

VOLATILE ANALYSIS BY PYROLYSIS OF REGOLITH: THE VAPOR INSTRUMENT DEVELOPMENT.

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ABSTRACT

The abundance, origin, and distribution of water and other volatiles at the lunar poles are still largely unknown. *In situ* analyses of the chemical and isotopic composition of the lunar regolith will be required to investigate these unknowns. The Volatile Analysis by Pyrolysis of Regolith (VAPoR) instrument is designed to analyze lunar regolith using pyrolysis mass spectrometry and measure abundances of volatiles and derive their origin. This paper gives a brief overview of the VAPoR instrument and some first results obtained by the VAPoR field unit.

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. A range of instruments based on this technique, summarized in Table 1,

have been developed and flown to several bodies in our Solar System. Within the same context the Volatile Analysis by Pyrolysis of Regolith (VAPoR) instrument is currently under development at NASA Goddard Space Flight Center (ten Kate et al., 2010, Getty et al., 2010). 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. There are at least three key lunar science measurement objectives that can be achieved by the VAPoR instrument: (1) confirm the amounts of water and/or OH identified by spectroscopic measurements made by LCROSS (www-1), Cassini VIMS (Clark, 2009), Chandrayaan-1 M3 (Pieters et al., 2009), and Deep Impact (Sunshine et al., 2009) 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;

and (3) measure the isotopic composition of a selection of compounds to establish the origin of the volatiles.

	Viking ²	TEGA ³	COSAC ⁴
Temperature range	50, 200, 350, and 500 °C	Ambient – 950 °C	Ambient – 600 °C
Oven material	Ceramic.	Nickel. Platinum resistance wire. Ceramic coating.	Platinum. Platinum resistance wire. Glass.
Oven size diameter	2 mm	7.2 mm	3 mm
length	19 mm	21.6 mm	6 mm
volume	~60 mm ³	~38 µl	
Number of ovens	3	8	2
	Ptolemy ⁵	SAM ⁶	VAPoR ¹
Temperature range	Ambient – 800 °C	Ambient – 1000 °C	Ambient – 1200 °C
Oven material	Platinum. Platinum resistance wire. Glass.	Quartz cup in alumina. Platinum resistance wire.	Zirconia. Platinum resistance wire.
Oven size diameter	3 mm		
length	6 mm		
volume		~500 mm ³	~100 mm ³
Number of ovens	3	2 ovens, 74 sample cups	6

References: ¹ten Kate et al., 2010; ²Biemann et al., 1977; ³Boynton et al., 2001; ⁴Goesmann et al., 2007; ⁵Wright et al., 2007; ⁶Mahaffy, 2007.

THE VAPOR INSTRUMENT

Instrument setup

The VAPoR instrument includes a sample manipulation system (SMS) and vacuum pyrolysis unit, gas processing system, and mass spectrometer. The VAPoR SMS consists of a 6-cup exchangeable carousel mechanism designed to receive lunar regolith samples of ~10-100 mg, and heat the samples to temperatures up to 1200 °C. 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. The lunar regolith surface or subsurface

samples can be delivered to the VAPoR instrument solid sample inlet robotically by a lander/rover scoop or drill, or collected and delivered to the inlet by an astronaut. The instrument package is designed such that it can both be integrated into an autonomous robotic and be used as a stand-alone human deployed package.

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 the target volatiles of VAPoR and their release temperatures.

Table 2: Release temperatures of target gases for the VAPoR pyrolysis mass spectrometer instrument.¹

	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 ²⁻⁴
	¹³ C/ ¹² C ratio of CO ₂	100-1400 ³
	¹⁵ N/ ¹⁴ N ratio in N ₂	600-1400 ³
	HDO/H ₂ O ratio	0-1400
Noble Gases	He, Ne, Ar	300-1400 ^{3,7}
	Isotope ratios (³ He/ ⁴ He, ³⁶ Ar/ ⁴⁰ Ar)	He: 200-500 ³ Ar: 300-1400 ^{3,6}
	¹³ C/ ¹² C ratio in CO ₂ from organics combustion	400-500 ⁷
Organics	Volatile hydrocarbons: methane, ethane, benzene, amines, alcohols, formaldehyde	300-1000 ³
	Water-ice in regolith	0-100
Resources	O ₂	1100-1400 ⁵
	Reduced inorganic gasses such as HCN, NH ₃ , and H ₂ S	HCN/NH ₃ : 100-900 ³ H ₂ S: 700-1300 ⁴
	³ He relative abundance	He: 200-500 ³
	³ He relative abundance	He: 200-500 ⁵

