Stanford University Stable Isotope Lab
On-line Manual
(Prepared by David A. Mucciarone)

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Section 1A: Finnigan MAT252 with Kiel III carbonate device

I) Operation Principles for $\delta^{18}O$, and $\delta^{13}C$ Analyses in carbonates:

Before you can operate the Finnigan MAT252 mass spectrometer, you must have training. Once trained, the following procedures will serve as an operational guide. The Kiel III carbonate device (KCIII) is connected to the MAT252 mass spectrometer changeover valve via a capillary. To get an understanding on how this process works, I will use calcium carbonate ($CaCO_3$) as an example and go from reaction of this material to mass spectrometer analysis. When $CaCO_3$ is reacted with purified phosphoric acid, at 70°C in our lab, CO_2 and H_20 gas are produced (Eq. 1).

$$2H_3PO_4 + 3CaCO_3 = 3CO_2 + 3H_20 + Ca_3(PO_4)_2 \qquad \text{(Eq. 1)}$$

The water is removed by a method called fractional freezing. Since water has a freezing temperature warmer than CO_2 the traps on the KCIII can heat or cool the trap as needed to control the transfer of CO_2. The KCIII works in the following manner (see Fig 1). The sample is acidified with two drops of purified phosphoric acid. Both CO_2 and H_2O are frozen into Trap 1 at -196°C. The reaction time is 470 seconds. At the end of the reaction, non-condensable gases are pumped away for 30 seconds. Trap 1 is then warmed to -115°C to keep the H_2O frozen but allows the CO_2 to evolve as a gas. Trap 2 is then cooled to -196°C to trap

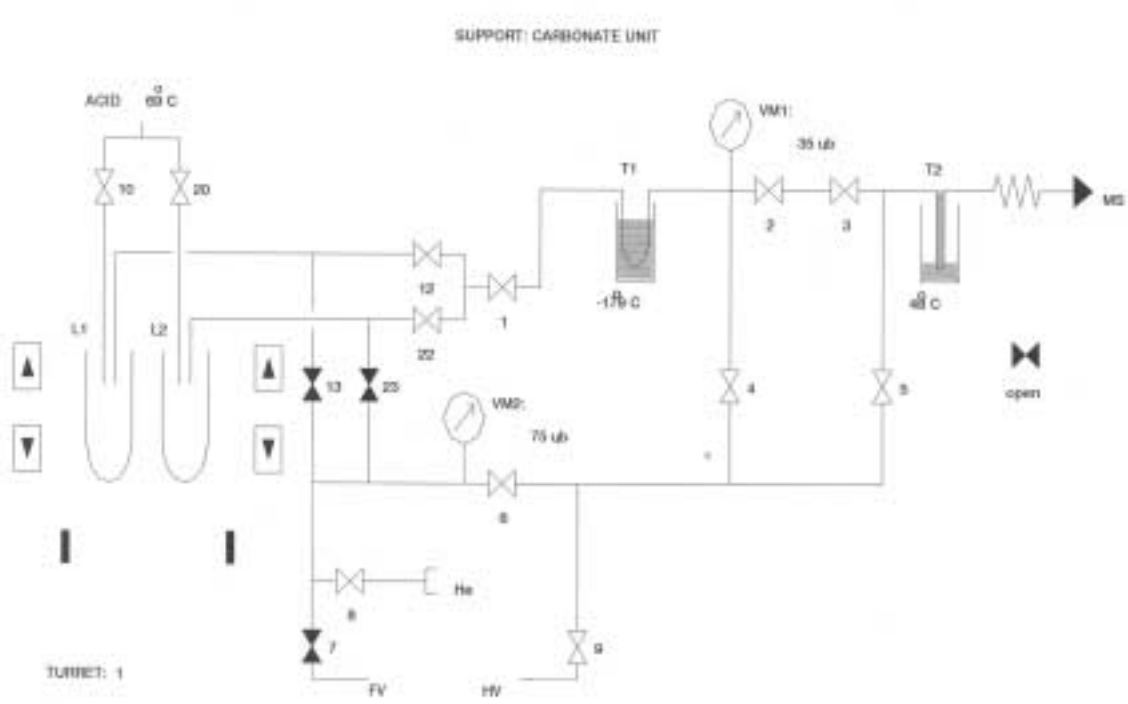

Figure 1: Schematic diagram of Kiel III carbonate device. The numbers denote valve identification, T1 and T2 represent Traps 1 and 2 respectively. HV represents high vacuum, which includes roughing and 60L turbo pump, FV is for fore vacuum which only has a roughing pump. Turret # indicates position of carousel. VM1 and 2 monitor vacuum integrity. MS indicates capillary attaching Kiel III carbonated device to changeover valve on the MAT252 mass spectrometer.

the CO_2 gas. After 120 seconds at -196°C, Trap 2 is isolated from Trap 1 by a series of valves. Trap 2 is then warmed to 30°C and the resulting CO_2 then travels down the capillary to the changeover valve.

Attached to the other side of the changeover valve is a capillary connected to the mass spectrometer inlet system (Fig 2). The inlet system is a symmetrical valve system composed of a reference and sample side where the valve volume and configuration are identical on both sides. Also equipped on

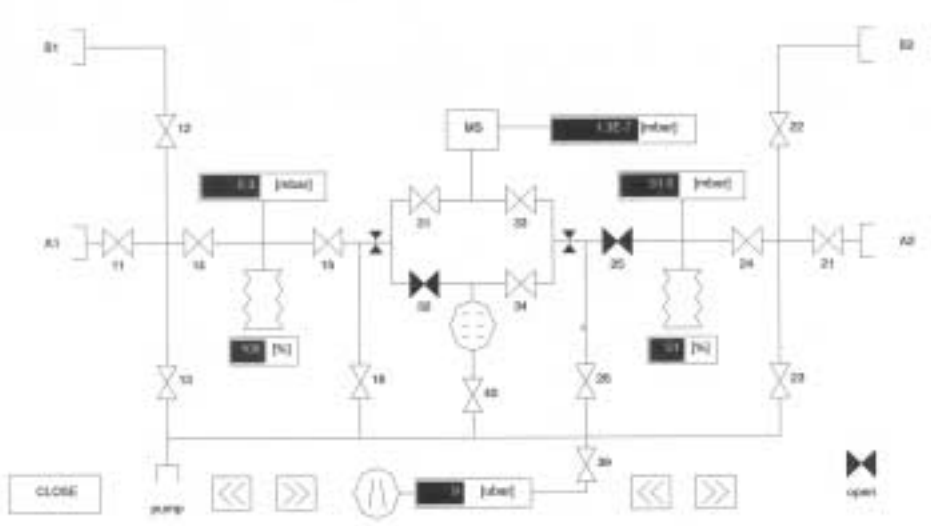

Figure 2: Schematic diagram of MAT252 inlet system. The numbers denote valve identification, valve numbers 31 - 34 represent the changeover valve. Volume of inlet bellows are indicated in %, inlet gas pressures are measured in mbar and roughing vacuum in µbar. MS indicates capillary attaching the inlet system to changeover valve on the MAT252 mass spectrometer.

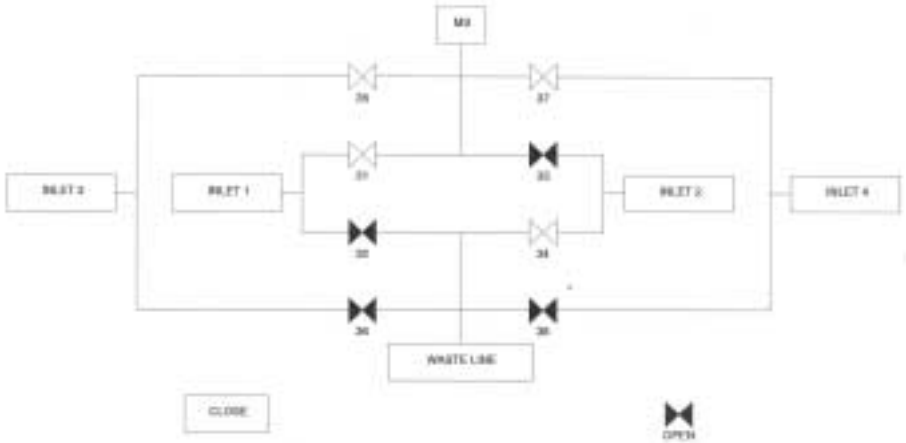

Figure 3: Schematic diagram of MAT252 changeover valve. Inlet 1 connects to the left side (sample) of inlet system, Inlet 2 connects to the right side (reference) of the inlet system, Inlet 3 connects to the Kiel III carbonate device, and Inlet 4 is a spare. MS indicates capillary attaching the inlet system to changeover valve on the MAT252 mass spectrometer.

the inlet system are variable reservoirs (flexible bellows) which allow for additional control of inlet gas pressures. A reference CO_2 gas (gas of known isotopic composition) is placed into the reference side of the inlet system for comparison with a known or unknown sample gas from the carbonate device. A series of standards of known isotopic composition are commonly run through the carbonate device to assure proper reference gas calibration and sampling protocol. The reference gas is a large quantity of gas that occupies the entire reference side of the inlet including the bellows. This gas will remain in the inlet throughout many known and unknown sample runs. In order to obtain useful isotopic data it is necessary to balance the pressure and volume of the known (reference gas) and unknown (sample from carbonate device) gas. This is done using the reference bellows and valves in the inlet system. Gas in the inlet system (Reference side) and carbonate device flow down capillaries and through changeover valves (Fig 3) into the ion source. These capillaries have an extremely small inside diameter. At the end of the capillaries are crimps, which are adjusted so that the flow and depletion rates of sample and reference CO_2 gas are identical. The crimps are also the transition point between low vacuum viscous ($< 10^{-4}$ Torr) and high vacuum molecular ($>10^{-4}$ Torr) gas flow. The capillaries are connected to a set of changeover valves that control the input of the inlet gases allowing for only one gas to be analyzed at a time.

Once the gas passes through the changeover valves it enter the source through an inlet probe (not to be confused with the inlet system) which simply directs the gas flow directly into the source block, more precisely the ionization chamber (see Fig 4). The gas flow in the ion source is always molecular. Attached to the source block are the filament (cathode), trap, ion extraction plates, and focusing plates (Fig. 5).

a) The filament (cathode), often tungsten, emits electrons in a helical orbit under the influence of small source magnets in which the CO_2 gas molecules collide with the electron beam making a CO_2^+ ion. The electron beam is at right angles to the ion trajectory.
b) The trap collects all electrons not involved in the collision with the CO_2, and is positioned opposite the filament.
c) The extraction plates accelerate ions out of the ionization chamber and direct the ions toward the exit slits and focusing plates. The accelerating voltage on the MAT252 is 10kV.

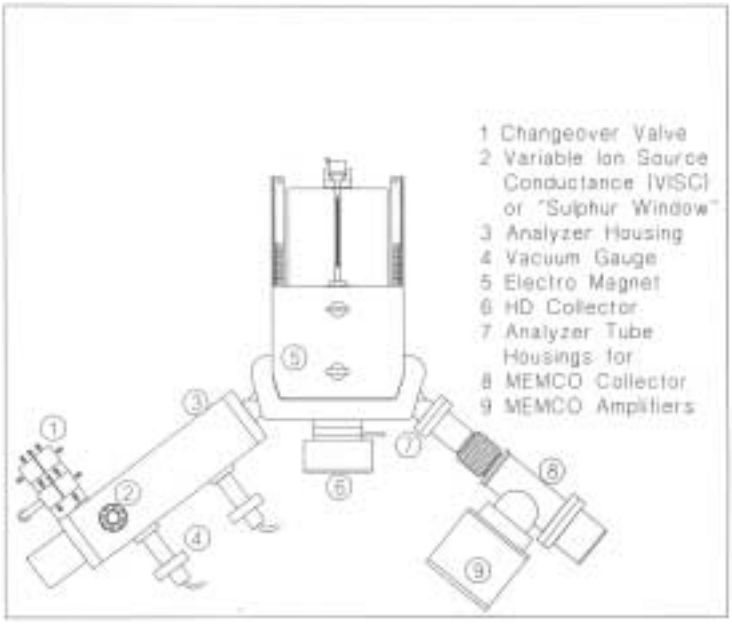

Figure 4: Schematic representation of the MAT252 analyzer system and the arrangement of components. Illustration is from the Finnigan operations manual.

d) There are a number of different focusing plates that are designed to progressively focus the ion beam leaving the source. The voltage is variable depending on the isotopic species being analyzed.
e) The final focusing plate defines the maximum beam width prior to passage into the flight tube.

