Quality Assurance - Data Management

Data Validation

SIRFER makes extensive use of a LIMS system to control samples and process data. LIMS records information about the samples, stores the analytical raw results, corrects and normalizes the analytical results using standardized algorithms and templates and corrects the results to international scales. LIMS monitors instrument parameters and provides notification to the analyst of abnormalities. The LIMS database provides statistics on laboratory reference materials (long-term precision and reproducibility) plus a record of all correction factors.

Validation of the data consists of a three-step process:

- Step 1 – Analyst Review
- Step 2 – LIMS Validation
- Step 3 – QA Approval

Analyst Review is the primary responsibility of the analyst. The analyst monitors instrument stability and is responsible for the initial examination of the IRMS data. The analyst assesses the quality of the work based on the following guidelines:

- The appropriate Standard Operating Procedure (SOP) has been followed.
- Sample preparation is correct and complete.
- Analytical results are correct and complete.
- QC samples are within established acceptable limits.

LIMS Validation identifies data outliers, assesses instrument stability, notifies the analyst of non-conforming instrument parameters and verifies that the corrected/normalized data meet the criteria set forth in the SOP.

QA Approval is the final assessment of the data before acceptance. QA Approval is an independent assessment of the final data by a researcher other than the analyst and must confirm the following:

- The reported results meet tolerances specified in the SOP.
- The results are traceable to internationally accepted standards.
- The results for a given sample are traceable throughout the entire analytical process. (This traceability is maintained through LIMS (which stores all of the pertinent data associated with the sample) and by the use of logbooks, instrument electronic files, and spreadsheets).

Quality Assurance – Reference Materials

$\delta^{13}C$, $\delta^{15}N$, $\delta^{2}H$, $\delta^{18}O$, $\delta^{34}S$, Solids, Continuous Flow

Two different primary laboratory reference materials (PLRM) of known isotopic composition are included in every run for normalization purposes. In addition, quality control secondary laboratory reference materials (SLRM) are included in each analytical run. For $\delta^{13}C$, $\delta^{15}N$, $\delta^{2}H$, $\delta^{18}O$, and $\delta^{34}S$ analysis there is at least one PLRM for every twelve unknowns. For $\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$ analysis of solid material, individual samples are analyzed once during an analytical run with the following exception: two unknown samples are run in duplicate during an analytical run. For $\delta^{18}O$ and $\delta^{2}H$ analysis of solid material, all samples are analyzed in duplicate during an analytical run.

$\delta^{13}C$, Liquids, Continuous Flow

Two different primary laboratory reference materials (PLRM) of known isotopic composition are included with the samples for normalization purposes. In addition, quality control secondary laboratory reference materials (SLRM) are included. Individual samples are analyzed in duplicate during an analytical run.

$\delta^{2}H$ and $\delta^{18}O$, Water, Continuous Flow

Waters of known isotopic signatures are included in every run for normalization purposes, including PLRM and SLRM. These reference materials have been calibrated against accepted NIST and/or IAEA water reference materials. These PLRM and SLRM are analyzed after ten samples with the order of analysis reversed every set to allow LIMS to correct for memory effects and signal drift. All sample vials are analyzed in duplicate during an analytical run.

$\delta^{13}C$, $\delta^{15}N$, $\delta^{18}O$, $\delta^{2}H$, Pure Gases, Dual Inlet

Samples are compared to two PLRM gases of known isotopic composition using dual inlet methods. The PLRM gases are generated offline via in-tube combustion followed by cryogenic trapping and collection of the product gas. All gases (PLRM and unknown) are run against calibrated reference gases. The reference gases have been calibrated against accepted NIST and/or IAEA reference materials.

$\delta^{13}C$ and $\delta^{18}O$, Atmospheric Gas

Samples are analyzed for $\delta^{13}C$ and $\delta^{18}O$ using continuous flow methods and the samples are compared to multiple atmospheric PLRM of known isotopic signatures and CO_2 concentrations. The $\delta^{13}C$ and $\delta^{18}O$ isotopic composition of the PLRM is measured by extracting the CO_2 from the mixture and comparing this extracted CO_2 to pure gases of known isotopic composition using DI-IRMS.

