

Seasonal temperature changes recorded in carbonate clumped isotopes of tufas

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The carbonate clumped isotopes thermometry is a novel technique to reconstruct the temperature of mineral precipitation without the isotopic information of the parent water. The abundance anomaly of ⁴⁷CO₂ (Δ_{47}) generated by acid digestion of calcite is an index of temperature (Ghosh *et al.* 2006). However, natural samples often show unexpected Δ_{47} values likely due to kinetic effect. We analyzed the clumped isotopes of two sample sets, synthetic calcites and natural tufa deposits. The calcites synthesized at four different temperatures (2.9–61.0°C) were in equilibrium for the oxygen isotopes. Tufa samples were collected from two sites, Shimokuraida (Okayama Pref.) and Shirokawa (Ehime Pref.), every month during a period from December 1998 to December 2000 (Kano *et al.*, 2003; Kawai *et al.*, 2006). Analyzed materials were carefully collected from the superficial 0.5 mm of each tufa sample which has a depositional interval of around 45 days.

Our Δ_{47} -temperature calibration by the synthetic calcites is undistinguishable from many previous studies. A typical inter-measurement error was 0.0078‰ (1 σ) estimated by in-house standard, which corresponds to 1.2°C in temperature.

The tufa Δ_{47} exhibited clear seasonal patterns ranged from 0.695‰ (Dec. 2000) to 0.731‰ (Aug. 2000) in Shimokuraida and from 0.696‰ (Jan. 2000) to 0.733‰ (Oct. 1999) in Shirokawa. These ranges correspond to 10.1–22.5°C and 9.7–22.3°C and these temperature ranges are 0–7°C higher than the actual water temperatures (ranging from 5.6 to 16.0°C). The temperature offset at both sites became the largest in late summer and early autumn, when the water had high *p*CO₂ and precipitation rate. It is assumed that active CO₂ degassing and rapid calcite precipitation caused the temperature offset. Although absolute temperature calibration of natural samples is in need of improvement, our tufa Δ_{47} values exhibited clearer seasonal patterns rather than in conventional $\delta^{18}\text{O}$ thermometry.

Reference

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Keywords: carbonate, clumped isotopes, tufa, oxygen isotope