

First record of changes on chloride and stable isotopes from an ice accumulation in the Torca de La Grajera (Burgos, N Spain)

María Jesús Turrero¹, Antonio Garralon¹, Lorenzo Sanchez¹, Ana Isabel Ortega^{2,3}, Paloma Gómez¹, Miguel Ángel Martín³, Javier Martín-Chivelet⁴

1. Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas, CIEMAT (Madrid, Spain)
2. Centro Nacional de Investigación sobre la Evolución Humana, CENIEH (Burgos, Spain)
3. Grupo Espeleológico Edelweiss, GEE (Burgos, Spain)
4. Universidad Complutense de Madrid, UCM (Madrid, Spain)

The ice accumulation investigated in this work refers to layered ice, 14.5 m thick, formed in the Torca de La Grajera pothole from a number of snow precipitation events. The hole is a natural open space -185 m depth, directly connected to the surface, in which over time the snow has become ice. It is a clear example of ice preserved in mid-latitudes and is potentially useful for paleoclimate reconstructions. Ice sample collection was made in two campaigns performed in September 2015 and 2016. The Grupo Espeleológico Edelweiss (GEE from its Spanish initials) was responsible for arranging all the equipment to descent into the hole and was in charge of taking samples as well. Sampling was made by drilling at different depths from the bottom of the hole, perpendicular to the axis of the growth. The external layer of ice was removed before drilling. The drilling machine coupled a stainless steel cylindrical core drill, 10 cm in diameter and 25 cm in length. Ice cores were stored in polypropylene bags to avoid contamination and placed on site in an insulated cooler containing dry ice to prevent ice melting, and then into a refrigerator maintained at -30 °C to keep samples during transport to the laboratory up to analysis. This procedure ensures that samples are maintained as close as possible to in situ conditions. Eight and fifteen samples of ice were collected in 2015 and 2016 sampling campaigns, respectively.

Samples were partially melted and filtrated through Millipore filters with pore size 0.45 μm for complete chemical and isotopic characterization in a way that minimizes the exposition to air. Common ions were analyzed using ion chromatography. Values of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ were determined using CRDS spectroscopy (Cavity Ring-Down Spectroscopy) that can simultaneously determine the isotopic relations of both isotopes in aqueous samples. To evaluate variability in the analyses and data quality at least one duplicate per sample was made, as well as sample blanks and charge balance calculations.

Preliminary profiles of chloride (Cl^-), $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in the ice samples were obtained. The composition indicates that the ice accumulation can be divided into two sections. The average values of lower section (0-8 m) are: $\text{Cl}^- = 0.011$ mmol/L, $\delta^{18}\text{O} = -6.1$ ‰_{SMOW} and $\delta^2\text{H} = -44$ ‰_{SMOW} and the average values of the upper section (8-14 m) are: $\text{Cl}^- = 0.025$ mmol/L, $\delta^{18}\text{O} = -8.5$ ‰_{SMOW} and $\delta^2\text{H} = -55$ ‰_{SMOW}. In both sections the profiles of Cl^- , $\delta^2\text{H}$ and $\delta^{18}\text{O}$ have similar shape and show the same general trend: the lighter the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values, the more chloride in the ice, which excludes the evaporation effect and indicates that temperature conditions at the moment of the recharge were different. These findings, with other data (e.g. Sánchez et al., this workshop) are serving to

undertake interpretation and modelling in terms of sources of precipitation and climatic conditions prevailing at the time of deposition.

Acknowledgment

Contribution to Projects CGL2013-43257-R and CGL2017-83287-R (MINECO, Spain) and to research group “Paleoclimatology and Global Change” of the UCM (Spain). We thank Junta de Castilla y León for permissions and Grupo Espeleológico Edelweiss (GEE) for speleological work and taking ice samples.