The CO_2 concentrations of the primary cylinders have been measured by the NOAA/CMDL/CCGG (National Oceanic and Atmospheric Administration / Climate Monitoring and Diagnostics Laboratory / Carbon Cycle Gases Group). This measurement by NOAA/CMDL places SIRFER on the WMO (World Meteorological Organization) CO_2 mole fraction scale.

Note on N_2O:
Correcting atmospheric CO_2 for the presence of N_2O is necessary if the $\delta^{13}C$ and $\delta^{18}O$ values of CO_2 need to be measured accurately because the raw CO_2 isotopic data contains a N_2O contribution, which accounts for about 0.2% of the mass 44 signal.

SIRFER employs the following method to eliminate N_2O:
Gas chromatography separation of N_2O and CO_2. This method results in complete separation of N_2O and CO_2 using a packed Porapak Q column. The method allows automated on-line applications and is invaluable for samples with high and/or variable N_2O content.

Quality Assurance -Analytical Methods

Carbon Isotope Ratio Analysis of Soils and Biological Materials

Soils and biological samples submitted for carbon isotope ratio determination are analyzed using continuous flow isotope ratio mass spectrometry. Quality assurance is based on the standard uncertainty of the known value of the SLRM calculated on multiple analyses of SLRM using LIMS. If the standard uncertainty is greater than 0.15 ‰, the unknowns are re-analyzed (until the 2-sigma expanded standard uncertainty of the result is better than 0.3 ‰). The isotopic composition is reported in per mil relative to VPDB on a scale such that USGS40 glutamic acid and USGS41 glutamic acid, respectively, are -26.24 ‰ and +37.76 ‰.

Nitrogen Isotope Ratio Analysis of Soils and Biological Materials

Soils and biological samples submitted for nitrogen isotope ratio determination are analyzed using continuous flow isotope ratio mass spectrometry. Quality assurance is based on the standard uncertainty of the known value of the SLRM calculated on multiple analyses of SLRM using LIMS. If the standard uncertainty is greater than 0.2 ‰, the unknowns are re-analyzed (until the 2-sigma expanded standard uncertainty of the result is better than 0.4 ‰). The isotopic composition is reported in per mil relative to nitrogen in AIR on a scale such that USGS40 glutamic acid and USGS41 glutamic acid, respectively, are -4.52 ‰ and +47.57 ‰.

Sulfur Isotope Ratio Analysis of Soils and Biological Materials

Samples submitted for sulfur isotope ratio determination are analyzed using continuous flow isotope ratio mass spectrometry. Quality assurance is based on the standard uncertainty of the known value of the SLRM calculated on multiple analyses of SLRM using LIMS. If the standard uncertainty is greater than 0.4 ‰, the unknowns are re-analyzed (until the 2-sigma expanded standard uncertainty of the result is better than 0.8 ‰). The isotopic composition is reported in per mil on a scale relative to VCDT such that IAEA-S-1 silver sulfide and IAEA-S-2 silver sulfide, respectfully, are, -0.3 ‰ and +22.7 ‰.

Hydrogen Isotope Ratio Analysis of Water

The prepared samples are analyzed for δ^2H using a High Temperature Conversion/Elemental Analyzer coupled to a Thermo Finnigan Delta Plus XL Isotope Ratio Mass Spectrometer through an open split interface. Each water sample is analyzed in duplicate. Quality assurance is based on the standard uncertainty of the known value of the SLRM of multiple analyses of SLRM using LIMS. If the standard uncertainty is larger than 2 ‰, the sample is re-analyzed (until the 2-sigma expanded standard uncertainty of the result is better than 4 ‰). The isotopic composition is reported in per mil relative to VSMOW water on a scale such that VSMOW and SLAP water, respectively, are 0 ‰ and -428 ‰.

