Updated 19.12.2023

$\delta^{13}C$ and $\delta^{15}N$ analysis of soils, sediments and other mineral rich samples (e.g. archaeological food crusts, and bulk bone/tooth powders)

Soil and sediment samples contain variable amounts of organic material, whose the $\delta^{13}C$ and/or $\delta^{15}N$ values we can analyze if the organic (and thus C and N) contents are high enough. We do not provide analyses of small particulate samples collected on glass fiber filters as a standard service.

General considerations

Typically, the N content of mineral rich matrices like natural soils and sediments is so low and the C content at the same time so high, that two separate subsamples of the same material must be weighed and analyzed to obtain both $\delta^{13}C$ and $\delta^{15}N$ values for the sample, but there are exceptions – see further below.

The C and N contents in different types of soils, sediments and mineral rich materials can display significant variability. The amount of sample weighed in for analysis depends on the C and N content of the material. When submitting these types of samples for analysis**, we ask you to provide a *best guess estimate* of the typical nitrogen/carbon weight-% that is representative of your samples**. Please, search for typical mean values for your specific sample type and circumstances from scientific literature if you have no measurement data for your own sample set. The **minimum acceptable contents of C and N is 0.2 Wt-%** for routine analysis**.** In certain cases we can measure samples down to 0.1 Wt-% C or N content at an additional charge, but the feasibility is reviewed on a case by case basis.

Examples of typical organic C and N dry Wt-% values in some mineral rich sample matrices are listed in the table below for reference. Archaeological food crust samples may have significantly less C (<5%) and N (<1 %) depending on the amount of pottery material incorporated into the sample during sampling. For soils, total C may be much higher depending on soil carbonate content. The sample masses listed are calculated for the lowest Wt-% value in the given typical range, i.e. lower sample masses apply if your material has higher contents of the element. The value in parentheses () is the minimum applicable sample mass for still acceptable analysis quality, but these should not be applied unless the availability of sample material is a problem. To find out the exact required weighing amounts for your samples, contact us at stableisotopes@helsinki.fi with the expected C and/or N weight-% values for your samples.

	C (org) wt-%	**sample mass for C, µg**	**N wt-%**	**sample mass for N, µg**
Arch. food crusts	10-70	750 (150)	1-10	4600 (2400)
Bone, dentine (bulk)	10-15	750 (150)	3-6	1500 (780)
Low organic soil	0.3-1.5	max. 15000	0.03-0.15	max. 15000
Mid organic soil	2-3	3800 (750)	0.2-0.3	max. 15000
High organic soil	5-15	1500 (300)	0.3-1	max. 15000

The combustion of the sample prior to IRMS-analysis takes place at 1020 °C. At this temperature, any carbonate that is present in the sample, will decompose and release carbon which will contribute to the $\delta^{13}C$ value. If your samples contain carbonate, and you want to get the $\delta^{13}C$ value of the organic fraction only, remember to pretreat your samples or request for carbonate removal as an additional service when submitting samples.

Updated 19.12.2023

Due to their generally high and variable mineral content, these sample types samples are more unpredictable and harder on the IRMS systems. They are difficult to combust, necessitate more frequent reactor maintenance, cause more frequent reactor breakage, and take up more staff working hours. Due to these reasons, prices per replicate for soils and sediments are higher than those for pure organic samples.

These sample types usually display a higher degree of heterogeneity, usually leading to lower precision, than pure organic materials, and we **recommend analyzing more than one replicate per sample** to get a realistic estimate of the uncertainty for the isotope value. Note that this is a different thing than analytical uncertainty quoted in the analytical report, which only measures the precision of the instrument. If analyzing the whole set of samples in duplicate/triplicate is not feasible, we recommend choosing a representative set of samples, e.g. 10-30% of total sample number, to be analyzed in duplicate or triplicate. However, as prices are charged per analyzed replicate, the decision of replicate IRMS measurements is left up to the customer's discretion. To help in making the decision, we recommend you follow examples typical in the scientific literature of your specific field.

Special case 1: Material with low C/N ratio

The δ13C and δ15N values of mineral-rich samples that have a sufficiently low C/N ratio (ratio of carbon weight-% to nitrogen weight-%; dry weight) can be analyzed from a single subsample, i.e. it is not necessary to prepare two subsamples to get both values. To qualify for CN-dual analysis, your sediment/soil sample must have a C/N <16.5, and at the same time, the N weight-% must be above 0.2%.

Special case 2: Archaeological food crusts

Archaeological food crust samples are a variable mixture of mineral matter (pottery material + possible burial earth remains), modern detrital organic remains and archaeological organic material, of which usually the latter is of interest. Prior to analysis, the material must be inspected, larger grains of mineral matter must be removed if present, and a sample must be obtained from the most homogenic, organic fraction. This often requires treatment of the sample under binoculars, and some times various methods of gravitational separation prior to sampling. The unpredictability and very high variability of C and N contents in food crust samples often leads to the necessity of several IRMS reanalyses per sample, leading also to a higher than typical sample amount demand. Typical sample amounts range from 0.5 to 20 mg dry weight. Due to the above challenges the price of $\delta^{13}C$ and/or $\delta^{15}N$ analysis of archaeological food crusts varies: it consists of a fixed rate of IRMS analysis (incl. reanalyses as needed) given in the price list, and on top of that, an hourly charge depending on the preparatory work needed to inspect and clean the sample for analysis. A minimum charge of one hour per sample applies.

