for the elements allowed in DB and NETPATH. Analytical data are stored in the .PAT file in units of millimoles per kilogram H_2O in the range 0.00001 to 9999.999. A listing of the DB.DAT file is given in Attachment B. Once the .PAT file is created, the WATEQFP output file is saved as [Filename].OUT. This file, with only minor changes, contains the full output from WATEQF (Plummer and others, 1976), including mineral saturation indices.

Quit

DB is terminated.

RUNNING NETPATH

Wherever practical in NETPATH, <Enter> results in the most common or natural selection being chosen or the current state of the value being requested to be retained. At prompts with no single preferable option or no previous reasonable value, <Enter> usually has no effect. Therefore, when the user is presented with a series of prompts, <Enter> will quickly run through them with no changes to current values.

NETPATH also handles incorrect input without abnormal termination. Values out of range or of incorrect type are handled without improper program termination. For example, when the program expects a real (noninteger) number input, an integer will be read and converted to a real value in the program. Entering letters at a prompt for a numerical value will not cause any major problem, although the value will have to be reentered.

File Selection

Once the user has prepared a file of water analyses using DB, and created the .PAT file for these data, NETPATH may be started. In running NETPATH, a list of all the available .PAT files of data (listed in NETPATH.FIL) is first displayed, and the user is instructed to select one. Next, NETPATH displays a list of model files (stored in MODEL.FIL) previously saved under the selected well file. If no model file is selected (or present), NETPATH requests whether the problem involves mixing of initial waters, and if so prompts for the number of waters mixing (maximum of 5). NETPATH then requests selection of initial and final wells from the .PAT file. If an existing model file is selected, the user has the option of accepting the model, deleting it from the list, or returning to the model list for another selection. If a previously saved model file is selected, lists of constraints and phases in the model are displayed along with the wells to be modeled. The user has the option of selecting the model or selecting phases and constraints individually later. If accepted, the phases and constraints may later be modified by choosing the appropriate options from the main screen of NETPATH.

Main Screen Functions

Once the desired files or wells have been selected, the main screen is displayed. This screen contains many of the important facts about the current model under consideration. The currently selected wells, the constraints and phases being used, and some parameters are displayed. When initially setting up a model, the screen is blank under the headings Constraints and Phases (see Add below). By responding to a few prompts, any part of the model can be edited. Warnings may be displayed if inappropriate choices are made. This is a sample main screen:

```
Initial Well: Madison.Recharge #3                          NETPATH 2.0
Final Well  : Madison.Mysse                               June 21, 1994
================================================================================
     Constraints: 10      |        Phases: 10           |      Parameters
--------------------------|-----------------------------|----------------------
Carbon       Sulfur       |+DOLOMITE CALCITE +ANHYDRIT |Mixing: No
Calcium      Magnesium    |+"CH2O"   GOETHITE-PYRITE   |Evaporation: No
Sodium       Potassium    | EXCHANGE+NaCl     SYLVITE  |Rayleigh Calcs: Yes
Chloride     Iron         | CO2 GAS                    |Exchange: Ca/Na
Redox        Sulfur-34    |                            |Init C-14  52.33 (TDC)
                          |                            |(Mass Balance)
================================================================================
Select: <A>dd, <D>elete, <E>dit, <R>un, <S>ave, <V>iew, or <Q>uit
```

From the main screen, the user can branch to <A>dd, <D>elete, <E>dit, <R>un, <S>ave, <V>iew, or <Q>uit. A description of each of these options follows.

Add

Once <A>dd is selected, the user may choose to add either constraints or phases. Constraints and phases were discussed earlier in the section IMPORTANT CONCEPTS IN NETPATH. If constraints are chosen, all available element, redox and isotopic constraints are listed for selection.

A selection of commonly used phases is stored in the file NETPATH.DAT. This file is read by NETPATH and, after choosing to add a phase, any mineral in the file can be selected. As the prompt states, typing L at the prompt will return a list of the phases read from NETPATH.DAT, their corresponding numbers, and their default precipitation-dissolution limitations. Typing the number of a phase at the <A>dd, Phase prompt will select a previously stored phase to be considered as part of the model. If the desired phase is not included in NETPATH.DAT, the desired phase, its stoichiometric coefficients, and redox state can be entered and the resulting phase saved into NETPATH.DAT for later use. New phases are entered by selecting the phase number corresponding to "Other" (82 in release version 2.0). The number corresponding to "Other" is incremented with each new phase stored in the NETPATH.DAT file. The isotopic compositions of phases are entered and (or) edited through the <E>dit, Isotopic data selection from the Edit menu and can be stored in model files, but not in NETPATH.DAT. Changes to default isotopic values for phases stored in NETPATH.DAT must be made by editing the NETPATH.DAT file with a text editor.

After a phase is selected or defined, the user is presented with some questions about the phase. Usually, the default, selected by <Enter>, is all that is needed. Each phase must be marked in one of four ways: (1) dissolution only, (2) precipitation only, (3) dissolution or precipitation allowed, or (4) isotopic exchange. Options 1-2 limit the total possible number of models. Sometimes it is not known whether the phase is a reactant or product, in which case option 3 is selected. Option 4, isotopic exchange, allows the user to specify an amount (in mmol/kg H_2O) of a phase that dissolves and precipitates in an isotopic exchange. If isotopic exchange is selected for a phase, the phase will also be allowed to dissolve or precipitate a net mass transfer along the flow path. After specifying the amount of a phase to undergo isotopic exchange, the isotopic composition of the phase in the exchange reaction may be specified. The isotopic composition of the exchanging phase can differ from that defined under <E>dit, Isotopic data, the latter of which is used if there is net dissolution of the phase. This option is useful if, for example two separate calcite phases occur in the system, one undergoing net dissolution and another, perhaps more stable phase undergoing

precipitation (recrystallization). The default selection applies the same isotopic composition defined under <E>dit, Isotopic data to the exchange reaction.

Another option allows the user to specify whether every model must contain that phase (termed forcing). Below is an example of the main screen showing kaolinite forced to be included in every model and allowing dissolution only (+) for NaCl, gypsum, and plagioclase feldspar, and precipitation only, (−), for kaolinite and Ca-montmorillonite:

```
Initial Well: Sierra Nevada (Ephemeral Spr.)            NETPATH 2.0
Final Well  : Sierra Nevada (Perennial Spr.)           June 21, 1994
================================================================================
     Constraints:  8      |        Phases:  9          |      Parameters
--------------------------|-----------Forced-----------|----------------------
Carbon       Sulfur       |-KAOLINIT                   |Mixing: No
Calcium      Magnesium    |----------Unforced----------|Evaporation: No
Sodium       Chloride     |+NaCl    +GYPSUM  -Ca-MONT  |Rayleigh Calcs: No
Silica       Aluminum     | CO2 GAS  CALCITE  SiO2     |
                          | BIOTITE +PLAGAN38          |
================================================================================
Warning: There is no data for Aluminum in 2 of the wells: zero will be used
================================================================================
Select: <A>dd, <D>elete, <E>dit, <R>un, <S>ave, <V>iew, or <Q>uit
```

If a new phase were entered (through the phase number corresponding to "Other"), the user may identify the phase to be saved in the NETPATH.DAT file. The NETPATH.DAT file is updated during execution of the <Q>uit command.

Delete

The <D>elete option allows phases or constraints to be removed from consideration in the model. More than one constraint or phase may be deleted before returning to the main screen. Within the Delete option the only way to delete all the phases or constraints is one at a time from the list displayed.

Edit

This selection is used to change a wide range of conditions and parameters in the models. Initiation of <E>dit prints an Edit menu on the screen, for example:

```
 General
   1) Well file              : class
   2) Entire model
   3) Phases
Wells
   4) Mixing                 : No
   5) Initial well           : Madison.Recharge #3
      Final well             : Madison.Mysse
 Parameters
   6) Evaporation/Dilution   : No
   7) Ion exchange           : Ca/Na
   8) Redox state of DOC
 Isotope calculations
   9) Rayleigh calculations  : Yes
  10) Isotopic data
  11) Model for initial C14  : Mass Balance
  12) Carbon fract. factors  : Mook
--------------------
Edit which? (<Enter> when done)
```

By selecting the appropriate number from the Edit menu it is possible to (1) change the well file to another set of wells (if other .PAT files exist), (2) change the model, if models have been previously saved under the current well file, (3) change or edit phases, (4) switch between mixing and nonmixing models, (5) select different initial and final waters from the well file, (6) switch on or off the evaporation/dilution option, (7) select various options affecting cation exchange, (8) redefine the redox state of DOC in initial and final waters (for the current model), (9) switch on or off the Rayleigh calculations and, if the Rayleigh calculations are invoked, (10) edit isotopic data on phases, isotopic values of dissolved methane and DOC, and isotope fractionation factors, (11) select a method for defining the initial ^{14}C content, A_0, for radiocarbon dating, and (12) select either the Mook or Deines and others sets of fractionation factors for the inorganic carbonate system defined previously. The above numbers of options in the Edit menu can change depending on selection of phases (EXCHANGE and CO2-CH4), and whether mixing or Rayleigh calculations are called for. If the phase CO2-CH4 is added, an additional parameter is displayed for definition of the fraction of CO_2 gas in the mixture. NETPATH returns to the edit menu after completion of each task. Some of the general features of <E>dit are described below.

Editing well files

This option allows the user to select another .PAT file from the well file (listed in NETPATH.FIL). If no other .PAT file exists in the directory, only the current .PAT file can be selected. When changing .PAT files, a previously defined model may be retained and applied to waters from a different well file.

Editing model files

This option allows the user to return to the list of models (in NETPATH.FIL) previously saved under the current well file and select another model file. Once selected, the set of constraints and phases previously defined for the model are displayed and the user has the option of deleting the model from the list of models, selecting another model, or accepting the model.

Editing phases

After this option is chosen, a list of the current phases in the model is displayed. A phase can be selected from the list by number and then edited. The entire phase can be replaced by either a previously entered phase or a user-entered phase, or simply kept. Selecting "Phases" from the Edit menu allows the user to modify any phase in the model, changing its name, stoichiometry, and dissolution, precipitation and forcing attributes. In defining new names of phases, the only limitations are that "CO2" should not be the first three letters of the phase name and the phase should not be called "EXCHANGE". These keywords initiate phase-specific routines that are not appropriate for most phases. To include additional phases in the model, use <A>dd from the main menu (see above).

Once a phase name has been entered, the stoichiometry of the phase may be defined one element (or redox state) at a time, along with the corresponding stoichiometric coefficient in the phase. Once this process is over, the defined stoichiometry is displayed, and may be edited, deleted, or more constraints can be added. <Enter> ends this editing. Once dissolution/precipitation and forced/unforced information has been entered, the phase may be stored in NETPATH.DAT. If the name is the same as a phase already in the file, it can be saved under a new name or it can replace the current phase in NETPATH.DAT. The initial designation of dissolution/precipitation behavior is stored as a default value for the phase and recalled each time the phase is added to a model. This default designation can be changed by editing the phase in the model and (or) overwriting the phase in the NETPATH.DAT file with a new default condition. It is not possible to edit the default isotopic compositions of phases in the NETPATH.DAT file within NETPATH (see <E>dit, Isotopic data). If the program is terminated in any way other than <Q>uit, additions to NETPATH.DAT will not be saved.

Editing mixing

With this option (option 4), the user can select whether mixing is to be considered. If mixing is invoked, the screen prompts for the number of waters that mix (maximum of 5 in NETPATH version 2.0), then displays the list of wells from the well file for selection. If the mixing option is subsequently turned off, only the first initial well among the previously-defined initial wells is retained in the model.

Editing wells (selecting wells within the well file)

Option 5 (and 4, if mixing) allows the user to select new initial and final wells from the [Filename].PAT file. Editing wells provides a means to apply a previously defined model to a new set of initial and final water analyses. <Enter> at any of the prompts keeps the current value, unless no value has been previously entered. By changing to a new well file (<E>dit, Well file), an existing model can be applied to waters from another [Filename].PAT file.

Editing parameters

Parameters can be used to include the possibility of evaporation or dilution (with pure water) during the evolution of the initial water(s) to the final water, define various ways cation exchange

can be calculated among Ca^{2+}, Mg^{2+}, and Na^{+} in the model, define the fraction of CO_2 gas in the CO2-CH4 gas mixture, and adjust the redox state of the DOC for each well within the model. Changes to the redox state of DOC in NETPATH do not effect the original data stored in either the .LON or .PAT files. Current values of all parameters are saved for a model using the <S>ave option from the main screen. The phases EXCHANGE and CO2-CH4 must be present in the model before they can be edited through the Edit menu. For further information, see the section "Phases" in IMPORTANT CONCEPTS IN NETPATH.

Editing isotope calculations

A toggle to allow Rayleigh calculations is accessed through the Edit menu. Once Rayleigh calculations are allowed, isotopic data may be edited. The data entered into this part of the program are used both for isotope mass balance and Rayleigh calculations. Even if the problem is one of the strictly valid isotope mass balance cases discussed above (see ISOTOPIC CALCULATIONS), it is still necessary to enable the Rayleigh calculations to edit the isotopic data. If Rayleigh calculations are selected, and phases containing carbon, sulfur, nitrogen, and (or) strontium are included in the model, three more options appear on the Edit menu, enabling the user to (1) Edit Isotopic data, which includes editing the isotopic compositions of phases in the model, editing the isotopic composition of DOC and CH_4 in initial and final waters, and editing fractionation factors, (2) select various means of defining the initial ^{14}C activity, A_0, in the recharge water, and (3) select one of two internal sets of carbonate-system fractionation factors (Mook set; Deines and others set).

The option <E>dit, Isotopic data allows values for the $\delta^{13}C$, ^{14}C (pmc), $\delta^{34}S$, $\delta^{15}N$, and the $^{87}Sr/^{86}Sr$ ratio to be defined for all carbon, sulfur, nitrogen, and Sr-bearing phases in the model. Control passes to a second screen under this option to allow editing of the carbon isotopic composition of dissolved methane and DOC, if either are present in any of the selected wells. Finally a third screen appears to allow editing of fractionation factors. The next choice from the Edit menu allows definition of the initial ^{14}C content (A_0, pmc), or calculation of A_0 from the adjustment models defined previously (see RADIOCARBON DATING). The final choice from the Edit menu allows selection of either the Mook set or Deines and others set of fractionation factors of inorganic carbon. The editing of isotopic data is discussed in more detail below.

Editing the isotopic composition of phases.

The first screen under <E>dit, Isotopic data deals with the isotopic composition of phases selected on the main screen. If there are any phases containing carbon, sulfur, nitrogen, or strontium, the first screen displayed under the <E>dit, Isotopic data option contains the isotopic compositions of $\delta^{13}C$, ^{14}C (pmc), $\delta^{34}S$, $\delta^{15}N$, and $^{87}Sr/^{86}Sr$ in those phases. An example of this screen is as follows:

```
                        Isotopic Compositions

Num Phase     Carbon-13  C14 % mod  Sulfur-34    Sr-87       N-15
-------------------------------------------------------------------
 1: DOLOMITE    4.000      0.000
 2: CALCITE     0.000      0.000
 3: ANHYDRIT                          15.500
 4: "CH2O"    -25.000      0.000
 5: PYRITE                          -22.090
 6: CO2 GAS   -16.200    100.000

Enter number of phase to edit. <Enter> when done.
```

In this example there were no Sr- or N-bearing phases in the model.

The isotopic compositions of the phases have either been entered by the user, retrieved from a saved model file, retrieved from NETPATH.DAT, or they are undefined. If "CO2-CH4" is a selected phase, δ^{13}C and ^{14}C (pmc) values will be displayed separately for the two gases in the gas mixture. The values will be combined according to the ratio determined by the fraction of CO_2 in the phase (see previous discussion of the CO2-CH4 phase). The listed isotopic compositions will be used in mass-balance calculations if δ^{13}C, ^{14}C, δ^{34}S, δ^{15}N, or ^{87}Sr/^{86}Sr are included as constraints. These isotopic compositions apply to both dissolution and precipitation (outgassing) processes when the isotope is included as a constraint. Alternatively, if Rayleigh calculations are made, these isotopic values are used for incoming sources only. Dissolution is considered a non-fractionating process. The δ^{13}C, ^{14}C, δ^{34}S, δ^{15}N, and ^{87}Sr/^{86}Sr isotopic compositions of all outgoing phases containing these elements are determined according to defined fractionation factors and the general analytical solution to the Rayleigh distillation problem of N incoming phases and M fractionating out-going phases (Wigley and others, 1978, 1979). The isotopic compositions have the following units: δ^{13}C in per mil relative to PDB, ^{14}C in percent modern carbon of the NBS oxalic acid standard, $\delta^{34}S$ in per mil relative to CDT, δ^{15}N in per mil relative to air, and Strontium-87 as the isotope ratio, ^{87}Sr/^{86}Sr.

Editing the isotopic composition of dissolved methane and dissolved organic carbon

If the concentrations of dissolved CH_4 and (or) DOC were entered in DB, they are stored in the .PAT file for use in NETPATH where they are summed with the dissolved inorganic carbon in defining the total dissolved carbon in solution. For isotopic calculations of δ^{13}C, it is also necessary to know the δ^{13}C composition of the dissolved CH_4 and DOC. Because these data are not routinely measured, there is no provision to store them through DB and into the .PAT file. Instead NETPATH accepts data for the δ^{13}C composition of dissolved CH_4 and DOC for a particular model. If data are given in DB for the concentrations of dissolved CH_4 and (or) DOC, and carbon is selected as a constraint in the NETPATH model, a second screen appears under <E>dit, Isotopic data for entering (and adjusting) the δ^{13}C and ^{14}C composition of dissolved CH_4 and DOC. An example of this screen follows:

```
                Isotopic compositions of Carbon in solution

                                  Carbon-13  C14 %mod   Carbon-13  C14 %mod
#  Well Name                       of CH4     of CH4     of DOC     of DOC
-------------------------------------------------------------------------
1: Nashville #4                                          -25.000     0.000
2: FAA Hilliard                                          -25.000     0.000
Enter number of well to change, <Enter> when done.
```

In the above example, the .PAT file contained no data for the concentration of dissolved CH_4. The .PAT file does contain analytical data for DOC and here its $\delta^{13}C$ is defined to be -25 per mil and its ^{14}C content is defined to be 0 pmc.

The isotopic compositions of dissolved nitrogen, sulfur and strontium species are entered separately in DB and stored in the .PAT file, along with the $\delta^{13}C$ and ^{14}C activity of TDIC.

Editing fractionation factors

Editing of fractionation factors is accessed through the third screen which appears under the <E>dit, Isotope data option of the Edit menu. Additive fractionation factors, ϵ, in per mil relative to the average isotopic composition of the element in solution may be specified for any precipitating (or outgassing) phase containing carbon, sulfur, nitrogen, or strontium.

Although fractionating processes may be included for the $^{87}Sr/^{86}Sr$ ratio, isotope fractionation is not expected for strontium owing to the relatively high mass. The strontium isotope ratio is included with carbon, sulfur, and nitrogen isotopes because all are treated using isotope evolution equations (Wigley and others, 1978, 1979) when Rayleigh calculations are invoked. The default additive fractionation factor for $^{87}Sr/^{86}Sr$ of 0.0 per mil should be utilized in this case. If sufficient data are available in the DB database, NETPATH computes default additive fractionation factors for $\delta^{13}C$, $\delta^{14}C$, and $\delta^{34}S$ relative to the average isotopic composition of that element in solution. The calculated per mil equilibrium additive fractionation factor for ^{14}C species is taken as two-fold the $\delta^{13}C$ fractionation (Craig, 1954). Alternatively, the ^{14}C fractionation factors can be defined under <E>dit, Isotope data.

The additive fractionation factors are calculated for the conditions at the final well (default $X = 1$), but may be specified at the initial well conditions ($X = 0$), or at any value in the interval $0 \leq X \leq 1$ where X is the fraction of the flow path between initial and final well. In NETPATH, fractionation factors calculated based on well data are shown with an asterisk. In mixing cases the initial fractionation factor is defined as the mean of the fractionation factors for the two initial waters. An example of the second isotope screen displayed for definition of fractionation factors is as follows:

```
             Additive Fractionation Factors (in per mil)
                        Relative to solution
Num Phase    Carbon-13  C14 % mod  Sulfur-34    Sr-87       N-15
-------------------------------------------------------------------
 1: CALCITE     2.381*     4.761*
 2: PYRITE                            -37.896@
 3: CO2 GAS    -5.924*   -11.848*
* = based on computed value at 0.50 fraction between init and final waters
@ = based on computed value at final water

Enter number of phase to edit, '0' for fraction along path, <Enter> when done.
```

Run

Selection of <R>un executes a modified version of BALANCE (Parkhurst and others, 1982) which has been named NEWBAL (Parkhurst, unpublished data on file in the Branch of Regional Research, Central Region, U.S. Geological Survey). However, the matrix–solving routine of NEWBAL was replaced with a more flexible version (Barrodale and Roberts, 1980). NETPATH first

displays the data to be input to NEWBAL, with prompts to abort should unexpected data be recognized. The following abbreviations are used in the display of the input data to the mass balance:

Abr.	Long Name	Abr.	Long Name	Abr.	Long Name	Abr.	Long Name
18	Oxygen-18	D	Deuterium	K	Potassium	P	Phosphate
AK	Alkalinity	F	Fluoride	LI	Lithium	RS	Redox
AL	Aluminum	FE	Iron	MG	Magnesium	S	Sulfur
B	Boron	HS	Sulfide	MN	Manganese	SH	34SH2S
BA	Barium	I1	Carbon-13	NA	Sodium	SI	Silica
BR	Bromide	I2	C-14 (% mod)	NH	Ammonium	SO	Sulfate
C	Carbon	I3	Sulfur-34	NO	Nitrate	SR	Strontium
CA	Calcium	I4	Sr-87/Sr-86	O2	Diss. O2	SS	34SSO4
CL	Chloride	I5	Nitrogen-15	OC	Organic C	TR	Tritium

This information can be used to check that the appropriate compositions of phases are being used. Also listed as input to NEWBAL are the compositions of the final and initial waters in mmol/kg H_2O.

All combinations of phases are checked to see if mass transfers can be found that satisfy the chosen constraints. The total number of models found, if any, is then displayed. If many more phases are included than constraints, the total number of models can be very large. Relatively long computation times may be required to find all possible models. While running NETPATH, the screen displays the total number of models to be tested, the cumulative total number of models tested (update in increments of 100 models), and the updated total number of models found. As discussed in IMPORTANT CONCEPTS IN NETPATH, the total number of models can be reduced by deleting unnecessary phases, editing phases by marking them for dissolution or precipitation only, and including appropriate forcing conditions for phases.

Alternatively, if no models are found, the program will determine if models can be found by ignoring precipitation/dissolution constraints. The output indicates which constraints could be ignored to find models. This procedure is sometimes useful in guiding the modeling exercise. If only one model is found, it will be displayed. If more than one model is found, the user is prompted whether to display the models all at once, one at a time, or not at all. At any prompt in this section, the user may return to the main screen.

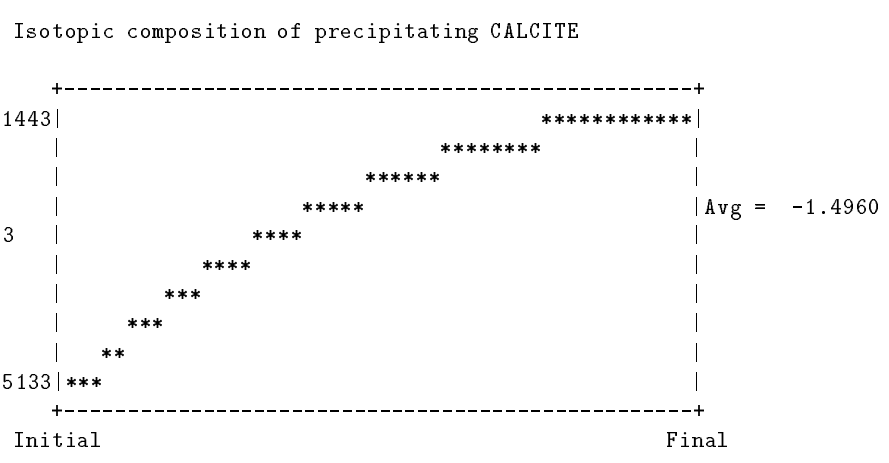
Isotope calculations during run

When the Rayleigh calculations are enabled (through the Edit menu), isotopic values are calculated for each of the five isotopes δ^{13}C, δ^{14}C, δ^{34}S, δ^{15}N, and ^{87}Sr/^{86}Sr. The message "Insufficient data" is displayed if there are data missing that are needed in the calculation. Explanation of the "Insufficient data" message is given for each isotope so marked by selecting <E> (to explain insufficient data). It may be necessary to return to DB to add appropriate isotopic data to the water analysis, save a new .LON file, and make a new .PAT file. Alternatively, the error message could result from failure to define appropriate isotopic data required in making the Rayleigh calculations. In this case it is necessary to return to <E>dit, Isotopic data to add the missing data.