Oxygen Isotope Ratio Analysis of Water

The prepared samples are analyzed for $\delta^{18}O$ using a High Temperature Conversion/Elemental Analyzer coupled to a Thermo Finnigan Delta Plus XL Isotope Ratio Mass Spectrometer through an open split interface. Every sample is analyzed in duplicate. Quality assurance is based on the standard uncertainty of the known value of the SLRM calculated on multiple analyses of SLRM using LIMS. If the standard uncertainty is larger than 0.15 ‰, the samples in the manifold are all re-analyzed (until the 2-sigma expanded standard uncertainty of the result is better than 0.3 ‰). The isotopic composition is reported in per mil relative to VSMOW water on a scale such that VSMOW and SLAP water, respectively, are 0 ‰ and -55.5 ‰.

Hydrogen Isotope Ratio Analysis of Organic and Inorganic Materials (solid)

The prepared samples are analyzed for $\delta^{2}H$ using a High Temperature Conversion/Elemental Analyzer coupled to a Thermo Finnigan Delta Plus XL Isotope Ratio Mass Spectrometer through an open split interface. Quality assurance is based on the standard uncertainty of the known value of the SLRM calculated on multiple analyses of SLRM using LIMS. If the standard uncertainty is larger than 2.5 ‰, the samples in the manifold are all re-analyzed (until the 2-sigma expanded standard uncertainty of the result is better than 4 ‰). The isotopic composition is reported in per mil relative to VSMOW water scale such that VSMOW and SLAP water, respectively, are 0 ‰ and -55.5 ‰.

Oxygen Isotope Ratio Analysis of Organic and Inorganic Materials (solid)

The prepared samples are analyzed for $\delta^{18}O$ using a High Temperature Conversion/Elemental Analyzer coupled to a Thermo Finnigan Delta Plus XL Isotope Ratio Mass Spectrometer through an open split interface. Quality assurance is based on the standard uncertainty of the known value of the SLRM calculated on multiple analyses of SLRM using LIMS. If the standard uncertainty is larger than 0.15 ‰, the samples in the manifold are all re-analyzed (until the 2-sigma expanded standard uncertainty of the result is better than 0.3 ‰). The isotopic composition is reported in per mil relative to VPDB on a scale such that L-SVEC $LiCO_3$ carbonate and NBS 19 $CaCO_3$, respectively, are -26.7 ‰ and +28.6 ‰.

Carbon, Oxygen and Hydrogen Isotope Ratio Analysis of Pure Gases

Gas samples are analyzed for $\delta^{13}C$, $\delta^{18}O$ and $\delta^{2}H$ in dual inlet mode using a Thermo Finnigan Delta Plus Advantage Isotope Ratio Mass Spectrometer. A minimum of two PLRM reference gases are generated from solid PLRM materials and analyzed along with the unknown gases. The standard uncertainty for $\delta^{13}C$ in CO_2 is defined as +/- 0.05 ‰, $\delta^{18}O$ in CO_2 is +/- 0.10 ‰, and $\delta^{2}H$ in H_2 is +/- 2.0 ‰. The carbon isotope composition is reported in per mil relative to VPDB on a scale such that NIST-19 $CaCO_3$ is 1.95 ‰. The oxygen isotope composition is reported in per mil relative to VSMOW on a scale such that NIST-19 $CaCO_3$ is +28.6 ‰. The hydrogen isotopic composition is reported in per mil relative to VSMOW water on a scale such that VSMOW water is 0 ‰.

