Supplementary Information

The supporting information contains 23 pages, one AutoIt computer script, one MATLAB script, one Table, two Figures, and available as an attachment is 1 .csv file.

1 Experimental Section

1.1 AutoIt computer script

```
#cs Start of comment

This script is based on timed mouse clicks and keyboard entries.

In order that the script works, the user needs to have a monitor with the same screen resolution as the one used for our case (1366 x 768 pixels).

If not, the parameters passed to the functions regarding positioning of mouse clicks will need to be changed in order that the script works properly.

This script deals entirely with the software controlling the AIRICA by means of automating its operation.

It consists of a large infinite loop (While 1 … WEND) that has two main parts: the first part is optimizes sampling and analysis for concentration measurements, while the second part optimizes them for isotopic measurement.

Learn more about AutoIt for Laboratory Automation from Practical Laboratory Automation Made easy with AutoIt by Matheus Carvalho ISBN: 978-3-527-34158-0.

#ce End of comment



opt("Wintitlematchmode",1)

While 1

WinMove("AIRICA measurement","",0,0)

WinActivate("AIRICA measurement")


;************

;Start of first part of the script

;************
```

```
;clicking on edit sample list
MouseClick("left",50,180)
Sleep(1000)

;adding sample name
MouseClick("left",440,508)
Sleep(1000)
Send("{BACKSPACE 50}{DEL 50}")
Send("Sample")
Send(@YDAY&@HOUR&@MIN)
Sleep(500)
MouseClick("left",520,508)
Sleep(500)
MouseClick("left",645,508)
Sleep(1000)

;clicking on edit calculation mode
MouseClick("left",200,255)
Sleep(1000)
MouseClick("left",300,265)
Send("{BACKSPACE 5}{DEL 5}")
Send("2")
Sleep(1000)
MouseClick("left",320,305)
Sleep(1000)
```

```
Send("{UP 10}")
Send("{ENTER}")
MouseClick("left",475,305)
Sleep(1000)
Send("{ENTER}")
Sleep(1000)

;clicking on edit extraction parameters
MouseClick("left",175,325)
Sleep(1000)
MouseClick("left",645,175)
Send("{BACKSPACE 5}{DEL 5}")
Send("210")
Sleep(500)
MouseClick("left",645,200)
Send("{BACKSPACE 5}{DEL 5}")
Send("50")
Sleep(500)
MouseClick("left",645,225)
Send("{BACKSPACE 5}{DEL 5}")
Send("60")
Sleep(500)
MouseClick("left",645,250)
Send("{BACKSPACE 5}{DEL 5}")
Send("0")
```

```
Sleep(500)
MouseClick("left",645,370)
Send("{BACKSPACE 5}{DEL 5}")
Send("80")
Sleep(500)
MouseClick("left",645,418)
Send("{BACKSPACE 5}{DEL 5}")
Send("2")
Sleep(500)
MouseClick("left",645,440)
Send("{DOWN 5}{UP}")
Send("{ENTER}")
MouseClick("left",635,535)
Sleep(1000)
Send("{ENTER}")
Sleep(1000)
Send("{ENTER}")
Sleep(1000)

;click on set flow parameter
MouseClick("left",910,85)
Sleep(1000)
MouseClick("left",630,325)
Send("{BACKSPACE 5}{DEL 5}")
Send("300")
```

```
MouseClick("left",630,388)
Sleep(1000)
Send("{ENTER}")
Sleep(1000)

;click on set blank
MouseClick("left",560,85)
Sleep(1000)
MouseClick("left",500,420)