After a model is displayed, more details about the isotopic evolution model can be displayed. The data input into the Rayleigh calculations can be displayed separately for each isotope by selecting <S> (to show Rayleigh data). This operation displays the initial carbon-13 and initial carbon-14 values for total dissolved carbon in the initial solution, and the initial sulfur-34 and initial

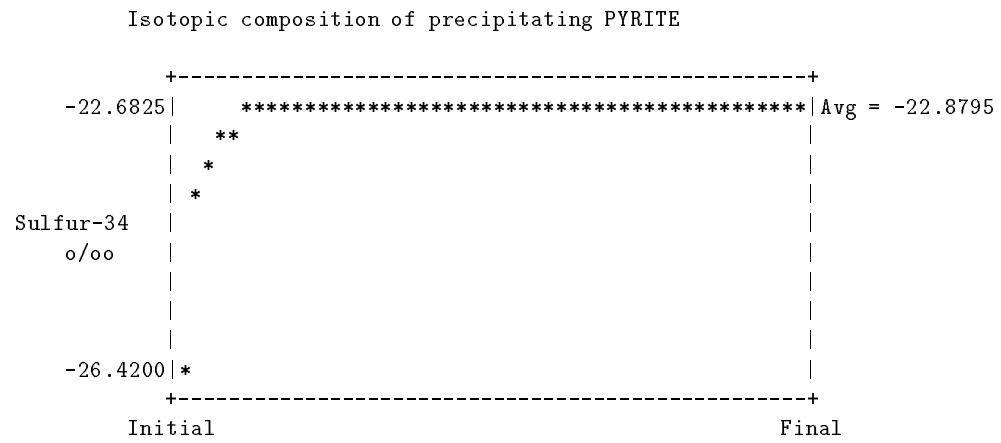
nitrogen-15 per mil value for total dissolved sulfur and nitrogen in the initial solution. Option <S> also displays phase mass transfers, additive fractionation factors, the average isotopic composition of the total amount of the phase precipitated or outgassed. Selecting <Enter> switches the display to the next isotope considered in Rayleigh distillation calculations, or by striking any key other than <Enter>, NETPATH plots a model calculation of the isotopic evolution of the outgoing phase along the flow path between the initial and final water. The model calculations of isotopic values along the flow path assume the relative rates of mineral-water reactions are constant between the initial and final water in proportion to the computed net mass transfer. A constant average additive fractionation factor defined in <E>dit, Isotope data, is used in the calculation. An example display is as follows:

```
 Data used for Carbon-13

 Initial Value:     -6.9900        Modeled Final Value:     -2.2137

  2 dissolving phases:
 Phase       Delta C     Isotopic composition (o/oo)
 DOLOMITE    7.06000             4.0000
 "CH2O"      0.87077           -25.0000

  2 precipitating phases:                              Average
 Phase       Delta C     Fractionation factor Isotopic composition (o/oo)
 CALCITE    -5.31723             2.3806               -1.4960
 CO2 GAS    -0.04355            -5.9240               -9.7684

 Hit <Enter> to continue, any other key to see graphs of
   the isotopic composition of precipitating phases.

x
```




```
 Hit <Enter> to continue
```

```
         Isotopic composition of precipitating CO2 GAS

            +-------------------------------------------------+
     -8.1417|                                     ************|
            |                              ********           |
            |                         ******                  |
            |                    *****                        |Avg =  -9.7684
Carbon-13   |               ****                              |
    o/oo    |           ****                                  |
            |        ***                                      |
            |     ***                                         |
            |   **                                            |
    -12.7606|***                                              |
            +-------------------------------------------------+
         Initial                                           Final

Hit <Enter> to continue


Data used for C-14 (% mod)

Initial Value:     52.3256        Modeled Final Value:     12.2689

 2 dissolving phases:
Phase       Delta C     Isotopic composition (% modern)
DOLOMITE    7.06000             0.0000
"CH2O"      0.87077             0.0000

 2 precipitating phases:                            Average
Phase       Delta C     Fractionation factor Isotopic composition (% modern)
CALCITE    -5.31723             4.7611              26.2549
CO2 GAS    -0.04355           -11.8479              25.8209

Hit <Enter> to continue, any other key to see graphs of
  the isotopic composition of precipitating phases.


Data used for Sulfur-34

Initial Value:      9.7300        Modeled Final Value:     15.8130

 1 dissolving phases:
Phase       Delta S     Isotopic composition (o/oo)
ANHYDRIT   20.14723            15.5000

 1 precipitating phases:                            Average
Phase       Delta S     Fractionation factor Isotopic composition (o/oo)
PYRITE     -0.18823           -37.8958             -22.8795

Hit <Enter> to continue, any other key to see graphs of
  the isotopic composition of precipitating phases.

x
```




```
Hit <Enter> to continue

Data used for Strontium-87

Data used for Nitrogen-15

No more models, hit <S> to show Rayleigh data,
<C> to run all C-14 models, <E> to explain insufficient data.
```

To apply all of the ^{14}C A_0 models to the initial water and calculate all the corresponding ages (travel times) of (to) the final water, <C> can be entered. An example of this screen is as follows:

Model (for initial A0)	A0 (initial)	Computed (no decay)	Observed	age (final)
Original Data	33.05	7.75	0.80	18771.
Mass Balance	52.33	12.27	0.80	22570.
Vogel	85.00	19.93	0.80	26580.
Tamers	53.46	12.54	0.80	22747.
Ingerson and Pearson	52.33	12.27	0.80	22570.
Mook	65.91	15.45	0.80	24478.
Fontes and Garnier	52.31	12.27	0.80	22568.
Eichinger	47.57	11.15	0.80	21783.
User-defined	100.00	23.45	0.80	27924.

Save

NETPATH allows the user to save two types of files, (1) the model file and (2) the results of the mass balance calculation. The saved model file contains all wells, data, parameters, selections, and attributes needed to repeat the identical calculation, and may be retrieved interactively by selecting <E>dit, Entire model (under the appropriate Well file) or, upon initiation of a new NETPATH session. The name of the model file is specified by the user after selecting <S>ave. It is important to save the model file before executing the <Q>uit command, if it is anticipated that the model could be used in subsequent calculations.

The results of the mass balance and isotopic calculations can also be saved to a separate file, but can always be reproduced if the model file has been saved. In some cases NETPATH reports models that exist only if certain mineral dissolution or precipitation constraints are ignored.

Although reaction information is displayed on the screen when models are found only by ignoring dissolution/precipitation constraints, the information is not saved to a results file. In this case the results file would indicate that no models were found. In saving a model or result, if a previous file already exists for the model or result, the filename is returned to the screen and the user has the option to overwrite the existing file, or specify a new filename.

View

The <V>iew option, selected from the main screen of NETPATH, allows all chemical and isotopic data stored in the .LON file by DB to be displayed for each water analysis included in the current model. With this feature it may be unnecessary to return to DB to check specific analytical data during the modeling process. However, if there are errors in the data base that need correcting, it is necessary to (1) save the current model file, (2) quit NETPATH, (3) return to DB, making necessary corrections, (4) save a new .LON file, (5) make a new .PAT file, (6) quit DB, and (7) return to NETPATH.

Quit

Once all modeling is completed and all desired files saved, the user selects <Q>uit to exit the program. The changes made to NETPATH.DAT are written at this point, so it is important that this option be used to exit the program.

EXAMPLES AND TEST PROBLEMS

This section treats 7 examples that serve the dual functions of demonstrating specific applications of NETPATH and testing code performance on other computers. The distribution diskette (see section How to Obtain the Software) contains model files that reproduce the results of the examples that appear below. The file names are listed in the file MODEL.FIL on the diskette, and identified in the text below.

Example 1: Silicate Weathering in the Sierra Nevada

In their classic paper "Origin of the Chemical Compositions of some Springs and Lakes", Garrels and Mackenzie (1967) performed a chemical mass balance on two spring compositions from the Sierra Nevada reported by Feth and others (1964). The two spring compositions are given below:

[*Values from Garrels and Mackenzie (1967) in millimoles per liter*]

	pH	SiO_2	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^{-}	SO_4^{2-}	Cl^{-}
Ephemeral Spr.	6.2	0.273	0.078	0.029	0.134	0.028	0.328	0.010	0.014
Perennial Spr.	6.8	.410	.260	.071	.259	.040	.895	.025	.030

Garrels and Mackenzie performed a "reverse" mass balance reconstituting the original granitic rock from the differences in water composition. The mass-balance approach used here and "reverse" mass-balance approach of Garrels and Mackenzie (1967) are identical in principle. From the "reverse" mass-balance approach the result is (Garrels and Mackenzie, 1967):

[*Mass transfer in millimoles per kilogram H_2O*]

Phase	Composition	Mass Transfer
"Halite"	$NaCl$	0.016
"Gypsum"	$CaSO_4$	.015
Kaolinite	$Al_2Si_2O_5(OH)_4$	-.033
Ca-Montmorillonite	$Ca_{0.17}Al_{2.33}Si_{3.67}O_{10}(OH)_2$	-.081
CO_2 gas	CO_2	.427
Calcite	$CaCO_3$	.115
Silica	SiO_2	.0
Biotite	$KMg_3AlSi_3O_{10}(OH)_2$	.014
Plagioclase	$Na_{0.62}Ca_{0.38}Al_{1.38}Si_{2.62}O_8$	.175

This problem repeats the calculation of Garrels and Mackenzie (1967) in NETPATH using the Ephemeral spring as the initial water and the Perennial spring as the final water. Garrels and Mackenzie (1967) adjusted the difference in bicarbonate concentrations to attain charge balance. In this problem the mass balance is solved using the original (charge imbalanced) waters. A temperature of 25 °C was assumed for both waters (actual temperature not given). The phase compositions chosen by Garrels and Mackenzie are given above.

WATEQFP was used to calculate the total inorganic carbon. Aluminum was taken to be zero (the default for unknown concentrations is zero in NETPATH). The following constraints and phases were included in NETPATH:

[See file **np-1a.dat** on the diskette]

```
Initial Well: Sierra Nevada (Ephemeral Spr.)            NETPATH 2.0
Final Well  : Sierra Nevada (Perennial Spr.)           June 21, 1994
================================================================================
     Constraints:  9      |        Phases:  9          |      Parameters
--------------------------|----------------------------|----------------------
Carbon       Sulfur       |+NaCl    +GYPSUM   KAOLINIT |Mixing: No
Calcium      Magnesium    | Ca-MONT  CO2 GAS  CALCITE  |Evaporation: No
Sodium       Chloride     | SiO2     BIOTITE +PLAGAN38 |Rayleigh Calcs: No
Silica       Aluminum     |                            |
Potassium                 |                            |
================================================================================
Warning: There is no data for Aluminum in 2 of the wells: zero will be used
================================================================================
Select: <A>dd, <D>elete, <E>dit, <R>un, <S>ave, <V>iew, or <Q>uit
```

On selecting <R>un, NETPATH first displays the data to be used (concentrations in the initial and final waters are always in millimoles per kilogram H_2O:

```
Initial Well : Sierra Nevada (Ephemeral Spr.)
Final Well   : Sierra Nevada (Perennial Spr.)
         Final     Initial
C       1.1993      0.7825
S       0.0250      0.0100
CA      0.2600      0.0780
MG      0.0710      0.0290
NA      0.2590      0.1340
CL      0.0300      0.0140
SI      0.4100      0.2730
AL      0.0000      0.0000
K       0.0400      0.0280
Hit <Q> to quit, or <Enter> to continue

NaCl     NA   1.0000 CL   1.0000
GYPSUM   CA   1.0000 S    1.0000 RS   6.0000 I3  22.0000
KAOLINIT AL   2.0000 SI   2.0000
Ca-MONT  CA   0.1670 AL   2.3300 SI   3.6700
CO2 GAS  C    1.0000 RS   4.0000 I1 -25.0000 I2 100.0000
CALCITE  CA   1.0000 C    1.0000 RS   4.0000 I1   0.0000 I2   0.0000
SiO2     SI   1.0000
BIOTITE  AL   1.0000 MG   3.0000 K    1.0000 SI   3.0000
PLAGAN38 CA   0.3800 NA   0.6200 AL   1.3800 SI   2.6200
Hit <Q> to quit, or <Enter> to continue
```

Notice that in the above listing of phase data some information is given for RS, I1, I2, and I3 that was not used in this problem. Possible redox reactions were not considered (though pyrite oxidation and precipitation of FeOOH; and perhaps aerobic oxidation of organic matter might be included). The isotopes were not considered in this problem either (notice on the main screen that Rayleigh Calcs: "No" is given). Isotopes were not included in the mass-balance calculations because they were not chosen as constraints. Nevertheless default isotopic (and RS) values are stored for each appropriate mineral in the file NETPATH.DAT. The default isotope parameters I1 and I2 are δ^{13}C (per mil) and ^{14}C (pmc), and I3 is δ^{34}S (per mil).

Returning to our problem there are 9 constraints and 9 phases. No models are found. The display is:

```
No models found. Hit <Enter> to continue.
```

When this occurs it is necessary to re-examine the chosen phases, and how they can satisfy the chemical variation in the chosen constraints. In this case the problem is fairly simple to see. Notice that potassium and magnesium have only one mineral source, biotite. If K and Mg are only derived from biotite then the change in concentrations of Mg and K in the waters must be in proportion to their stoichiometry in biotite, 3:1. Examination of the water composition shows that this is not exactly so. Therefore, NETPATH finds no models. There are several ways around this problem which must be guided by geological, hydrological, and geochemical intuition. Some of the possibilities are (1) there may be more K and (or) Mg phases reacting (such as K-spar), (2) the two waters may not be truly evolutionary, or (3) there may be small analytical error in K and (or) Mg. If K-spar is added to the phases, the models precipitate K-spar rather than dissolve it (very unlikely for these dilute waters). Inspection of the analysis of Garrels and Mackenzie (1967) shows that these authors actually ignored the potassium in their calculation, basing the amount of biotite reacted on the change in magnesium concentration. The same logic needs to be applied in NETPATH. This is done by deleting the K constraint. The revised main screen is now:

[See file **np-1b.dat** on the diskette]

```
Initial Well: Sierra Nevada (Ephemeral Spr.)            NETPATH 2.0
Final Well  : Sierra Nevada (Perennial Spr.)           June 21, 1994
================================================================================
     Constraints:  8      |        Phases:  9          |      Parameters
--------------------------|----------------------------|----------------------
Carbon       Sulfur       |+NaCl    +GYPSUM   KAOLINIT |Mixing: No
Calcium      Magnesium    | Ca-MONT  CO2 GAS  CALCITE  |Evaporation: No
Sodium       Chloride     | SiO2     BIOTITE +PLAGAN38 |Rayleigh Calcs: No
Silica       Aluminum     |                            |
================================================================================
Warning: There is no data for Aluminum in 2 of the wells: zero will be used
================================================================================
Select: <A>dd, <D>elete, <E>dit, <R>un, <S>ave, <V>iew, or <Q>uit
```

The revised input is as follows:

```
Initial Well : Sierra Nevada (Ephemeral Spr.)
Final Well   : Sierra Nevada (Perennial Spr.)

         Final     Initial
C       1.1993      0.7825
S       0.0250      0.0100
CA      0.2600      0.0780
MG      0.0710      0.0290
NA      0.2590      0.1340
CL      0.0300      0.0140
SI      0.4100      0.2730
AL      0.0000      0.0000
Hit <Q> to quit, or <Enter> to continue

NaCl     NA   1.0000 CL   1.0000
GYPSUM   CA   1.0000 S    1.0000 RS   6.0000 I3  22.0000
KAOLINIT AL   2.0000 SI   2.0000
Ca-MONT  CA   0.1670 AL   2.3300 SI   3.6700
CO2 GAS  C    1.0000 RS   4.0000 I1 -25.0000 I2 100.0000
CALCITE  CA   1.0000 C    1.0000 RS   4.0000 I1   0.0000 I2   0.0000
SiO2     SI   1.0000
BIOTITE  AL   1.0000 MG   3.0000 K    1.0000 SI   3.0000
PLAGAN38 CA   0.3800 NA   0.6200 AL   1.3800 SI   2.6200
Hit <Q> to quit, or <Enter> to continue
```

Nine models were tested and five found that satisfied the chemical constraints:

```
                  9 models checked
                  5 models found
Display them <A>ll at once, <Return> for each, or <N>one.

          MODEL   1
 NaCl     +          0.01600
 GYPSUM   +          0.01500
 KAOLINIT           -0.03355
 Ca-MONT            -0.08136
 CO2 GAS             0.30296
 CALCITE             0.11380
 BIOTITE             0.01400
 PLAGAN38 +          0.17584
Hit <Enter> to continue, any other key to quit.

          MODEL   2
 NaCl     +          0.01600
 GYPSUM   +          0.01500
 KAOLINIT           -0.82741
 Ca-MONT             0.60007
 CO2 GAS             0.41676
 SiO2               -0.91311
 BIOTITE             0.01400
 PLAGAN38 +          0.17584
Hit <Enter> to continue, any other key to quit.

          MODEL   3
 NaCl     +          0.01600
 GYPSUM   +          0.01500
 KAOLINIT            2.07993
 Ca-MONT            -1.89550
 CALCITE             0.41676
 SiO2                2.43096
 BIOTITE             0.01400
 PLAGAN38 +          0.17584
Hit <Enter> to continue, any other key to quit.

          MODEL   4
 NaCl     +          0.01600
 GYPSUM   +          0.01500
 KAOLINIT           -0.12833
 CO2 GAS             0.31655
 CALCITE             0.10021
 SiO2               -0.10902
 BIOTITE             0.01400
 PLAGAN38 +          0.17584
Hit <Enter> to continue, any other key to quit.
```

```
           MODEL   5
 NaCl      +          0.01600
 GYPSUM    +          0.01500
 Ca-MONT              -0.11015
 CO2 GAS               0.29815
 CALCITE               0.11861
 SiO2                  0.03859
 BIOTITE               0.01400
 PLAGAN38  +           0.17584
No more models, hit <Enter> to continue
```

All five models dissolve biotite and plagioclase, as expected (because no other sources of Mg and Na were included). Kaolinite and Ca-montmorillonite are expected to be products, rather than reactants, in this weathering environment, therefore models 1-2 and 1-3 are probably not valid (though this opens the question of the thermodynamics of clay minerals and their dissolution behavior). Because kaolinite is expected to be a weathering product in this system, model 1-5 is probably unrealistic. This narrows models among the selected phases down to 1-1 and 1-4, and possibly model 1-2, if we allow dissolution of previously formed montmorillonite. Is dissolved silica conserved among the aluminosilicate phases or is some form of silica a product in the system? Returning to the WATEQFP output generated by DB it is seen that both waters are oversaturated with respect to quartz, and even more so if the waters are colder than the assumed 25 °C. The final water (Perennial spring) is oversaturated with chalcedony (SI = 0.14 and 0.32 at 25 and 10 °C, respectively). The initial water (Ephemeral spring) is very close to saturation with chalcedony (SI = -0.04 and 0.14 at 25 and 10 °C, respectively). The conclusion from WATEQFP is that a common form of silica could precipitate from the Sierra Nevada waters. Thus, either models 1-1 or 1-4, and possibly 1-2 are most likely for the chosen phases. Petrographic evidence for the abundance of Ca-montmorillonite would help resolve this question further.

We could have used some of the above reasoning in the initial selection of phases to narrow the possibilities. For example it could be required that kaolinite be included in every model, and both kaolinite and Ca-montmorillonite be products in the system. This can be accomplished in NETPATH Using <E>dit, Phase. The revised screen shows that kaolinite is "Forced" to be included in every model and the minus signs in front of kaolinite and Ca-montmorillonite mean that only models that precipitate these phases will be displayed. The plus signs for NaCl, gypsum, and plagioclase mean that only models dissolving these phases will be displayed.

[See file **np-1c.dat** on the diskette]

```
Initial Well: Sierra Nevada (Ephemeral Spr.)            NETPATH 2.0
Final Well  : Sierra Nevada (Perennial Spr.)           June 21, 1994
================================================================================
     Constraints:  8      |        Phases:  9          |      Parameters
--------------------------|----------Forced-----------|----------------------
Carbon       Sulfur       |-KAOLINIT                  |Mixing: No
Calcium      Magnesium    |----------Unforced---------|Evaporation: No
Sodium       Chloride     |+NaCl    +GYPSUM  -Ca-MONT |Rayleigh Calcs: No
Silica       Aluminum     | CO2 GAS  CALCITE  SiO2    |
                          | BIOTITE +PLAGAN38         |
================================================================================
Warning: There is no data for Aluminum in 2 of the wells: zero will be used
================================================================================
Select: <A>dd, <D>elete, <E>dit, <R>un, <S>ave, <V>iew, or <Q>uit
```

The calculations below show that eight models were tested of which only two meet the requirements.

```
Initial Well : Sierra Nevada (Ephemeral Spr.)
Final Well   : Sierra Nevada (Perennial Spr.)
         Final     Initial
C       1.1993      0.7825
S       0.0250      0.0100
CA      0.2600      0.0780
MG      0.0710      0.0290
NA      0.2590      0.1340
CL      0.0300      0.0140
SI      0.4100      0.2730
AL      0.0000      0.0000
Hit <Q> to quit, or <Enter> to continue

KAOLINIT AL   2.0000 SI   2.0000
NaCl     NA   1.0000 CL   1.0000
GYPSUM   CA   1.0000 S    1.0000 RS   6.0000 I3  22.0000
Ca-MONT  CA   0.1670 AL   2.3300 SI   3.6700
CO2 GAS  C    1.0000 RS   4.0000 I1 -25.0000 I2 100.0000
CALCITE  CA   1.0000 C    1.0000 RS   4.0000 I1   0.0000 I2   0.0000
SiO2     SI   1.0000
BIOTITE  AL   1.0000 MG   3.0000 K    1.0000 SI   3.0000
PLAGAN38 CA   0.3800 NA   0.6200 AL   1.3800 SI   2.6200
Hit <Q> to quit, or <Enter> to continue

                   8 models checked
                   2 models found
Display them <A>ll at once, <Return> for each, or <N>one.

           MODEL   1
 KAOLINIT  - F       -0.03355
 NaCl      +          0.01600
 GYPSUM    +          0.01500
 Ca-MONT   -         -0.08136
 CO2 GAS               0.30296
 CALCITE               0.11380
 BIOTITE               0.01400
 PLAGAN38  +          0.17584
Hit <Enter> to continue, any other key to quit.

           MODEL   2
 KAOLINIT  - F       -0.12833
 NaCl      +          0.01600
 GYPSUM    +          0.01500
 CO2 GAS               0.31655
 CALCITE               0.10021
 SiO2                 -0.10902
 BIOTITE               0.01400
 PLAGAN38  +          0.17584
No more models, hit <Enter> to continue
```

The results of the silica-conserved model (model 1-1) are again nearly identical to that of Garrels and Mackenzie (1967). The only significant difference is in the CO_2 gas mass transfer. The difference follows from the fact that Garrels and Mackenzie (1967) made a mass balance on HCO_3^-, and NETPATH makes the mass balance on TDC. For the same amount of bicarbonate, the Ephemeral Spring would have more total dissolved carbon than the Perennial Spring because of the lower pH and greater concentration of CO_2(aq). The results of NETPATH take this difference into

account by considering the total dissolved carbon in the system. The CO_2 gas mass transfer cannot be correctly calculated from the bicarbonate balance alone. In addition, NETPATH found another model (model 1-2) that produces SiO_2 rather than Ca-montmorillonite. In reality the waters may evolve as a linear combination of models 1-1 and 1-2.

The validity of the final model(s) depends in part on the selection of phases. For every change in the anorthite mole fraction of the plagioclase, there is another model. How well is the plagioclase composition known? How much actual variation is there in the plagioclase composition? What are the actual clay compositions? The more that is known about the compositions of the phases in the system, the more that can be learned about the mass transfer. At this point we could return to DB and re-make the .PAT file selecting the charge-balancing option, as one means of examining uncertainties in the analytical data.

Example 2: Evaporation of Dilute Inflow in Origin of Great Salt Lake, Utah

In this admittedly simplified problem, Great Salt Lake (GSL), Utah is modeled as a closed-basin lake resulting from evaporative concentration of dilute inflow from rivers with accompanying mineral precipitation. This problem uses NETPATH to determine the evaporation factor necessary to produce GSL water and mass transfer of a given set of phases. Water analyses have been selected from Hahl and Mitchell (1963). The dilute inflow is the weighted average inflow for the water year 1961 for the Bear River (site 39 of Hahl and Mitchell, 1963), and the lake composition is a single (representative) analysis of a water sample collected at site 123 just south of the railroad crossing in October 1960. The two water analyses are as follows:

[*Great Salt Lake data, in millimoles per kilogram* H_2O]

Constituent	Inflow	Lake
Ca	1.698	11.216
Mg	1.730	491.925
Na	9.449	5428.616
K	.435	166.479
Cl	9.234	5834.640
SO_4	.698	291.427
TDIC	6.021	6.304
pH	8.1	7.5

The original data were in parts per million. Because the lake water brine is too concentrated to be reliably speciated using the ion association model of WATEQFP, the two waters were speciated in PHRQPITZ (Plummer and others, 1988) to define the total dissolved inorganic carbon using the reported field alkalinity and pH, and assuming a temperature of 15 °C. The mmolal concentrations from PHRQPITZ are given above and entered into DB. Although DB speciates the water through WATEQFP, the final total concentration of inorganic carbon is unaffected for data entered in molal (mmolal) units.

Saturation indices from PHRQPITZ (calculated at 15 °C) indicate the lake water is very nearly saturated with halite (SI_{Halite} = -0.005), slightly oversaturated with aragonite ($SI_{Aragonite}$ = 0.45) and gypsum (SI_{Gypsum} = 0.13), and somewhat undersaturated with mirabilite ($Na_2SO_4 \cdot 10H_2O$; $SI_{Mirabilite}$ = -0.44). The calculated log P_{CO_2} is -2.4 atmospheres, so there is potential for CO_2 outgassing. The PHRQPITZ calculations show that mirabilite solubility is quite sensitive to variations in temperature, relative to the other phases considered here. For example, at 5 °C, the lake

water is slightly oversaturated with mirabilite ($SI_{Mirabilite} = 0.03$) while the saturation indices of aragonite, gypsum, halite, and log P_{CO_2} are hardly changed. Spencer and others (1985a,b) note the presence of halite, mirabilite, and aragonite in lake sediment. Although aragonite, halite, and gypsum precipitation, and CO_2 gas loss from the lake could occur throughout the year, the thermodynamic calculations from PHRQPITZ indicate that the mirabilite found in the sediment of GSL probably forms during the winter. Here NETPATH is used to solve for the extent of evaporation of the dilute inflow and the mass transfers of halite, mirabilite, gypsum, aragonite, and CO_2 gas that would result if no other reactions or hydrologic processes were occurring.

