

**MEASUREMENT OF TOTAL ORGANIC AND TOTAL INORGANIC CARBON ON MARS, A. P. Zent<sup>1</sup>, R. C. Quinn<sup>2</sup>, J. L. Lambert<sup>3</sup>, S. Kounaves<sup>4</sup>, S. Young<sup>4</sup>, J. Bell<sup>3</sup>, M. Hecht<sup>3</sup>, C. Taylor<sup>2</sup>,** <sup>1</sup> NASA Ames Research Center, Moffett Field, CA, 94035 ([Aaron.P.Zent@nasa.gov](mailto:Aaron.P.Zent@nasa.gov)), <sup>2</sup> SETI Institute, Mountain View CA, 94035 <sup>3</sup> Jet Propulsion Lab, Pasadena CA, 91106, <sup>4</sup> Tufts University, Boston MA 02155.

Two of NASA's key goals over the next several decades of planetary exploration are to determine whether life developed on any planetary bodies in the solar system other than Earth, and to learn more about the origins of life on Earth by studying the evolution of complex organic molecules on other planetary bodies. Detailed information on both inorganic and organic carbon concentrations and  $^{13}\text{C}/^{12}\text{C}$  isotope ratios for planetary bodies is essential for addressing the above goals and for modeling planetary formation and geochemical evolution.

Our instrument concept (TIC-TOC: Total Inorganic Carbon - Total Organic Carbon) is based on the assumption that the strategy adopted for assessing the abundance of organic matter and possible biological derivation of organic matter on other planetary bodies should be broad in scope and as similar as possible to strategies adopted on Earth for detecting traces of ancient life. One of the most fundamental measurements made on terrestrial samples of interest for their fossil microbiological content is to quantify the total carbon content of the sample in terms of aggregate inorganic and organic fractions and to compare their stable carbon isotope ratios. Comparison of  $^{13}\text{C}/^{12}\text{C}$  ratios for coexisting organic and carbonate fractions of sediment is a powerful indicator of past biological activity that is commonly used to establish the provenance of organic matter in terrestrial sediments as old as several billion years. For biologically-derived samples, the  $^{13}\text{C}/^{12}\text{C}$  ratio for the organic carbon in a sample is typically reduced by 2 to 4% (20 to 40 parts per thousand, per mil, or ‰) relative to coexisting inorganic carbon. Comparison of the stable carbon isotope ratios between coeval reduced and inorganic carbon fractions of Martian sediments is one way of constraining conjecture regarding the existence of life on Mars (Schidlowski, 1992; Rothschild and DesMarais, 1989; Sauke and Becker, 1998; Wright and Pillinger, 1998; Jakosky et al., 1999). A fundamental challenge with total carbon analyses of geologic samples is effecting separate measurements of the carbonates and organic carbon. We have opted to do our separations *via* wet chemistry rather than thermally, chiefly because of uncertainties due to overlapping breakdown temperatures of organic and inorganic C-bearing compounds.

