



VAPoR – Volatile Analysis by Pyrolysis of Regolith – an instrument for *in situ* detection of water, noble gases, and organics on the Moon

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ABSTRACT

We present the Volatile Analysis by Pyrolysis of Regolith (VAPoR) instrument design and demonstrate the validity of an *in situ* pyrolysis mass spectrometer for evolved gas analyses of lunar and planetary regolith samples. *In situ* evolved gas analyses of the lunar regolith have not yet been carried out and no atmospheric or evolved gas measurements have been made at the lunar poles. VAPoR is designed to do both kinds of measurements, is currently under development at NASA's Goddard Space Flight Center, and will be able to heat powdered regolith samples or rock drill fines up to 1400 °C *in vacuo*. To validate the instrument concept, evolved gas species released from different planetary analogs were determined as a function of temperature using a laboratory breadboard. Evolved gas measurements of an Apollo 16 regolith sample and a fragment of the carbonaceous meteorite Murchison were made by VAPoR and our results compared with existing data. The results imply that *in situ* evolved gas measurements of the lunar regolith at the polar regions by VAPoR will be a very powerful tool for identifying water and other volatile signatures of lunar or exogenous origin as potential resources for future human exploration.

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1. Introduction

In situ volatile and isotopic measurements of water and potential biomarkers including simple hydrocarbons at solar system bodies such as Mars, the Moon, Titan, Enceladus, Europa, asteroids, and comets may lead to potential breakthroughs in the quest for the origin and history of volatiles in the solar system and the presence (or absence) of complex organic compounds important to life. Moreover, *in situ* volatile measurements would enable a ground-truth assessment of the availability of resources such as water and oxygen, important for a sustained human presence on the Moon or elsewhere. Isotopic measurements that are critical for establishing the origin of any volatiles, including organic compounds, will require a mass spectrometer with a high mass resolution, dynamic range, and sensitivity across a wide mass range. For example, they will serve as a detector of water and potential biomarkers, such as simple hydrocarbons that are

precursors for life, and measure C, H, and N isotopic compositions of these, which can be fractionated by biological processes.

There are several approaches to extract volatiles from regolith samples, such as crushing and mechanical agitation (Gibson and Andrawes, 1978), but the most efficient way to obtain the release of the widest range of volatiles is by vacuum pyrolysis, especially if the sample has been crushed prior to heating (Anderson et al., 1972). Several missions have used this approach, an overview of which is given in Table 1: The Viking landers in the 1970s were the first to carry and successfully apply pyrolysis gas chromatograph mass spectrometry (GCMS) on the surface of another solar system body, Mars. The Viking GCMS instruments were equipped with ovens that could heat regolith samples up to 500 °C causing the release of volatile organic material by vaporization and finally thermal decomposition of more refractory substances (Anderson et al., 1972; Biemann et al., 1977). More recently, the Thermal and Evolved Gas Analyzer (TEGA; Boynton et al., 2001), landed on the surface of Mars, onboard the Phoenix lander. The TEGA ovens heated polar regolith samples up to 1000 °C and the evolved gases were analyzed using a mass spectrometer (Boynton et al., 2001). The Philea lander of the Rosetta mission, currently on its way to comet 67 P/Churyumov–Gerasimenko, carries two evolved gas analyzers:

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Table 1
Overview of solar system pyrolysis ovens and their temperature profiles.

	Viking ^a	TEGA ^b	COSAC ^c	Ptolemy ^d	SAM ^e	VAPoR
Temperature range	50, 200, 350, and 500 °C	ambient–950 °C	ambient–600 °C	ambient–800 °C	ambient–1000 °C	ambient–1200 °C
Oven material	Ceramic	Nickel wrapped with platinum resistance wire and ceramic coating	Platinum wrapped with platinum resistance wire encased in glass.	Platinum wrapped with platinum resistance wire encased in glass.	Quartz cup in alumina wrapped with platinum resistance wire.	Platinum resistance wire encased in Zirconia.
Oven size diameter	2 mm: inner	7.2 mm	3 mm	3 mm	~500 mm ³	~100 mm ³
length	19 mm	21.6 mm	6 mm	6 mm		
volume	~60 mm ³	~38 µl				
Number of ovens	3	8	2	3	2 ovens, 74 sample cups	6

References:

- ^a Biemann et al. (1977).
^b Boynton et al. (2001).
^c Goesmann et al. (2007).
^d Wright et al. (2007).
^e Mahaffy (2008).

the Cometary Sampling and Composition experiment (COSAC; Goesmann et al., 2007) and Ptolemy (Wright et al., 2007). Both COSAC and Ptolemy will measure the elemental, isotopic, chemical, and mineralogical composition of the comet's surface and subsurface material. COSAC will analyze the evolved gases from near surface material using a GCMS, and is optimized for molecular and chiral analyses (Goesmann et al., 2007). Ptolemy will analyze (sub)surface material by direct sampling of the nucleus/coma and analyzing evolved gases using a GCMS, aiming at measuring isotopic ratios of lighter elements (Wright et al., 2007). Finally, the Mars Science Laboratory, planned for launch in 2011, will carry the Sample Analysis at Mars (SAM) instrument suite (Mahaffy, 2008), comprised of a pyrolysis oven system, six gas chromatographic (GC) columns equipped with thermal conductivity detectors, a mass spectrometer that can be coupled to the GC, and a tunable laser spectrometer to analyze the evolved gases and to make direct atmospheric measurements of water, CO₂, and CH₄. In this paper, we will describe and test a preliminary setup of a new instrument based on SAM design heritage called VAPoR (Volatile Analysis by Pyrolysis of Regolith), which is currently being developed at NASA's Goddard Space Flight Center (GSFC).