Send("{BACKSPACE 10}{DEL 10}")
Send("2")
MouseClick("left",595,430)
Sleep(1000)

;clicking on sample to start measurement
MouseClick("left",224,134)
Sleep(1000)
MouseClick("left",95,95)
Sleep(1000)
Send("{ENTER}")
Sleep(1000)
Send("{ENTER}")
Sleep(1000)

;monitoring a pixel in order to deal with different analysis times, if necessary
```

```
Sleep(10*1000)
$TargetPixelColor = PixelGetColor(268,63)
While $TargetPixelColor <> 6684444
        Sleep(5000)
        $TargetPixelColor = PixelGetColor(268,63)
WEnd
Sleep(20*1000)

;************
;Start of second part of the script
;************

;clicking on edit sample list
WinMove("AIRICA measurement","",0,0)
WinActivate("AIRICA measurement")
MouseClick("left",50,180)
Sleep(1000)

;adding sample name
MouseClick("left",440,508)
Sleep(1000)
Send("{BACKSPACE 50}{DEL 50}")
Send("Sample")
Send(@YDAY&@HOUR&@MIN)
Sleep(500)
```

```
MouseClick("left",520,508)
Sleep(500)
MouseClick("left",645,508)
Sleep(1000)

;clicking on edit calculation mode
MouseClick("left",200,255)
Sleep(1000)
MouseClick("left",300,265)
Send("{BACKSPACE 5}{DEL 5}")
Send("1")
Sleep(1000)
MouseClick("left",320,305)
Sleep(1000)
Send("{UP 10}")
Send("{ENTER}")
MouseClick("left",475,305)
Sleep(1000)
Send("{ENTER}")
Sleep(1000)

;clicking on edit extraction parameters
MouseClick("left",175,325)
Sleep(1000)
MouseClick("left",645,175)
```

```
Send("{BACKSPACE 5}{DEL 5}")
Send("380")
Sleep(500)
MouseClick("left",645,200)
Send("{BACKSPACE 5}{DEL 5}")
Send("25")
Sleep(500)
MouseClick("left",645,225)
Send("{BACKSPACE 5}{DEL 5}")
Send("45")
Sleep(500)
MouseClick("left",645,250)
Send("{BACKSPACE 5}{DEL 5}")
Send("0")
Sleep(500)
MouseClick("left",645,370)
Send("{BACKSPACE 5}{DEL 5}")
Send("15")
Sleep(500)
MouseClick("left",645,418)
Send("{BACKSPACE 5}{DEL 5}")
Send("1")
Sleep(500)
MouseClick("left",645,440)
Send("{UP 6}")
```

```
Send("{ENTER}")
MouseClick("left",635,535)
Sleep(1000)
Send("{ENTER}")
Sleep(1000)
Send("{ENTER}")
Sleep(1000)

;click on set flow parameter
MouseClick("left",910,85)
Sleep(1000)
MouseClick("left",630,325)
Send("{BACKSPACE 5}{DEL 5}")
Send("70")
Sleep(1000)
MouseClick("left",630,388)
Sleep(1000)
Send("{ENTER}")
Sleep(1000)

;click on set blank
MouseClick("left",560,85)
Sleep(1000)
MouseClick("left",500,420)
Send("{BACKSPACE 10}{DEL 10}")
```

```
Send("200")
Sleep(1000)
MouseClick("left",595,430)
Sleep(1000)

;clicking on sample to start measurement
MouseClick("left",224,134)
Sleep(1000)
MouseClick("left",95,95)
Sleep(1000)
Send("{ENTER}")
Sleep(1000)
Send("{ENTER}")
Sleep(1000)

Sleep(10*1000)
$TargetPixelColor = PixelGetColor(268,63)
While $TargetPixelColor <> 6684444
        Sleep(5000)
        $TargetPixelColor = PixelGetColor(268,63)
WEnd

MouseClick("left",938,124)
Sleep(1000)
MouseClick("left",670,405)
```

```
Send("{BACKSPACE 10}{DEL 10}")

Send("300")

Sleep(8000)

MouseClick("left",765,400)

Sleep(1000)


Sleep(50*1000)

WEnd
```