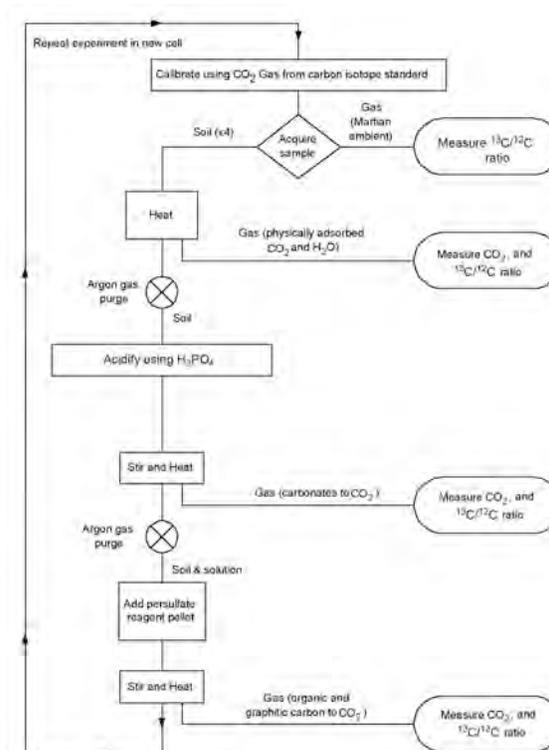


Fig. 1. Flow diagram of the TIC-TOC Experiment

Our approach is to fully convert carbonate

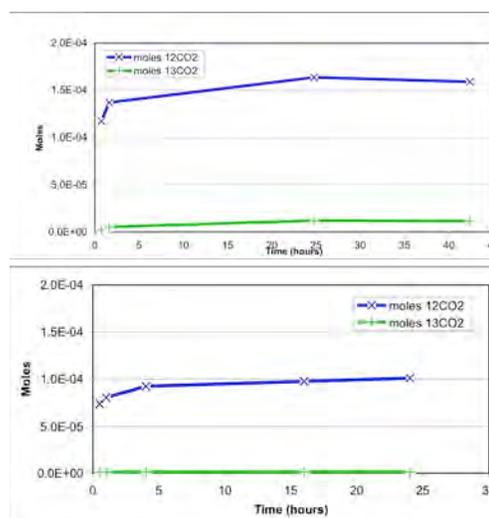


Fig. 2. Quantitative retrieval of  $^{13}\text{C}$ -labeled glucose and unlabeled reagent  $\text{CaCO}_3$  (top). Quantitative retrieval of  $\text{CaCO}_3$  by  $\text{H}_3\text{PO}_4$ ;  $^{13}\text{C}$ -labeled formic acid in the sample was not oxidized (bottom).

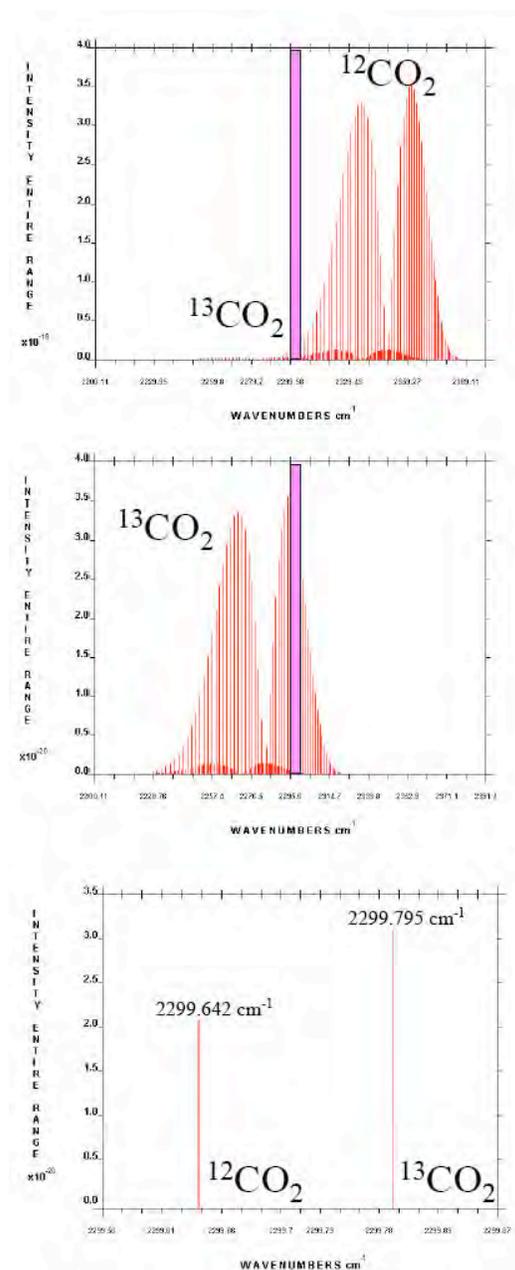


Fig. 3. Matched line strengths occur at  $2299\text{cm}^{-1}$ .

species to  $\text{CO}_2$  with hot  $\text{H}_3\text{PO}_4$ , followed by oxidation of the organic species with potassium persulphate ( $\text{K}_2\text{S}_2\text{O}_8$ ). This approach takes advantage of considerable analytical experience in carbon analysis. A few of the substantial number of protocol chemistry results are shown in Figure 2.