VAPoR is a vacuum pyrolysis mass spectrometer, designed specifically for operation on the lunar surface, but similar measurements can also be made on the surface of other airless bodies such as comets and asteroids without significant modifications in the instrument design. The rationale for VAPoR is the following: evolved gas analyses (EGA) are especially valuable for both science and exploration to determine the origins of water-ice and potentially other volatiles including organic compounds on the Moon. Previous observations by Clementine and the Lunar Prospector (LP) showed that the polar regions contain enhanced levels of hydrogen that may indicate the presence of water-ice (Bussey et al., 2005). Later, Saal et al. (2008) detected water concentrations of 30 part-per-million (ppm) by reanalysis of Apollo samples, which are higher than previously thought. The very recent detection of H₂O/OH by 3 independent missions, the M³ instrument on Chandrayaan (Pieters et al., 2009), the EPOXI (extended Deep Impact) mission (Sunshine et al., 2009), and the VIMS instrument on Cassini (Clark, 2009) further support the case for water-ice and/or hydrated minerals on the Moon. Preliminary data from the Lunar CRater Observation and Sensing Satellite (LCROSS) impact recently showed evidence for water-ice in the

Cabeus crater, about 100 km from the South Pole (*www-1*), and confirmed previous Clementine and LP data. Several processes are suggested to have contributed to the lunar volatile content. Water and other volatiles could have been delivered to the lunar surface by repeated cometary and meteorite impacts, for example, during the heavy bombardment period of 4.1–3.8 Ga (Mottmann, 1977; Cohen et al., 2000; Jørgensen et al., 2009), followed by migration and concentration at the cold permanently shadowed regions of the lunar poles. Remote D/H measurements of HCN from comet Hale-Bopp show that the volatiles are heavily enriched in deuterium compared to volatiles from other sources (Bockelée-Morvan et al., 2004), therefore if comets were the primary source of volatiles on the Moon they would also be expected to be enriched in deuterium. Another significant source that may add to or alter the lunar volatile content is the solar wind. It is possible that the hydrogen signal at the lunar poles is due to hydrogen implanted by the solar wind, which is delayed from diffusing out of the permanently shadowed regolith by low temperatures (Crider and Vondrak, 2002). Solar implanted C and H in the lunar equatorial soils have been found to be depleted in ¹³C and D, with isotope ratios that are distinct from terrestrial organics, comets, and carbonaceous meteorites (Kaplan, 1972; Hashizume et al., 2004; Busemann et al., 2006). The solar wind also plays a role, among other potential sources, in the ¹⁵N/¹⁴N ratios on the lunar surface, which may have varied significantly over the last 4 billion years (Kerridge, 1993; Kim et al., 1995; Hashizume et al., 2000). Though controversial (Buratti et al., 2000), lunar transient events (Cameron, 1977) have been proposed to be a third potential source of volatiles on the Moon. Cameron (1977), Middlehurst (1977), and Crotts (2008) have suggested that the transient phenomena that appear over the surface may be the same phenomena as the apparent venting noted during Apollo 14 (Freeman et al., 1972). Fig. 1 shows the isotopic signatures of different sources of organics.

The asymmetric distribution of water (and possibly other volatiles) between the lunar equator and poles suggested by the missions discussed previously may lend credibility to the hypothesis that the volatiles delivered to the lunar surface in this period have migrated to the polar cold trap regions of the Moon over time (Crider and Vondrak, 2000). Lunar hydrogen reservoirs seem to include water-ice, solar wind deposits, and hydrated minerals. The distribution of hydrogen between these reservoirs awaits measurement.

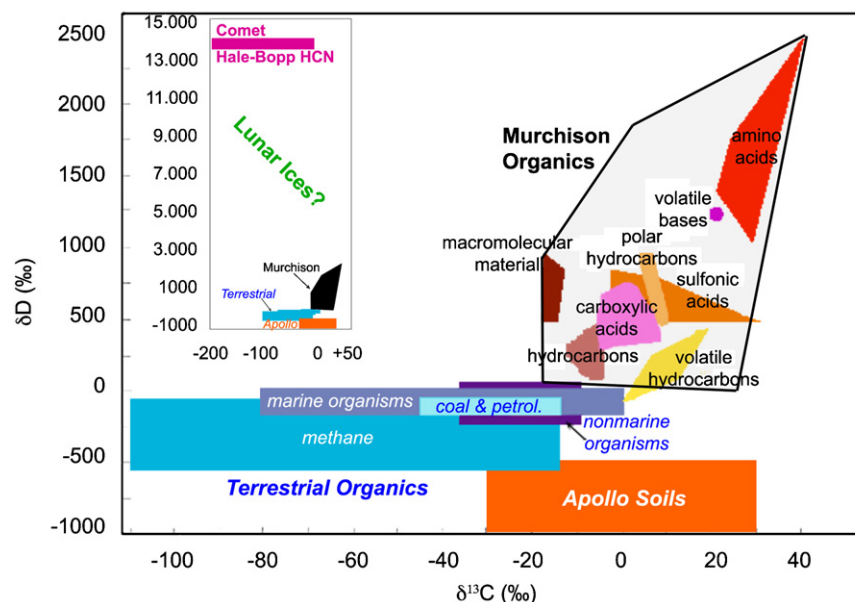


Fig. 1. The gas flow diagram of VAPoR, showing a schematic overview of the instrument. Regolith samples are introduced into one of the six pyrolysis cups through the solid sample inlet tube. This cup is then heated and the evolved gases flow into the ion source of the mass spectrometer. Direct atmospheric measurements are made through the atmospheric inlet, which feeds the gases directly into the mass spectrometer. In static mode a high conductance valve can be opened to an active gas getter for noble gas enrichment. Calibration gas will be used to calibrate the instrument at the lunar surface.

Although there is increasing evidence for an asymmetric distribution of water concentration on the Moon, it is still unknown whether or not other volatiles are present in the regolith (including hydrocarbons) and how the distribution of volatiles in the regolith at the lunar poles compares with other regions. The volatile inventory of the lunar equatorial region is well known through the analyses of samples recovered during the Apollo missions (De Maria et al., 1971; Gibson and Johnson, 1971; Simoneit et al., 1973). To thoroughly understand the volatile abundance, distribution, and isotopic composition of the lunar regolith, *in situ* analysis will be required, and for the permanently shadowed regions, unless extraordinary measures are taken (e.g. collection and Earth return at 50 K), a large fraction of the original volatile material would be lost prior to analyses on Earth.

