Isotopes

R. Francey

Division of Atmospheric Research
CSIRO

FRANCEY

CO_2 STABLE ISOTOPES

MAIN OBJECTIVE:

Partition atmosphere-surface exchange of CO_2 between oceans and terrestrial biota ($\delta^{13}CO_2$).

SECONDARY OBJECTIVES:

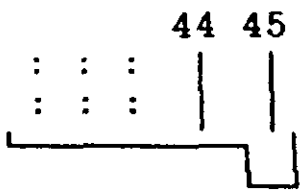
* Role of the biosphere in the global hydrological cycle ($\delta^{18}CO_2$)

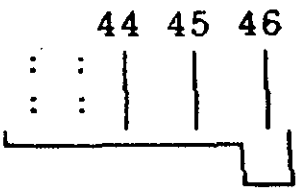
* Stratospheric-tropospheric exchange ($\delta^{18}CO_2$)

MASS SPECTROMETER MEASUREMENT OF CO_2

$$\delta^{13}C = \left[\frac{(^{13}C/^{12}C)_S}{(^{13}C/^{12}C)_R} - 1 \right] . 1000 \ (‰)$$

VG Micromass 602D





Measure: $\delta^{45}{}' = (m45/m44)_S/(m45/m44)_R - 1$
$\delta^{46}{}' = (m46/(m44+m45))_S/(m46/(m44+m45))_R - 1$

Slit Correction: $\delta^{45} = \delta^{45}{}'$
$\delta^{46} = \delta^{46}{}'(1 - R^{45}\delta^{45}/(R^{45}+1))$

^{17}O Correction: $\delta^{13} = R^{45}\delta^{45}/R^{13} - R^{17}\delta^{46}/R^{13}$
$\delta^{18} = \delta^{46} - R^{17}R^{45}\delta^{46}/R^{18}$

N_2O Correction:

$$\delta^{13}{}_C - \delta^{13} = (R^{45}C^{45}/R^{13} - R^{17}C^{46}/R^{13})\ rE$$
$$\delta^{18}{}_C - \delta^{18} = (R^{46}C^{46}/2R^{18} - R^{17}R^{45}C^{45}/R^{18})\ rE$$

{$r=N_2O/CO_2$, E=rel.ioniz.efficiency, $C^n=(1-S_N{}^n/Sc^n)$}

Conversion to PDB≡CO_2:

$$\delta_{PDB}{}^{13}S = \delta_{PDB}{}^{13}R + \delta_R{}^{13}S + 10^{-3}.\delta_{PDB}{}^{13}R.\delta_R{}^{13}S$$
$$\delta_{PDB}{}^{18}S = \delta_{PDB}{}^{18}R + \delta_R{}^{18}S + 10^{-3}.\delta_{PDB}{}^{18}R.\delta_R{}^{18}S$$

S = SAMPLE
R = REFERENCE
R^n = 'known' isotope ratios of R

CO_2 STABLE ISOTOPES

MAIN OBJECTIVE:

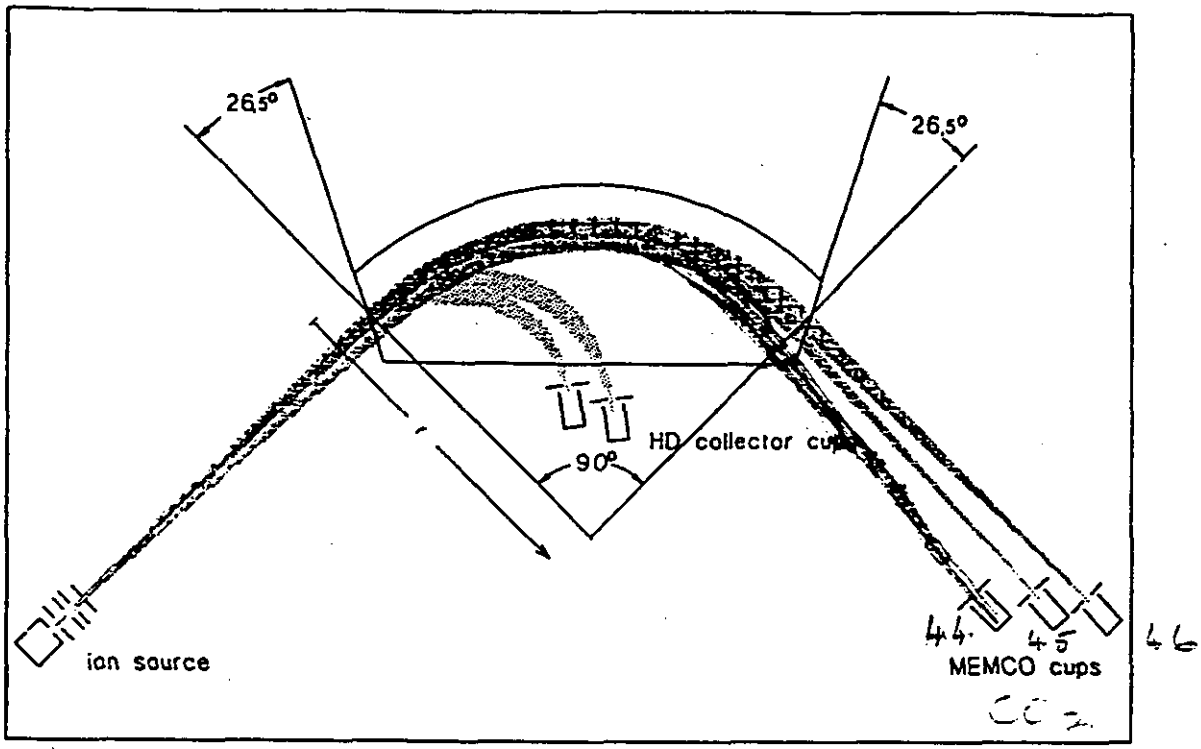
Partition atmosphere-surface exchange of CO_2 between oceans and terrestrial biota ($\delta^{13}CO_2$).

SECONDARY OBJECTIVES:

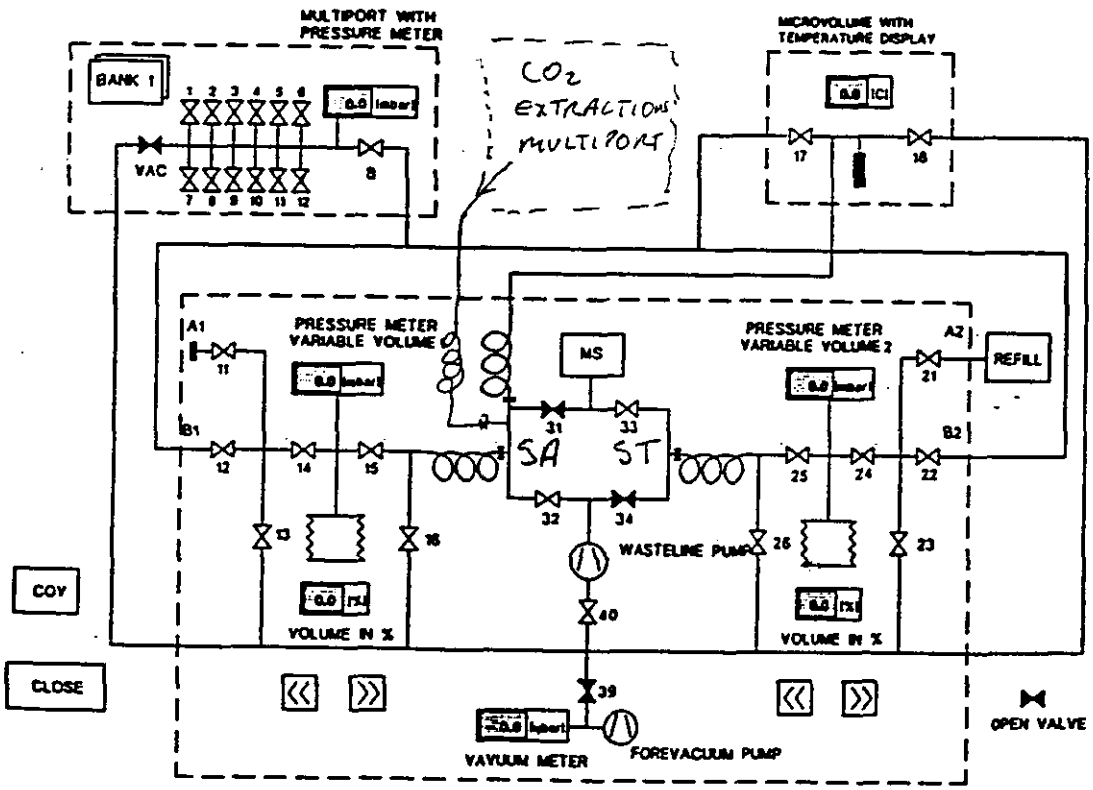
* Role of the biosphere in the global hydrological cycle ($\delta^{18}CO_2$)

* Stratospheric-tropospheric exchange ($\delta^{18}CO_2$)

