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Seasonal change in Soil CO2 and carbon isotopic model in a tufa-depositing stream.

Masako Hori[1]

[1] Earth and Planetary Systems Sci., Hiroshima Univ

Tufas are freshwater carbonates developed in limestone areas. They become recognized to be available as terrestrial paleoclimatic media since recent studies have confirmed that they recorded climatic information in stable isotopic composition. Their growth rate reaches a few cm/year, is much higher than that of speleothems, and allows high-resolution analysis. In spite of these advantages, questions still remain in the principal processes that record paleoclimate in geochemical proxies. The main purpose of this research is to evaluate the local characteristics that influence carbon isotopic behaviors, and to identify the mechanisms in isotopic reactions of water and tufa.

A tufa-bearing stream water at Nagaya (Takahashi City, Okayama Prefecture) issues from a catchment of Permian-Carboniferous Nakamura limestone group. In this study, a laminated tufa developed in the stream is analyzed for high-resolution stable isotopic records. Furthermore, oxygen isotopes of spring water and rain water, water chemistry, carbon isotopes of DIC, and soil CO2 (PCO2 and carbon isotopes) are analyzed.

High-resolution stable isotopic records of Nagaya tufa are characterized by 1) the disordered d18O curve and 2) significantly smoothed d13C curve. Chapter 1 might be due to influence from heavy rainfall. Continuous measurement of spring water and rainwater shows that heavy rainfall in the period of 1-5 July has lighter oxygen isotopic ratio (-13.1%0) and resulted to a 1%0 decrease in d18O value of the stream water. Such influence would be more remarkable in a small aquifer that is supported by the large annual amplitude of spring water temperature (7.0C). The small aquifer at Nagaya has low ability buffing temperature and oxygen isotopic ratio. In this way, temperature index of oxygen isotopic ratios are sometimes perturbated.

The smoothed change in d13C shoule be associated with a process, temperature-depending such as natural ventilation. However, seasonal change in soil air composition can be alternatively a cause of such a smooth change in the carbon isotope, and was tested in this study. Carbon isotopic ratio from biogenic CO2, such as roots respiration and decomposition of organic matter is likely constant throughout a year. But, soil air is the mixture of biogenic CO2 and open air CO2, and this mixing ratio can change. Contribution from open air increases the d13C value, and decrease PCO2 of the soil air. Soil PCO2 collected at two of three stations has been responded to rainfalls that restrict air diffusion in the upper soil layer. However, soil CO2 at one station involves less serious alternation from mixing of open air, and shows good correlation with air temperature.

Carbon isotopic record can be explained by the seasonal change in soil air compositions. Firstly, rain water reaches to equilibrium with soil air CO2, and dissolves limestone in a closed system. Two moles of dissolved carbon consist of one originated from host limestone, and another from CO2 in a soil layer. Thus, the budget isotopic composition is in the mean value between the soil CO2 and the limestone (one-by-one water). Next, the cave air is assumed to be the same level of PCO2 and is in the isotopic equilibrium with this water (one-by-one air). However, there is influence from a soil air flux. Cave water is then in equilibrium with the air which consists of one-by-one air and soil air. The mixing ratio is valuated with d14C which is available in other locality. Calculated values well coincide with the actual spring water values at Nagaya spring. Carbon isotope of DIC in water changes seasonally with initial sources, principally soil CO2.