

Supporting information to:

NETPATH-WIN: An Interactive User Version of the Mass-Balance Model, NETPATH

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As an example of using DB-WIN and NETPATH-WIN, we examine radiocarbon dating in part of the Floridan aquifer of Florida, USA as originally investigated by Plummer and Sprinkle (2001). For demonstration purposes, radiocarbon dating is applied to water from well 3.5 (well 5 on flow path III, Figure 3 in the Note). All the data for this example are available in the distribution file of NETPATH-WIN. Figure S1 illustrates the opening screen of DB-WIN.

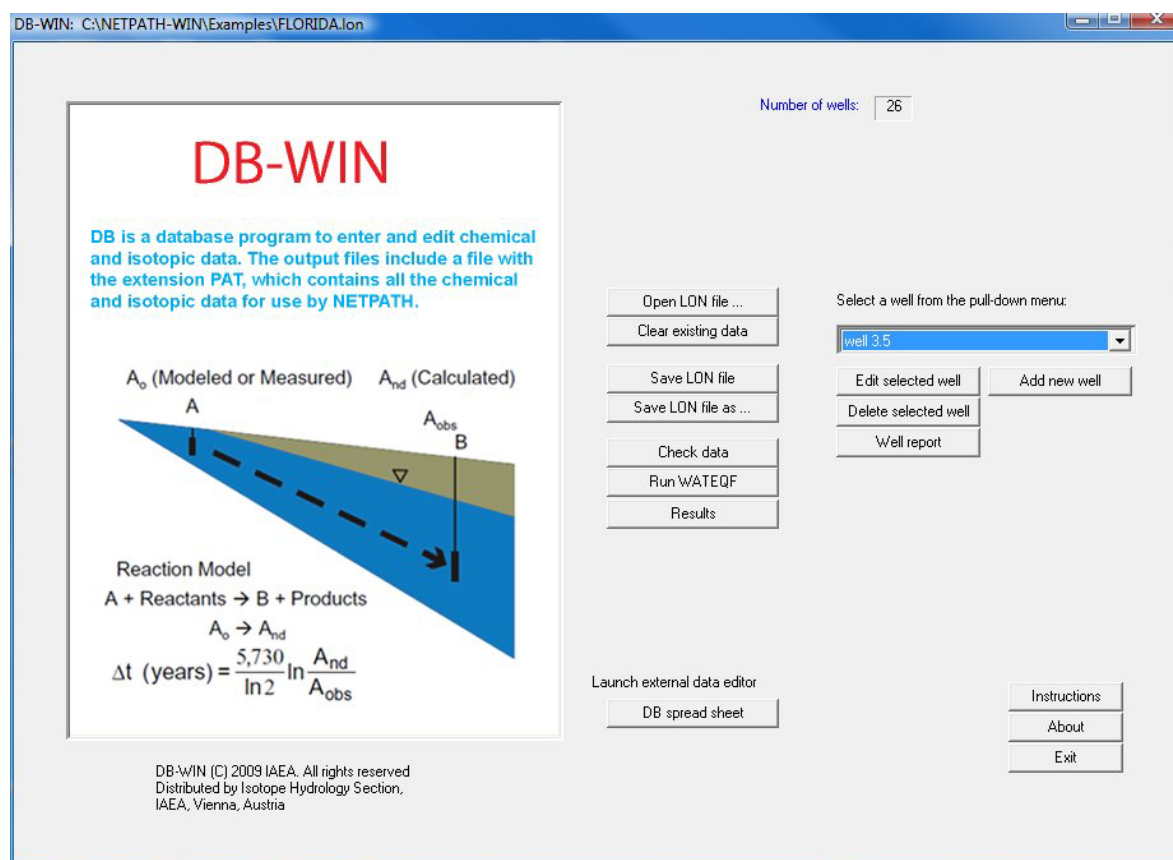


Figure S1. The opening screen of DB-WIN showing various options. Steps start by selecting "Open LON file..." followed by other selections including manipulating the well data, running the thermodynamic speciation code, WATEQF, and examining the WATEQF results. A specific well to edit is chosen from the pull-down menu, which is well 3.5 in this screen.

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The screen includes an instruction button that provides information on the use of DB-WIN. In addition to opening an existing LON file, one can launch a spreadsheet for new data entry, save the LON file, check the LON file for erroneous data, identify missing critical values, such as temperature and pH, check charge imbalance, speciate the water analyses in the LON file using the WATEQF speciation model, and view the text file of the WATEQF results (Figure S1).

From this screen, it is possible to edit the existing data for a chosen well, add a new well to the database, delete a well, print a text file of the chemical and isotopic data for the well, and select various options to be used in speciation of the analysis in WATEQF. This screen allows paging from well to well in the database for additional editing, and saving the new well data for each well in the LON file. The edited LON file can be saved under a new name and/or location.

Example steps in using DB-WIN

Some of the steps in using DB-WIN are summarized for an example from the Floridan aquifer.

1. Open the file FLORIDA.LON.
2. Select well 3.5 from the drop-down menu as seen in Figure S1.
3. Choose "Edit selected well" and examine various well data and various flags (Figure S2). The latter include "Units" of concentration, choice of model to calculate "Activity coefficients", "Carbon choices" (options for unit of concentration of dissolved inorganic carbon), and "pe calculation choices" (options for calculation of pe). Detailed information about well data and flags are available in the original model documentation (Plummer et al., 1994).
4. If needed, changes can be easily made and saved.
5. Run WATEQF from the main menu to create the FLORIDA.PAT file. Before WATEQF is run, an option appears (Figure S3) that permits adjusting the water analyses for charge imbalance in creating the PAT file. (This is normally not recommended but can be an option later to test model sensitivity to possible charge imbalance uncertainty in the analytical data). DB-WIN then asks for the location of the thermodynamic database used by WATEQF, "DB.IN" (Figure S4). Unless alternate thermodynamic data are to be used, one normally selects the default option in opening DB.IN. WATEQF is then run and the PAT file created (Figure S5) that contains all the data needed to run NETPATH-WIN for the chosen LON file. By clicking on the "Results" tab from the main menu of DB-WIN, the user can page through an ascii file of the output from WATEQF, viewing, for example, the distribution of aqueous species in each water sample, dissolved gas partial pressures, and mineral saturation indices. Having closed the WATEQF "Results" window, the user is returned to the main screen of DB-WIN where additional options are available ("Add a new well" to the LON file, "Delete the selected well" from the LON file). The analytical data for the well selected in the main screen, well 3.5 in this case, can be displayed (and printed) by selecting the "Well report" tab (Figure S6).

WELL NAME: well 3.5

Well information

Well number: 2

	Entry
Well name	well 3.5
Address, line 1	
Address, line 2	
Address, line 3	
Address, line 4	
Address, line 5	

Flags

Units: mg/l

Activity coefficient: Debye-Huckel

Carbon choices: Field alk. (as HCO₃⁻)

PE calculation choices: Redox ignored

Well data

	Value
1. Temp.	26.0
2. pH	8.16
3. Diss. O ₂	0.0
4. Alkalinity	184.4
5. Tritium	-0.03
6. H ₂ S	3.47
7. Ca ²⁺	22.
8. Eh	0.
9. Mg ²⁺	29.
10. Na ⁺	145.
11. K ⁺	9.5
12. Cl ⁻	113.
13. SO ₄ ²⁻	158.
14. F ⁻	1.8
15. SiO ₂	14.
16. Br ⁻	0.29
17. B	0.400
18. Ba ²⁺	0.027
19. Li ⁺	0.007

Well sequence

Previous well 12 Next well

Accept changes for this well Close

Figure S2. Example showing the Edit well screen from DB-WIN. The pull-down menus allow editing of specific information pertaining to the well (location, aquifer, date/time sampled, well depth, amount of casing, and land-surface elevation), concentration data for the sample, and Flags that set units of concentration, activity coefficient option used in WATEQF, concentration unit of inorganic carbon, and choice of redox option.

Question

Adjust the .pat file to approximate charge balance in input data?

[Not normally recommended. Used to check model sensitivity to charge imbalances in original analytical data. See original program documentation for further details]

Yes No Cancel

Figure S3. Prior to specifying the LON data set in WATEQF, an option is available to adjust the chemical analyses for charge imbalance, in proportion to their equivalents in the analysis. Selecting “Yes” will alter all the analytical data in creating the PAT file (the original LON file is unaltered). This can be a useful option for testing existing NETPATH-WIN models for uncertainties in analytical data, but is not recommended for initial model construction.