1.2 Matlab script

```
%Matlab Script for processing CRDS data from PICARRO (csv export) 01/08/2016
%Inquiries please direct to K.G. Schulz (kai.schulz@scu.edu.au)

%1) Remove headers from PICARRO output csv (see PICARRO_out.csv for details)
%2) Replace comma by space in PICARRO output csv
%3) Remove occasional 'Z' in last line of PICARRO output csv
%4) PICARRO output csv has to start below peak cut-off def., i.e. pCO2 below 400
%5) Remove any prolonged portions above the cut-off def., which
  %are not associate to peaks from seawater injections
  %(e.g. measurements of laboratory air). Otherwise those parts will be
  %identified as peaks and inflate the matrix.
%6) Delta13C_DIC values for the large CRDS injections and
  %corresponding times are stored in a matrix called 'FinalOutput'

clear all
close all

fread='PICARRO_out.csv';  %name of PICARRO input csv in same folder as
                          %this script

%means of carrier gas (instrument air) C12 and C13 concentrations
%and isotopic signature determined from several hours of continuous measurements
```

```
carriergas12=285.8;

carriergas13=3.181;

carriergasdelta=-10.09;


%BE CAREFUL WHEN MAKING CHANGES BEYOND THIS POINT

%---------------------------------------------------------

[DATE TIME AMPM FRAC_DAYS_SINCE_JAN1 FRAC_HRS_SINCE_JAN1 JULIAN_DAYS EPOCH_TIME ALARM_STATUS INST_STATUS CavityPressure CavityTemp WarmBoxTemp EtalonTemp DasTemp MPVPosition solenoid_valves OutletValve MeasurementMode species HP_12CH4 HP_12CH4_dry HP_13CH4 HR_13CH4 Delta_iCH4_Raw HP_Delta_iCH4_Raw HP_Delta_iCH4_30s HP_Delta_iCH4_2min HP_Delta_iCH4_5min HR_12CH4 HR_12CH4_dry HR_Delta_iCH4_Raw HR_Delta_iCH4_30s HR_Delta_iCH4_2min HR_Delta_iCH4_5min ChemDetect H2O X12CO2 X12CO2_dry X13CO2 Delta_Raw_iCO2 Delta_30s_iCO2 Delta_2min_iCO2 Delta_5min_iCO2 peak87_baseave_spec peak88_baseave peakheight_5 peak0_spec ch4_splinemax peak30_spec peak_30]=textread(fread,'%s %s %s %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f');


fclose('all')


%normalize time axis to beginning of experiment on Jan 19th 12:00

time=JULIAN_DAYS-19.5;


%find all 12C data above 400ppm and the start and end point for

%each peak

pfsa=find(X12CO2>400);

dpfsa=find(diff(pfsa)>10);
```

```
%Compiling peak area data in a single matrix each

peaks12=ones(max(diff(dpfsa)),round(length(dpfsa)))*NaN;
peaks13=ones(max(diff(dpfsa)),round(length(dpfsa)))*NaN;
deltaC=ones(max(diff(dpfsa)),round(length(dpfsa)))*NaN;
peakstime=ones(max(diff(dpfsa)),round(length(dpfsa)))*NaN;



peaklength(1:(pfsa(dpfsa(1))-pfsa(1)+1),1)=(pfsa(dpfsa(1))-pfsa(1)+1);
peaks12(1:(pfsa(dpfsa(1))-pfsa(1)+1))=X12CO2([pfsa(1):pfsa(dpfsa(1))]);
peaks13(1:(pfsa(dpfsa(1))-pfsa(1)+1),1)=X13CO2([pfsa(1):pfsa(dpfsa(1))]);
deltaC(1:(pfsa(dpfsa(1))-pfsa(1)+1),1)=Delta_Raw_iCO2([pfsa(1):pfsa(dpfsa(1))]);
peakstime(1:(pfsa(dpfsa(1))-pfsa(1)+1))=time([pfsa(1):pfsa(dpfsa(1))]);


for i=2:length(dpfsa)
peaks12(1:(pfsa(dpfsa(i))-pfsa(dpfsa(i-1)+1)+1),i)= ...
        X12CO2([pfsa(dpfsa(i-1)+1):pfsa(dpfsa(i))]);
peaks13(1:(pfsa(dpfsa(i))-pfsa(dpfsa(i-1)+1)+1),i)= ...
        X13CO2([pfsa(dpfsa(i-1)+1):pfsa(dpfsa(i))]);
deltaC(1:(pfsa(dpfsa(i))-pfsa(dpfsa(i-1)+1)+1),i)= ...
        Delta_Raw_iCO2([pfsa(dpfsa(i-1)+1):pfsa(dpfsa(i))]);
peakstime(1:(pfsa(dpfsa(i))-pfsa(dpfsa(i-1)+1)+1),i)= ...
        time([pfsa(dpfsa(i-1)+1):pfsa(dpfsa(i))]);
