Using stable isotope geochemistry to investigate the source(s) of volatiles in the lunar regolith

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Using Stable Isotope Geochemistry to Investigate the Source(s) of Volatiles in the Lunar Regolith

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1: Introduction:

- Previous laboratory analyses of lunar soil samples have documented a range of volatile species present within the regolith that blankets the lunar surface.

- Thermal gas release studies (heating soil samples at rates of 4-6 °C/min up to temperatures just exceeding their initial melting points) released noble gases, CH_4, CO, CO_2, H_2, H_2O, N_2, and sulphur-bearing species H_2S and SO_2 ([1], [2]). The temperatures at which these gases are released can be used to tentatively identify their sources; for example, solar-wind derived hydrogen and helium are released between 300-700 °C [2].

- Acid and deuterated acid dissolution studies (treating lunar soil samples with HF, DF, and DCl) released several ppm of 'lunar' methane (CH_4) and reaction-produced CD_4 (most likely from hydrolysable carbon (C_{hyd} is carbon associated with nanophase Fe^0) contributed by meteorite impacts and solar wind interactions [3]. Such methane and C_{hyd} compounds are concentrated in the finer fractions of lunar soils (48-152 µm diameter), being located on the surfaces/outer layers of grains [4].

- Isotopic studies have also been conducted; isotopic values are expressed using the delta notation, where: $\delta\,\text{Heavier isotope} = \left(\dfrac{\left(\frac{\text{Heavier isotope}}{\text{Lighter isotope}}\right)_{sample} - \left(\frac{\text{Heavier isotope}}{\text{Lighter isotope}}\right)_{standard}}{\left(\frac{\text{Heavier isotope}}{\text{Lighter isotope}}\right)_{standard}} \right) \times 1000$

- These studies have revealed that total C $\delta^{13}C$ values for lunar soils range from -30 ‰ to +30 ‰ [5]. Given that the values for possible terrestrial contaminants range between -20 ‰ to +20 ‰ [6], and that end-member solar wind carbon has a calculated $\delta^{13}C$ value of < -105 ‰ [7], it was suggested that lunar soil carbon is most likely from a meteoritic/cometary source [6]. However, this does not take into account C speciation, or the individual isotopic values of carbon-bearing gases in lunar soils.

- Therefore, focusing on CH_4 in lunar soils, the overall aim of this project is to measure its carbon isotopic signature as a means of fingerprinting the likely source(s) of such carbon.

- Given that methane in lunar soils is calculated to make up only around 15 to 25 % of the total carbon in lunar soils [8], such isotopic measurements will need to be performed on highly sensitive instrumentation, capable of handling relatively small amounts of sample gas

- To that end, this poster describes initial evaluation work carried out on the IonCam 2020 mass spectrometer at the Open University, to assess its suitability for use with lunar samples.

2: IonCam 2020 Gas Analysis Mass Spectrometer

- The IonCam 2020 mass spectrometer was purchased from OI Analytical (of Alabama, USA) in the autumn of 2012

- It is a miniaturised, 'transportable', non-scanning mass spectrometer, allowing for simultaneous detection of all masses present in a gas sample.

- The 'IonCCD' detector (Charge-Coupled Device) within the machine is described as pressure independent, and highly linear*, suggesting that it should function well with small amounts of gas (ideal for lunar soil samples). *A linear response here would mean that gas flow (measured as gas intensity at the detector) should be proportional to pressure squared.