The flight tube has a 90^{o} deflection path (Fig. 4) having a radius of R fitted with a permanent magnet of strength B . The MAT252 is equipped with an electromagnet with a maximum field strength of 0.77 Tesla providing a mass range up to 150 amu at full accelerating voltage. Therefore the radius is fixed and the magnet is variable but constant for any given gas species. At a constant accelerating voltage (V) and magnet strength, the lighter mass will be deflected (bend) more than the heavier mass. In the case of CO_2, mass 44 is bent more than 45 and 46. However, in order to analyze another gas such as N_2 or SO_2 with a fixed magnet, the accelerating voltage needs to increase or decrease, respectively or the accelerating voltage can remain the same and the magnetic field strength can be varied. Therefore, the relation of all these parameters is given as:

$$m/z = K * H^2$$

Where: m/z is the mass to charge ratio
$K = R^2/2U$ = constant
H is the magnet strength
R is the Radius of flight tube
U is the acceleration voltage

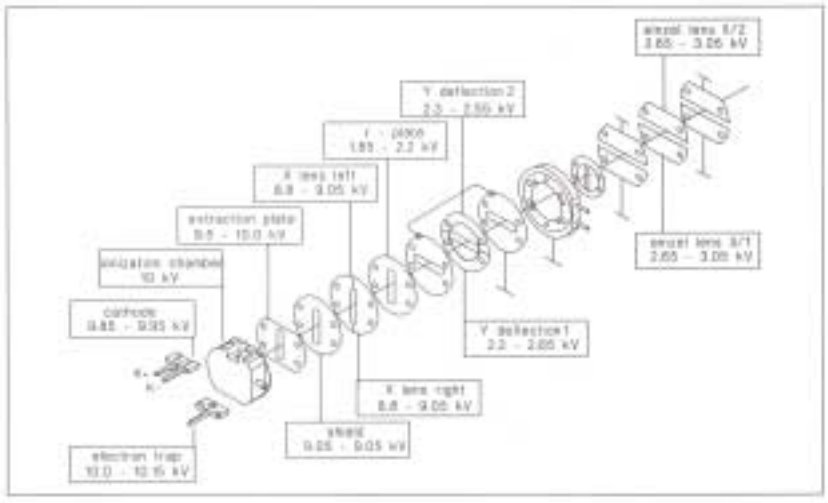

Figure 5: Schematic of MAT252 ion source. Values are ion source potential in relation to ground at 10kV ion acceleration voltage.

After leaving the flight tube, the separate ion beams of different masses are directed into 2 (1 major and 1 minor) or 3 (1 major and 2 minor) collectors (Faraday cups) depending on the type of mass spectrometer (Fig. 6). These cups are grounded through high ohm resistors. As the ion current passes to ground the drop in the resistor acts as a measure of the ion current. There are two types of collectors, major and minor. The major collector is larger and less sensitive than the minor collector. These collectors can either be fixed to a correct spacing for a particular set of masses or adjustable. In the case of CO_2, a triple collector mass spectrometer can detect all three masses (44-major, 45-minor, and 46-minor) and calculate $\delta^{18}O$ and $\delta^{13}C$ in one run. On a double collector with CO_2 the accelerating voltage is changed to direct the appropriate masses into the 2 collectors in order to calculate $\delta^{18}O$ and $\delta^{13}C$ (44-major, 45-minor for $\delta^{13}C$, 44 & 45-major, 46-minor for $\delta^{18}O$).

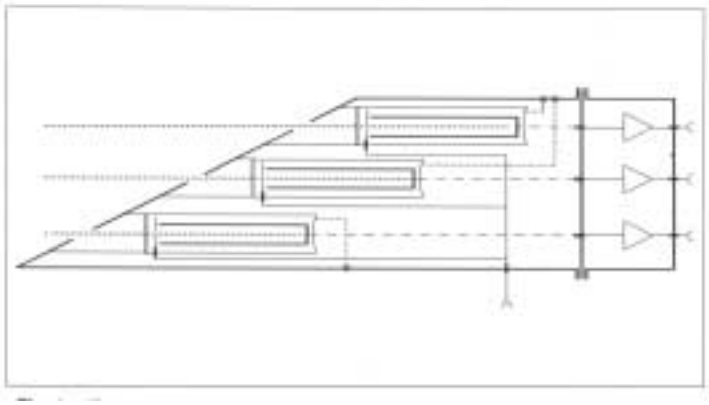

Figure 6: Schematic representation of faraday cup (collectors) on the MAT252.

The signals received by the collectors are amplified and transferred to voltage to frequency converters (VFC) on a system control board in a microprocessor. This system board basically digitizes the analog signal for processing by an interfaced computer. The analog and digital output is then sent to disk and a printer. In the course of one analysis for $\delta^{18}O$ and $\delta^{13}C$ on the MAT252 mass spectrometer, 8 reference/sample/reference sets (8 traces or 24 changeover valve cycles) are analyzed. All of the data are expressed in conventional delta (δ) notation, where the isotopic ratios of $\delta^{18}O$ /$\delta^{16}O$ and $\delta^{13}C/\delta^{12}C$ are relative to the international PDB standard (Eq. 2) as defined by:

$$\delta\ ^{o}/_{oo} = [(Ratio_{sample} - Ratio_{standard})/(Ratio_{standard})] \times 1000 \qquad \text{(Eq. 2)}$$

PDB refers to a Cretaceous belemnite called *Belemnitella americana* from the Peedee formation in South Carolina and is defined as 0 for both $\delta^{13}C$ and $\delta^{18}O$ and has been exhausted (however, there may me a few labs that still have a small quantity remaining). The carbonate standard NBS-19 or TS limestone (NBS is an acronym for the National Bureau of Standards which was replaced by NIST) is presently a substitute for PDB and has been given a fixed isotopic value for $\delta^{13}C$ of 1.95$^{o}/_{oo}$ and for ^{d18}O of -2.2$^{o}/_{oo}$. Many laboratories use internationally known standards such as NBS-19 obtained from facilities such as the National Institute of Standards and Technologies (NIST) or from the International Atomic Energy Agency (IAEA) to calibrate their instruments and reference gases. To reduce the possibility of exhausting these international standards, laboratories establish working standards that have been calibrated against various known standards and with other laboratories, to use routinely in the laboratory.

Although PDB is always used for reporting $\delta^{13}C$ results, in addition to PDB, the term SMOW is also used when referring to $\delta^{18}O$ in carbonates and water. SMOW is and acronym for Standard Mean Ocean Water introduced by H. Craig (1961b). Like PDB, SMOW is defined as 0 for $\delta^{18}O$, however, SMOW does not equal PDB. To convert PDB to SMOW or vice versa Friedman and O'Neil (1977) generated the following equations.

$$\delta^{18}O_{(SMOW)} = 1.03091(\delta^{18}O_{(PDB)}) + 30.91 \qquad \text{(Eq. 3)}$$

or

$$\delta^{18}O_{(PDB)} = 0.97002(\delta^{18}O_{(SMOW)}) + 29.98 \qquad \text{(Eq. 4)}$$

You may also find this standard referred to as Vienna-Standard Mean Ocean Water or V-SMOW which was prepared by H. Craig for the IAEA in Vienna, Austria (Hoefs, 1980). Two other water standards used are SLAP (Standard Light Antarctic Precipitation) which was introduced by Gonfiantini in 1976

(Gonfiantini, 1978) for the IAEA, and GISP (Greenland Ice Sheet Precipitation) which was prepared by W. Dansgaard. Listed in Table 1 are the isotopic compositions of commonly used standards, most of these can be obtained from the National Institute of Standards and Technology (NIST) in Gaithersburg, MD 20899-0001. For more information consult the reference list below.

Table 1: Isotopic compositions of standard reference materials.

Standard.	Description (‰)	$\delta^{18}O_{(PDB)}$(‰)	$\delta^{18}O_{(SMOW)}$(‰)	$\delta^{13}C_{(PDB)}$(‰)
PDB	Peedee belemnite	0.00		0.00
SMOW	Standard Mean Ocean Water		0.00	
NBS-1	Water		-7.86	
NBS-1A	Water		-24.21	
NBS-18	Carbonatite	-23.05		-5.04
NBS-19	TS limestone	-2.20	28.65	1.95
NBS-20	Solenhofen limestone	-4.18	26.64	-1.06
NBS-21	Graphite			-28.10
NBS-22	Oil			-29.63
SLAP	Standard Light Antarctic Precipitation		-55.50	
GISP	Greenland Ice Sheet Precipitation		-24.85	

II) References:

Coplen, T.B., C. Kendall, J. Hopple, 1983. Comparison of stable isotope reference samples, *Nature*, 302:236-238.

Craig, H., 1957. Isotopic standards for carbon and oxygen and correction factors for mass spectrographic analyses of carbon dioxide, *Geochim. Cosmochim. Ac*ta, 12:133-149.

Craig, H., 1961b. Standard for reporting concentrations of deuterium and oxygen-18 in natural waters, *Science*, 133:1833-1834.

Epstein, S., R. Buchsbaum, H. Lowenstam, and H.C. Urey, 1953. Carbonate-water isotopic temperature scale, *Geol. Soc. Am. Bull.*, 62:417-426.

Friedman, I., and J.R. O'Neil, 1977. Complation of stable isotope fractionation factors of geochemical interest, *in*: Data Geochem, 6th Ed U.S. Geol. Surv. Prof. Pap. 440-KK.

Gonfiantini, R., 1978. Standards for stable isotope measurements in natural compounds, *Nature*, 271:534-536.

Hoefs, J., 1980. Stable Isotope Geochemistry, Springer-Verlag, Berlin, 208p.

McCrea, J.M., 1950. On the isotopic chemistry of carbonates and a paleotemperature scale, *J. Chem. Phys*., 18:849-857.

Shama, T., and R.N. Clayton, 1965. Measurement of $^{18}O/^{16}O$ ratios in total oxygen of carbonates, *Geochim. Cosmochim. Ac*ta, 29:1347-1353.

Swart, P.K., S.J. Burns, and J.J. Leder, 1991. Fractionation of the stable isotopes of oxygen and carbon in carbon dioxide during the reaction of calcite with phosphoric acid as a function of temperature and technique, *Chem. Geology*, 86:89-96.

Walters Jr., L.J., G.E. Claypool, and P.W. Choquette, 1972. Reaction rates and d18O variation for the carbonate-phosphoric acid preparation method, *Geochim. Cosmochim. Ac*ta, 36:129-140.