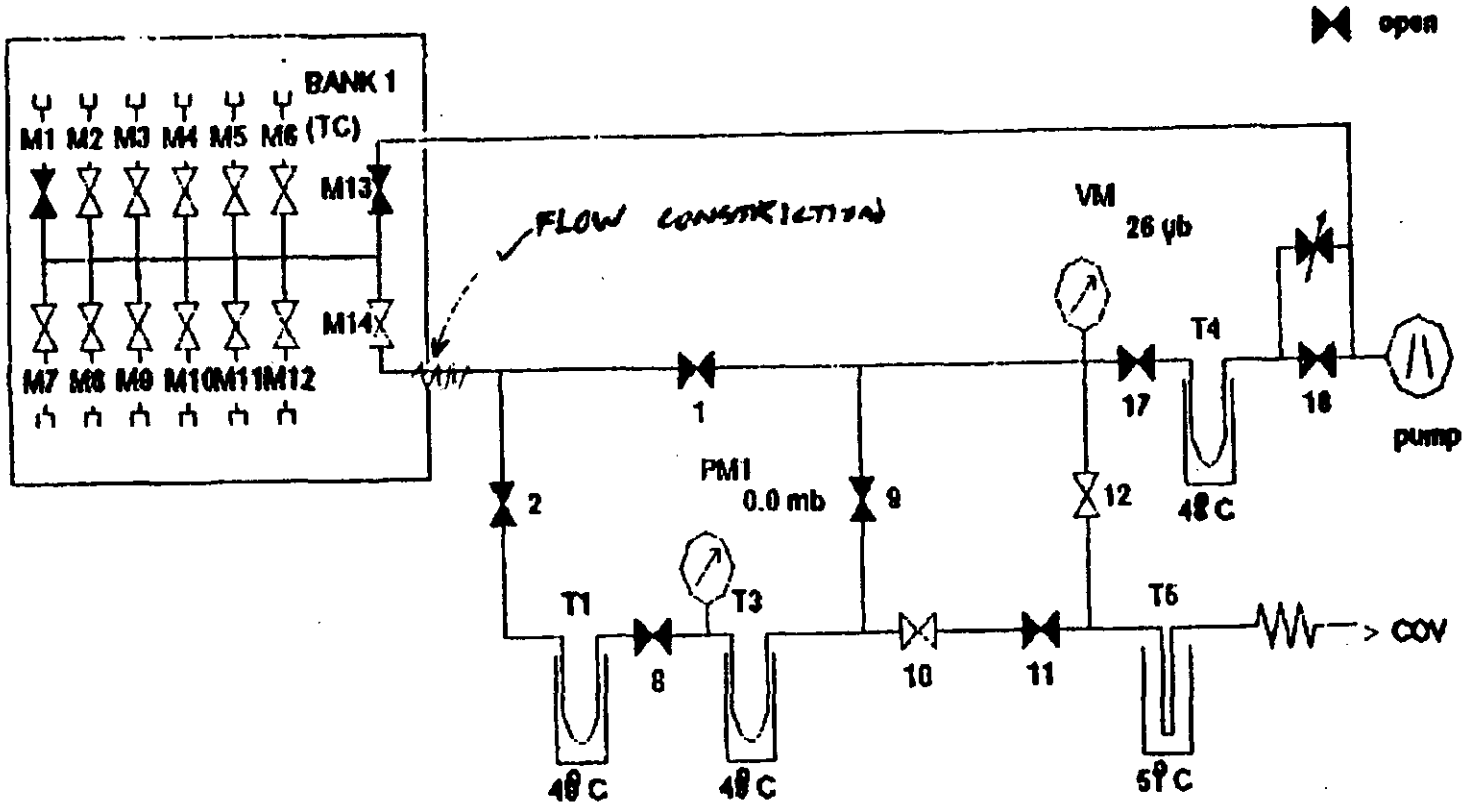
the scheme of the ion path



The scheme of an inlet system with a multiport and microvolume

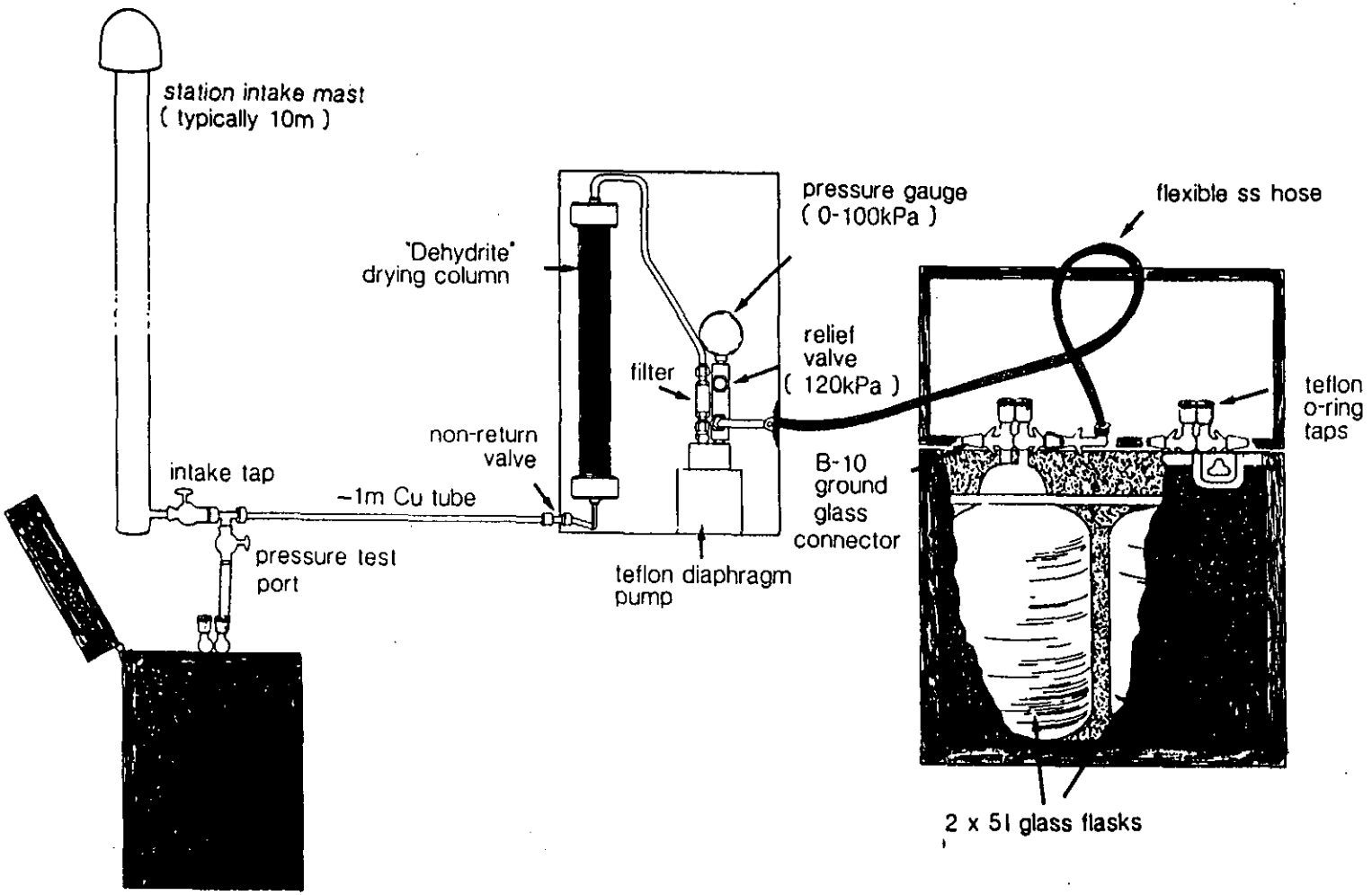


SUPPORT: MT – BOX – C PERIPHERAL



REVIEW CAPE GRIM SAMPLING STRATEGY:

* In situ CO_2 extraction (4/month)
* 5L air flasks (1/month)
* 0.5L air flasks (6/month)
* High pressure cylinders (2/year)


station intake mast
(typically 10m)
'Dehydrite'
drying column
pressure gauge
(0-100kPa)
flexible ss hose
relief
valve
(120kPa)
filter
teflon
o-ring
taps
non-return
valve
intake tap
~1m Cu tube
B-10
ground
glass
connector
pressure test
port
teflon diaphragm
pump
2 x 5l glass flasks

GASLAB ATMOSPHERIC COMPOSITION MEASUREMENTS 1991

Existing, (limited) *Planned (* upgrade)*

GLOBAL SURVEY OF CONTEMPORARY ATMOSPHERE

Species:

CO_2, $\delta^{13}C$, $\delta^{18}O$, ($\Delta^{14}C$) O_2/N_2
CH_4, ($\delta^{13}C$) δ^3H
CO, (H_2)
(N_2O, F-11, F-12, F-113, CCl_4, CH_3Cl, CH_3CCl_3)

Sites:

AES	**Alert** (82°N), Fraserdale (50°N)	
NOAA	**Barrow** (71°N), Niwot ridge (40°N)	
	Mauna Loa (20°N), (Samoa, 14°S)	Samoa*
	South Pole (90°S)	
UW	Cheeka Peak (48°N)	
CGBAPS	**Cape Grim** (41°S)	
AAD	Macquarie Is (54°S), Mawson (68°S)	MQ*, MA*
		Casey?
		Heard Is?
other	Darwin (12°S), GBReef (19°S)	India
Aircraft:		
	Australian Airlines 727 (39°S)	737's*
	Light hire (41°S)	Qantas?
		NASA/PEM
Balloons:		
	Kiruna (68°N)	tropics?
Ships:		
	Aurora, Franklin	*