peaklength(i)=(pfsa(dpfsa(i))-pfsa(dpfsa(i-1)+1)+1);
```

```
end

deltaC_added=((peaks12+peaks13).*deltaC-(carriergas12+ ...
                        carriergas13)* ...
    carriergasdelta)./(peaks12+peaks13-carriergas12- ...
                    carriergas13);

mean_peakstime=nanmean(peakstime);

%filter for outliers, i.e. off by more than 2 std in comparison to
%mean

deltaC_mean=nanmean(deltaC_added);
deltaC_std=nanstd(deltaC_added);

deltaC_added_it1=deltaC_added;

for i=1:length(dpfsa)
    deltaC_added_it1(find( abs(deltaC_mean(i)-deltaC_added(:,i)) > abs(deltaC_std(i).*2)),i)=NaN;
end

deltaC_mean_it1=nanmean(deltaC_added_it1);
deltaC_std_it1=nanstd(deltaC_added_it1);

%%%%%%%%%%%%%%%%%%%%%second itteration
```

```
deltaC_added_it2=deltaC_added_it1;

for i=1:length(dpfsa)
    deltaC_added_it2(find( abs(deltaC_mean_it1(i)-deltaC_added_it1(:,i)) > abs(deltaC_std_it1(i).*2)),i)=NaN;
end

deltaC_mean_it2=nanmean(deltaC_added_it2);
deltaC_std_it2=nanstd(deltaC_added_it2);

%%%%%%%%%%%%%%%%%%%%third itteration

deltaC_added_it3=deltaC_added_it2;

for i=1:length(dpfsa)
    deltaC_added_it3(find( abs( deltaC_mean_it2(i)-deltaC_added_it2(:,i)) > abs(deltaC_std_it2(i).*2)),i)=NaN;
end

deltaC_mean_it3=nanmean(deltaC_added_it3);
deltaC_std_it3=nanstd(deltaC_added_it3);

%%%%%%%%%%%%%%final itteration

deltaC_added_final=deltaC_added;
```

```
deltaC_mean_final=deltaC_mean;
deltaC_std_final=deltaC_std;
for g=1:40
for i=1:length(dpfsa)
        deltaC_added_final(find( abs(deltaC_mean_final(i)-deltaC_added_final(:,i)) > abs(deltaC_std_final(i).*2)),i)=NaN;
end

deltaC_mean_final=nanmean(deltaC_added_final);
 deltaC_std_final=nanstd(deltaC_added_final);
end

%distinguish between small peaks for DIC measurements and large for
%d13C_DIC

large=find(peaklength>170&peaklength<450);
small=find(peaklength<150&peaklength>25);

%create matrix with data for large peaks only
C12_pm_large=peaks12(:,large);
delta_pm_large=deltaC(:,large);
time_pm_large=peakstime(:,large);

%final output
%measurement time and isotopic composition
FinalOutput=[mean_peakstime(large)' deltaC_mean_final(large)']
```

```
%some data visualiziation

figure
axes('Position',[0.15 0.5 0.8 0.4])

plot(time, X12CO2,'k')

ylabel('^{12}CO_2 (ppmv)')
xlabel('Time since start of the Experiment')

text(7.695,-400, 'Please note the two small peaks (seawater injections for determination of DIC)')
text(7.695,-490, 'followed by a large peak (injection for determination of carbon isotope signature)')

axis([7.695 7.84 0 1000])

figure
axes('Position',[0.15 0.5 0.8 0.4])

plot(time_pm_large,C12_pm_large)

ylabel('^{12}CO_2 (ppmv)')
xlabel('Time since start of the Experiment')
```

```
text(7.695,-400, 'Large peaks as identified by the script, resulting from the slow seawater')

text(7.695,-490, '\rm injection, and used for subsequent $\rm \delta^{13}C_{DIC}$
calculations','Interpreter','latex')


axis([7.695 7.84 0 1000])


figure

axes('Position',[0.15 0.5 0.8 0.4])

plot(mean_peakstime(large), deltaC_mean_final(large),'ko','MarkerFaceColor','k')


ylabel('\rm \delta^{13}C_{DIC} (^{\fontsize{7}o}/{\fontsize{7}oo})','Interpreter','tex')

xlabel('Time since start of the Experiment')


text(7.695,-3.4, 'Calculated $\rm \delta^{13}C_{DIC}$, using the large paeks','Interpreter','latex')


axis([7.695 7.84 -3 -2])

end
```