Stanford University Stable Isotope Lab
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Section 1B: Finnigan MAT252/Kiel III Carbonate Device Operation

I) Run terminated without error (NORMAL)

1. Click on ALT-T (upper left screen). This will exit CNF-B, ACON-B
2. Click on CNF-B, SUPP-B. This will enter Kiel support screen
3. Click on TAKE MAG (F7). This will remove vials from ports (Fig. P1).
4. Lower and remove liquid nitrogen (LN_2) dewar and remove ice (Fig. P2). This is necessary if beginning a new run or if run terminated by error and was sitting many hours.
5. Remove carousel (Fig. P3). Be careful not to hit capillaries or drip counter.
6. Install new carousel (Fig. P3), again be careful not to hit the drip counters or capillaries.
7. Clean acid drip counter, and capillaries with 2-propanol (Fig. P4).
8. Clean o-rings on both ports with 2-propanol and then lightly grease o-rings with Apiezon L (Fig. P5).
9. Click on KBD INPUT (F5) Type P5 <Enter>, Click on KBD INPUT again Type P1 <Enter> this will reset the carousel.
10. If ice around cold traps has been removed and LN_2 is ready (*i.e.*, LS160 dewars and small blue dewar replaced and approximately 1" from top), click on T1 then click on analog temperature bar at approximately -170°C to -180°C. This will fill the blue LN_2 dewar. Remember as it begins to fill, approximately 1/2, bring the dewar snug to the cold trap plate.
11. If LN_2 is not ready, click on LOAD MAG (F6). This will load the vials on the ports (Fig. P6).
12. Click on CNF-B, EDIT-B, 2-SEQUENCE EDITOR. Prepare a new table by copying a previous sequence. **The filename should be in the format operators first and last initial followed by the date (*e.g.*, DM041902).** Enter new run information. Make sure that the reference refills (RR=120) are in the correct locations. When finished, save and exit Sequence Editor, then Click on ALT-T.
13. Return to CNF-B, SUPP-B, if acid temperature is at 69°C and LN_2 dewar is filled and cold trap is at the temperature you selected above then Click ALT-T.
14. Click on CNF-B, ACON-B, 2-SEQUENCE ACQ, Click on TABLE DIR (Shift F10),
    a. TABLE NAME: (*e.g.*, DM041702)
    b. START LINE: 1,
    c. END LINE: 46, make sure start and end line numbers are correct (*e.g.*, 1 and 46 for a full carousel run)
    d. MODE: DAY
    e. FILENAME: **should be as follows: Path D:\DATA\filename.WKS (Filename is 8 characters.WKS). The filename should have the format operators first initial, date, followed by a letter beginning with A ending with .WKS (e.g., D041702A.WKS).** Type in the path and filename then press <Enter> (*e.g.*, the line should read as follows D:\DATA\D041702A.WKS).
    f. LIST TYPE: FORMAT3 **(ONLY)**
    g. FILE TYPE: LOT
    h. SAVE DATA TO DATABASE: COL
15. Click SAVE to save sequence.
16. To transfer the run data from hard disk to floppy disk you Press Ctrl and 2 (from the number keypad). Using DOS (*i.e.*, CD\DATA and DIR and COPY) commands go to the directory D:\DATA and copy the file to floppy disk (*e.g.*, at prompt D:\DATA> Type COPY D041700A.WKS A:). Press Ctrl and 1 (from the number keypad) to return to ISODAT.
17. Click MEASURE to begin run. Make sure there is plenty of paper in printer to complete the run.

Stanford University Stable Isotope Laboratory Finnigan MAT252 mass spectrometer with 24 port manifold, and Kiel II carbonate device.

Stanford University MAT252/Kiel III Carbonate Device Operation

II) Run terminated with error

1. Click on ALT-T (upper left screen). This will exit CNF-B, ACON-B
2. Click on CNF-B, SUPP-B, 1-CARBONATE UNIT. This will enter Kiel support screen
3. Remove liquid nitrogen (LN_2) dewar and remove ice (Fig. P2). This is necessary if run was terminated by error and was sitting many hours.
4. If ice around cold traps has been removed and LN_2 is ready (*i.e.*, LS160 dewars and small blue dewar replaced and small blue dewar is approximately 1" from top), click on T1 then click on analog temperature bar at approximately -170°C to -180°C. This will fill the blue LN_2 dewar. Remember as it begins to fill, approximately 1/2, bring the and small blue dewar snug to the cold trap plate.
5. Click on CNF-B, EDIT-B, 2-SEQUENCE EDITOR. Select table that was terminated by error and add and/or delete reference refills (RR=120) and make sure that the RR=120 are in the correct locations. When finished, save and exit Sequence Editor, then Click on ALT-T.
6. Return to CNF-B, SUPP-B, if acid temperature is at 69°C and LN_2 dewar is filled and cold trap is at the temperature you selected above then Click ALT-T
7. Click on CNF-B, ACON-B, 2-SEQUENCE ACQ, Click on TABLE DIR (Shift F10),
   a. TABLE NAME: reselect the correct table name (*e.g.*, DM041702)
   b. START LINE: begin where the error took place
   c. END LINE: 46 if for a full carousel run
   d. MODE: NIGHT
   e. FILENAME: should be as follows: **Path D:\DATA\filename.WKS (Filename is 8 characters.WKS). The filename should have the format, operators first initial, date, followed by a next letter in the sequence after the original that began A and followed by .WKS (*e.g.*, D041702B.WKS).** Type in the path and filename then press <Enter> (*e.g.*, the line should read as follows D:\DATA\D041702B.WKS).
   f. LIST TYPE: FORMAT3 **(ONLY)**
   g. FILE TYPE: LOT
   h. SAVE DATA TO DATABASE: COL
8. Click SAVE to save sequence. Make sure there is plenty of paper in printer to complete the run.
9. To transfer the run data from hard disk to floppy disk you Press Ctrl and 2 (from the number keypad. Using DOS (*i.e.*, CD\DATA and DIR and COPY) commands go to the directory D:\DATA and copy the file to floppy disk (*e.g.*, at prompt D:\DATA> Type COPY D041702A.WKS A: or COPY D041702*.*: A to copy all associated files). Press Ctrl and 1 (from keypad) to return to ISODAT.
10. Click MEASURE to begin run.

Stanford University MAT252/Kiel III Carbonate Device Operation

III) Run interrupted by error

1) PART 1: Able to escape out of error

A. If a gray window with at red bar will be displayed on the screen obstructing the normal display. Locate the source of the error (*e.g.*, high voltage out). Fix error then attempt to press ESC. If the error display disappears and the instrument appears to be working watch it carefully because it may actually be hung up and just going through the motions. It is best to just press TERMINATE and allow the sample that is in acquisition to finish. If the error appeared a short time ago it is just a simple matter of restarting the sequence as follows

1. Click on ALT-T (upper left screen). This will exit CNF-B, ACON-B.
2. Click on CNF-B, ACON-B, 2-SEQUENCE ACQ, Click on TABLE DIR (Shift F10),
   a. TABLE NAME: reselect the correct table name (*e.g.*, DM041702).
   b. START LINE: begin where the error took place.
   c. END LINE: 46 if for a full carousel run).
   d. MODE: DAY
   e. FILENAME: should be as follows: **Path D:\DATA\filename.WKS (Filename is 8 characters.WKS). The filename should have the format, operators first initial, date, followed by a next letter in the sequence after the original that began A and followed by .WKS (*e.g.*, D041702B.WKS).** Type in the path and filename then press <Enter> (*e.g.*, the line should read as follows D:\DATA\D041702B.WKS).
   f. LIST TYPE: FORMAT3 **(ONLY)**
   g. FILE TYPE: LOT
   h. SAVE DATA to database: COL
3. Click SAVE to save sequence. Make sure there is plenty of paper in printer to complete the run.
4. Click MEASURE to begin run.
5. If you were able to escape from the error or the run was able to continue the data was saved to the database (called ISOBASE) and to the filename you created. On the other hand, if you were not able to escape and had to refer to Part 2 of this section then the data was only saved to the database and not to the file you created in the SEQUENCE ACQ screen. This file will only have 128K. You will need to review the recover data section (IV) for instructions on how to obtain the run data.

Stanford University MAT252/Kiel III Carbonate Device Operation

2) PART 2: Unable to escape out or error

A. If a gray window with at red bar will be displayed on the screen obstructing the normal display. If after looking for the fault and do not see one then attempt to press ESC. If the error display does not disappear to the point where the screen freezes then you will have to reboot the computer by following the reboot sequence.

1. Press Ctrl, Alt, Del to reboot computer.
2. At the Load Real/32 prompt, Type N <Enter> this will load Win95
3. At login prompt, Type sil <OK>
4. Click on Scan Disk (on desktop). Let the program delete any fragments - DO NOT FIX THEM, just delete them.
5. Restart the computer using the START button
6. At the Load Real/32 prompt, Type Y <Enter> this will load ISODAT v7.2 allow the microprocessor to reset before doing anything (message is displayed at top of screen).

B. Continue as follows to prepare the run:

1. Click on CNF-B, SUPP-B, 1-CARBONATE UNIT. This will enter Kiel support screen.
2. Depending on where the carousel stopped rotating (check to see its present position) you will have to enter this value because the **Turret position will default to 0 (zero)**. This must be reset. (*e.g.*, the carousel failed at position 5. Using KBD INPUT Type P5, then Type P1. The carousel will not rotate at the first input but will rotate to position 1 on the second. If the carousel failed at position 1 then you only need to Type P1, the carousel will not rotate but the turret will be reset.
3. Remove liquid nitrogen (LN_2) dewar and remove ice. This is necessary if run was terminated by error and was sitting many hours (Fig. P2).
4. If ice around cold traps has been removed and LN_2 is ready (*i.e.*, LS160 dewars and small blue dewar replaced and small blue dewar is approximately 1" from top) Click on T1 then Click on analog temperature bar at approximately -170°C to -180°C. This will fill the blue LN_2 dewar. Remember as it begins to fill, approximately 1/2, bring the and small blue dewar snug to the cold trap plate.
5. Click on CNF-B, EDIT-B, 2-SEQUENCE EDITOR. Select table that was terminated by error and add and/or delete reference refills (RR=120) and make sure that the RR=120 are in the correct locations. When finished, save and exit Sequence Editor, then Click on ALT-T.
6. Return to CNF-B, SUPP-B, if acid temperature is at 69°C or 70°C and LN_2 dewar is filled and cold trap is at the temperature you selected above then Click ALT-T

Stanford University MAT252/Kiel III Carbonate Device Operation

2) PART 2: Unable to escape out or error (CONTINUED)

7. Click on CNF-B, ACON-B, 2-SEQUENCE ACQ, Click on TABLE DIR (Shift F10),
   a. TABLE NAME: reselect the correct table name (*e.g.*, DM041702).
   b. START LINE: begin where the error took place.
   c. END LINE: 46 if for a full carousel run).
   d. MODE: DAY
   e. FILENAME: should be as follows: **Path D:\DATA\filename.WKS (Filename is 8 characters.WKS). The filename should have the format, operators first initial, date, followed by a next letter in the sequence after the original that began A and followed by .WKS (*e.g.*, D041702B.WKS).** Type in the path and filename then press <Enter> (*e.g.*, the line should read as follows D:\DATA\D041702B.WKS).
   f. LIST TYPE: FORMAT3 **(ONLY)**
   g. FILE TYPE: LOT
   h. SAVE DATA to database: COL
8. Click SAVE to save sequence. Make sure there is plenty of paper in printer to complete the run.
9. You need to remember that when a run is terminated by error in this way the data is saved to the database (called Isobase) only and not to the file you created in the SEQUENCE ACQ screen. This file will only have 128K. You will need to review the recover data section (IV) for instructions on how to obtain the run data.
10. Click MEASURE to begin run.