GASLAB ATMOSPHERIC COMPOSITION MEASUREMENTS 1991

Existing, (limited) *Planned (* upgrade)*

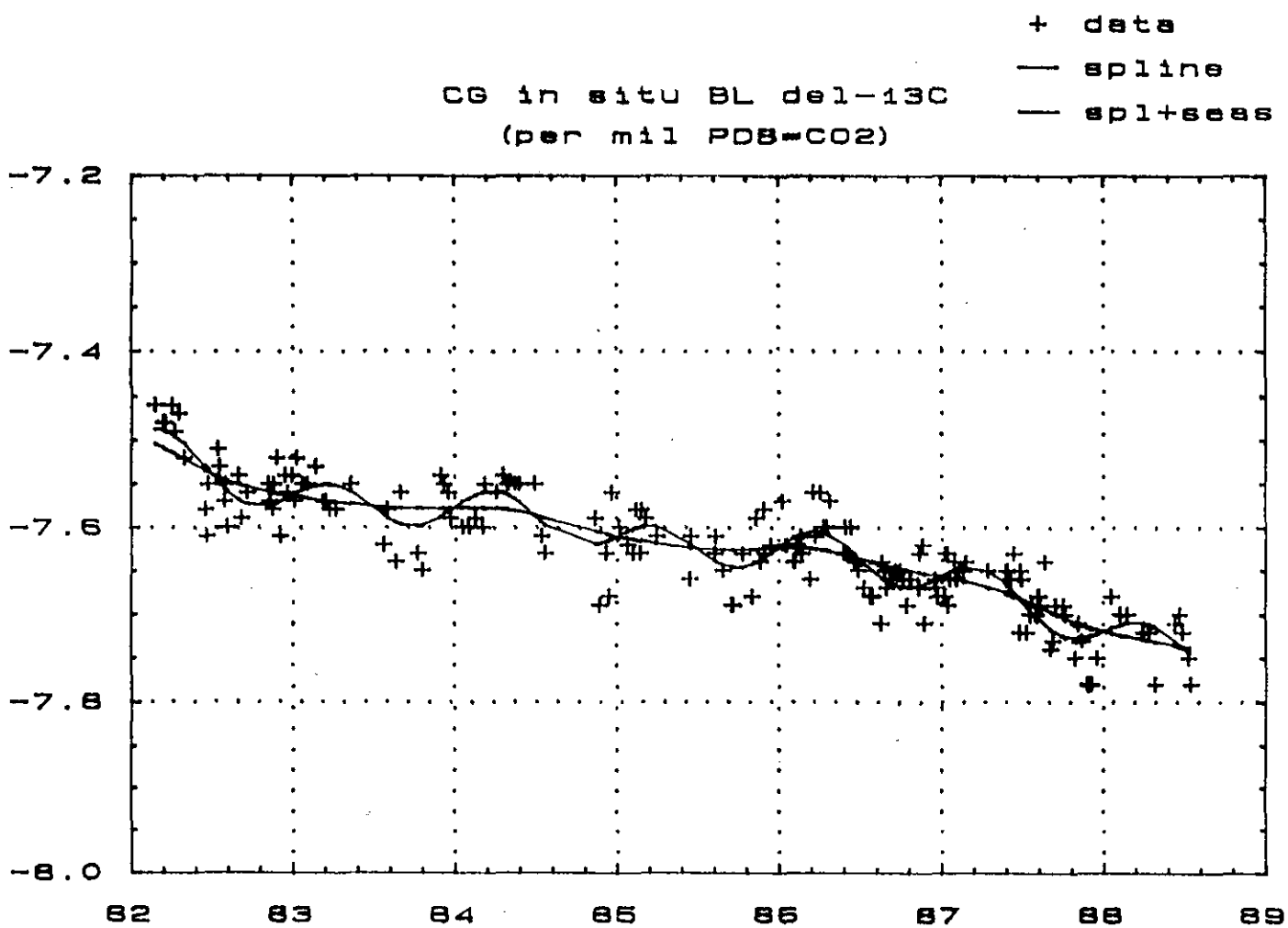
THE PAST ATMOSPHERE

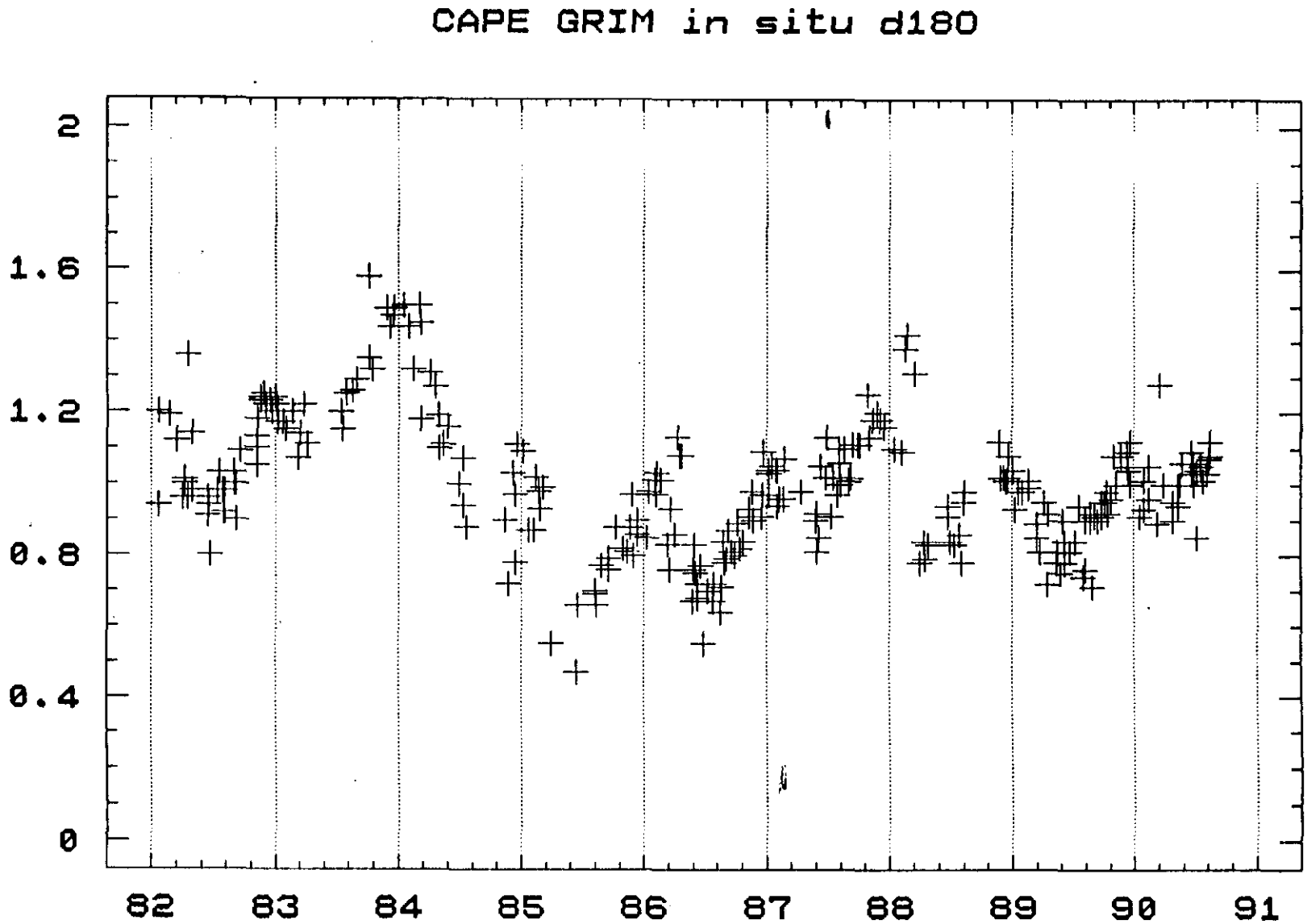
Species:

O_2/N_2, $\delta^{34}O$, $\delta^{29}N$
CO_2, ($\delta^{13}C$) ($\Delta^{14}C$),
CH_4, ($\delta^{13}C$)
N_2O CFC's,O_3

Source:

Cape Grim Archive (1978 -)
DEO8 Ice Core (1850 -) DSS(10KBP)


+ data
spline
spl+seas
CG in situ BL del-13C
(per mil PDB-CO2)
-7.2
-7.4
-7.6
-7.8
-8.0
82
83
84
85
86
87
88
89