The constraints Ca, Na, C, S, and Cl were included with the phases CO_2 gas, halite, aragonite, mirabilite, and gypsum. Evaporation was selected using <E>dit. The default dissolution-only option for NaCl from the NETPATH.DAT file was edited, using <E>dit, Phase, to allow either dissolution or precipitation of halite to occur. The main screen appears as follows:

[See file **np-2.dat** on the diskette]

```
Initial Well: GSL, Bear R. weighted 1961                NETPATH 2.0
Final Well  : GSL, S. arm at RR Oct. 1960.             June 21, 1994
================================================================================
     Constraints:  5      |        Phases:  5          |      Parameters
--------------------------|----------------------------|-----------------------
Carbon       Sulfur       | CO2 GAS  NaCl     ARAGONIT |Mixing: No
Calcium      Sodium       | MIRABILI GYPSUM            |Evaporation: Yes
Chloride                  |                            |Rayleigh Calcs: No
================================================================================
Select: <A>dd, <D>elete, <E>dit, <R>un, <S>ave, <V>iew, or <Q>uit
```

The input to NETPATH and results are as follows:

```
Initial Well : GSL, Bear R. weighted 1961
Final Well   : GSL, S. arm at RR Oct. 1960.
         Final     Initial
C       6.3060      6.0210
S     291.4270      0.6980
CA     11.2170      1.6980
NA   5428.6160      9.4490
CL   5834.6400      9.2340
Hit <Q> to quit, or <Enter> to continue

CO2 GAS  C    1.0000 RS   4.0000 I1 -25.0000 I2 100.0000
NaCl     NA   1.0000 CL   1.0000
ARAGONIT CA   1.0000 C    1.0000 RS   4.0000
MIRABILI NA   2.0000 S    1.0000 RS   6.0000
GYPSUM   CA   1.0000 S    1.0000 RS   6.0000 I3  22.0000
Hit <Q> to quit, or <Enter> to continue

                    5 models checked
                    3 models found
Display them <A>ll at once, <Return> for each, or <N>one.

           MODEL   1
 CO2 GAS             -4.32887
 NaCl                -2.26579
 ARAGONIT            -1.68460
 MIRABILI            -0.34995
 Evaporation factor:    837.323      1.194g H2O remain
Hit <Enter> to continue, any other key to quit.
```

```
          MODEL   2
 CO2 GAS             -4.13876
 ARAGONIT            -1.87226
 MIRABILI            -0.42879
 GYPSUM               0.19201
 Evaporation factor:    631.865      1.583g H2O remain
Hit <Enter> to continue, any other key to quit.

          MODEL   3
 NaCl                49.32956
 ARAGONIT            -5.95771
 MIRABILI            -2.14518
 GYPSUM               4.37229
 Evaporation factor:     99.629     10.037g H2O remain
No more models, hit <Enter> to continue
```

Three models were found. Each indicates different amounts of evaporation and mass transfer of different phases. We can test the validity of the models by comparing the signs of the calculated mass transfers to the known saturation states. For example, it may be possible to eliminate model 2-2, which indicates net dissolution of gypsum, because the PHRQPITZ calculation of saturation state indicated that gypsum should precipitate, regardless of reasonable temperature variations for GSL. Also, model 2-2 would not require halite mass transfer, which is unlikely because halite is present in the lake sediment. Model 2-3 can be eliminated using several lines of evidence. First, model 2-3 also indicates gypsum dissolution. In addition, model 2-3 does not include CO_2 gas as a phase. Because CO_2 gas has a partial pressure in GSL that is 10-fold that of the atmosphere, a flux of CO_2 gas to the atmosphere is expected. It is also unlikely that during the overall evaporation process halite would dissolve, since it is present in the lake sediment and has obviously formed at some time in the past. Therefore, only one of the 3 models found is consistent with what is known (model 2-1). The initial problem could be modified to produce only model 2-1 by using <E>dit, Phase to force CO_2 gas to be in every model and marking gypsum for precipitaiton only, or by forcing CO_2 and halite to be in every model.

The results indicate that the solutes contained in 1 kg of water from the Bear River would be concentrated by a factor of 837.323, leaving only 1.194 g H_2O remaining to produce water of composition of GSL. Or, every kg of H_2O in GSL has been evaporated on the average from 837 kg H_2O from the Bear River. From the initial solutes contained in 1 kg of H_2O from Bear River, 4.3 mmol of CO_2 gas would be transferred from the lake to the atmosphere, with precipitation of 2.3, 1.7, and 0.3 mmols of halite, aragonite, and mirabilite, respectively, to the lake sediment. Model 2-1 does not include a mass transfer for gypsum, however this finding does not produce an inconsistency because gypsum is not reported in the sediment (Spencer and others, 1985a,b).

It might be possible to check model 2-1 partially by calculating a mass balance for the lake-sediment system. Other complicating factors at Great Salt Lake are discussed by Spencer and others, (1985a, 1985b), and include historical variation in inflow composition, spatial differences in brine composition in different parts of the lake, additional brines trapped in pore fluids, outflow during paleo-high stands, input from geothermal sources, and diffusion of solutes into the sediment. These processes could also be considered in NETPATH, but their evaluation would require additional data.

Using the evaporation factor of 837, conservative concentration of Mg and K in the average inflow would produce lake concentrations of 1.4 molal for Mg compared to the observed 0.49 molal; and 0.36 molal for K compared to the observed 0.17 molal concentration in the lake. Obviously,

sinks for Mg and K are indicated. Spencer and others (1985a,b) attribute this loss of Mg and K to diffusion into the sediment pore fluid and incorporation into diagenetic minerals.

Additional modeling could take into account diagenetic sinks for K and Mg, and the possibility of redox reactions accompanying microbial oxidation of organic matter in the sediment.

Example 3: Origin of Sodium Bicarbonate Waters in the Atlantic Coastal Plain

Sodium-bicarbonate waters are very common in Atlantic and Gulf Coastal Plain sediments. For example, Foster (1950) reports ground water from the Coastal Plain of Mississippi containing more than 1500 mg/L HCO_3^- with high Na^+. The origin of this water type is generally attributed to dissolution of calcium carbonate and cation exchange of Ca^{2+} for Na^+ on marine clays. It has long been recognized that a source of CO_2 is required to react with calcium carbonate to form bicarbonate (Cederstrom, 1946; Foster, 1950), otherwise the dissolution-exchange reaction would produce sodium-carbonate water (pH>10.3). The sodium bicarbonate waters typically have pH values near 8.4.

As the Coastal Plain ground-water systems become confined downgradient, an atmospheric or soil-zone source for the CO_2 is unlikely. The source of CO_2 has generally been attributed to organic material oxidized by microbial activity and has been a subject of considerable research lately (see for example Thorstenson and others, 1979; Chapelle and Knobel, 1985; Chapelle and others, 1987, Chapelle and others, 1988). Of particular interest and impact on the geochemical modeling of these waters is the actual electron-acceptor in the overall oxidation of the organic matter. The most obvious possibilities are (1) oxygen (system open to the atmosphere), (2) iron reduction (Lovley, 1987), (3) sulfate reduction, and (4) methanogenesis. Finally, we consider the possibility of forming the sodium bicarbonate waters by inorganic reactions involving exchange of sodium and protons for calcium.

This problem examines analyses of two waters from the Aquia aquifer of Maryland given by Chapelle and Knobel (1985). Three general compositional zones are recognized by Chapelle and Knobel (1985): an upgradient calcium-magnesium-bicarbonate-type water (zone I) evolving to a sodium-calcium-magnesium-bicarbonate-type water (zone II) and then to a sodium-bicarbonate-type water (zone III). This example considers the evolution of the zone I water (at well Fd-12) to the zone III water (at well Ff-35). The chemical data are given in the table below:

[*Data from Chapelle and Knobel (1985) in milligrams per liter. Temperature of 17 °C assumed for well Fd-12*]

Zone	I	III
Well Number	Fd-12	Ff-35
Temperature	17	19
pH	7.6	8.4
Calcium	41	3
Magnesium	13	1.9
Sodium	3.8	140
Potassium	7.1	7.8
Bicarbonate	178	367
Chloride	1.5	2.4
Sulfate	19	13
Silica	14	11

Dissolved iron and hydrogen sulfide were not reported but are assumed to be very low (zero). For illustration purposes, only the carbon, calcium, and sodium data initially are considered. As additional processes are added, the constraints of redox, iron and sulfur will also be included.

The following models are considered:

Model 3-1 – Calcite, CO_2, and Ca/Na exchange for the constraints Ca, Na, and C. This should identify the amount of CO_2 needed to make the zone III sodium bicarbonate-type water.

Model 3-2 – Begin considering possible redox process for the CO_2 source identified in model 3-1. Replace CO_2 with CH_2O and include O_2 gas among the phases and "redox" among the constraints. This is the case of aerobic oxidation of organic matter.

Model 3-3 – Close the system to O_2 gas (that is, remove O_2 gas as a phase from the model). Assume the terminal electron accepting process (TEAP) is reduction of Fe (III) to Fe (II). The source of Fe (III) is assumed to be goethite. Because Fe (II) concentrations are very low in the water, formation of Fe (II) mineral(s) must be proposed. Two possible sinks for Fe(II) are considered: cation exchange of Fe (II) for Na^+, Fe/Na ion exchange, and precipitation of magnetite. The waters are likely to be undersaturated with respect to siderite, at least initially (plus some unrealistic redox results follow using siderite). Model 3-3 is a redox problem involving iron reduction, so the constraints of iron and redox need to be included. Note that both a source(s) and sink(s) of iron are needed because it is assumed that the Fe_T concentration is very low in both waters.

Model 3-4 – This model builds on model 3-3 by including sulfate reduction. Because dissolved iron and H_2S concentrations are low in the ground water, it is necessary to include sources and sinks for sulfur and iron. In this example, the iron sink in model 3-3 is replaced with pyrite, and gypsum is included as a source for sulfur. Although gypsum is not present in the sediments, the pore waters in the adjacent confining units have been shown to be calcium-sulfate waters near gypsum saturation (see for example Pucci and Owens, 1989). Inclusion of gypsum necessitates inclusion of sulfur among the constraints.

Model 3-5 – This model investigates the possibility of methanogenesis. Methanogenesis does not occur in the presence of dissolved sulfate (Lovley and Klug, 1986). Here, the sulfate reduction system (deleting iron and sulfur as constraints, and pyrite, gypsum and goethite as phases) is replaced with CH_4 gas while retaining the redox constraint and CH_2O as a phase. Dissolved CH_4 was not reported in the water analysis. Because we entered through DB a value of 0 for

the concentration of dissolved CH_4, NETPATH should find a negative mass transfer for CH_4 gas, which, in this case, will be the amount of CH_4 that would be expected to occur in the final water, if methanogenesis were actually occurring.

Model 3-6 – In models 3-2 to 3-5 redox reactions considered the oxidation state of carbon in "organic matter" to be zero – comparable to that of carbohydrates (CH_2O). It is likely that the source of the organic matter is lignite rather than carbohydrate. As discussed earlier in this report, the oxidation state of carbon in lignite is approximately -0.4. Model 3-6 repeats Model 3-4 (sulfate reduction) with lignite rather than carbohydrates.

Model 3-7 – Finally, we consider the possibility of Ca^{2+} exchange for Na^+ and H^+ on an exchanger, such as lignite in the system. The proton exchange reaction was defined earlier in the section IMPORTANT CONCEPTS IN NETPATH, sub-section Phases. In this case the protons released from the exchanger would combine with CO_3^{2-} from calcite to produce the HCO_3^- in the final water. This model largely replaces the need for redox reactions in producing HCO_3^-. We return to models 3-6 and 3-7 in Example 5 to use carbon isotopes to further test the reaction possibilities.

The primary choice of phases included calcite, Ca/Na exchange and a carbon source. This differs somewhat from the treatment of Chapelle and Knobel (1985) who dissolved 10 mole percent Mg-calcite and precipitated 2 mole percent Mg-calcite. It is now known that calcites of only low Mg content and aragonite are present in the clays, silts, and sands of the Aquia Formation of Paleocene age. For illustration purposes, reactions involving Mg have been ignored.

Model 3-1: Open to Carbon Dioxide Gas

The problem was set up as follows:

[See file **np-3-1.dat** on the diskette]

```
Initial Well: Chapelle-Knobel (1985) Fd-12              NETPATH 2.0
Final Well  : Chapelle-Knobel (1985) Ff-35             June 21, 1994
================================================================================
     Constraints:  3      |        Phases:  3          |      Parameters
--------------------------|----------------------------|-----------------------
Carbon       Calcium      | CALCITE  EXCHANGE CO2 GAS  |Mixing: No
Sodium                    |                            |Evaporation: No
                          |                            |Rayleigh Calcs: No
                          |                            |Exchange: Ca/Na
================================================================================
Select: <A>dd, <D>elete, <E>dit, <R>un, <S>ave, <V>iew, or <Q>uit
```

"EXCHANGE" is a general phase in NETPATH.DAT for Ca-Mg/Na ion exchange. Pure Ca/Na exchange is the default value. Once EXCHANGE is selected as a phase, the Ca/Mg ratio in the exchange can be edited using the Edit menu. Alternatively, we could have constructed a new phase named, for example, Ca-Na Ex, using the <A>dd, Phase, Other option. The Ca/Na exchange corresponds to the reaction

$$Na_2X + Ca^{2+} \rightarrow CaX + 2Na^+ \ .$$

The stoichiometric coefficients of the "phase" are defined as Na: 2, Ca: -1. Thus, if a positive mass transfer is calculated in NETPATH, the reaction proceeds to the right, uptake of Ca and release of Na. Negative mass transfer for this phase would indicate the reaction proceeded to the left, that is, uptake of Na on the exchanger. In general, positive mass transfers indicate that the

phase entered the aqueous solution, indicating dissolution (of a phase) or ingassing (of a gas). Negative mass transfers indicate precipitation or outgassing.

Model 3-1 is not a redox problem as defined, thus "redox" is not among the constraints. Mixing and evaporation are not considered in this problem and the capability to make isotopic calculations is not selected.

Selecting <R>un lists the input, and calculates the result.

```
Initial Well : Chapelle-Knobel (1985) Fd-12
Final Well   : Chapelle-Knobel (1985) Ff-35

         Final     Initial
C       5.9742      3.0740
CA      0.0749      1.0232
NA      6.0930      0.1653
Hit <Q> to quit, or <Enter> to continue

CALCITE  CA   1.0000 C    1.0000 RS   4.0000 I1   0.0000 I2   0.0000
EXCHANGE CA  -1.0000 NA   2.0000 MG   0.0000
CO2 GAS  C    1.0000 RS   4.0000 I1 -25.0000 I2 100.0000
Hit <Q> to quit, or <Enter> to continue

                     1 model checked
                     1 model found

           MODEL   1
 CALCITE              2.01547
 EXCHANGE             2.96382
 CO2 GAS              0.88467
No more models, hit <Enter> to continue
```

The reaction is calcite dissolution, Ca for Na ion exchange (release of Na to solution), and ingassing of CO_2. Other models could be considered including mineral sources of Mg such as low Mg-calcite, Mg-montmorillonite dissolution, and Mg/Na exchange; but this obscures the redox points being demonstrated in the subsequent models developed for this example. Overall, model 3-1 is basically the reaction sought, but it is not particularly realistic when considering the possible mechanisms for CO_2 entering into the aquifer. If the magnitude of the CO_2 gas mass transfer were on the order of 0 to 0.1 mmol/kg H_2O, it would be likely that the system is closed to CO_2, considering likely uncertainties in total carbon in the initial and (or) final waters. In the results above, the CO_2 gas term is large and a plausible source of CO_2 gas is needed. Chapelle and Knobel (1985) note that the ground water initially contains dissolved oxygen but becomes anoxic down gradient in the presence of lignitic material. Possible redox reactions are now considered.

Model 3-2: Aerobic Oxidation of Organic Matter

In considering the possibility of aerobic oxidation of organic matter, the phase CO_2 is replaced with "CH_2O" and O_2, and the constraint "redox" is added. The new problem looks like this:

[See file **np-3-2.dat** on the diskette]

```
Initial Well: Chapelle-Knobel (1985) Fd-12              NETPATH 2.0
Final Well  : Chapelle-Knobel (1985) Ff-35             June 21, 1994
================================================================================
     Constraints:  4      |        Phases:  4          |      Parameters
--------------------------|----------------------------|----------------------
Carbon       Calcium      | CALCITE  EXCHANGE+O2 GAS   |Mixing: No
Sodium       Redox        |+"CH2O"                     |Evaporation: No
                          |                            |Rayleigh Calcs: No
                          |                            |Exchange: Ca/Na
================================================================================
Select: <A>dd, <D>elete, <E>dit, <R>un, <S>ave, <V>iew, or <Q>uit
```

and the results are as follows:

```
Initial Well : Chapelle-Knobel (1985) Fd-12
Final Well   : Chapelle-Knobel (1985) Ff-35
         Final     Initial
C       5.9742      3.0740
CA      0.0749      1.0232
NA      6.0930      0.1653
RS     23.8967     12.2961
Hit <Q> to quit, or <Enter> to continue

CALCITE  CA   1.0000 C    1.0000 RS   4.0000 I1   0.0000 I2   0.0000
EXCHANGE CA  -1.0000 NA   2.0000 MG   0.0000
O2 GAS   RS   4.0000
"CH2O"   C    1.0000 I1 -25.0000 I2   0.0000
Hit <Q> to quit, or <Enter> to continue

                    1 model checked
                    1 model found

           MODEL   1
 CALCITE              2.01547
 EXCHANGE             2.96382
 O2 GAS    +          0.88467
 "CH2O"    +          0.88467
No more models, hit <Enter> to continue
```

This reaction could occur, but there would have to be a mechanism for introducing the 0.8 mmol of O_2 per kg of water. Chapelle and Knobel noted 5 to 10 mg/L dissolved oxygen (DO) in the recharge waters. These are typical values for the solubility of O_2 in water (about 8 mg/L at 25 °C). The maximum DO content of 10 mg/L of O_2 of molecular weight 32 corresponds to 0.3 mmol of O_2 per liter. Thus, nearly three times as much oxygen in recharge waters would have to enter the ground water for aerobic oxidation to account for CO_2 production. This could happen only in the unsaturated zone where the system is open to atmospheric oxygen. Chapelle and Knobel note that the sodium–bicarbonate waters only form in the deeper, confined, anoxic part of the Aquia aquifer. Therefore, the model is invalid because there is no plausible source of O_2 between the initial and final wells; so other electron acceptors must be considered.

Model 3-3: Ferric Iron Reduction

It is commonly observed in Coastal Plain sand aquifers, in proceeding from oxygenated recharge downgradient, that as the O_2 begins to vanish, there is an abrupt increase in dissolved ferrous ion. Lee and Strickland (1988) noted dissolved iron contents of 2 mg/L in Coastal Plain sediments of Cretaceous age in Georgia, and South Carolina. These values are large compared with background values of tens of micrograms per liter dissolved Fe in the oxygenated zone. The source of iron is presumably FeOOH. Our particular problem becomes a little unrealistic here because Chapelle and Knobel (1985) did not report dissolved iron data. It has been assumed that the dissolved iron concentration is zero. If all the reduced iron remained in solution, FeOOH alone would be included in the phases along with "redox" as a constraint. In our cases, because dissolved iron concentrations are low, both a source and sink of iron are needed. Even if 2 mg/L (0.04 mmol/kg H_2O) were reasonable for the iron reduction zone of the Aquia aquifer, this is not enough iron to account for the total electron transfer, so a sink of iron still would have to be proposed. The waters are probably undersaturated with siderite, so siderite was not considered as a sink. For example, sinks of Fe/Na ion exchange and magnetite (not a likely phase) were considered. The two cases of iron sinks were considered separately to avoid constructing even less likely models involving reactions between Fe/Na exchange and magnetite. Considering Fe(II)/Na ion exchange, the phase was created using <A>dd, Phase. The stoichiometry is Fe: -1, Na: 2, RS: -2. The model and results are as follows:

[See file **np-3-3a.dat** on the diskette]

```
Initial Well: Chapelle-Knobel (1985) Fd-12              NETPATH 2.0
Final Well  : Chapelle-Knobel (1985) Ff-35             June 21, 1994
================================================================================
     Constraints:  5      |        Phases:  5          |      Parameters
-------------------------|--------------------------|----------------------
Carbon       Calcium     | CALCITE +"CH2O"   GOETHITE |Mixing: No
Sodium       Redox       | FeII-Na  CO2 GAS           |Evaporation: No
Iron                     |                            |Rayleigh Calcs: No
================================================================================
Warning: There is no data for Iron in 1 of the wells: zero will be used
================================================================================
Select: <A>dd, <D>elete, <E>dit, <R>un, <S>ave, <V>iew, or <Q>uit
```

Note that NETPATH prints a warning under the main screen. Because iron data were not entered in DB for these analyses, they are undefined. NETPATH assumes that the undefined concentrations in solution are zero and prints a warning. If this is not appropriate, it is necessary to return to DB and enter appropriate missing data.

```
Initial Well : Chapelle-Knobel (1985) Fd-12
Final Well   : Chapelle-Knobel (1985) Ff-35

          Final     Initial
C       5.9742      3.0740
CA      0.0749      1.0232
NA      6.0930      0.1653
RS     23.8967     12.2961
FE      0.0000      0.0000
Hit <Q> to quit, or <Enter> to continue
```

```
CALCITE  CA   1.0000 C    1.0000 RS   4.0000 I1   0.0000 I2   0.0000
"CH2O"   C    1.0000 I1 -25.0000 I2   0.0000
GOETHITE FE   1.0000 RS   3.0000
FeII-Na  FE  -1.0000 NA   2.0000 RS  -2.0000
CO2 GAS  C    1.0000 RS   4.0000 I1 -25.0000 I2 100.0000
Hit <Q> to quit, or <Enter> to continue

                    1 model checked
                    1 model found

           MODEL   1
 CALCITE             -0.94835
 "CH2O"    +          0.74096
 GOETHITE             2.96382
 FeII-Na              2.96382
 CO2 GAS              3.10753
No more models, hit <Enter> to continue
```

The above result indicates the reduction of nearly 3 mmols of ferric hydroxide with the Fe(II) replacing Na on the exchanger. CO_2 gas was included because an impossible reaction (precipitating organic matter) results if Na-Ca exchange is retained. The model requires an unrealistic and large source of CO_2 gas entering the ground water.

Next, another reduced iron sink, magnetite is considered. The average oxidation state of iron in magnetite is $8/3 = 2.67$. Thus magnetite is more reduced than FeOOH (+3). The model is as follows:

[See file **np-3-3b.dat** on the diskette]

```
Initial Well: Chapelle-Knobel (1985) Fd-12              NETPATH 2.0
Final Well  : Chapelle-Knobel (1985) Ff-35             June 21, 1994
================================================================================
     Constraints:  5      |        Phases:  5          |      Parameters
--------------------------|----------------------------|----------------------
Carbon       Calcium      | CALCITE  EXCHANGE+"CH2O"   |Mixing: No
Sodium       Redox        | GOETHITE MAGNETIT          |Evaporation: No
Iron                      |                            |Rayleigh Calcs: No
                          |                            |Exchange: Ca/Na
================================================================================
Warning: There is no data for Iron in 1 of the wells: zero will be used
================================================================================
Select: <A>dd, <D>elete, <E>dit, <R>un, <S>ave, <V>iew, or <Q>uit

Initial Well : Chapelle-Knobel (1985) Fd-12
Final Well   : Chapelle-Knobel (1985) Ff-35

         Final     Initial
C       5.9742      3.0740
CA      0.0749      1.0232
NA      6.0930      0.1653
RS     23.8967     12.2961
FE      0.0000      0.0000
Hit <Q> to quit, or <Enter> to continue
```

```
CALCITE  CA   1.0000 C    1.0000 RS   4.0000 I1   0.0000 I2   0.0000
EXCHANGE CA  -1.0000 NA   2.0000 MG   0.0000
"CH2O"   C    1.0000 I1 -25.0000 I2   0.0000
GOETHITE FE   1.0000 RS   3.0000
MAGNETIT FE   3.0000 RS   8.0000
Hit <Q> to quit, or <Enter> to continue

                    1 model checked
                    1 model found

          MODEL   1
 CALCITE              2.01547
 EXCHANGE             2.96382
 "CH2O"    +          0.88467
 GOETHITE            10.61604
 MAGNETIT            -3.53868
No more models, hit <Enter> to continue
```

This type of reaction could occur, but there would have to be mineralogical evidence of a reduced iron phase in the system. There is no evidence for this reaction in the Aquia Formation. It seems logical to conclude that in the absence of very high concentrations of dissolved iron, a different iron phase must be produced. Production of an iron sulfide mineral during sulfate reduction is a plausible mechanism.

Model 3-4: Combined Sulfate and Iron Reduction

It is commonly observed that the concentration of dissolved iron is very low during sulfate reduction because of the very low solubilities of iron sulfide phases. The models below consider pyrite as a product, recognizing that the phase "pyrite" can represent a range of semicrystalline FeS or FeS_2 phases. If sulfate reduction were occurring (in the absence of iron reactions), all the hydrogen sulfide produced would be found in solution. This would generate a noticeable amount of H_2S considering the amount of CO_2 that must be produced. Therefore, if sulfate reduction is occurring in the Aquia aquifer, there must be a source and sink for sulfur and iron. The models below assume FeOOH for the source of iron. The question of the source of sulfate remains. This is particularly acute because there are no evaporite beds or nodules of gypsum in the formation. There is the possibility that SO_4 substitutes in the lattice of marine calcite (Busenberg and Plummer, 1985), but, because the calcites have recrystallized in freshwater, most of the sulfate has probably already been released during previous diagenesis. Recently Pucci and Owens (1989) observed calcium sulfate waters approaching several thousand milligrams per liter in pore fluids of the confining units of Coastal Plain aquifers in New Jersey. Chapelle and McMahon (1991) and McMahon and Chapelle (1991) considered the confining units as sources of sulfate in South Carolina. In the models below, $CaSO_4$ is included as a "phase". The problem could be more realistically modeled as mixing (diffusion) of a calcium sulfate water into the Aquia aquifer. The model is –

[See file **np-3-4.dat** on the diskette]

```
Initial Well: Chapelle-Knobel (1985) Fd-12              NETPATH 2.0
Final Well  : Chapelle-Knobel (1985) Ff-35             June 21, 1994
================================================================================
     Constraints:  6      |        Phases:  6          |      Parameters
--------------------------|----------------------------|----------------------
Carbon       Calcium      | CALCITE  EXCHANGE+"CH2O"   |Mixing: No
Sodium       Redox        | GOETHITE+GYPSUM  -PYRITE   |Evaporation: No
Iron         Sulfur       |                            |Rayleigh Calcs: No
                          |                            |Exchange: Ca/Na
================================================================================
Warning: There is no data for Iron in 1 of the wells: zero will be used
================================================================================
Select: <A>dd, <D>elete, <E>dit, <R>un, <S>ave, <V>iew, or <Q>uit

Initial Well : Chapelle-Knobel (1985) Fd-12
Final Well   : Chapelle-Knobel (1985) Ff-35

         Final     Initial
C       5.9742      3.0740
CA      0.0749      1.0232
NA      6.0930      0.1653
RS     24.7091     13.4832
FE      0.0000      0.0000
S       0.1354      0.1978
Hit <Q> to quit, or <Enter> to continue

CALCITE  CA   1.0000 C    1.0000 RS   4.0000 I1   0.0000 I2   0.0000
EXCHANGE CA  -1.0000 NA   2.0000 MG   0.0000
"CH2O"   C    1.0000 I1 -25.0000 I2   0.0000
GOETHITE FE   1.0000 RS   3.0000
GYPSUM   CA   1.0000 S    1.0000 RS   6.0000 I3  22.0000
PYRITE   FE   1.0000 S    2.0000 RS   0.0000 I3 -60.0000
Hit <Q> to quit, or <Enter> to continue

                    1 model checked
                    1 model found

           MODEL   1
 CALCITE              1.13822
 EXCHANGE             2.96382
 "CH2O"    +          1.76192
 GOETHITE             0.46985
 GYPSUM    +          0.87725
 PYRITE    -         -0.46985
No more models, hit <Enter> to continue
```

The above result is possible, but should be investigated using carbon and sulfur isotopic data. For example if the sulfate of the confining unit were marine in origin (about 22 per mil, CDT), the remaining sulfur in solution would be enriched due to microbial fractionation. It is interesting to note that so much calcium enters the solution with the sulfate that very little calcite dissolution is indicated. This model is reconsidered in Example 5 to demonstrate applications of carbon isotopic data.