Stanford University MAT252/Kiel III Carbonate Device Operation

IV) Recover run data from database

1. Click on CNF-A, EVAL-A, 1-OFF LINE
2. (6) SEQUENCE NAME: (*e.g.*, DM041702) Search by sequence name of run.
3. Click on DIRECTORY (Shift F5).
4. Click on TAG ALL (F5) if all of the runs need to be transferred to disk or use TAG (F6) to select the runs needed to be transferred.
5. Click on FORMAT (F8) and then enter the following exactly:
   a. OUTLIER TEST: D2
   b. STANDARD IDENT: SIL#2
   c. LIST TYPE: NO
   d. GRAPHICS: NO
   e. ALPHA (CO3) CORRECTION: YES
   f. ALPHA (H2O) CORRECTION: NO
   g. ATOM% / APE REPORT: NO
   h. FILENAME: D:\DATA\FILENAME.WKS (e.g., D041702A.WKS). **Make sure the filename you select will not overwrite data on the disk. The computer will not prompt you.**
   i. LIST TYPE: FORMAT3
   j. FILE TYPE: LOT
6. Click on EVALUATE (F7). This will begin the data transfer. Wait for the transfer to be complete before pressing ALT-T.
7. To transfer the run data you just transferred from hard disk to floppy disk you Press Ctrl and 2 (from the number keypad). Using DOS (*i.e.*, CD\DATA and DIR and COPY) commands go to the directory D:\DATA and copy the file to floppy disk (*e.g.*, at prompt D:\DATA> Type COPY D041702A.WKS A: or COPY D041702*.*: A to copy all associated files). Press Ctrl and 1 (from the number keypad) to return to ISODAT.

Stanford University MAT252/Kiel III Carbonate Device Operation

V) Acid Drip Test Procedure

1. Click on CNF-B, SUPP-B, 1-CARBONATE UNIT. This will enter the Kiel support screen.
2. Open acid valve 10 and 20. Both can be open at the same time. Allow each to drop 2 to 3 drops of acid per reaction vessel or let them go until they time out (approximately 15 drops). Do not leave this unattended because it is possible for the vials to fill and flood valve system if counter fails to work correctly.
3. Close acid valve 10 and 20.
4. Click on TAKE MAG. This will remove both reaction vessels. Wait for both vessels to be removed before proceeding to Step 5.
5. Click on LOAD MAG. This will automatically load both reaction vessels.
6. Finished.

Figure P1: Finnigan Kiel III carbonate device oven and carousel assembly outside (upper left photo) and inside (upper right photo). In order to service the ports or to replace the carousel (middle left photo) it is necessary to remove vials from Port 1 (middle right photo) and 2 (bottom left photo). Once both vials are removed (bottom right photo) you can service ports.

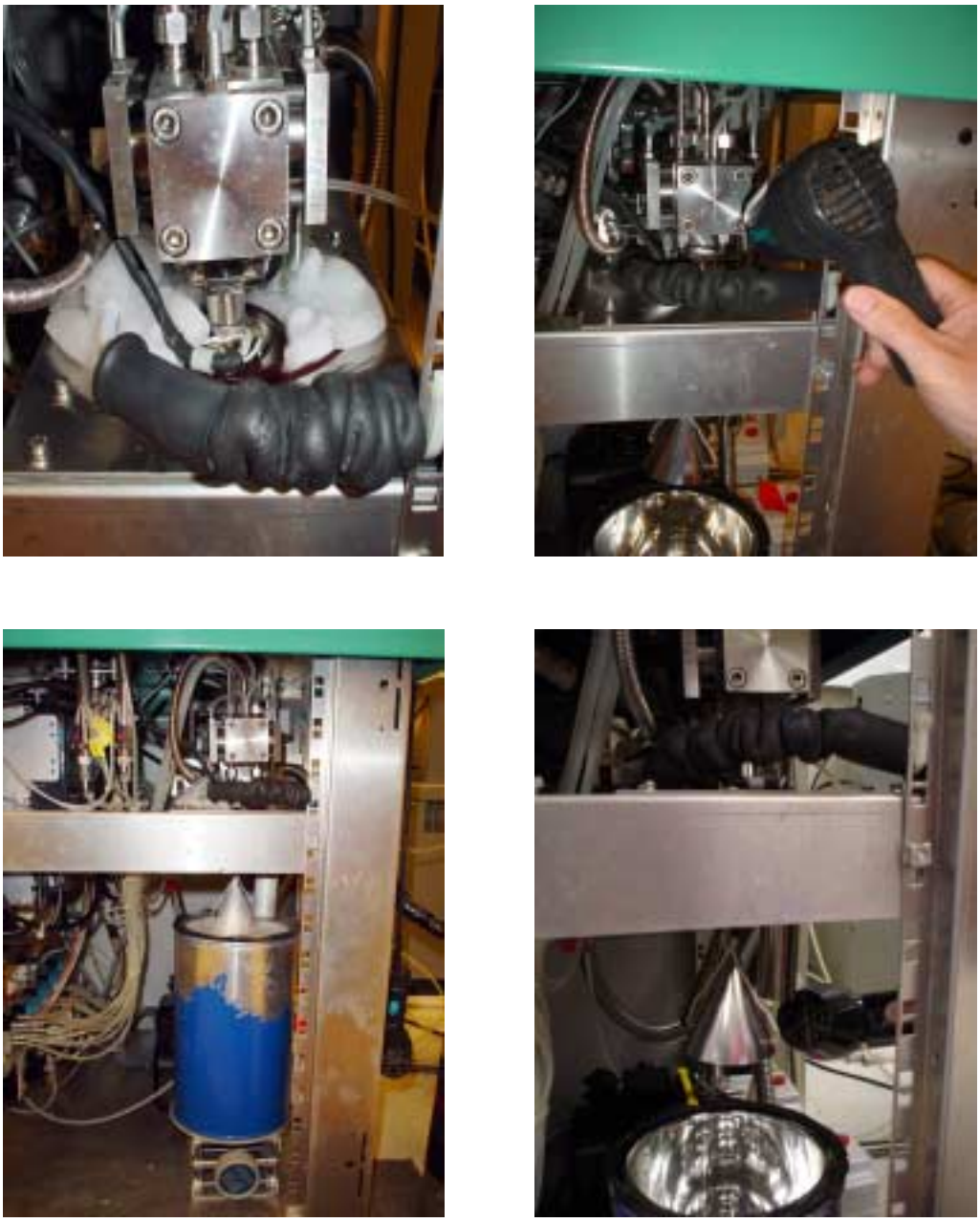

Figure P2: Removing ice build up on the Finnigan Kiel III cold finger assembly. It is normal for ice to build up around the cold finger valve assembly (top left photo) but too much ice can cause problems and damage. Lower jack-stand to expose cold finger assembly (bottom left photo) and then remove LN_2 dewar. Use the blow dryer to expedite removal of ice around the top (top right photo) and around the bottom of the cold finger assembly (bottom right photo), do not pry or force the removal of the ice this could damage components of the entire assembly.

Figure P3: Removing and installing the sample carousel on the Finnigan Kiel III. To remove, carefully lift the carousel to free the shaft from the pivot base (left photo). Slide carousel out without touching the capillaries, counters, or pistons with the carousel or vials. To install, taking the same precautions as above, carefully slide the carousel in and gently place the carousel shaft onto the pivot base (middle photo). You will need to align the pin on the carousel shaft with the slot on the pivot base as well as the slot on the carousel top shroud with the vertical rod at the back of the unit (right photo).

Figure P4: Clean the acid drip counters and capillaries on both Port 1 (left photo) and Port 2 (right photo) using 2-propanol and a cotton swab. Extra care should be taken not to alter the alignment between the counter and capillary.

Figure P5: Servicing the o-rings on the Finnigan Kiel III ports. Clean both the o-rings and stainless steel areas around Ports 1 (upper left photo) and 2 (upper right photo) using 2-propanol and a cotton swab. Place a small portion of Apiezon L on your index finger and lightly grease Ports 1 (lower left photo) and 2 (lower right photo).

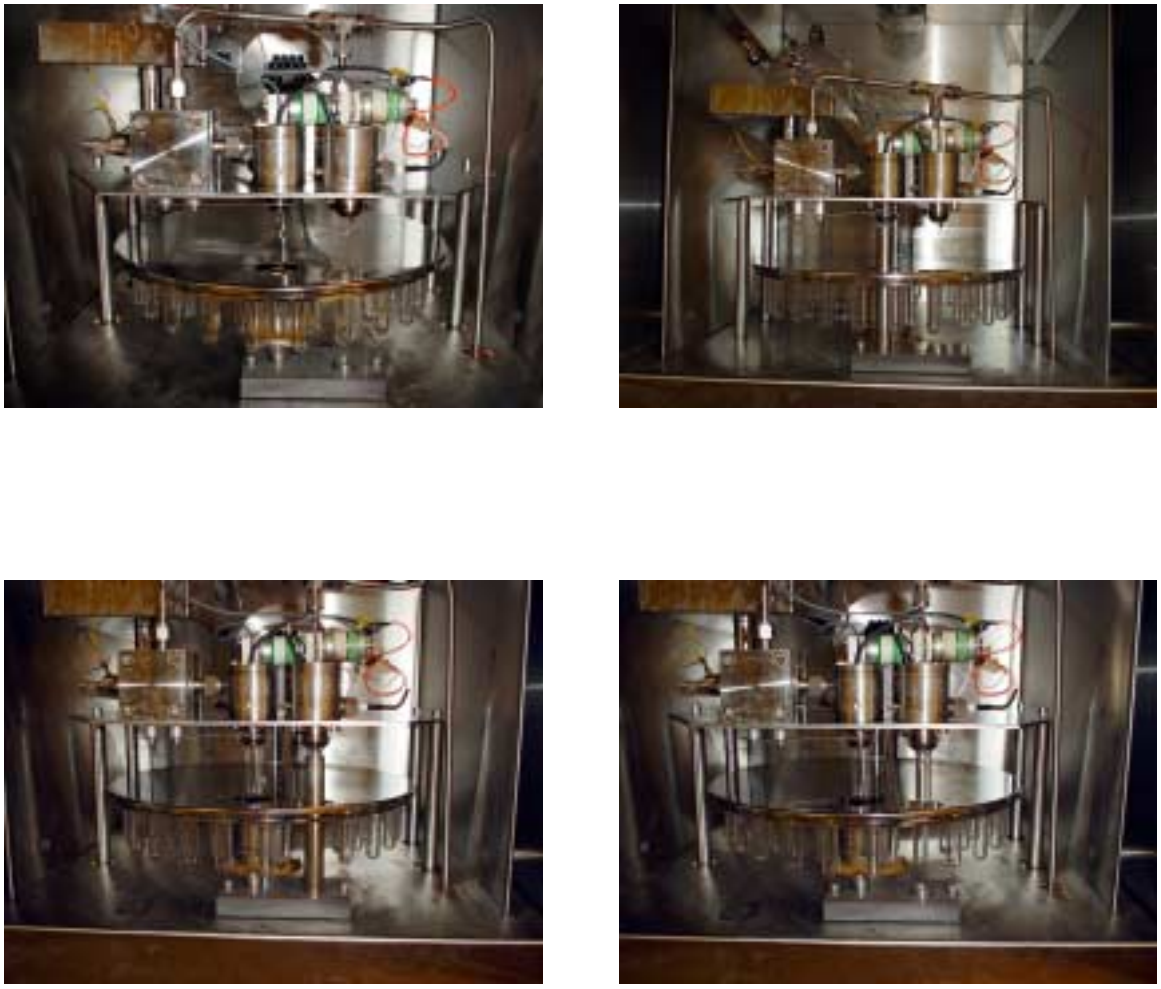

Figure P6: Reloading the sample vials after cleaning and greasing Ports 1 and 2 (top left to bottom right).

