Temperature change since the latest Pleistocene deglaciation stage recorded in carbonate clumped isotopes of a stalagmite collected in Hiroshima Prefecture, Japan

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Stalagmite Hiro-1 from northeastern Hiroshima Prefecture is a valuable material for terrestrial paleoclimate in Japan (Shen *et al.* 2010; Hori *et al.* 2013). However, it is not always easy to separate the temperature and the moisture signals from the stalagmite oxygen isotopic profile. A possible solution for this problem is carbonate clumped isotopes that is independent on isotopic value of water (Ghosh *et al.* 2006) and has been applied to some stalagmites (Affek *et al.* 2014). Carbonate clumped isotopes means the concentration anomaly of mass-47 carbon dioxide generated from the reaction of calcium carbonate and phosphoric acid, and is generally in inverse proportion to the square of the absolute temperature. Here we measured the clumped isotopes for 40 horizons of Hiro-1 stalagmite reacted with phosphoric acid at 70°C.

The generated carbon dioxide was carefully purified in column cooled at -10°C, and measured by MAT 253 with applying the baseline 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 within 0.015 permil (1s) 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).

After eliminating obvious offsets, the temperatures based on the clumped isotope of Hiro-1 was in 29.7–20.7°C (24.8°C in average) during Holocene (11–4 ka), and in 22.4–14.3°C (18.0°C in average) during the latest Pleistocene (18–12 ka). These temperatures are likely higher than the real, by considering that the modern temperature of this cave is 10.7°C. The temperature offset is common between several speleothem studies reflecting Kinetic Isotopic Effect associated with CO_2 degassing (e.g. Affek *et al.* 2014). Although our evaluation involves some uncertainties, we suggest that the temperature difference between Holocene and latest Pleistocene was 6–7°C. This preliminary estimation is broadly consistent to the 1.5 permil difference in oxygen isotope between Holocene and Pleistocene observed in Hiro-1 (Shen *et al.* 2010).

Keywords: stalagmite, clumped isotopes, temperature change, last glacial period, Holocene