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O and C stable isotopes in cryogenic cave calcite (CCC) – possible proxy for past climate changes

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Perennial ice deposits in caves host various proxies of past climate variability, most notable, the isotopic composition of ice, which has been shown to reflect, generally, the temperature outside the cave during the formation of ice (usually, autumn though spring). This ice forms by the freezing of water, water that contains large amounts of dissolved calcium carbonate. The freezing is accompanied by degassing of CO_2, and precipitation of cryogenic cave calcite (CCC) under strong kinetic conditions. These kinetic processes could lead to the alteration of the original putative climatic signal carried by the isotopic composition of CCC. Here, we present a possibly climatic explanation of the isotopic composition of CCC from a 1000 years old cave ice deposit from Scărișoara Ice Cave (SIC) in Romania, Eastern Europe.

In a 7 m core from the Great Hall of SIC we have analyzed the isotopic composition of the water (oxygen and hydrogen) and CCC (oxygen and carbon) from individual ice layers in the core, as well as that of precipitation , outside the cave. The isotopic composition of precipitation from the cave area varies between -3.6 ‰ for δ[U+02E1]^{8}O and -22 ‰ for δ^{2}H in summer, and -17.8 ‰ for δ[U+02E1]^{8}O and -22 ‰ for δ^{2}H in winter, with mean values of -9.1 ‰ for δ[U+02E1]^{8}O and -62 ‰ for δ^{2}H. A positive correlation between air temperature and the isotopic composition of precipitation, as well as drip water in the cave has been found. The mean values in the ice core during the past 1000 years are -10.3‰ for δ18O and -71 ‰ for δ^{2}H. The water isotopic values in the ice core show low values up to 900 AD, higher values between 900 and ∼1300 AD (Medieval Warm Period, MWP), and again lower values after 1300 AD (Little Ice Age, LIA), reaching their minimum after 1800 AD. The isotopic composition of CCC shows slightly higher values in the MWP and lower in LIA, possibly suggesting a climatic influence. Modern observations are too short to be able to calibrate this putative signal. Further, clumped isotope thermometry has shown that the kinetic fractionation that dominates during the freezing of water leads to unusual reconstructed formative temperature: +20ºC. However, δ[U+02E1]^{3}C and δ[U+02E1]^{8}O values in CCC have higher values for samples from the MWP than those from the LIA. CCC results from the deposition of $CaCO_3$ from Ca(CO_3)2. The main source of CO_2 to form carbonic acid is soil CO_2, produced by root respiration. Previous studies have shown that δ[U+02E1]^{8}O of this CO_2 is in equilibrium with the δ[U+02E1]^{8}O of water, so that the higher (lower) δ[U+02E1]^{8}O values of CCC could reflect warmer (colder) conditions during the MPW (LIA). The interpretation of δ[U+02E1]^{3}C values of CCC is less straightforward. Higher δ[U+02E1]^{3}C values in soil CO_2 are determined by moisture limitation on plants, either due to low moisture or higher evaporative conditions. While the MWP was warmer in the study area, conflicting data exists on precipitation, with studies suggesting both drier and wetter conditions, so that is difficult to interpret our carbon isotope data. Apart from the direct climatic influence, the depth of soil could have also played a part, as deeper soils, as expected under birch forests that dominated during the MWP, would have had more enrichment in the heavy isotopes with depth, than the thiner soils of the LIA (formed under mostly spruce forests). Further, drought/higher temperatures could also influence the kinetics of the reaction, which can be large enough to overprint any soil signal in δ[U+02E1]^{3}C.