To date, the only *in situ* surface measurements of the volatile composition of the lunar exosphere were made by the Lunar Atmosphere Composition Experiment (LACE) mass spectrometer on Apollo 17 (Hoffmann et al., 1973, Apollo Preliminary Science Report) and there have been no *in situ* volatile measurements (atmosphere or regolith) at the lunar poles. Therefore, VAPoR has been designed to analyze regolith at the lunar surface *in situ* to (1) confirm the amounts of water and/or OH identified by spectroscopic measurements made by LCROSS, Cassini VIMS, Chandrayaan-1 M³, and Deep Impact and discriminate between adsorbed water and water released from hydrated minerals; (2) detect other volatiles, including the ones found in the Apollo samples, to establish whether differences exist in composition and concentration between the poles and the equator; (3) measure the isotopic composition of a selection of compounds to establish the origin of the volatiles, and (4) assess hazardous or useful compounds for possible future man-based lunar bases. Volatile measurements by VAPoR at the lunar poles could also yield astrobiologically important information on the delivery of volatiles and pre-biotic organic materials by comets to the early Earth.

VAPoR is designed to operate on a rover or lander that can land and operate in remote and inaccessible locations, such as permanently shadowed craters. In both cases, samples would be collected and delivered to the VAPoR instrument solid sample inlet tube via a robotic arm. However, it can also be deployed and

operated as a portable instrument by an astronaut, who can collect and deliver rock samples directly to the instrument. Elements of VAPoR are based on the design of the SAM instrument suite (Mahaffy, 2008), but VAPoR is a smaller, more portable, instrument designed for shorter mission durations. It will have an oven designed specifically to heat samples to higher temperatures than SAM (see Table 1), enabling the detection of oxygen released from silicates and allowing efficient release of radiogenic (decay-produced) and spallation-produced noble gases. This paper describes the VAPoR instrument, its current implementation as a breadboard prototype, and our initial tests with extraterrestrial samples. These initial breadboard results confirm previous evolved gas analyses of Apollo and Murchison samples (see Results and Discussions sections).

2. The VAPoR instrument

2.1. Specific scientific targets

VAPoR will focus on the analyses of C, H, O, N, and S containing volatiles and their isotopes, and the pyrolysis program used was optimized for the detection of simple aliphatic and aromatic hydrocarbons such as methane, ethane, benzene, and toluene. In addition, VAPoR will take measurements of the distribution and isotopic composition of the noble gases He, Ne, and Ar. These measurements are important to understand the contribution of noble gases from solar wind implantation and cosmic-ray bombardment and potentially even outgassing from the lunar interior. Measurements of ⁴⁰Ar released from rock samples by VAPoR could be important for K–Ar age dating if K abundances can be derived by another measurement technique. Table 2 gives an overview of VAPoR's target volatiles and their release temperatures.

2.2. Instrument setup

VAPoR will consist of a sample carousel containing 6 individual pyrolysis oven crucibles to heat solid samples using a specified

heating ramp up to 1400 °C, attached to a mass spectrometer to analyze the evolved gases. The basic operation of VAPoR is as follows: (i) a predefined volume of crushed sample or rock fragment (corresponding to a sample mass in the order of ~10–100 mg) is dropped through the sample inlet into one of 6 oven crucibles, either by a robotic scoop on a rover, or by an astronaut; (ii) the oven is rotated by a sample manipulation

system directly underneath the inlet of the mass spectrometer and lifted to form a leak tight seal to the mass spectrometer inlet; (iii) the oven is then heated (step or linear ramp) to a maximum temperature of 1400 °C and the evolved gases are analyzed directly by the mass spectrometer.

Table 1 gives an overview of the characteristics of current solar system pyrolysis ovens. The VAPoR ovens will be designed to achieve much higher temperatures (up to 1400 °C) compared to previous flight pyrolysis units (Table 1). The ability to heat regolith samples to these temperatures is critical for releasing oxygen and some noble gases that are only released at temperatures in excess of 1200 °C under vacuum. In addition to evolved gas measurements of regolith, VAPoR is also capable of operating in another mode where direct volatile measurements of the lunar exosphere can be made through an atmospheric inlet. In the static operation mode a getter will pump the active gases and enrich the noble gases. The gas flow diagram of VAPoR is shown in Fig. 2. With the inclusion of a turbo pumping system on VAPoR, volatile measurements can also be made during field-testing on Earth, and on other bodies of astrobiological interest, including Mars and Titan. Although the current VAPoR breadboard is fairly massive (~40 kg) and requires significant power to operate (~200 W average), due to the need for a large turbomolecular pump, the VAPoR flight unit, based on the SAM design, will be much smaller ~20 dm³, weighing ~10–15 kg. The aimed power consumption for a typical evolved gas analysis up to 1400 °C based on extrapolation of required power for operation of the SAM flight pyrolysis ovens is in the 40–60 W range.

The SAM instrument uses a quadrupole mass spectrometer with unit mass resolution from 2 to 535 amu. We are currently testing a miniature TOF-MS with a much higher mass resolution and mass range ($m/\Delta m \sim 500$) to be used by VAPoR (Getty et al., 2007; King et al., 2008; Roman et al., 2008). The intrinsic sensitivity of this mass spectrometer is ~10⁻⁴ (counts/second)/(particle/cc) for N₂. The ability to perform isotopic analysis

Table 2
Release temperatures of target gases for the VAPoR pyrolysis mass spectrometer instrument.

Instrument target gases		Temperature range (°C)
CHONS–Inorganics	Atmospheric volatiles	Not applicable
	H ₂ O, H ₂ , CO ₂ , CO, N ₂ , SO ₂	0–1400 ^{a,b,c}
	¹³ C/ ¹² C ratio of CO ₂	100–1400 ^b
	¹⁵ N/ ¹⁴ N ratio in N ₂	600–1400 ^b
Noble Gases	HDO/H ₂ O ratio	0–1400
	He, Ne, Ar	300–1400 ^{b,e}
	Isotope ratios (³ He/ ⁴ He, ³⁶ Ar/ ⁴⁰ Ar)	He: 200–500 ^d , Ar: 300–1400 ^{b,e}
Organics	¹³ C/ ¹² C ratio in CO ₂ from organics combustion	400–500 ^f
	Volatile hydrocarbons: methane, ethane, benzene, amines, alcohols, formaldehyde	300–1000 ^b
	Water–ice in regolith	0–100
Resources	O ₂	1100–1400 ^d
	Reduced inorganic gasses such as HCN, NH ₃ , and H ₂ S	HCN/NH ₃ : 100–900 ^b , H ₂ S: 700–1300 ^c
	³ He relative abundance	He: 200–500 ^d
	³ He relative abundance	He: 200–500 ^d

References:

- ^a Simoneit et al. (1973).
- ^b Holland et al. (1972).
- ^c Gibson and Johnson (1971).
- ^d De Maria et al. (1971).
- ^e Lord (1968).
- ^f Court et al. (2005).