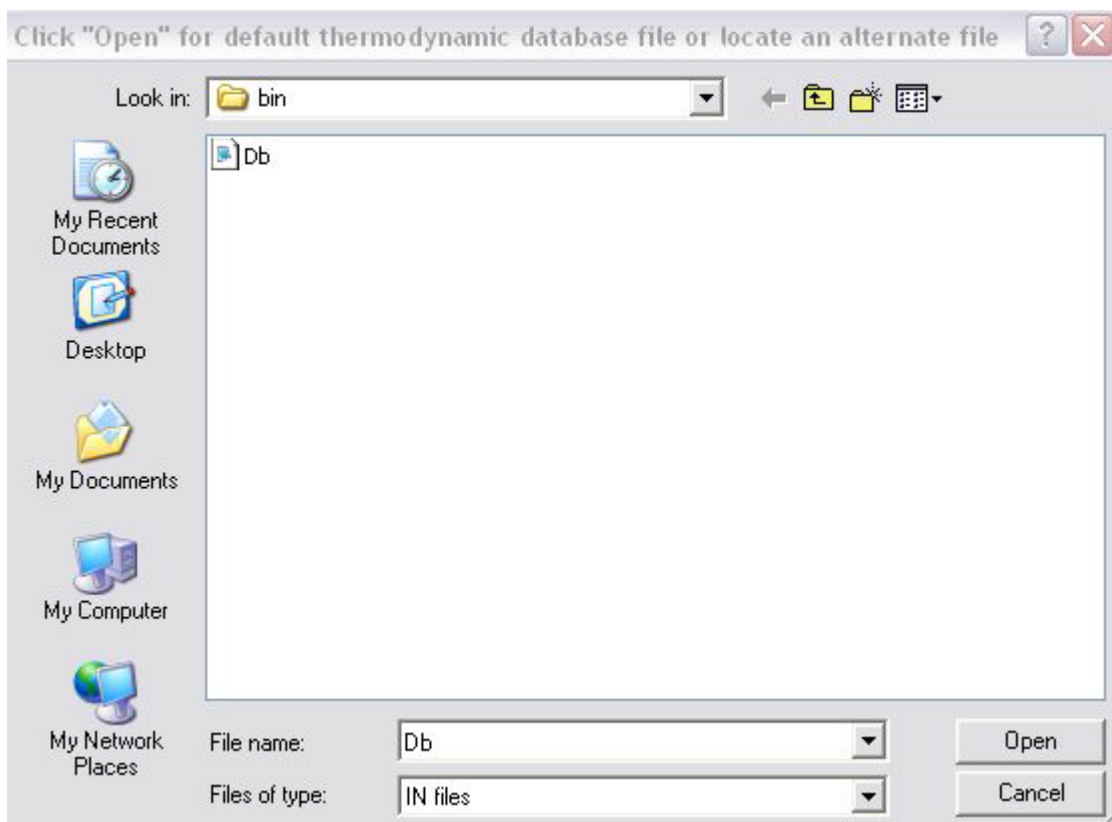


Figure S4. More advanced users may construct their own thermodynamic data files for WATEQF. Here the option is given to select an alternate thermodynamic data file, or to select “Open” to use the data file provided with the distribution package for NETPATH-WIN. The existing thermodynamic data are consistent with the original NETPATH (Plummer et al., 1994).

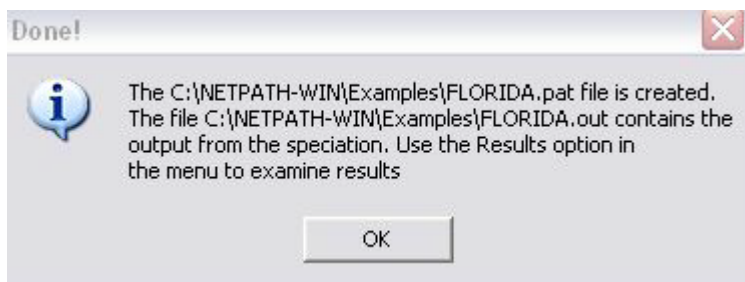


Figure S5. The water analyses in the FLORIDA.LON file were speciated and the NETPATH-WIN data file, FLORIDA.PAT, was created. DB-WIN then returns to the main screen (Figure S1).

Freport - Notepad			
File Edit Format View Help			
well name	:	well 3.5	
owner	:		
site ID	:	Larson	
Latitude/longitude	:		
Date/time sampled	:		
Temperature	26.0 degrees C	Nitrate	0.020 mg/l as N
Sp. Cond.	940.	Ammonium	0.380 mg/l as N
pH	8.16	N2 (aq)	N.D. mg/l as N
Eh	N.D. volts	Phosphate	0.010 mg/l as P
Density	1.0 g/cm3	Boron	0.400 mg/l
Dissolved oxygen	0.0 mg/l	Aluminum	0.0 mg/l
Alkalinity #	184.4 mg/l	Silica	14. mg/l as SiO2
Calcium	22. mg/l	DOC	1.800 mg/l as C
Magnesium	29. mg/l	RS of DOC	0.
Sodium	145. mg/l	CH4 (aq)	N.D. mg/l
Potassium	9.5 mg/l	Delta C-13 TDIC	-1.60 o/oo
Barium	0.027 mg/l	Carbon 14 TDIC	0.23 % modern
Strontium	15.000 mg/l	Delta S-34 (SO4)	31.3 o/oo
Iron	0.009 mg/l	Delta S-34 (H2S)	-31.9 o/oo
Manganese	0.002 mg/l	Sr 87/86	N.D.
Lithium	0.007 mg/l	N-15 of Nitrate	N.D. o/oo
Chloride	113. mg/l	N-15 of Ammonium	N.D. o/oo
Sulfate	158. mg/l	N-15 of N2 (aq)	N.D. o/oo
H2S as S	3.47 mg/l	Delta Deuterium	-5.5 o/oo
Fluoride	1.8 mg/l	Delta O-18	-1.60 o/oo
Bromide	0.29 mg/l	Tritium	-0.03 TU

N.D. = not determined			
TDIC = Total Dissolved Inorganic Carbon			
DOC = Dissolved Organic Carbon			
Sp. Cond. = Specific Conductivity (us/cm)			
RS = Redox State			
# = uncorrected, reported as HCO3-			

Figure S6. Display of the analytical data in the LON file for the selected well in the main screen of DB-WIN. Close the window to exit this display.

Having speciated the FLORIDA.LON data set in DB-WIN, we run NETPATH-WIN and select the FLORIDA.PAT file, as seen in Figure S7. This PAT file contains all the compositional data for each water analysis (in mmols/kg water) and isotopic data for each sample. If previous models have been saved that are associated with the PAT file, they appear in the list of DAT files. Each model file (DAT file) contains all the parameters, phases, constraints, isotope values, etc., needed to re-run the model using the saved PAT file. From the main screen of NETPATH-WIN, new model files (DAT files) can be created or existing files modified and saved with new or existing names.