CAPE GRIM in situ d18O
2
1.6
1.2
0.8
0.4
0
82
83
84
85
86
87
88
89
90
91

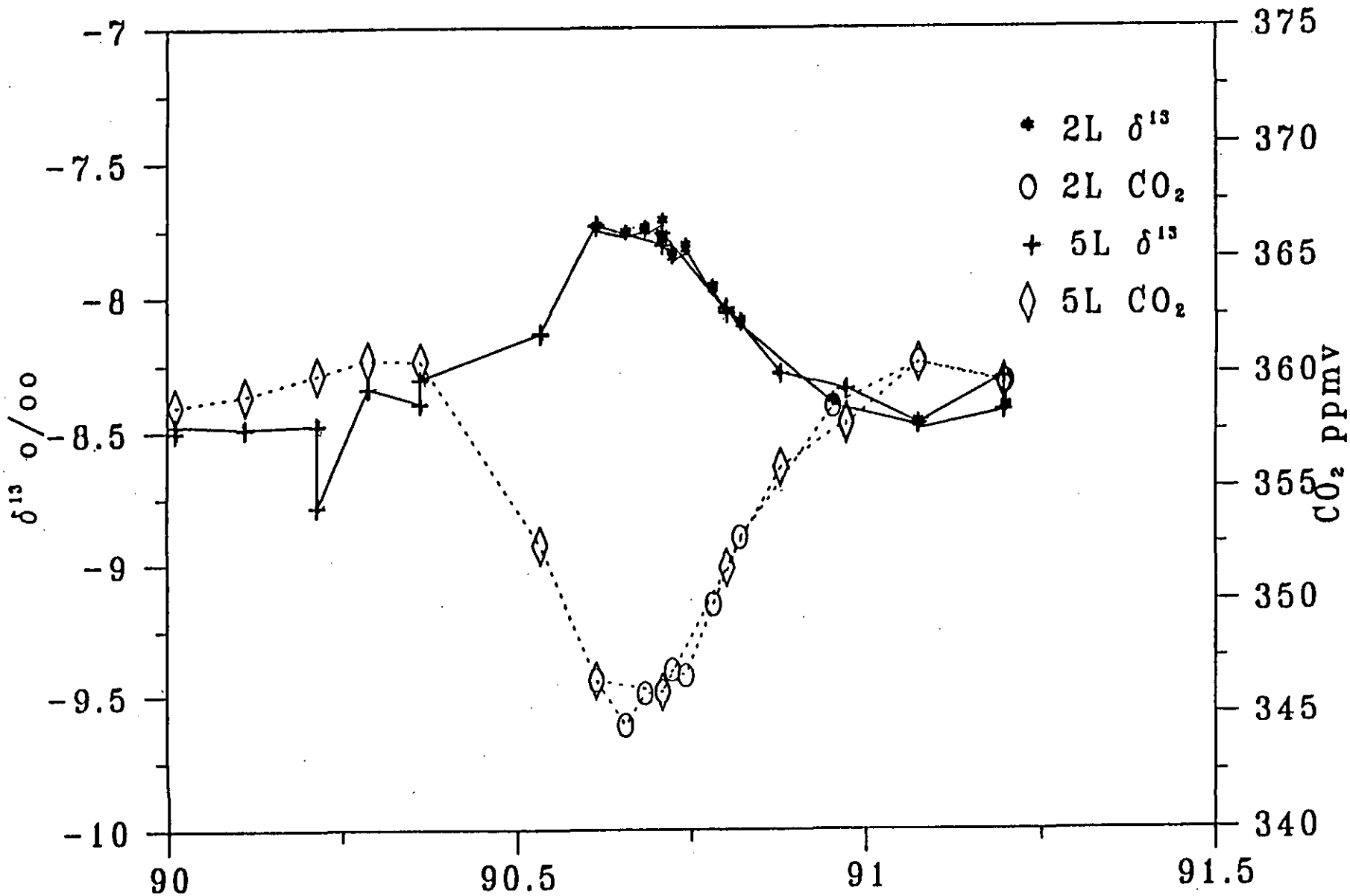
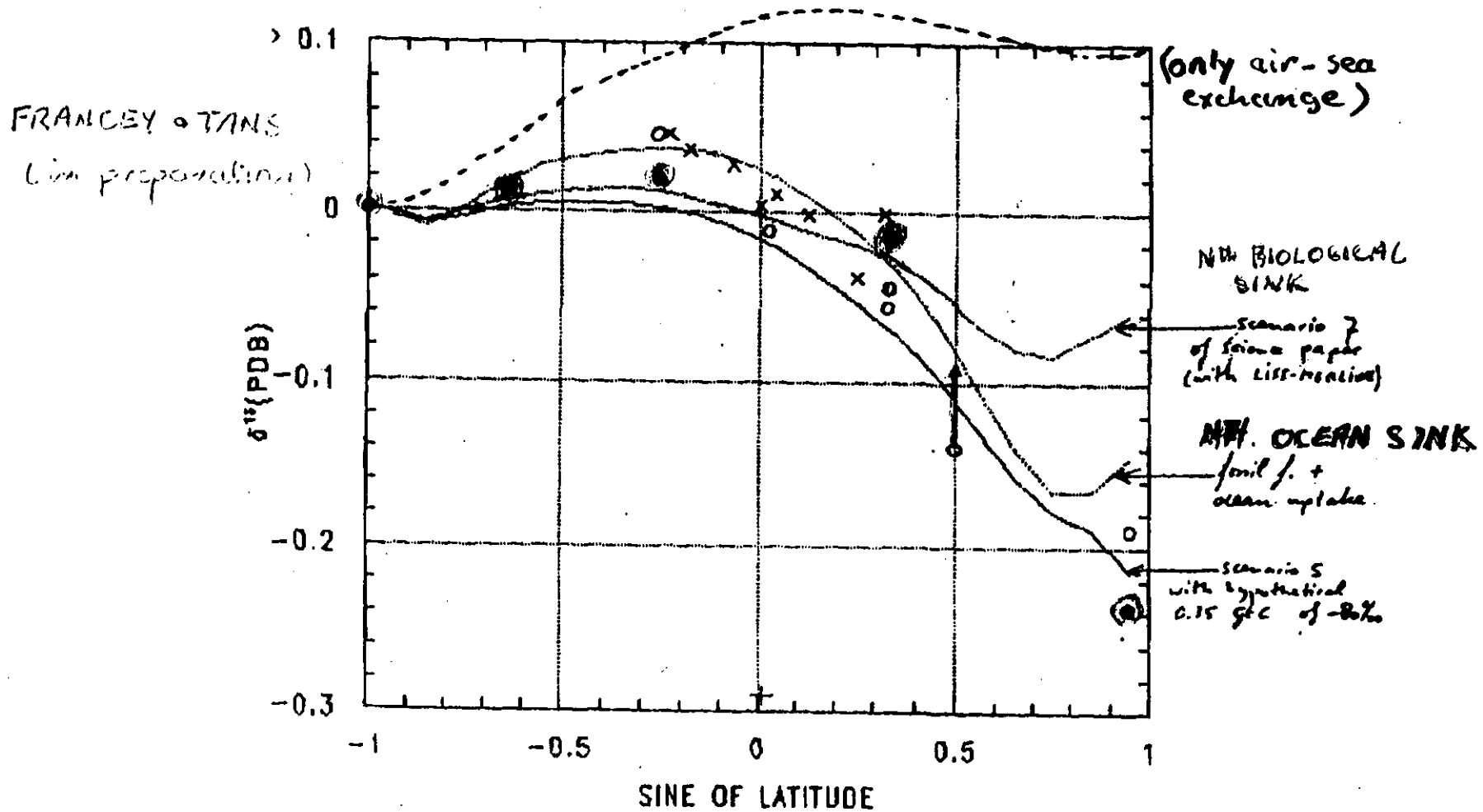

COMPARISON OF δ13 AND CO2 - ALERT
2L δ13
2L CO2
5L δ13
5L CO2
δ13 o/oo
CO2 ppmv
-7
-7.5
-8
-8.5
-9
-9.5
-10
375
370
365
360
355
350
345
340
90
90.5
91
91.5

Figure 1



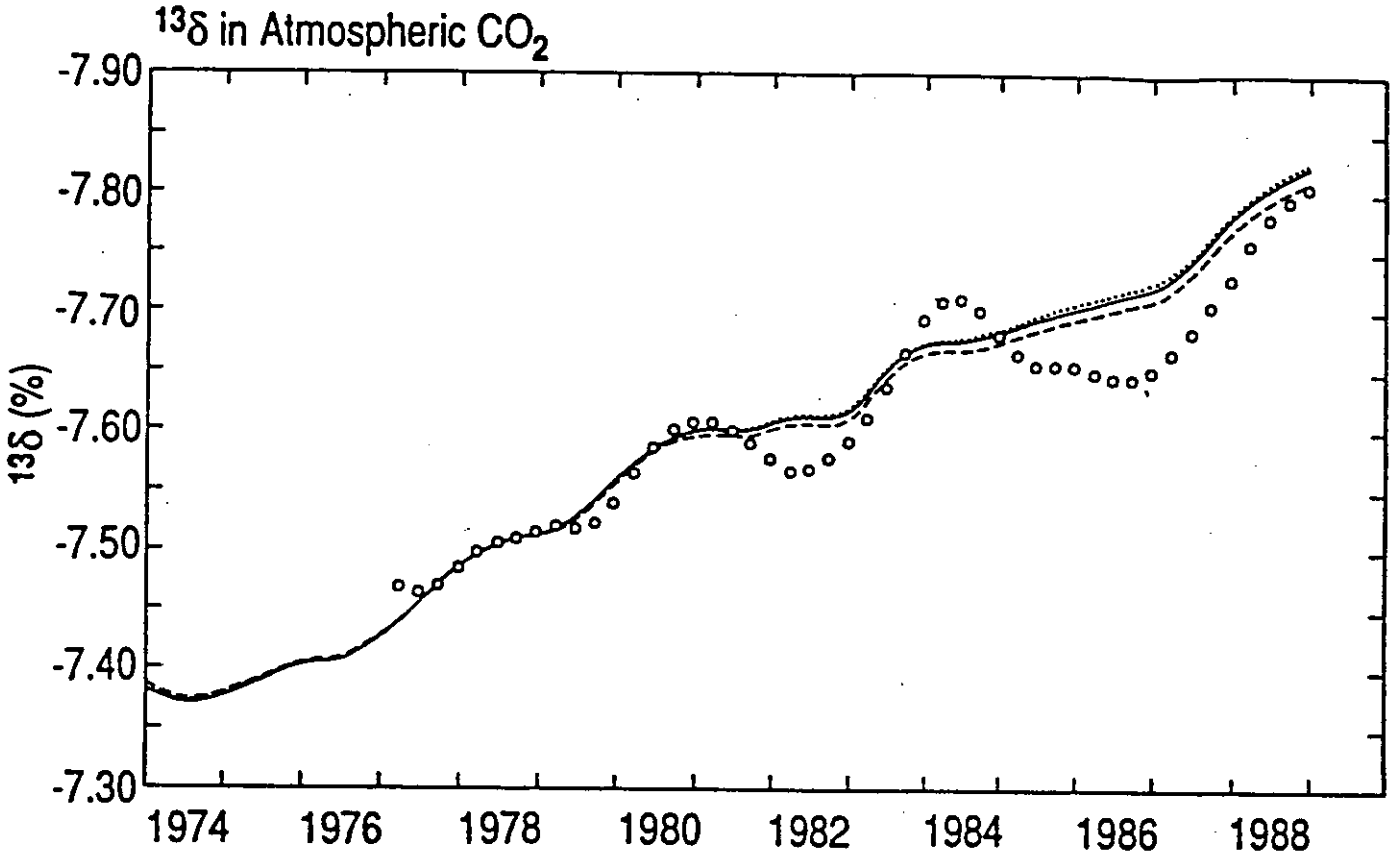


Fig. D.2. Observed and predicted time trend of $^{13}\delta$, in per mil, showing details of the plot of Figure D.1 for the recent period. Direct measurements are again shown as plus marks. The solid curve, upper curve after 1978, again shows a prediction of the box diffusion model calibrated by stationary radiocarbon. The predictions of the oceanic circulation model and the box diffusion model calibrated by bomb radiocarbon (shown below the curve for stationary radiocarbon) are indistinguishable.