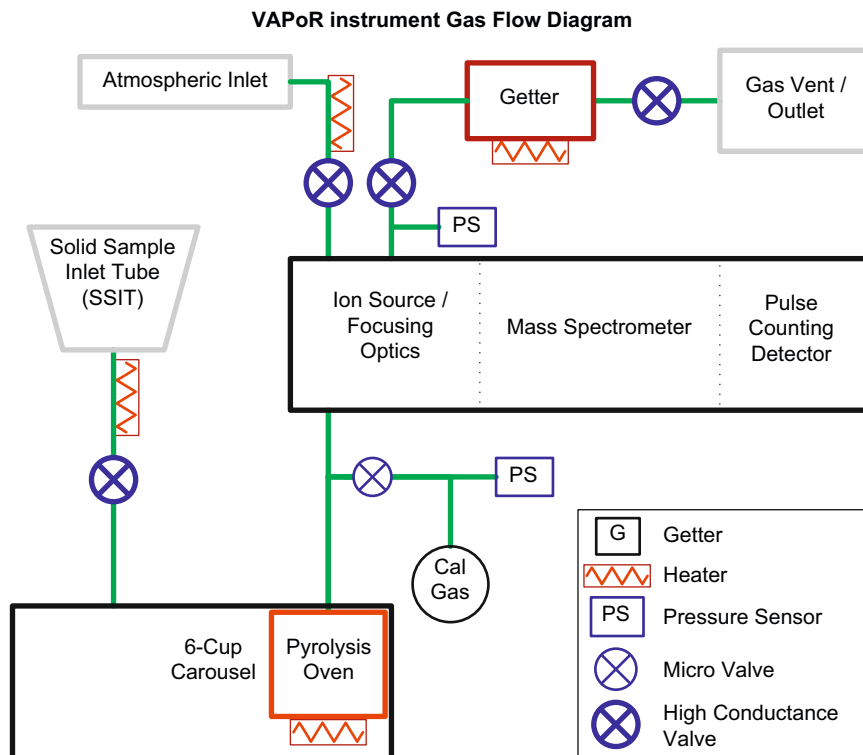


Fig. 2. Possible sources of lunar organic material and its isotopic signatures (after Sephton and Botta (2005) with additional data from Bockelée-Morvan et al. (2004); Kaplan (1972)).

depends on several factors, including abundance, integration time, mass resolution ($m/\Delta m$), and sensitivity. Whereas this mass spectrometer will be able to distinguish ^3He and ^4He , HDO and H_2O , as well as HD and ^3He , it does not have sufficient mass resolution to separate isobaric interferences in the amu 28 channel due, for example, to CO and N_2 . Tests are currently underway to further specify the isotopic measurements that VAPoR will be able to make. Table 3 gives an overview of current state-of-the-art mass spectrometers as well as how the VAPoR TOF-MS and the residual gas analyzer, which is part of the VAPoR breadboard (see Section 3), relate to these instruments.

To validate the VAPoR instrument concept a breadboard has been developed to test different heating rates and instrument components. This VAPoR breadboard has been assembled from commercial components that resemble those that would be incorporated into a flight instrument. The maximum sample temperature used for the breadboard laboratory experiments carried out as part of this research was 1200°C , however we are currently testing an oven crucible capable of achieving 1400°C under vacuum. In the following sections we describe the status of the current VAPoR laboratory breadboard and the results obtained from the analysis of an Apollo 16 lunar regolith sample and a sample of the Murchison meteorite. The Murchison meteorite sample was selected as an analogue for a carbonaceous asteroid or comet.

3. The VAPoR breadboard and the analytical protocol

The VAPoR breadboard consists of a stainless steel vacuum chamber, equipped with a turbo-diaphragm pumping station (Pfeiffer Vacuum TSU071E, TC600), a pressure gauge (Pfeiffer Vacuum PKR 251), and a residual gas analyzer (RGA; Stanford Research Systems RGA 300; sensitivity of the faraday cup detector: 2×10^{-4} A/torr; see Table 3). The breadboard is shown in Fig. 3. Samples were pyrolyzed using a modified Knudsen cell (WA Technology, Cambridge, UK, Fig. 4A), with a quartz sample holder (Fig. 4B) placed in a graphite crucible that is mounted inside an alumina heater threaded with tungsten heater wire. The heater is held in place by a stainless steel tube in a stainless steel water-cooled jacket. The sample was heated using a Watlow temperature controller (SD 6C-HF-AA-AARG) with an Omega solid-state relay (SSR240DC25), and a Variac power source (type 033-2558). A Pt-10%Rh thermocouple was used to measure the temperature of the heater. The breadboard is setup such that there is direct line of sight from the heated sample to the ionization region of the RGA. A similar configuration is envisioned for a flight instrument.

The quartz holders (Fig. 4B) that were used to pack the sample were cleaned in an ultrasonic bath for 10 min in deionized water (Cole–Palmer IonXchanger), followed by 10 min in 95% HPLC

Table 3
State-of-the-art space flight mass spectrometers, the VAPoR TOF-MS and breadboard RGA[#].