- It is capable of performing fast analyses of samples, which allows transient processes to be monitored and recorded in 'real-time'.
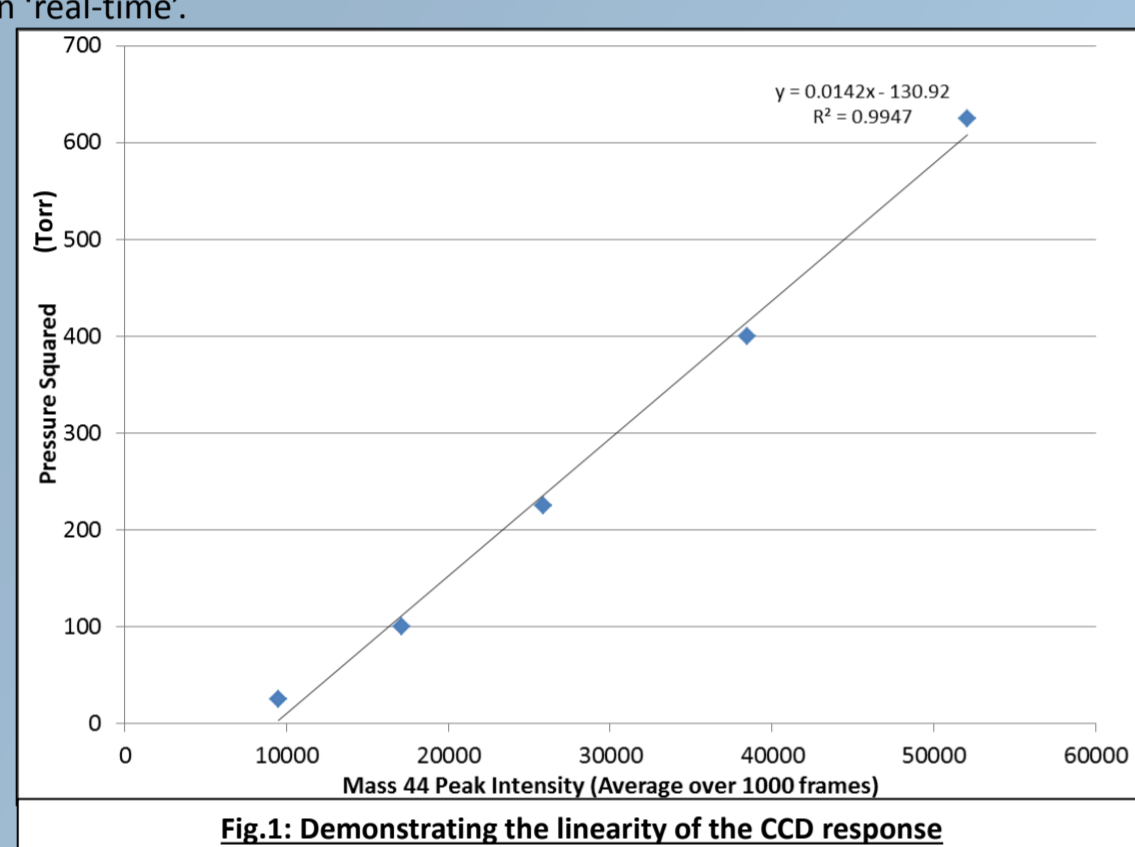
Fig.1: Demonstrating the linearity of the CCD response

- To investigate the IonCam's suitability for use with lunar soil volatile samples, it was attached to a continuous-flow reference gas line, via the inlet capillary on the front of the machine casing.

- Because the machine has no internal pressure gauge, a Baratron pressure transducer (1000 Torr) was incorporated into this reference gas line, allowing us to monitor how much gas is flowing into the mass spectrometer at any given time, and also how the machine performs at a range of different pressures of sample gas.

- The standard reference gas used to characterise the machine's performance was carbon dioxide (CO_2), which displays peaks at masses 44, 45, and 46 on a mass spectrum.

