MEASUREMENT OF TERRESTRIAL METHANE CONCENTRATIONS COMPARABLE TO PROPOSED METHANE CONCENTRATIONS ON MARS

K. D. Webster[1], G. Etiope[2], A. Drobniak[3], A. Schimmelmann[1], and L. M. Pratt[1], [1]Indiana University, Bloomington, Department of Geological Sciences, 1001 E 10th St. Bloomington, IN 47405, kevdwebs@indiana.edu, aschimme@indiana.edu, prattl@indiana.edu, [2]Istituto Nazionale di Geofisica e Vulcanologia, Sezione Roma 2, Italy, etiope@ingv.it, [3]Indiana Geological Survey, Indiana University, 611 North Walnut Grove, Bloomington, Indiana 47405, agdrobni@indiana.edu

INTRODUCTION:

Caves are a globally distributed environment on Earth, occuring in several different lithologies. Caves provide shielding from radiation, are nearly isothermal environments, and can preserve biological structures made by microorganisms; thus caves are highly favorable places in the universe to look for extraterrestrial life [1]. Even though the total volume of cave ecosystems is unknown [2], it is estimated that karst environments, which commonly host caves, cover 20% of the Earth's surface [3]. Additionally, caves serve as a suitable testing ground for instruments for planetary missions due to their tight spaces which require small, lightweight, and durable instrumentation for *in situ* measurements.

***Figure 1**: The entrance of Lost River Cave in Kentucky*

Despite the fact that cave ecosystems provide diverse niches for organisms and microorganisms on Earth, relatively little is known about the biogeochemistry of methane (CH_4) in cave ecosystems. The CH_4 molecule is capable of acting as a biomarker. Methanogenesis (Archaeal generation of CH_4) preferentially enriches ^{12}C to ^{13}C and methanotrophy (bacterial consumption of methane) preferentially consumes ^{12}C and the residual methane molecules are enriched in ^{13}C [4]. Observations of methane in the martian atmosphere have triggered speculation about present-day life on Mars [5]. Therefore, an improved understanding of the biogeochemistry of methane in terrestrial caves will help in assessment of martian caves as a plausible habitat for methanotrophic organisms or methanogens.

METHODS:

A Boreal open-path laser (tunable diode laser), a WEST Systems CH_4- CO_2 fluxmeter, with CH_4-laser sensor (tuneable diode laser) and a Gasmet DX4030 (Fourier Transform infra-red spectrometer) were deployed in three caves in Kentucky (Lost River Cave, Diamond Caverns, and Mammoth Cave) and one cave in Indiana (Buckner Cave) to search for CH_4 (Figure 1).

Open-path laser (OPL) measurements were used to monitor the CH_4 present in Diamond Caverns, Mammoth Cave, and in Buckner Cave. Laser transects ranged from 29.9 – 37.0 m in length and lasted for 45 minutes – 1 hour in duration (Fugure 2). The laser was programmed to produce a data point every 73 seconds. All of the data points were then averaged to determine a mean concentration in the path length over the time interval. The OPL was used to measure the CH_4 concentration in one part of the cave system. Error in the measurements was assessed using:

$$E = U([CH_4]) + (\{\Sigma([CH_4]_d - [CH_4])^2\}/n)^{1/2} + 0.1m([CH_4])/(L) \qquad (1)$$

***Figure 2**: Deployment of the open-path laser (OPL) in a room in Mammoth Cave*

Where E is the average error associated with the mean methane concentration, U is the OPL's mean uncertainty in the measurement of CH_4 in the laser-path length, $[CH_4]$ is the mean concentration in the path length over the time interval, $[CH_4]_d$ is the mean concentration of CH_4 in discrete measuremet periods, n is the total number of adjustments in the measurement, and L is the measured path length in meters (m).

METHODS CONT:

The error of individual data points was assessed using:

$$e = u([z_{CH4}]) + 0.1m([z_{CH4}])/(L) \qquad (2)$$

Where e is the error associated with the individual data point, u is the OPL's uncertainty in the measurement of CH_4 in the laser-path length and, $[z_{CH4}]$ is an individual CH_4 concentration measurement. The detection limit for the open-path laser is one part per million multiplied by meters divided by L: (ppm · m)/(L).

***Figure 3**: The WEST systems insturment measuring the CH_4 concentation in Diamond Caverns.*

The WEST Systems instrument was deployed in Lost River Cave, Diamond Caverns and Mammoth Cave. The system has an error of 0.1 ppm and a detection limit of 0.1 ppm. Cave atmosphere was continuously analyzed along the visited paths and rooms of the cave (Figure 3). The instrument was also used to search for CH_4 flux from the cave walls (Figure 4).