$\text{H}_3\text{PO}_4$  is a non-oxidizing acid, and  $\text{K}_2\text{S}_2\text{O}_8$  is acidic, so inorganic carbon must be analyzed first.

While rapid decarbonation of all carbonates, including siderite is possible at  $\text{H}_3\text{PO}_4$

temperatures near  $100^\circ\text{C}$ , it is more effective to decrease the solution temperature and use high concentrations of  $\text{K}_2\text{S}_2\text{O}_8$  during the oxidation step, because decomposition of  $\text{K}_2\text{S}_2\text{O}_8$  increases with temperature. Excess  $\text{K}_2\text{S}_2\text{O}_8$  also alleviates known interference of the oxidation reactions by  $\text{Cl}^-$  in concentrations greater than  $0.02\text{ M}$ . The organics most resistant to oxidation with persulphate solution are saturated hydrocarbons and halogenated alkanes (Huang et al., 2005).

To address difficulty with oxidation of some species via persulphate, we are simultaneously investigating the utility of electrochemical oxidation of soluble organics with boron-doped diamond electrodes

Our detection system is based on spectroscopic measurement of  $\text{CO}_2$  absorption in the headspace. In selecting a wavelength for measurement, there is tradeoff between precision of isotopic ratio measurements  $\Delta\delta$  and required temperature stability  $\Delta T$  which varies as a function of the difference between the lower state transition energies  $\Delta E$  of the two spectral lines given by:  $\Delta\delta = (\Delta E \Delta T)/(kT^2)$ , where  $k$  is Boltzman's constant. Matching lower state transition energies usually means the absorption lines of isotopes are of different strengths thus requiring two cells for analysis. We would prefer a temperature stabilized single cell with matched line strengths (Fig. 3).

Assuming a desire to detect ppb organic levels, we calculate that a  $1\text{ng}$  sample of evolved  $\Sigma\text{CO}_2$ , pressurized at  $100\text{ torr}$  in a cell with a volume of  $10\text{cm}^3$  would require a pathlength of  $4.68 \times 10^3\text{ m}$  to obtain a 50% transmission at the peak of the  $\nu = 2299.795\text{ cm}^{-1}$   $^{13}\text{CO}_2$  absorption line. This will require eventual development of a cavity ringdown system. We are proceeding with development and demonstration with the lower-power Difference Frequency Generation laser shown schematically in Fig. 4.

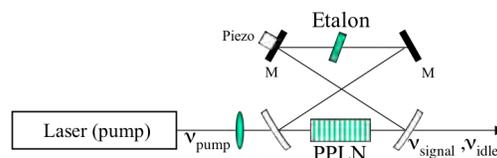


Fig. 4. TIC-TOC DFG detection system.

- Jakosky, B.M. *Orig. Life Evol. Biosph.*, **29**:47-57 1999.  
 Huang K. C., et al., *Chemosphere*, **61**, 551-560, 2005.  
 Rothschild, L.J. DesMarais, D. *Adv. Space Res.*, **9**, 159-65, 1989  
 Sauke, T.B. Becker, J.F. *Planet. Space. Sci.*, **46**, 805-12. 1998  
 Schidlowski, M. *Adv. Space Res.*, **12**, 101-10, 1992  
 Wright, I.P. Pillinger, C.T., *Planet. Space Sci.*, **46**, 813-23. 1998