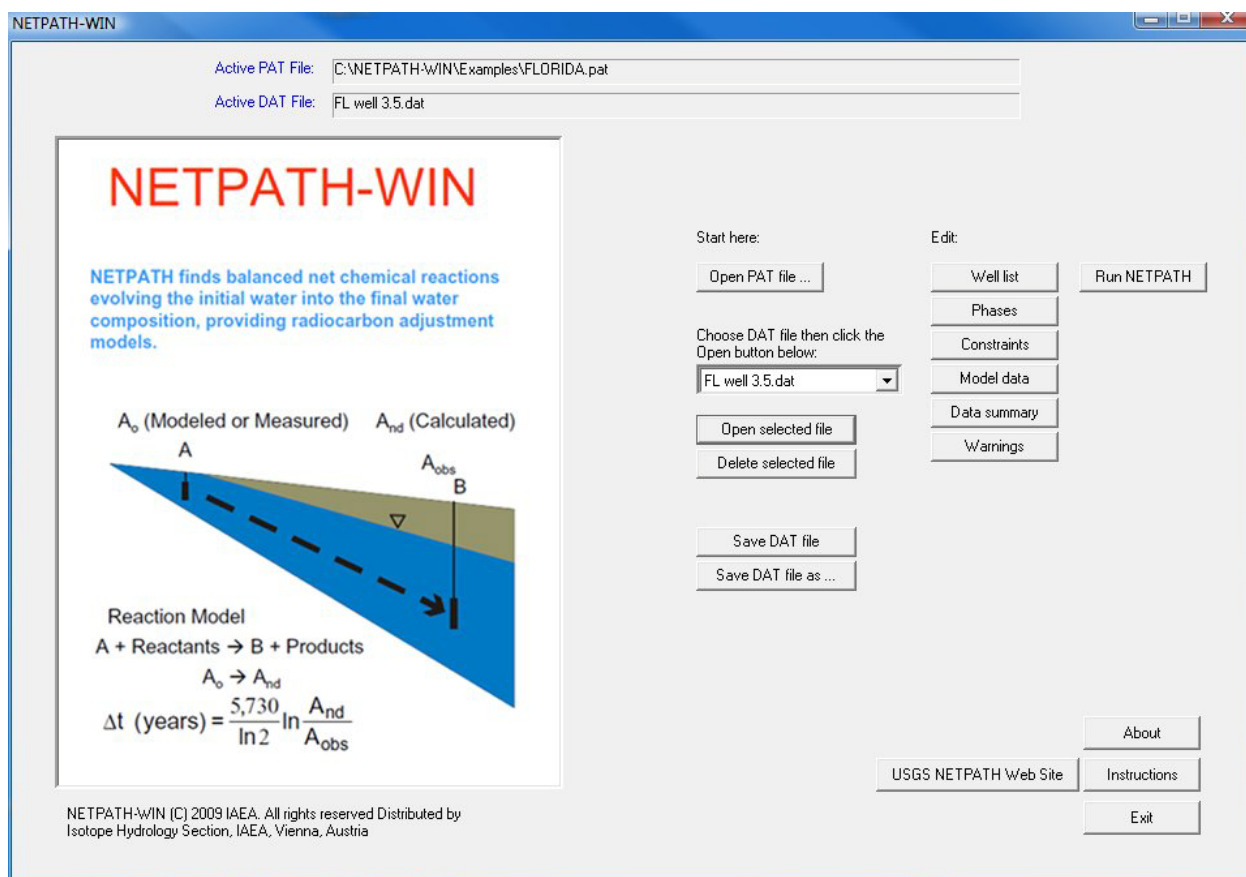


Figure S7. The opening screen of NETPATH-WIN showing various options. Steps start by opening an existing PAT file (FLORIDA.pat, in this example), followed by opening a selected DAT file (a model file) from the pull-down menu (which can be edited and saved). New models (DAT files) can be created using tabs under the Edit option, and saved using the tabs “Save DAT file” or “Save DAT file as”. Existing DAT files can be deleted using the “Delete selected file” tab. Various actions under the “Edit” heading include the “Well list” (permits selection of wells to be included in the model), “Phases” (selection of phases to consider in the model), “Constraints” (selection of chemical and isotopic constraints in the model), and “Model data” (definition of specific parameters applicable to the model). Options also include examining “Data summary”, “Warnings” (includes identifying missing data), and running NETPATH, “Run NETPATH”.

Example steps in using NETPATH-WIN

Example steps are summarized below to demonstrate construction and/or editing of the model file (DAT file) for well 3.5 using NETPATH-WIN. In this example it was assumed that the initial water was similar in chemical and isotopic composition to water 1.1 from the recharge area (Figure 3 in the Note), that it may have mixed with a fraction of saline water, using an average seawater composition, and evolved via water-rock reaction to the composition of water 3.5, following criteria originally selected in Plummer and Sprinkle (2001).

1. Having opened the FLORIDA.pat file in NETPATH-WIN, we select the DAT file previously saved for well 3.5 from the drop-down menu and press the button “Open selected file” (Figure S7).
2. Under the Edit heading, we click on the “Well list” tab to display and/or modify the initial and final wells to be included in the model. Only 1 final water analysis can be selected but as many as 5 initial waters can be included as mixing along the flow path to the final well (Figure S8).

Well List

Used wells

	Number in list	Name
Initial 1	1	well 1.1
Initial 2	25	Sea Water (DKN et al mg/kg soln)
Initial 3		
Initial 4		
Initial 5		
Final	12	well 3.5

Total list of wells (make changes here; maximum 5 initial wells, one final well)

Number	Name	Initial?	Final?
1	well 1.1	<input checked="" type="checkbox"/>	<input type="checkbox"/>
2	well 1.2	<input type="checkbox"/>	<input type="checkbox"/>
3	well 1.3	<input type="checkbox"/>	<input type="checkbox"/>
4	well 2.2	<input type="checkbox"/>	<input type="checkbox"/>
5	well 2.3	<input type="checkbox"/>	<input type="checkbox"/>
6	well 2.4	<input type="checkbox"/>	<input type="checkbox"/>
7	well 2.5	<input type="checkbox"/>	<input type="checkbox"/>

Select wells of choice (one final well and maximum of 5 initial wells) then click "Use selected wells" to activate choice.

Use selected wells

OK

Figure S8. From the “Well list” tab, the model file (FL well 3.5.dat) for well 3.5 includes two initial waters, water from well 1.1 and a Sea Water analysis (upper panel displaying wells used in the model). The lower panel contains a list that permits changing the wells in the model. The wells in the model are updated by clicking the “Use selected wells” tab. Finally click the “OK” button to return to the main menu of NETPATH-WIN.

3. The phases menu (“Add or Remove Phases”) permits selection of phases that are considered possible reactants and products in the evolution of the initial to final water composition (minerals and gases), (Figure S9). The phases menu permits adding or removing phases from the model, marking them to be included in every model

(“forcing”), and selecting their transfer behaviour (dissolution only, precipitation only, both, and isotopic exchange). This procedure can be used to cause NETPATH-WIN to exclude some unreasonable models, such as those that precipitate organic matter, precipitate iron sulphides in aerobic groundwater, or dissolve calcite in under-saturated groundwater. The “forcing” option causes NETPATH-WIN to display all models that contain the selected (forced) phase(s). Using the Phases menu (Figure S9), the following phases were included as possible reactants and products (as in Plummer and Sprinkle, 2001): organic carbon (carbon of zero oxidation state, denoted CH₂O), isotopic exchange of 5.5 mmols/kg water of calcite, dissolution of dolomite, and inclusion of Ca/Na₂ ion exchange, iron oxyhydroxide (goethite), gypsum (anhydrite), NaCl, pyrite and CO₂ gas. The results were limited to models that only oxidize organic carbon, dissolve dolomite, gypsum, and NaCl; that only precipitate pyrite, and that can proceed in either direction for ion exchange, goethite reaction and CO₂ gas exchange. The CO₂ gas mass transfer is expected to be near zero for closed-system evolution, but this phase was included to allow for some uncertainty in initial conditions.

Add or Remove Phases

Used phases

Select phase to remove then click the remove button. Change data in table as desired then click the update button.

Phase No.	Phase ID from phase list below	Phase Name	Phase in every model?	Transfer (choose from drop-down menu)	Amount to exchange	
<input type="checkbox"/>	1	"CH2O"	<input type="checkbox"/>	dissolution		
<input type="checkbox"/>	2	11	CALCITE	<input type="checkbox"/>	isotopic exchange	5.5000
<input type="checkbox"/>	3	21	DOLOMITE	<input type="checkbox"/>	dissolution	
<input type="checkbox"/>	4	22	EXCHANGE	<input type="checkbox"/>	both diss. & prec.	
<input type="checkbox"/>	5	29	GOETHITE	<input type="checkbox"/>	both diss. & prec.	
<input type="checkbox"/>	6	30	GYPSUM	<input type="checkbox"/>	dissolution	

Remove selected phase
Update

Complete phase list

Use the complete list of phases to add to those above, by selecting the phase of choice then clicking the add button. Phase will appear at end of list in table above.

To edit this complete list, run the Phase Editor that is included in the NETPATH-WIN package. After saving the changes, (re)open the PAT file to update the list of phases here.

Phase ID	Phase Name	1	2	3	4	5	6	7	8	9
<input type="checkbox"/>	1	"CH2O"	+	C	1.000	I1	-25.00	I2	0.00	
<input type="checkbox"/>	2	ALBITE	+	NA	1.000	AL	1.000	SI	3.000	
<input type="checkbox"/>	3	ALUNITE		K	1.000	AL	3.000	S	2.000	RS 12
<input type="checkbox"/>	4	ANALCIME	+	NA	1.000	AL	1.000	SI	2.000	
<input type="checkbox"/>	5	ANNITE	+	K	1.000	FE	3.000	AL	1.000	SI 3.0
<input type="checkbox"/>	6	ANORTH	+	CA	1.000	AL	2.000	SI	2.000	
<input type="checkbox"/>	7	ARAGONIT		CA	1.00	C	1.00	RS	4.00	
<input type="checkbox"/>	8	BARITE		BA	1.000	S	1.000	RS	6.000	

Add selected phase
OK

Figure S9. The “Phases” menu for the selected model (FL well 3.5.dat). The upper panel allows phases to be removed from the model and the lower panels allows addition of phases to the model (by marking the open boxes on the left of each panel and then clicking the “Remove selected phase” or “Add selected phase” tab). In the upper panel a phase included in the model can be marked to be included in every model. In cases where multiple models

are found in NETPATH-WIN, this option forces NETPATH to display only models that contain the phase or phases selected with a mark in the box “Phase in every model?”. By clicking on the cell for “Transfer (choose from drop-down menu)”, a phase can be marked for “dissolution only”, “precipitation only”, “both” (permitting NETPATH to display models in which the phase either dissolves or precipitates), and “isotopic exchange”, where the amount of the phases to be exchanged, in mmols/kg water, is entered in the last column to the right of the upper panel. The case of isotopic exchange in NETPATH includes the option “both” (permitting net dissolution or net precipitation) plus isotopic exchange of the prescribed mass of the phase. Additional phases in the model can be displayed using the list, which includes 74 phases in its default database (only the first 8 are shown here). The list can be edited by running the Phase Editor program in the NETPATH-WIN distribution package.