	Strofiio Bepi-Colombo	SAM QMS MSL	COSAG Rosetta	Ptolemy Rosetta	VAPoR TOF-MS design goals	test bed RGA
Mass Spectrometer						
Type	TOF	Scanning Quadrupole	TOF	Ion trap MS	Reflectron TOF	Scanning Quadrupole
Mass Range	1–60 Da	2–535 Da	1–1500 Da	12–100; 40–150 Da	1–1000 Da	1–300 Da
Electron Emitter	Thermionic	Thermionic	Thermionic	Nanotips	CNT Field	Thermionic
Arrayed Emitters	No	No	No	Yes	Yes	No
Sensitivity/N_2 (cps/molecule/cc)	1.4×10^{-1}	5×10^{-3}	–	–	1×10^{-4}	$\sim 4 \times 10^{-2}$
Resource Requirements						
Power (avg, W)	~ 1	14.5	8	10	~ 1	60
Mass (kg)	1.7	1.3	4.9	4.5	< 0.4	2.7
Volume (cm^3)	1000	3000	4700	198	< 1000	855

[#] Modified and updated from King et al. (2008)

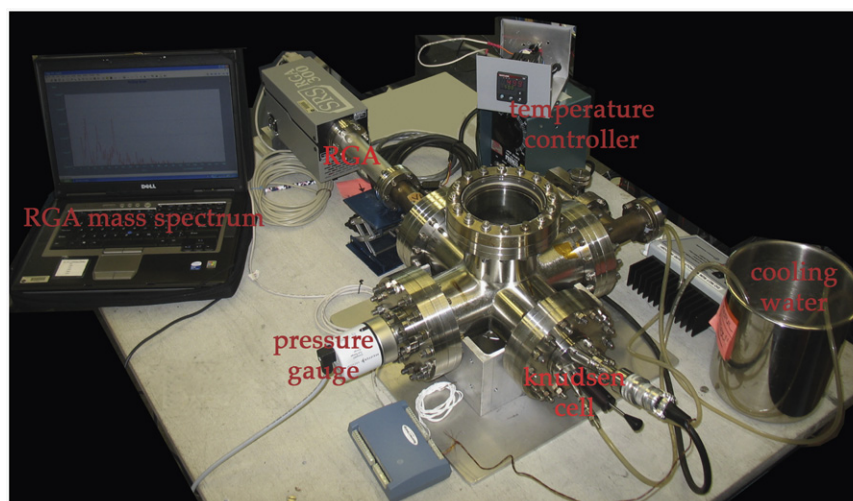


Fig. 3. The laboratory breadboard used to demonstrate the VAPoR instrument concept, with the stainless steel cross in the middle, equipped with an RGA, a pressure gauge, a Knudsen cell and a turbo-diaphragm pumping station.

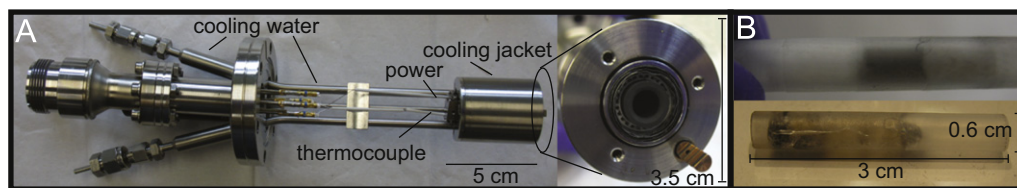


Fig. 4. A) The modified Knudsen cell used as a high temperature vacuum pyrolysis oven. The Knudsen cell pyrolysis oven is designed to reach a maximum temperature of 1200 °C. B) Quartz sample holder with sample before (top) and after (bottom) pyrolysis. The soil sample is kept in place with quartz wool on both sides. A next generation pyrolysis oven is being designed to reach 1400 °C.

grade n-hexane (Fisher Scientific), and 10 min in 99.5% absolute 200 proof ethanol (Fisher Scientific), the holders wrapped in aluminum foil and then baked for 2 h in air at 500 °C in an air oven. Borosilicate pipettes used for filling the quartz tubes were also cleaned by baking for 2 h at 500 °C in air. The samples that were analyzed are described in more detail in Section 4. The Apollo 16 regolith sample (64801,53) was a very fine-grained sample and did not require crushing. The Murchison meteorite fragment was crushed using a clean mortar and pestle prior to analysis and the powder passed through a stainless steel 150 μm sieve. Approximately 60 mg of Apollo regolith, and two separate Murchison meteorite powdered aliquots (8 and 60 mg) were inserted into separate quartz tubes and then packed with a small layer of quartz wool to ensure that the powder remained inside the quartz tube during heating (Fig. 4B). Each sample was then placed into the graphite crucible and the Knudsen cell was mounted into the vacuum chamber in direct line of sight with the ion source region of the RGA. The chamber was pumped down to a pressure of $\sim 1 \times 10^{-8}$ mbar prior to heating. At this pressure the RGA was switched on and the filament left on for an hour to warmup. With the filament on, the pressure inside the chamber increased to $\sim 1 \times 10^{-7}$ mbar. After warmup, the Knudsen cell cooling water was turned on and the linear heating ramp initiated. The start temperature was 25 °C and the samples were heated at a rate of 5 °C per min up to 1200 °C.

4. Samples Studied

The current development of VAPoR is focused primarily on the polar regions of the Moon that contain evidence for water; however, no good regolith analogs for the polar regions exist. Therefore, we selected a lunar regolith sample from the Apollo 16 mission for this study. The Murchison carbonaceous chondrite was selected for testing since this meteorite has been extensively studied and serves as a good analogue for *in situ* analysis on the surface of a comet or carbonaceous asteroid.

4.1. Apollo 16 sample 64801,53

Lunar regolith sample 64801,53, a sub-sample of sample 64801, is an Apollo 16 sample from station 4 in the Descartes region of the lunar highlands, with a sieve fraction of regolith < 1 mm. This sample is a key sample for lunar geology as it is part of a set of samples used to study the ejecta blankets of craters and relative albedos (Heymann et al., 1975). Sample 64 801 was specifically “shielded” from the South Ray Crater and has an apparent cosmic-ray exposure age of 310 million years from cosmogenic ^{21}Ne measurements (Walton et al., 1973). The soil has been well analyzed and its chemical characteristics are relatively simple, with a high abundance of aluminum and calcium (Bansal et al., 1972; Korotev, 1981). Four rock types have been identified in the samples, cataclastic anorthosites, partially molten breccias,

igneous and high-grade metamorphic rocks, and polymict breccias (Apollo 16 Preliminary Examination Team, 1973).