1.3

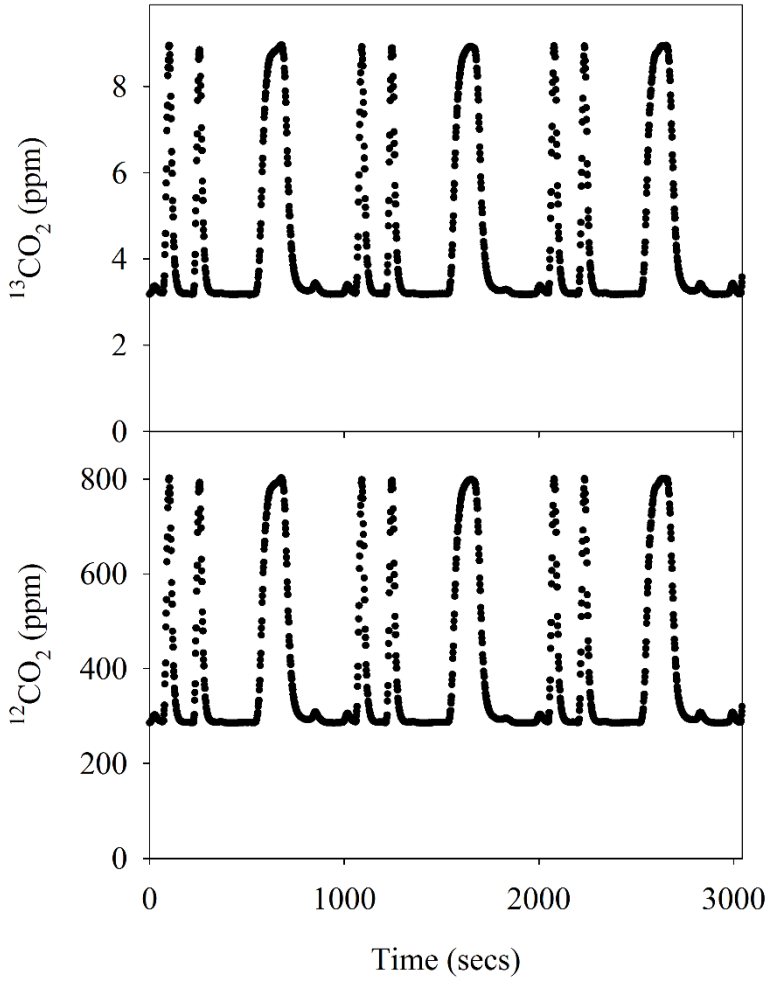

Figure S1. Typical output from the CRDS showing 3 measurements cycles for $^{13}CO_2$ (top) and $^{12}CO_2$ (bottom). An individual measurement cycle consists of the AIRICA system acidifying 3 aliquots of water. The first is a rinse, the second used to determine DIC concentration, and the third to determine δ^{13}C-DIC.