4. The “Constraints” tab on the main screen of NETPATH-WIN (Figure S7) allows us to select appropriate chemical and isotopic constraints in finding valid reaction models consistent with the observed chemical and isotopic data. The upper panel of the “Constraints” tab displays all the constraints selected for the model. The lower panel of the “Constraints” tab is used to modify the constraints in the model (Figure S10). Using the “Constraints” menu (Figure S10), the following chemical and isotopic constraints were selected to determine the calculated mass transfers of the proposed phases in each model: carbon, sulphur, calcium, magnesium, redox (conservation of electrons in redox reactions), sulphur-34 isotope mass balance, sodium, chloride and iron.

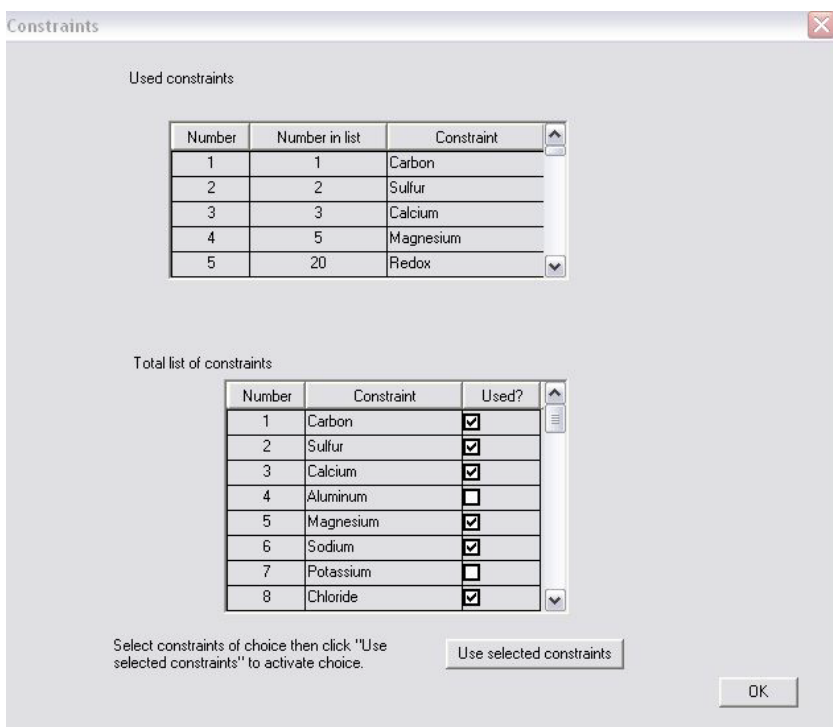


Figure S10. Example showing the “Constraints” menu which was accessed from the main menu of NETPATH-WIN. The upper panel shows the list of constraints selected in the model (use the side arrows to display all the constraints in the model). The lower panel permits adding or removing constraints in the model. The “Use selected constraints” button updates the list of constraints in the model. Click “OK” to return to the main menu of NETPATH-WIN.

5. The “Model data” button from the main screen of NETPATH-WIN opens the “Model parameters” window (Figure S11) that has three tabs: 1. Geochemical parameters, 2. Isotopic data, and 3. Data for ^{14}C Ao models. These three features are described briefly below.

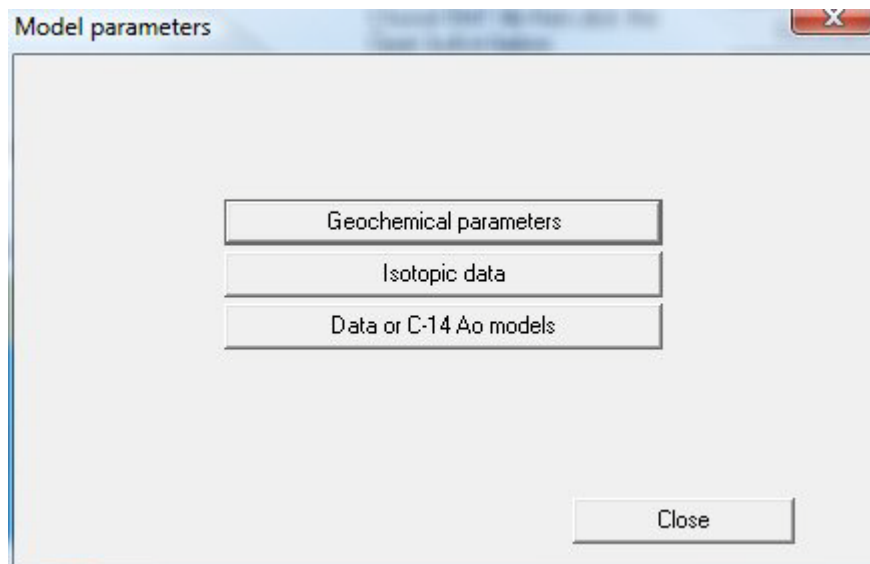


Figure S11. Display of the “Model parameters” window that branches to many chemical and isotopic details of the phases and models.

6. The “Geochemical parameters” window (Figure S12) summarizes some of the features previously set for the model: 1. Number of solutions that are allowed to mix along the flow path; 2. A switch to turn on or off evaporation or dilution; 3. A switch that turns on (yes) or off (no) Rayleigh isotope calculations (this needs to be “on” for isotope evolution calculations to be included for the model); 4. A menu that permits selection of the way cation exchange is computed when the phase “EXCHANGE” is included in the model (see Plummer et al., 1994 for further details). The middle panel of the “Geochemical parameters” menu permits entering tentative values of the ^{14}C content of the sample in percent modern carbon (pmc) for each water analysis. Entering values in the white (active) cells will override the original values in the LON file for the well. These are temporary changes for testing sensitivity of modelled radiocarbon ages to uncertainties in ^{14}C data. The lower-most panel of the “Geochemical parameters” window applies to the special cases of inclusion of either of the phases “CO₂-CH₄” or EXCHANGE. In the first case, it is possible to specify the fraction of CO₂ in a CO₂-CH₄ gas mixture, that, for possible kinetic reasons, fractionates as it degasses, such as from a landfill. In the second case it is possible to specify the ratio of Ca/Mg in cation exchange with Na, prompted by selecting “Variable CaMg” under the Ion Exchange menu and including the phase EXCHANGE in the model (see Plummer et al., 1994 for further details).

Geochemical parameters

Mixing (as specified in the "Well list" screen): 2 solutions mix

Parameters

Evaporation/Dilution
☐ Yes
☒ No

Ion Exchange
☐ Computed from Ca/Mg ratio
☐ 50/50 Ca/Mg
☒ Ca/Na, no Mg
☐ Variable CaMg

Rayleigh calculations
☒ Yes
☐ No

	Well name	Original Value	User defined value
Initial 1	well 1.1	0.00000	
Initial 2	Sea Water (DKN et al mg/kg soln)	0.00000	
Initial 3			
Initial 4			
Initial 5			
Final	well 3.5	0.00000	

If user values are defined, the values are used instead of the original values.

	Value
Fraction CO ₂ in CO ₂ -CH ₄	
Fraction Ca in Ca/Mg	

Cancel OK

Figure S12. Example of the "Geochemical parameters" menu. In this example, the model includes two initial waters that are allowed to mix, evaporation or dilution is not permitted, simple Ca/Na cation exchange is allowed (that is, options involving Ca-Mg/Na exchange are not considered), the model will use the original ¹⁴C data as defined in the LON file, and no data for the fraction of CO₂ in a CO₂-CH₄ gas mixture is permitted because the phase was not included in the model and the fraction of Ca in Ca/Mg exchange is not allowed because the "Variable CaMg" option was not selected under the "Ion Exchange" panel.

- The "Isotopic data" window (Figure S13), accessed from the "Geochemical parameters" window (Figure S11), is used to define: 1. The carbon-13 and carbon-14 isotopic composition of all carbon-bearing phases (solids and gases) that can enter the aqueous phase (such as through oxidation of organic carbon, dissolution of CO₂ gas, carbonate mineral dissolution), 2. The fractionation factors of carbon-13 and carbon-14 for the carbon-bearing phases relative to the isotopic composition in the solution, i.e. additive fractionation factors, as calculated in NETPATH (Wigley et al., 1978; Plummer et al., 1994), and 3. The carbon-13 and carbon-14 composition of dissolved methane and dissolved organic carbon. Default values of the additive fractionation factors (middle panel, Figure S13) are automatically calculated in NETPATH-WIN. However, the

“Isotopic data” window permits the user to override these values. A cell beneath the middle panel permits the calculation of the pH-dependent additive fractionation factors at an intermediate point along the flow path, by interpolation between the pH values of the initial and final waters. In the example shown in Figure S13, the additive fractionation factors are calculated at the pH of the final water analysis (a fraction along the flow path of 1.0). The lower panel of the “Isotopic data” window permits definition of the $\delta^{13}\text{C}$ and ^{14}C isotopic composition of dissolved methane and dissolved organic carbon, if present in the analytical data of the LON file. In the example shown (Figure S13), the initial and final water analyses contained DOC (but no methane) and their $\delta^{13}\text{C}$ and ^{14}C composition were defined to be -25 per mil and 0 pmc.

