Isotopes: Fingerprinting the Sources and Sinks of Martian Methane

G.H.Morgan, I.P.Wright, C.T.Pillinger

PSSRI, The Open University, Walton Hall, Milton Keynes, MK7 6AA.

g.h.morgan@open.ac.uk

Methane on Mars

- Krasnopolsky *et al.* **
  - (1997) 70 ± 50 ppb
  - (1999/2004) 10 ppb

- Mumma *et al.* **
  - (2004) High Latitude = 20-60 ppb
    Equatorial < 250 ppb

- Formisano *et al.*
  - (2004) 10.5 ppb

PSSRI

CEPSAR
Centre for Earth, Planetary, Space & Astronomical Research

Abundance, Sources and Sinks

Distribution

- Uniform?
- Enhanced [CH_4] & [H_2O] in some areas?
- Strong methane gradient between equator and poles (250 to 50 ppb)?

Sources

Methanogens?
Geothermal (e.g. serpentization of basalts)
Significance of abiogenic (Comets, Meteorites, IPD) sources?
Volcanoes not thought to be a source (THEIMS – no hot spots / TEXES – [SO2] < 0.5 ppb)

Sinks

Photochemical only?
Hydrogen Peroxide Dust?
Methanotrophs?

Why Use Isotopes?

- The stable isotopic composition of a species, at natural abundance levels, is indicative of the physical and chemical history of the species.

- Measuring the isotopic composition of the species in a cycle, enables one to infer:
  - Formation processes
  - Sink processes
  - Influence of other physical processes (e.g. transport)

- Terrestrial biological systems discriminate between isotopomers, preferring to utilise the lighter isotope, resulting in very depleted species.

Stable Isotope Notation

All systems will result in fractionation, therefore instead of an absolute abundance being measured the isotope ratio of a sample is compared to that of a reference standard.

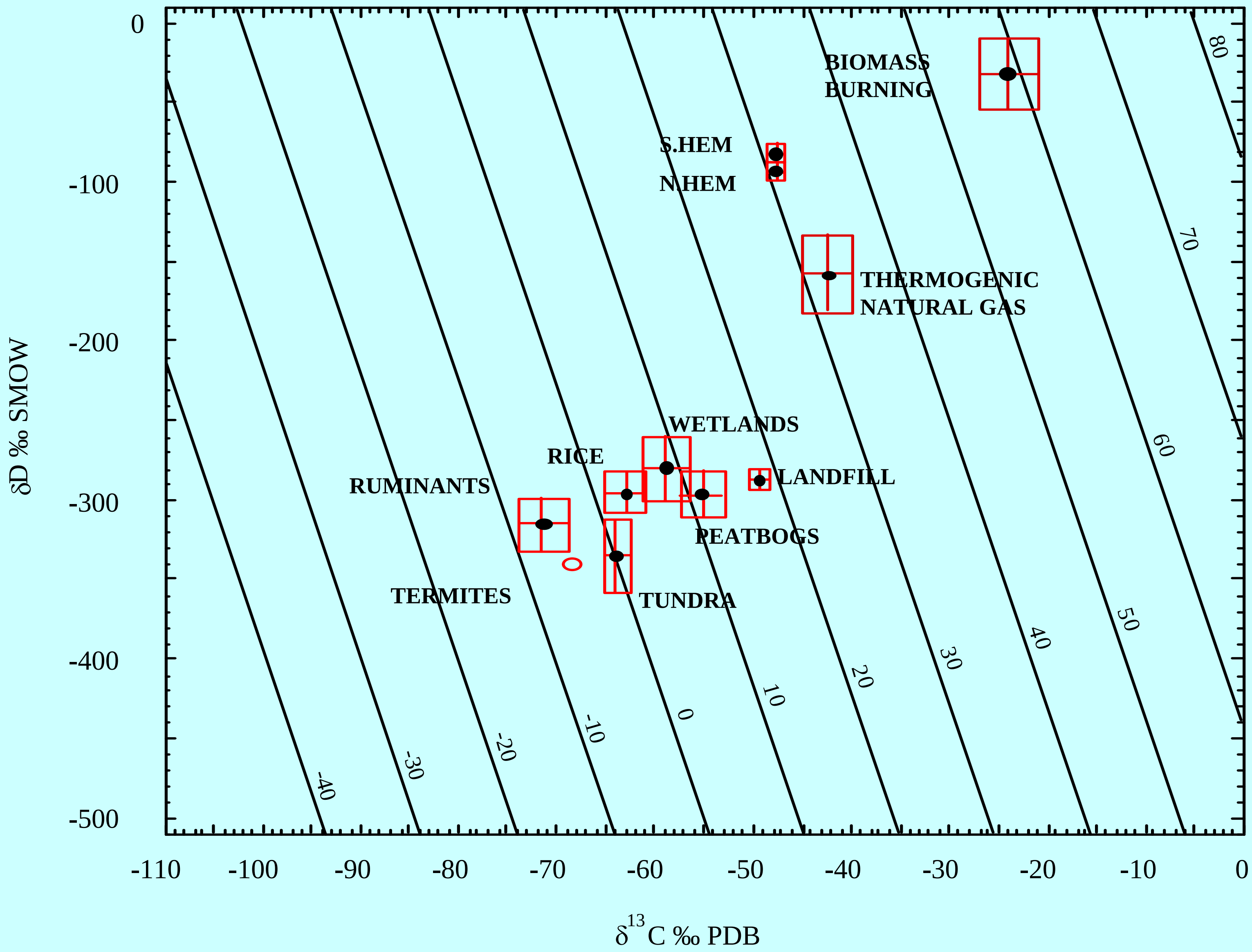
$$\delta^{13}C\ (‰) = \left(\left[\left({}^{13}C/{}^{12}C \right)_{sam} / \left({}^{13}C/{}^{12}C \right)_{ref} \right] - 1 \right) \times 1000$$