References: ¹ten Kate et al., 2010; ²Simoneit et al. (1973); ³Holland et al. (1972); ⁴Gibson and Johnson (1971); ⁵de Maria et al. (1971); ⁶Lord (1968); ⁷Court et al. (2005).

THE VAPOR FIELD UNIT

The VAPoR field unit (Fig 1.) consists of a small stainless steel cross, equipped with a turbodiaphragm 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). Samples were pyrolyzed using a specially designed zirconia oven, with a quartz sample holder. The sample was heated using a Watlow temperature controller. 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.



Figure 1. The VAPoR Field Unit.

Approximately 10 mg of sample was 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. The chamber was pumped down to a pressure of $\sim 1 \times 10^{-8}$ mbar prior to heating, and the samples were heated at a rate of 5-20 °C per minute up to 1200 °C.

SOME PYROLYSIS RESULTS

VAPoR field-testing was performed in the framework of the International Lunar Surface Operation - In-Situ Resource Utilization Analogue Test 2010, at the Mauna Kea volcano on Hawaii. Figure 2 and 3 show evolved gases of a surface sample taken at the test site (Getty et al., 2010).

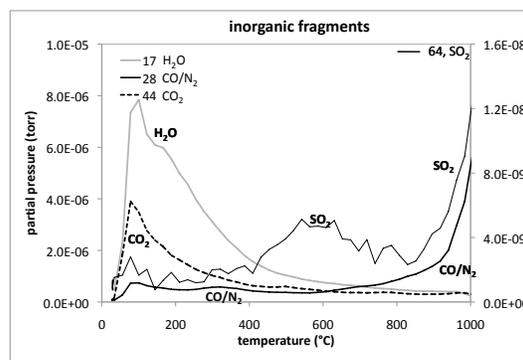


Figure 2. Selected inorganic volatiles released from the Mauna Kea soil sample as function of sample temperature. CO and N₂ cannot be separated with the RGA used and are therefore plotted together. H₂O, CO/N₂, and CO₂ are plotted on the right y-axis, SO₂ on the left y-axis. Mass 17 is used to represent H₂O, because of the high water content of the sample. Mass 18 has an $\sim 4 \times$ higher partial pressure.

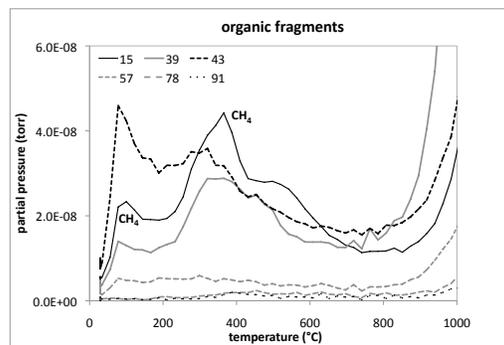


Figure 3. Selected alkane and aromatic hydrocarbons released from the Mauna Kea soil sample as function of sample temperature. Mass 15 corresponds to a fragment of CH₄; masses 39, 43, and 57 correspond to various alkane

fragments, and masses 78 and 91 correspond to benzene, and alkylbenzene (toluene), respectively.

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 (ten Kate et al., 2010). 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. 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. 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.

ACKNOWLEDGEMENTS

We recognize the NASA Lunar Sortie Science Opportunities (grant #06-LSSO06-0002) and Astrobiology Science and Technology Instrument Development (grant #07-ASTID07-0020) programs, as well as NASA Goddard Internal Research and Development funding for

supporting this research.

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