- Data was collected over several weeks, in both 'raw' form (measured intensity in each pixel on the CCD detector (mass peaks being roughly 20 pixels wide, and centred on specific pixels), and using the machine's 'TIC' or 'Total Ion Chromatogram' function (logging the real-time intensity of the three masses of interest (m/z 44, 45, and 46) in femtoamps (fA)).
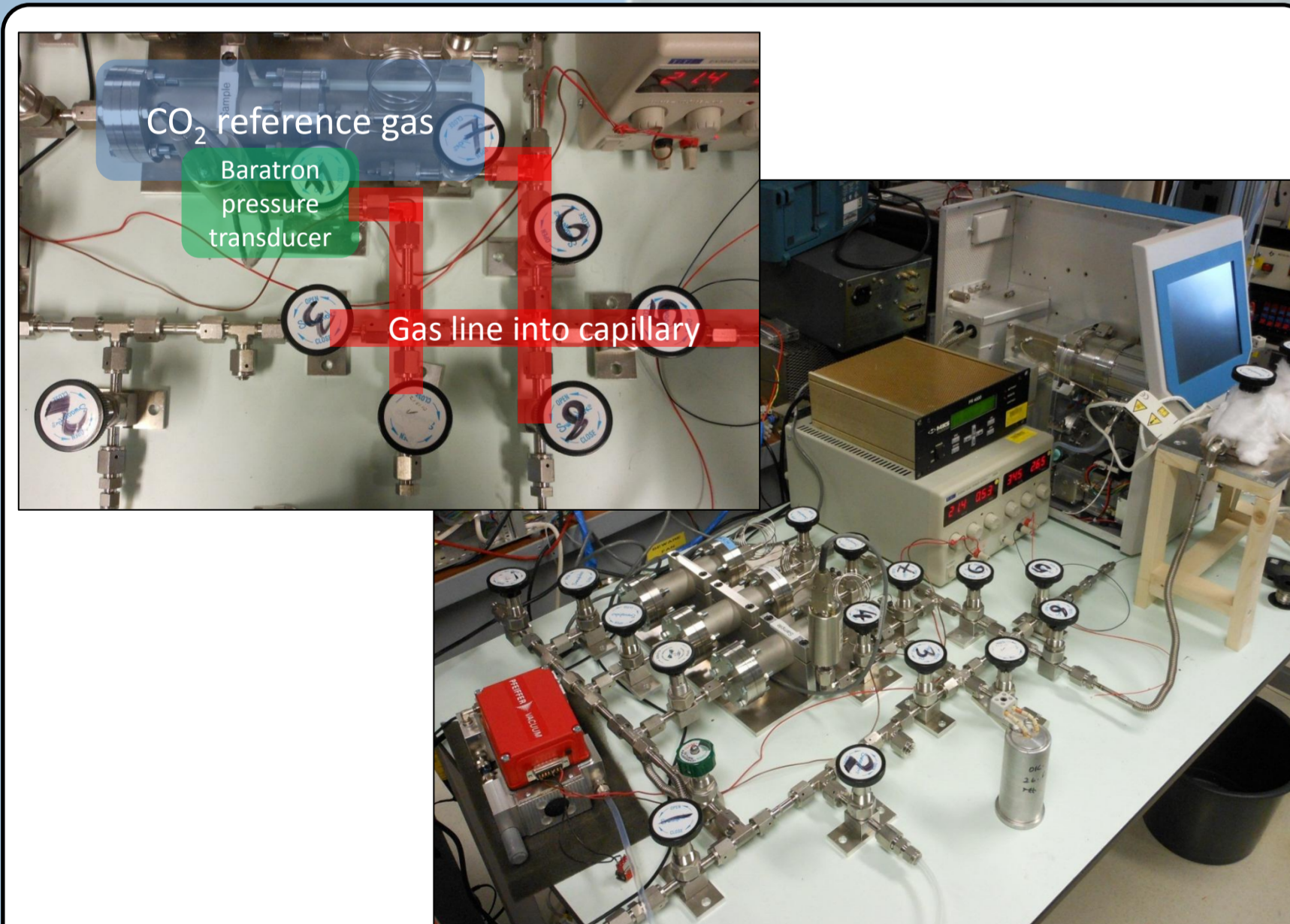
CO_2 reference gas
Baratron pressure transducer
Gas line into capillary