Sample preparation, all sample types

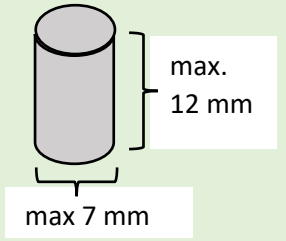
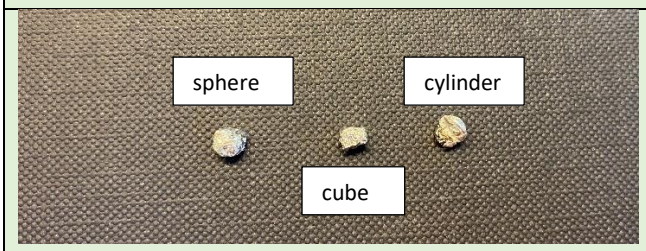
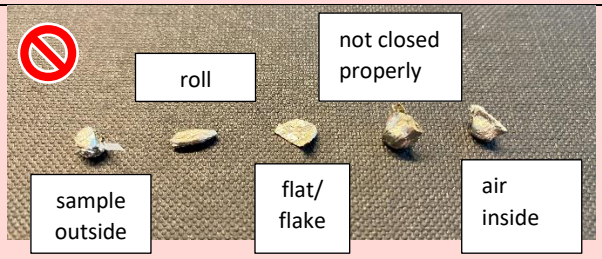
Properly dried and homogenized sample powders are weighed into tin (Sn) capsules of appropriate volume (see Table below). Capsule size is chosen to enable proper closing and folding of the cup without material leaking or protruding outside. If your samples are in silver (Ag) cups after acid treatment for carbonate removal, encapsulate the entire crimped Ag cup within another cup made of tin and be sure to let us know about this. The tin functions as an important catalyst of the combustion reaction. If using silver, use high purity cups (Ag 99.99%).

If you're weighing and closing your samples yourself, please see tips for encapsulating samples below, and note that the Wt-% results are dependent on the accuracy of your weighing. You should use a microbalance giving you 3 decimal digits below 1 mg, i.e. 0.001 mg / 1 µg precision. Aim at a precision of ± 10% in weighing. For example, when aiming at a mean weight of 1.00 mg, you would accept sample weights from 0.90 to 1.10 mg.

Updated 19.12.2023

Encapsulating samples:

The aim is to have all the sample material inside, all the air squeezed out, nothing leaking out, and have a shape that is bulky (3D) enough that it will not get stuck and wedged in the narrow spaces left between the moving and stationary parts of the autosampler.

YES	NO
☺ compress, squeeze out air from sample+capsule	☹ squeeze/fold only top part of tin cup closed
☺ make bulky shape: spherical, cubical, cylinder…	☹ folded into a flat/ flake-like/ roll-like shape
☺ fold and crimp in the opening	☹ sample is leaking or protruding out of cup
 After closing and compaction, capsule must fit in a cylidrical shape of max 7 x 12 mm	NOTE THAT IF YOU'RE SAMPLES ARE SOMETHING DESCRIBED ABOVE OR PICTURED BELOW, WE WILL HAVE TO REPACK/ RESHAPE THEM AT AN ADDITIONAL CHARGE.
	

Manufacturer	Product	ID	Size (mm)	Common for sample types
IVA Analysentechnik GmbH & Co. KG	Tin capsules for solids	SA76980002	3.2 x 4	animal tissues, collagen, plants, fungi…
IVA Analysentechnik GmbH & Co. KG	Tin capsules for solids, light	SA76980702L	4 x 6	plant N, soils, sediments, food crust (arch)
IVA Analysentechnik GmbH & Co. KG	Tin capsules for solids	SA76980902	5 x 8	plant N, soils, sediments, food crust (arch)

Table 1: Tin cups commonly used for C and N isotope analyses at the Laboratory of Chronology. Corresponding capsules are available from many other manufacturers.

IRMS-analysis and data normalization

The isotopic composition of carbon and nitrogen is measured on a Carlo Erba NC2500 elemental analyzer coupled to a Thermo Scientific Delta V series isotope ratio mass spectrometer in continuous flow mode. Alongside samples, each analytical run contains ca. 30% reference materials that are used for normalization of isotope values and for quality control. The isotope values of the samples and QC materials are normalized using the known isotope values of *at least two different* calibration reference materials included in the run. We use several internationally recognized secondary reference materials for this purpose: USGS-40, USGS-41, IAEA-N1, IAEA-N2, IAEA-CH3, IAEA-CH6 and IAEA-CH7. The QC materials are chosen to correspond to the analyzed sample matrix as closely as possible. Data normalization is performed using the 'LIMS for Light Stable Isotopes' software developed by Tyler Coplen of the Reston Stable Isotope Laboratory at the US Geological Survey. The long-term analytical precision is ± 0.2 for both $\delta^{13}C$ and $\delta^{15}N$ values.

In addition to the requested isotope values, the report of analysis also includes the Weight-% of the element(s) in the samples, a method description and standard deviations of the reference materials to

evaluate internal precision. If the customer wishes to also receive a copy of the uncorrected, ‘raw’ data, this can be made available **upon prior agreement**.