$$\delta D\ (‰) = \left(\left[\left(D/H \right)_{sam} / \left(D/H \right)_{ref} \right] - 1 \right) \times 1000$$

Urey (1948)

Stable Isotope Ratios

- $(^{13}C/\,^{12}C)_{PDB}$ = 0.0112372 (Craig, 1957)
- $(D/H)_{SMOW}$ = 0.00015576 (Hagemann, 1970)
- Where:
  - PDB = Pee Dee Belemnite
  - SMOW = Standard Mean Ocean Water



A.L. Butterworth, OU PhD (1997), Adapted from M.Wahlen (1994)

CEPSAR Centre for Earth, Planetary, Space & Astronomical Research

The Issue of Sample Size

$\delta^{13}C$ Determination

- Combustion of CH_4 to CO_2 (water removed)
- Originally required 70 litres of ambient air per analysis
- Currently between 10-100 ml of ambient air per analysis

δD Determination

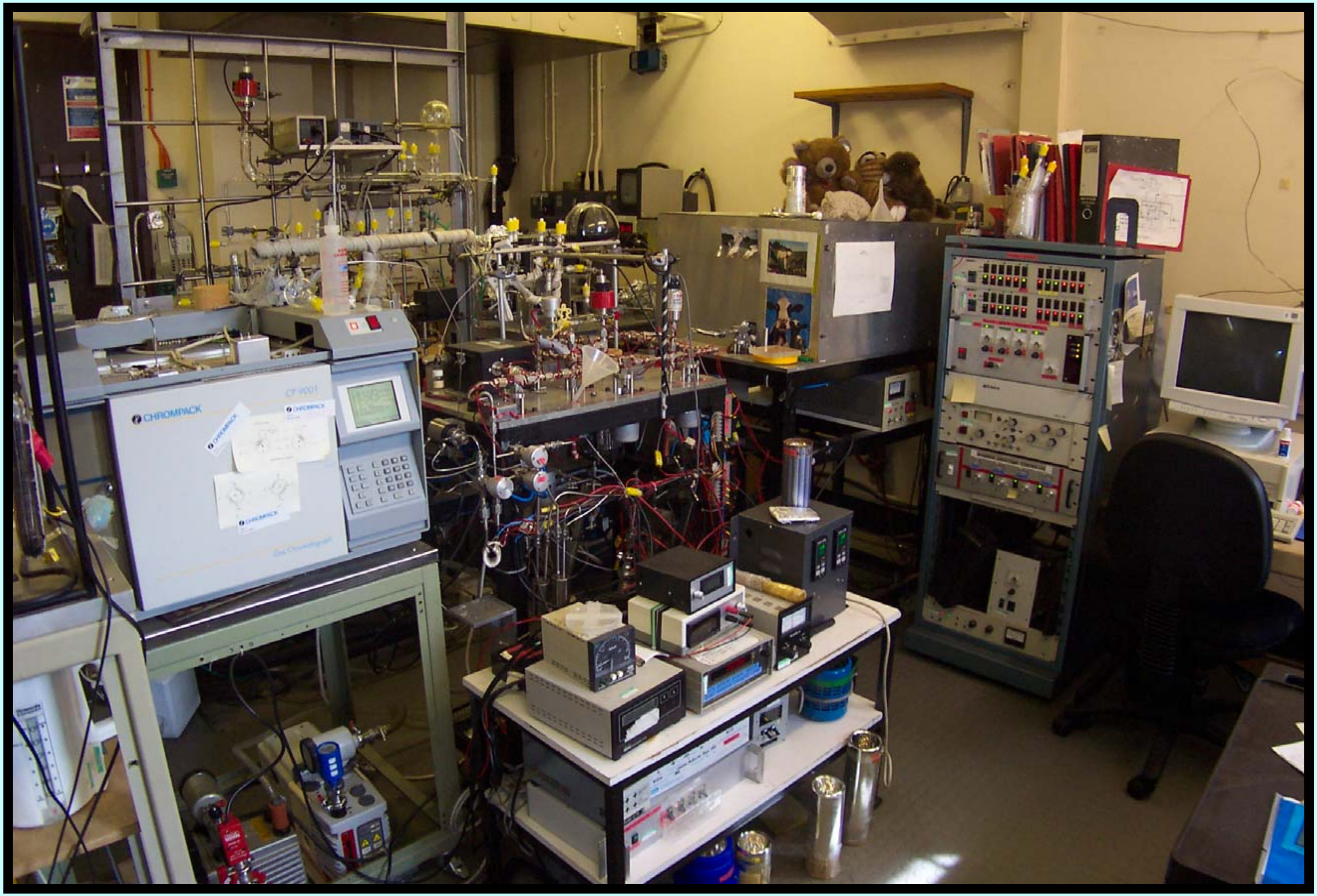
- Combustion of CH_4 to H_2O (CO_2 removed), then conversion of H_2O to H_2
- Originally required 1.5 m^3 of ambient air per analysis
- Currently ca 1.5 litres of ambient per analysis
- (Thermal Decomposition to H_2 directly, at 1400 C)

