Variations in atmospheric helium isotopes

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The purpose of this work is to look for variations in the isotopic helium composition in the atmosphere. Anthropogenic activities such as oil and gas exploitation release crustal helium, which has excess ^{4}He compared to atmospheric helium. This may give rise to detectable spatial and temporal variations in the atmospheric ^{3}He/^{4}He [1].

These differences, if they exist, would be very small [2], and thus require very high precision measurements. However, high precision measurements of atmospheric helium presents a significant analytical challenge because helium is only present in trace quantities in the air (5.24 ppm) and there are are many of orders of magnitude difference in the abundance of the two isotopes (^{3}He/^{4}He$_{air}$ = 1.38 x10^{-6}). We are designing a method to reliably measure ^{3}He/^{4}He with 2‰ or better precision.

Air samples are collected in copper tubes which are then sealed manually at the sample site with steel clamps. Each tube holds a volume of approximately 20 cm^3. Samples collected cover a wide range of longitudes and latitudes, with a particular emphasis on sampling across many latitudes since the largest spatial variation is expected to be seen in latitude.

For each measurement we purify a relatively large amount of gas (~5-15 cm^3) so that we can make many repeat analyses of the same sample gas. We have constructed an automated extraction line which can rapidly switch between measuring aliquots of sample with standards. A major component of our method features an adjustable bellows on the sample aliquot volume that enables us to adjust the size of a sample aliquot to precisely match the standard, eliminating biases arising from nonlinear pressure effects in the mass spectrometer. The measurements are made using a Helix split flight tube multi-collector mass spectrometer.

At present, the measured ratios of a sample have a 1σ reproducibility of 2-3‰, which is still too large to detect variations. We have planned several changes to further improve the next round of measurements including installing a quadrupole mass spectrometer to monitor the gas purification process and the addition of a cold trap to the mass spectrometer volume.

[1] Oliver *et al.* (1984) *GCA* **48**, 1759–1767. [2] Sano *et al.* (2010) *GCA* **74**, 4893–4901.

On the origins of dissolved natural organic matter (DNOM) in rivers and lakes

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One of the most important characteristics of DNOM, at least with respect to reversible chemical reactivity, is its aromatic carbon content. The DNOM (measured as dissolved organic carbon, DOC) that dominates most rivers and lakes is derived primarily from land plants, including various species of woody trees and shrubs, grasses, fungi and mosses. The specific ultraviolet absorbance (SUVA, absorbance at 254 nm in a 1.0 cm cell divided by DOC in mgL^{-1}) of DNOM provides a simple, widely applicable indication of a sample's aromatic content. Examination of SUVA values of water samples from rivers and lakes, then comparison of these to SUVA values for DNOM samples derived from precursor materials, shows little apparent commonality. These precursor materials consist of senescent materials from plant species common to the catchment basins of the rivers and lakes. This paper examines the effects of geochemical processes on the SUVA values of natural waters and associated precursor materials in order to develop an understanding of the primary factors affecting the origins and aromatic content of DNOM in natural waters.