2 Results and Discussion

2.1 Table S1. $\delta^{13}C$ values – IRMS (‰)

	$\delta^{13}C$ – IRMS (‰)	$\delta^{13}C$ DIC – AIRICA-CRDS (‰)
Carbonate Standard 1 (Na_2CO_3)	-3.2 ± 0.1 (n = 3)	
Standard 1 (~500 µmol)		-3.47 ± 0.63 (n = 7)
Standard 1 (~1000 µmol)		-3.77 ± 0.17 (n = 6)
Standard 1 (~1900 µmol)		-3.68 ± 0.16 (n = 57)
Standard 1 (~2800 µmol)		-3.60 ± 0.11 (n = 6)
Standard 1 (~3600 µmol)		-3.58 ± 0.07 (n = 8)
Carbonate Standard 2 (K_2CO_3)	-26.8 ± 0.1 (n = 3)	
Standard 2 (~2000 µmol)		-26.67 ± 0.17 (n = 7)

2.2

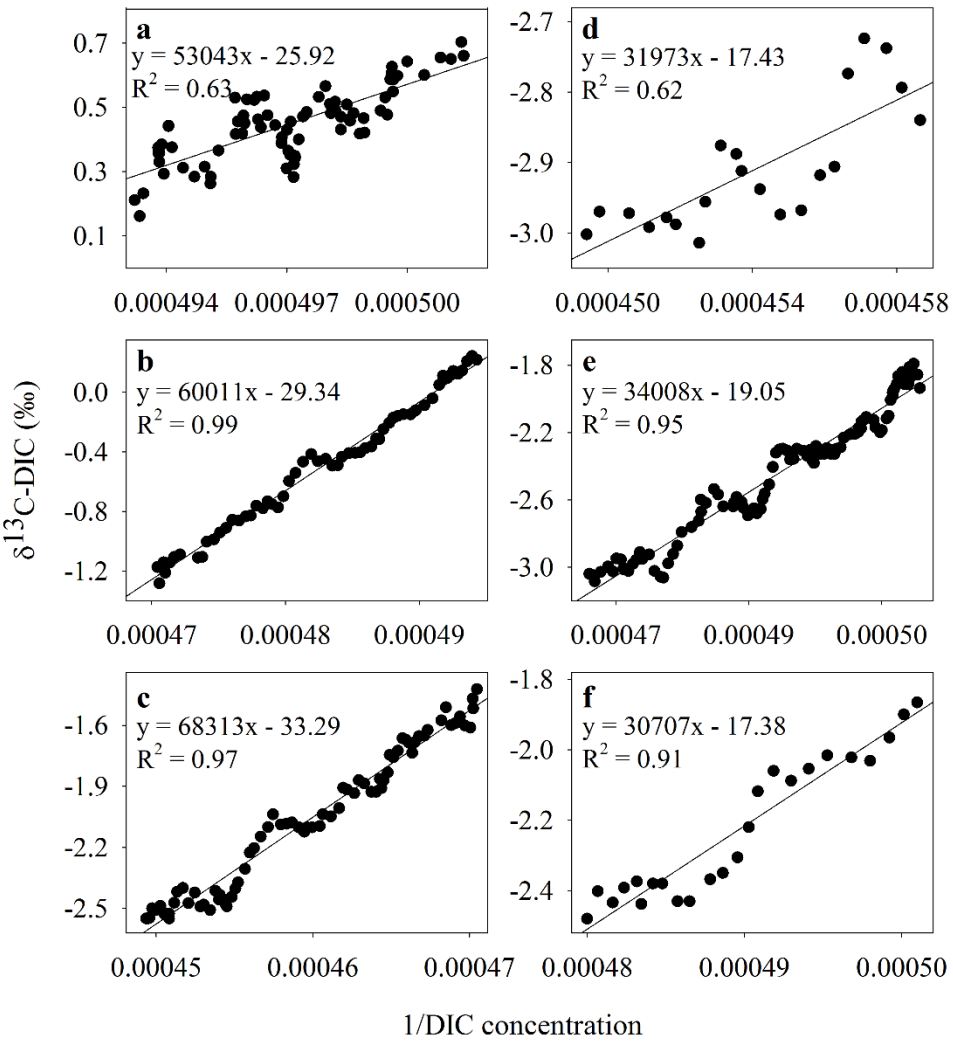

Figure S2. Regressions of 1/DIC concentration vs. δ^{13}C-DIC values (Keeling plots). Letters correspond with the linear increase/decrease in DIC concentrations shown in Figure 4.