Stanford University Stable Isotope Lab
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Section 1C: Finnigan MAT252/24x Multiport Operation

I) Run terminated without error (NORMAL)

1. Click on ALT-T (upper left screen). This will exit CNF-A, ACON-A
2. Click on CNF-A, SUPP-A, and 2-MULTIPORT CTRL. This will enter multiport support screen.
3. Note fore vacuum baseline (Fig. P1) and open the following valves in order. Click on valves 39, 13, 12, and 14 (Fig. 1). Allow vacuum to regain baseline.
4. Prepare and order sample tubes to be loaded into tube cracker manifold. Using a file or Dremel Tool to score the glass in the middle of the sample tube (Fig. P2). Make sure the scoring goes completely around the sample tube.
5. Click on CNF-A, EDIT-A, 3-SEQUENCE EDITOR Prepare a new table by copying a previous sequence. **The filename should be in the format operators first and last initial followed by the date (*e.g.*, DM091702).** Enter new run information. Make sure that the reference refills (RR=120) are in the correct locations. When finished, press exit/save (F10) Sequence Editor, then Click on ALT-T.
6. Unloading/loading sample tubes in crackers (Fig. P3).
   a. Open the bottom of the crackers by loosening the Swagelok cap fitting on the bottom. This can be done by hand or with two 9/16" wrenches.
   b. Remove spent ampoules from crackers.
   c. Place scored ampoules into cracker and secure with Swagelok cap fitting. Tighten fitting by hand or use two 9/16" wrenches. Be careful not to over tighten the fitting.
7. Click on CNF-A, SUPP-A, and 2-MULTIPORT CTRL (Fig. 1).
   a. Click on the Bank1 (or Bank2) on the upper left of the screen until the correct bank is selected.
   b. Close valve 14.
   c. Click on BANK (F7) and type BOPEN <ENTER>. This will open all 12 ports to the selected bank including valve B. The atmospheric pressure in the crackers will exit through valves B, 12, 13, 39.

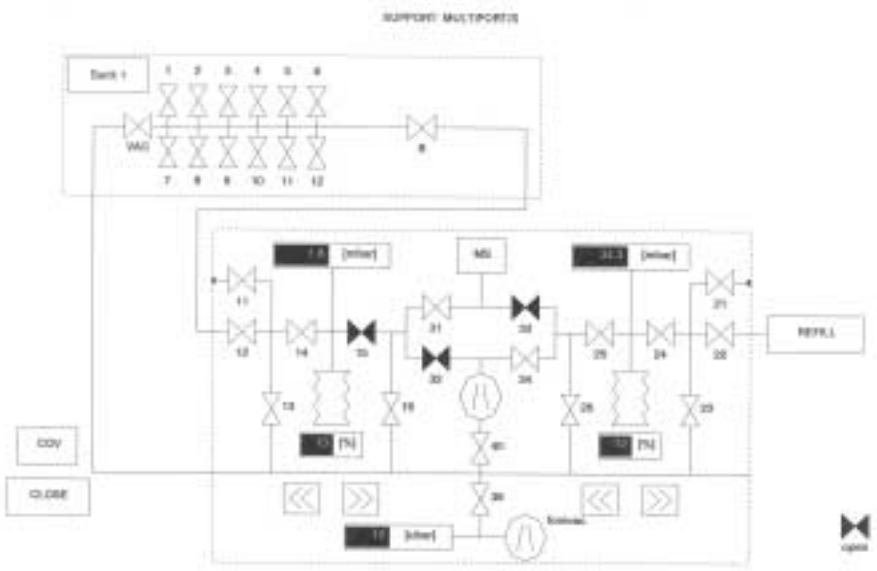

Figure1: Schematic representation of the MAT252 inlet system and multiport manifold.

8. Repeat Step 6a and 6c for the other bank.
9. Allow a minimum of 15 minutes for the crackers to evacuate before starting the run. This can be monitored from the inlet screen display on CNF-A, SUPP-A, and 2-MULTIPORT CTRL.
10. Click on CNF-A, ACON-A, 2-SEQUENCE ACQ, Click on TABLE DIR (Shift F10),
    a. TABLE NAME: (*e.g.*, DM091702)
    b. START LINE: 1,
    c. END LINE: 12, make sure start and end line numbers are correct (*e.g.*, 1 and 12 for a full bank; 1 and 24 for both banks)
    d. MODE: DAY
    e. FILENAME: **should be as follows: Path D:\DATA\filename.WKS (Filename is 8 characters.WKS). The filename should have the format operators first initial, date, followed by a letter beginning with A ending with .WKS (e.g., D091702A.WKS).** Type in the path and filename then press <Enter> (*e.g.*, the line should read as follows D:\DATA\D091702A.WKS).
    f. LIST TYPE: FORMAT1 **(ONLY)**
    g. FILE TYPE: LOT
    h. SAVE DATA TO DATABASE: COL
10. Click SAVE (F9) to save sequence
11. To transfer the run data from hard disk to floppy disk you Press Ctrl and 2 (from the number keypad). Using DOS (*i.e.*, CD\DATA and DIR and COPY) commands go to the directory D:\DATA and copy the file to floppy disk (*e.g.*, at prompt D:\DATA> Type COPY D091702A.WKS A:). Press Ctrl and 1 (from the number keypad) to return to ISODAT.
12. Click MEASURE (F5) to begin run. Make sure there is plenty of paper in printer to complete the run.
13. When the run display has refreshed (i.e., updated screen display), you can crack all sample tubes (Fig. 4). Try and do this in an orderly manner so you do not miss any tubes.
14. It takes approximately 4 hours to run one bank of samples. Two complete runs (4 banks) can easily be run in a day. To accomplish this you will need to have your samples prepared in advance.

Stanford University Stable Isotope Laboratory Finnigan MAT252 mass spectrometer with dual inlet and 24 port manifold.

Stanford University MAT252/24x Multiport Operation

II) Run terminated with error

1. Click on ALT-T (upper left screen). This will exit CNF-A, ACON-A
2. Determine source of the problem and fix. When problem is resolved begin run where it was terminated.
3. Click on CNF-A, ACON-A, 2-SEQUENCE ACQ, Click on TABLE DIR (Shift F10),
   a. TABLE NAME: reselect the correct table name (*e.g.*, DM091701).
   b. START LINE: begin where the error took place.
   c. END LINE: 24 if both banks are being run (12 if only 1 bank)
   d. MODE: DAY
   e. FILENAME: should be as follows: **Path D:\DATA\filename.WKS (Filename is 8 characters.WKS). The filename should have the format, operators first initial, date, followed by a next letter in the sequence after the original that began A and followed by .WKS (*e.g.*, D091702B.WKS).** Type in the path and filename then press <Enter> (*e.g.*, the line should read as follows D:\DATA\D091702B.WKS).
   e. D:\DATA\D091700B.WKS).
   f. LIST TYPE: FORMAT1 **(ONLY).**
   G. FILE TYPE: LOT
   H. SAVE DATA TO DATABASE: COL
4. Click SAVE (F9) to save sequence. Make sure there is plenty of paper in printer to complete the run.
8. To transfer the run data from hard disk to floppy disk you Press Ctrl and 2 (from the number keypad. Using DOS (*i.e.*, CD\DATA and DIR and COPY) commands go to the directory D:\DATA and copy the file to floppy disk (*e.g.*, at prompt D:\DATA> Type COPY D091702A.WKS A: or COPY D091702*.*: A to copy all associated files). Press Ctrl and 1 (from keypad) to return to ISODAT.
5. Click MEASURE (F5) to begin run.

Stanford University MAT252/24x Multiport Operation

III) Run interrupted by error

1) PART 1: Able to escape out or error

A. If a gray window with at red bar will be displayed on the screen obstructing the normal display. Locate the source of the error (*e.g.*, high voltage out). Fix error then attempt to press ESC. If the error display disappears and the instrument appears to be working watch it carefully because it may actually be hung up and just going through the motions. It is best to just press ALT-T to terminate the run. If the error appeared a short time ago it is just a simple matter of restarting the sequence as follows

1. Click on ALT-T (upper left screen). This will exit CNF-A, ACON-A
2. Click on CNF-A, ACON-A, 2-SEQUENCE ACQ, Click on TABLE DIR (Shift F10)
   a. Table name: reselect the correct table name (*e.g.*, DM091701).
   b. Start Line: begin where the error took place.
   c. End Line: 24 if both banks are being run (12 if only 1 bank).
   d. Mode: DAY
   e. Filename: should be as follows: Path D:\DATA\filename.WKS (Filename is 8 **characters.WKS). The filename should have the format, operators first initial, date, followed by a next letter in the sequence after the original that began A and followed by .WKS (*e.g.*, D091702B.WKS).** Type in the path and filename then press <Enter> (*e.g.*, the line should read as follows D:\DATA\D091702B.WKS).
   f. List Type: FORMAT1 **(ONLY)**
   g. File TYPE: LOT
   h. Save DATA to database: COL
3. Click SAVE (F9) to save sequence. Make sure there is plenty of paper in printer to complete run..
4. Click MEASURE to begin run.
5. If you were able to escape from the error or the run was able to continue the data was saved to the database (called ISOBASE) and to the filename you created. On the other hand, if you were not able to escape and had to refer to Part 2 of this section then the data was only saved to the database and not to the file you created in the SEQUENCE ACQ screen. This file will only have 128K. You will need to review the recover data section (IV) for instructions on how to obtain the run data.

Stanford University MAT252/24x Multiport Operation

2) PART 2: Unable to escape out or error

A. If a gray window with at red bar will be displayed on the screen obstructing the normal display. If after looking for the fault and do not see one then attempt to press ESC. If the error display does not disappear to the point where the screen freezes then you will have to reboot the computer by following the reboot sequence.

1. Press Ctrl, Alt, Del to reboot computer.
2. At the Load Real/32 prompt, Type N <Enter> this will load Win95
3. At login prompt, Type sil <OK>
4. Click on Scan Disk (on desktop). Let the program delete any fragments - DO NOT FIX THEM, just delete them.
5. Restart the computer using the START button.
6. At the Load Real/32 prompt, Type Y <Enter> this will load ISODAT v7.2 allow the microprocessor to reset before doing anything (message is displayed at top of screen).

B. Continue as follows to prepare the run:

1. Click on ALT-T (upper left screen). This will exit CNF-A, ACON-A
2. Click on CNF-A, ACON-A, 2-SEQUENCE ACQ, Click on TABLE DIR (Shift F10)
   a. TABLE NAME: reselect the correct table name (*e.g.*, DM091701).
   b. START LINE: begin where the error took place.
   c. END LINE: 24 if both banks are being run (12 if only 1 bank).
   d. MODE: DAY.
   e. FILENAME: should be as follows: **Path D:\DATA\filename.WKS (Filename is 8 characters.WKS). The filename should have the format, operators first initial, date, followed by a next letter in the sequence after the original that began A and followed by .WKS (*e.g.*, D091702B.WKS).** Type in the path and filename then press <Enter> (*e.g.*, the line should read as follows D:\DATA\D091702B.WKS).
   f. List Type: FORMAT1 **(ONLY)**
   g. FILE TYPE: LOT
   h. SAVE DATA to database: COL
3. Click SAVE (F9) to save sequence. Make sure there is plenty of paper in printer to complete the run.
4. You need to remember that when a run is terminated by error in this way the data is saved to the database (called Isobase) only and not to the file you created in the SEQUENCE ACQ screen. This file will only have 128K. You will need to review the recover data section (IV) for instructions on how to obtain the run data.
5. Click MEASURE to begin run.