Model 3-5: Methanogenesis

Fermentative bacteria metabolize complex organic matter to produce acetate, H_2, and CO_2, among other compounds. If sulfate is present, sulfate-reducers will metabolize H_2 and acetate to reduce sulfate. If sulfate is absent, methanogenic bacteria metabolize H_2 with acetate to produce CH_4. For methanogenesis with acetate, CO_2 and CH_4 enter the solution simultaneously in 1:1 stoichiometric proportion, although they are not produced by the same metabolic process. The CO_2 is produced by fermentative bacteria and the CH_4 by methanogens. (See Lovley and Klug, 1986, for details and further references).

This having been said, how is methanogenesis modeled for the Aquia aquifer? In the simplest case, consider an initial water as pure water and final water containing 1 mmol/L of total dissolved carbon (only). In addition to the carbon, there are no other elements other than hydrogen and oxygen in the final solution. This is a redox problem, so the two constraints are "carbon" and "redox". The two phases are CH_2O and CH_4.

The CH_4 mass transfer into or out of the solution will depend on the redox state of the aqueous solution - that is, the oxidation state of carbon in the final solution. If methanogenesis had occurred according to the net reaction

$$2CH_2O \rightarrow CO_2 + CH_4 \ ,$$

the 1 mmol of carbon in the final solution would be present as 0.5 mmol CO_2 and 0.5 mmol of CH_4. The redox state of this solution is

$$\mathrm{RS} = 4m_{CO_2} - 4m_{CH_4} \ ;$$

for this example of pure methanogenesis, RS is 0. Solving the carbon mass balance and redox balance equations, it can be shown that ΔCH_4 is 0.0 and ΔCH_2O is 1.0. This has sometimes been a point of confusion. Here, it was just concluded that methanogenesis was occurring, but a CH_4 mass transfer of zero is calculated. In this case, methanogenesis surely did occur and the CH_4 that was produced, 0.5 mmol, is in the solution. The redox state of the solution reflects this. NETPATH calculates that none of the CH_4 that was produced has left the aqueous solution; thus, the CH_4 mass transfer is zero.

Now, consider the possibility that the RS of the final solution is +4, and the solution contains 1 mmol of CO_2. Methanogenesis did again occur, but this time all the CH_4 produced (1 mmol) has left the aqueous solution. In this case 2 mmols of "CH_2O" were consumed in methanogenesis producing 1 mmol of CO_2, which remains in the final solution, and 1 mmol of CH_4 which has left the aqueous solution, presumably through outgassing. With this in mind, the waters from the Aquia aquifer are reconsidered.

In the model below, carbohydrates and CH_4 have been included among the phases, retaining "redox" as a constraint. The iron and sulfur constraints and phases are deleted (using <D>elete). The methanogenesis model is as follows:

[See file **np-3-5.dat** on the diskette]

```
Initial Well: Chapelle-Knobel (1985) Fd-12              NETPATH 2.0
Final Well  : Chapelle-Knobel (1985) Ff-35             June 21, 1994
================================================================================
     Constraints:  4      |        Phases:  4          |      Parameters
--------------------------|----------------------------|-----------------------
Carbon       Calcium      | CALCITE  EXCHANGE CH4 GAS  |Mixing: No
Sodium       Redox        |+"CH2O"                     |Evaporation: No
                          |                            |Rayleigh Calcs: No
                          |                            |Exchange: Ca/Na
================================================================================
Select: <A>dd, <D>elete, <E>dit, <R>un, <S>ave, <V>iew, or <Q>uit

Initial Well : Chapelle-Knobel (1985) Fd-12
Final Well   : Chapelle-Knobel (1985) Ff-35

         Final     Initial
C       5.9742      3.0740
CA      0.0749      1.0232
NA      6.0930      0.1653
RS     23.8967     12.2961
Hit <Q> to quit, or <Enter> to continue

CALCITE  CA   1.0000 C    1.0000 RS   4.0000 I1   0.0000 I2   0.0000
EXCHANGE CA  -1.0000 NA   2.0000 MG   0.0000
CH4 GAS  C    1.0000 RS  -4.0000 I1 -40.0000 I2   0.0000
"CH2O"   C    1.0000 I1 -25.0000 I2   0.0000
Hit <Q> to quit, or <Enter> to continue

                    1 model checked
                    1 model found

           MODEL   1
 CALCITE              2.01547
 EXCHANGE             2.96382
 CH4 GAS             -0.88467
 "CH2O"    +          1.76934
No more models, hit <Enter> to continue
```

The results above show that if methanogenesis has occurred in the Aquia aquifer, all the CH_4 produced (0.886 mmols/kg H_2O) has, somehow, left the system, because we assumed a zero concentration of CH_4 in the Aquia aquifer when entering the data in DB. Alternatively, the methanogenesis model cannot be eliminated if analysis of the Aquia aquifer indicates the presence of some 14 mg/l. However, reported analyses for CH_4 are very low in the Aquia aquifer (Chapelle and Knobel, 1985), which eliminates the possibility of methanogenesis as a viable reaction in the Aquia aquifer. Notice that in the calculations, there is exactly a 2:1 mass transfer ratio of organic matter:CH_4 mass transfer, as dictated by the reaction stoichiometry.

Recalling our original definition of Redox State of aqueous solutions and its dependence on choice of constraints in the model, inspection of results from models 3-4 and 3-5 shows different values of RS for the solutions. In model 3-4 RS is based on the dissolved C, Fe, and S data, and in model 3-5 RS is based only on the dissolved C data.

Model 3-6: Sulfate Reduction, Iron Reduction and Lignite

Recognizing that "CH_2O" may not be the most appropriate form of organic carbon source, the possibility of oxidation of lignite is considered. As discussed earlier, the oxidation state of carbon in lignite is approximately -0.4. This model repeats model 3-4, sulfate reduction, with a lignite carbon source.

[See file **np-3-6.dat** on the diskette]

```
Initial Well: Chapelle-Knobel (1985) Fd-12              NETPATH 2.0
Final Well  : Chapelle-Knobel (1985) Ff-35             June 21, 1994
================================================================================
     Constraints:  6      |        Phases:  6          |      Parameters
--------------------------|----------------------------|----------------------
Carbon       Calcium      | CALCITE  EXCHANGE GOETHITE |Mixing: No
Sodium       Redox        |+GYPSUM  -PYRITE  +LIGNITE  |Evaporation: No
Iron         Sulfur       |                            |Rayleigh Calcs: No
                          |                            |Exchange: Ca/Na
================================================================================
Warning: There is no data for Iron in 1 of the wells: zero will be used
================================================================================
Select: <A>dd, <D>elete, <E>dit, <R>un, <S>ave, <V>iew, or <Q>uit

Initial Well : Chapelle-Knobel (1985) Fd-12
Final Well   : Chapelle-Knobel (1985) Ff-35

         Final     Initial
C       5.9742      3.0740
CA      0.0749      1.0232
NA      6.0930      0.1653
RS     24.7091     13.4832
FE      0.0000      0.0000
S       0.1354      0.1978

CALCITE  CA   1.0000 C    1.0000 RS   4.0000 I1   0.0000 I2   0.0000
EXCHANGE CA  -1.0000 NA   2.0000 MG   0.0000
GOETHITE FE   1.0000 RS   3.0000
GYPSUM   CA   1.0000 S    1.0000 RS   6.0000 I3  22.0000
PYRITE   FE   1.0000 S    2.0000 RS   0.0000 I3 -60.0000
LIGNITE  C    1.0000 RS  -0.4000 I1 -25.0000 I2   0.0000
Hit <Q> to quit, or <Enter> to continue

                    1 model checked
                    1 model found

           MODEL   1
 CALCITE              0.91087
 EXCHANGE             2.96382
 GOETHITE             0.58352
 GYPSUM    +          1.10460
 PYRITE    -         -0.58352
 LIGNITE   +          1.98927
No more models, hit <Enter> to continue
```

Note above in listing the problem input, the RS for lignite is indicated as -0.4. The results using lignite are similar to those of Model 3-4 with "CH_2O", yet indicating increases in amounts of organic matter oxidation, goethite dissolution, sulfate reduction and pyrite formation, and small decreases in the amounts of calcite dissolved.

Model 3-7: Proton Exchange

Proton exchange refers to the exchange of both sodium and protons on an exchanger for dissolved calcium. There has been some interest in the process recently (Appelo, 1994) and it appears a viable mechanism to be considered. The exchanger may be lignitic material in the aquifer, which may account for the nearly coincident occurrence of redox reactions and abrupt increases in dissolved Na^+ and HCO_3^- (reaction fronts). In the example below we assume a constant Na^+:H^+ ratio of 4:1 on the exchanger, which exchanges for Ca^{2+}. The reaction was described earlier in the chapter IMPORTANT CONCEPTS IN NETPATH. Here we replace the Ca/Na exchange in model 3-1 with proton exchange, as described above. The model input and result are as follows:

[See file **np-3-7.dat** on the diskette]

```
Initial Well: Chapelle-Knobel (1985) Fd-12              NETPATH 2.0
Final Well  : Chapelle-Knobel (1985) Ff-35             June 21, 1994
================================================================================
     Constraints:  3      |        Phases:  3          |      Parameters
--------------------------|----------------------------|----------------------
Carbon       Calcium      | CALCITE  CO2 GAS  H-Exch   |Mixing: No
Sodium                    |                            |Evaporation: No
                          |                            |Rayleigh Calcs: No
================================================================================
Select: <A>dd, <D>elete, <E>dit, <R>un, <S>ave, <V>iew, or <Q>uit

Initial Well : Chapelle-Knobel (1985) Fd-12
Final Well   : Chapelle-Knobel (1985) Ff-35

         Final     Initial
C       5.9742      3.0740
CA      0.0749      1.0232
NA      6.0930      0.1653
Hit <Q> to quit, or <Enter> to continue

CALCITE  CA   1.0000 C    1.0000 RS   4.0000 I1   0.0000 I2   0.0000
CO2 GAS  C    1.0000 RS   4.0000 I1 -25.0000 I2 100.0000
H-Exch   NA   1.6000 CA  -1.0000
Hit <Q> to quit, or <Enter> to continue

                    1 model checked
                    1 model found

           MODEL   1
 CALCITE              2.75643
 CO2 GAS              0.14371
 H-Exch               3.70478
No more models, hit <Enter> to continue
```

The results indicate that the Aquia aquifer waters may actually be explained rather simply without the redox reactions of models 3-2 to 3-6. Proton exchange yields (within the uncertainty of the analytical data) a ground-water system closed to CO_2 gas, which is expected. With proton exchange (model 3-7) additional calcite is dissolved by the protons released from the exchanger, eliminating the need for an additional CO_2 source in the aquifer, which was the problem in model 3-1. The reaction, as treated here, can only be considered qualitative because the Na^+:H^+ ratio of the exchanger was assumed, and held constant over the length of the flow path. We will return to this problem in Example 5 by examining possible carbon-isotope evolution.

One final comment. All of the above models are possible until eliminated by introduction of additional data or observations, such as contradictions with saturation indices, inappropriate choice of phases, inconsistency with observed carbon and sulfur isotopic data for the solution and solids, etc. Furthermore, the modeling is based on the assumption that the two chosen waters are truly on the same flow path in the Aquia aquifer, or are representative of waters on the same flow path, and that the ground-water system is at chemical steady state.

Example 4: Mixing and Reaction – Acid Mine Drainage at Pinal Creek, Near Globe, Arizona

The chemistry and migration of an acidic plume that has leaked from a waste pond used by a porphyry copper mining operation near Globe, Arizona, is currently being studied (Eychaner, 1989). The plume mixes in part with the natural background water in the basin-fill conglomerate. An overview of the hydrochemical setting is given in Eychaner and others (1989). Glynn (1991) made geochemical mass-balance models for the waters of the Pinal Creek site. The example below is an attempt to model the evolution of the final water in the plume at site 402 (pH 4-5) as a result of mixing of acidic water from the plume at site 51 (pH<4) with the regional background water (site 404) plus reaction with the mineralogy of the basin-fill conglomerate. Rock types contributing to the conglomerate in the area include diabase, schist, granite, quartz monzonite, granodiorite, and quartzite. Limestones and dolostones are also present in the area. The three water analyses are as follows:

[*Concentrations in milligrams per liter*]

Parameter	Site 404	Site 51	Site 402
Temperature °C	19	18	18
pH	7.65	3.74	4.27
Eh (volts)	.16	.43	.43
Dissolved O_2	5.9	.5	.6
Alk. or TDIC	[1]228	[2]254	[2]285
Calcium	40	440	540
Magnesium	13	390	190
Sodium	27	210	110
Iron	.0	2,800	540
Manganese	.1	75	66
Chloride	8	340	140
Sulfate	18	8,800	3,300
Silica (SiO_2)	32	100	96
Aluminum	.0	250	10

[1]Total alkalinity as HCO_3^-.

[2]TDIC as HCO_3^-.

In constructing the .PAT file, the measured Eh (0.43 volts) was used for sites 402 and 51. No Eh was available for site 404, so Eh was based on the Sato relation (see Truesdell and Jones, 1974; Plummer and others, 1976). In NETPATH, a mixing problem was set up where the two initial waters were from sites 404 and 51, and the final water was from site 402. The shallow unconfined system is considered open to CO_2 and O_2 gas. Models for this system are examined below in determining the mixing proportions of the two initial waters.

The following constraints were considered: C, S, Ca, Al, Mg, Na, Cl, Si, Fe, RS, and Mn. Chloride was considered to be conservative, so no chloride phases were included, and the mixing ratio was automatically based on Cl. Calcite, dolomite, and CO_2 were included for the carbonate

system. There is a significant loss of dissolved iron in the plume, so the phase goethite was included. MnOOH was included to account for changes in dissolved Mn. To a first approximation, the alumino-silicate reactions were modeled using albite, SiO_2, gibbsite, and kaolinite. Clearly, many other silicate phases should ultimately be considered here, especially plagioclase feldspar(s). The system was considered open to O_2 gas and CO_2 gas. Organic matter is probably not present in significant quantities. The problem appears as follows in NETPATH:

[See file **np-4.dat** on the diskette]

```
Initial Well: Pinal Cr. background, #404
Initial Well: Pinal Cr pH<4 plume, #51                  NETPATH 2.0
Final Well  : Pinal Cr pH 4-5, #402                    June 21, 1994
================================================================================
     Constraints: 11      |        Phases: 11          |      Parameters
--------------------------|----------------------------|----------------------
Carbon       Sulfur       | CALCITE  CO2 GAS  GYPSUM   |Mixing: Yes
Calcium      Aluminum     |+ALBITE  +O2 GAS   GIBBSITE |Evaporation: No
Magnesium    Sodium       | GOETHITE+DOLOMITE MnOOH    |Rayleigh Calcs: No
Chloride     Silica       | KAOLINIT SiO2              |
Iron         Manganese    |                            |
Redox                     |                            |
================================================================================
The mixing ratio will be determined by Chloride
Warning: There is no data for Aluminum in 1 of the wells: zero will be used
================================================================================
Select: <A>dd, <D>elete, <E>dit, <R>un, <S>ave, <V>iew, or <Q>uit

Initial Well 1 : Pinal Cr. background, #404
Initial Well 2 : Pinal Cr pH<4 plume, #51
Final well     : Pinal Cr pH 4-5, #402

         Final    Initial 1   Initial 2
C       4.6956      3.9020      4.2204
S      34.5357      0.1875     92.8765
CA     13.5447      0.9984     11.1301
AL      0.3726      0.0000      9.3939
MG      7.8567      0.5349     16.2636
NA      4.8102      1.1749      9.2610
CL      3.9699      0.2257      9.7230
SI      1.6062      0.5328      1.6874
FE      9.7207      0.0000     50.8313
MN      1.2078      0.0018      1.3841
RS    247.9553     17.4741    678.6413
Hit <Q> to quit, or <Enter> to continue
```

```
CALCITE  CA   1.0000 C    1.0000 RS   4.0000 I1   0.0000 I2   0.0000
CO2 GAS  C    1.0000 RS   4.0000 I1 -25.0000 I2 100.0000
GYPSUM   CA   1.0000 S    1.0000 RS   6.0000 I3  22.0000
ALBITE   NA   1.0000 AL   1.0000 SI   3.0000
O2 GAS   RS   4.0000
GIBBSITE AL   1.0000
GOETHITE FE   1.0000 RS   3.0000
DOLOMITE CA   1.0000 MG   1.0000 C    2.0000 RS   8.0000 I1   0.0000
         I2   0.0000
MnOOH    MN   1.0000 RS   3.0000
KAOLINIT AL   2.0000 SI   2.0000
SiO2     SI   1.0000
Hit <Q> to quit, or <Enter> to continue

                  11 models checked
                   3 models found
Display them <A>ll at once, <Return> for each, or <N>one.

          MODEL   1
 Init 1   + F        0.60576
 Init 2   + F        0.39424
 CALCITE              9.62443
 CO2 GAS            -11.19808
 GYPSUM              -2.19327
 ALBITE   +           0.44746
 O2 GAS   +           2.32125
 GIBBSITE            -3.05421
 GOETHITE           -10.31891
 DOLOMITE +           1.12089
 MnOOH                0.66099
 KAOLINIT            -0.36204
Hit <Enter> to continue, any other key to quit.

          MODEL   2
 Init 1   + F        0.60576
 Init 2   + F        0.39424
 CALCITE              9.62443
 CO2 GAS            -11.19808
 GYPSUM              -2.19327
 ALBITE   +           0.44746
 O2 GAS   +           2.32125
 GIBBSITE            -3.77829
 GOETHITE           -10.31891
 DOLOMITE +           1.12089
 MnOOH                0.66099
 SiO2                -0.72409
Hit <Enter> to continue, any other key to quit.
```

```
          MODEL   3
 Init 1    + F        0.60576
 Init 2    + F        0.39424
 CALCITE               9.62443
 CO2 GAS             -11.19808
 GYPSUM               -2.19327
 ALBITE    +           0.44746
 O2 GAS    +           2.32125
 GOETHITE            -10.31891
 DOLOMITE  +           1.12089
 MnOOH                 0.66099
 KAOLINIT             -1.88915
 SiO2                  3.05421
No more models, hit <Enter> to continue
```

For this set of phases, three models were found. The mixing fractions calculated from the chloride indicate that 61 percent of the final water is from the background basin-fill ground water (sample #404) and 39 percent is from the acid plume water (sample #51). The three models are similar, differing in the mass transfer of kaolinite, gibbsite, and silica. The predominate reactions appear to be calcite dissolution, outgassing of CO_2, precipitation of goethite, precipitation of gypsum, and ingassing of O_2 gas. It would be possible to check the mixing ratios on the basis of δD and δ^{18}O data, but these isotopic data are not currently available. It may be possible to check the carbonate reactions using carbon isotopic data.

Even though primary silicate minerals (feldspars, quartz, etc.) predominate in the mineralogy of the basin-fill material at Globe, Arizona, the mass-balance modeling indicates that reactions with these minerals are secondary to those of the more reactive carbonates, and precipitation of kaolinite, gibbsite, ferric hydroxides, and gas exchange across the water table with the unsaturated zone. As a general comment in setting up mass balance models, it is important to recognize the most reactive phases in the system, even though they may not be the predominant mineralogy.

Finally, it should be recognized that the mixing fractions computed by NETPATH apply to the compositions of waters withdrawn from the wells installed at the Pinal Creek site and may not necessarily represent the mixing proportions of the waters in place along flow lines. It is possible that at least part of the mixing indicated by NETPATH was caused by the convergence of many flow lines into the well screens during pumping. If further study can eliminate this possibility, then the computed mixing is a function of the dispersive properties of the system.

Example 5: Application of Carbon Isotope Data to Example 3

In Example (3), seven models were solved for formation of sodium bicarbonate-type water in the Aquia aquifer of southern Maryland. The models considered different sources and sinks for carbon. Consequently, if the carbon isotopic composition of incoming carbon, and the fractionations when carbon leaves the aqueous phase (precipitation or outgassing) are known, it is possible to calculate values of δ^{13}C at the final well for comparison with the observed. Because a valid mass-balance model must predict the observed δ^{13}C, models that fail to predict the observed δ^{13}C can be eliminated. Evaluation of the δ^{13}C in the reaction is also a useful step in evaluating ^{14}C data and radiocarbon ages.

To solve this problem, it is first necessary to return to DB to add δ^{13}C values for dissolved carbon species for the initial and final waters in the Aquia aquifer from Chapelle and Knobel (1985). Although Chapelle and Knobel (1985) did not measure ^{14}C, Purdy and others (1992) reported ^{14}C

activities of the dissolved inorganic carbon of 33.9 and 3.1 pmc for an upgradient and downgradient water, respectively. The site selected by Purdy and others (1992) for the upgradient water is in the recharge area for the Aquia aquifer and is probably representative of the initial well, Fd-12, of Chapelle and Knobel (1985). The downgradient well of Chapelle and Knobel (1985), well Ff-35, is approximately 36 miles further downgradient than the well sampled by Purdy and others (1992) for a downgradient water. Therefore, the reported 3.1 pmc for the downgradient water of Purdy and others (1992) is a maximum value applicable to well Ff-35 of Chapelle and Knobel (1985). In DB the two wells Fd-12 and Ff-35 were edited to obtain δ^{13}C values for TDIC of -12.6 and -6.2 per mil (Chapelle and Knobel, 1985), respectively, and ^{14}C values of TDIC of 33.9 and 3.1 pmc, respectively. The revised .LON file was saved using <S>ave/<S>peciate in DB to make a new .PAT file.

Returning to NETPATH, the saved model file from Example 3, model 3-6 (iron reduction coupled with sulfate reduction using lignite) is retrieved. This model is considered the most realistic of the redox models considered for the Aquia aquifer. The retrieval is accomplished through the Edit menu. The listing below shows the retrieval of model 3-6 from Example 3:

```
 -----------------
 CHOOSE MODEL FILE
 -----------------
   1:  np-1a.dat
   2:  np-1b.dat
   3:  np-1c.dat
   4:  np-2.dat
   5:  np-3-1.dat
   6:  np-3-2.dat
   7:  np-3-3a.dat
   8:  np-3-3b.dat
   9:  np-3-4.dat
  10:  np-3-5.dat
  11:  np-3-6.dat
  12:  np-3-7.dat
  13:  np-4.dat
  14:  np-5-1.dat
  15:  np-5-2.dat
 Enter number of file, 0 for none, or <ENTER> to see more files:
11

 ---------------------------------------
 np-3-6.dat
 ---------------------------------------
 Initial well: Chapelle-Knobel (1985) Fd-12
 Final well  : Chapelle-Knobel (1985) Ff-35

 CONSTRAINTS:
 Carbon         Calcium        Sodium         Redox          Iron
 Sulfur

 PHASES:
 CALCITE        EXCHANGE       GOETHITE       GYPSUM         PYRITE
 LIGNITE
 Use this file?  (N)o, (D)elete, or <ENTER> to accept:
```

```
Initial Well: Chapelle-Knobel (1985) Fd-12              NETPATH 2.0
Final Well  : Chapelle-Knobel (1985) Ff-35             June 21, 1994
================================================================================
     Constraints:  6      |        Phases:  6          |      Parameters
--------------------------|----------------------------|----------------------
Carbon       Calcium      | CALCITE  EXCHANGE GOETHITE |Mixing: No
Sodium       Redox        |+GYPSUM  -PYRITE  +LIGNITE  |Evaporation: No
Iron         Sulfur       |                            |Rayleigh Calcs: No
                          |                            |Exchange: Ca/Na
================================================================================
Warning: There is no data for Iron in 1 of the wells: zero will be used
================================================================================
Select: <A>dd, <D>elete, <E>dit, <R>un, <S>ave, <V>iew, or <Q>uit
```

Having retrieved model 3-6 from Example 3, the Rayleigh calculations are invoked through the Edit menu. This is done by selecting <E>dit. Below is an example:

```
e

  General
    1) Well file              : class
    2) Entire model
    3) Phases
 Wells
    4) Mixing                 : No
    5) Initial well           : Chapelle-Knobel (1985) Fd-12
       Final well             : Chapelle-Knobel (1985) Ff-35
  Parameters
    6) Evaporation/Dilution   : No
    7) Ion exchange           : Ca/Na
    8) Redox state of DOC
  Isotope calculations
    9) Rayleigh calculations  : No
 --------------------
 Edit which? (<Enter> when done)
9
 Do Rayleigh calculations? (<Enter> for No )
y
```

Having selected the Rayleigh calculations, the Edit menu is expanded to allow entering and editing other isotopic data. In the example below, option 10 is selected to edit the isotopic data for carbon (and sulfur) phases in the model.

```
 General
   1) Well file               : class
   2) Entire model
   3) Phases
Wells
   4) Mixing                  : No
   5) Initial well            : Chapelle-Knobel (1985) Fd-12
      Final well              : Chapelle-Knobel (1985) Ff-35
 Parameters
   6) Evaporation/Dilution    : No
   7) Ion exchange            : Ca/Na
   8) Redox state of DOC
 Isotope calculations
   9) Rayleigh calculations   : Yes
  10) Isotopic data
  11) Model for initial C14   : Original Data
  12) Carbon fract. factors   : Mook
 --------------------
Edit which? (<Enter> when done)
10
```

Chapelle and Knobel (1985) report the $\delta^{13}C$ for calcite (aragonite) from the Aquia aquifer to be +1.1 per mil. Organic matter in the Coastal Plain sediments is approximately -22 per mil in $\delta^{13}C$. It is assumed that ingassing of CO_2 is from fermentation of organic matter and, thus, also has a $\delta^{13}C$ of -22 per mil. All carbon sources within the aquifer are assumed to be old and their ^{14}C content is defined to be 0 pmc.