Fig.2: Reference gas line and IonCam set-up
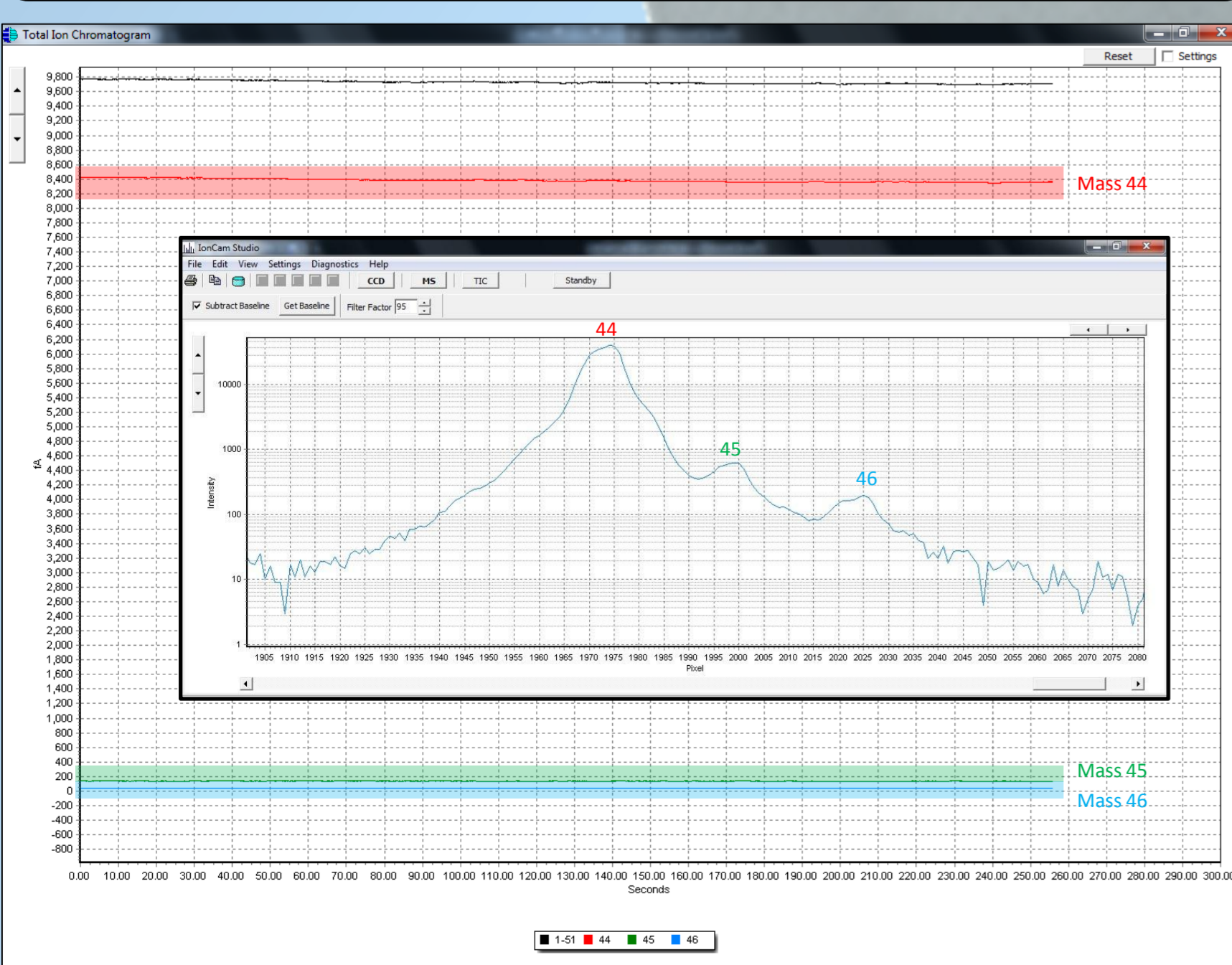
Mass 44
44
45
46
Mass 45
Mass 46