Stanford University MAT252/24x Multiport Operation

IV) Recover run data from database

1. Click on CNF-A, EVAL-A, 1-OFF LINE
2. (6) SEQUENCE NAME: (*e.g.*, DM091701) Search by sequence name of run.
3. Click on DIRECTORY (Shift F5)
4. Click on TAG ALL (F5) if all of the runs need to be transferred to disk or use TAG (F6) to select the runs needed to be transferred.
5. Click on FORMAT (F8) and then enter the following exactly:
   a. OUTLIER TEST: D2
   b. STANDARD IDENT: SIL#2
   c. LIST TYPE: NO
   d. GRAPHICS: NO
   e. ALPHA (CO3) CORRECTION: NO
   f. ALPHA (H2O) CORRECTION: NO
   g. ATOM% / APE REPORT: NO
   h. FILENAME: D:\DATA\FILENAME.WKS (e.g., D041700A.WKS). **Make sure the filename you select will not overwrite data on the disk. The computer will not prompt you.**
   i. LIST TYPE: FORMAT1
   j. FILE TYPE: LOT
6. Click on EVALUATE (F7). This will begin the data transfer. Wait for the transfer to be complete before pressing ALT-T.
7. To transfer the run data you just transferred from hard disk to floppy disk you Press Ctrl and 2 (from the number keypad). Using DOS (*i.e.*, CD\DATA and DIR and COPY) commands go to the directory D:\DATA and copy the file to floppy disk (*e.g.*, at prompt D:\DATA> Type COPY D091702A.WKS A: or COPY D091702*.*: A to copy all associated files). Press Ctrl and 1 (from the number keypad) to return to ISODAT.

Figure P1: Perform a fore vacuum check by pressing the black FV Inlet button on the far right and monitor by reading the lower green bar (left photo). When finished press the black HV source button on the far right and monitor by reading the upper red bar (right photo).

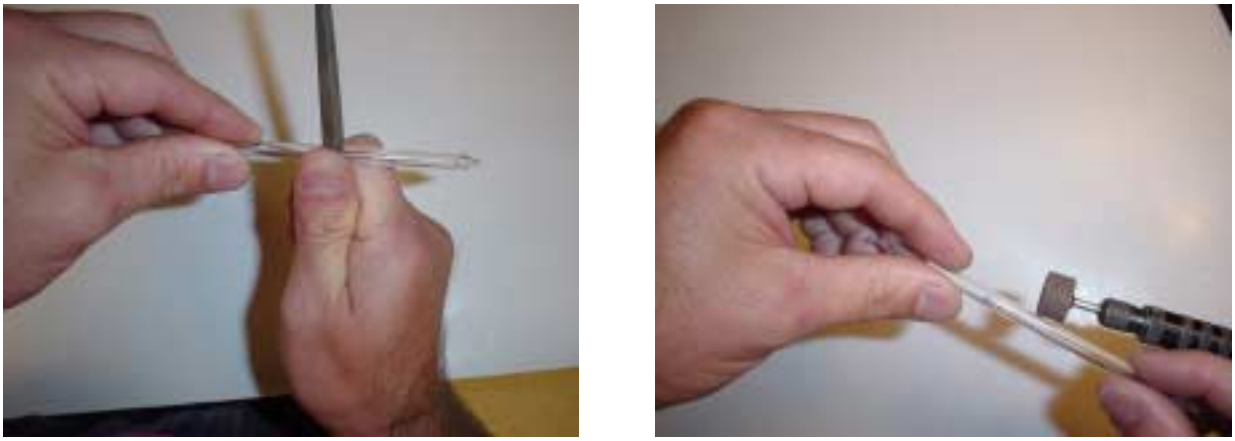

Figure P2: Scoring sample tubes using file (left photo) or the Dremel Tool. With either technique it is necessary to make a score completely around the glass sample tube. Also, care should be taken not to break the glass sample tube or cutting your hand. With the file technique (left photo) apply enough pressure with your thumb to allow the file to cut into the glass while also allowing you to rotate the sample tube with the opposite hand. When using the Dremel Tool (right photo) set the Variac controller on 20 to 25 (out of 100), press the sample tube against grinding wheel and rotate making a score completely around the sample tube.

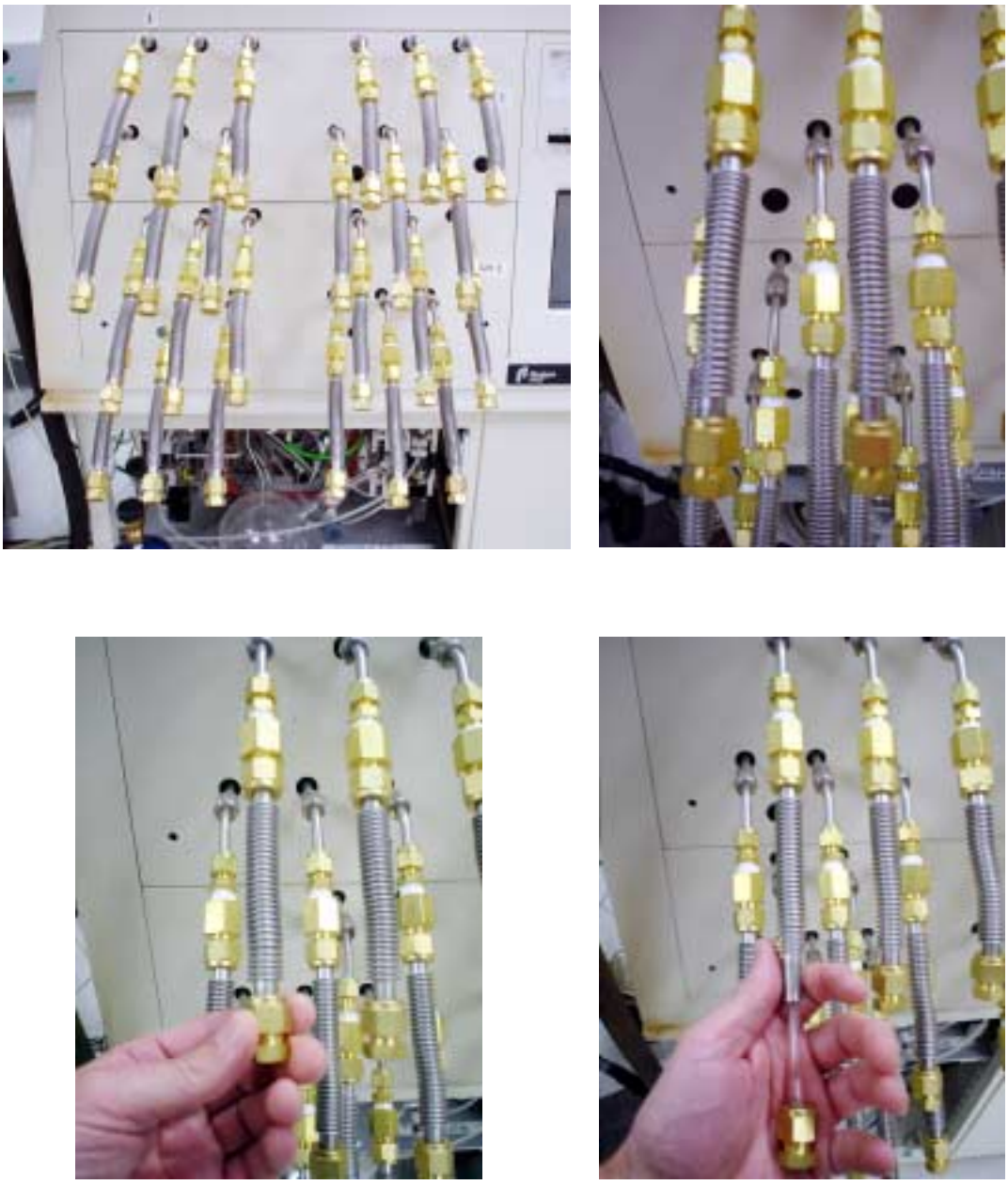

Figure P3: Loading sample tubes into tube crackers of the Finnigan MAT 252 24 port manifold (upper left photo). Note the orientation of the tube crackers on the 24 port manifold. Bank 2 (B2)-Tube cracker 1 (T1) is located at the upper left (top row) counting to the right to B2-T6, second row B2-T7 to B2-T12, third row Bank 1 (B1)-T1 to B1-T6, forth (bottom row) B1-T7 to B1-T12. Select tube cracker (upper right photo) then loosen and remove end cap from tube cracker (lower left photo). Remove previous sample tube, if present, and

install new scored sample tube into tube cracker (lower right photo) then replace and tighten end cap.

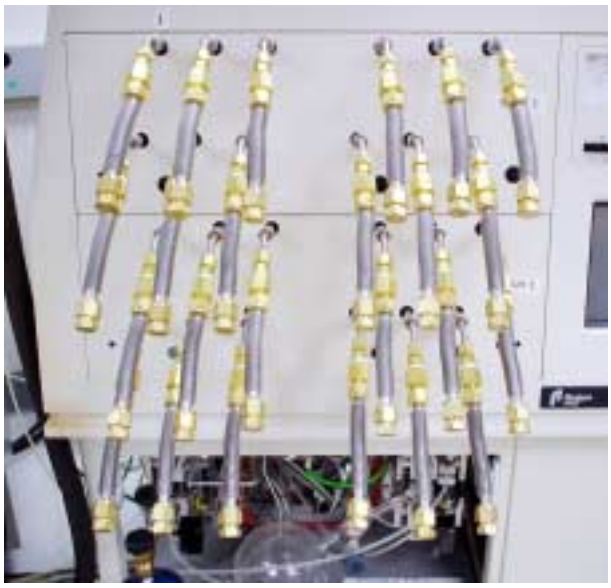

Figure P4: After you press measure (F5) you need to crack all sample tubes. It is best to do this in an orderly manner so you do not miss any samples. Crack sample tubes by bending the bellows tube until you hear the glass sample tube break (right photo).

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(Prepared by David A. Mucciarone)

Section 1D: Preparation of 100% Phosphoric Acid (H_3PO_4) for Kiel Carbonate Device

This procedure is designed to prepare approximately 425 ml of 100% phosphoric acid (H_3PO_4). The entire procedure should be performed under a fume hood. Goggles, rubber gloves and a lab coat/apron are required throughout the acid preparation.

Materials: Ar grade 85% Phosphoric acid (H_3PO_4).

Equipment: Graduated cylinder 500 ml, 1000 ml beaker, hot plate or heating mantle with controller, ring stand with clamp, thermometer 200°C, storage bottle/flask with ground glass stopper.

1. Calibrate 1000 ml flask or beaker to account for 15% (~75 ml) loss of water during the heating process.

2. In a fume hood place 500 ml ACS grade 85% Phosphoric acid (H_3PO_4) into a calibrated 1000 ml beaker or round flask.

3. Insert thermometer and heat flask on hot plate or in heating mantle at 140°C for approximately 12 hrs or until enough water evaporates to reach the 15% calibration mark. Note: once temperature is stable at 140°C, remove thermometer.

4. When calibration make is reached turn of hot plate or heating mantle and allow to cool.

5. Measure the density of the acid with a hydrometer. The specific gravity is 1.89 - 1.90. This is adequate for the Kiel. The acid resides in the oven at 70°C and flow well at this density. If the acid is more dense the acid begins to polymerize and clog the capillaries and tubing. The isotopic results are +/-0.03$^{o}/_{oo}$ for $\delta^{13}C$ and +/- 0.05$^{o}/_{oo}$ for $\delta^{18}O$ on standards

References:

Bowen, R., 1966, Paleotemperature analysis: Elsevier Publishing Company, New York.

Keish, B., J.W. Kennedy, and A.C. Wahl, 1958, The exchange of oxygen between phosphoric acid and water, Anal. Chem. v. 80, p. 4778-4782.

McCrea, J.M., 1950, On the isotopic chemistry of carbonates and a paleotemperature scale: Jour. Chem. Phys., v. 18, p. 849-857.

Wachter, E.A. and J.M. Hayes, 1985, Exchange of oxygen isotopes in carbon dioxide-phosphoric acid systems: Isot. Geosci., v. 52, p. 365-374.