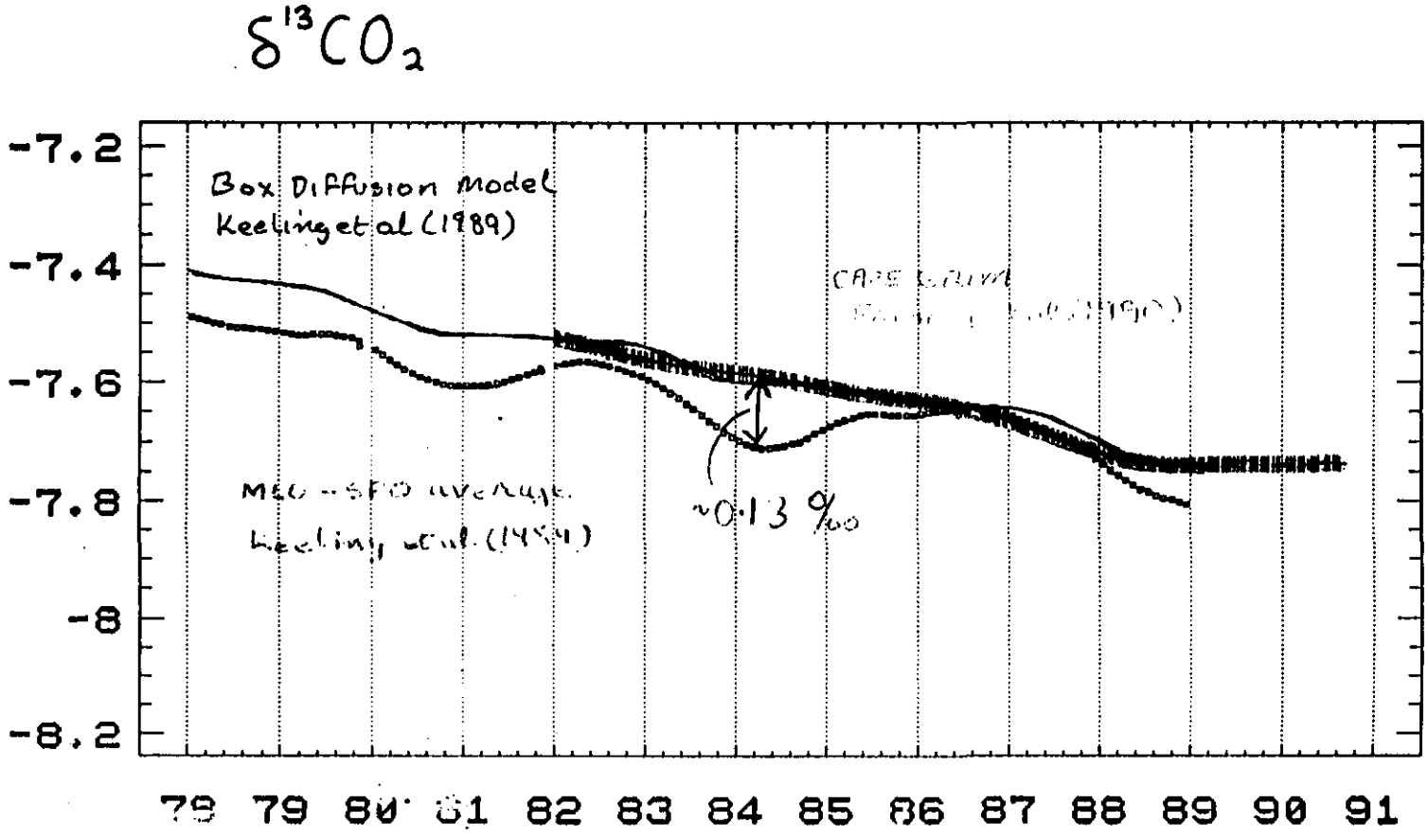

$\delta^{13}CO_2$
-7.2
-7.4
-7.6
-7.8
-8
-8.2
Box Diffusion model
Keeling et al (1989)
MLO - SPO average
Keeling et al. (1989)
~0.13 ‰
79 79 80 81 82 83 84 85 86 87 88 89 90 91

FIGURE 2

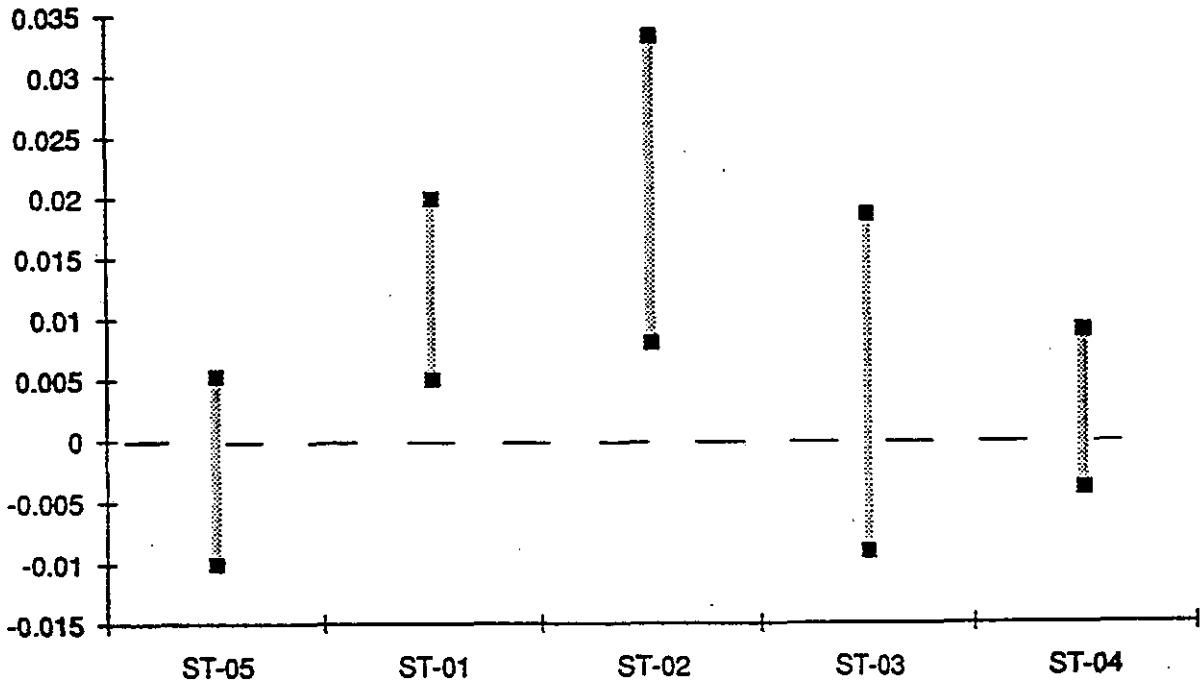


Figure 3: Measurements of the CO_2 isotope standards made on the MAT252 in October 1991.

TABLE 3: COMPARISON OF THE SPECIFICATIONS OF THE MAT252 AND THE VG602D/DAR MASS SPECTROMETER SYSTEMS FOR $\delta^{13}C$ IN CO_2 EXTRACTED FROM AIR SAMPLES.

Sensitivity and external precision

	MAT252		VG602D	
	Air sample size (bar.L)	$\delta^{13}C$ $2\sigma_{10}$ (‰)	Air sample size (bar.L)	$\delta^{13}C$ $2\sigma_{10}$ (‰)
normal sample	0.5 (175 bar.µL CO_2)	0.01	10.0 (3500 bar.µL CO_2)	0.03
(Factory test	0.026	0.009)		
(Laboratory test	0.010	0.010)		

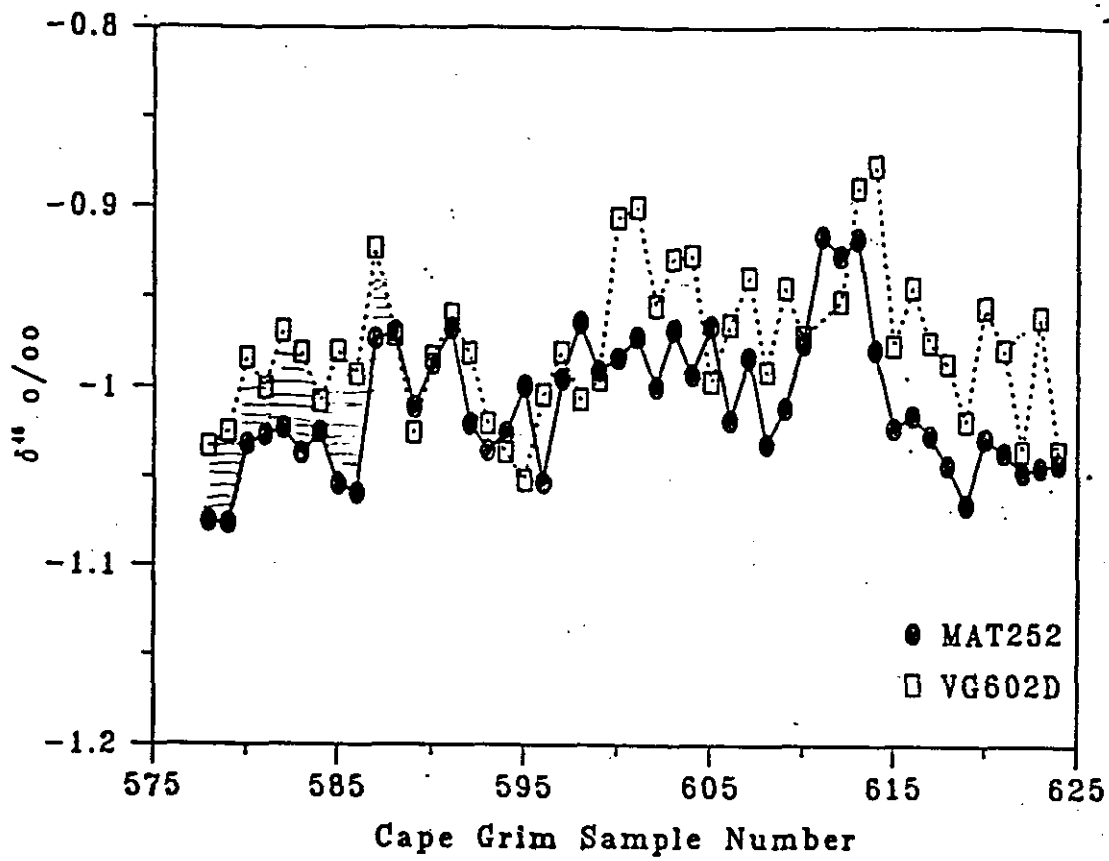
(NOTE : $2\sigma_{10}$ ($\delta^{18}O$) is approximately twice $2\sigma_{10}$ ($\delta^{13}C$).