Fig.3: Real-time monitoring of specific masses using the 'TIC' function, and (inset) the corresponding raw CCD pixel display for the same masses (20 Torr)
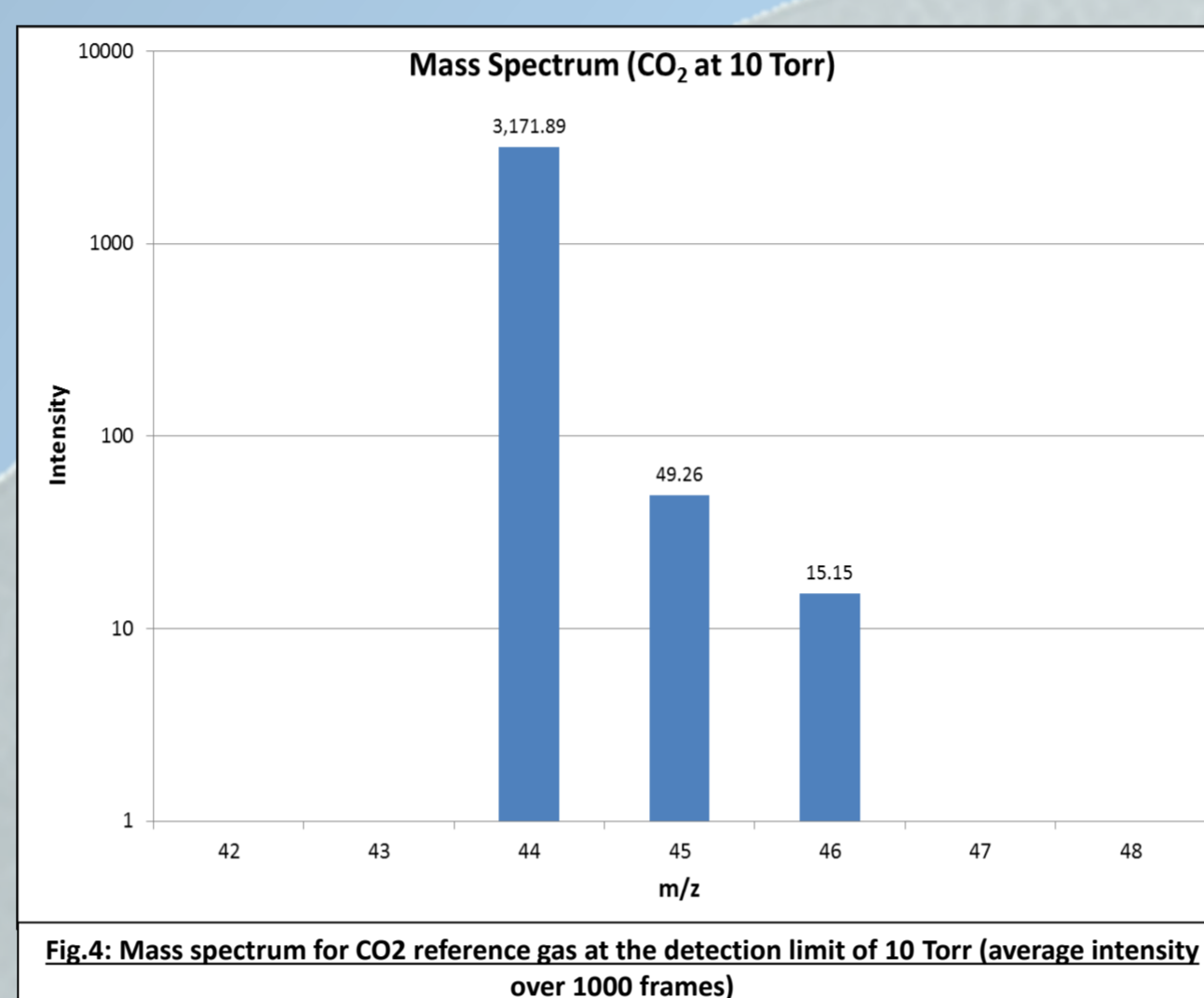
3: Detection Limit

