Gas Source Isotope Ratio Mass Spectrometer (commonly IRMS, herein MS)

Measures relative amounts of stable isotopes of one or more elements in a single gas, e.g. for

O2: 18O/16O and 17O/16O 34/32, 33/32

This particular unit is a Thermo-Finnigan MAT253 (now MAT253”plus” at Thermo-Fisher) that has a 10 kV acceleration voltage and a 10-cup primary collector, and can also analyze

CO: 18O/16O and 13C/12C 30/28, 29/28

CO2: 18O/16O and 13C/12C 46/44, 45/44, and m47, 48, 49, for clumped good luck

N2:15N/14N 29/28

SO2: 34S/32S 66/64

SF6: 36S/32S, 34S/32S, and 33S/32S 131/127, 129/127, 128/127, as SF5+

A separate collector is located much closer to the ion source to account for the much smaller flight path/radius of hydrogen

H2: 2H/1H commonly expressed as D/H

For the highest accuracy and precision, the MS is operated in Dual Inlet (DI) mode at high vacuum

(~10-11 bar), where the only entrants in the flight tube are the sample and reference gases. Sample and reference gas pressures and resulting collector voltages must be balanced using a pair of compressible bellows assemblies, because linearity issues otherwise.

(Rambling statement by tour guide here on so called reference gas vs. actual standards. Bonus points if “matrix effects” can be made to be understood by all, and with context, in a clear and concise manner.)

Continuous Flow Peripherals

Automated Continuous Flow (CF) mode analyses use a helium carrier gas to bring the both sample and reference gases into the MS flight tube ion source from peripheral devices.

TC/EA – Thermal Conversion/Elemental Analyzer option with Conflo III

Measures D/H and 18O/16O in water, either directly or as water extracted from hydrous solid samples, e.g. mica, clay minerals, hydrous volcanic glass, or organic compounds. Solid samples are introduced by a rotary autosampler into the furnace at 1450 °C which is lined with vitreous carbon and where the helium carrier gas is always flowing. Even for solid mineral samples (~1 mg @ 3wt% H2O, 30µg), the water is released in a few milliseconds and is subject to the essentially instantaneous pyrolysis reaction:

H2O(g) + C(s) → H2(g) + CO(g)

The mixed gas sample is pushed immediately by the helium carrier gas stream into a GC column where H2 and CO are resolved with a separation of about two minutes. The MS then measures D/H, jumps to the CO configuration, and then measures 18O/16O. Pulses of reference gas are metered to the MS by the attendant Conflo III peripheral device that can also used with other types of elemental analyzers. The autosampler is timed so that the H2 sample/standard peak arrives in the MS just after the last H2 reference gas peak, and the CO sample/standard peak finishes just before the first CO reference gas peak. The Conflo III meters out pulses of reference gas, and decreases gas pressures to atmospheric, suitable for introduction into the MS flight tube.

GasBench II option

In our lab, it measures 18O/16O and 13C/12C in carbonate minerals, mostly CaCO3 of high purity from sea shell carbonates for the Dept. of Anthropology, but also in nodules from soil and sediments for folks in Earth Science. Other capabilities, done in the past but generally abandoned are 18O/16O in water via equilibration with CO2, and 13C/12C in dissolved inorganic carbon. The Gasbench II operates with both a robotic autosampler, and a heating block at 70 °C which holds 96 samples/standards

For carbonate minerals, ~100 μg of pure (more for impure) CaCO3 is put into a 12 ml glass test tube (“exetainer”), threaded for an airtight septum cap. The exetainers are flushed with helium to exclude atmosphere, two at a time with those flush needles, and then eight drops of ortho-phosphoric acid are injected by hand, yielding the following reaction:

3CaCO3(s) + 2H3PO4(l) → 3CO2(g) + 3H2O(l) + 2Ca3(PO4)2(aq)

During the reaction, one third of the oxygen is left behind in solution. Fortunately, this temperature-dependent fractionation has already been well quantified by the work of others, and at 70 °C equilibrium is attained in ~15 minutes. Similar to the Conflo, the GasBench meters pulses of both reference and sample gases, in helium carrier gas at atmospheric pressure, to the MS.

Laser Fluorination

Laser fluorination is a process by which O2 gas is extracted from oxygen-bearing compounds. In our lab that is almost always a silicate mineral. For the simplest of silicate minerals, quartz, with the fluorinating agent BrF5, yields the following (not balanced) reaction:

SiO2(qtz) + BrF5(g) → SiF4(g) + O2(g) + BrF, BrF3, BrF5 (g)

Except for O2, all of the reaction products freeze at the liquid nitrogen (LN2) temperature (-196°C).For other silicates solid products are also present, and might include NaF, KF, CaF2, MgF2, FeF3, AlF3, etc. The fluorination line is kept at high vacuum so that only the sample and BrF5 are present at the time of fluorination. Generally the reaction is exceedingly slow at room T, so an infrared laser (CO2, 9.6 μm, 100W) is used to heat the sample to ~1800 °C. Note that the sample chamber window must be transparent to infrared radiation, and so is composed of BaF2. Some reactive samples e.g. whole rock powders will react at room T, so they are transferred singly to the sample chamber via an airlock. When the reaction is visibly complete, the SiF4 and spent reagent wastes are frozen with LN2, and the sample is passed through an Hg diffusion pump to remove any remaining traces of wastes not frozen, as HgFx(s), HgBrX(s). The sample is then converted to CO2 over hot carbon. Since CO2 freezes at the T of LN2, it can easily be moved further along the vacuum line to the MS inlet using only LN2.

If O-17 is of interest, the procedure is a bit more complicated, as the sample must be analyzed in the MS directly as O2, rather than CO2. Thus the sample must be moved among molecular sieve (zeolite) traps, which are also cooled with LN2, but instead of freezing O2, molecular adsorption of O2 on the zeolite surface. The sample is then passed through a GC column to separate the sample from any NF3 interfering contaminant, if present. The traps and GC column must also be outgassed under vacuum or helium carrier gas, by heating after each sample, so the process takes much longer than the CO2 method.