

Sulfur isotope analysis by near-infrared optical feedback cavity enhanced absorption spectroscopy

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The sulfur biogeochemical cycle is a collection of fundamental processes that help maintaining physical, chemical and biological equilibrium in the environment. Sulfuric acid, the end oxidation product, has profound environmental impacts; notably, acidification of precipitation, changes in Earth's radiative balance, sewage pipe deterioration, and respiratory health effects. Anthropogenic emissions due to fossil fuel burning have surpassed natural (marine and volcano) emissions, with unknown consequences for the biodiversity and the climate. Sulfur isotope (^{32}S (95%), ^{34}S (4.2%), ^{33}S (0.7%), ^{36}S (0.002%)) analysis has proven to be applicable in a wide range of studies, from, e.g., sourcing atmospheric sulfur pollution [1], chronicling the emergence of life [2], and determining when atmospheric oxygen became abundant [3]. However, it has been severely hampered by the complexities and difficulties associated with conventional isotope ratio mass spectrometry (IRMS). Indeed, sulfur isotopes are usually analyzed in either SO_2 or SF_6 . The first is easily obtained after combustion of sulfur compounds, but has problems of mass-overlap between $^{33}\text{SO}_2$ and OS^{17}O . The latter is obtained after a long and potentially dangerous chemical conversion.

For these reasons we have developed a new method based on near-infrared spectroscopy of H_2S . $\text{H}_2\text{S(g)}$ has the advantage to be produced easily by reduction of sulfur compounds and requires no specific chemical installation. In fact, it is normally produced in one of the first steps of the chemical reactions used to produce SO_2 or SF_6 . This allows using optical feedback cavity enhanced absorption spectroscopy (OFCEAS [4]) near $1.6\text{ }\mu\text{m}$ on a sample of 100 nmol H_2S , which is competitive with the sulfur quantity needed by IRMS. Additionally, OFCEAS has a built-in frequency scale calibration, enabling highly accurate model fits to the recorded spectra, an important feature for the quantitative measurement. Averaging over tens of minutes to improve precision is possible due to good thermal and pressure stabilization of the optical setup.

We report first results obtained for static measurements on three H_2S samples synthesized and verified by IRMS to have relative enrichments of 0‰ 42.6‰ and 83.6‰ for $\delta^{34}\text{S}$, and 0‰ 2.81‰ and 5.39‰ for $\delta^{33}\text{S}$. The laser measurements agree to within 1‰ with the IRMS values. Performing 3 measurements lasting 12 minutes each, a precision of 0.08‰ is reached.

References:

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