Efficiency

	MAT252 multiport inlet/ automated cryo-traps/ triple collector	VG602D manual cryo-traps/ manual inlet/ dual collector
Analysis and preparation time (minutes)		
1 sample	40	260
12 samples	400	3240
Operator time (minutes)		
1 sample	10	260
12 samples	40	3240

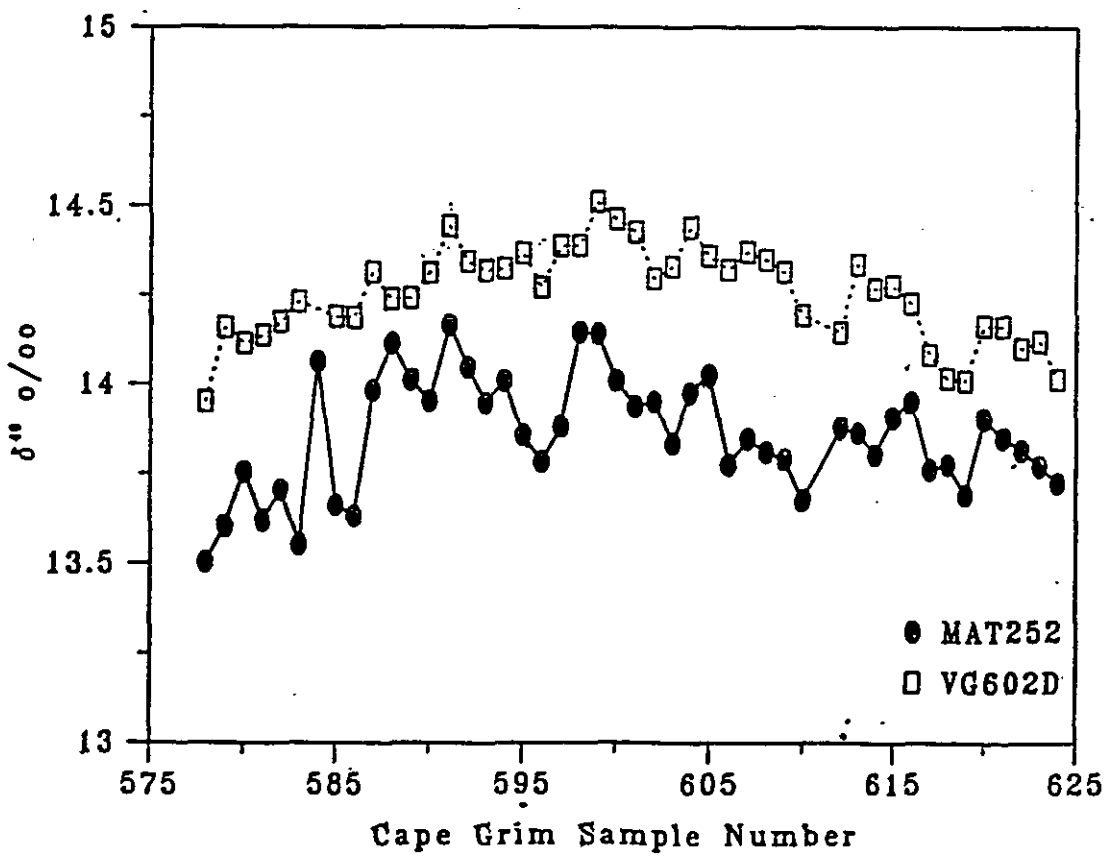
CAPE GRIM in situ δ^{46} RECORD

Averages



CAPE GRIM in situ δ^{46} RECORD

Averages not corrected for δ^{46} measurement



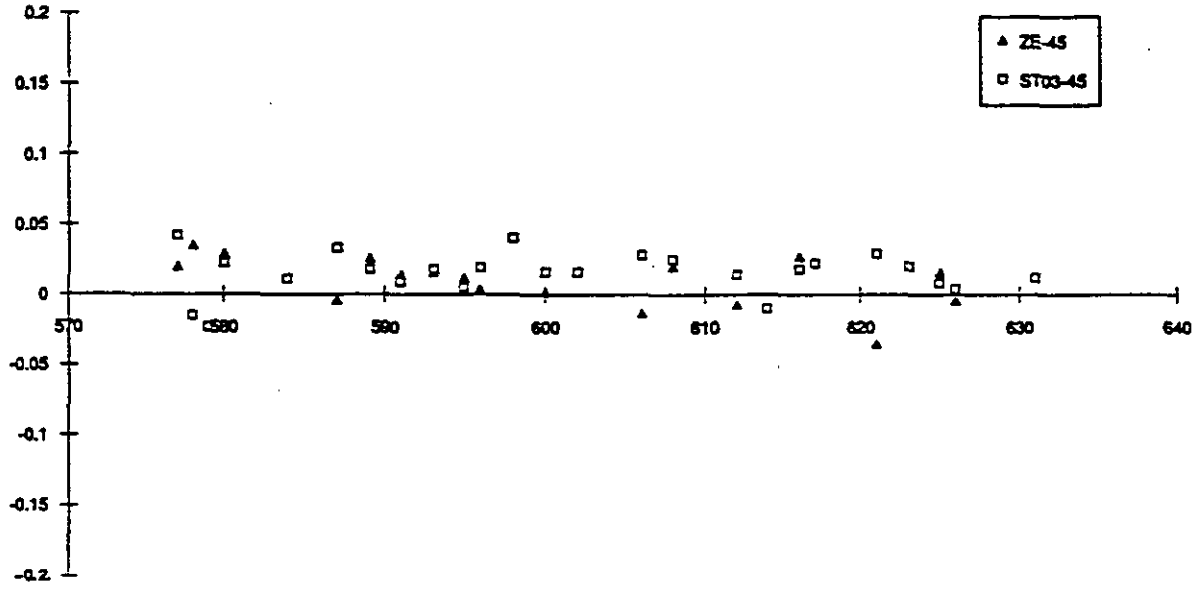


Figure 4(a): Zero-enrichment and ST-03 v ST-03 results corresponding to analyses of Cape Grim in situ samples #587-#632 on the VG602D.

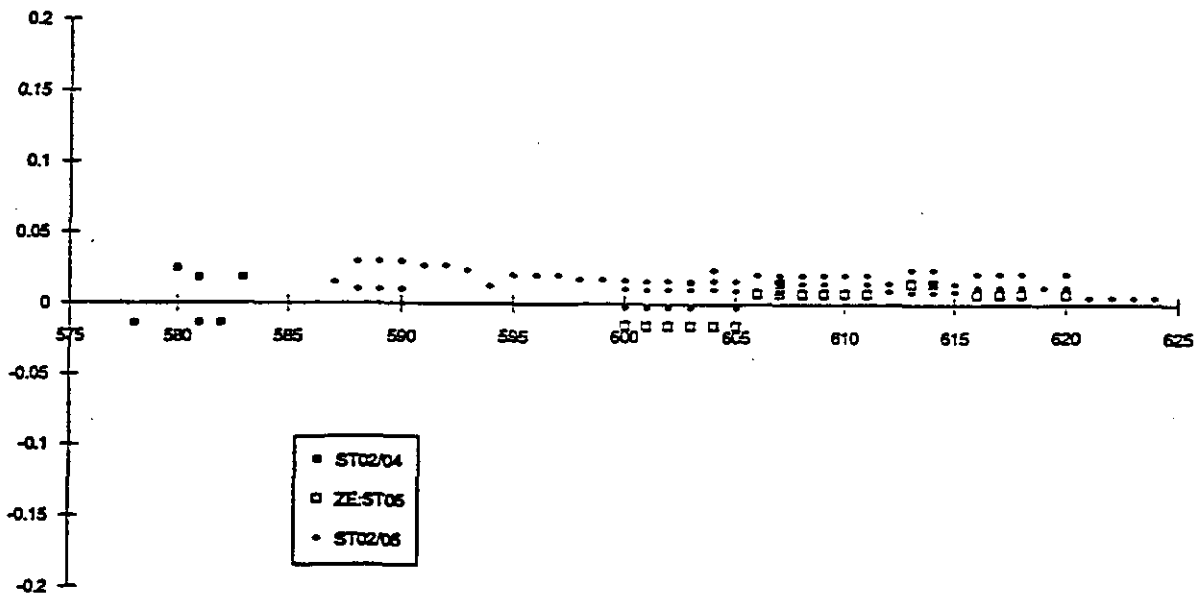


Figure 4(b): Zero-enrichment and "standard v standard" results corresponding to analyses of samples #587-#632 on the MAT252.

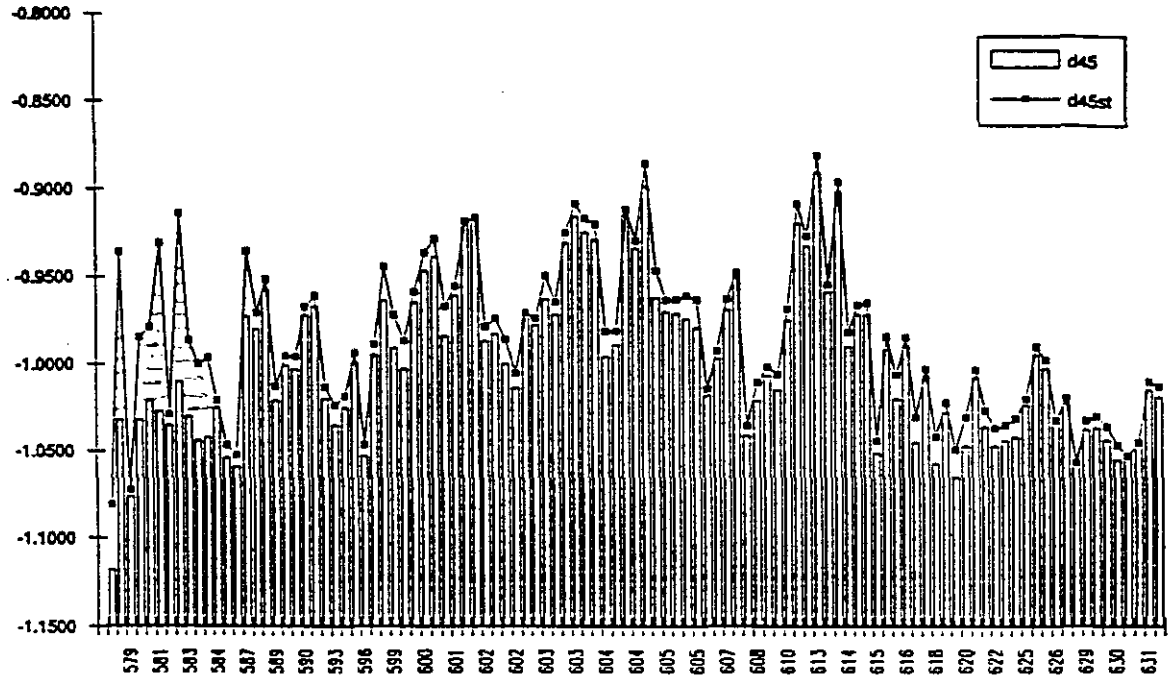


Figure 6: MAT252 raw measured δ^{45} (bars) and corrected δ^{45} (points) using the time of storage of the STANDARD and a -0.002 ‰ hr^{-1} coefficient due to fractionation in the capillary bleed.