4.2. Murchison meteorite

The Murchison meteorite fell on September 28, 1969, near Murchison, Victoria, Australia, and is a CM2-type carbonaceous chondrite (Ehmann et al., 1970). The organic composition of this meteorite has been well characterized (e.g. Engel and Macko, 1997; Botta and Bada, 2002; Sephton, 2002; and Martins et al., 2008). The mineralogical composition of the Murchison meteorite is dominated by fine-grained intergrowths produced by aqueous alteration (Rubin et al., 2007). XRD-PSD analysis suggests tochilinite/cronstedtite (58.5%), serpentine (22.8%), olivine (Fo₁₀₀ (7.4%), Fo₈₀ (2.2%), Fo₅₀ (2%)), and small amounts of Fe–Ni metal, orthopyroxene (enstatite), pyrrhotite, pentlandite, magnetite, and calcite (Bland et al., 2004). The Murchison meteorite sample studied (USNM 6650,2) was provided for this study by the curator at the Smithsonian Museum of Natural History. The 6 g interior fragment was crushed and sieved to < 150 μm, from this 68 mg was allocated to this study.

5. VAPoR breadboard results and discussion

The evolved gas data for the samples are shown in Figs. 5–8. We have focused on a number of representative volatiles, which are represented by their mass-to-charge ratios, m/z. The volatiles H₂O⁺, CO⁺ / N₂⁺, and CO₂⁺, are shown in Fig. 5. Methane (CH₄⁺) and the noble gases ⁴He⁺ and ⁴⁰Ar⁺ are shown in Fig. 6. Fig. 7 shows series of simple aromatic and alkane hydrocarbon fragment represented by m/z 29, 39, 23, 57, 78, and 91, where fragments 78 and 91 correspond to benzene (C₆H₆⁺) and toluene (C₇H₈⁺), respectively. Sulfur-bearing species, H₂S⁺, SO₂⁺, COS⁺ and CS₂⁺ and oxygen, which is an important target for future *in situ* resource exploration, are shown in Fig. 8. Fig. 9 shows a procedural blank of the system taken before the first sample was analyzed. The mass spectrometer used in this study does not have sufficient resolution to distinguish between CO⁺ and N₂⁺, or S⁺ and O₂⁺ therefore these are plotted together. Only the evolved gas patterns of the 8 mg Murchison sample are shown, because the 60 mg sample caused saturation of the RGA due to high pressures observed from sample outgassing (predominately H₂O⁺ released from hydrated minerals). The partial pressures of the evolved gases varied considerably between the two samples, and in order to plot the outgassing profiles of the two samples in the same figure, the samples are plotted on different pressure scales. Both samples have a similar increase in m/z 12 (C⁺), 16 (CH₄⁺ or O⁺, not distinguishable at these higher temperatures from fragmentation patterns), 28⁺ (N₂ or CO⁺), and 29 peaks (12 and 16 are not shown), at temperatures above 1000 °C. This increase is not observed at experiments that only ran up to 1000 °C, or in the blank run. Previous evolved gas analyses of lunar samples showed similar results, which were attributed to bursting of

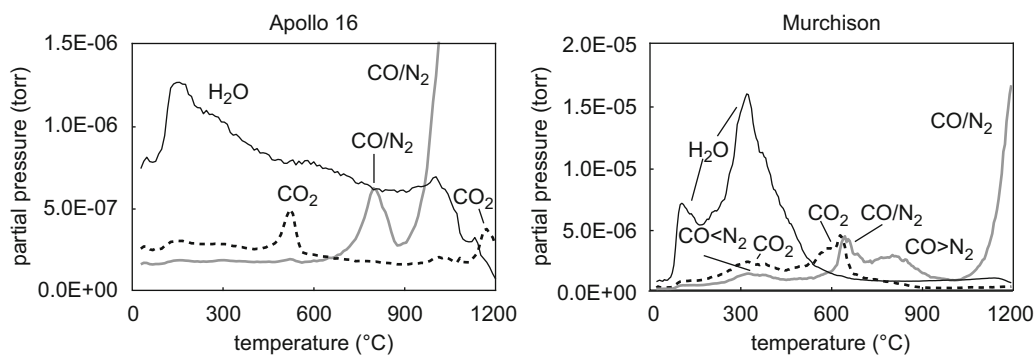


Fig. 5. Water, CO/N₂, and CO₂ evolved gas profiles as function of temperature for Apollo 16 and Murchison. Please note different scales on y-axis.

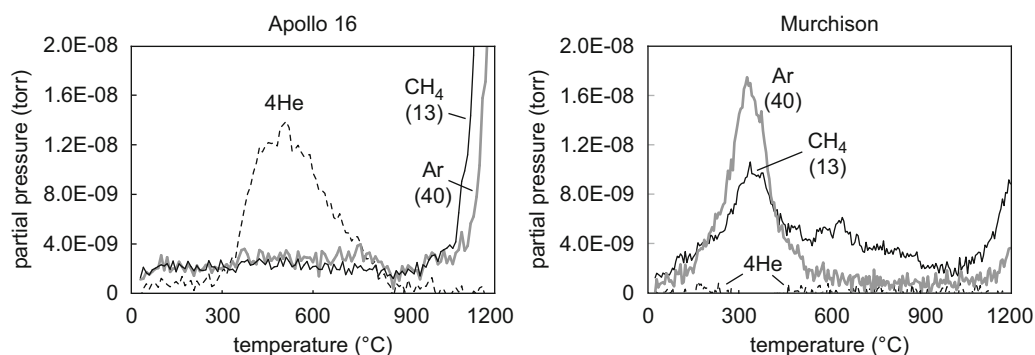


Fig. 6. Noble gases helium and argon, and methane (represented by m/z 13) evolved gas profiles as function of temperature for Apollo 16 and Murchison. The CH-fragment, m/z 13, of methane is shown because the methane contribution in its other fragments (12, 14, 15, 16, and 17) is too small to be distinguishable from other fragments at these m/zs. Please note different scales on y-axis.