The sulfur isotopes are also treated in this problem, although the data are quite limited. The mass-transfer results are unaffected by lack of isotopic data because isotopic constraints were not included. In the Rayleigh calculations performed for each mass-balance model, it is assumed that incoming sulfate (presumably from pore spaces in the confining unit) is originally of marine origin having a $\delta^{34}S$ of 22 per mil. Since FeS_2 phases are sinks for iron and sulfur in the Aquia (that is, they do not dissolve in the system), it is not necessary to define the $\delta^{34}S$ of pyrite, but it is necessary to define the sulfur-isotope fractionation factor for precipitating pyrite. For example purposes it is assumed that pyrite is depleted in $\delta^{34}S$ by 40 per mil relative to that of total dissolved sulfur in solution. The listing below shows the default isotopic data for phases in the model.

```
                        Isotopic Compositions

 Num Phase    Carbon-13  C14 % mod  Sulfur-34    Sr-87       N-15
 ------------------------------------------------------------------
  1: CALCITE     0.000      0.000
  2: GYPSUM                             22.000
  3: PYRITE                            -30.000
  4: LIGNITE   -25.000      0.000
 Enter number of phase to edit. <Enter> when done.
```

Every carbon-bearing phase in the model appears on the screen. NETPATH also considers Rayleigh processes with sulfur, nitrogen, and strontium isotopes, and any phases containing these elements will also appear for editing. The default isotopic values for calcite, gypsum, pyrite, and lignite that are stored in the NETPATH.DAT file are displayed. The example below shows the editing of the carbon isotopic values:

```
 Enter number of phase to edit. <Enter> when done.
1

 Enter isotopic composition of Carbon-13 for 'CALCITE '.
 <Enter> to use    0.0000
1.1

 Enter isotopic composition of Carbon-14 for 'CALCITE '.
 <Enter> to use    0.0000

                        Isotopic Compositions
 Num Phase    Carbon-13  C14 % mod  Sulfur-34    Sr-87       N-15
 ---------------------------------------------------------------------
  1: CALCITE     1.100      0.000
  2: GYPSUM                            22.000
  3: PYRITE                           -30.000
  4: LIGNITE   -25.000      0.000
 Enter number of phase to edit. <Enter> when done.

4

 Enter isotopic composition of Carbon-13 for 'LIGNITE '.
 <Enter> to use  -25.0000

-22

 Enter isotopic composition of Carbon-14 for 'LIGNITE '.
 <Enter> to use    0.0000

                        Isotopic Compositions
 Num Phase    Carbon-13  C14 % mod  Sulfur-34    Sr-87       N-15
 ---------------------------------------------------------------------
  1: CALCITE     1.100      0.000
  2: GYPSUM                            22.000
  3: PYRITE                           -30.000
  4: LIGNITE   -22.000      0.000
 Enter number of phase to edit. <Enter> when done.
```

None of the phases contain strontium or nitrogen, so there is no need to specify the $^{87}Sr/^{86}Sr$ ratio or $\delta^{15}N$. Note that the isotopic values displayed for phases are used in NETPATH for any incoming source mineral. In this case, all dissolving calcite will enter the solution with $\delta^{13}C$ of $+1.1$ per mil and ^{14}C content of 0.0 pmc. These isotope values do not apply to precipitation which involves an isotopic fractionation process.

The next screen that appears under the Edit, Isotopic data option of the Edit menu allows editing of isotopic fractionation factors used in the Rayleigh calculations.

```
              Additive Fractionation Factors (in per mil)
                        Relative to solution
 Num Phase    Carbon-13  C14 % mod  Sulfur-34    Sr-87       N-15
 ---------------------------------------------------------------------
  1: CALCITE     0.705*     1.410*
  2: PYRITE                           Undefined

 * = based on computed value at 1.00 fraction between init and final waters
 Enter number of phase to edit, '0' for fraction along path, <Enter> when done.
```

Note that all fractionation factors are given relative to the average isotopic composition of that element **in solution**. The "*" denotes values calculated using published equilibrium fractionation factors (either the Mook, or Deines and others sets). In the case of pyrite the correlation from Plummer and others (1990) for the kinetic fractionation observed in the Madison aquifer is used. Use of the Madison aquifer correlation depends on data for δ^{34}S of sulfate (and temperature) in the final well (when the fraction $X = 1.00$). Because δ^{34}S of sulfate is not known in our final well, NETPATH shows the pyrite-solution sulfur fractionation as "undefined". For example purposes below, the pyrite fractionation is edited giving a value of -40. This means that any pyrite formed will be depleted in δ^{34}S by 40 per mil relative to that of the aqueous solution. It is often instructive to examine the sensitivity of modeling results to uncertainties in isotopic data, including fractionation factors. The next test problem (Example 6) is perhaps a more realistic application of sulfur isotopic data. Because of the mass difference between δ^{13}C and ^{14}C, it is theoretically predicted that ^{14}C fractionation factors will be approximately twice those of δ^{13}C (Craig, 1954). Alternatively, the ^{14}C fractionation factors can be edited to user-defined values. The listing above shows the calculated and (or) default fractionation factors. Below is an example of editing the pyrite fractionation factor to the suggested value of -40 per mil:

```
 Enter number of phase to edit, '0' for fraction along path, <Enter> when done.
2

 Enter additive fractionation factor of Sulfur-34 for 'PYRITE  '.
-40

              Additive Fractionation Factors (in per mil)
                        Relative to solution
 Num Phase    Carbon-13  C14 % mod  Sulfur-34    Sr-87       N-15
 ------------------------------------------------------------------
  1: CALCITE     0.705*     1.410*
  2: PYRITE                            -40.000

 * = based on computed value at 1.00 fraction between init and final waters
 Enter number of phase to edit, '0' for fraction along path, <Enter> when done.
```

Once the selection of fractionation factors has been made, control is returned to the Edit menu. Because estimates of ^{14}C values for the initial and final wells are included, it is necessary to select the option from the Edit menu to define the initial ^{14}C value. Here, models to define the initial ^{14}C value for the recharge water (prenuclear detonation, A_0) are selected. These A_0 models are examined in more detail in Example 6. The present problem selects a "user-defined" value of 50 pmc, similar to that computed by many of the A_0 models. The reported ^{14}C activity of 33.9 pmc indicates that this sample is likely several thousand years old. The listing below is an example of the selection procedure:

```
 General
   1) Well file               : class
   2) Entire model
   3) Phases
Wells
   4) Mixing                  : No
   5) Initial well            : Chapelle-Knobel (1985) Fd-12
      Final well              : Chapelle-Knobel (1985) Ff-35
 Parameters
   6) Evaporation/Dilution    : No
   7) Ion exchange            : Ca/Na
   8) Redox state of DOC
 Isotope calculations
   9) Rayleigh calculations   : Yes
  10) Isotopic data
  11) Model for initial C14   : Original Data
  12) Carbon fract. factors   : Mook
--------------------
Edit which? (<Enter> when done)

       Initial Carbon-14, A0, (percent modern)
            for Total Dissolved Carbon

        Model             Initial well

  1 : Original Data       :     33.90
  2 : Mass Balance        :     55.75
  3 : Vogel               :     85.00
  4 : Tamers              :     52.75
  5 : Ingerson and Pearson:     50.40
  6 : Mook                :     34.25
  7 : Fontes and Garnier  :     50.35
  8 : Eichinger           :     47.91
  9 : User-defined        :    100.00

 Enter number of model to use (<Enter> for 'Original Data')
9


 Hit <Enter> to input data for 'User-defined',
 any other key to enter data for all models.


 Enter value of user-defined C-14 activity for Chapelle-Knobel (1985) Fd-12,
 <Enter> for    100.00
50
```

```
       Initial Carbon-14, A0, (percent modern)
            for Total Dissolved Carbon

        Model             Initial well

  1 : Original Data       :     33.90
  2 : Mass Balance        :     55.75
  3 : Vogel               :     85.00
  4 : Tamers              :     52.75
  5 : Ingerson and Pearson:     50.40
  6 : Mook                :     34.25
  7 : Fontes and Garnier  :     50.35
  8 : Eichinger           :     47.91
  9 : User-defined        :     50.00

Enter number of model to use (<Enter> to quit, 0 to edit data for all models)
```

Having provided the needed isotopic data, NETPATH returns to the Edit menu.

```
 General
   1) Well file               : class
   2) Entire model
   3) Phases
Wells
   4) Mixing                  : No
   5) Initial well            : Chapelle-Knobel (1985) Fd-12
      Final well              : Chapelle-Knobel (1985) Ff-35
 Parameters
   6) Evaporation/Dilution    : No
   7) Ion exchange            : Ca/Na
   8) Redox state of DOC
 Isotope calculations
   9) Rayleigh calculations   : Yes
  10) Isotopic data
  11) Model for initial C14   : User-defined
  12) Carbon fract. factors   : Mook
--------------------
Edit which? (<Enter> when done)
```

If satisfied with isotopic data and other parameters set through the Edit menu, <Enter> returns to the main screen and selecting <R>un solves the problem, as shown below.

[See file **np-5-1.dat** on the diskette]

```
Initial Well: Chapelle-Knobel (1985) Fd-12              NETPATH 2.0
Final Well  : Chapelle-Knobel (1985) Ff-35             June 21, 1994
================================================================================
     Constraints:  6      |        Phases:  6          |      Parameters
--------------------------|----------------------------|-----------------------
Carbon       Calcium      | CALCITE  EXCHANGE GOETHITE |Mixing: No
Sodium       Redox        |+GYPSUM  -PYRITE  +LIGNITE  |Evaporation: No
Iron         Sulfur       |                            |Rayleigh Calcs: Yes
                          |                            |Exchange: Ca/Na
                          |                            |Init C-14  50.00 (TDC)
                          |                            |(User-defined)
================================================================================
Warning: There is no data for Iron in 1 of the wells: zero will be used
================================================================================
Select: <A>dd, <D>elete, <E>dit, <R>un, <S>ave, <V>iew, or <Q>uit
```

```
r

 Initial Well : Chapelle-Knobel (1985) Fd-12
 Final Well   : Chapelle-Knobel (1985) Ff-35

          Final     Initial
 C       5.9742      3.0740
 CA      0.0749      1.0232
 NA      6.0930      0.1653
 RS     24.7091     13.4832
 FE      0.0000      0.0000
 S       0.1354      0.1978
 Hit <Q> to quit, or <Enter> to continue

 CALCITE  CA   1.0000 C    1.0000 RS   4.0000 I1   1.1000 I2   0.0000
 EXCHANGE CA  -1.0000 NA   2.0000 MG   0.0000
 GOETHITE FE   1.0000 RS   3.0000
 GYPSUM   CA   1.0000 S    1.0000 RS   6.0000 I3  22.0000
 PYRITE   FE   1.0000 S    2.0000 RS   0.0000 I3 -60.0000
 LIGNITE  C    1.0000 RS  -0.4000 I1 -22.0000 I2   0.0000
 Hit <Q> to quit, or <Enter> to continue

                     1 model checked
                     1 model found

            MODEL   1
  CALCITE               0.91087
  EXCHANGE              2.96382
  GOETHITE              0.58352
  GYPSUM    +           1.10460
  PYRITE    -          -0.58352
  LIGNITE   +           1.98927

                Computed    Observed
 Carbon-13      -13.6412     -6.2000
 C-14 (% mod)    25.7277*     3.1000
 Sulfur-34       66.9880   Undefined
 Strontium-87      Insufficient data
 Nitrogen-15       Insufficient data
 ------------------------------------------------------------------------
 Adjusted C-14 age in years:  17494.*     * = based on User-defined

 No more models, hit <S> to show Rayleigh data,
 <C> to run all C-14 models, <E> to explain insufficient data.
```

The computed mass transfer is, as expected, identical to that found previously in model 3-6. But having included carbon isotopic data, the consistency of the model can be tested with the δ^{13}C data (and other isotopic data if they are available). The above result shows that the calculated δ^{13}C is far too negative in comparison to that observed at the final well (-13.6 per mil calculated relative to the observed value of -6.2 per mil). It can be shown that, by editing the isotopic data, unreasonably enriched organic matter or calcite is required for the model to predict the observed δ^{13}C. That is, the modeled δ^{13}C is inconsistent within the uncertainties in the known isotopic data. Therefore, the reaction model is very likely incorrect.

Several other models could result in enriched ^{13}C values at the final well– (1) methanogenesis, (2) carbon isotope exchange with the carbonate minerals, and (3) proton exchange combined with

calcite dissolution. We have already eliminated methanogenesis as a possible reaction because dissolved CH_4 concentrations are near zero in the final well. The calculations that follow consider the possibility of carbon isotope exchange (recrystallization of calcite) and proton exchange.

Returning to the main screen, the Edit menu is entered to edit the phase calcite to allow isotopic exchange of an estimated 5.2 mmol of calcite per kg H_2O. The listings below show this selection and the computed result.

```
 Initial Well: Chapelle-Knobel (1985) Fd-12              NETPATH 2.0
 Final Well  : Chapelle-Knobel (1985) Ff-35             June 21, 1994
 ================================================================================
      Constraints:  6      |        Phases:  6          |      Parameters
 --------------------------|----------------------------|----------------------
 Carbon       Calcium      | CALCITE  EXCHANGE GOETHITE |Mixing: No
 Sodium       Redox        |+GYPSUM  -PYRITE  +LIGNITE  |Evaporation: No
 Iron         Sulfur       |                            |Rayleigh Calcs: Yes
                           |                            |Exchange: Ca/Na
                           |                            |Init C-14  50.00 (TDC)
                           |                            |(User-defined)
 ================================================================================
 Warning: There is no data for Iron in 1 of the wells: zero will be used
 ================================================================================
 Select: <A>dd, <D>elete, <E>dit, <R>un, <S>ave, <V>iew, or <Q>uit
e

  General
    1) Well file              : class
    2) Entire model
    3) Phases
 Wells
    4) Mixing                 : No
    5) Initial well           : Chapelle-Knobel (1985) Fd-12
       Final well             : Chapelle-Knobel (1985) Ff-35
  Parameters
    6) Evaporation/Dilution   : No
    7) Ion exchange           : Ca/Na
    8) Redox state of DOC
  Isotope calculations
    9) Rayleigh calculations  : Yes
   10) Isotopic data
   11) Model for initial C14  : User-defined
   12) Carbon fract. factors  : Mook
 --------------------
 Edit which? (<Enter> when done)
3

 List of phases

   1:   CALCITE            2:   EXCHANGE           3:   GOETHITE
   4:   GYPSUM             5:   PYRITE             6:   LIGNITE

 Input phase to edit.  <Enter to abort>
1
```

```
 Phase editing choices for CALCITE
      1) Replace phase entirely
      2) Edit phase composition
      3) Edit forcing and dissolution/precipitation only
 Enter your choice, or <Enter> to abort the edit:
3

 Enter transfer allowed for 'CALCITE '. (1) dissolution, (2) precipitation,
 (3) both, or (4) isotopic exchange.
 Hit <Enter> for both.
4

 Enter amount to exchange.  (0 to cancel).
5.2
 Enter isotopic composition of Carbon-13 in exchanging mineral:
 (Hit <Enter> to use the phase value, or enter a new value)


 Enter isotopic composition of Carbon-14 (% mod) in exchanging mineral:
 (Hit <Enter> to use the phase value, or enter a new value)


 Should 'CALCITE ' be included in every model?
 <Enter> for no.


  General
    1) Well file               : class
    2) Entire model
    3) Phases
 Wells
    4) Mixing                  : No
    5) Initial well            : Chapelle-Knobel (1985) Fd-12
       Final well              : Chapelle-Knobel (1985) Ff-35
  Parameters
    6) Evaporation/Dilution    : No
    7) Ion exchange            : Ca/Na
    8) Redox state of DOC
  Isotope calculations
    9) Rayleigh calculations   : Yes
   10) Isotopic data
   11) Model for initial C14   : User-defined
   12) Carbon fract. factors   : Mook
 --------------------
 Edit which? (<Enter> when done)
```

[See file **np-5-2.dat** on the diskette]

```
 Initial Well: Chapelle-Knobel (1985) Fd-12              NETPATH 2.0
 Final Well  : Chapelle-Knobel (1985) Ff-35             June 21, 1994
 ================================================================================
      Constraints:  6      |        Phases:  6          |      Parameters
 --------------------------|----------------------------|----------------------
 Carbon       Calcium      |*CALCITE  EXCHANGE GOETHITE |Mixing: No
 Sodium       Redox        |+GYPSUM  -PYRITE  +LIGNITE  |Evaporation: No
 Iron         Sulfur       |                            |Rayleigh Calcs: Yes
                           |                            |Exchange: Ca/Na
                           |                            |Init C-14  50.00 (TDC)
                           |                            |(User-defined)
 ================================================================================
 Warning: There is no data for Iron in 1 of the wells: zero will be used
 ================================================================================
 Select: <A>dd, <D>elete, <E>dit, <R>un, <S>ave, <V>iew, or <Q>uit

r

 Initial Well : Chapelle-Knobel (1985) Fd-12
 Final Well   : Chapelle-Knobel (1985) Ff-35

          Final     Initial
 C       5.9742      3.0740
 CA      0.0749      1.0232
 NA      6.0930      0.1653
 RS     24.7091     13.4832
 FE      0.0000      0.0000
 S       0.1354      0.1978
 Hit <Q> to quit, or <Enter> to continue

 CALCITE  CA   1.0000 C    1.0000 RS   4.0000 I1   1.1000 I2   0.0000
 EXCHANGE CA  -1.0000 NA   2.0000 MG   0.0000
 GOETHITE FE   1.0000 RS   3.0000
 GYPSUM   CA   1.0000 S    1.0000 RS   6.0000 I3  22.0000
 PYRITE   FE   1.0000 S    2.0000 RS   0.0000 I3 -60.0000
 LIGNITE  C    1.0000 RS  -0.4000 I1 -22.0000 I2   0.0000
 Hit <Q> to quit, or <Enter> to continue

                     1 model checked
                     1 model found

            MODEL   1
  CALCITE              0.91087        5.200 exchanged
  EXCHANGE             2.96382
  GOETHITE             0.58352
  GYPSUM    +          1.10460
  PYRITE    -         -0.58352
  LIGNITE   +          1.98927
```

```
                Computed    Observed
Carbon-13        -6.2067     -6.2000
C-14 (% mod)      7.8030*     3.1000
Sulfur-34        66.9880   Undefined
Strontium-87       Insufficient data
Nitrogen-15        Insufficient data
-------------------------------------------------------------------------
Adjusted C-14 age in years:   7631.*     * = based on User-defined

No more models, hit <S> to show Rayleigh data,
<C> to run all C-14 models, <E> to explain insufficient data.
```

The amount of calcite exchanged, 5.2 mmol/kg H_2O, was determined by "trial and error", iterating between Edit, Phase and <R>un. Notice that phases marked for isotopic exchange are identified with an "*" on the main screen, and the amount exchanged is displayed next to its calculated net mass transfer. In the above model, 0.91 mmol of calcite dissolved and an additional 5.2 mmol exchanged for every kilogram of H_2O along the flow path to the final well. In NETPATH "isotope exchange" or "recrystallization" refers to dissolution and subsequent precipitation of the same mass of the same phase. In the precipitation step, a fractionation occurs between precipitate and solution, and therefore, the Rayleigh calculations are used in NETPATH. In the case of recrystallization of calcite, a less stable calcite dissolves and is replaced by precipitation of another, more stable, calcite. In the dissolution/precipitation step, carbon from the mineral is exchanged with carbon in the aqueous solution. When the carbonates are significantly enriched relative to the solution, as for the marine carbonates in this problem, isotope exchange will introduce more enriched carbon without changing the total concentration of calcium or carbon in solution (only the $\delta^{13}C$ of the solution is affected).

The ^{13}C results show that this particular model could be valid if there were substantial recrystallization of the carbonates. This is similar to the model that Chapelle and Knobel (1985) used, if aragonite were substituted for the 10 mol percent Mg-calcite reactant assumed by Chapelle and Knobel (1985). The above model could be modified by replacing reactant calcite with aragonite and including a low Mg-calcite as product. By changing the Mg mole fraction in low-Mg calcite, the recrystallization mass transfer changes. There may be some Mg content for the secondary calcite necessary to cause agreement in ^{13}C. An alternative model could consider Mg/Na ion exchange.

Notice that recrystallization causes the modeled ^{14}C age to be substantially younger. There are limits to the extent of isotopic exchange that could occur, taking into account the travel time for the water and the actual observed ^{14}C content of the water. The calculated amount of isotopic exchange, 5.2 mmol/kg H_2O, is unrealistically large, especially for the predominantly clastic mineralogy of the Aquia aquifer. Actual measurements of the ^{14}C activity in the Aquia aquifer at well Ff-35 will likely place constraints on the amount of recrystallization that is possible. Purdy and others (1992) used dissolved chloride and stable isotope data to show that waters recharged during the last glacial maximum (some 18,000 to 20,000 years ago) occur in the Aquia aquifer. Because the adjusted ^{14}C age is quite sensitive to the amount of recrystallization, it may be possible to eliminate isotope exchange as an important reaction in the Aquia aquifer.

With increasing amounts of isotopic exchange, the modeled $\delta^{13}C$ of the final water will approach an asymptotic value. The asymptotic value for $\delta^{13}C$ of the final solution is modeled for a large mass of isotopic exchange (Wigley and others, 1978). This is found by editing the mass of calcite exchanged to a very large amount, for example, 999.999 mmol/kg H_2O. The value 999.999 is the largest amount of exchange that can be saved in a model using the <S>ave option (although even larger values can be used within the model). The results are as follows:

[See file **np-5-3.dat** on the diskette]

```
Initial Well : Chapelle-Knobel (1985) Fd-12
Final Well   : Chapelle-Knobel (1985) Ff-35

         Final     Initial
C       5.9742      3.0740
CA      0.0749      1.0232
NA      6.0930      0.1653
RS     24.7091     13.4832
FE      0.0000      0.0000
S       0.1354      0.1978
Hit <Q> to quit, or <Enter> to continue

CALCITE  CA   1.0000 C    1.0000 RS   4.0000 I1   1.1000 I2   0.0000
EXCHANGE CA  -1.0000 NA   2.0000 MG   0.0000
GOETHITE FE   1.0000 RS   3.0000
GYPSUM   CA   1.0000 S    1.0000 RS   6.0000 I3  22.0000
PYRITE   FE   1.0000 S    2.0000 RS   0.0000 I3 -60.0000
LIGNITE  C    1.0000 RS  -0.4000 I1 -22.0000 I2   0.0000
Hit <Q> to quit, or <Enter> to continue

                    1 model checked
                    1 model found


           MODEL   1
 CALCITE              0.91087      999.999 exchanged
 EXCHANGE             2.96382
 GOETHITE             0.58352
 GYPSUM    +          1.10460
 PYRITE    -         -0.58352
 LIGNITE   +          1.98927

                Computed    Observed
Carbon-13         0.3510     -6.2000
C-14 (% mod)      0.0000      3.1000
Sulfur-34        66.9880   Undefined
Strontium-87       Insufficient data
Nitrogen-15        Insufficient data

No more models, hit <S> to show Rayleigh data,
<C> to run all C-14 models, <E> to explain insufficient data.
```

Thus, if a very large amount of calcite (aragonite) were involved in recrystallization, the δ^{13}C of the ground water would approach about +0.4 per mil (+0.351 per mil calculated for 999.999 mmols of calcite exchanged) for equilibrium exchange conditions. It was not actually necessary to run NETPATH to find this out. Because the equilibrium isotopic fractionation factor for carbon between calcite and solution is 0.705 per mil for the final well (as shown on the Fractionation Factor screen), it is expected that the final water will be depleted in ^{13}C by 0.705 per mil relative to the calcite. The ^{13}C isotopic composition of calcite was defined to be +1.1 per mil, so the equilibrium δ^{13}C value for inorganic carbon in the final water is $+1.1 - 0.705 = +0.395$ per mil. This value is reached only after an infinite amount of recrystallization. Recrystallization of 999.999 mmol/kg H_2O results in a solution δ^{13}C value of +0.351 per mil which is near the asymptotic value (+0.395 per mil). For very large amounts of recrystallization, NETPATH approaches an asymptotic value of +0.395 per mil for this problem.

The above calculations indicate, however, that if the ^{14}C content of the final water is approximately 3 pmc, there can be little isotopic exchange in the Aquia aquifer, because the adjusted age is consistent with the expected age for waters recharged during the last glacial maximum (18,000 to 20,000 years B.P.).

The Rayleigh calculations were not carried out for the sulfur isotopic data, as indicated by the statement "Insufficient data", even though the isotopic composition of sulfur-containing phases and the pyrite-solution fractionation factor were defined. In this case, the missing data are the sulfur isotopic composition of dissolved sulfate in the initial well and final well. Preliminary calculations assigning 22 per mil to the dissolved sulfate for the initial and final waters (entered through DB) show that the modeled isotopic composition of total dissolved sulfur (sulfate plus sulfide) at the final well (not shown here) would be substantially heavier than the pre-defined incoming sulfur from gypsum of 22 per mil (modeled $\delta^{34}S$ is 67 per mil at the final well). This is to be expected under conditions of sulfate reduction in systems of low dissolved sulfate content. Obviously, actual data on the sulfur isotopic composition of this system would be very useful in further refining the model.

Finally, we consider the possibility of proton exchange (without isotopic exchange of calcite). The phase EXCHANGE was replaced in the previous model with a proton-exchange reaction ($Na^+_{1.6}H^+_{0.4}/Ca^{2+}$). All other isotopic values used previously in model 5-2 were unchanged. The problem is solved as follows:

[See file **np-5-4.dat** on the diskette]

```
 Initial Well: Chapelle-Knobel (1985) Fd-12              NETPATH 2.0
 Final Well  : Chapelle-Knobel (1985) Ff-35             June 21, 1994
 ================================================================================
      Constraints:  6      |        Phases:  6          |      Parameters
 --------------------------|----------------------------|-----------------------
 Carbon       Calcium      | CALCITE  GOETHITE+GYPSUM   |Mixing: No
 Sodium       Redox        |-PYRITE  +LIGNITE  H-Exch   |Evaporation: No
 Iron         Sulfur       |                            |Rayleigh Calcs: Yes
                           |                            |Init C-14  50.00 (TDC)
                           |                            |(User-defined)
 ================================================================================
 Warning: There is no data for Iron in 1 of the wells: zero will be used
 ================================================================================
 Select: <A>dd, <D>elete, <E>dit, <R>un, <S>ave, <V>iew, or <Q>uit
r

 Initial Well : Chapelle-Knobel (1985) Fd-12
 Final Well   : Chapelle-Knobel (1985) Ff-35

          Final     Initial
 C       5.9742      3.0740
 CA      0.0749      1.0232
 NA      6.0930      0.1653
 RS     24.7091     13.4832
 FE      0.0000      0.0000
 S       0.1354      0.1978
 Hit <Q> to quit, or <Enter> to continue
```

```
CALCITE  CA   1.0000 C    1.0000 RS   4.0000 I1   1.1000 I2   0.0000
GOETHITE FE   1.0000 RS   3.0000
GYPSUM   CA   1.0000 S    1.0000 RS   6.0000 I3  22.0000
PYRITE   FE   1.0000 S    2.0000 RS   0.0000 I3 -60.0000
LIGNITE  C    1.0000 RS  -0.4000 I1 -22.0000 I2   0.0000
H-Exch   NA   1.6000 CA  -1.0000
Hit <Q> to quit, or <Enter> to continue

                    1 model checked
                    1 model found

          MODEL   1
 CALCITE              2.70351
 GOETHITE             0.05768
 GYPSUM    +          0.05292
 PYRITE    -         -0.05768
 LIGNITE   +          0.19663
 H-Exch               3.70478

               Computed    Observed
Carbon-13       -6.7097     -6.2000
C-14 (% mod)    25.7277*     3.1000
Sulfur-34       30.4161   Undefined
Strontium-87      Insufficient data
Nitrogen-15       Insufficient data
-------------------------------------------------------------------------
Adjusted C-14 age in years:  17494.*     * = based on User-defined

No more models, hit <S> to show Rayleigh data,
<C> to run all C-14 models, <E> to explain insufficient data.
```

Only two phases in the above proton-exchange model have significant mass transfer, dissolution of 2.7 mmol of calcite and 3.7 mmol of the defined proton-exchange reaction per kg H_2O. All other mass transfers are small and within the uncertainties of the analytical data. For example, if the initial water had only 0.2 mmol of TDIC less than that of well Fd-12, no lignite oxidation would be computed, and the modeled $\delta^{13}C$ would be essentially identical to the observed $\delta^{13}C$ for well Ff-35. The additional dissolution of calcite resulting from the release of protons from the exchanger brought the modeled $\delta^{13}C$ for the final water very near the observed (-6.7 vs -6.2 per mil). Also, the modeled ^{14}C age remained old and consistent with an expected last glacial maximum age (however, no conclusions can be drawn without actual ^{14}C data at well Ff-35). There is presently no field evidence for redox reactions of the types required by models 3-2 to 3-6 in the Aquia aquifer, and the simplest hypothetical reaction model is one involving proton exchange, which remains to be tested.

