

## $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ isotopic analysis of solid materials

Isotope Science Laboratory – Applied Geochemistry Group (ISL-AGg)  
Geoscience Department  
University of Calgary

### Overview:

Analyses of  $\delta^{13}\text{C}$ , wt%C,  $\delta^{15}\text{N}$  and wt%N of solid matter are done using Continuous Flow-Elemental Analysis-Isotope Ratio Mass Spectrometry (CF-EA-IRMS) technology. In the ISL-AGg, a Thermo DeltaV<sup>Plus</sup>® mass spectrometer is interfaced with either an Elementar *Isotope CUBE*® or Costech 4010® elemental analyzer via a ConFloIV® device. All materials (RMs, QA/QCs and unknowns) are packed in tin cups of varying and appropriate size, which are dropped by auto sampler onto a quartz tube combustion reactor. The temperature of this reactor is maintained at ~1000°C and 'flash-combustion' is achieved by injecting a pulse of O<sub>2</sub>(gas) exactly at the time of sample drop. The eluent gases are then swept by the helium carrier stream through a reduction reactor (~650°C), thus reducing NO<sub>x</sub> species to N<sub>2(gas)</sub>. GC separation of N<sub>2</sub> and CO<sub>2</sub> is achieved before the gas stream is leaked through the ConFlo-IV open split into the ion source of the mass analyzer.  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values are determined by comparing the respective sample peak areas, as [Vs], to reference gas peaks also inlet through the open split. For materials with widely varying [C:N] ratios,  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  analyses must be done separately. For samples whose C:N ratio approaches [3:1] (i.e. bone collagen) the peak jumping feature of the mass spectrometer can be used and a single sample suffices. These instruments are fully automated and computer controlled using ISODAT 3.88 software. Prior to sample analysis instrument conditions: reactor temperature(s), carrier gas flows, ion beam background(s), ion source stability and signal linearity are checked and recorded ("*Daily check*" routine).

Stable isotope ratios are expressed as delta ( $\delta$ ) and are measures of a 'per mill' (‰), or parts per thousand difference between the isotope ratio of a sample and that of a known (International) standard material. Values are reported relative to 'Vienna Pee Dee Belemnite' (VPDB) formation for Carbon (Craig, 1957) and 'Atmospheric air' for Nitrogen (Air-N<sub>2</sub>).

**Internal lab standards:**

Standard	Supplier	Prod. #	Formula
Caffeine	Sigma Aldrich	C-0750	C <sub>8</sub> H <sub>10</sub> N <sub>4</sub> O <sub>2</sub>
Gelatin	Sigma Aldrich	G-9382	unknown
Glycine	MP Biomedicals	100570	C <sub>2</sub> H <sub>5</sub> NO <sub>2</sub>
Keratin	MP Biomedicals	902111	unknown

**International standards:**

Identifier	$\delta^{13}\text{C}$ (‰) <sub>VPDB</sub>	$\delta^{15}\text{N}$ (‰) <sub>Air-N<sub>2</sub></sub>
USGS 24	-16.0 ± 0.1	
IAEA-CH-6	-10.4 ± 0.2	
IAEA-CH-7	-31.8 ± 0.2	
NBS 22	-30.03 ± 0.2	
USGS 40	-26.39 ± 0.2	-4.52 ± 0.2
USGS 41	37.63 ± 0.2	+47.57 ± 0.2
USGS 25		-30.40 ± 0.2
USGS 26		+53.70 ± 0.2
USGS 34		-1.80 ± 0.2
USGS 35		+2.70 ± 0.2
IAEA N1		+0.43 ± 0.2
IAEA N2		+20.32 ± 0.2
IAEA NO <sub>3</sub>		+4.69 ± 0.2

- Internal lab standards are used at the beginning, between (~ every 5th) and the end of each sequence to correct for instrument drift and to normalize the data to internationally accepted standards
- Six (6) replicates of different weights are placed near the beginning of each sequence to allow for element wt.% determination and 'non-linearity' correction
- Internal lab standards have been characterized against the International Standards listed above and are re-checked periodically
- USGS LIMS is used for drift correction, normalization and data management. (<http://water.usgs.gov/software/LIMS/>)

**Accuracy and Precision:**

$\delta^{13}\text{C}_{\text{Organic}} \pm 0.2$  per mil (n=10 internal lab standards)

$\delta^{15}\text{N}_{\text{Organic}} \pm 0.2$  per mil (n=10 internal lab standards)

Elemental wt%C, wt%N and C/N ratio = ± 5% (relative error)

### References:

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R.A. Werner and W.A. Brand, Referencing strategies and techniques in stable isotope ratio analysis, *Rapid Communications in Mass Spectrometry*, 2001: 15: 501-519

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