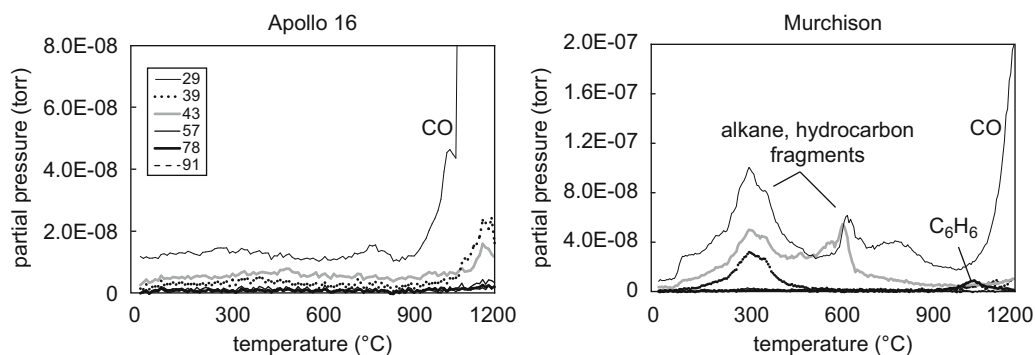


Fig. 7. Evolved gas profiles of hydrocarbon and alkane fragments as function of temperature for Apollo 16 and Murchison. Please note different scales on y-axis.

gas-containing vesicles (Gibson and Johnson, 1971) or other traps, or high temperature nitrides (Flory et al., 1972). In the case of the Murchison sample, an estimate about the majority of CO⁺ or N₂⁺ in the CO⁺/N₂⁺ ratio could be made based on analysis of the fragments of the CO⁺ and N₂⁺ mass spectra (12 and 16 for CO⁺, and 14 for N₂⁺). Similar analysis of the Apollo 16 sample did not provide conclusive information about the CO⁺/N₂⁺ ratio. The Apollo 16 sample shows a minor 39 and 43 peak around 1100 °C. Pump oil has been suggested; however no traces of this contaminant have been detected in the blank sample. Organics have been detected in a different Apollo 16 sample (Table 4; Simoneit et al. 1973), but at much lower temperatures (250–500 °C), therefore this peak is most likely contamination of either the sample or the quartz holder used for this measurement.

The lack of other alkane and hydrocarbon fragments in the Apollo 16 sample suggests that this sample was not significantly contaminated by organics during collection and curation over the past 37 years. Oxygen is not expected to be released at temperatures below 1000–1200 °C, therefore the S⁺/O₂⁺ profiles in both the Apollo 16 and the Murchison sample are expected to be S⁺, especially when compared to the H₂S⁺, SO₂⁺, and CS₂⁺ profiles.

Table 4 summarizes the evolved gas results for the Apollo 16 and Murchison samples and compares them with existing evolved gas samples. The Apollo 16 sample analyzed in this study has not previously been examined and is therefore compared to another Apollo 16 soil sample (61221,7; Simoneit et al., 1973), an Apollo 14 sample (14163,178; Gibson and Moore, 1972), and an Apollo 15 (15601,31; Gibson and Moore, 1972) soil sample. Table 4

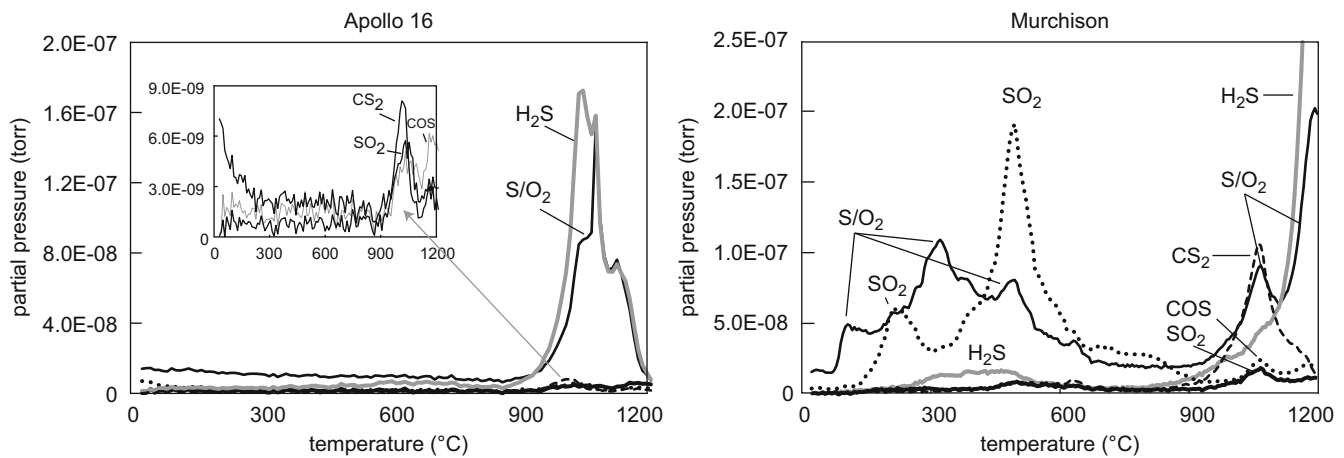


Fig. 8. Evolved gas profiles of the sulfur-bearing species SO_2 , H_2S , COS and CS_2 , and S/O_2 as function of temperature for Apollo 16 and Murchison. The inset in the Apollo 16 plot shows SO_2 , COS , and CS_2 traces on a different scale as well to highlight their profiles at higher temperatures. Please note different scales on y-axis.