Mass Spectrum (CO_2 at 10 Torr)

3,171.89

49.26

15.15

Fig.4: Mass spectrum for CO2 reference gas at the detection limit of 10 Torr (average intensity over 1000 frames)

- For the purposes of making an isotope measurement, the detection limit of the machine is taken as the smallest amount of gas needed to generate a stable, measureable peak in the mass spectrum for the least abundant isotope, in this case mass 46.

- By logging mass spectra at a range of different pressures (as measured by the gauge on the reference gas line), starting at 25 Torr, and decreasing in steps down to 5 Torr pressure, we found that the peak for mass 46 disappears at around 10 Torr, which, using the Ideal Gas equation (PV=nRT, where P= pressure, V= volume of gas, n= number of moles of gas, R= ideal gas constant, and T= temperature of the gas), corresponds to 9081.8 nmoles of CO_2 reference gas. (At this pressure, the leak rate from the reference gas line into the mass spectrometer inlet capillary is calculated to be 3.13982 x 10^{-6} mbar l/s)

- Thus, assuming data is being collected for 5 minutes to make one isotope measurement, 19 nmoles of CO_2 are required for the measurement, out of the total 9081.8 nmoles needed to maintain at least 10 Torr of pressure flowing into the machine.

	P(pascals)	V	R	T (K)		moles	nmol	ng	g	mg
25 Torr	3289.473684	0.000017	8.21	300		2.27044E-05	22704.44687	998995.6621	0.000998996	0.998996
20 Torr	2631.578947	0.000017	8.21	300		1.81636E-05	18163.55749	799196.5297	0.000799197	0.799197
15 Torr	1973.684211	0.000017	8.21	300		1.36227E-05	13622.66812	599397.3973	0.000599397	0.599397
10 Torr	1315.789474	0.000017	8.21	300		9.08178E-06	9081.778746	399598.2648	0.000399598	0.399598
5 Torr	657.8947368	0.000017	8.21	300		4.54089E-06	4540.889373	199799.1324	0.000199799	0.199799

Gas into machine in 1 second	6.30679E-11 moles per second
Gas into machine in 5 mins	1.89204E-08 moles
	18.92037239 nmol

4: Stability

- In order to make reliable, precise isotope measurements, the response seen on the detector needs vary as little as possible over the time taken to make a measurement (in this case, over 5 minutes).

- Given that $\delta^{13}C$ values from previous studies of lunar soils range from -30 ‰ to +30 ‰, to be able to distinguish between different potential sources of carbon, a variation over measurement time of < ± 1 ‰ would be ideal.

- To assess the variation in the measurements the IonCam makes, data collected at the machine's detection limit of 10 Torr CO_2 was used.

- The real-time counts of masses 44, 45, and 46 from the 'TIC' function (which logged 2850 frames of data over 5 minutes/300 seconds) were converted into isotope ratios (45/44 and 46/44) for each frame logged.

- The average ratios for both 45/44 and 46/44 were then calculated for each consecutive group of 100 frames over the 300 second measurement period, and these 100 frame average ratios were converted into 'per mil' (‰) variations from a 'standard' by comparing them to the average ratios for the following group of 100 frames, in a 'zero enrichment' calculation.

- Because this data was collected right at the detection limit of the machine, occasionally mass 46 would not be abundant enough to be measured; this results in the largest variations of ± several hundred ‰.

- However, when mass 46 was detected, the isotope ratios varied by around ± 20 ‰ over the course of the 5 minute measurement period, with 2σ relative errors in the region of ± 3 ‰ for the 45/44 isotope ratio, and ± 5 ‰ for the 46/44 ratio.

