$\delta^{18}O$ isotopic analysis of inorganic and organic solids by Thermal Conversion

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Overview:

The $^{18}O/^{16}O$ ratio of pure inorganic and organic materials (e.g. $BaSO_4$ or plant cellulose) is determined using a high temperature reactor coupled to a Continuous Flow - Isotope Ratio Mass Spectrometer (CF-IRMS). The system is comprised of a HEKA High Temperature Oxygen analyzer (HTO)® interfaced to a Thermo Delta+XL® mass spectrometer via a Conflow-III® open split/interface. Oxygen-containing compounds are quantitatively converted to CO at temperatures between 1350˚C and 1450˚C. After GC separation, the CO gas is swept by a carrier gas into the mass spectrometer and raw $\delta^{18}O$ values are determined. Results are expressed in the usual per mil notation relative to the international V-SMOW standard. The instruments are fully automated and computer controlled using ISODAT 2.0 software. Prior to sample analysis all instrument conditions (reactor temperatures, GC oven temperature, carrier gas flow, ion beam background(s), ion source stability and signal linearity) are checked and recorded ("*Daily check*" routine).

Stable isotope ratios are expressed as delta (δ) 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.

Online (CF-IRMS) technique:

1. Approximately 300µg of pure, homogenized sample are weighed into high purity silver cups (Elemental Microanalysis p/n: D2000)

2. The sample-containing cups are dropped into the high temperature (HTO) pyrolysis reactor using a Costech Zero Blank® autosampler

3. The HTO is maintained at temperatures between 1350˚C and 1450˚C for organic (e.g. cellulose) and inorganic (e.g. $BaSO_4$) materials respectively

4. Carrier flow is ~90 ml/min of UHP 5.0 helium

5. The carrier gas sweeps the gaseous pyrolysis products through a GC column (Elemental MicroAnalysis p/n: E3042) in which CO is separated from N_2

6. CO is introduced via an open split/interface directly into the ion source of the mass-spectrometer

7. Ion currents of masses 28 and 30 are measured simultaneously and the 30/28 ratio of the sample gas is compared to that of a standard CO reference (GTS-Praxair p/n: CO 4.7Z-AS)

8. 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 the international VSMOW-SLAP scale

9. Six (6) replicates of different weights are placed near the beginning of each sequence to allow for element wt.% determination and 'non-linearity' correction

10. Internal lab standards have been characterized against the International Standards listed below and are re-checked periodically

11. USGS LIMs is used for drift correction, normalization and data management (http://water.usgs.gov/software/LIMS/)

International Reference Materials for ^{18}O solids:

Material	$\delta^{18}O_{VSMOW}$
IAEA NO_3	+25.32 ±0.29‰
USGS34	-27.78 ±0.37‰
USGS35	+56.81 ±0.31‰
NBS 127	+8.59 ±0.26‰
IAEA SO5	+12.13 ±0.33‰
IAEA SO6	-11.35 ±0.31‰
IAEA 601	+23.14 ±0.19‰
IAEA 602	+71.28 ±0.36‰
VSMOW2	0‰
SLAP	-55.5‰

Accuracy and Precision:

Accuracy and precision of $\delta^{18}O$ determinations on cellulose, $AgNO_3$ and $BaSO_4$ are generally better than ±0.3‰ (one standard deviation based on n=50 lab standards).

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