In the final model of this example (model 5-5) we modify model 3-7 to treat reactions in the Aquia aquifer as entirely inorganic, non-redox reactions.

[See file **np-5-5.dat** on the diskette]

```
 Initial Well: Chapelle-Knobel (1985) Fd-12              NETPATH 2.0
 Final Well  : Chapelle-Knobel (1985) Ff-35             June 21, 1994
 ================================================================================
      Constraints:  3      |        Phases:  3          |      Parameters
 --------------------------|----------------------------|----------------------
 Carbon       Calcium      | CALCITE  H-Exch   CO2 GAS  |Mixing: No
 Sodium                    |                            |Evaporation: No
                           |                            |Rayleigh Calcs: Yes
                           |                            |Init C-14  50.00 (TDC)
                           |                            |(User-defined)
 ================================================================================
 Select: <A>dd, <D>elete, <E>dit, <R>un, <S>ave, <V>iew, or <Q>uit
r

 Initial Well : Chapelle-Knobel (1985) Fd-12
 Final Well   : Chapelle-Knobel (1985) Ff-35

          Final     Initial
 C       5.9742      3.0740
 CA      0.0749      1.0232
 NA      6.0930      0.1653
 Hit <Q> to quit, or <Enter> to continue

 CALCITE  CA   1.0000 C    1.0000 RS   4.0000 I1   1.1000 I2   0.0000
 H-Exch   NA   1.6000 CA  -1.0000
 CO2 GAS  C    1.0000 RS   4.0000 I1 -22.0000 I2   0.0000
 Hit <Q> to quit, or <Enter> to continue

                     1 model checked
                     1 model found

            MODEL   1
  CALCITE              2.75643
  H-Exch               3.70478
  CO2 GAS              0.14371

                Computed    Observed
 Carbon-13       -6.5051     -6.2000
 C-14 (% mod)    25.7277*     3.1000
 Sulfur-34        0.0000   Undefined
 Strontium-87       Insufficient data
 Nitrogen-15        Insufficient data
 ------------------------------------------------------------------------
 Adjusted C-14 age in years:  17494.*     * = based on User-defined

 No more models, hit <S> to show Rayleigh data,
 <C> to run all C-14 models, <E> to explain insufficient data.
```

The small amount of CO_2 gas mass transfer could easily be explained by natural variations in TDIC of initial and (or) final waters in the Aquia aquifer. The small differences between modeled and observed $\delta^{13}C$ can be accounted for by natural variations in $\delta^{13}C_{Calcite}$ and the Na^+:H^+ ratio in the exchange reaction for Ca^{2+}. The ^{13}C data have eliminated all proposed redox reactions as a source for the required CO_2 identified in model 3-1. Isotopic exchange cannot be eliminated without further study of the ^{14}C content of the Aquia aquifer waters. However, the relatively large amount of isotopic exchange indicated for the predominantly clastic sand aquifer is unlikely. Proton

exchange, coupled with calcite dissolution is a viable reaction, if it can be demonstrated to occur in the Aquia aquifer (Appelo, 1994).

Example 6: Applications of ^{13}C, ^{14}C, and ^{34}S Data in Mass-Balance Modeling, Madison Aquifer

Reactions in the Madison aquifer in parts of Wyoming, Montana and South Dakota were investigated by Plummer and others (1990). These authors showed that the predominant reactions were dedolomitization (calcite precipitation driven by dissolution of dolomite and anhydrite), sulfate reduction, iron reduction, cation exchange, and halite dissolution. Reaction models were found that reproduced the observed $\delta^{13}C$ and $\delta^{34}S$ at the final wells along eight flow paths. These reaction models were then applied to the initial ^{14}C data along the flow paths to estimate adjusted radiocarbon ages at the final wells.

In the example that follows, one reaction model from the Madison study is repeated to show combined uses of stable isotope data and examine the ^{14}C models for A_0. The chemical and isotopic data are taken from Plummer and others (1990) and summarized below for two waters, Recharge #3 and Mysse; Recharge #3 evolves to Mysse in south-central Montana.

[*Data from Madison Aquifer, concentrations in millimoles per kilogram H_2O*]

Constituent	Recharge #3	Mysse
Temperature °C	9.9	63
pH	7.55	6.61
Dissolved O_2	.0	.0
Eh (volts)	.0	-.244[1]
Ca^{2+}	1.2	11.28
Mg^{2+}	1.01	4.54
Na^{+}	.02	31.89
K^{+}	.02	2.54
Fe^{2+}	.001	.0004
Cl^{-}	.02	17.85
SO_4^{2-}	.16	19.86
H_2S_T	.0	.259
TDIC	4.30	6.87
DOC	n.d.[2]	n.d.[2]
$\delta^{13}C$ (TDIC[3])	-6.99	-2.34
^{14}C (TDIC[3]) in pmc	33.05	.8
Tritium (TU)	19.8	n.d.[2]
$\delta^{34}S_{SO_4}$	9.73	16.30
$\delta^{34}S_{H_2S}$	n.d.[2]	-22.09

[1]Eh of Mysse well calculated from SO_4/H_2S data in WATEQFP

[2]n.d. – not determined

[3]TDIC – total dissolved inorganic carbon calculated from pH and field alkalinity in WATEQFP

Other data used by Plummer and others (1990) define $\delta^{13}C$ of dolomite, calcite, and organic matter as +4.0, +4.0, and -25.0 per mil, respectively, and $\delta^{34}S$ of anhydrite and pyrite as +15.5 and -22.09 per mil, respectively. The ^{14}C content of all carbon sources along the flow path are 0.0 pmc.

In defining A_0 using the mass-balance model, the $\delta^{13}C$ of soil gas CO_2 and calcite and dolomite were taken to be -13.36 and 0.0 per mil. Below is a listing of the main screen for this problem.

[See file **np-6.dat** on the diskette]

```
Initial Well: Madison.Recharge #3                        NETPATH 2.0
Final Well  : Madison.Mysse                             June 21, 1994
================================================================================
     Constraints: 10      |        Phases: 10          |      Parameters
--------------------------|----------------------------|----------------------
Carbon       Sulfur       |+DOLOMITE CALCITE +ANHYDRIT |Mixing: No
Calcium      Magnesium    |+"CH2O"   GOETHITE-PYRITE   |Evaporation: No
Sodium       Potassium    | EXCHANGE+NaCl     SYLVITE  |Rayleigh Calcs: Yes
Chloride     Iron         | CO2 GAS                    |Exchange: Ca/Na
Redox        Sulfur-34    |                            |Init C-14  52.33 (TDC)
                          |                            |(Mass Balance)
================================================================================
Select: <A>dd, <D>elete, <E>dit, <R>un, <S>ave, <V>iew, or <Q>uit
```

Notice that the constraint Sulfur-34 was selected. In this case the sulfur isotopic data will be treated as a mass-balance problem, even though there is a fractionating output of sulfur in precipitated pyrite. As discussed by Plummer and others (1990), the sulfur isotopic composition of anhydrite was adjusted to bring the CO_2 gas mass transfer to near zero, as expected for deep confined aquifers isolated from the atmosphere (that is, the system is expected to be closed to CO_2 gas). Before running the model, the Edit menu is used to view the isotopic data selected for the model.

```
e

  General
    1) Well file              : class
    2) Entire model
    3) Phases
 Wells
    4) Mixing                 : No
    5) Initial well           : Madison.Recharge #3
       Final well             : Madison.Mysse
  Parameters
    6) Evaporation/Dilution   : No
    7) Ion exchange           : Ca/Na
    8) Redox state of DOC
  Isotope calculations
    9) Rayleigh calculations  : Yes
   10) Isotopic data
   11) Model for initial C14  : Mass Balance
   12) Carbon fract. factors  : Mook
--------------------
Edit which? (<Enter> when done)
```

```
10

                        Isotopic Compositions

 Num Phase    Carbon-13  C14 % mod  Sulfur-34    Sr-87       N-15
 ------------------------------------------------------------------
  1: DOLOMITE    4.000      0.000
  2: CALCITE     4.000      0.000
  3: ANHYDRIT                           15.500
  4: "CH2O"    -25.000      0.000
  5: PYRITE                          -22.090
  6: CO2 GAS   -16.200    100.000
 Enter number of phase to edit. <Enter> when done.

              Additive Fractionation Factors (in per mil)
                         Relative to solution
 Num Phase    Carbon-13  C14 % mod  Sulfur-34    Sr-87       N-15
 ------------------------------------------------------------------
  1: CALCITE     2.381*     4.761*
  2: PYRITE                          -37.896@
  3: CO2 GAS    -5.924*   -11.848*

 * = based on computed value at 0.50 fraction between init and final waters
 @ = based on computed value at final water
 Enter number of phase to edit, '0' for fraction along path, <Enter> when done.
```

Notice that the carbon system fractionation factors are defined at the midpoint between the chemistries of the initial and final waters ($X = 0.5$). This was changed from the default value of $X = 1$.

The pyrite fractionation factor indicates that pyrite precipitated along the flow path is 37.8958 per mil lighter than the average isotopic composition of total dissolved sulfur in solution (SO_4+H_2S). This is calculated using the sulfur isotopic data at the Mysse well of $\delta^{34}S_{SO_4}$ of +16.3 and $\delta^{34}S_{H_2S}$ of -22.09 per mil. The total concentrations of sulfate and sulfide are 19.86 and 0.259 mmol. Thus, the average isotopic composition of S_T is 15.8058 per mil. Assuming that the pyrite will precipitate without further fractionation from the dissolved sulfide, the additive fractionation factor relative to the solution is

$$\epsilon_{\mathrm{pyr-soln}} = \delta^{34}S_{H_2S} - \delta^{34}S_T = -22.09 - 15.8058 = -37.8958 \; .$$

If, however, the pyrite were fractionated by 1 per mil heavier than the dissolved sulfide, the pyrite solution fractionation factor could be changed to -36.8958.

The next screen pertains to various models for defining A_0 for ^{14}C calculations. These are accessed through the Edit menu.

```
e

  General
    1) Well file              : class
    2) Entire model
    3) Phases
 Wells
    4) Mixing                 : No
    5) Initial well           : Madison.Recharge #3
       Final well             : Madison.Mysse
  Parameters
    6) Evaporation/Dilution   : No
    7) Ion exchange           : Ca/Na
    8) Redox state of DOC
  Isotope calculations
    9) Rayleigh calculations  : Yes
   10) Isotopic data
   11) Model for initial C14  : Mass Balance
   12) Carbon fract. factors  : Mook
 --------------------
 Edit which? (<Enter> when done)

11

        Initial Carbon-14, A0, (percent modern)
             for Total Dissolved Carbon

         Model             Initial well
   1 : Original Data       :     33.05
   2 : Mass Balance        :     52.33
   3 : Vogel               :     85.00
   4 : Tamers              :     53.46
   5 : Ingerson and Pearson:     52.33
   6 : Mook                :     65.91
   7 : Fontes and Garnier  :     52.31
   8 : Eichinger           :     47.57
   9 : User-defined        :    100.00
 Enter number of model to use (<Enter> for 'Mass Balance')

 Hit <Enter> to input data for 'Mass Balance',
 any other key to enter data for all models.

t

 Enter value of C-14 activity in carbonate minerals (% modern),
 <Enter> for      0.00

 Enter value of C-14 activity in soil gas CO2 (% modern),
 <Enter> for    100.00

 Enter value of C-14 activity in dolomite (% modern),
 <Enter> for      0.00

 Enter value of C-14 activity in calcite (% modern),
 <Enter> for      0.00
```

```
Choices for C-13 (TDIC) in initial solution
  (Used only in A0 models)
 0 : Original Value
 1 : User-defined Value

Choose method for defining C-13 (TDIC) in initial solution,
<Enter> to use Original Value.



Enter value of delta C-13 (per mil) in carbonate minerals,
<Enter> for      0.00

Choices for delta C-13 (per mil) in soil gas CO2
 0 : User-defined Value
 1 : Mass Balance - no fractionation
 2 : Mass Balance - with fractionation
 3 : Open System (gas-solution equilibrium)




Choose method for defining delta C-13 (per mil) in soil gas CO2,
<Enter> to use Mass Balance - no fractionation.

Enter value of delta C-13 (per mil) in dolomite,
<Enter> for      0.00




Enter value of delta C-13 (per mil) in calcite,
<Enter> for      0.00

C-13 of CO2 gas for initial well:  -13.359
Hit <Enter> to continue

       Initial Carbon-14, A0, (percent modern)
            for Total Dissolved Carbon

        Model             Initial well
  1 : Original Data       :     33.05
  2 : Mass Balance        :     52.33
  3 : Vogel               :     85.00
  4 : Tamers              :     53.46
  5 : Ingerson and Pearson:     52.33
  6 : Mook                :     65.91
  7 : Fontes and Garnier  :     52.31
  8 : Eichinger           :     47.57
  9 : User-defined        :    100.00
Enter number of model to use (<Enter> to quit, 0 to edit data for all models)
```

```
 General
   1) Well file               : class
   2) Entire model
   3) Phases
Wells
   4) Mixing                  : No
   5) Initial well            : Madison.Recharge #3
      Final well              : Madison.Mysse
 Parameters
   6) Evaporation/Dilution    : No
   7) Ion exchange            : Ca/Na
   8) Redox state of DOC
 Isotope calculations
   9) Rayleigh calculations   : Yes
  10) Isotopic data
  11) Model for initial C14   : Mass Balance
  12) Carbon fract. factors   : Mook
--------------------
Edit which? (<Enter> when done)
```

Returning to the main screen, the problem is run with the following result.

```
Initial Well : Madison.Recharge #3
Final Well   : Madison.Mysse

          Final     Initial
C        6.8700      4.3000
S       20.1190      0.1600
CA      11.2800      1.2000
MG       4.5400      1.0100
NA      31.8900      0.0200
K        2.5400      0.0200
CL      17.8500      0.0200
FE       0.0004      0.0010
RS     146.1228     18.1620
I3     317.9967      1.5568
Hit <Q> to quit, or <Enter> to continue

DOLOMITE CA   1.0000 MG   1.0000 C    2.0000 RS   8.0000 I1   8.0000
         I2   0.0000
CALCITE  CA   1.0000 C    1.0000 RS   4.0000 I1   4.0000 I2   0.0000
ANHYDRIT CA   1.0000 S    1.0000 RS   6.0000 I3  15.5000
"CH2O"   C    1.0000 I1 -25.0000 I2   0.0000
GOETHITE FE   1.0000 RS   3.0000
PYRITE   FE   1.0000 S    2.0000 RS   0.0000 I3 -44.1800
EXCHANGE CA  -1.0000 NA   2.0000 MG   0.0000
NaCl     NA   1.0000 CL   1.0000
SYLVITE  K    1.0000 CL   1.0000
CO2 GAS  C    1.0000 RS   4.0000 I1 -16.2000 I2 100.0000
Hit <Q> to quit, or <Enter> to continue
```

```
                    1 model checked
                    1 model found

           MODEL   1
 DOLOMITE  +          3.53000
 CALCITE              -5.31723
 ANHYDRIT  +         20.14723
 "CH2O"    +          0.87077
 GOETHITE              0.09351
 PYRITE    -         -0.09411
 EXCHANGE              8.28000
 NaCl      +         15.31000
 SYLVITE               2.52000
 CO2 GAS              -0.04355
Hit <Enter> to continue

               Computed    Observed
Carbon-13       -2.2137     -2.3400
C-14 (% mod)    12.2689*     0.8000
Sulfur-34       15.8130     15.8058
Strontium-87      Insufficient data
Nitrogen-15       Insufficient data
-------------------------------------------------------------------------
Adjusted C-14 age in years:  22570.*     * = based on Mass Balance

No more models, hit <S> to show Rayleigh data,
<C> to run all C-14 models, <E> to explain insufficient data.
```

Below, "S" is selected to show data used in the Rayleigh calculations and "C" to show radiocarbon ages calculated for the mass transfer model, but assuming different models for A_0.

```
s

 Data used for Carbon-13

 Initial Value:     -6.9900        Modeled Final Value:     -2.2137

  2 dissolving phases:
 Phase       Delta C     Isotopic composition (o/oo)
 DOLOMITE    7.06000              4.0000
 "CH2O"      0.87077            -25.0000

  2 precipitating phases:                            Average
 Phase       Delta C     Fractionation factor Isotopic composition (o/oo)
 CALCITE    -5.31723             2.3806               -1.4960
 CO2 GAS    -0.04355            -5.9240               -9.7684

 Hit <Enter> to continue, any other key to see graphs of
   the isotopic composition of precipitating phases.
```

```
 Data used for C-14 (% mod)

 Initial Value:     52.3256        Modeled Final Value:     12.2689

  2 dissolving phases:
 Phase       Delta C     Isotopic composition (% modern)
 DOLOMITE    7.06000              0.0000
 "CH2O"      0.87077              0.0000

  2 precipitating phases:                              Average
 Phase       Delta C     Fractionation factor Isotopic composition (% modern)
 CALCITE    -5.31723              4.7611               26.2549
 CO2 GAS    -0.04355            -11.8479               25.8209

 Hit <Enter> to continue, any other key to see graphs of
   the isotopic composition of precipitating phases.


 Data used for Sulfur-34

 Initial Value:      9.7300        Modeled Final Value:     15.8130

  1 dissolving phases:
 Phase       Delta S     Isotopic composition (o/oo)
 ANHYDRIT   20.14723             15.5000

  1 precipitating phases:                              Average
 Phase       Delta S     Fractionation factor Isotopic composition (o/oo)
 PYRITE     -0.18823            -37.8958              -22.8795

 Hit <Enter> to continue, any other key to see graphs of
   the isotopic composition of precipitating phases.


 Data used for Strontium-87


 Data used for Nitrogen-15

 No more models, hit <S> to show Rayleigh data,
 <C> to run all C-14 models, <E> to explain insufficient data.
c
     Model                 A0     Computed  Observed    age
 (for initial A0)      (initial) (no decay)           (final)
 ------------------------------------------------------------
 Original Data           33.05      7.75      0.80    18771.
 Mass Balance            52.33     12.27      0.80    22570.
 Vogel                   85.00     19.93      0.80    26580.
 Tamers                  53.46     12.54      0.80    22747.
 Ingerson and Pearson    52.33     12.27      0.80    22570.
 Mook                    65.91     15.45      0.80    24478.
 Fontes and Garnier      52.31     12.27      0.80    22568.
 Eichinger               47.57     11.15      0.80    21783.
 User-defined           100.00     23.45      0.80    27924.

 No more models, hit <S> to show Rayleigh data,
 <C> to run all C-14 models, <E> to explain insufficient data.
```

For this particular set of conditions, the A_0 values are quite similar in many of the models, and therefore similar ages are found, typically 21,000 to 23,000 years.

Example 7: Degradation of Dissolved Organic Carbon Released from Crude Oil

In the previous six examples, the carbon system was limited to total dissolved inorganic carbon. In this problem, chemical and isotopic evolution in waters containing dissolved inorganic carbon, dissolved CH_4 and dissolved organic carbon are investigated. The example is taken from the studies of Baedecker and Cozzarelli (1991) and Baedecker and others (1993) on the degradation of organic carbon released from crude oil that contaminates a shallow sand aquifer near Bemidji, Minnesota. Hult (1984) gives background data for the study. The uncontaminated glacial outwash material of the aquifer is primarily quartz sand with about 6 percent carbonate minerals (calcite), 30 percent feldspars, less than 5 percent clay minerals, and less than 0.2 percent organic carbon. Since 1979 when the oil spill occurred, contaminants have been transported more than 180 meters downgradient in a narrow plume. Beyond the plume, the DOC concentration in the ground water is less than 2 mg/L. Within the plume, the DOC concentration exceeds 50 mg/L.

Baedecker and Cozzarelli (1991) modeled the degradation of the dissolved organic carbon released from the oil using a pre-release version of NETPATH for the primary reactions (1) methanogenesis of DOC, (2) outgassing of CO_2 and CH_4 from the water table into the unsaturated zone, (3) dissolution of calcite and goethite, and (4) precipitation of a Ca-siderite ($Fe_{0.7}Ca_{0.3}CO_3$). Baedecker and others (1993) subsequently modified the reaction model replacing calcite with siderite and changing the composition of the calcium-siderite from 30 percent to 20 percent calcium (RS=5.6). Two models were considered, one in which outgassing of CO_2 and CH_4 from the aquifer into the unsaturated zone was in proportion to the Henry's law partial pressures in the aquifer (their model 1 using the phase "CO_2-CH_4" with a CO_2 fraction in the gas mixture of 0.14), and a second model (model 2) in which CO_2 and CH_4 were treated as separate phases.

Below we present a slightly modified re-construction of model 1 of Baedecker and others (1993). The reaction is modeled between two water compositions in the plume; the upgradient water, Site AA, near the oil body, and Site BB about 40 meters downgradient. The model differs from that of Baedecker and others (1993) on two points: (1) calcite and siderite are included as separate pure phases, removing the Ca-siderite of Baedecker and others (1993). This change allows the mass balance to determine the net mass transfers for the end-member components which can be used to imply the composition of the Ca-siderite forming (if a single solid solution forms) or to place constraints on the range of compositions of siderites and calcites that can form (if more than one phase forms). (2) Baedecker and others (1993) apparently used -1.0 for the RS of DOC at the initial point (Site AA) and RS of 0.0 for DOC at the final point (Site BB). This choice did not produce an exact match in computed and observed $\delta^{13}C$ at the final well. In the present model, sets of values of RS of DOC at the initial and final sites are found that lead to agreement in the computed and observed $\delta^{13}C$. This analysis places constraints on the possible range of compositions of organic compounds being degraded at Bemidji. All other aspects of the present model are those of Baedecker and others (1993). Listed below are the chemical and isotopic data for the water at Sites AA and BB taken mainly from Baedecker and others (1993):

[*Data from Baedecker and Cozzarelli (1991), and Baedecker and others (1993), in millimoles per liter*]

Property or Constituent	Site A	Site B
Temperature °C	10	9
pH	6.78	6.93
Eh (volts)	-.15	-.09
Dissolved O_2	.0	.0
Ca^{2+}	3.322	3.046
Mg^{2+}	1.770	1.366
Na^{+}	.135	.091
K^{+}	.169	.036
Fe^{2+}	1.055	.079
Mn^{2+}	.016	.127
Cl^{-}	.009	.010
$SO_4{}^{2-}$	.005	.012
H_2S	<.0006	<.0006
TDIC	17.165	10.572
DOC	4.171	1.515
CH_4(aq)	1.353	.386
$NH_4{}^{+}$	.028	.005
SiO_2	1.018	.508
$\delta^{13}C_{TDIC}$ (per mil)	-5.80	-5.95
$\delta^{13}C_{CH_4(aq)}$	-56.1	-53.6

Other data needed to re-construct the modified model 1 are unknown and were estimated by Baedecker and others (1993). The $\delta^{13}C$ of the DOC was assumed to be -25 per mil. Baedecker and others (1993) state that the oxidation state of reactive carbon in the DOC at Site AA could range between -2.3 and -1.0. Because DOC is being oxidized at Bemidji, the residual DOC at Site BB should be more oxidized than that at Site AA. In the present model values of RS of DOC at Site AA were assumed in the range of -2.3 to -1.0 and then values of RS for the residual DOC at Site BB were found by trial and error that produce calculated values of $\delta^{13}C$ of total dissolved carbon that are identical to the observed at Site BB. The process of sorption of NH_4^+ on clays (without cation exchange) was retained, though its mass transfer is small and has insignificant effect on the other modeled results. A small increase in dissolved Mn^{2+} was attributed to reduction of MnO_2. It was assumed that the fraction of CO_2 in the CO_2-CH_4 gas mixture was 0.14, as would be expected if Henry's law were obeyed across the water table into the unsaturated zone (Baedecker and others, 1993), using the calculated partial pressures of CH_4 and CO_2 in the ground water at Site BB. Methane was assumed to leave the aqueous solution without further fractionation and CO_2 was fractionated according to the equilibrium fractionation between CO_2 gas and the aqueous inorganic carbon species, using the speciation at Site BB. The modified model 1 that follows is nonunique, but does show that for reasonable values of unknown parameters, reactions can be found that are consistent with the chemical and isotopic data. The following is a listing of the main screen for this problem and critical data used (displayed from the Edit menu):

[See file **np-7.dat** on the diskette]

```
 Initial Well: Bemidjii Site AA                          NETPATH 2.0
 Final Well  : Bemidjii Site BB                         June 21, 1994
 ================================================================================
      Constraints:  6      |        Phases:  6          |      Parameters
 --------------------------|----------------------------|----------------------
 Carbon       Calcium      | MnO2     GOETHITE SIDERITE |Mixing: No
 Iron         Manganese    | Sorb NH4 CO2-CH4  CALCITE  |Evaporation: No
 Nitrogen     Redox        |                            |Rayleigh Calcs: Yes
                           |                            |X CO2 in CO2-CH4: 0.14
                           |                            |Init C-14   0.00 (TDC)
                           |                            |(Original Data)
 ================================================================================
 Select: <A>dd, <D>elete, <E>dit, <R>un, <S>ave, <V>iew, or <Q>uit

e

  General
    1) Well file               : class
    2) Entire model
    3) Phases
 Wells
    4) Mixing                  : No
    5) Initial well            : Bemidjii Site AA
       Final well              : Bemidjii Site BB
  Parameters
    6) Evaporation/Dilution    : No
    7) Fraction CO2 in CO2-CH4 : 0.140
    8) Redox state of DOC
  Isotope calculations
    9) Rayleigh calculations   : Yes
   10) Isotopic data
   11) Model for initial C14   : Original Data
   12) Carbon fract. factors   : Mook
 --------------------
 Edit which? (<Enter> when done)
```

