

## A calculational procedure for determining $^{17}\text{O}/^{16}\text{O}$ ratio in water by an equilibration method

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Stable isotope ratios of water ( $^2\text{H}/^1\text{H}$  and  $^{18}\text{O}/^{16}\text{O}$ ) are useful for studies of the modern and past hydrologic cycle. In addition,  $^{17}\text{O}/^{16}\text{O}$  ratio in water provides a parameter which reflects relative humidity changes above the ocean,  $^{17}\text{O}$ -excess [1]. However, the  $\delta^{17}\text{O}$  data of water are very limited due to the technical difficulties of precise measurement involving fluorination reaction to convert water to gaseous  $\text{O}_2$ . Recent study showed that the equilibration method can be used for  $\delta^{17}\text{O}$  measurement, and proposed to use a chemical buffer in the water to keep the pH value [2].

We have developed a relatively simple calculation scheme for retrieving the  $\delta^{17}\text{O}$  of water from the 45/44  $\text{CO}_2$  ion-abundance data ( $^{45}\text{R}$ ) obtained by the conventional equilibration method. Our calculation takes into account a decrease in pH value due to high partial pressure of  $\text{CO}_2$  during the equilibration process. Further, we rephrase the equations in terms of  $\delta$  value. This reveals that the  $\delta^{17}\text{O}$  of water can be determined precisely when the relative  $\delta^{13}\text{C}$  differences between working standards and sample are negligible.

Application of the calculation scheme to the IAEA standard waters show the  $\delta^{17}\text{O}$  of GISP is consistent with that of previous studies. We also have applied this method to the deep ice core drilled at the Dome Fuji station, Antarctica. A 130m section around MIS9.3 (~ 330kyr BP) was measured with continuous 10-cm sampling. The profile of  $\delta^{17}\text{O}$  shows a marked similarity to that of  $\delta^{18}\text{O}$ . The changes in  $^{17}\text{O}$ -excess during the glacial-interglacial shift can be detected by averaging many data points.

[1] Barkan & Luz (2007) *Rapid Communications in Mass Spectrometry* **21**, 2999-3005. [2] Elsig & Leuenberger (2008) *Analytical Chemistry* **80**, 3244-3253.

## Carbonyl sulfide (OCS) in the Archean atmosphere

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The mass independent fractionation of sulfur isotopes (S-MIF) in geological samples would provide a record of the past atmospheric composition, though the mechanism of photochemical S-MIF is still poorly understood [1]. We determined the high-precision UV absorption spectra of  $\text{SO}_2$  isotopologues [2] and calculated isotope fractionation factor of  $\text{SO}_2$  photolysis as a function of wavelength. Using these results, we show that the estimated fractionation factors give mass independent distributions and are highly sensitive to the atmospheric concentrations of  $\text{O}_2$ ,  $\text{O}_3$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CS}_2$ ,  $\text{NH}_4$ ,  $\text{N}_2\text{O}$ ,  $\text{H}_2\text{S}$ , OCS and  $\text{SO}_2$  itself, because these molecules can modify spectra of actinic UV flux. Although various UV-shielding scenarios can be considered, we found that the negative  $\Delta^{33}\text{S}$  observed in all the Archean sulfate deposits [1,3] could be expected only when OCS was present in the atmosphere. This is because OCS uniquely absorbs >200 nm region of solar UV flux. Further, we performed numerical simulation of atmospheric reactions including OCS chemistry and found that ppm-level OCS could be accumulated in a  $\text{O}_2$ -free reducing atmosphere when  $\text{CO}/\text{CO}_2$  ratio is greater than 1. Therefore, appreciable amount of OCS is likely to have existed in the reducing Archean atmosphere. Such a high level of OCS also absorbs infrared light from 8 to 13  $\mu\text{m}$ , which is not absorbed by water vapor. Hence, OCS could be an alternative or even more efficient greenhouse gas than  $\text{CO}_2$  to resolve the faint young Sun paradox [4]. Furthermore, OCS also has absorption band in lethal UVC region like ozone, thus could be an alternative UV-shielding molecule in an  $\text{O}_2$ -free reducing atmosphere. The decline of OCS might have caused the late Archean Pongola glaciation (2.9 Ga) and possibly resulted in UV crisis of terrestrial and shallow water ecosystems until the rise of oxygen.

[1] Farquhar *et al.* (2001) *JGR* **106**, 32829. [2] Danielache *et al.* (2008) *JGR* **113**, D17314. [3] Ueno *et al.* (2008) *GCA* **72**, 5675. [4] Sagan & Mullen (1972) *Science* **177**, 52.