Isotopic data

Isotopic Compositions

Number	Phase	Carbon-13	C14 % mod	Sulfur-34	Sr-87	N-15
1	"CH2O"	-25.000	0.000			
2	CALCITE	0.000	0.000			
3	DOLOMITE	0.000	0.000			
4	GYP SUM			22.000		

-9999.00 means undefined.

Isotopic Compositions: Additive Fractionation Factors (in per mil) relative to solution

Number	Phase	Carbon-13	Carbon-14	Sulfur-34	Sr-87	N-15
1	CALCITE	2.232	4.465	*		
2	PYRITE			-59.298	@	
3	CO2 GAS	-6.542	-13.084	*		

To get a computed value, leave the cell blank and hit Update.
 * = based on computed value at 1.0000 fraction between initial and final waters
 @ = based on computed value at final water (insufficient data in initial water)
 # = based on computed value at initial water (insufficient data in final water)
 -9999.00 means undefined.

Isotopic compositions of Carbon in solution

Number	Well name	Carbon-13 of CH4	C14 %mod of CH4	Carbon-13 of DOC	C14 %mod of DOC
1	well 1.1			-25.000	0.000
2	well 3.5			-25.000	0.000

Cancel Update OK

Figure S13 Example of the “Isotopic data” menu accessed from the “Geochemical parameters” window (Figure S11). In this example, the upper panel allows definition of the $\delta^{13}\text{C}$, ^{14}C , ^{34}S , ^{87}Sr , and ^{15}N isotopic composition of all carbon- sulphur- strontium- and nitrogen-bearing phases in the model. The middle panel displays calculated default values of the additive fractionation factors (relative to the isotopic composition in solution) which can be re-defined in this panel, and the lower panel is used to define the $\delta^{13}\text{C}$ and ^{14}C composition of dissolved organic carbon and dissolved methane in the water analyses.

8. The “Data for C-14 Ao models” window (Figure S14) is accessed from the “Geochemical parameters” window (Figure S11). The pull-down button in the upper left corner of the window allows selection of the traditional radiocarbon adjustment model that is to be applied to the initial water composition to estimate the initial ^{14}C content, such as “Mass Balance”, “Vogel”, Tamers, Ingerson and Pearson, Fontes and Garnier, and Eichinger (see Plummer et al., 1994 for definition of the Ao models used in NETPATH). Checking the box to the right (Edit data for all models) permits editing the parameters used in all of the available Ao models. Two sets of carbon-isotope fractionation factors are available in NETPATH-WIN and this example uses those of Mook (Plummer et al., 1994). Depending on the Ao model selected, additional values of input parameters are called for including: 1. Method for defining $\delta^{13}\text{C}$ of the initial solution, 2. Method for defining the $\delta^{13}\text{C}$ of soil gas CO_2 , 3. $\delta^{13}\text{C}$ and ^{14}C values used in the Ao models, 4. User-defined ^{14}C values for the initial wells, and definition of $\delta^{13}\text{C}$ of CO_2 gas in the initial waters. Values defined in the “Data for C-14 Ao models” menu apply only to calculation of Ao, and are not used outside of the Ao calculation. For example, the $\delta^{13}\text{C}$ composition of calcite defined in the Isotopic data window (Figure S13) is not used in the Ao models unless redefined in the “Data for C-14 models” window (Figure S14).

Data for C-14 Ao models

Choose Ao model from the list:

Original Data ☐ Edit data for all models

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

	Model	Initial 1	Initial 2
1	Original Data	40.624	2.000
2	Mass Balance	45.942	-1614.210
3	Vogel	74.726	85.000
4	Tamers	45.492	50.309
5	Ingerson and Pearson	45.942	-999.000
6	Mook	37.569	53.448
7	Fontes and Garnier	46.214	50.309
8	Eichinger	43.607	113.138
9	User-defined	100.000	100.000

Carbon fract. factors

☒ Mook
☐ Deines, et al.

Method for C-13 of initial solution

☒ Original Value
☐ User-defined Value

Method for C-13 of soil gas CO_2

☐ User-defined Value
☒ Mass Balance - no fractionation
☐ Mass Balance - with fractionation
☐ Open System (gas-solution equilibrium)

Parameters for the Ao models

	Value
C-14 activity in carbonate minerals (% mo...)	0.000
C-14 activity in soil gas CO_2 (% modern)	100.000
C-14 activity in dolomite (% modern)	0.000
C-14 activity in calcite (% modern)	0.000
delta C-13 (per mil) in the solution	0.000
delta C-13 (per mil) in carbonate minerals	0.000
delta C-13 (per mil) in soil gas CO_2	-25.000
delta C-13 (per mil) in dolomite	0.000
delta C-13 (per mil) in calcite	0.000

User-defined C-14 activity

	Well name	Value
1	well 1.1	100.00
2	Sea Water (DKN et al mg/kg s)	100.00
3		
4		
5		

	Initial 1	Initial 2	Initial 3	Initial 4	Initial 5
C-13 of CO_2 gas for initial well(s)	-21.719	0.00000			

Cancel Update OK

Figure S14. Example of the “Data for C-14 Ao models” window accessed from the “Geochemical parameters” window (Figure S11). This window permits selection of a radiocarbon adjustment model that is to be applied to the initial water composition to estimate Ao. The pull-down tab displays seven models (options) for defining Ao. Depending on selection of the Ao model, NETPATH-WIN permits definition of other values needed in the model calculations. Using the default values shown, NETPATH-WIN calculates estimates of Ao based on these models.

9. Finally we return to the main screen of NETPATH-WIN and click on “Run NETPATH”. The first screen (Figure S15) shows the chemical data, phases, wells, and constraints on which the calculation will be based.

DATA

Well	Name
Initial well 1	well 1.1
Initial well 2	Sea Water (DKN et al mg/kg soln)
Final well	well 3.5

Ename	Final	Initial 1	Initial 2	Initial 3	Initial 4	Initial 5
C	3.0462	2.7558	2.1276			
S	1.7542	0.1250	29.2610			
CA	0.5493	0.9483	10.6619			
MG	1.1937	0.3333	55.0711			
RS	21.2443	10.4424	184.9318			

Pname	elem	coef	elem	coef	elem	cc
"CH2O"	C	1.0000	I1	-25.0000	I2	0.00
CALCITE	CA	1.0000	C	1.0000	RS	4.00
DOLOMITE	CA	1.0000	MG	1.0000	C	2.00
EXCHANGE	CA	-1.0000	NA	2.0000	MG	0.00

CANCEL RUN

Figure S15. Pull-down menus that display water samples, constraints, phases and chemical composition data to be used in the NETPATH-WIN model calculations. The vertical and horizontal arrows permit viewing of all the values.

10. Clicking on “Run” in the lower right corner runs NETPATH-WIN for the described model displaying the screen shown in Figure S16. The upper panel of the NETPATH-WIN “Results” gives the calculated mass transfers in mmols/kg water under the column labelled “Delta” (negative for phase precipitation or gas loss, positive for phase dissolution or addition of a gas to the groundwater). The lower panel compares computed and observed values of isotopic data. $\delta^{13}\text{C}$ data are given for dissolved inorganic carbon and total dissolved carbon. The model radiocarbon age, “22,779” years of the total dissolved carbon in the final well, well 3.5, appears below the panel of calculated and observed isotopic data.

