4000 years of climate change in Northern Spain from speleothem records

J. MARTÍN-CHIVELET[1]*, M.B. MUÑOZ-GARCÍA[1], M.J. TURRERO[2], A.I. ORTEGA[3], D. DOMÍNGUEZ-VILLAR[4]

[1]Universidad Complutense, Dpt. Estratigrafía, Facultad de Ciencias Geológicas, 28040 Madrid, Spain (*corr.author: j.m.chivelet@geo.ucm.es, mbmunoz@geo.ucm.es)
[2]Ciemat. Dpt. Medio Ambiente, 28040 Madrid, Spain (mj.turrero@ciemat.es)
[3]Universidad de Burgos, Dpt. CC. Históricas. Facultad de Humanidades., 09001 Burgos Spain (paleonto@ubu.es)
[4]Universidad Complutense, Dpt. Geodinámica, Fac. CC. Geológicas, 28040 Madrid Spain (ddomingu@geo.ucm.es)

Coetaneous stalagmites from three different caves in N. Spain (Ojo Guareña, Atapuerca and Cobre) have been investigated in order to reconstruct the regional paleoenvironmental conditions related to the North Atlantic climatic variability through the last four millennia. This reconstruction, based on a multi-proxy approach which includes oxygen and carbon isotope profiles and microfacies analysis, has been calibrated by means of present-day hydrogeochemical monitoring programs of the environment of the caves as well as historical archives in the area.

The investigated caves, located inland Spain, show significantly different local climatic conditions, ranging from the high-mountain climate of the Cantabrian Ranges (Cobre Cave) to the drier and warmer climate of the Meseta (Atapuerca), and are thought to be strongly sensitive to medium to long-term NAO oscillations.

Comparative analysis of the reconstructed series demonstrates an overall correspondence which allows establishing the regional pluvio-thermal changes at decadal to millennial scales for the 4000 years, but also notable differences that are attributed to local or karst-related factors. Spectral analysis of stable isotope values yields significant periodicities that could correspond to known solar cycles, supporting the idea that long-term NAO changes strongly respond to solar forcing.

Also, comparison of geochemistry of recent and ancient espeleothems reveals quite unique, extreme climate conditions for the last years, related to 20th Century global warming. Comparable conditions to those of today were reached only during few, relatively short intervals, throughout the last four millennia in N Spain.

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Surface charge and zeta-potential of metabolically active and dead cyanobacteria

RAUL E. MARTINEZ, OLEG S. POKROVSKY, JACQUES SCHOTT AND ERIC H. OELKERS

LMTG - UMR 5563 CNRS, Université Paul-Sabatier Observatoire Midi-Pyrénées, 14, avenue Edouard Belin, 31400 Toulouse, France (raul.martinez@lmtg.obs-mip.fr, oleg@lmtg.obs-mip.fr, schott@lmtg.obs-mip.fr, oelkers@lmtg.obs-mip.fr)

Zeta potential and acid base titrations of living, inactivated, and dead *Planktothrix* sp. and *Synechococcus* sp. cyanobacteria were performed to determine the degree to which cell surface electric potential and proton/hydroxyl adsorption are controlled by metabolism or cell membrane structure. Surface OH- excess from potentiometric data shows differences in surface charge between active and dead cyanobacteria for the pH range of 3 to 10. An average zero salt effect pH of 5.8 ± 0.1 and 6.3 ± 0.1 was obtained for active *Planktotrhix* sp. and *Synechococcus* sp. respectively. Zeta potentials of active *Planktothrix* sp. *and Synechococcus* sp. were positive at alkaline conditions, with a maximum of +13.7 ± 1.5 mV at a pH of 9.0 ± 0.1 for both species. This positive potential diminished in the presence of 1 mM HCO_3^-. The zeta potential of *Planktothrix* sp. and *Synechococcus* sp. cells was negative at alkaline pH following their exposure to NaN_3, a metabolic inhibitor. Their average potential was -18.4 ± 1.8 mV at a pH of 9.14 ± 0.02 following a 3 hours exposure to NaN_3. The zeta potential of dead cyanobacteria was negative for *Planktothrix* sp., in the pH range of 2.5 to 10.5, at -30 to -20 mV. Dead *Synechococcus* sp. recorded negative potentials to a minimum of -30 mV at pH 8, positive potentials were recovered to a maximum of +10 mV at pH 9.1. Zeta potentials for dead, but non-acidified *Synechococcus* sp. remained negative at -30 mV from an initial pH of 5.6 to 10.5, reflecting differences in cell wall structure between these species. Taken together, these results indicate that *Planktothrix* sp. and *Synechococcus* sp. may metabolically control their surface charge to electrostatically attract bicarbonate anions at alkaline pH, required for photosynethesis.