Once the gas passes through the SGE valves it enter the source through an inlet which simply directs the gas flow directly into the source block, more precisely the ionization chamber (see Fig 2). The gas flow in the ion source is always molecular. Attached to the source block are the filament (cathode), trap, ion extraction plates, and focusing plates (Fig. 3).

a) The filament (cathode), often tungsten, emits electrons in a helical orbit under the influence of small source magnets in which the CO_2 gas molecules collide with the electron beam making a N_2^+ or CO_2^+ ion. The electron beam is at right angles to the ion trajectory.
b) The trap collects all electrons not involved in the collision with the N_2 or CO_2, and is positioned opposite the filament.
c) The extraction plates accelerate ions out of the ionization chamber and direct the ions toward the exit slits and focusing plates. The accelerating voltage on the Delta plus is 3kV.
d) There are a number of different focusing plates that are designed to progressively focus the ion beam leaving the source. The voltage is variable depending on the isotopic species being analyzed.
e) The final focusing plate defines the maximum beam width prior to passage into the flight tube.

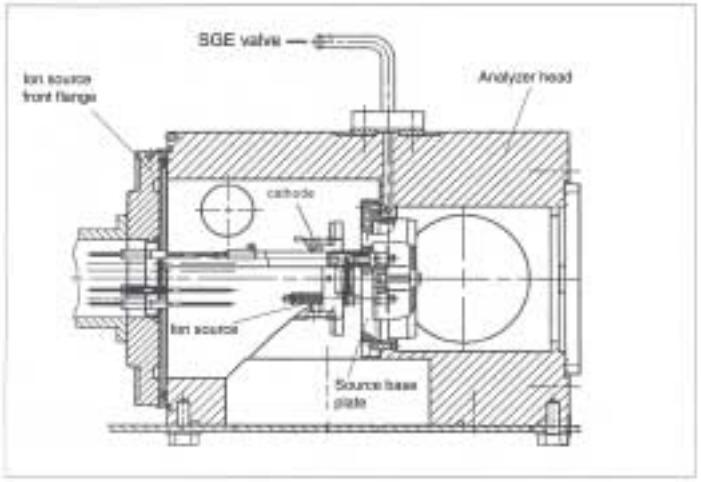

Figure 2: Schematic of Delta plus ion source within the source housing (analyzer head). Gases enter through the SGE valve into the ionization chamber. Illustration is from Finnigan users manual.

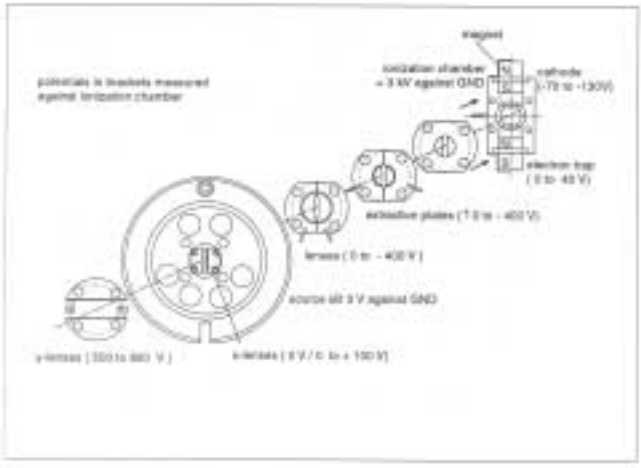

Figure 3: Schematic of Delta plus ion source components. Values are ion source potential in relation to ground at 3kV ion acceleration voltage. Illustration is from Finnigan user manual.

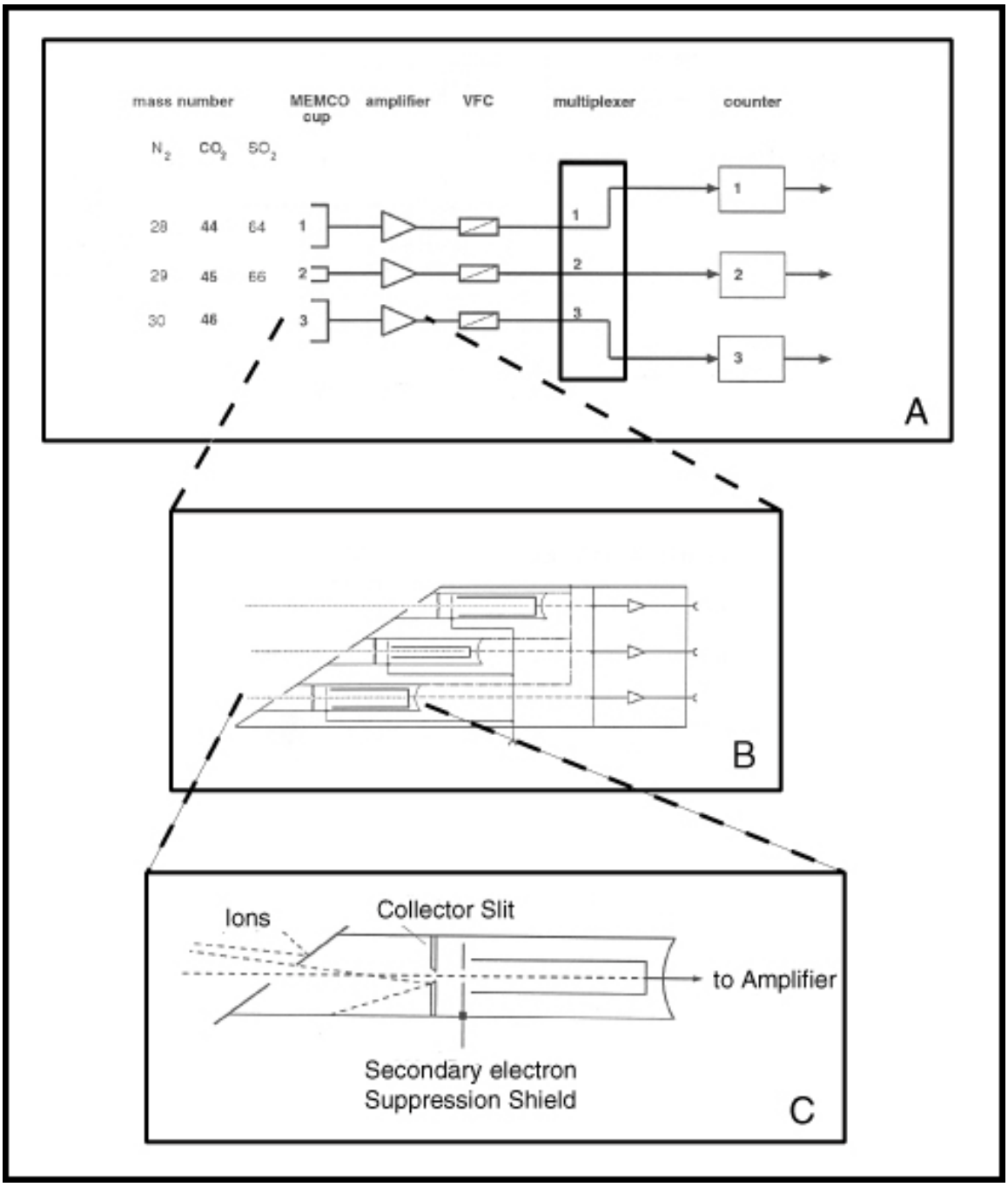

Figure 4: Schematic representation of faraday cup (collectors) on the Delta plus. A represents an overview of the collector system. B is an enlarged view of the collectors and amplifiers. Note that cup 2 is smaller than cups 1 and 3 but is more sensitive than cup 3 but less than cup 1. The resistor on cup 1 = 3×10^8, cup 2 = 3×10^{10}, and cup 3 = 3×10^{11} for N_2 and CO_2. C is a detail representation of an individual collector.

The flight tube has a 90° deflection path (Fig. 1) having a radius of R fitted with a permanent magnet of strength B (BDAC). The Delta plus is equipped with an electromagnet with maximum field strength of 0.75 Tesla providing a mass range from 10 to 70 amu at full accelerating voltage of 3kV. Therefore the radius is fixed and the magnet is variable but constant for any given gas species. At a constant accelerating voltage (V) and magnet strength, the lighter mass will be deflected (bend) more than

the heavier mass. In the case of CO_2, mass 44 is bent more than 45 and 46. However, in order to analyze another gas such as N_2 or SO_2 with a fixed magnet, the accelerating voltage needs to increase or decrease, respectively or the accelerating voltage can remain the same and the magnetic field strength can be varied. Therefore, the relation of all these parameters is given as:

$$m/z = K * H^2$$

Where: m/z is the mass to charge ratio
$K = R^2/2U$ = constant
H is the magnet strength
R is the Radius of flight tube
U is the acceleration voltage

After leaving the flight tube, the separate ion beams of different masses are directed into 3 (1 major and 2 minor) collectors (Faraday cups) depending on the type of mass spectrometer (Fig. 4). These cups are grounded through high ohm resistors. As the ion current passes to ground the drop in the resistor acts as a measure of the ion current. In addition, each collector also has a feedback resistor, therefore each amplifier can be matched to the isotope collected in a particular faraday cup. There are two types of collectors, major and minor. The major collector is usually larger and less sensitive than the minor collector. These collectors can either be fixed to a correct spacing for a particular set of masses or adjustable. In the case of N_2 or CO_2 a triple collector mass spectrometer can detect all three masses (28-major, 29-minor or 44-major, 45-minor, and 46-minor) and calculate $\delta^{15}N$ and $\delta^{13}C$ in one run without changing feedback resistors. The ISODAT software cup configuration utility does this automatically.

The signals received by the collectors are amplified and transferred to voltage to frequency converters (VFC) on a system control board in a microprocessor. This system board basically digitizes the analog signal for processing by an interfaced computer. The analog and digital output is then sent to disk and a printer. In the course of one analysis for $\delta^{15}N$ and $\delta^{13}C$ on the Delta plus mass spectrometer, one reference and one sample injection are measured to determine the concentration and isotopic composition. All of the data are expressed in conventional delta (δ) notation, where the isotopic ratio of $\delta^{15}N$ /$\delta^{14}N$ is expressed relative to Air and $\delta^{13}C/\delta^{12}C$ relative to the international PDB standard (Eq. 1) as defined by:

$$\delta\ ^{o}/_{oo} = [(Ratio_{sample} - Ratio_{standard})/(Ratio_{standard})] \times 1000 \qquad \text{(Eq. 1)}$$

PDB refers to a Cretaceous belemnite called *Belemnitella americana* from the Peedee formation in South Carolina and is defined as 0 for both $\delta^{13}C$ and has been exhausted (however, there may be a few labs that still have a small quantity remaining). The carbon standard NBS-21, USGS-24 (both graphite), NBS-22 (oil), and NIST-1547 (peach leaves), where NBS is an acronym for the National Bureau of Standards which was replaced by NIST or the National Institute of Standards and Technology, and USGS or U.S. Geologic Survey are standards used to calibrate to PDB. The CO_2 reference gas used is research grade and has been calibrated to PDB using these standards. Nitrogen isotopes are compared to Air, which is defined as zero. The N_2 reference gas we use is research grade and has been calibrated to Air using IAEA-N1 and IAEA-N3, USGS-26, where IAEA is an acronym for the International Atomic Energy Agency. To reduce the possibility of exhausting these international standards, laboratories establish working standards that have been calibrated against various known standards and with other laboratories, to use routinely in the laboratory. Listed in Table 1 are the isotopic compositions of commonly used standards, most of these can be obtained from the National Institute of Standards and Technology (NIST) in Gaithersburg, MD 20899-0001. For more information consult the reference list below.

Now that you have a general understanding on how the Finnigan Delta plus operates you can continue with Part B of this section to see how the gases generated by the EA move through the system and how they are analyzed. Consult Section 2A for a discussion on the ConFloII interface and Section 2 C for the quick reference guide to the operation of the EA and the Delta plus.

Table 1: Isotopic compositions of standard reference materials (Coplen et al., 2002).