The Gasmet was only used in one area of Mammoth cave and produced a data point every 10 seconds of CH_4 monitoring. The Gasmet has a detection limit of 0.1 ppm.

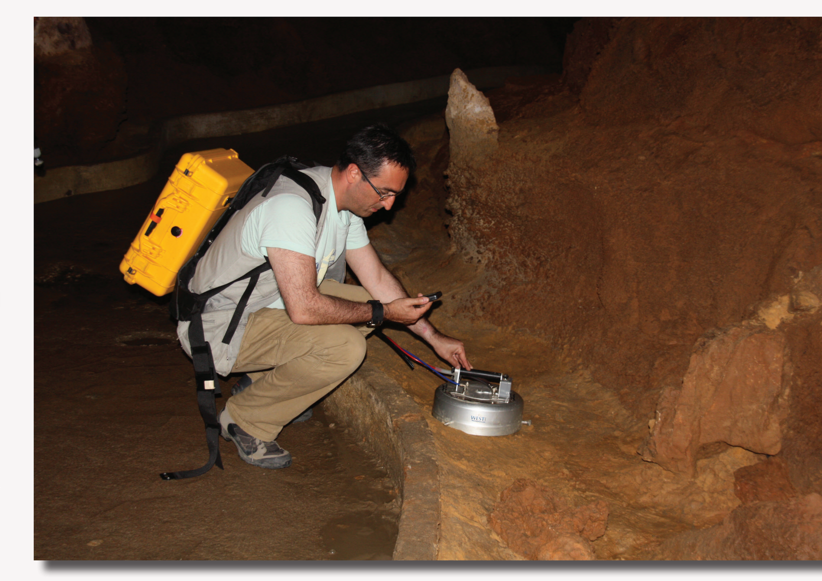

***Figure 4**: The WEST systems insturment measuring the flux of CH_4 in Diamond Caverns*

RESULTS:

Figure 5: *OPL measurement of CH_4 in the "Bendy Rock Room" of Buckner Cave (BC BRR).*

Figure 6: *The OPL measurement of CH_4 in Mammoth Cave (MC 3).*

Table 1: *Comparison of CH_4 concentrations at several different localities within the caves as measured with the different instruments. LRC = Lost River Cave, DC = Diamond Caverns, MC = Mammoth Cave, BC = Buckner Cave, Bckgrnd = Background.*

DISCUSSION:

The sub-atmospheic concentration of CH_4 in the four caves suggests that caves generally are quasi-CH_4-free environments. Therefore, they are special terrestrial environments where the CH_4 concentrations are similar to those proposed in the martian atmosphere. The concentration of CH_4 in the Martian atmosphere has been estimated to be locally as high as 0.03 ppm [5]. Ground-based detection of methane on the surface of Mars will require instrumentation with errors less than 0.01 ppm. The 0.03 ppm and 0.015 ppm error associated with the OPL measurements from Mammoth Cave and Buckner Cave demonstrate that an OPL is a tenable instrument for future martian missions. Most of the error in the measurement of methane in these two caves was due to the low number of methane molecules in the laser's path length. Boreal suggests that having 10 ppm · m molecules of CH_4 in the path length will reduce the laser's internal error [6]. Martian atmospheric pressure is roughly 0.006 bar [7], so at a concentration of 0.03 ppm, a path length of 60 km or greater on the Martian surface would help reduce the laser's internal error. Assuming 0.03 ppm CH_4 in the Martian atmosphere and a pathlength of 60 km, the error in an OPL measurement may be as low as 0.0006 ppm. Furthermore, since low pressure narrows the infra-red absorption bands of methane, path lengths shorter than 60 km will still be able to generate data with high precision and accuracy.

IMPLICATIONS FOR MARS:

1 **Caves provide a suitable testing ground for instrumentation being designed for future martian missions**

2 **An open-path laser system can provide an accurate way to measure local atmosphereic CH_4 concentrations on Mars**

3 **If an OPL was mounted on a landed platform and multiple reflectors were deployed by a rover, then repeat measurements of methane concentrations could be made across landscape features of hundreds of meters to a few kilometers**

ACKOWLEDGEMENTS: This research was funded by NASA, Astrobiology Science and Technology for Exploring Planets (Award # NNX11AJ01G) and from the U.S. Department of Energy, Basic Energy Sciences (Grant # DE-FG02-11ER16246). We thank Joe Forsythe of Lost River Cave and Rickard S. Toomey III of Mammoth Cave National Park for facilitating access. R. Droppo povided graphical assistance during this project. Boreal Laser Company helped in the data analysis.

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