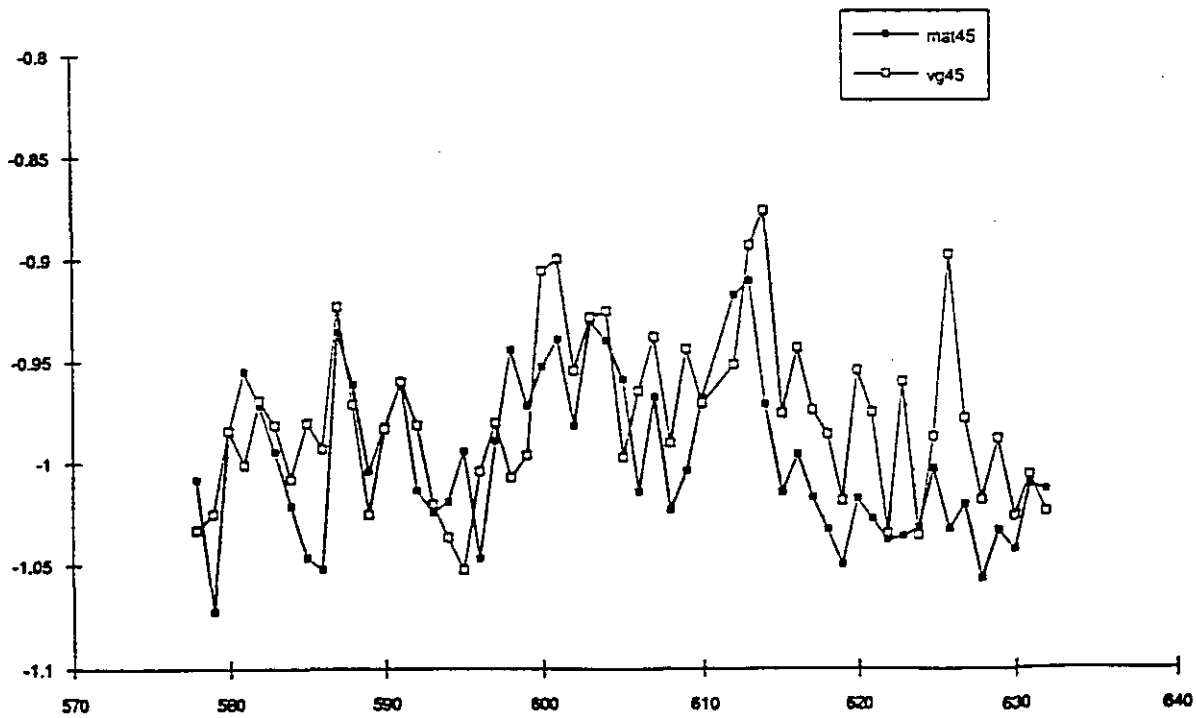


Figure 7: Cape Grim in situ CO_2 measured on both the MAT252 and VG602D mass spectrometers.

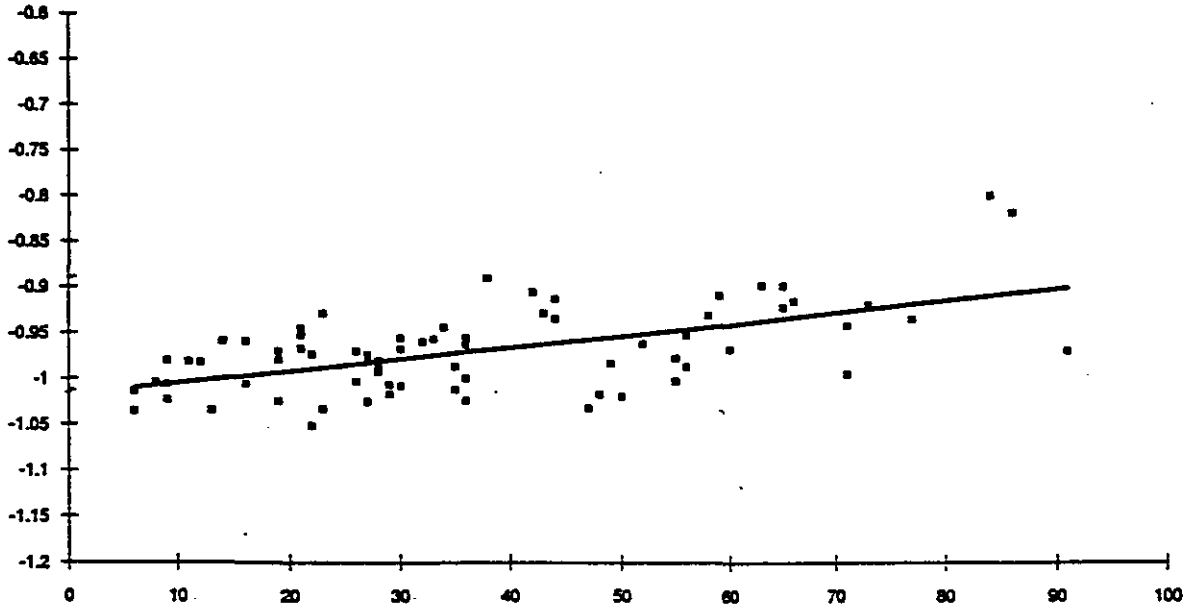


Figure 5(a): VG602D δ^{45} values of Cape Grim in situ CO_2 samples #587-#632 as a function of storage time (days) in the 100 ml flasks with Teflon O-ring seal stopcocks.

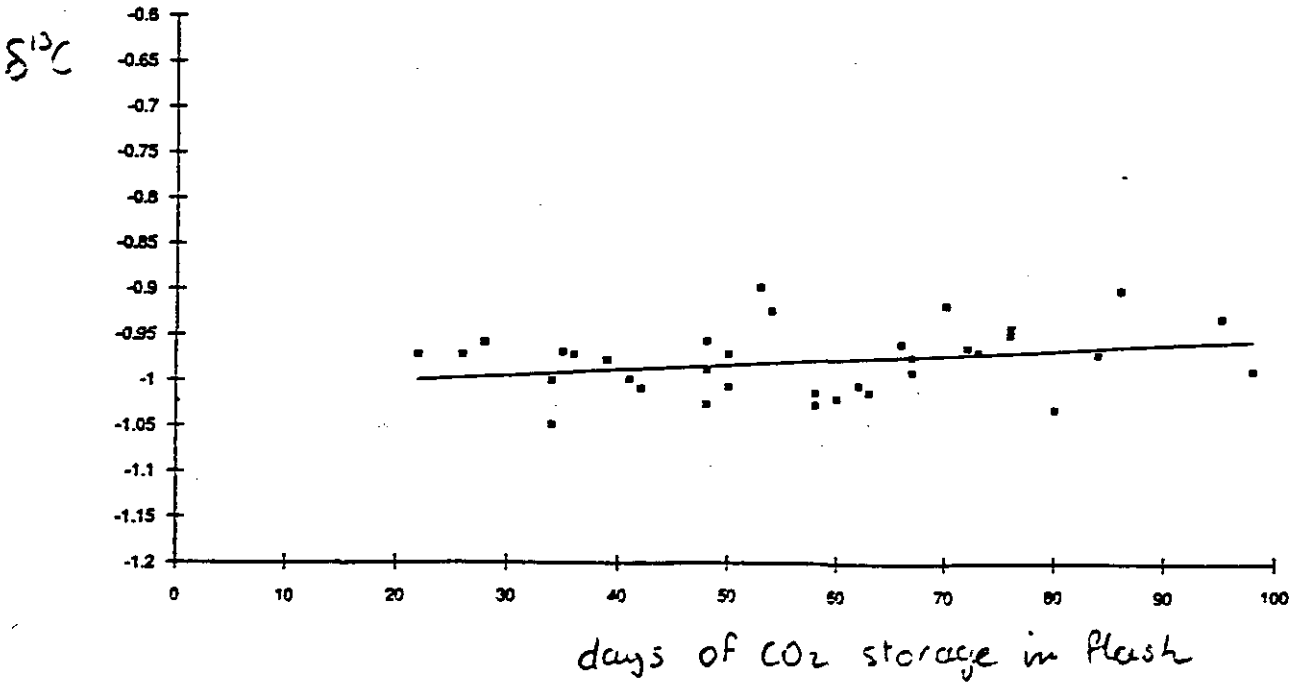
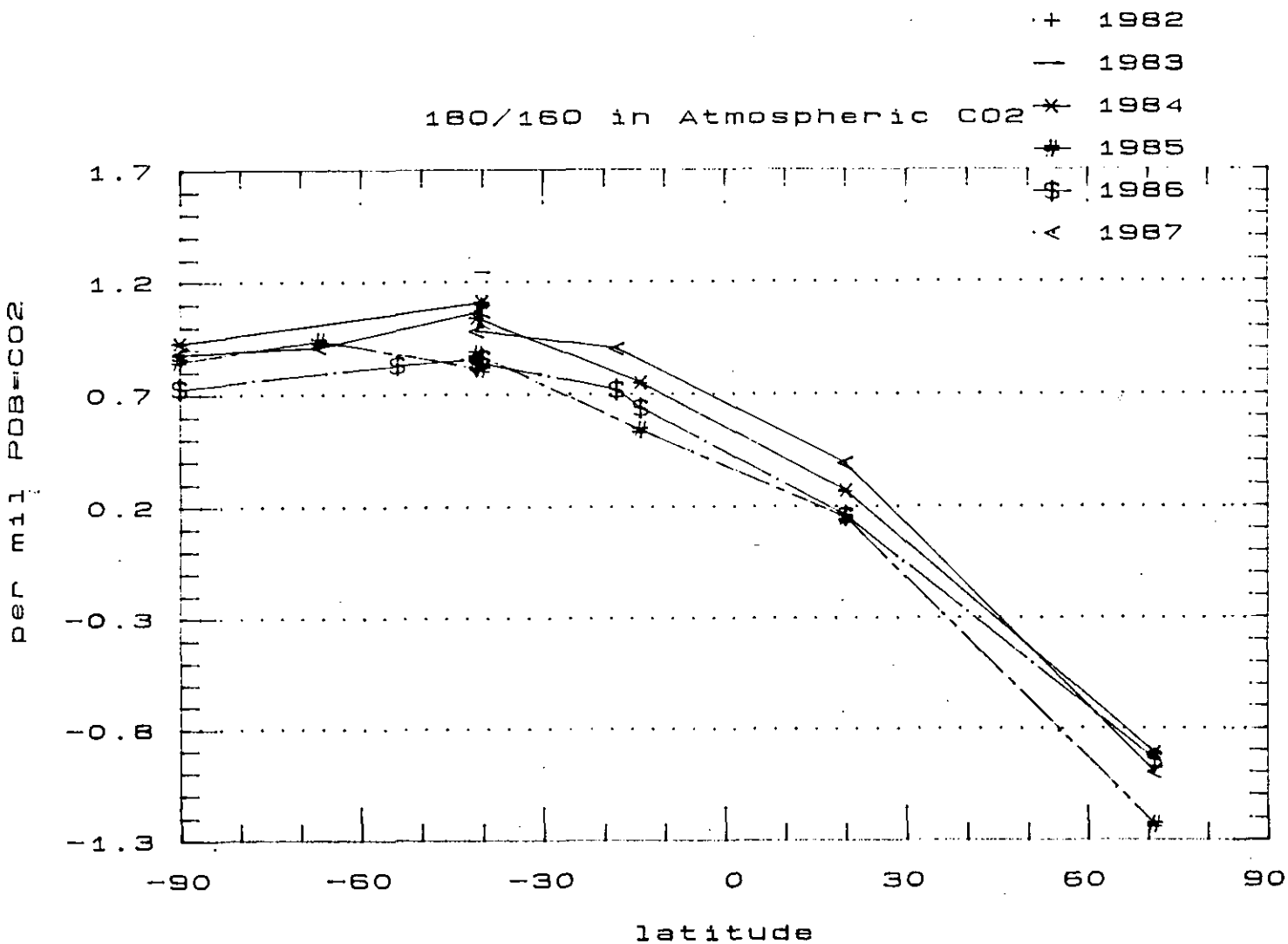