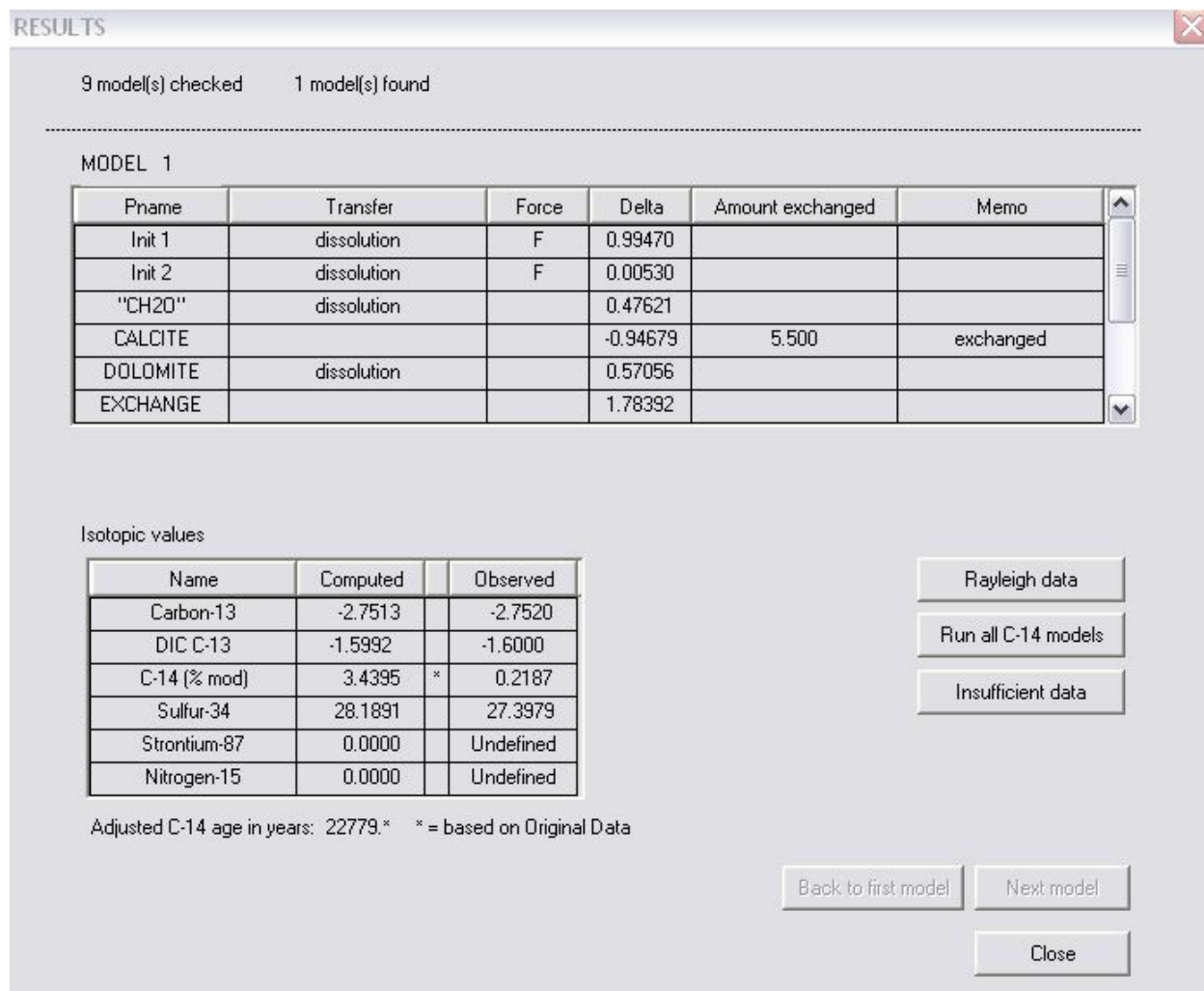


Figure S16. The Results page from NETPATH-WIN. The upper panel shows the calculated phase transfers for each phase in the model (negative for precipitation, positive for dissolution). The mixing fractions of initial solutions 1 and 2 (well 1.1 and sea water, respectively) are 0.9947 and 0.0053. The lower panel gives computed and observed isotopic data. The modeled radiocarbon age is shown below the lower panel, 22,779 years in this case.

- Next we click on the "Rayleigh data" tab of the "Results" window. This produces a potentially long ascii file displaying all the isotopic data at increments along the flow path (Figure S17). In our example only data for $\delta^{13}\text{C}$, ^{14}C and ^{34}S were computed. Shown are the calculated results for the isotopic composition of precipitating (out-going) phases at increments of 10% of the overall net reaction from the initial point to the final point.

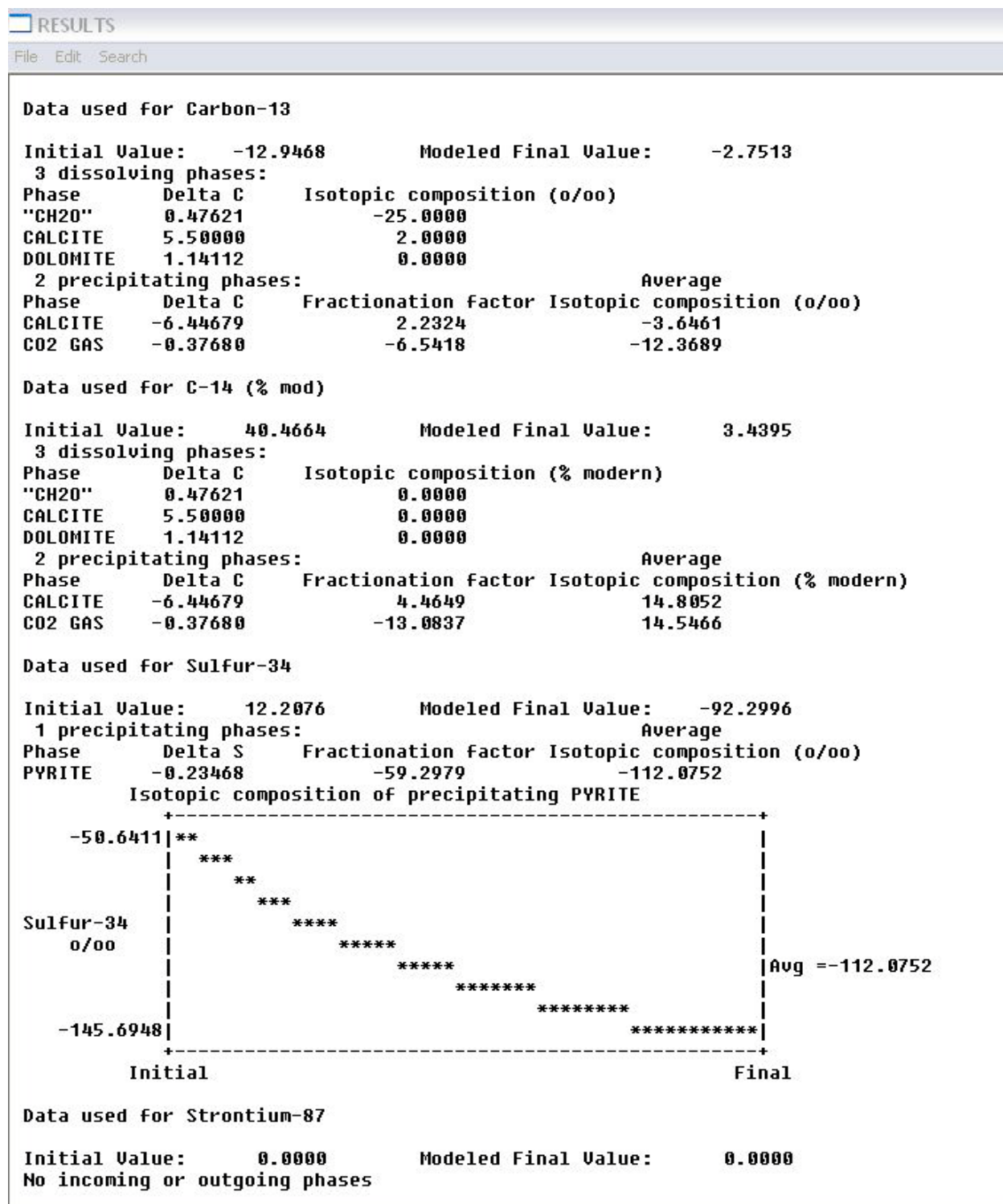


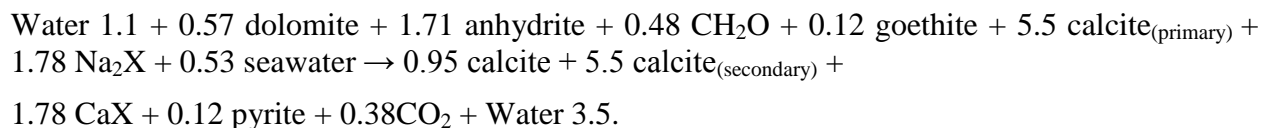
Figure S17. Calculated Rayleigh distillation paths of the isotopic composition of precipitating phases along the flow path.

12. By clicking on “Run all C-14 models” from the “Results” page, the ^{14}C adjusted model ages are displayed for all the ^{14}C Ao models of NETPATH-WIN (Figure S18).