PSSRI

CEPSAR Centre for Earth, Planetary, Space & Astronomical Research

PSSRI

CEPSAR
Centre for Earth, Planetary, Space & Astronomical Research



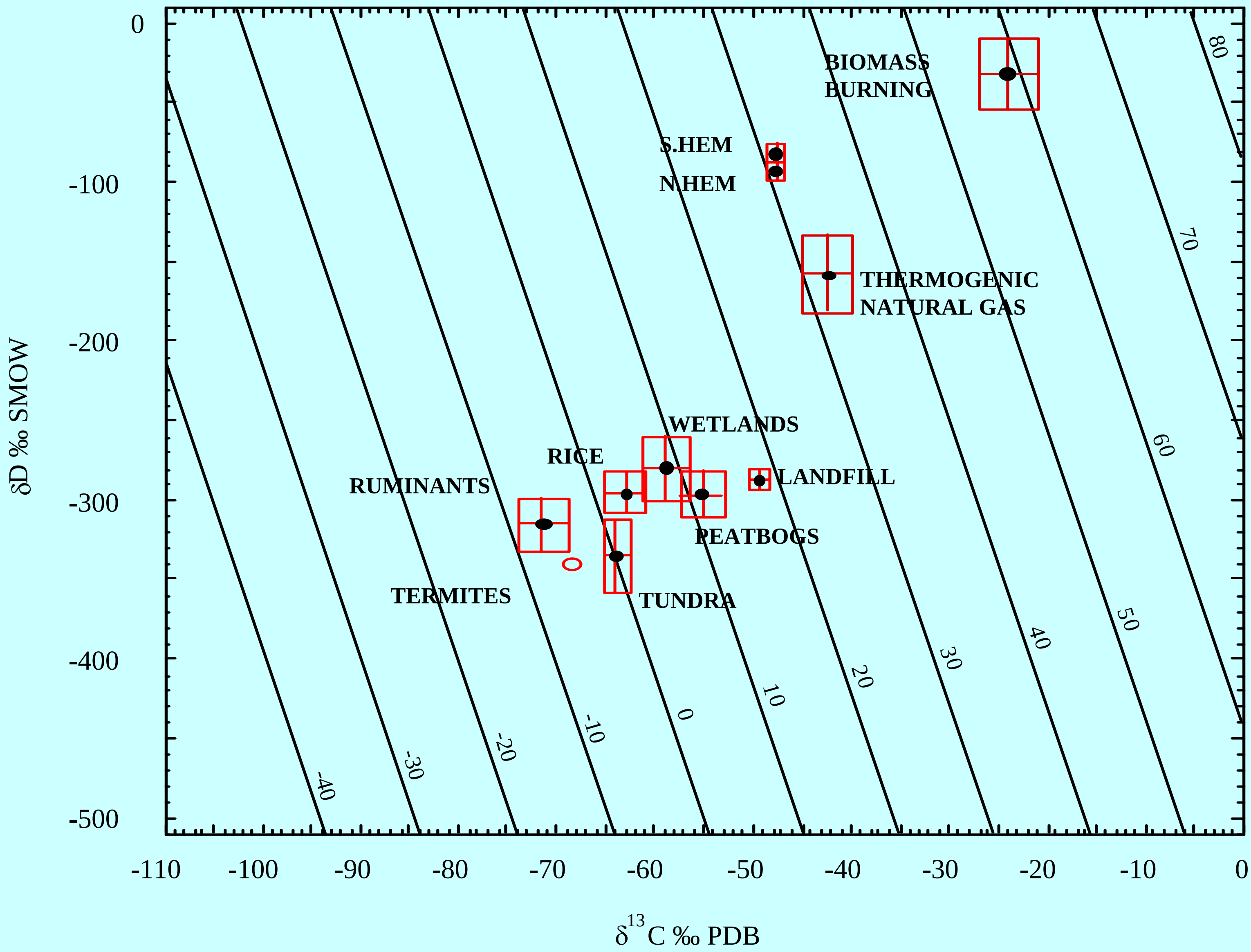
MIRANDA

MIRANDA

- Uniquely uses CH_4 as the analyte
- Static Mass Spectrometer
- Quantity of analyte = 0.3 nmoles
- Equivalent to 5 ml of ambient air
- δ^{17}M (δ^{13}C allows δD to be derived)
- Precision = ± 0.5 ‰
- Originally driven by Meteorite analysis programme