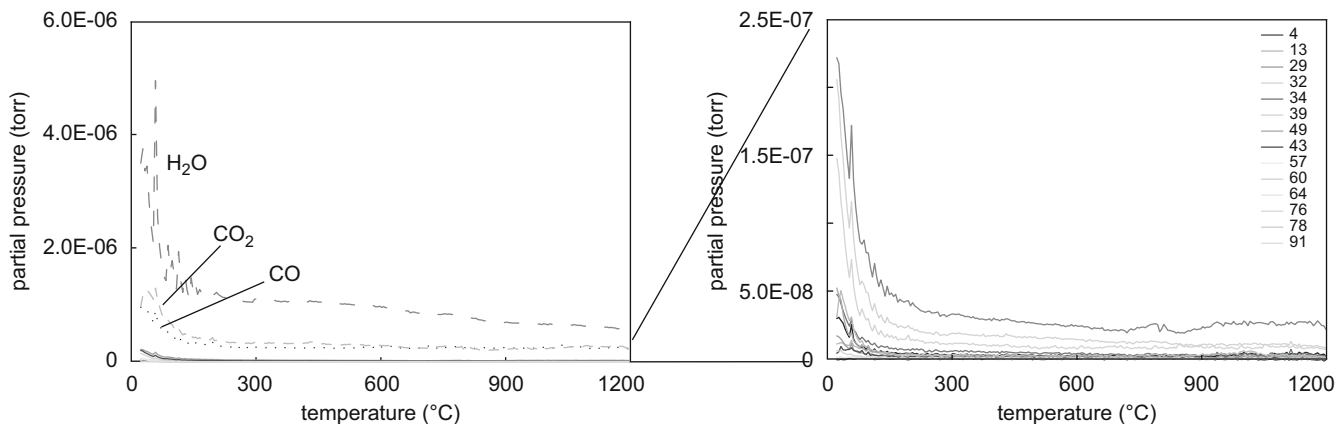


Fig. 9. Background evolved gas profiles of the VAPoR breadboard with an empty quartz sample holder. The left-hand plot shows all the fragments analyzed in this study. In the right-hand plot all fragments except H_2O , CO/N_2 , and CO_2 are shown on a smaller scale.

shows that our data are consistent with existing data, although neither CS_2^+ nor COS^+ have been reported for Apollo samples and are only present in very minor amounts in our sample (see Fig. 8, inset in Apollo data). Apollo 16 sample 61221,7 is referred to as rich in complex volatiles (Gibson and Johnson, 1971) and “unique” (unclear whether North or South Ray Ejecta) in the same classification where 64 801 is classified as “dark soil” (Heymann et al., 1975). Furthermore, both samples come from a different region, 61 221 from Station 1 on the rim of Plum Crater and 64 801 from Station 4 in a shielded position from South Ray Crater (Heymann et al., 1975). This most likely explains the low temperature evolved SO_2 and the presence of more volatiles than seen in sample 68401,53 (this study). H_2S^+ has been detected in our analysis, but could not be confirmed as an outgassing product of the lunar or Murchison meteorite samples due to a high H_2S^+ background of the system. The Murchison sample is compared to previous work by Simoneit et al. (1973) and shows consistent results as well. S^+/O_2^+ is not reported for the earlier Murchison analysis and our analysis did not show the COS^+ fragment. Our samples were heated at a rate of $5^\circ\text{C}/\text{min}$, the other Apollo 16 and Murchison sample at a rate of $14^\circ\text{C}/\text{min}$ and the Apollo 14 and 15 samples at a rate of $6^\circ\text{C}/\text{min}$. Preliminary experiments performed using the VAPoR breadboard (data not shown) suggested that a faster heating rate causes considerable widening of evolved gas peaks, even when the rate was doubled from 5 to $10^\circ\text{C}/\text{min}$. This

could explain the broader evaporation rates of some of the fragments in the earlier Apollo 16 and Murchison data. In general the VAPoR breadboard produces results comparable to existing data.

6. Conclusion

Evolved gas analyses of the lunar regolith have not yet been carried out *in situ* and no atmospheric or evolved gas measurements have been made at the lunar poles. The VAPoR instrument presented here is capable of making both kinds of measurements. The data obtained with the VAPoR breadboard instrument demonstrates that vacuum pyrolysis up to 1200°C coupled with line of sight volatile detection by mass spectrometry is an attractive technique for volatile analysis of the lunar regolith. The VAPoR flight instrument concept will include a mass spectrometer with a higher resolution than currently being tested, a pyrolysis oven capable of achieving higher temperatures with lower oven outgassing, a much shorter distance between the oven and the ion source region and smaller chamber volume which should greatly improve sensitivity. In particular, the sensitivity for noble gases (e.g. Ne) will be improved in the VAPoR flight instrument design by minimizing the volume and distance between the pyrolysis oven and the mass spectrometer

Table 4
Comparison of VAPoR Apollo 16 and Murchison evolved gas profiles with selected existing analyses.

SAMPLE	EVOLVED GASES									
Apollo 16, 64801,53 (this work)	H ₂ O									
	CO ₂					CO/N ₂		CO/N ₂		
Apollo 14, 14163,178 (Gibson & Moore, 1972)	H ₂ O									
	CO ₂	H ₂					CO/N ₂		CO ₂	
Apollo 15, 15601,31 (Gibson & Moore, 1972)	H ₂ O									
	CO ₂					CO/N ₂		CO ₂		
Apollo 16, 61221,7 (Simonet et al., 1973)	H ₂ O									
	CO ₂	CH ₄	HCN	NO	SO ₂	CO/N ₂		SO ₂		
Murchison (this work)	H ₂ O									
	CO ₂					CO/N ₂		CO/N ₂		
Murchison (Simonet et al., 1973)	H ₂ O									
	CO ₂					CO		H ₂ S		

ion source. The VAPoR instrument is designed to operate in dynamic mode, where the gases can be vented to lunar ambient, and in static mode. In this static mode the getter (Fig. 1) will pump the active gases and concentrate noble gas species released

from the regolith. This getter will be an important part of the instrument to concentrate noble gases, but even without the getter as demonstrated in these experiments, we can still measure solar wind implanted He.

The purpose of this work was not to calibrate the instrument; therefore, no attempt has been made to quantify the amount of evolved gases and the acquired data were only compared to existing data showing the gas release profiles as a function of temperature. The comparison of the analyses performed with the VAPoR breadboard and previous work demonstrates the capability of VAPoR to identify a range of different volatile species in the lunar regolith, from solar wind implanted helium, to mass fragments characteristic of aliphatic and aromatic hydrocarbons.

VAPoR aims to identify specific adsorbed species, organic compound classes, and hydrated minerals on the Moons and other small airless bodies including asteroids and comets. Upcoming work will correlate the outgassing profiles of pure standards with the outgassing profiles of natural samples, in order to further calibrate this method. Future versions of VAPoR with increased mass spectrometer sensitivity and resolution, a higher maximum pyrolysis temperature, and reduced oven outgassing should make it possible to identify some of the species (e.g. Ne) that we are currently unable to detect in the Apollo regolith sample using the VAPoR breadboard. Future *in situ* volatile and isotopic measurements at the polar regions and a comparison of the relative distribution of volatiles released from the polar regolith to the Apollo samples collected at the equatorial regions will provide important constraints on the source of water and possible other volatiles on the Moon.

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