**Supplementary discussion on the nature of mixing hyperbolas in the ∆47/δ18OC13 system**

Non-linear mixing of ∆47 values can be calculated relatively simply using the δ18OC13 notation presented in this manuscript. The key is to calculate the mixed values using a mixing hyperbola, relative to the abundance of carbon-13 ([13C], see S-1 for full definition).

For any end-member isotope ratio mixing model where the concentrations of the element of interest are CA and CB, and the isotopic compositions of the end members are δA and δB, a mixture consisting of some fraction of the two (FA and FB, where FB = 1-FA) will have an isotopic composition defined by equation B-1.

(B-1)

If this mixing model is applied to δ18OC13, using the concentration carbon-13 in then the δ18OC13 of a mixed system is defined by equation B-2.

(B-2)

The ∆47 value of the mixed system can then be calculated using this δ18OC13mix value, producing the familiar non-linear mixing paths described by Defliese and Lohmann (2015). Figure S2-1 shows the results of the 15°C equilibration experiment compared to a mixing line between initial and equilibrium values, note the convex-upward nature of the mixing line and the convex-downward nature of the experimental data.



Figure S2-1: ∆47 value plotted relative to δ18O value of a mixed system between initial and equilibrium compositions of the 15°C experiment (Grey circles), plotted with experimental data for equilibration at 15°C (Green circles). End-member values for δ13C are -17‰ and -15‰, δ18O values for the two end-members are -18.55‰ and -1.37‰, ∆47 values for the endmembers are

0.543‰ and 0.689‰. Note positive curvature of mixing line.

A mixing model which produces the concave-up curvature of the measured results of ∑DIC equilibration discussed in the main text, and shown in figure S2-1, would require a negative correlation between the end-member δ13C and δ18O values. This is illustrated in figure S2-2, which simulates the mixing of endmember δ13C values of -15‰ and 0‰, δ18O values of +15‰ and 0‰ and ∆47 values of 0.75‰ and 0.70‰.



Figure S2-2: ∆47 value plotted relative to δ18O value of a mixed system of two end-members with δ13C values of -15‰ and 0‰, a δ18O values of +15‰ and 0‰ and ∆47 values of 0.70 and 0.75. A Matlab script has been provided which creates the above figure, input values can be modified as desired.

Matlab code for calculating and plotting mixed models. Input δ13C, δ18O and ∆47 values can be changed as desired. As written, script outputs figure S2-2.

%%%%%%%

% D47 mixing model

% Graphs the mixing line for endmember d13C, d18O and D47 values

% Calculates mixing hyperbola for d18OC13 using C-13 concentration

% Script written by Philip Staudigel

% May 2018

%%%%%%%

clear all

%% Input end-member values here

d13CA = -15; % d13C of end-member A

d13CB = 0; % d13C of end-member B

d18OA = +15; % d18O of end-member A

d18OB = 0; % d18O of end-member B

D47A  = .7; % D47 of end-member A

D47B  = .75; % D47 of end-member B

%% Calculate Concentrations of 13C and d18OC13 values for end-members

r13A = (d13CA/1000+1)\*0.0118; %Chang and Li, 1990

r13B = (d13CB/1000+1)\*0.0118;

C13A = r13A/(1+r13A);

C13B = r13B/(1+r13B);

d18O13A= unclump(d13CA, d18OA, D47A)

d18O13B= unclump(d13CB, d18OB, D47B);

%% Fraction of end-member A for model

FA = [0:.1:1];

%% Simple mixing of d13C and d18O

d13Cm = d13CA\*FA + d13CB\*(1-FA);

d18Om = d18OA\*FA + d18OB\*(1-FA);

%% Calculate mixing hyperbola for d18OC13

r13m = (d13Cm./1000+1).\*0.0118; %Chang and Li, 1990

C13m = r13m./(1+r13m);

d18O13m = (FA\*d18O13A\*C13A + (1-FA)\*d18O13B\*C13B)./C13m;

D47m = clump(d13Cm, d18Om, d18O13m);

%% Plot the mixed system D47 relative to d18O

close all

plot(d18Om,D47m,'color',[0 0 0])  % plot the line

hold on

plot(d18Om,D47m,'o','markeredgecolor',[0 0 0],'markerfacecolor',[.7 .7 .7],'markersize',10) % plot the dots

% make it pretty

set(gca,'tickdir','both','linewidth',1,'xcolor','black','ycolor','black','fontsize',16);

% axis labels

xlabel('\delta^{18}O (  ^{\fontsize{8}o}/{\fontsize{8}o o} VPDB)','fontname','calibri','fontsize',16);

ylabel('\Delta\_{47}(^{ \fontsize{8}o}/{\fontsize{8}o o})','fontname','calibri','fontsize',16);

%% Two scripts for clumping / unclumping

function [D47] = clump(d13C,d18O,d18O13)

% Values for PDB and lambda

R13PDB = 0.0118; %Chang and Li, 1990

R18PDB = 0.00208839; % Modified from Baertschi 1976

R17PDB = 0.0003931; % Assonov and Brenninkmeijer, 2003

l = 0.528; % Lambda: Barkan and Luz, 2005. R17 = (R18s/R18pdb)^l x R17pdb

r13 = (d13C./1000+1).\*R13PDB;

r18 = (d18O./1000+1).\*R18PDB;

r17 = R17PDB\*(r18/R18PDB).^l;

r1813 = (d18O13./1000+1).\*R18PDB;

r1713 = R17PDB.\*(r1813./R18PDB).^l;

C12 = 1./(1+r13);

C13 = r13./(1+r13);

C16 = 1./(1+r17+r18);

C17 = r17./(1+r17+r18);

C18 = r18./(1+r17+r18);

C1613 = 1./(1+r1713+r1813);

C1713 = r1713./(1+r1713+r1813);

C1813 = r1813./(1+r1713+r1813);

R47stoc = (C13.\*C17.\*C17 + 2.\*C13.\*C18.\*C16 + 2.\*C12.\*C17.\*C18)./(C12.\*C16.\*C16);

R47real = (C13.\*C1713.\*C1713 + 2.\*C13.\*C1813.\*C1613 + 2.\*C12.\*C17.\*C18)./(C12.\*C16.\*C16);

D47 = (R47real./R47stoc-1).\*1000;

end

function [d18O13] = unclump(d13C,d18O,D47)

 steps = 5; % number of iterations for solving d18O13

 d18O13 = d18O+D47; % an initial approximation for d18O13, to be refined iteratively

 for i=1:steps

     Diff = clump(d13C,d18O,d18O13)-D47;

     d18O13 = d18O13-Diff;

 end

end