

Investigations into temporal and spatial variations in atmospheric helium isotopes

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This work describes the development of a method to measure atmospheric helium isotopes at a very high precision (0.2% or better). The primary motivation is to look for potential temporal or spatial variations in the helium isotopic composition of the atmosphere. Since crustal helium has a large excess of ⁴He relative to atmospheric helium, recent anthropogenic activities such as fossil fuel exploitation may give rise to a change in the atmospheric composition [1, 2]. However, previous measurements have put an upper limit on this near current measurement abilities [3, 4]. There are significant analytical challenges to improving the precision of atmospheric helium measurements as helium is only present in trace quantities in the air (5.24 ppm) and there are many orders of magnitude difference in the abundance of the two isotopes (³He/⁴He_{air} = 1.38 × 10⁻⁶).

To improve our ability to measure helium isotopes precisely, we have constructed an automated extraction line which can rapidly switch between measuring aliquots of sample with standards. For each measurement we purify a relatively large amount of gas (~20 cm³) so that we can make many repeat analyses of the same sample gas. 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.

Prior to analysis we remove the neon (and any other gases remaining after purification) with a cryo trap. This lowers the pressure in the mass spectrometer and makes it easier to be sure that the standard and sample aliquots are the same size. There is an additional cryo trap on the mass spectrometer volume to maintain low background levels. Adding the cryo trap reduced the statistical errors of repeated standard analysis within one day from 0.5% to 0.3% (2σ). Meanwhile the absolute scatter of measurements over several days fell from ~5% before the addition of the cryo trap to better than 0.5%. We believe much of this remaining scatter can be attributed to an instability discovered in the high voltage power supply of the source.

All of the previous measurements were made on a GV Instruments Helix split flight tube multi-collector mass spectrometer, which was specifically designed for helium isotope measurements. Future measurements will be made on a new version of the same machine built by Thermo Scientific and recently installed in our lab (January 2012). The new machine has already demonstrated approximately three times higher sensitivity as well as better electronic stability. First results with the new machine will be presented at the conference.

[1] Oliver *et al.* (1984) *GCA* **48**, 1759-1767. [2] Pierson-Wickman *et al.* (2001) *EPSL* **194**, 165-175. [3] Sano *et al.* (2010) *GCA* **74**, 4893-4901. [4] Lupton and Evans (2004) *GRL* **31**, L13101.

Metagenome-enabled investigation of microbial sulfur precipitation in a carbonate aquifer

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Microbial coupling between carbon and sulfur elemental cycles in iron-poor, carbonate-rich environments results in the dissolution of carbonate minerals, precipitation of gypsum, and/or the precipitation and dissolution of elemental S. In particular, the incomplete oxidation of sulfide to elemental S strongly affects the availability of H₂S and H₂SO₄, acids which contribute to limestone dissolution. The sulfidic Frasassi caves provide a superb model environment for understanding biotic and abiotic controls on the balance of these processes, which affect porosity development and fluid flow in sedimentary aquifers and the diagenesis of marine carbonates.

In the Frasassi system, four types of sulfide-oxidizing biofilm communities develop in separate niches defined by dissolved sulfide: oxygen ratios and hydrodynamic shear [1]. Elemental analyses suggest that S precipitates most rapidly in locations where turbulent mixing brings sulfidic water in contact with cave air, resulting in biofilms that are 40-80% sulfur by mass. Major populations in the biofilms include members of widely-dispersed and uncultivated sulfur-oxidizing clades, including Gammaproteobacteria related to "Thiobacillus barengensis" (Tbar) and Sulfurovumales-group Epsilonproteobacteria. Based on FISH population counts with genus and group-specific probes, Sulfurovumales are successful only when the sulfide: oxygen ratio exceeds 150. In contrast, Tbar populations are not correlated with concentrations of sulfide, oxygen, or the dissolved sulfide: oxygen ratio.

To further investigate the geochemical and ecological factors that favor the growth of Tbar and Sulfurovumales populations, and implications for sulfur precipitation and limestone dissolution, we investigated the metabolic capabilities of the sulfur-precipitating biofilms using enrichment culturing and metagenomics. Initial enrichment culturing efforts suggest that Tbar and Sulfurovumales populations are autotrophic or mixotrophic, and that batch (rather than flow-through) culturing methods favor the growth of Tbar over Sulfurovumales. Four metagenomes derived from biofilms naturally enriched in Tbar and Sulfurovumales populations are currently in production, and will provide genetic clues necessary to enhance enrichment culturing efforts and constrain the metabolic potential of these ecologically successful groups, including pathways for partial or complete S oxidation, S reduction, C and N fixation, heterotrophy, and biofilm formation.

[1] Macalady (2008) *ISME Journal* **2**, 590-601.