Standard.	Description (‰)	$\delta^{15}N_{(Air)}$(‰)	$\delta^{18}O_{(SMOW)}$(‰)	$\delta^{13}C_{(PDB)}$(‰)
PDB	Peedee belemnite		30.91	0.00
SMOW	Standard Mean Ocean Water		0.00	
Air	Air	0.00		
IAEA-N1	Ammonium sulfate	0.43		
IAEA-N3	Potassium nitrate	4.69		
USGS-26	Ammonium sulfate	53.62		
NBS-19	TS limestone		28.65	1.95
USGS-24	Graphite			-15.99
NBS-21	Graphite			-28.10
NBS-22	Oil			-29.74

II) Chromatography and Isotopic Analysis

The Delta plus is connected to an EA via a ConFloII open split interface. Helium carrier gas flowing through the entire system in conjunction with the length of the GC column and the temperature of the GC oven will control the retention times of the N_2 and CO_2. These parameters have been selected so that we can maximize both separation and chromatography (shape) of the sample peaks. These two factors are important for a couple of reasons. First, separation between peaks is needed so that them Delta plus mass spectrometer can peak jump from N to C. Peak jumping involves changing the electromagnet current (BDAC) while maintaining the source voltage (HVDAC) constant. This process takes time and therefore adequate time must be budgeted to allow completion of this task. Second, proper peak shape is needed to obtain accurate concentration and isotopic measurements. Long tails on peaks will increase error in both calculations. Our system is setup to perform a slow jump routine between the nitrogen and carbon run. Our premise for using this routine is because it allows more maximum tuning of the source prior to analyses of N and C. The fast peak jump routing requires the software to be instructed on how to change the electromagnet current. This value will not be adjusted during the entire run sequence. All things remaining equal this routine will perform satisfactory, however, through the course of a given run sequence the electromagnet and/or source voltage can drift. Thereby introducing the possibility of errors and instability. If the retention times between peaks are close due to EA limitations or because of preference then the operator will benefit by using the fast peak jump routine. In reality, the mass spec will drift slightly over the course of a run sequence. So, by modifying the configuration and parameters of the EA we have created enough separation between the N and C peaks in a manner that we feel maximizes concentration and isotopic precision without compromising chromatography. See Table 1 for the configurations of the Delta plus/EA.

A typical run for nitrogen and carbon on the Delta plus is as follows. The run begins with a peak jump of the electromagnet current (BDAC) to N_2 and centers the high voltage (HVDAC) on mass 29 or beam 2. When complete a new graphics display will appear on the screen. A signal is sent to the EA to begin 1 second into the run and turn off at 25 seconds. The ConFloII solenoid will activate at approximately 14 seconds into the run indicated by the start of the LCD timer and the activation of the oxygen injection solenoid on the EA. When the EA timer reaches 20 seconds, the zero blank carousel will rotate one position dropping the sample into the combustion/oxidation column. At 90 seconds into the run a signal is sent to the ConFloII interface and N_2 reference gas is injected into the mass spectrometer for 20 seconds. The timer on the EA will reset at 120 seconds. At about 175 seconds into the run the N_2 peak from the sample will elute out of the 4 m GC column. Depending on the amount of N in the sample the peak will have a retention time of approximately 50 to 80 seconds. One second prior to the end of the nitrogen run the helium dilution solenoid is activated and at 275 seconds the nitrogen portion of the run is terminated (Fig. 1).

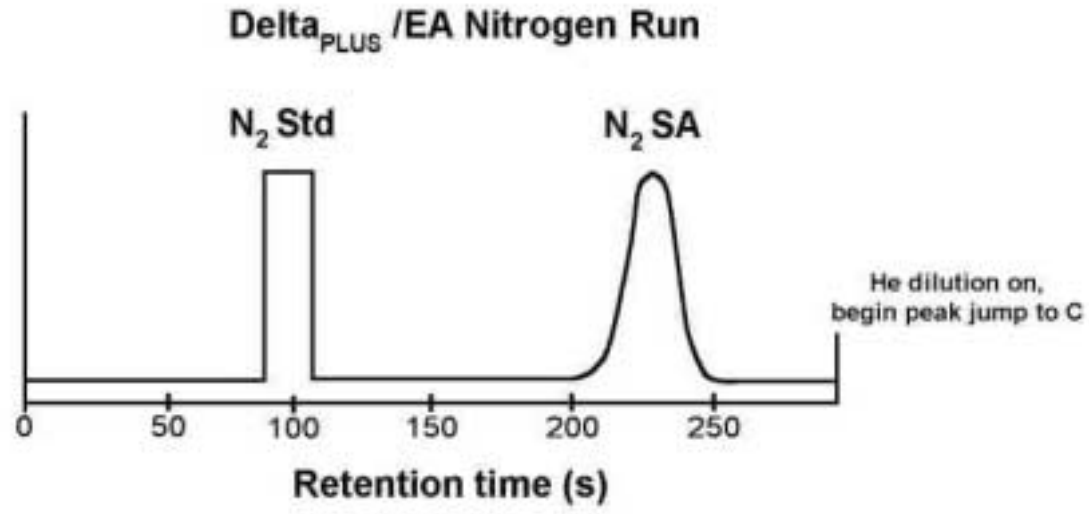

Figure 1: Schematic representation of the nitrogen portion of a nitrogen/carbon analysis. Notice that the N2 reference gas is injected prior to the unknown N2 sample peak.

A slow peak jump routine is performed as the instrument prepares to analyze CO_2. This routine require about 75 seconds and involves a change in electromagnet current (BDAC), injection of CO_2 reference gas from the ConFloII interface, and centers the high voltage (HVDAC) on mass 45 or beam 2. When complete a new graphics display window will appear. Approximately 18 seconds into the run the CO_2 peak from the sample will elute out of the 4 m GC column. Depending on the amount of C in the sample the peak will have a retention time of approximately 75 to 130 seconds. At 185 seconds a signal is sent to the ConFloII interface and CO_2 reference gas is injected into the mass spectrometer for 20 seconds. One second before the end of the run the helium dilution is turned off and the carbon portion of the run has ended and the analysis of the sample is completed (Fig. 2). This method of analysis continues until the run sequence in finished.

The above discussion has been about obtaining elemental and isotopic values from N and C from the same sample. Table 2 is a quick reference on how the EA and ConFloII are configured to run N and C on the same sample. It is also possible to run only N or C where peak jumping is not required. It is however, necessary to configure a Method in ISODAT to perform this task correctly. In addition, it is also possible to configure the EA differently to run O in the form of CO (Section 2D) or S in the form of SO_2 (Section 2E). To do this it is necessary to reconfigure the EA with different reactor and/or reactor/reduction columns and GC columns. New Methods will need to be created in ISODAT to accommodate the modifications in the EA. Aside from running an EA on our Delta plus, other peripherals can be attached that run via continuous flow. For example we have a HP5890 GC configured to do compound specific GC-C-IRMS (Section 2F).

It is necessary to review and understand the operation of the elemental analyzer before operating the mass spectrometer. This section was written a synopsis and as a guide to the safe operation of the Delta plus. You will receive all of the necessary information for operating the instrument from your training. However, you can find more details on the mass spectrometer and elemental analyzer in the sorted Finnigan Delta plus and Carlo Erba user manuals.

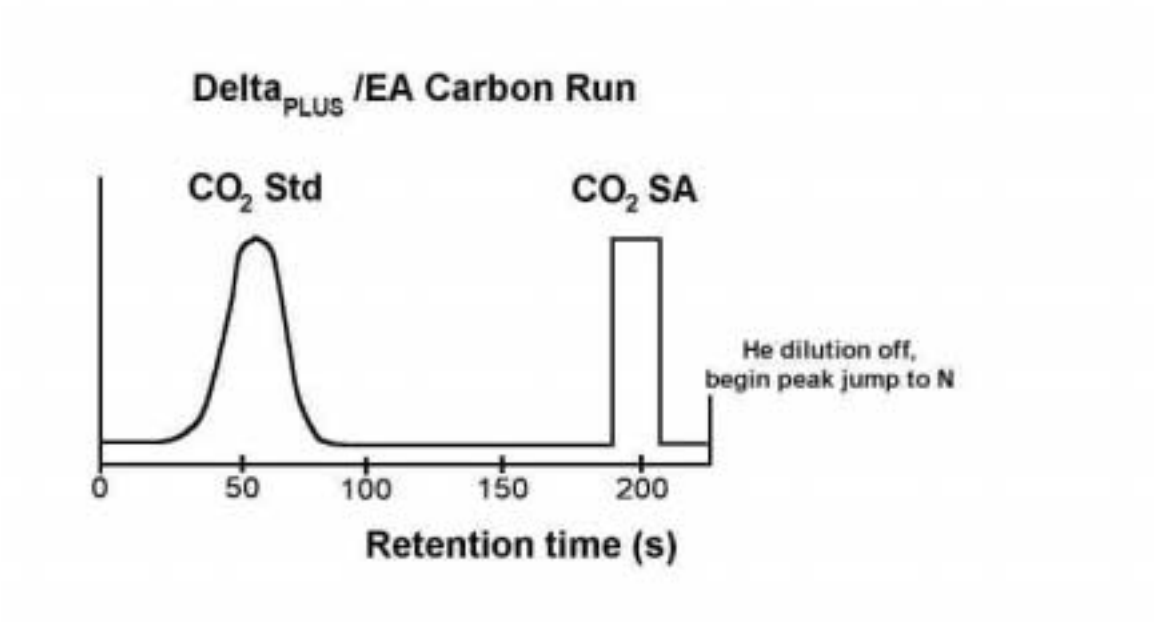

Figure 2: Schematic representation of the carbon portion of the nitrogen/carbon analysis. Notice that unlike the nitrogen run the CO_2 reference gas is injected after the unknown CO_2 sample peak this is because of the slow peak jump routine from N to C.

Table 2: Set up parameters for C and N analysis using the Carlo Erba Na1500 Series 2 elemental analyzer.

Instrument Temperatures (°C)	
Combustion oven	1020
Reduction oven	650
Chromatographic column	60
Filament	190
Flow Rates (ml min^{-1}) and gas pressures	
Helium carrier gas, Grade 4.6, Zero (90 - 100kPa on EA)	55-65
Oxygen Grade 4.3, UHP (100 - 105kPa on EA)	25-30
Nitrogen Research Grade 6.0 (100 - 105kPa on CFII)	
Carbon dioxide Research Grade 4.6 (100 - 105kPa on CFII)	
Helium Grade 4.6, Zero (90 - 100kPa on CFII)	
Element Retention Times (seconds)	
Nitrogen as N_2 reference gas injection	80-100
Nitrogen as N_2	175-260
Carbon as CO_2	20-120
Carbon as CO_2 reference gas injection	185-205
Additional Parameters on EA (seconds)	
Cycle time	110
Sample time begin/end	20 & 21
Oxygen injection	70
Run Parameters (seconds)	
Run time for N	265
Peak jump to C	~90-100

Table 2 (cont.): Set up parameters for C and N analysis using the Carlo Erba Na1500 Series 2 elemental analyzer.

Run time for C	225
Peak jump to N at end of run	30
Run time for N and C	630s (10.5 min)
Column Configuration (cm)	
Quartz combustion column (l x w)	45.0 x 1.8
From bottom to top:	
-Quartz wool	4.0
-Silvered cobalic oxide (Co_3O_4 + Ag)	6.0
-Quartz wool	0.5
-Chromium oxide (Cr_2O_3)	10.5
-Quartz wool	0.5
Quartz reduction column (l x w)	45.0 x 1.8
From bottom to top:	
-Quartz wool	4.0
-Reduced copper wires (approx. 150g)	30.0
-Quartz (silica) chips	9.0
-Quartz wool	1.5

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