

Seasonal change recorded in carbonate clumped isotope of tufa deposits

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Clumped isotope of CO₂ generated by acid reaction of calcite is only dependent on temperature of mineral precipitation (Ghosh et al. 2006). However, this carbonate clumped isotope often offsets from the equilibrium value of an expected temperature likely due to kinetic effect. We applied the clumped isotope to tufa deposits that are generally equilibrium in conventional carbon and oxygen isotopes. Samples were collected at two tufa sites in Ehime and Okayama Prefecture, every month during a period from December 1999 to December 2000 (Kano et al., 2003; Kawai et al., 2006). The analyzed material was collected from the surface of each sample, which is 0.5 mm thick.

The generated carbon dioxide was carefully purified in column cooled at -10°C, and measured by MAT 253 with applying the background correction of He et al. (2012). Each value was adjusted on the absolute reference frame of Dennis et al. (2011). A typical measuring error was 0.015 permil (1σ) that corresponds to 3°C in the temperature range of Hiro-1. We applied the temperature equation based on our own measurements of synthesized calcites of known temperatures, which is very similar to the theoretical equation of Guo et al. (2009).

The tufas from Ehime Prefecture indicated a clear seasonal changes of temperature ranging from 3.7 to 20.9°C, which is consistent with measured temperature range of 5-19°C. A similar consistent result from the Okayama tufa indicates that the carbonate clumped isotope of tufa can be used for a thermometer. CO₂ degassing was observed in these tufa sites, but did not result in a recognizable disequilibrium. We suspect that the kinetic effect was insignificant in a pH condition around 8.3 where the dominant carbonate species is bicarbonate.

Keywords: Clumped isotope, tufa, thermometer