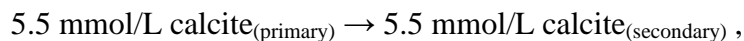
RESULTS				
File Edit Search				
Model (for initial A0)	A0 (initial)	Computed (no decay)	Observed	age (final)
Original Data	40.47	3.44	0.22	22779.
Mass Balance	45.75	3.89	0.22	23794.
Vogel	74.77	6.35	0.22	27854.
Tamers	45.51	3.87	0.22	23750.
Ingerson and Pearson	45.75	3.89	0.22	23794.
Mook	37.63	3.20	0.22	22179.
Fontes and Garnier	46.23	3.93	0.22	23879.
Eichinger	43.89	3.73	0.22	23450.
User-defined	100.00	8.50	0.22	30257.

Figures S18. Display of the adjusted radiocarbon ages of total dissolved carbon at well 3.5 based on application of a range of Ao models to the initial water. In our case the original data were used to define Ao corresponding to an adjusted radiocarbon model age of 22,779 years.

From the NETPATH-WIN results, the overall net mass balance reaction can be written:



The part of the overall reaction pertaining to calcite recrystallization (isotopic exchange),



represents recrystallization of an estimated mass of 5.5 mmols of calcite (of marine origin, $\delta^{13}\text{C}_{\text{calcite}} \equiv 2$ per mil) per liter of aquifer, to form 5.5 mmols of secondary calcite (accounting for isotopic fractionation in calcite precipitation) in freshwater. One of the findings from the NETPATH modeling was that without calcite recrystallization, the modeled values of $\delta^{13}\text{C}_{\text{DIC}}$ were significantly depleted in ^{13}C relative to the observed. The mmols/kg of water of calcite recrystallization was that needed in the NETPATH models to match the observed $\delta^{13}\text{C}_{\text{DIC}}$. During recrystallization, a fractionation occurs that enriches the secondary calcite with ^{14}C from the DIC, lowering the ^{14}C content of DIC in the dissolved HCO_3^- . Therefore, recrystallization of calcite lowers the value of A_{nd} (Figure 2 in the Note), and thus lowers the adjusted radiocarbon

age. The adjusted radiocarbon age of total dissolved carbon at well 3.5 is (rounded to the nearest 100 years) 22,800 yr, as in Plummer and Sprinkle (2001).

Application of Traditional Radiocarbon Adjustment Models to Single Water Samples

Next we use NETPATH-WIN to apply traditional adjustment models to the final water, as in Figure 1 in the Note. The steps are as follows:

1. Beginning with the DAT file for well 3.5 (Figure S7), the file is edited with NETPATH-WIN using the “Well list” menu to define the initial and final water to both be well 3.5, and seawater is removed (Figure S19).

Well List

Used wells

	Number in list	Name
Initial 1	12	well 3.5
Initial 2		
Initial 3		
Initial 4		
Initial 5		
Final	12	well 3.5

Total list of wells (make changes here; maximum 5 initial wells, one final well)

Number	Name	Initial?	Final?
10	well 3.3	<input type="checkbox"/>	<input type="checkbox"/>
11	well 3.4	<input type="checkbox"/>	<input type="checkbox"/>
12	well 3.5	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>
13	well 3.6	<input type="checkbox"/>	<input type="checkbox"/>
14	well 3.7	<input type="checkbox"/>	<input type="checkbox"/>
15	well 4.2	<input type="checkbox"/>	<input type="checkbox"/>
16	well 4.3	<input type="checkbox"/>	<input type="checkbox"/>

Select wells of choice (one final well and maximum of 5 initial wells) then click "Use selected wells" to activate choice.

Use selected wells

OK

Figure S19. From the “Well list” menu under the Edit heading of NETPATH-WIN, the FL well 3.5 DAT file is modified choosing well 3.5 as both the initial and final well and removing seawater as an additional initial water. Other options are described in Figure S8.

- Under phases, isotopic exchange is changed to dissolution (only) (Figure S20). The constraints and phases can be left as they were since the initial and final waters are identical in composition, and thus all net mass transfer will be zero. No changes are needed to the geochemical parameters or isotopic compositions of phases, because, again, their mass transfers will be zero.

Add or Remove Phases

Used phases

Select phase to remove then click the remove button. Change data in table as desired then click the update button.

Phase No.	Phase ID from phase list below	Phase Name	Phase in every model?	Transfer (choose from drop-down menu)	Amount to exchange
<input type="checkbox"/>	1	"CH2O"	<input type="checkbox"/>	dissolution	
<input type="checkbox"/>	2	11	11	dissolution	
<input type="checkbox"/>	3	21	21	dissolution	
<input type="checkbox"/>	4	22	22	both diss. & prec.	
<input type="checkbox"/>	5	29	29	both diss. & prec.	
<input type="checkbox"/>	6	30	30	dissolution	

Remove selected phase Update

Complete phase list

Use the complete list of phases to add to those above, by selecting the phase of choice then clicking the add button. Phase will appear at end of list in table above.

To edit this complete list, run the Phase Editor that is included in the NETPATH-WIN package. After saving the changes, (re)open the PAT file to update the list of phases here.

Phase ID	Phase Name	1	2	3	4	5	6	7	8	9	10
<input type="checkbox"/>	1	"CH2O"	+	C	1.000	11	-25.00	12	0.00		
<input type="checkbox"/>	2	ALBITE	+	NA	1.000	AL	1.000	SI	3.000		
<input type="checkbox"/>	3	ALUNITE		K	1.000	AL	3.000	S	2.000	RS	12
<input type="checkbox"/>	4	ANALCIME	+	NA	1.000	AL	1.000	SI	2.000		
<input type="checkbox"/>	5	ANNITE	+	K	1.000	FE	3.000	AL	1.000	SI	3.0
<input type="checkbox"/>	6	ANORTH	+	CA	1.000	AL	2.000	SI	2.000		
<input type="checkbox"/>	7	ARAGONIT		CA	1.00	C	1.00	RS	4.00		
<input type="checkbox"/>	8	BARITE		BA	1.000	S	1.000	RS	6.000		

Add selected phase OK

Figure S20. Screen showing the "Phases" menu in which calcite was changed to dissolution (only), removing the option of isotopic exchange with calcite. Other features of the "Phases" menu are described in Figure S9.

- Isotopic data used in the traditional adjustment models are defined in the "Data for C-14 Ao models" screen. Here we check the box to Edit data for all models (Figure S21). Following the selections of Plummer and Sprinkle (2001), the soil gas $\delta^{13}\text{C}$ was defined using the open system model, the Mook set of fractionation factors were selected (Plummer et al., 1994), the ^{14}C content of carbonate minerals was defined to be 0 pmc and for soil gas CO_2 , 100 pmc. The $\delta^{13}\text{C}$ of dissolving carbonate minerals was defined to be 0 per mil.

Data for C=14 Ao models

Choose Ao model from the list:

User-defined ☒ Edit data for all models

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

	Model	Initial 1	Initial 2
1	Original Data	0.219	
2	Mass Balance	91.892	
3	Vogel	80.816	
4	Tamers	48.173	
5	Ingerson and Pearson	18.684	
6	Mook	83.337	
7	Fontes and Garnier	14.714	
8	Eichinger	7.093	
9	User-defined	100.000	

Carbon fract. factors

☒ Mook
☐ Deines, et al.

Method for C-13 of initial solution

☒ Original Value
☐ User-defined Value

Method for C-13 of soil gas CO₂

☐ User-defined Value
☐ Mass Balance - no fractionation
☐ Mass Balance - with fractionation
☒ Open System (gas-solution equilibrium)

Parameters for the Ao models

	Value
C-14 activity in carbonate minerals (% modern)	0.000
C-14 activity in soil gas CO ₂ (% modern)	100.000
C-14 activity in dolomite (% modern)	0.000
C-14 activity in calcite (% modern)	0.000
delta C-13 (per mil) in the solution	0.000
delta C-13 (per mil) in carbonate minerals	0.000
delta C-13 (per mil) in soil gas CO ₂	-25.000
delta C-13 (per mil) in dolomite	0.000
delta C-13 (per mil) in calcite	0.000

User-defined C-14 activity

	Well name	Value
1	well 3.5	100.00
2		
3		
4		
5		

	Initial 1	Initial 2	Initial 3	Initial 4	Initial 5
C-13 of CO ₂ gas for initial well(s)	-8.1418				

Cancel Update OK

Figure S21. This screen permits selection of the Ao model to be applied to the initial water, and allows editing of all data used in all the Ao models. Cells that can be edited have white background (active), depending on selected model and/or options. Two optional sets of carbon-isotope fractionation factors are available. It is possible to define an alternative value of the $\delta^{13}\text{C}$ of DIC in the initial water, possibly accounting for paleoclimatic variations in C_3/C_4 plant abundance. Four options are provided for defining the $\delta^{13}\text{C}$ of soil-gas CO_2 .

4. Selecting "Run NETPATH" from the main screen of NETPATH-WIN (Figure S7), displays a "DATA" window that lists the wells in the model, their chemical composition in mmols/kg water corresponding to the selected (and displayed) constraints, and all of the selected phases in the model (Figure S22).