- Because many of the isotope ratio variations appear to be significantly larger than the calculated 2σ error values, it seems that the CCD detector in this machine is inherently unstable at this high level of precision; indeed, these measurements already take the detector below the manufacturer's stated sensitivity parameters, thus limiting the possibility of further improvements to stability.
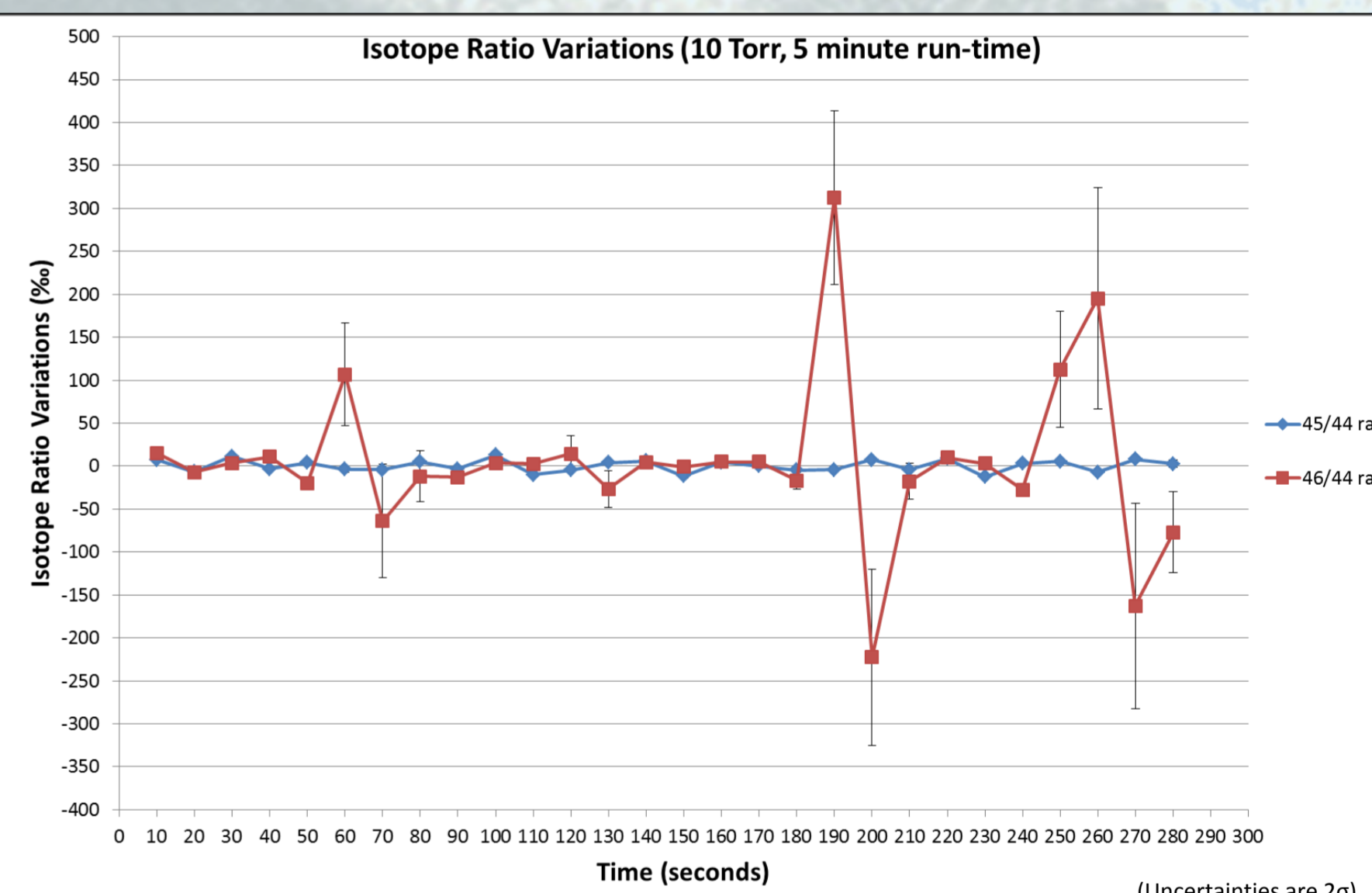
Isotope Ratio Variations (10 Torr, 5 minute run-time)