Carbon and Oxygen Isotope Ratio Analysis of Atmospheric Gases

Dual Inlet Method:

Gas samples (CO_2) are analyzed for $\delta^{13}C$ and $\delta^{18}O$ in dual inlet mode using a Thermo Finnigan Delta Plus Advantage Isotope Ratio Mass Spectrometer. The standard uncertainty for $\delta^{13}C$ is defined as +/- 0.05 ‰ and $\delta^{18}O$ is +/- 0.10 ‰. Quality assurance is based on the standard uncertainty of the known value of the SLRM calculated on multiple analyses of SLRM using LIMS. For $\delta^{13}C$, if the standard uncertainty is larger than 0.05 ‰, the sample is re-analyzed (until the 2-sigma expanded standard uncertainty of the result is better than 0.1 ‰). For $\delta^{18}O$, if the standard uncertainty is larger than 0.1 ‰, the sample is re-analyzed (until the 2-sigma expanded standard uncertainty of the result is better than 0.2 ‰). The carbon isotope composition is reported in per mil relative to VPDB on a scale such that NIST-19 $CaCO_3$ is +1.95 ‰. The oxygen isotope composition is reported in per mil relative to VSMOW on a scale such that NIST-19 $CaCO_3$ is +28.6 ‰.

Continuous Flow Method:

Gas samples are analyzed for $\delta^{13}C$ and $\delta^{18}O$ using an flask autosampler coupled to a Thermo Finnigan Delta Plus Advantage Isotope Ratio Mass Spectrometer through an open split interface.. Quality assurance is based on the standard uncertainty of the known value of the SLRM calculated on multiple analyses of SLRM using LIMS. If the standard uncertainty is larger than 0.15 ‰, the samples in the manifold are rejected. The carbon isotope composition is reported in per mil relative to VPDB on a scale such that NBS 19 $CaCO_3$ is +1.95 ‰. The oxygen isotope composition is reported in per mil relative to VSMOW on a scale such that NIST-19 $CaCO_3$ is +28.6 ‰.

Carbon and Oxygen Isotope Ratio Analysis of Equilibration Gases

Gas samples are analyzed for $\delta^{13}C$ and $\delta^{18}O$ using a gas chromatograph coupled to a Thermo Finnigan Delta Plus Advantage Isotope Ratio Mass Spectrometer through an open split interface. Quality assurance is based on the standard uncertainty of the known value of the SLRM calculated on multiple analyses of SLRM using LIMS. If the standard uncertainty is larger than 0.15 ‰, the sample is re-analyzed (until the 2-sigma expanded standard uncertainty of the result is better than 0.3 ‰). The carbon isotope composition is reported in per mil relative to VPDB on a scale such that NBS 19 $CaCO_3$ is +1.95 ‰. The oxygen isotope composition is reported in per mil relative to VSMOW on a scale such that NIST-19 $CaCO_3$ is +28.6 ‰.

Carbon Isotope Ratio Analysis of DIC Samples

Gas samples are analyzed for $\delta^{13}C$ and $\delta^{18}O$ using gas chromatograph coupled to a Thermo Finnigan Delta Plus Advantage Isotope Ratio Mass Spectrometer through an open split interface. Quality assurance is based on the standard uncertainty of the known value of the SLRM calculated on multiple analyses of SLRM using LIMS. If the standard uncertainty is larger than 0.2 ‰, the sample is re-analyzed (until the 2-sigma expanded standard uncertainty of the result is better than 0.4 ‰). The carbon isotope composition is reported in per mil relative to VPDB on a scale such that NBS 19 $CaCO_3$ is +1.95 ‰.

Carbon and Oxygen Isotope Ratio Analysis of Elevated [CO_2] Samples

Elevated [CO_2] gas samples are analyzed for $\delta^{13}C$ and $\delta^{18}O$ using gas chromatograph coupled to a Thermo Finnigan Delta Plus Advantage Isotope Ratio Mass Spectrometer through an open split interface. Quality assurance is based on the standard uncertainty of the known value of the SLRM calculated on multiple analyses of SLRM using LIMS. If the standard uncertainty is larger than 0.2 ‰, the sample is re-analyzed (until the 2-sigma expanded standard uncertainty of the result is better than 0.4 ‰). The carbon isotope composition is reported in per mil relative to VPDB on a scale such that NBS 19 $CaCO_3$ is +1.95 ‰. The oxygen isotope composition is reported in per mil relative to VSMOW on a scale such that NIST-19 $CaCO_3$ is +28.6 ‰.