Figure 5(b): MAT252 δ^{45} values of Cape Grim in situ CO_2 samples #587-#632 as a function of storage time (days) in the 100 ml flasks with Teflon O-ring seal stopcocks.


180/160 in Atmospheric CO2
1982
1983
1984
1985
1986
1987
per mil PDB-CO2
1.7
1.2
0.7
0.2
-0.3
-0.8
-1.3
-90
-60
-30
0
30
60
90
latitude

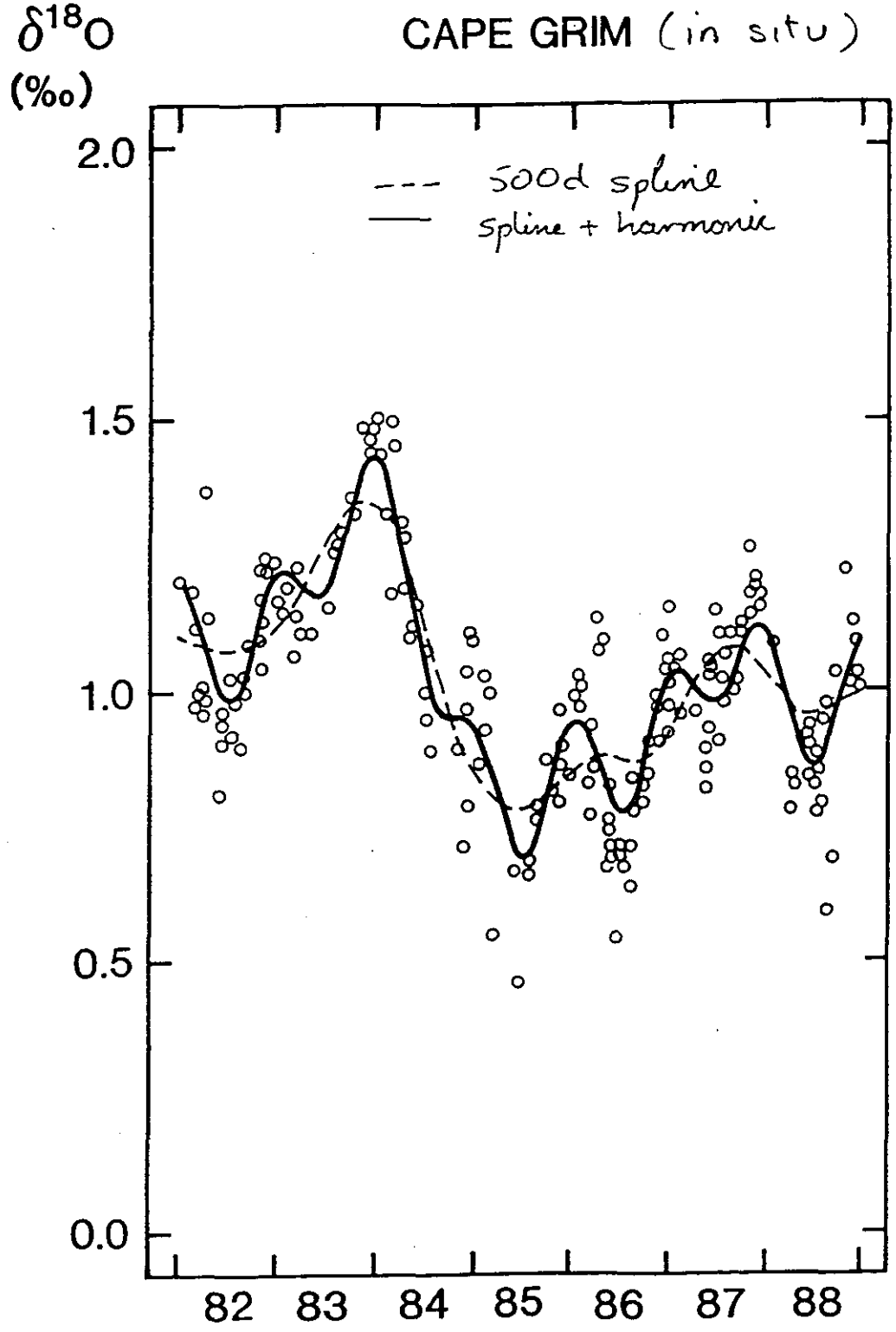

δ18O
(‰)
CAPE GRIM (in situ)
500d spline
spline + harmonic
2.0
1.5
1.0
0.5
0.0
82
83
84
85
86
87
88

FIG 1

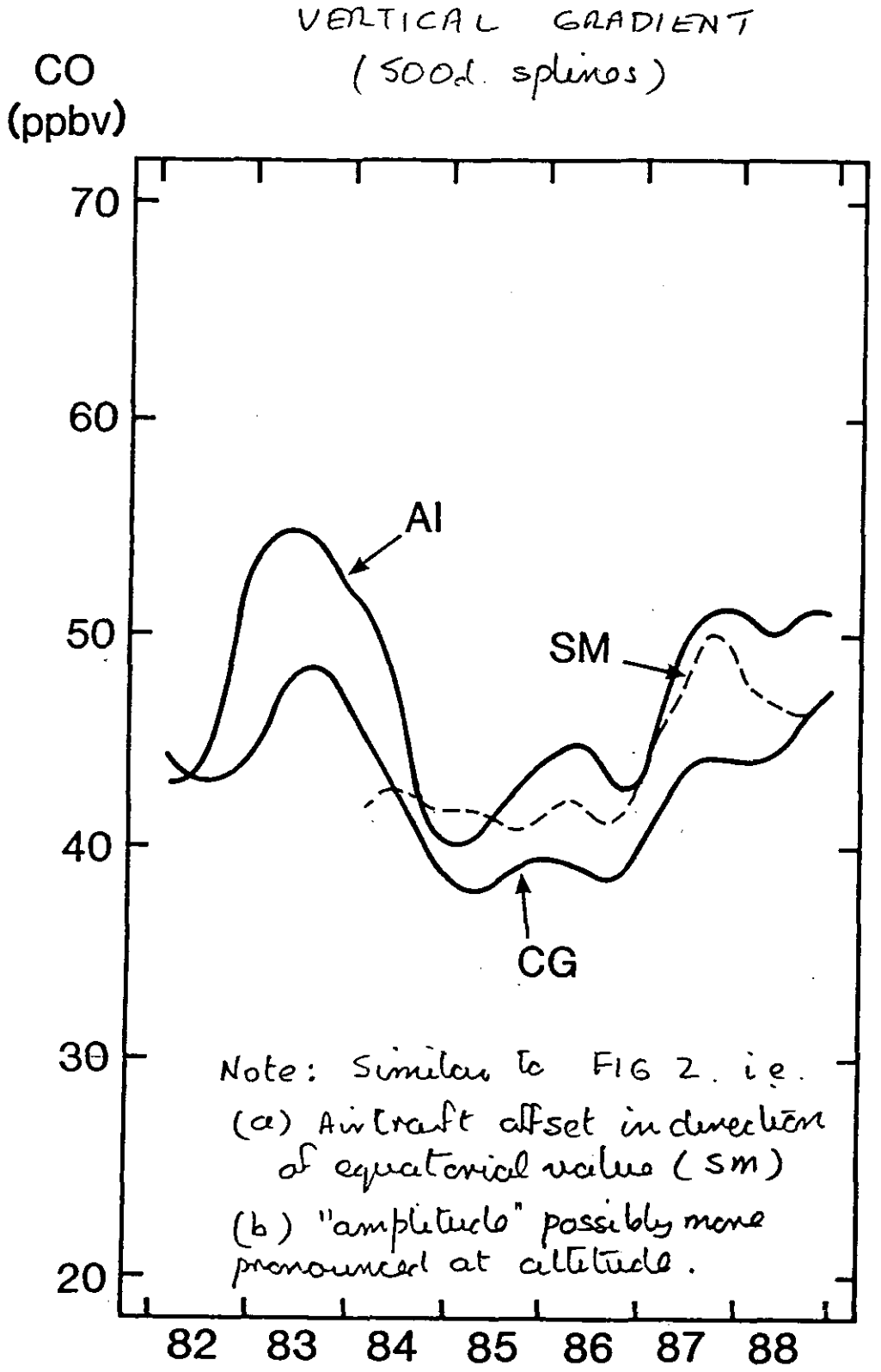


FIG. 7

(CSIRO / FRASER)