Archean sulfur may power modern microbial life in the deep subsurface in the Canadian Shield

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Saline fracture water in Archean rocks in the Canadian Shield and South Africa have been found to host microbes (mainly sulfate reducers) as deep as 3 km. This provides an important analog for the study of life on the early Earth and for search for life on other planets (e.g. Mars). In order to understand the source and sustainability of the sulfate that supports these deep microbial ecosystems, we carried out multiple sulfur (S) isotope analyses for dissolved sulfate and sulfide in the saline waters from up to 2.7 km depth in the Canadian Shield near Timmins, Ontario (ON) and Thompson, Manitoba (MN).

Prevalent S isotope mass independent fractionations (MIF) were observed: dissolved sulfate at the ON sites had $\delta^{34}S$ values from 3.3 to 8.4‰ and $\Delta^{33}S$ from -0.07 to -0.20‰. Dissolved sulfate at the MN sites had $\delta^{34}S$ values from 21.1 to 26.0‰ and $\Delta^{33}S$ from 0.13 to 0.19‰. One dissolved sulfide sample at the MN sites had $\delta^{34}S$ of 4.4‰ and $\Delta^{33}S$ of 0.13‰. The negative $\Delta^{33}S_{sulfate}$ values at ON are comparable to those of local 2.7Ga sulfide deposits. At MN, the S source of the hosting Proterozoic ore deposits has been inferred to be at least partially from recycling of sulfide in local Archean sedimentary rocks. The observed MIF of the saline waters suggests the possibility that the ultimate S sources of sulfate in these deep groundwater systems are the Archean sulfides. The large $\delta^{34}S$ and consistent $\Delta^{33}S$ between dissolved sulfate and sulfide, and the significantly elevated $\delta^{34}S_{sulfate}$ values in the MN samples relative to the reported values for the ore (2-6‰) suggest significant sulfate reduction (SR). The $\delta^{34}S_{sulfate}$ of the ON samples are also elevated by 1-6‰ compared to the published values of local ore deposits (0-2‰), implying SR may be also taking place at this site. Because all of these groundwaters have temperatures less than 30°C, the SR is most likely biological in origin. Our data raise the possibility that present-day elemental cycling by deep microbial communities can be supported by Archean S sources.

Measurement of intramolecular carbon isotopic distribution of acetaldehyde emitted from plant leaves

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Stable isotopic signatures within molecules record a wide range of phenomena in the chemical, biological, environmental, and earth sciences.

Here, we focus on acetaldehyde, which is an important metabolic intermediate in biological systems. Until now, there was only one study on intramolecular carbon isotopic composition ($\delta^{13}C$) of acetaldehyde, which derived from pyruvate decarboxylase during yeast incubation experiments [1]. However, in this study, the analytical protocol and the precision of the method, and the brief description made suggests that the technique was cumbersome, since it predated GC-IRMS techniques.

In this study, we examine the applicability of measurements of intramolecular $\delta^{13}C$ in acetaldehyde through GC-C-IRMS approaches. Using GC-C-IRMS combined with an off-line pyrolysis, we determined the certified values of the intramolecular $\delta^{13}C$ in acetaldehyde samples. Then, based on the certified value, we developed GC-Py-GC-C-IRMS combined with headspace solid-phase microextraction (time-saving and more sensitive than off-line pyrolysis) for the accurate determination of $\delta^{13}C$ of acetaldehyde. This method was applied to samples collected form chamber in which plants were grown. The results shown that the intrmolecular $\delta^{13}C$ of acetaldehyde emitted from plants was influenced by environmental factors, such as temperature, sunlight or humidity. These results suggest that environmental factors influence the fluxes related to acetaldehyde metabolism in plants, which gives us new insights into plant metabolic pathways and potentially plant-atmosphere interactions.

[1] DeNiro, M. & S. Epstein (1977) *Science* **197**, 261–263.