DATA

Well	Name
Initial well 1	well 3.5
Final well	well 3.5

Ename	Final	Initial 1	Initial 2	Initial 3	Initial 4	Initial 5
C	3.0462	3.0462				
S	1.7542	1.7542				
CA	0.5493	0.5493				
MG	1.1937	1.1937				
RS	21.2443	21.2443				

Pname	elem	coef	elem	coef	elem	cc
"CH2O"	C	1.0000	I1	-25.0000	I2	0.00
CALCITE	CA	1.0000	C	1.0000	RS	4.00
DOLOMITE	CA	1.0000	MG	1.0000	C	2.00
EXCHANGE	CA	-1.0000	NA	2.0000	MG	0.00

CANCEL RUN

Figure S22. The first screen that appears after selecting “Run NETPATH” displays the wells in the model. The initial and final wells are identical in the case of application of traditional adjustment models in radiocarbon dating, as in this example. The screen also previews the constraints and compositions of solutions and phases in the model. Since the initial and final solutions are defined identically, the calculated mass transfer will be zero.

- Next we click on “RUN” from the “DATA” screen which displays the NETPATH “Results” screen (Figure S23). This example shows the expected zero mass transfer for all phases and identical computed and observed isotopic values. The ^{14}C age assuming an initial ^{14}C content of 100 pmc is 50,600 years (Figure S23).

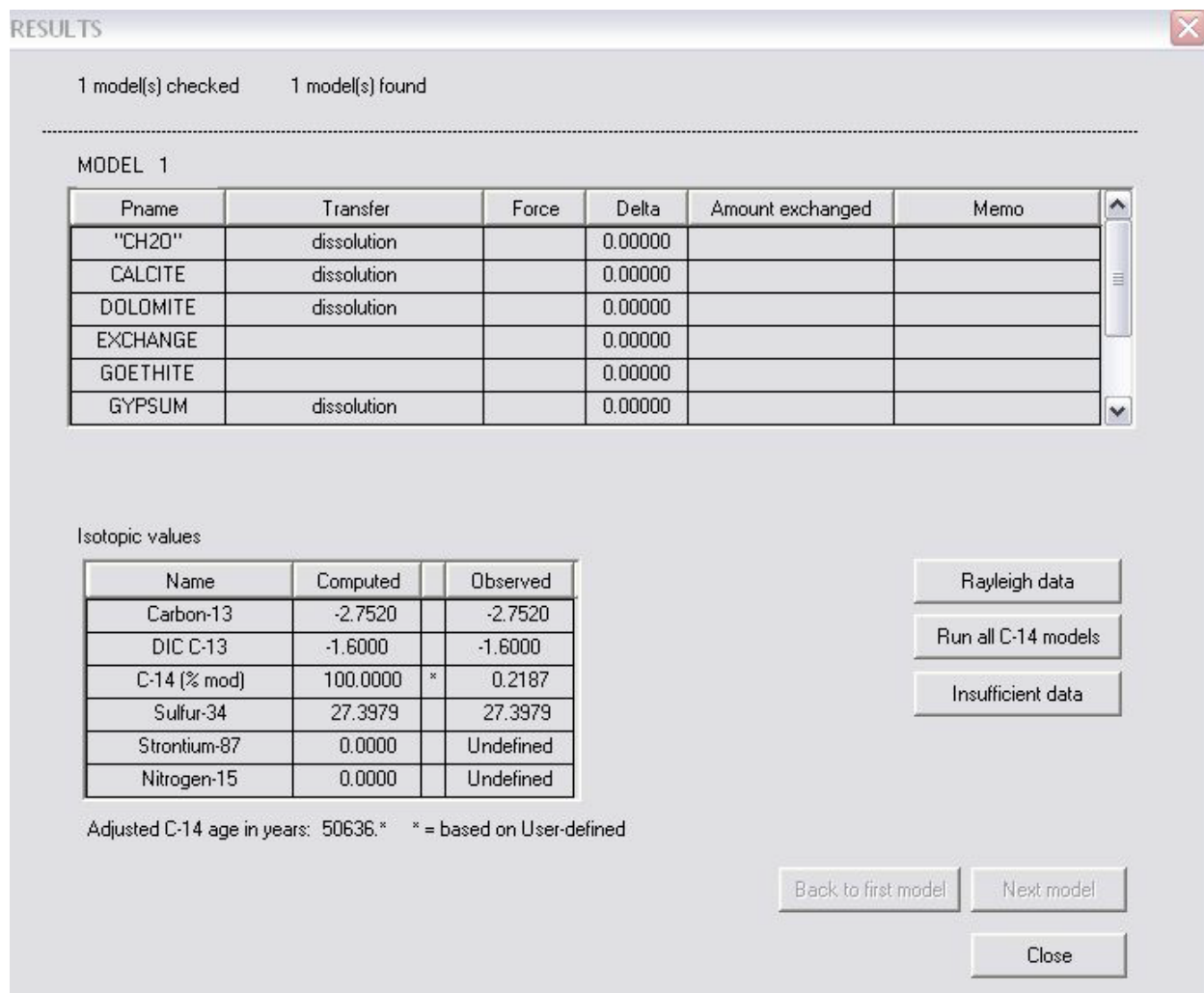


Figure S23. The "Results" window of NETPATH-WIN showing zero mass transfer of phases in this example applying traditional adjustment models and identical computed and observed isotopic values.

- Clicking on "Run all C-14 models" in this particular case calculates the radiocarbon ages from the traditional models (Figure S24): Unadjusted age, 50,600 yrs; Tamers (1975), 44,600 yrs; Ingerson and Pearson (1964), 36,800 yrs; Mook (1972), 49,100 yrs; Eichinger (1983), 28,800; and Fontes and Garnier (1979), 34,800 yrs (ages rounded to nearest 100 years). The unadjusted age, and those adjusted radiocarbon ages utilizing the traditional adjustment models are, in this case, all considerably older than the adjusted age (22,800 yrs, Figures S16) generated at the end of the flow path from well 1.1 to well 3.5 with correction for additional geochemical reactions that are not included in the traditional adjustment models.

RESULTS				
File Edit Search				
Model (for initial A0)	A0 (initial)	Computed (no decay)	Observed	age (final)
Original Data	0.22	0.22	0.22	0.
Mass Balance	91.89	91.89	0.22	49937.
Vogel	80.82	80.82	0.22	48875.
Tamers	48.17	48.17	0.22	44598.
Ingerson and Pearson	18.68	18.68	0.22	36769.
Mook	83.34	83.34	0.22	49129.
Fontes and Garnier	14.71	14.71	0.22	34794.
Eichinger	7.09	7.09	0.22	28762.
User-defined	100.00	100.00	0.22	50636.

Figure S24. The “Results” screen showing all radiocarbon ages of total dissolved carbon in FL well 3.5 as calculated from all the traditional adjustment models in NETPATH (and NETPATH-WIN).

Closing Comment

Selected traditional adjustment models are best suited for geochemical systems undergoing relatively simple water-rock reactions, such as usually occur in shallow recharge areas, but, depending on choice of model, can be applied to radiocarbon dating of DIC in groundwater systems undergoing carbonate-mineral dissolution, gypsum dissolution, Ca/Na ion exchange, CO₂ gas dissolution, and isotope exchange between soil CO₂, calcite, and dissolved inorganic carbon during recharge. In general, many more geochemical reactions can occur in groundwater systems that are often overlooked. Some of the more important reactions that are not accounted for in traditional adjustment models include degradation of organic matter accompanying various redox reactions, such as iron reduction, sulphate reduction, methanogenesis, degradation of dissolved organic carbon, isotopic fractionation in precipitation of carbonate phases, and recrystallization of carbonate minerals.

Adjusted radiocarbon ages will likely be overestimated if calculated from traditional adjustment models in systems undergoing more complex geochemical reactions than those considered in the traditional adjustment models. Because of the internal consistency in ability to import and export analytical data through spreadsheet files from PHREEQC, NetpathXL (that uses Microsoft Excel® (Parkhurst and Charlton, 2008)), and NETPATH-WIN (that has been constructed to migrate NETPATH and NetpathXL applications into the Microsoft WINDOWS® environment), more complete geochemical calculations can be made. For example, it is now possible to reconstruct NetpathXL or NETPATH-WIN models in PHREEQC in-order to consider uncertainty in analytical data, or to consider in PHREEQC possible geochemical evolutionary reaction paths in aquifers from net geochemical models generated in NetpathXL or NETPATH-WIN. Alternatively, analytical data from PHREEQC can be exported to NetpathXL or NETPATH-WIN in-order to apply some of the more advanced radiocarbon dating options of NETPATH (and NetpathXL or NETPATH-WIN).

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