By selecting option (8), the redox state of the DOC reacting in the ground water was changed from the default value of 0.0 originally stored in the .PAT file from DB to values in the range -2.0 to -1.0 for DOC at site AA, and corresponding values of RS for DOC at Site BB were selected by trial and error to find values that reproduce the observed $\delta^{13}C$ at Site BB. Baedecker and Cozzarelli (1991) found a range of aromatic hydrocarbons were released to the ground water from the oil, including benzene (C_6H_6) and the alkylbenzenes (C_6 to C_{10}). Eganhouse (1987) and Cozzarelli and others (1990) describe the microbial degradation of the aromatic hydrocarbons at Bemidji. Returning to the Edit menu we display the carbon isotopic data used in the revised model 1.

```
 General
   1) Well file               : class
   2) Entire model
   3) Phases
Wells
   4) Mixing                  : No
   5) Initial well            : Bemidjii Site AA
      Final well              : Bemidjii Site BB
 Parameters
   6) Evaporation/Dilution    : No
   7) Fraction CO2 in CO2-CH4 : 0.140
   8) Redox state of DOC
 Isotope calculations
   9) Rayleigh calculations   : Yes
  10) Isotopic data
  11) Model for initial C14   : Original Data
  12) Carbon fract. factors   : Mook
--------------------
Edit which? (<Enter> when done)

                        Isotopic Compositions

Num Phase    Carbon-13  C14 % mod  Sulfur-34    Sr-87       N-15
-------------------------------------------------------------------
 1: SIDERITE    0.000      0.000
 2: Sorb NH4                                                Undefined
 3: CO2       -24.700      0.000
    CH4       -53.600      0.000
 4: CALCITE     0.000      0.000
Enter number of phase to edit. <Enter> when done.
```

Although realistic ^{13}C values are given for CO_2 and CH_4 in the gas mixture, and for the siderite and calcite, the calculations are independent of these values (above) because the mass transfers for these phases are, in this case, all negative, that is, they outgas or precipitate. Therefore, their isotopic compositions are determined by isotopic fractionation. Next we display carbon isotopic data used for dissolved CH_4 and DOC.

```
                Isotopic compositions of Carbon in solution

                                    Carbon-13  C14 %mod   Carbon-13  C14 %mod
#  Well Name                         of CH4     of CH4     of DOC     of DOC
-------------------------------------------------------------------------------
1: Bemidjii Site AA                  -56.100     0.000     -25.000     0.000
2: Bemidjii Site BB                  -53.600     0.000     -25.000     0.000

Enter number of well to change, <Enter> when done.
```

The ^{13}C (and ^{14}C) values for dissolved CH_4 and DOC are not commonly measured, therefore, they are not entered in DB. However, in considering carbon isotopic effects in modeling reactions with waters containing these forms of carbon, it is necessary to know the carbon isotopic compositions of all carbon species to define the isotopic composition of total dissolved carbon. The above screen only appears for initial and (or) final waters that contain either dissolved CH_4 and (or) DOC. In the calculations that follow the isotopic composition of dissolved CH_4 was determined by Baedecker and Cozzarelli (1991) and that of the DOC was assumed.

```
              Additive Fractionation Factors (in per mil)
                        Relative to solution
Num Phase     Carbon-13  C14 % mod  Sulfur-34    Sr-87       N-15
-------------------------------------------------------------------
 1: SIDERITE    6.461*    12.921*
 2: Sorb NH4                                                Undefined
 3: CO2        -3.423*    -6.845*
    CH4       -43.900     0.000
 4: CALCITE     6.461*    12.921*
*based on computed value at 1.00 fraction between init and final waters
Enter number of phase to edit, '0' for fraction along path, <Enter> when done.
```

The above screen defines the fractionation factors for all carbon-bearing phases that occur in the model. These fractionation factors are used only for precipitation or outgassing. Note that all fractionation factors are calculated or defined relative to the average isotopic composition of the element in aqueous solution, which in this case is -9.74 per mil for total dissolved carbon at the final well ($X = 1$). The CH_4 fractionation factor between CH_4(aq) and CH_4 gas was assumed to be zero. Therefore, the $\delta^{13}C$ composition of CH_4 gas = $\delta^{13}C$ of CH_4 (aq) = -53.6 per mil. And the fractionation factor for CH_4 gas relative to the ^{13}C of the total dissolved carbon is $-53.6 - (-9.74) = -43.9$ per mil. In outgassing of the CO_2-CH_4 gas mixture, the two gases are assumed to leave the aqueous solution independently according to their mole fractions in the mixture. Therefore, the average fractionation factor for the gas mixture is computed as a linear proportion of the end-member fractionation factors. In this case, ϵ for the gas mixture containing 14 percent CO_2 is $0.14(-3.4225) + 0.86(-43.9) = -38.233$ per mil relative to the solution. The problem could be further refined by study of the siderite fractionation factor. Here the siderite fractionation factor was assumed equal to that of calcite. Next, the main screen is invoked to run NETPATH.

```
 General
   1) Well file               : class
   2) Entire model
   3) Phases
Wells
   4) Mixing                  : No
   5) Initial well            : Bemidjii Site AA
      Final well              : Bemidjii Site BB
 Parameters
   6) Evaporation/Dilution    : No
   7) Fraction CO2 in CO2-CH4 : 0.140
   8) Redox state of DOC
 Isotope calculations
   9) Rayleigh calculations   : Yes
  10) Isotopic data
  11) Model for initial C14   : Original Data
  12) Carbon fract. factors   : Mook
--------------------
Edit which? (<Enter> when done)
```

```
 Initial Well: Bemidjii Site AA                          NETPATH 2.0
 Final Well  : Bemidjii Site BB                         June 21, 1994
 ================================================================================
      Constraints:  6      |        Phases:  6          |      Parameters
 --------------------------|----------------------------|----------------------
 Carbon       Calcium      | MnO2     GOETHITE SIDERITE |Mixing: No
 Iron         Manganese    | Sorb NH4 CO2-CH4  CALCITE  |Evaporation: No
 Nitrogen     Redox        |                            |Rayleigh Calcs: Yes
                           |                            |X CO2 in CO2-CH4: 0.14
                           |                            |Init C-14   0.00 (TDC)
                           |                            |(Original Data)
 ================================================================================
 Select: <A>dd, <D>elete, <E>dit, <R>un, <S>ave, <V>iew, or <Q>uit

r

 Initial Well : Bemidjii Site AA
 Final Well   : Bemidjii Site BB

          Final     Initial
 C      12.4730     22.6890
 CA      3.0460      3.3220
 FE      0.0790      1.0550
 MN      0.1270      0.0160
 N       0.1450      0.1680
 RS     38.1867     56.9640
 Hit <Q> to quit, or <Enter> to continue

 MnO2     MN   1.0000 RS   4.0000
 GOETHITE FE   1.0000 RS   3.0000
 SIDERITE FE   1.0000 C    1.0000 RS   6.0000 I1   0.0000 I2   0.0000
 Sorb NH4 N   -1.0000 RS   3.0000
 CO2-CH4  C    1.0000 RS  -2.8800 I1 -49.5540 I2   0.0000
 CALCITE  CA   1.0000 C    1.0000 RS   4.0000 I1   0.0000 I2   0.0000
 Hit <Q> to quit, or <Enter> to continue

                     1 model checked
                     1 model found

            MODEL   1
  MnO2                0.11100
  GOETHITE            6.48751
  SIDERITE           -7.46351
  Sorb NH4            0.02300
  CO2-CH4            -2.47649
  CALCITE            -0.27600

                Computed    Observed
 Carbon-13       -9.7411     -9.7385
 DIC C-13        -5.9531     -5.9500
 C-14 (% mod)      Insufficient data
 Sulfur-34        0.0000   Undefined
 Strontium-87      Insufficient data
 Nitrogen-15       Insufficient data

 No more models, hit <S> to show Rayleigh data,
 <C> to run all C-14 models, <E> to explain insufficient data.
```

The results are similar to those of Baedecker and others (1993), but, because of changes in redox state of DOC and composition of the carbonate mineral solid solutions, not identical to those of model 1 given by Baedecker and others (1993). The slightly revised model 1 of Baedecker and others (1993) indicates dissolution of approximately 0.11 mmols of MnO_2, and 6.49 mmol of goethite, precipitation of 0.28 mmol of calcite, 7.46 mmols of siderite, sorption of 0.023 mmol of NH_4^+, and outgassing of 2.48 mmols of a CO_2-CH_4 gas mixture containing 14 mole percent CO_2. These mass transfers cause the calculated $\delta^{13}C$ of TDC to be equal to the observed (-9.74 per mil) whenever the redox states of DOC at Sites AA and BB are modeled according to the relation

$$\mathrm{RS}_{DOC\ (SiteBB)} = 3.60 + 2.78\mathrm{RS}_{DOC\ (SiteAA)}.$$

The above relationship applies only to the selected model and data, but can be used to place constraints on the redox state of reactive DOC at Site AA. Because the RS of DOC at Site BB must be equal to or more positive than the RS of DOC at Site AA, the above relation indicates that, if all other aspects of model 1 are unchanged, the RS of DOC at Site AA cannot be more negative than approximately -2.0, otherwise, values of RS of DOC at Site BB more negative than those at Site AA are calculated. Furthermore, the above relationship indicates that the modeled RS of DOC at Site BB would be greater than zero if RS of reactive DOC at Site AA were greater than -1.3, which is also unlikely. The RS of DOC at Site BB is equal to that at Site AA if RS of DOC at Site AA is approximately -2.0. Therefore, NETPATH modeling between Sites AA and BB indicates that dissolved hydrocarbons that are actively being oxidized at Bemidji can have an average carbon oxidation state of -2.0 to probably not greater than -1.3.

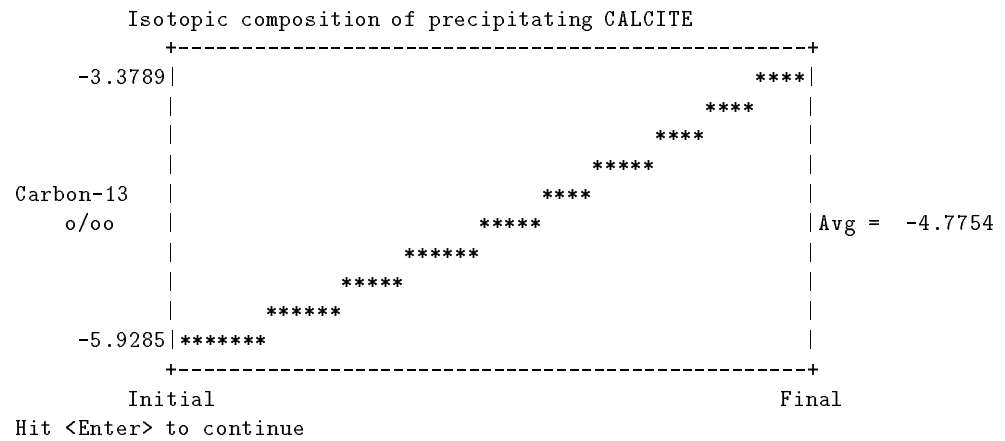
Notice that when DOC and (or) CH_4 are included, NETPATH prints the modeled and observed ^{13}C of TDC and of TDIC. Below, the Rayleigh data are displayed by entering <S> showing that NETPATH used, in this case, the fractionation factor of -38.233 per mil for the CO_2-CH_4 gas mixture, which can be calculated from the fractions of the individual fractionation factors for CO_2 and CH_4, as discussed above. No data for ^{14}C, ^{34}S, ^{15}N, or $^{87}Sr/^{86}Sr$ were available for this study.

```
s

 Data used for Carbon-13

 Initial Value:    -12.3291        Modeled Final Value:     -9.7411

  4 precipitating phases:                              Average
 Phase       Delta C     Fractionation factor Isotopic composition (o/oo)
 SIDERITE   -7.46351             6.4606               -4.7754
 CO2 GAS    -0.34671            -3.4225              -14.5482
 CH4 GAS    -2.12978           -43.9000              -54.5738
 CALCITE    -0.27600             6.4606               -4.7754

 Hit <Enter> to continue, any other key to see graphs of
   the isotopic composition of precipitating phases.
```

```
Data used for C-14 (% mod)

Data used for Sulfur-34

Initial Value:      0.0000        Modeled Final Value:      0.0000

No incoming or outgoing phases

Hit <Enter> to continue



Data used for Strontium-87

Initial Value:      0.0000        Modeled Final Value:      0.0000

No incoming or outgoing phases

Hit <Enter> to continue



Data used for Nitrogen-15

No more models, hit <S> to show Rayleigh data,
<C> to run all C-14 models, <E> to explain insufficient data.

Initial Well: Bemidjii Site AA                          NETPATH 2.0
Final Well  : Bemidjii Site BB                         June 21, 1994
================================================================================
     Constraints:  6      |        Phases:  6          |      Parameters
--------------------------|----------------------------|----------------------
Carbon       Calcium      | MnO2     GOETHITE SIDERITE |Mixing: No
Iron         Manganese    | Sorb NH4 CO2-CH4  CALCITE  |Evaporation: No
Nitrogen     Redox        |                            |Rayleigh Calcs: Yes
                          |                            |X CO2 in CO2-CH4: 0.14
                          |                            |Init C-14   0.00 (TDC)
                          |                            |(Original Data)
================================================================================
Select: <A>dd, <D>elete, <E>dit, <R>un, <S>ave, <V>iew, or <Q>uit
```

During selection of the <S> command, it is possible to display plots of isotopic values for the phases modeled along the reaction path from the initial point to final point. Below we give the plots for the carbon-bearing phases along the path from Site AA to Site BB.

```
x
          Isotopic composition of precipitating SIDERITE
             +-------------------------------------------------+
      -3.3789|                                            ****|
             |                                        ****    |
             |                                    ****        |
             |                                *****            |
 Carbon-13   |                            ****                 |
     o/oo    |                       *****                     |Avg =  -4.7754
             |                  ******                         |
             |             *****                               |
             |       ******                                    |
      -5.9285|*******                                          |
             +-------------------------------------------------+
          Initial                                            Final
 Hit <Enter> to continue

          Isotopic composition of precipitating CO2 GAS
             +-------------------------------------------------+
     -13.1654|                                            ****|
             |                                        ****    |
             |                                    ****        |
             |                                *****            |
 Carbon-13   |                            ****                 |
     o/oo    |                       *****                     |Avg = -14.5482
             |                  ******                         |
             |             *****                               |
             |       ******                                    |
     -15.6900|*******                                          |
             +-------------------------------------------------+
          Initial                                            Final
 Hit <Enter> to continue

          Isotopic composition of precipitating CH4 GAS
             +-------------------------------------------------+
     -53.2471|                                            ****|
             |                                        ****    |
             |                                    ****        |
             |                                *****            |
 Carbon-13   |                            ****                 |
     o/oo    |                       *****                     |Avg = -54.5738
             |                  ******                         |
             |             *****                               |
             |       ******                                    |
     -55.6692|*******                                          |
             +-------------------------------------------------+
          Initial                                            Final
 Hit <Enter> to continue
```



The Rayleigh calculations indicate that siderite and calcite precipitated along the path between Site AA and Site BB would average about -4.8 per mil in $\delta^{13}C$, varying between about -5.9 to -3.3 per mil from Site AA to Site BB, respectively. The plots indicate that CH_4 entering the unsaturated zone from the water table at Site BB would have a $\delta^{13}C$ composition of about -53.2 per mil compared to -13.1 per mil for CO_2. Recent analyses of gases above the water table at Bemidji at a point slightly farther downgradient from Site BB and following by approximately 5 years the date of the original measurements of Baedecker and Cozzarelli (1991) indicate that CH_4 gas is rapidly oxidized to CO_2 gas in the unsaturated zone, resulting in highly depleted CO_2 gas near -44.3 per mil, with no discernible CH_4 gas remaining (Revesz and others, 1994; K.M. Revesz, unpublished data, 1994). If all the CH_4 gas entering the unsaturated zone at Site BB were oxidized to CO_2 gas, the NETPATH results indicate that unsaturated-zone CO_2 at Site BB would have a $\delta^{13}C$ isotopic composition of approximately -47.6 per mil at the time of original sampling (1987) conducted by Baedecker and Cozzarelli (1991) and Baedecker and others (1993). The isotopic composition of CO_2 measured recently by Revesz (Revesz and others, 1994; K.M. Revesz, unpublished data, 1994) is consistent with a trend in isotopic enrichment of inorganic carbon at Bemidji with time (Baedecker and others, 1993) and supports the assumption of Baedecker and Cozzarelli (1991) and Baedecker and others (1993) of Henry's law behavior for CO_2 and CH_4 gas mass transfer into the unsaturated zone.

At this point, the user could continue with this problem using NETPATH to examine the sensitivity of modeling results to uncertainties in the compositional and isotopic data. Such analysis is useful in eliminating some reaction possibilities and helps focus the investigation on critical data needed to improve understanding of the reaction system. In this problem, the most significant data needed appear to be the redox state of the reacting DOC (at sites AA and BB). Other studies should investigate the mechanism of CO_2-CH_4 outgassing and its effect on gas composition. Furthermore, because this problem deals with a point source of contamination, it may be necessary to evaluate the effect of hydrodynamic dispersion on the water chemistry. This could be accomplished through digital simulation of the flow and solute transport.

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Attachment A: Description of BALNINPT

An interactive program for mass-balance calculations

BALNINPT is an interactive Fortran 77 computer program designed to quantify chemical reactions between ground water and minerals and (or) gases. Using (1) the chemical compositions of water samples from two points along a flow path and (2) a set of mineral phases hypothesized to be the reactive phases in the system, the program calculates the mass transfer of phases necessary to account for the observed changes in composition between the two water samples. The program determines every combination of the specified minerals that can account for the observed changes. Additional constraints can be included in the problem formulation to account for mixing of two end-member waters, redox reactions, and, in a simplified form, isotopic composition. Extensive help facilities are provided interactively by the program.

BALNINPT is largely superseded by the program NETPATH. All of the modeling capabilities of BALNINPT are included in NETPATH, with one exception: mass-balance on any element or isotope is possible with BALNINPT, while NETPATH is restricted to a fixed set of elements and isotopes. There is no data base or speciation program attached to BALNINPT, as DB is to NETPATH, nor are Rayleigh calculations and radiocarbon dating possible with BALNINPT.

BALNINPT solves a set of linear equations that account for mass conservation for each specified element. The unknowns in these equations are the mass transfers of minerals and gases. In the matrix that corresponds to the set of linear equations, the columns are the stoichiometries of the hypothesized reactant minerals. The right-hand side of the equations are determined from the analytical data for the elements in solution. If the number of mineral and gas phases equals the number of elements (and the stoichiometries of the phases are linearly independent), the equations can be solved producing a single model. If the number of phases exceeds the number of elements, the system of equations is overspecified. In this case, BALNINPT exhaustively searches for all combinations of minerals that, when used to form the left-hand side of the simultaneous equations, result in a solution to the equations. Phases may be constrained to dissolve or precipitate; any solutions to the equations that violate these constraints are not printed. It is also possible to limit the combinations of minerals that are tested to those that include selected minerals.

Proper use of the program requires adequate knowledge of geochemistry and a proper formulation of the problem. Input includes the total element concentrations of two (or three in the mixing case) solutions and the stoichiometric compositions of all the minerals and gases that are hypothesized to react. The elements and phases included can be entered interactively. Mineral formulas may be selected interactively, edited, or defined by the user; the default data file contains approximately 75 minerals and gases.

The user may selectively choose to save model files (formatted files containing all information necessary to repeat the calculations), which can subsequently be retrieved, rerun, and (or) edited. It is also possible to print results of selected models.

BALNINPT is written in standard Fortran 77 and, generally, is easily installed on new platforms. PC and Unix versions are available by anonymous ftp to brrcrftp.cr.usgs.gov. (See How to Obtain the Software).

