METHANE AS AN INDICATOR OF LIFE ON MARS: NECESSARY MEASUREMENTS AND SOME POSSIBLE MEASUREMENT STRATEGIES. B. M. Bebout[1], N. E. Bramall[2], C. A. Kelley[3], J. P. Chanton[4], A. Tazaz[4], J. Poole[3], B. Nicholson[3], A. Detweiler[1], and M. Gupta[2], and A. J. Ricco[1], [1]NASA Ames Research Center, (Brad.M.Bebout@nasa.gov, MS 239-4, Moffett Field, CA 94035-1000), [2]Los Gatos Research, (Mountain View, CA 94041-1518), [3]Department of Geological Sciences, University of Missouri, (Columbia, MO 65211), [4]Department of Earth, Ocean and Atmospheric Science, Florida State University, (Tallahassee, FL 32306-4320).

Introduction: Seasonal methane releases [1], as well as planetary atmospheric methane concentrations of approximately 10 ppb have been reported on Mars [1-3]. If confirmed, these detections of methane, and particularly the seasonal variations of methane, would be tantalizing evidence in support of the presence of a near surface, or subsurface microbial biosphere. Methane can, however, also be produced by non-biological processes, and so discriminators capable of distinguishing biologically produced methane are necessary.

The Stable Isotopic Composition of Methane: Naturally occurring biogenic (biologically-produced) methane is characterized by a low $^{13}C/^{12}C$ ratio, with $\delta^{13}C_{CH4}$ values ranging from –110‰ to –50‰, whereas thermogenic methane (methane produced by the thermal alteration of organic matter) generally has $\delta^{13}C$ values > –50 ‰ and is characterized by progressive enrichment in ^{13}C content with increasing maturity, eventually approaching the $^{13}C/^{12}C$ of the original organic matter [4, 5]. Biogenic methane has a wide range in $\delta^{2}H_{CH4}$ values, varying from –400‰ to –150‰, whereas the $\delta^{2}H_{CH4}$ values of thermogenic methane generally range from –275‰ to –100‰ [5]. Geologic methane production from low-temperature water-rock reactions (e.g., serpentinization) varies between $\delta^{13}C$ of –40‰ to –10‰ and $\delta^{2}H_{CH4}$ values of –100‰ to –400‰ although it is less well characterized [5, 6]. When used separately, both carbon and hydrogen isotopes show considerable overlap between sources (biogenic, thermogenic, and geologic). However, the use of both $\delta^{13}C_{CH4}$ and $\delta^{2}H_{CH4}$ in combination allows for useful separation between the general fields of biogenic, thermogenic, and geologic methane [6].

Methane to Alkane Ratios: The presence of higher n-alkane hydrocarbon gases, such as ethane, can also be used to distinguish between methane sources. Biogenic methane production is usually not accompanied by significant ethane production [7-9] whereas the processes that form thermogenic and geologic methane also produce ethane [7, 8, 10, 11]. It has been proposed that a methane/ethane ratio of over 1,000 is indicative of a biogenic source, while a ratio of less than 50 suggests a thermogenic source [7, 9].

Characterization of Methane from Mars Analog Environments on Earth: Our recent work has shown that a number of processes operating in hypersaline environments similar to presently existing or past hypersaline environments on Mars may conspire to make the interpretation of the isotopic composition of Mars methane more difficult. In particular, the limitation of biological methane production by low substrate concentrations reduces the discrimination against ^{13}C, and therefore produces methane very enriched in ^{13}C [12]. In fact, methane produced in hypersaline environments on Earth has an isotopic composition and alkane content outside the values presently considered to indicate a biogenic origin [13].

Instruments and Strategies for the Detection and Characterization of Methane on Mars: Because determining the biogenicity of methane on Mars on the basis of its stable isotopic composition and the ratio of methane to higher order alkanes alone may be problematic, sampling the seasonal variability in these characteristics of methane to obtain the variations that might be expected as a result of changes in rates of biological activity becomes of paramount importance. Instruments for measurements of methane on Mars, whether from orbit, or landed, need to make measurements over several seasonal cycles. Therefore, instruments being designed to characterize methane on Mars should be extremely robust against changes in calibration that occur over time, or with temperature.

Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS): OA-ICOS is a technological marriage between Cavity Ringdown Spectroscopy (CRDS) and Tunable Diode Laser Absorption Spectroscopy (TDLAS). The technique combines the cavity-enhanced sensitivity of CRDS with the ultra-high resolution spectroscopic measurements of traditional TDLAS. The general instrument concept is shown in ***Figure 1***.

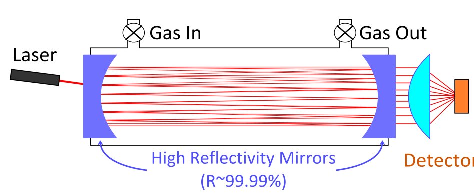

Figure 1: Layout of an OA-ICOS instrument.

High Sensitivity. Light from a diode laser is injected off-axis into a cavity formed by two highly-reflective mirrors $(R \approx 99.99\%)$. The transmitted light bounces between these mirrors thousands of times, creating an effective spectroscopic path length of up to tens of kilometers, depending on the mirror reflectivity. This is much higher than the tens of meters of path length achieved in traditional TDLAS multipass cells. As absorption is strongly dependent on optical path length, this makes for a very sensitive measurement.

High Dynamic Range. The dynamic range of OA-ICOS instruments is very high because on each reflection, a small amount of the laser light exits the cavity and is focused onto the detector-- so that even if a strong absorber is present, some light will always be detected. The dynamic range of an OA-ICOS instrument can easily cover ten orders of magnitude. This is a huge advantage when measuring isotope ratios.

High-resolution spectra. Just as in traditional TDLAS, the diode laser can be current-tuned to cover a range of several cm^{-1} to achieve high-resolution (<10 MHz), information-rich spectra which can allow for precise measurements of spectral lines. CRDS, at best, can achieve resolutions of only ~300 MHz and requires a lot of complicated mode-matching, wavelength-monitoring techniques and electronics which are not required for OA-ICOS.

Physically Robust. Because light is being injected into the cavity off-axis, many cavity modes are excited as opposed to traditional CRDS which is injected on-axis to excite a single mode. This means that OA-ICOS is extremely insensitive to any laser alignment issues. OA-ICOS instruments are even robust compared to multi-pass TDLAS instruments. It may even be a candidate for an impactor-type deployment.

Many Species. Because the laser is being injected off-axis, multiple lasers can be injected into the same cavity . This increases the number of target species that can be measured with a single apparatus.

Measuring Hydrocarbons with OA-ICOS. There are number of novel diode laser sources in the 3.3- to 3.4-μm range, which greatly enhances the existing spectroscopic detection limits of hydrocarbons. Using a combination of HiTran simulations and real-world experience with OA-ICOS instruments, we have determined that we could measure hydrocarbons in the parts-per-trillion (ppt) range, as listed in ***Table 1***.

Table 1: Estimated detection limits (1σ) in 5 seconds for hydrocarbon species and their isotopologues under Martian atmospheric conditions.

	CH_4	C_2H_6	C_3H_8	C_4H_{10}
Det. Limit	13 ppt	12 ppt	207 ppt	21 ppt

OA-ICOS Ready for Spaceflight: OA-ICOS instruments are, in principle, ready for space flight as nearly all of the key components have already been developed for the TLS instrument which is currently headed to Mars as part of the MSL mission. A candidate instrument concept for inclusion in landed missions to Mars is shown in *Figure 2*. This candidate instrument could be included in any number of low-cost lander platforms being developed for the exploration of Mars. With total mass under 1 kg and average power draw < 1 W, OA-ICOS can be a complementary or add-on instrument on even very small landers and small "hard landing" vehicles.

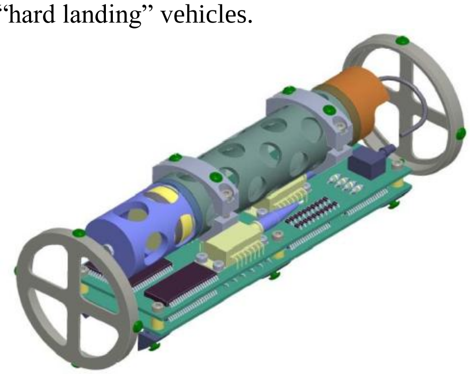

Figure 2: A miniature OA-ICOS instrument for the exploration of Mars. The packaged instrument measures 20.3 cm in length, 6.4 cm in diameter and mass< 1 kg. Shown are three diode lasers. Average Power draw < 1 Watt for ~2 measurements/hour.

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