Carbon Isotope Ratio Analysis of Pure CO_2 Samples

Pure gas samples are analyzed for $\delta^{13}C$ using DI-IRMS methods Quality assurance is based on the standard uncertainty of the known value of the SLRM calculated on multiple analyses of SLRM using LIMS. If the standard uncertainty is larger than 0.05 ‰, the sample is re-analyzed (until the 2-sigma expanded standard uncertainty of the result is better than 0.1 ‰). The carbon isotope composition is reported in per mil relative to VPDB on a scale such that NBS 19 $CaCO_3$ is +1.95 ‰.

Nitrogen Isotope Ratio Analysis of Pure N_2 Samples

Pure gas samples are analyzed for $\delta^{15}N$ using DI-IRMS methods. Quality assurance is based on the standard uncertainty calculated on multiple analyses of SLRM using LIMS. If the standard uncertainty is larger than 0.08 ‰, the sample is re-analyzed (until the 2-sigma expanded standard uncertainty of the result is better than 0.16 ‰). The nitrogen isotope composition is reported in per mil relative to AIR on a scale such that IAEA-N1 is +0.43 ‰.

Hydrogen Isotope Ratio Analysis of Pure H_2 Samples

Pure gas samples are analyzed for $\delta^{2}H$ using DI-IRMS methods. Quality assurance is based on the standard uncertainty of the known value of the SLRM calculated on multiple analyses of SLRM using LIMS. . If the standard uncertainty is larger than 2 ‰, the sample is re-analyzed (until the 2-sigma expanded standard uncertainty of the result is better than 4 ‰). The hydrogen isotope composition is reported in per mil relative to VSMOW on a scale such that VSMOW is +0 ‰.

Carbon and Oxygen Isotope Ratio Analysis of Carbonate Samples

Pure gas samples are analyzed for $\delta^{13}C$ and $\delta^{18}O$ using DI-IRMS methods. Quality assurance is based on the standard uncertainty of the known value of the SLRM calculated on multiple analyses of SLRM using LIMS. . If the standard uncertainty is larger than 0.05 ‰, the sample is re-analyzed (until the 2-sigma expanded standard uncertainty of the result is better than 0.1 ‰). The carbon isotope composition is reported in per mil relative to VPDB on a scale such that NBS 19 $CaCO_3$ is +1.95 ‰. The oxygen isotope composition is reported in per mil relative to VPDB on a scale such that NIST-19 $CaCO_3$ is -2.2 ‰.

Carbon Isotope Ratio Analysis of Gas Samples

Gas samples are analyzed for $\delta^{13}C$ using a elemental analyzer coupled to a Thermo Finnigan Delta Plus Advantage Isotope Ratio Mass Spectrometer through an open split interface. Quality assurance is based on the standard uncertainty of the known value of the SLRM calculated on multiple analyses of SLRM using LIMS. If the standard uncertainty is larger than 0.2 ‰, the sample is re-analyzed (until the 2-sigma expanded standard uncertainty of the result is better than 0.4 ‰). The carbon isotope composition is reported in per mil relative to VPDB on a scale such that NBS 19 $CaCO_3$ is +1.95 ‰.

Carbon Isotope Ratio Analysis of Liquid Samples

Liquid samples are analyzed for $\delta^{13}C$ using an elemental analyzer coupled to a Thermo Finnigan Delta Plus Advantage Isotope Ratio Mass Spectrometer through an open split interface. Quality assurance is based on the standard uncertainty of the known value of the SLRM calculated on multiple analyses of SLRM using LIMS. If the standard uncertainty is larger than 0.2 ‰, the sample is re-analyzed (until the 2-sigma expanded standard uncertainty of the result is better than 0.4 ‰). The carbon isotope composition is reported in per mil relative to VPDB on a scale such that NBS 19 $CaCO_3$ is +1.95 ‰.