Attachment B: Listing of the data file to DB, DB.DAT

```
C ------------------------------------
C       NETPATH 2.0 June 21, 1994
C                  by
C           Eric C. Prestemon
C
C    with technical assistance from
C L. Niel Plummer and David L. Parkhurst
C ------------------------------------

 Note: this is a modified phreeqe format database file for use with
 NETPATH. Comments may exist between groups of data (after the blank
 line, if between two keyword lines) or at the beginning of the file,
 as long as they do not match a key word.

 Warning: Changing or deleting any of the elements and/or master
 species will cause incorrect results. Other species or minerals input
 may be modified.

c   lexcept: 1=Carbon 2=CO3 3=HCO3 4=H2CO3 5=HS 6=SO4 7=NO3 8=NH4 9=O2 10=N2
c            11=CH4 12=DOC 13=DOX(entered) 14=O2(computed)
SPECIAL
  15  15  34  35  25  16  17  23  32  24  26  27  28  32

ELEMENTS
Ca          4   40.08       4  Ca+2
Mg          5   24.312      5  Mg+2
Na          6   22.9898     6  Na+
K           7   39.102      7  K+
Fe          8   55.847      8  Fe+2
Mn          9   54.9380     9  Mn+2
Al         10   26.9815    10  Al+3
Ba         11   137.34     11  Ba+2
Sr         12   87.62      12  Sr+2
Si         13   60.0848    13  SiO2
Cl         14   35.453     14  Cl-
C          15   61.0173    34  Carbon as HCO3
SO         16   96.0616    16  SO4-2
NO         17   14.0067    17  NO3- as N
B          18   10.81      18  B
P          19   30.9738    65  PO4-3 as P
F          20   18.9984    20  F-
Li         21   6.939      21  Li+
Br         22   79.904     22  Br-
NH         23   14.0067    23  NH4+ as N
N2         24   14.0067    24  N2 aq as N
HS         25   32.06      25  HS- as S
CH         26   16.0428    26  CH4
OC         27   12.011     27  DOC as C
DO         28   31.9988    28  O2 (user entered)

SPECIES
  1
H+           101 1.0       0.0       9.0       9.0                -1.0
 0.0       0.0
  1 1.0
  2
```

```
E-          100 -1.0      0.0       0.0                          0.0
 0.0       0.0
  2 1.0
  3
H2O         100 0.0       0.0       0.0                          0.0
 0.0       0.0
  3 1.0
  4
Ca+2        101 2.0       0.0       6.0       5.0       0.165    0.0
 0.0       0.0
  4 1.0
  5
Mg+2        101 2.0       0.0       8.0       5.5       0.20     0.0
0.0       0.0
  5 1.0
  6
Na+         101 1.0       0.0       4.0       4.0       0.075    0.0
0.0       0.0
  6 1.0
  7
K+          101 1.0       0.0       3.0       3.5       0.015    0.0
0.0       0.0
  7 1.0
  8
Fe+2        100 2.0       2.0       6.0                          0.0
0.0       0.0
  8 1.0
  9
Mn+2        100 2.0       2.0       6.0                          0.0
 0.0       0.0
  9 1.0
 10
Al+3        100 3.0       0.0       9.0                          0.0
 0.0       0.0
 10 1.0
 11
Ba+2        100 2.0       0.0       5.0                          0.0
 0.0       0.0
 11 1.0
 12
Sr+2        101 2.0       0.0       5.0       5.26      0.121    0.0
 0.0       0.0
 12 1.0
 13
H4SiO4      100 0.0       0.0       0.0                          0.0
 0.0       0.0
 13 1.0
 14
Cl-         101 -1.0      0.0       3.0       3.5       0.015    0.0
 0.0       0.0
 14 1.0
 15
CO3-2       101 -2.0      4.0       4.5       5.4       0.0      2.0
 0.0       0.0
 15 1.0
 16
SO4-2       101 -2.0      6.0       4.0       5.0       -0.04    0.0
 0.0       0.0
```

```
 16 1.0
 17
NO3-        100 -1.0      5.0       3.0                          0.0
 0.0       0.0
 17 1.0
 18
H3BO3       100 0.0       0.0       0.0                          0.0
0.0       0.0
 18 1.0
 19
PO4-3       100 -3.0      0.0       4.0                          2.0
 0.0       0.0
 19 1.0
 20
F-          100 -1.0      0.0       3.5                          0.0
 0.0       0.0
 20 1.0
 21
Li+         100 1.0       0.0       6.0                          0.0
0.0       0.0
 21 1.0
 22
Br-         100 -1.0      0.0       3.0                          0.0
0.0       0.0
 22 1.0
 23
NH4+        100  1.       -3.       2.5        0.0       0.0      0.
 0.0       0.0
 23 1.0
 24
N2          100  0.        0.        0.        0.0       0.0      0.
 0.0       0.0
 24 1.0
 25
HS-         100  -1.      -2.       3.5        0.0       0.0      1.
 0.0       0.0
 25 1.0
 26
CH4 AQ      100 0.0       -4.0      0.0                          0.0
 0.0       0.0
 26 1.0
 27
DOC         100  0.        0.        0.        0.0       0.0      0.
 0.0       0.0
 27 1.0
 28
DOX         100  0.        0.        0.        0.0       0.0      0.
 0.0       0.0
 28 1.0
 31
OH-         210 -1.0      0.0       3.5                          1.0
-14.000   13.362    -283.9710   -0.05069842 13323.0     102.24447   -1119669.0
  3 1.0     1 -1.0
 32
O2 AQ       300 0.0       4.0       0.0                          0.0
-86.08    134.79
  3 2.0     1 -4.0    2 -4.0
 33
```

```
H2 AQ       200 0.0       -2.0      0.0                            0.0
-3.15     -1.759
  1 2.0     2 2.0
 34
HCO3-       211 -1.0      4.0       4.5       5.4       0.0       1.0
 10.329    -3.561    107.8871    0.03252849  -5151.79    -38.92561   563713.9
 15 1.0     1 1.0
 35
H2CO3       310 0.0       4.0       0.0                            0.0
 16.681    -5.738    464.1965    0.09344813  -26986.16   -165.75951  2248628.9
 15 1.0     1 2.0     3 -1.0
 40
HSO4-       210 -1.0      6.0       0.0                            -1.0
 1.988     3.85      -56.889     0.006473    2307.9      19.8858
 16 1.0     1 1.0
 41
S-2         200 -2.0      -2.0      5.0                            2.0
-12.918    12.100
 25 1.0     1 -1.0
 43
H2S         200 0.0       -2.0      0.0                            0.0
 6.994     -5.300
 25 1.0     1 1.0
 48
NO2-        400 -1.0      3.0       3.0                            0.0
 28.57     -43.76
 17 1.0     1 2.0     2 2.0     3 -1.0
 50
NH3 AQ      200 0.0       -3.0      0.0                            1.0
-9.252    12.48
 23 1.0     1 -1.0
 52
NH4SO4-     200 -1.0      3.0       0.0                            0.0
1.11      0.0
 23 1.0    16 1.0
 57
H2BO3-      200 -1.0      0.0       0.0                            1.0
-9.240    3.224
 18 1.0     1 -1.0
 58
BFOH3-      200 -1.0      0.0       0.0                            0.0
-0.40     1.85
 18 1.0    20 1.0
 59
BF2OH2-     400 -1.0      0.0       0.0                            0.0
7.63      1.618
 18 1.0    20 2.0     1 1.0     3 -1.0
 60
BF3OH-      400 -1.0      0.0       0.0                            0.0
13.67     -1.614
 18 1.0     1 2.0    20 3.0     3 -2.0
 61
BF4-        400 -1.0      0.0       0.0                            0.0
20.28     -1.846
 18 1.0     1 3.0    20 4.0     3 -3.0
 65
HPO4-2      200 -2.0      0.0       4.0                            1.0
 12.346    -3.53
```

```
 19 1.0     1 1.0
 66
H2PO4-      200 -1.0      0.0       4.5                            0.0
 19.553    -4.52
 19 1.0     1 2.0
 69
HF AQ       210 0.0       0.0       0.0                            -1.0
 3.18      3.18      -2.033      0.012645    429.01
  1 1.0    20 1.0
 70
HF2-        200 -1.0      0.0       0.0                            -1.0
 3.76      4.55
  1 1.0    20 2.0
 75
CaOH+       300 1.0       0.0       0.0                            1.0
 -12.78
  4 1.0     3 1.0     1 -1.0
 76
CaCO3       210 0.0       4.0       0.0                            2.0
3.224     3.545     -1228.732   -0.299440   35512.75     485.818
  4 1.0    15 1.0
 77
CaHCO3+     311 1.0       4.0       0.0       5.4       0.0       1.0
11.435    -0.871    1317.0071   0.34546894  -39916.84    -517.70761  563713.9
  4 1.0    15 1.0     1 1.0
 78
CaSO4       200 0.0       6.0       0.0                            0.0
2.30      1.65
  4 1.0    16 1.0
 79
CaHSO4      300 1.0       6.0       0.0                            -1.0
3.068     0.0
  4 1.0    16 1.0     1 1.0
 80
CaPO4-      200 -1.0      0.0       0.0                            2.0
6.459     3.100
  4 1.0    19 1.0
 81
CaHPO4      300 0.0       0.0       0.0                            1.0
15.085    -0.230
  4 1.0     1 1.0    19 1.0
 82
CaH2PO4+    300 1.0       0.0       0.0                            0.0
20.961    -1.120
  4 1.0     1 2.0    19 1.0
 83
CaF+        200 1.0       0.0       0.0                            0.0
0.940     4.12
  4 1.0    20 1.0
 85
MgOH+       300 1.0       0.0       0.0                            1.0
-11.44
  5 1.0     3 1.0     1 -1.0
 86
MgCO3       210 0.0       4.0       0.0                            2.0
2.98      2.713      0.9910      0.00667
  5 1.0    15 1.0
 87
```

```
MgHCO3+     310 1.0       4.0       0.0                           1.0
11.399    -2.771    48.6721     0.03252849  -2614.335     -18.00263  563713.9
  5 1.0     1 1.0    15 1.0
 88
MgSO4       200 0.0       6.0       0.0                           0.0
2.37      4.55
  5 1.0    16 1.0
 89
MgPO4-      200 -1.0      0.0       0.0                           2.0
6.589     3.100
  5 1.0    19 1.0
 90
MgHPO4      300 0.0       0.0       0.0                           1.0
15.216    -0.230
  5 1.0     1 1.0    19 1.0
 91
MgH2PO4+    300 1.0       0.0       0.0                           0.0
21.066    -1.120
  5 1.0     1 2.0    19 1.0
 92
MgF+        200 1.0       0.0       0.0                           0.0
1.82       3.2
  5 1.0    20 1.0
 93
NaOH        300 0.0       0.0       0.0                           1.0
 -14.18   0.0
  6 1.0     3 1.0     1 -1.0
 94
NaCO3-      200 -1.0      4.0       0.0                           2.0
1.27      8.91
  6 1.0    15 1.0
 95
NaHCO3      300 0.0       4.0       0.0                           1.0
10.079
  6 1.0     1 1.0    15 1.0
 96
NaSO4-      200 -1.0      6.0       0.0                           0.0
0.70      1.12
  6 1.0    16 1.0
 97
NaHPO4-     300 -1.0      0.0       0.0                           1.0
12.636    -3.530
  6 1.0     1 1.0    19 1.0
 98
NaF aq      200 0.0       0.0       0.0                           0.0
 -0.24
  6 1.0    20 1.0
 99
KOH         300 0.0       0.0       0.0                           1.0
 -14.46   0.0
  7 1.0     3 1.0     1 -1.0
100
KSO4-       200 -1.0      6.0       0.0                           0.0
0.85       2.25
  7 1.0    16 1.0
101
KHPO4-      300 -1.0      0.0       0.0                           1.0
12.636    -3.530
```

```
  7 1.0     1 1.0    19 1.0
102
FeOH+       300 1.0       2.0       0.0                          1.0
-9.500    13.2
  8 1.0     3 1.0     1 -1.0
105
FeCl+       200 1.0       2.0       0.0                          0.0
 0.14
  8 1.0    14 1.0
106
FeCO3       200 0.0       6.0       0.0                          2.0
4.38
  8 1.0    15 1.0
107
FeHCO3+     300 1.0       6.0       0.0                          1.0
 12.329
  8 1.0    15 1.0     1 1.0
108
FeSO4       200 0.0       8.0       0.0                          0.0
2.25      3.23
  8 1.0    16 1.0
109
FeHSO4+     300 1.0       +8.0                                   -1.0
3.068
  8 1.0    16  1.0    1  1.0
110
Fe(HS)2     200 0.0       -2.0      0.0                          2.0
8.95
  8 1.0    25 2.0
111
Fe(HS)3-    200 -1.0      -4.0      0.0                          3.0
10.987
  8 1.0    25 3.0
112
FeHPO4      300 0.0       2.0       0.0                          1.0
15.946    -3.530
  8 1.0     1 1.0    19 1.0
113
FeH2PO4+    300 1.0       2.0       0.0                          0.0
22.253    -4.520
  8 1.0     1 2.0    19 1.0
114
FeF+        200 1.0       2.0       0.0                          0.0
 1.0
  8 1.0    20 1.0
115
Fe+3        200 3.0       3.0       9.0                          -2.0
-13.02     9.68
  8 1.0     2 -1.0
117
FeOH+2      400 2.0       3.0       0.0                          -1.0
-15.21    20.08
  8 1.0     3 1.0     2 -1.0    1 -1.0
118
FeOH2+      400 1.0       3.0       0.0                          0.0
-18.69    26.78
  8 1.0     3 2.0     1 -2.0    2 -1.0
119
```

```
FeOH3       400 0.0       3.0       0.0                        1.0
-25.58    34.48
  8 1.0     3 3.0     1 -3.0    2 -1.0
120
FeOH4-      400 -1.0      3.0       0.0                        2.0
-34.62    41.58
  8 1.0     3 4.0     1 -4.0    2 -1.0
121
Fe2OH2+4    400 4.0       6.0       0.0                        -2.0
-28.99    32.86
  8 2.0     3 2.0     1 -2.0    2 -2.0
122
Fe3OH4+5    400 5.0       9.0       0.0                        -2.0
-45.36    43.34
  8 3.0     3 4.0     1 -4.0    2 -3.0
123
FeCl+2      300 2.0       3.0       0.0                        -2.0
-11.54    15.28
  8 1.0    14 1.0     2 -1.0
124
FeCl2+      300 1.0       3.0       0.0                        -2.0
-10.89    9.68
  8 1.0    14 2.0     2 -1.0
125
FeCl3       300 0.0       3.0       0.0                        -2.0
-11.89    9.68
  8 1.0    14 3.0     2 -1.0
126
FeSO4+      300 1.0       9.0       0.0                        -2.0
-8.98     13.59
  8 1.0    16 1.0     2 -1.0
127
FeHSO4+2    400 2.0       +9.0                                 -3.0
-8.552
  8 1.0    16  1.0    1  1.0    2  -1.0
128
FeSO42-     300 -1.0      15.0      0.0                        -2.0
-7.64     14.28
  8 1.0    16 2.0     2 -1.0
129
FeHPO4+     400 1.0       3.0       0.0                        -1.0
 4.756    11.91
  8 1.0     1 1.0    19 1.0     2 -1.0
130
FeH2P+2     400 2.0       3.0       0.0                        -2.0
 11.963   5.48
  8 1.0     1 2.0    19 1.0     2 -1.0
131
FeF+2       300 2.0       3.0       0.0                        -2.0
-6.82     12.38
  8 1.0    20 1.0     2 -1.0
132
FeF2+       300 1.0       3.0       0.0                        -2.0
-2.22     14.48
  8 1.0    20 2.0     2 -1.0
133
FeF3        300 0.0       3.0       0.0                        -2.0
0.98      15.08
```

```
  8 1.0    20 3.0     2 -1.0
134
MnOH+       300 1.0       2.0       0.0                           1.0
-10.59    14.40
  9 1.0     3 1.0     1 -1.0
136
MnCl+       200 1.0       2.0       0.0                           0.0
 0.61      0.0
  9 1.0    14 1.0
137
MnCl2       200 0.0       2.0       0.0                           0.0
 0.25      0.0
  9 1.0    14 2.0
138
MnCl3-      200 -1.0      2.0       0.0                           0.0
 -0.31     0.0
  9 1.0    14 3.0
139
MnCO3       200 0.0       6.0       0.0                           2.0
4.90
  9 1.0    15 1.0
140
MnHCO3+     300 1.0       6.0       0.0                           1.0
 12.279    0.0
  9 1.0    15 1.0     1 1.0
141
MnSO4       200 0.0       8.0       0.0                           0.0
 2.25     3.37
  9 1.0    16 1.0
142
Mn(NO3)2    200 0.0       12.0      0.0                           0.0
0.6       -0.396
  9 1.0    17 2.0
143
MnF+        200 1.0       2.0       0.0                           0.0
 0.84      0.0
  9 1.0    20 1.0
144
Mn+3        200 3.0       3.0       0.0                           0.0
 -25.51    25.8
  9 1.0     2 -1.0
150
AlOH+2      310 2.0       0.0       0.0                           1.0
-5.00     11.49      -38.253     0.0         -656.27     14.327
 10 1.0     3 1.0     1 -1.0
151
AlOH2+      310 1.0       0.0       0.0                           2.0
-10.1     26.90      88.500      0.0         -9391.6     -27.121
 10 1.0     3 2.0     1 -2.0
152
AlOH3       310 0.0       0.0       0.0                           3.0
-16.9     39.89      226.374     0.0         -18247.8    -73.597
 10 1.0     3 3.0     1 -3.0
153
AlOH4-      310 -1.0      0.0       0.0                           4.0
-22.7     42.30      51.578      0.0         -11168.9    -14.865
 10 1.0     3 4.0     1 -4.0
154
```

```
AlSO4+      200 1.0       6.0       0.0                           0.0
 3.02      2.15
 10 1.0    16 1.0
155
AlSO42-     200 -1.0      12.0      0.0                           0.0
 4.92      2.84
 10 1.0    16 2.0
156
AlHSO4+2    300 2.0       +6.0                                    -1.0
2.448
 10 1.0    16  1.0    1  1.0
157
AlF+2       200 2.0       0.0       0.0                           0.0
 7.0       1.06
 10 1.0    20 1.0
158
AlF2+       200 1.0       0.0       0.0                           0.0
 12.7      1.98
 10 1.0    20 2.0
159
AlF3        200 0.0       0.0       0.0                           0.0
 16.8      2.16
 10 1.0    20 3.0
160
AlF4-       200 -1.0      0.0       0.0                           0.0
 19.4      2.20
 10 1.0    20 4.0
161
AlF5-2      200 -2.0      0.0       0.0                           0.0
 20.6      1.84
 10 1.0    20 5.0
162
AlF6-3      200 -3.0      0.0       0.0                           0.0
 20.6     -1.67
 10 1.0    20 6.0
164
H3SiO4-     210 -1.0      0.0       0.0                           1.0
 -9.83     6.12      -302.3724   -0.050698   15669.69    108.18466   -1119669.0
 13 1.0     1 -1.0
165
H2SiO4-2    210 -2.0      0.0       0.0                           2.0
 -23.0     17.6      -294.0184   -0.072650   11204.49    108.18466   -1119669.0
 13 1.0     1 -2.0
166
SiF6-2      400 -2.0      0.0       0.0                           -4.0
 30.18     -16.26
 13 1.0     1 4.0    20 6.0     3 -4.0
170
BaOH+       300 1.0       0.0       0.0                           1.0
 -13.47
 11 1.0     3 1.0     1 -1.0
171
BaCO3       210 0.0       4.0       0.0                           2.0
2.71       3.55      0.113       0.008721
 11 1.0    15 1.0
172
BaHCO3+     310 1.0       4.0       0.0                           1.0
 11.311    1.999     104.7933    0.04619749  -5151.79    -38.92561   563713.9
```

```
 11 1.0    15 1.0     1 1.0
173
BaSO4       200 0.0       6.0       0.0                           0.0
2.7
 11 1.0    16 1.0
176
SrOH+       301 1.0       0.0       5.0       5.0                 1.0
 -13.29
 12 1.0     3 1.0     1 -1.0
177
SrHCO3+     311 1.0       4.0       5.4       5.4                 1.0
 11.509    2.489    104.6391    0.04739549  -5151.79    -38.92561   563713.9
 12    1.0 15    1.0  1    1.0
178
SrCO3       210 0.0       4.0                                     2.0
 2.81      5.22     -1.019      0.012826
 12    1.0 15    1.0
179
SrSO4       200 0.0       6.0                                     0.0
 2.29      2.08
 12    1.0 16    1.0
180
LiOH        300 0.0       0.0       0.0                           1.0
 -13.64   0.0
 21 1.0     3 1.0     1 -1.0
181
LiSO4-      200 -1.0      6.0       0.0                           0.0
0.64      0.0
 21 1.0    16 1.0

LOOK MIN
Calcite    2   4.0       -8.480    -2.297         1
  15 1.0          4 1.0
-171.9065   -.077993    2839.319      71.595
Aragonit   2   4.0       -8.336    -2.589         1
  15 1.0          4 1.0
-171.9773   -.077993    2903.293      71.595
Dolomite   3   8.0       -17.09    -9.436         0
   4 1.0          5 1.0         15 2.0
Siderite   2   6.0       -10.89    -2.48          0
   8 1.0         15 1.0
Rhodochr   2   6.0       -11.13    -1.43          0
   9 1.0         15 1.0
Strontit   2   4.0       -9.271    -0.40          1
  12 1.0         15 1.0
155.0305               -7239.594   -56.58638
Witherit   2   4.0       -8.562    0.703          1
  11 1.0         15 1.0
607.642     0.121098    -20011.25   -236.4948
Gypsum     3   6.0       -4.58     -0.109         1
   4 1.0         16 1.0          3 2.0
68.2401                -3221.51    -25.0627
Anhydrite  2   6.0       -4.36     -1.71          1
   4 1.0         16 1.0
197.52                 -8669.8     -69.835
Celestit   2   6.0       -6.63     -1.037         1
  12 1.0         16 1.0
-14805.9622  -2.4660924  756968.533  5436.3588   -40553604.0
```

```
Barite     2   6.0       -9.97     6.35           1
  11 1.0         16 1.0
 136.035      0.0        -7680.41    -48.595
Hydroxap   4   0.0       -3.421    -36.155        0
   3 1.0         65 3.0          4 5.0          1 -4.0
Fluorite   2   0.0       -10.6     4.69           1
   4 1.0         20 2.0
66.348                  -4298.2     -25.271
SiO2 (a)   2   0.0       -2.71     3.34           1
  13 1.0          3 -2.0
 -0.26       0.0         -731.0
Chalcedy   2   0.0       -3.55     4.72           1
  13 1.0          3 -2.0
 -0.09       0.0         -1032.0
Quartz     2   0.0       -3.98     5.99           1
  13 1.0          3 -2.0
 0.41        0.0         -1309.0
Gibbs(c)   3   0.0       8.11      -22.8          0
  10 1.0          3 3.0          1 -3.0
Al(OH)3a   3   0.0       10.8      -26.5          0
  10 1.0          3 3.0          1 -3.0
Kaolinit   4   0.0       7.435     -35.3          0
   3 1.0          1 -6.0        13 2.0         10 2.0
Albite     4   0.0       -18.002   25.896         0
   6 1.0        153 1.0         13 3.0          3 -8.0
Anorth     4   0.0       -19.714   11.58          0
   4 1.0        153 2.0         13 2.0          3 -8.0
Kspar      4   0.0       -20.573   30.82          0
   7 1.0        153 1.0         13 3.0          3 -8.0
Kmica      4   0.0       12.703    -59.376        0
   7 1.0         10 3.0         13 3.0          1 -10.0
Chlorite   5   0.0       68.38     -151.494       0
   3 -6.0         1 -16.0        5 5.0          10 2.0         13 3.0
Ca-Mont    5   0.0       -45.027   58.373         0
   3 -12.0        4 0.165      153 2.33         13 3.67          1 2.0
Talc       4   0.0       21.399    -46.352        0
   5 3.0         13 4.0          3 -4.0          1 -6.0
Illite     6   0.0       -40.267   54.684         0
   3 -11.2        7 0.6          5 0.25        153 2.3          13 3.5
   1 1.2
Chrysotl   4   0.0       32.2      -46.8          1
   3 1.0          1 -6.0        13 2.0          5 3.0
13.248       0.0         10217.1     -6.1894     0.0
Sepiol c   4   0.0       15.76     -10.7          0
   5 2.0         13 3.0          1 -4.0          3  -0.5
Sepiol d   4   0.0       18.66     0.0            0
   5 2.0         13 3.0          1 -4.0          3  -0.5
Hematite   3   6.0       -4.008    -30.845        0
 115 2.0          3 3.0          1 -6.0
Goethite   3   3.0       -1.0      0.0            0
 115 1.0          3 2.0          1 -3.0
Fe(OH)3a   3   3.0       4.891     0.0            0
 115 1.0          3 3.0          1 -3.0
Pyrite     4   0.0       -18.479   11.3           0
   1 -2.0         2 -2.0         8 1.0          25 2.0
FeS ppt    3   0.0       -3.915    0.0            0
   8 1.0         25 1.0          1 -1.0
Mackinit   3   0.0       -4.648    0.0            0
```

```
   8 1.0         25 1.0          1 -1.0
Vivianit   3   6.0       -36.000   0.0            0
   8 3.0         19 2.0          3 8.0
Pyrolusi   4   4.0       41.38     -65.11         0
   9 1.0          3 2.0          1 -4.0         2 -2.0
Hausmani   4   8.0       61.03     -100.64        0
   9 3.0          3 4.0          1 -8.0         2 -2.0
Manganit   4   3.0       25.34     0.0            0
   9 1.0          3 2.0          1 -3.0         2 -1.0
Pyrochro   3   2.0       15.2      0.0            0
   9 1.0          3 2.0          1 -2.0
PCO2       1   4.0       -1.468    -4.776         1
  35 1.0
108.3865    0.01985076  -6919.53    -40.45154    669365.0
O2 gas     1   4.0       -2.96     -1.844         0
  32 1.0
H2 gas     1   -2.0      -3.15     -1.759         0
  33 1.0
N2 gas     1   0.0       -3.26     -1.358         0
  24 1.0
H2S gas    1   -2.0      -0.997    -4.57          0
  43 1.0
CH4 gas    1   -4.0      -2.86     -3.373         0
  26 1.0
NH3 gas    1   -3.0      1.77      -8.17          0
  50 1.0
Melanter   3   8.0       -2.209    4.91           1
   3 7.0          8 1.0         16 1.0
 1.447       -0.004153   0.0         0.0         -214949.0
Alunite    5   12.0      -1.4      -50.25         0
  10 3.0          3 6.0          1 -6.0         7 1.0         16 2.0
K-Jarosit  5   21.0      -9.21     -31.28         0
 115 3.0          3 6.0          1 -6.0         7 1.0         16 2.0

END


Data received from Jim Ball 12/10/89.  Major ions should be same as
Nordstrom and others, 1990 in Melchoir, D. C., and Bassett, R. L.,
eds., Chemical Modeling of Aqueous Systems II: American Chemical
Symposium Series 416, pages 398-413.

Changed Fe+3 to be 115 and Mn+3 to be 144.  Alumino-silicates taken
from WATEQ2 by D. Parkhurst.

12/2/92: Alkalinity updated. Negative values for H+, HSO4, Fe+3. Revised
alkalinities to be consistent.

5/93: Revised some data to be more consistent with WATEQ4F data tables.

4/17/94: Remove polysulfide species.

$Header: /z/dlprcolkr/home/dlpark/programs/unix/netpath.beta/data/RCS/db.dat,v 1.10 1994/05/24 14:56:11
dlpark Exp $
```

Attachment C: Listing of the data file to NETPATH, NETPATH.DAT

```
"CH2O"   +C  1.000  I1-25.00  I2 0.000
ALBITE   +NA 1.000  AL 1.000  SI 3.000
ALUNITE   K  1.000  AL 3.000  S  2.000  RS 12.000
ANALCIME +NA 1.000  AL 1.000  SI 2.000
ANNITE   +K  1.000  FE 3.000  AL 1.000  SI 3.000  RS 6.000
ANORTH   +CA 1.000  AL 2.000  SI 2.000
ARAGONIT  CA 1.000  C  1.000  RS 4.000  I1 0.000  I2 0.000
AUGITE   +CA  .400  MG  .800  FE  .700  AL  .200  SI 1.900  RS 1.400
BARITE    BA 1.000  S  1.000  RS 6.000
BIOTITE  +AL 1.000  MG 1.500  K  1.000  SI 3.000  FE 1.500  RS 3.000
BRUCITE   MG 1.000
CALCITE   CA 1.000  C  1.000  RS 4.000  I1 0.000  I2 0.000
CELESTIT  SR 1.000  S  1.000  RS 6.000  I8 0.000
CH4 GAS   C  1.000  RS-4.000  I1-50.00  I2 0.000
CHLORITE +MG 5.000  AL 2.000  SI 3.000
CHRYSOTL +MG 3.000  SI 2.000
CO2 GAS   C  1.000  RS 4.000  I1-25.00  I2100.00
CO2-CH4   C  1.000  I1-25.00  I20.0000  I3-50.00  I4 0.000
Ca-MONT   CA 0.167  AL 2.330  SI 3.670
DIOPSIDE +CA 1.000  MG 1.000  SI 2.000
DOLOMITE  CA 1.000  MG 1.000  C  2.000  RS 8.000  I1 0.000  I2 0.000
EXCHANGE
FLUORAP   CA 5.000  P  3.000  F  1.000
FLUORITE  CA 1.000  F  2.000
FORSTRIT +MG 2.000  SI 1.000
Fe-S      FE 1.000  S  1.000  RS 0.000  I3-30.00
FeII-Na   FE-1.000  NA 2.000  RS-2.000
GIBBSITE  AL 1.000
GOETHITE  FE 1.000  RS 3.000
GYPSUM    CA 1.000  S  1.000  RS 6.000  I322.000
H2 GAS    RS-2.000
H2S GAS   S  1.000  RS-2.000
HEMATITE  FE 2.000  RS 6.000
HORNBLND +CA 1.000  MG 1.000  FE 1.000  AL 1.000  SI 3.500  RS 2.000
HYDROXAP  CA 5.000  P  3.000
ILLITE    K  0.600  MG 0.250  AL 2.300  SI 3.500
K-SPAR   +K  1.000  AL 1.000  SI 3.000
K-MICA   +K  1.000  AL 3.000  SI 3.000
K-MONT    K  0.330  AL 2.330  SI 3.670
KAOLINIT  AL 2.000  SI 2.000
LIGNITE  +C  1.000  RS-0.400  I1-25.00  I2 0.000
MAGNESIT  MG 1.000  C  1.000  RS 4.000
MAGNETIT  FE 3.000  RS 8.000
MG.02CAL  C  1.000  CA 0.980  MG 0.020  RS 4.000  I1 0.000  I2 0.000
MIRABILI  NA 2.000  S  1.000  RS 6.000
MONT-FEL  CA  .100  K   .130  MG  .400  FE  .100  AL 1.990  SI 3.650  RS  .300
MONT-MAF  CA  .130  K   .070  MG  .400  FE  .100  AL 1.990  SI 3.650  RS  .300
Mg-MONT   MG 0.167  AL 2.330  SI 3.670
Mg/Na EX  NA 2.000  MG-1.000
MgSiO3   +MG 1.000  SI 1.000
Mn(OH)3   MN 1.000  RS 3.000
MnO2      MN 1.000  RS 4.000
MnOOH     MN 1.000  RS 3.000
N2 GAS    N  2.000  RS 0.000
NA-MONT   NA 0.330  AL 2.330  SI 3.670
NACLINOP  NA 1.000  AL 1.000  SI 5.000
```

```
NH3 GAS   N  1.000  RS-3.000
NH4/CAEX  N  2.000  CA-1.000  RS-6.000
Na-MONT   NA 0.330  AL 2.330  SI 3.670
Na2SO4    NA 2.000  S  1.000  RS 6.000
NaCl      NA 1.000  CL 1.000
NaHCOL    NA 1.000  C  1.000  RS 4.000
O2 GAS    RS 4.000
PHLOGOPI  K  1.000  MG 3.000  AL 1.000  SI 3.000
PLAGAN25 +CA  .250  AL 1.250  SI 2.750  NA  .750
PLAGAN30 +CA  .300  AL 1.300  SI 2.750  NA  .700
PALGAN33 +CA  .330  AL 1.330  SI 2.670  NA  .700
PLAGAN38 +CA  .380  NA  .620  AL 1.380  SI 2.620
PLAGAN45 +CA  .450  NA  .550  AL 1.450  SI 2.550
PREHNITE +CA 2.000  AL 2.000  SI 3.000
PYRITE    FE 1.000  S  2.000  RS 0.000  I3-30.00
RHODOCHR  MN 1.000  C  1.000  RS 6.000
SEPIOLIT  MG 2.000  SI 3.000
SIDERITE  FE 1.000  C  1.000  RS 6.000
STRENGIT  FE 1.000  P  1.000  RS 3.000
STRONITE  SR 1.000  C  1.000  RS 4.000  I8 0.000
SYLVITE   K  1.000  CL 1.000
SiO2      SI 1.000
TALC      MG 3.000  SI 4.000
VIVIANIT  FE 3.000  P  2.000  RS 6.000
WITHERIT  BA 1.000  C  1.000  RS 4.000
*OTHER**
```

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