45/44 ratio
46/44 ratio

(Uncertainties are 2σ)

Fig.5: Isotope ratio variations (‰) over 5 minutes at 10 Torr, comparing the 100-frame average ratio with that of the following 100 frames

5: Suitability

- Using these results to make some rough calculations, based on the expected yield of volatiles containing carbon from lunar soils, the IonCam would only need around 100 times more sample (in the region of hundreds of micrograms per measurement) to make one isotope measurement than other high-precision established isotope mass spectrometers used at the Open University. However, the amount of sample gas needed to build up enough pressure (≥ 10 Torr) to make such an isotope measurement must be taken into account; this takes the amount of lunar soil needed up to tens of grams, far beyond what is a feasible amount to use, and indeed far in excess of how much lunar soil is available to use.

- Further, at best, the detector is capable of making isotope measurements with a variation of ± 20 ‰. Knowing that the whole range of values for possible solar system sources of carbon is only ± 30 ‰, it would be impossible to distinguish between different sources for the carbon found in lunar soils, using the IonCam as it is currently performing.

- There are also a number of other issues surrounding the use of the IonCam instrument for isotope work, one of which is poor resolution between peaks of similar masses, leading to tailing peaks which interfere with the measured intensities of neighbouring peaks. Another problem is the occasional presence of a 'digital' or stepped response from the detector; this is possibly a feature of the gain of individual pixels within the CCD detector suddenly switching, although this requires further investigation.

- To conclude, in its current configuration, the IonCam 2020 instrument is not suitable for use with lunar soil samples. Making some fairly easy, quick changes, such as reducing the internal volume of the reference gas line, and making isotope measurements over a shorter time period would reduce the amount of sample needed by a factor of 100, for example, but to fully resolve the machine's various issues, more in-depth modifications (perhaps adding a gas chromatography (GC) module, or replacing the CCD with a more stable detector) are necessary. Such extensive adaptation may indeed be carried out by others at the Open University in the future, although that is beyond the scope of this lunar geochemistry project to document.

6: Other Instrumentation

- There are several well-established instruments at the Open University that are capable of making highly precise isotopic measurements on small sample sizes, so these will be the next possibilities to explore.

- The first of these is 'Finesse', a custom-built instrument which incorporates on-line pyrolysis/combustion of samples, with three dedicated static-mode mass spectrometers to simultaneously collect isotopic data for different elements, such as carbon and nitrogen. 'Finesse' is a high-precision piece of instrumentation, and typically requires < 10 mg of sample to make measurements over a range of temperature steps (up to 1400 °C) [9].

- The second instrument suitable for work with lunar soil samples is the Thermo MAT 253 isotope ratio monitoring gas chromatography mass spectrometer (*irm*-GCMS). Although with this machine, the initial pyrolysis of the lunar soil samples must be carried out off-line, it uses helium as a carrier gas to move the sample gas through the chromatographic column, where the various volatiles are separated so that they enter the mass spectrometer at different times. Initial test runs (using pure 100 % methane) conducted recently have shown an isotope ratio variation of ± 0.18 ‰, using a sample size of just 665.5 ng. Further experiments will be carried out in the coming weeks to test its precision using 10 % CH_4 in helium as a standard reference gas.

- Finally, if changes are made to the IonCam instrument, it can always be revisited to reassess its suitability for this project.

7: References

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