Carbon and Oxygen Isotope Ratio Analysis of Atmospheric CO_2 Samples

Gas samples are analyzed for $\delta^{13}C$ and $\delta^{18}O$ using a preconcentrator coupled to a Thermo Finnigan Delta S Isotope Ratio Mass Spectrometer through an open split interface. Quality assurance is based on the standard uncertainty of the known value of the SLRM calculated on multiple analyses of SLRM using LIMS. . If the standard uncertainty is larger than 0.2 ‰, the sample is re-analyzed (until the 2-sigma expanded standard uncertainty of the result is better than 0.4 ‰). The carbon isotope composition is reported in per mil relative to VPDB on a scale such that NBS 19 $CaCO_3$ is +1.95 ‰. The oxygen isotope composition is reported in per mil relative to VSMOW on a scale such that NIST-19 $CaCO_3$ is +28.6 ‰.

Nitrogen Isotope Ratio Analysis of Atmospheric N_2O Samples

Gas samples are analyzed for $\delta^{15}N$ using a preconcentrator coupled to a Thermo Finnigan Delta S Isotope Ratio Mass Spectrometer through an open split interface. Quality assurance is based on the standard uncertainty of the known value of the SLRM calculated on multiple analyses of SLRM using LIMS. If the standard uncertainty is larger than 0.2 ‰, the sample is re-analyzed (until the 2-sigma expanded standard uncertainty of the result is better than 0.4 ‰). The nitrogen isotope composition is reported in per mil relative to AIR on a scale such that IAEA-N1 is +0.43 ‰.

Carbon Isotope Ratio Analysis of Atmospheric CH_4 Samples

Gas samples are analyzed for $\delta^{13}C$ using a preconcentrator coupled to a Thermo Finnigan Delta S Isotope Ratio Mass Spectrometer through an open split interface. Quality assurance is based on the standard uncertainty of the known value of the SLRM calculated on multiple analyses of SLRM using LIMS. If the standard uncertainty is larger than 0.2 ‰, the sample is re-analyzed (until the 2-sigma expanded standard uncertainty of the result is better than 0.4 ‰). The carbon isotope composition is reported in per mil relative to VPDB on a scale such that NBS 19 $CaCO_3$ is +1.95 ‰.

Carbon and Oxygen Isotope Ratio Analysis of Carbonate Samples

Gas samples are analyzed for $\delta^{13}C$ using a common acid bath digestion autosampler coupled to a Thermo Finnigan MAT 252 Isotope Ratio Mass Spectrometer. Quality assurance is based on the standard uncertainty of the known value of the SLRM calculated on multiple analyses of SLRM using LIMS. If the standard uncertainty is larger than 0.12 ‰, the sample is re-analyzed (until the 2-sigma expanded standard uncertainty of the result is better than 0.24 ‰). The carbon isotope composition is reported in per mil relative to VPDB on a scale such that NBS 19 $CaCO_3$ is +1.95 ‰.

Carbon and Oxygen Isotope Ratio Analysis of Headspace CO_2 Samples

Gas samples are analyzed for $\delta^{13}C$ and $\delta^{18}O$ using a headspace autosampler coupled to a Thermo Finnigan MAT 252 Isotope Ratio Mass Spectrometer through an open split interface. Quality assurance is based on the standard uncertainty of the known value of the SLRM calculated on multiple analyses of SLRM using LIMS. If the standard uncertainty is larger than 0.2 ‰, the sample is re-analyzed (until the 2-sigma expanded standard uncertainty of the result is better than 0.4 ‰). The carbon isotope composition is reported in per mil relative to VPDB on a scale such that NBS 19 $CaCO_3$ is +1.95 ‰. The oxygen isotope composition is reported in per mil relative to VSMOW on a scale such that NIST-19 $CaCO_3$ is +28.6 ‰.