Evolved Gas Analysis coupled with Cavity Ringdown Spectrometry for *in situ* $\delta^{13}C$ measurements of Mars analog materials

JENNIFER C. STERN[1], AMY C. MCADAM[1], HEATHER B. FRANZ[1,2] AND PAUL R. MAHAFFY[1]

[1]NASA Goddard Space Flight Center, Code 699, Greenbelt, MD 20771. Jennifer.C.Stern@nasa.gov
[2]University of Maryland, College Park, MD 20742

Evolved Gas Analysis (EGA) was used on the Mars Phoenix Mission [1] and will be used on Sample Analysis at Mars (SAM) on the 2011 Mars Science Laboratory (MSL) to examine the chemical composition of gases evolved from stepped heating of Martian regolith. Briefly, a pyrolysis unit heats a solid sample to temperatures of ~1100° C and the gases evolved from this heating are detected by a quadrupole mass spectrometer. Results of SAM breadboard tests using carbonate standards and Mars analog materials show different carbon species are evolved at different temperatures. Fragments from various organics are detected 300° and 700° C. Between 700° and 800° C, CO_2 is evolved from the thermal decomposition of calcite ($CaCO_3$).

The SAM suite is equipped with tunable laser spectrometry (TLS) for both concentration and isotopic measurements of atmospheric gases such as methane and CO_2 [2]. The TLS will also be used to measure $^{13}C/^{12}C$ of CO_2 evolved from Martian regolith, which may contain carbonate based on recent identification of carbonates by both Mars Reconnaisance Orbiter (MRO) and Phoenix [3-4]. To perform laboratory tests to optimize $^{13}C/^{12}C$ measurements, we have interfaced an EGA pyrolysis unit with 2 different commercial benchtop cavity ringdown spectrometers (CRDS, Los Gatos Research Company and Picarro) capable of analyzing $^{13}C/^{12}C$ of CO_2 evolved from Mars analog samples.

This system is being developed to combust samples in the presence of oxygen to convert reduced organics to CO_2 for isotopic analysis. Ultimately, a front-end combustion unit interfaced with laser spectrometric technologies for bulk $^{13}C/^{12}C$ measurements is the first step in determining *in situ* the carbon isotopic composition of individual organic molecules including those with biological or prebiotic significance (amino acids, fatty acids, nucleobases).

[1] Hoffman, J. H. *et al.* (2008) *J Am Soc Mass Spectrom* **19**, 1377–1383. [2] Mahaffy, P.R. (2009) *Geochem. News* **121**. [3] Ehlmann, B. L. *et al.* (2008) *Science* **322**, 1828–1832. [4] Boynton, W. V. *et al.* (2009) *Science* **325**, 61–64.

Zircon oxygen isotopes by SIMS: Performance evaluation of the Canadian IMS1280

R.A. STERN* AND R.B. ICKERT

Canadian Centre for Isotopic Microanalysis (CCIM), Department of Earth and Atmospheric Sciences, University of Alberta, AB, Canada T6G 2E3 (*correspondence: rstern@ualberta.ca)

The flagship instrument of the CCIM is a Cameca IMS1280 ion microprobe, commissioned in late 2009. The instrument incorporates the latest technologies that have contributed to advancing the state-of-the-art in precision, accuracy, and throughput [1, 2] in measuring $\delta^{18}O_{VSMOW}$ in zircon, including normal incidence electron charge compensation, automated secondary ion tuning, and simultaneous measurement of $^{16}O^-$ and $^{18}O^-$ in Faraday cups. Nevertheless, as is well-known, the potential of SIMS instrumentation cannot be realized in the absence of optimum procedures for sample preparation and analysis. Protocols for the analysis of O-isotopes in zircon with the IMS1270/1280 vary significantly amongst practitioners, for example, the tuning of the Transfer (secondary column) section that results in significant differences in the relative transmission of ions (e.g. ~30–90%). The range of possible approaches to analysis demands that individual labs develop and test their preferred 'best practice.'

The results of the first CCIM experiment analyzing $^{18}O/^{16}O$ in various zircon oxygen-isotope reference materials [3] (RM) on a single grain mount are summarized in the Table. These preliminary results suggest that uncertainties of ±0.2‰ (2σ) per analysis from 10 μm spots are realistic, consistent with performance expectations. Additional work is planned to validate the analytical protocol, test for matrix effects, and contribute to an improved error analysis.

RM	N	mean raw $\delta^{18}O$	mean $\delta^{18}O$, corrected to TEM2	SD	RM $\delta^{18}O$
TEM2	15	8.22	8.20	0.10	8.20
KIM-5	6		5.24	0.09	5.09
91500	6		10.09	0.09	10.07
MOGOK	6		22.87	0.24	22.94
MUDTANK	6		5.10	0.07	5.03
ABER	6		5.07	0.03	5.05
OG1	6		6.01	0.07	

[1] Kita *et al.* (2009) *Chem. Geol.* **264**, 43–57. [2] Whitehouse & Nemchin (2009) *Chem. Geol.* **261**, 31–41. [3] Valley (2003) *Rev. Mineral Geochem* **53**, 343–385.