



Fluid inclusion stable isotopes and clumped isotopes thermometry study of Eastern Mediterranean paleoclimate

A. Matthews (1), M. Bar-Matthews (2), H.P. Affek (3), A. Ayalon (2), H.B. Vonhof (4), S. Zaarur (3), Y. Burstyn (1,2)

(1) Fredy and Nadine Hermann Institute of Earth Sciences, Hebrew University of Jerusalem, Jerusalem 91904, Israel (alan@vms.huji.ac.il, 97225662581), (2) Geological Survey of Israel, Jerusalem 95501, Israel, (3) Department of Geology and Geophysics, Yale University, New Haven, USA, (4) Faculty of Earth and Life Sciences, Vrije Universiteit Amsterdam, The Netherlands

Fluid inclusion (FI) stable isotopes and clumped isotopes thermometry provide powerful tools for reconstructing paleoclimates using speleothems. Clumped isotopes thermometry is a unique tool for paleotemperature determination using the mass 47 anomaly (Δ_{47}), but its application to speleothems is complicated by the occurrence of a kinetic isotope effect (KIE) that accompanies CO_2 degassing during carbonate precipitation¹. Experimental studies involving the surface precipitation of synthetic calcite² provide a Δ_{47} thermometer calibration that takes KIE into account and allows its direct application to speleothems. Complementary, the δD_w and $\delta^{18}\text{O}_w$ values of speleothem FI provide an important proxy for cave water-rainfall paleo-hydrological conditions, together with the data required for construction of the meteoric water line (MWL) relationship. Until recently the main studied parameter is δD_w , and the reliability of FI $\delta^{18}\text{O}_w$ has been questioned because of the possibility of post-depositional isotope exchange with the surrounding calcite. When speleothem calcite $\delta^{18}\text{O}_{cc}$ is measured, Δ_{47} temperatures allow $\delta^{18}\text{O}_w$ to be independently calculated using the calcite-water fractionation relationship. Methods for FI analysis using crushing in a helium stream, TC/EA and continuous flow mass spectrometry (Amsterdam system³) enable both δD_w and $\delta^{18}\text{O}_w$ to be determined, thus allowing measured $\delta^{18}\text{O}_w$ values to be compared with those calculated from Δ_{47} temperatures and $\delta^{18}\text{O}_{cc}$. We apply these methodologies to paleoclimate study in the Eastern Mediterranean (EM) region during the last 150 ky: in the Soreq Cave from the glacial stage 6 to the last interglacial stage 5e and the last glacial maximum (LGM) to the Holocene, and to the Alpine karst system of the Hermon mountain range (MS) cave⁴ during the last interglacial and brief warm intervals during the last glacial.

Soreq Cave Δ_{47} data show temperature minima at the termination of stage 6 and the LGM, but the LGM temperatures (*ca* 9°C) were several degrees lower than for glacial stage 6. Both minima were followed by sharp temperature rises into stage 5e and Holocene, respectively. Δ_{47} thermometry of the MS cave speleothems confirm that temperatures rose to several degrees above freezing during brief warming events in the otherwise frozen last glacial at this altitude (2224m). MWL relationships over the last 150 ky using FI δD_w and calculated $\delta^{18}\text{O}_w$ suggest that glacial periods are characterized by a MWL closer to that of the global system, whereas interglacial periods in the Soreq cave and warm glacial intervals in the MS cave show higher “d excesses” characteristic of the present day EM region. The MWL relationships of Soreq Cave speleothems in stage 5e are consistent with the ‘amount effect’ controlling $\delta^{18}\text{O}_w$, as found today and in the Holocene⁵. Comparison of measured with calculated $\delta^{18}\text{O}_w$ values show that it may also be possible to retrieve accurate values for $\delta^{18}\text{O}_w$ in suitable speleothems.

1. Affek, H., et al (2008). *Geochim. Cosmochim. Acta* 72, 5351-5360. 2. Zaarur, S. and Affek, H. In preparation. 3. Vonhof, H., et al. (2006). *Rapid Comm. Mass Spectrom.* 20, 2553-2555. 4. Ayalon et al (2012) In submission. 5. Bar Matthews, M., et al (2003). *Geochim. Cosmochim. Acta* 67, 3181-3199.