PSSRI

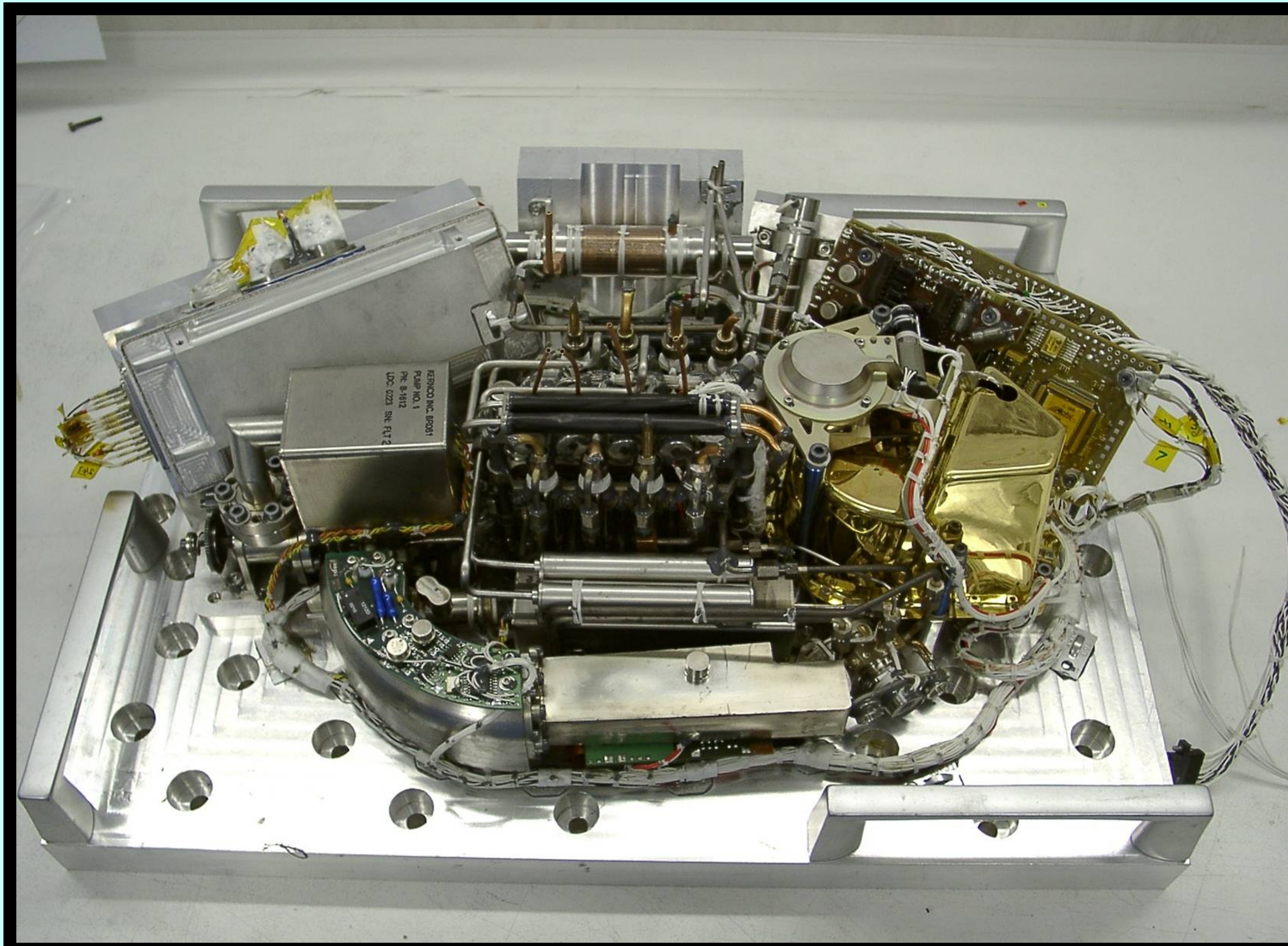
CEPSAR Centre for Earth, Planetary, Space & Astronomical Research



A.L. Butterworth, OU PhD (1997), Adapted from M.Wahlen (1994)

PSSRI

CEPSAR
Centre for Earth, Planetary, Space & Astronomical Research



The Gas Analysis Package (GAP)

PSSRI

CEPSAR Centre for Earth, Planetary, Space & Astronomical Research

	Earth	Mars
Pressure	1000 mbar	7 mbar
[CH_4]	1.7 ppm	10 ppb
Temperature	15 °C	-80 °C to 0 °C
Volume of sample (For 0.3 nmoles of CH_4)	4.5 ml	97 litres

* *PPARC funding post-doc to investigate way forward*

PSSRI

CEPSAR Centre for Earth, Planetary, Space & Astronomical Research

Issues / Constraints

- Quantity of analyte (1 litre = 3.1 E^{-12} moles)
- Complexity of matrix

  [CO_2] = 95.3%, [N_2] = 2.7%, [Ar] = 1.6%
- Budgets (Mass/Power/Volume, etc)
- Selectivity (must only measure methane)
- Practicality (e.g. chemical reagents)
- Survivability

PSSRI

CEPSAR Centre for Earth, Planetary, Space & Astronomical Research

Conclusions

1. Biogenic and abiogenic origins should be discriminated by *in situ* determination of the isotopic composition of methane in the Martian atmosphere ($\delta^{13}C$, $\delta^{17}M$, δD).

2. Technique needs to be highly sensitive and high precision

   (*i.e.* Magnetic Sector Mass Spectrometer)

Conclusions (II)

3. Measurement can not be performed in isolation, we require information on the other components of the Carbon and Water Cycles (and the kinetics of sink processes).

4. An evolution of the Gas Analysis Package (GAP), with a new inlet system, would be capable of such measurements.