Triple oxygen ($^{16}$O, $^{17}$O, $^{18}$O) and hydrogen ($^1$H, $^2$H) isotope analyses of rainfall events in Central-South Pyrenees.

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Few studies of rainfall isotopic composition are available in the northern Iberian Peninsula, and up to now none of them has provided detailed analyses of the triple oxygen isotopes ($d^{17}$O, $d^{18}$O and derived parameter $^{17}$O excess), preventing from the complete understanding of some atmospheric processes and their relationship with the current climate in this region. This information, together with the characterization of dripwater isotopic composition once transferred throughout the epikarst, is essential to the correct interpretation of paleoclimate records based on speleothem isotopic data.

We provide the first database of triple oxygen and hydrogen stable isotopes of rainwater in Central-South Pyrenees. We characterize local rainfall isotopic variability in a high altitude site and identify the main factors controlling the isotopic composition of rainwater. The samples were collected on a rainfall-event basis from July 2017 to June 2019 (n=216) at the interpretation center of “Las Güixas” touristic cave in Villanúa (Huesca, Spain), where other monitoring surveys are in progress. This site (42º40'59''N; 0º31'55''W; 957 m a.s.l.) is characterized by a transitional Mediterranean – Oceanic climate with a highly contrasted seasonality, mean annual temperature of 10ºC and mean annual precipitation of 1100 mm. We analyzed $d^{17}$O, $d^{18}$O and dD, and derived parameters $^{17}$O excess and d-excess in rainwaters using a Picarro L2140-i analyzer at the University of Almería (Spain), with mean precisions (1-standard error) of 5 per meg for $^{17}$O excess and 0.1‰ for d-excess. Meteorological variables (temperature, RH and rainfall amount) were monitored (every 10 min) at the sampling site during the length of this study.

During the two-years monitoring period, $d^{18}$O ranged from -21.7 to 8.7‰ and dD did from -170.8 to 34.1‰, with average values of -7.4‰ and -52.3‰, respectively. The $^{17}$O excess averaged 21±24 per meg and the mean d-excess was 7.1±7.7‰. The local meteoric water line is defined by dD=7.3$d^{18}$O+1.9 ($R^2=0.96$) and d$^{17}$O= 0.524·d$^{18}$O+0.0088 ($R^2=1$). The $d^{17}$O, $d^{18}$O and dD values were higher during summer (June to September; -2.1, -3.9 and -26.6‰, respectively; n=68) and were lower during the rest of the year (-4.7, -9.0 and -63.8‰, respectively; n=164). In contrast, the $^{17}$O excess and d-excess were lower during summer (3 per meg and 4.6‰, respectively) and higher (29 per meg and 8.2‰, respectively) during the remaining months. We found that the isotopic parameters are weakly correlated with rainfall amount during each event, but they strongly
depend on seasonal changes in air temperature and relative humidity. The extremely low $^{17}$O_{excess} and d-excess values observed in summer (down to -75 per meg and -35.6‰, respectively), cannot be explained by particular conditions at the source of moisture during water vapor formation, but by local meteorological parameters and rain drops re-evaporation during rainfall events.

Further processing of this database will consider other influencing factors in the isotopic composition of rainfall events, such as changes in the source moisture, synoptic pattern and type of rainfall, to further understand the complexity of atmospheric processes through the information stored in the triple oxygen isotopes of rainfall, with application to future $^{17}$O_{excess} studies in speleothems.