# Mountain permafrost in the Central Pyrenees: insights from 1

#### the Devaux ice cave 2

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#### 26 Abstract (250words)

27 Ice caves are one of the least studied parts of the cryosphere, particularly those

located in inaccessible permafrost areas at high altitudes or high latitudes. We 28

characterize the climate dynamics and the geomorphological features of Devaux 29

cave, an outstanding ice cave in the Central Pyrenees on the French-Spanish 30

border. Two distinct cave sectors were identified based on air temperature and 31

geomorphological observations. The first one comprises well-ventilated galleries 32 with large temperature oscillations likely influenced by a cave river. The second 33 sector corresponds to more isolated chambers, where air and rock temperatures 34 35 stay below 0°C throughout the year. Seasonal layered ice and hoarfrost occupy the first sector, while transparent, massive perennial ice is present in the isolated 36 chambers. Cryogenic calcite and gypsum are mainly present within the perennial 37 ice. During winter, the cave river freezes at the outlet, resulting in a damming and 38 back-flooding of the cave. We suggest that relict ice formations record past 39 damming events with subsequent formation of congelation ice.  $\delta^{34}S$  values of 40 gypsum indicate that the sulfate originated from the oxidation of pyrite present in 41 the bedrock. Several features including the air and rock temperatures, the 42 43 absence of drips, the low\_small loss of ice\_in the past seven decades, and the location of ice bodies in the cave indicate that the cave permafrost is the result of 44 a combination of undercooling by ventilation and diffusive heat transfer from the 45 surrounding permafrost, reaching a thickness of ~200 m below the surface. 46

Keywords: Ice cave, cave monitoring, cryogenic cave carbonates, cryogenic
gypsum, Devaux cavePyrenees.

## 49 1. Introduction

50 Mountain areas are one of the most susceptible among those environments to 51 most affected by current climate change (Hock et al., 2019). In the mid-latitudes, high-altitude areas are subject to mountain permafrost, a very sensitive and 52 unstable phenomenon that responds quickly to environmental changes (Harris et 53 al., 2003; Biskaborn et al., 2019) due to the number of factors. They influence the 54 spatial distribution of mountain permafrost, including snow cover distribution and 55 thickness, topography, water availability, surface temperature and rock 56 temperatureSnow cover distribution and thickness, topography, water availability, 57 and surface and rock temperature influence the spatial distribution of mountain 58 59 permafrost -(Gruber and Haeberli, 2009). In light of these processes, Due to this number of processes multidisciplinary studies including, among others, 60 measurements of rock temperature measurements in boreholes, and the bottom 61 temperatures of snow cover (BTS), a variety of geophysical techniques, and 62 thematic detailed maps mapping (geomorphology, thermal) are needed to gain a 63

**Comentado [M1]:** Reviewer #2. 155-57: (R) snow cover distribution and thickness

topography, water availability, surface and rock temperature all influence the spatial distribution of mountain permafrost

**Comentado [M2]:** Reviewer #2. 157-61: (R) In light of these processes, [ ... ] are needed to gain a comprehensive understanding of mountain permafrost.

comprehensive understanding of mountain permafrost (e.g. Lewkowicz and 64 Ednie, 2004; Serrano et al., 2019; Biskaborn et al., 2019). On the other hand, the 65 integrated study studies of paleo-permafrost (e.g. Vaks et al., 2020), e.g. Vaks et 66 al., 2020) and modern permafrost, specifically mountain permafrost (e.g., Supper 67 et al., 2014; Scandroglio et al., 2021), shede light on past, present and future 68 developments of permafrost areas, an issue of vital importance in the context of 69 global warming. Studies of past permafrost require sedimentary records, which 70 71 are locally preserved in caves located at high altitudes and/or high latitudes. Thus, Temporal and spatial changes in past permafrost distribution have been 72 identified using speleothems (stalagmites, flowstones) in high-73 latitudecircumpolar and polar regions (e.g., (Vaks et al., 2013, 2020; Moseley et 74 al., 2021; Li et al., 2021) as well as in mid-latitude regions (e.g., Lundberg and 75 McFarlane, 2007; Fankhauser et al., 2016; Lechleitner et al., 2020). 76

Ice caves are defined as cavities in rock hosting perennial ice that results from 77 the transformation of snow and/or the freezing of infiltrating water reaching the 78 cave (Persoiu and Lauritzen, 2018). Cave ice can be dated and used as a 79 valuable paleoclimate archive in non-polar areas (e.g., Stoffel et al., 2009; Spötl 80 et al., 2013; Perșoiu et al., 2017; Kern et al., 2018; Sancho et al., 2018a; Leunda 81 et al., 2019; Munroe, 2021; Racine et al., 2022). Furthermore, temporal and 82 spatial changes in past permafrost distribution have been identified using 83 speleothems (stalagmites, flowstones) in circumpolar and polar regions (e.g., as 84 well as in mid-latitude regions (e.g., Lundberg and McFarlane, 2007; Fankhauser 85 et al., 2016; Lechleitner et al., 2020). Recently, coarse cryogenic cave carbonates 86 (CCCcoarse), that form during slow freezing of water inside caves, have been used 87 88 as indicator of permafrost degradation, permafrost thickness, and subsurface ice formation (Žák et al., 2004, 2012; Richter et al., 2010a; Luetscher et al., 2013; 89 Orvošová et al., 2014; Spötl and Cheng, 2014; Bartolomé et al., 2015; 90 Dublyansky et al., 2018; Koltai et al., 2020; Munroe et al., 2021; Spötl et al., 91 2021). 92

Many ice caves are located in areas where the mean annual air temperature
(MAAT) outside the cave is above 0°C (Perşoiu and Lauritzen, 2018) and,
therefore, are highly susceptible to future climate warming (Kern and Perşoiu,
2013). These ice caves are local thermal anomalies which are controlled by the

Comentado [M3]: New reference added:

Li, T.-Y., Baker, J. L., Wang, T., Zhang, J., Wu, Y., Li, H.-C., Blyakharchuk, T., Yu, T.-L., Shen, C.-C., Cheng, H., Kong, X.-G., Xie, W.-L., and Edwards, R. L.: Early Holocene permafrost retreat in West Siberia amplified by reorganization of westerly wind systems, Commun. Earth Environ. 2, 1–11, https://doi.org/10.1038/s43247-021-00238z, 2021.

**Comentado [M4]:** Reviewer#1: lines 73-78: This sentence somehow doesn't fit to the other parts of this paragraph. Please consider omitting it or moving it to another place where it fits better.

Con formato: Inglés (Estados Unidos)

## Comentado [M5]: added:

Racine, T. M. F., Reimer, P. J., and Spötl, C.: Multicentennial mass balance of perennial ice deposits in Alpine caves mirrors the evolution of glaciers during the Late Holocene, Sci. Rep., 12, 11374, https://doi.org/10.1038/s41598-022-15516-9, 2022.

Con formato: Inglés (Estados Unidos)

Código de campo cambiado

Comentado [M6]: Moved from here to lines 70-75

#### Comentado [M7]: New reference added:

Spötl, C., Koltai, G., Jarosch, A. H., and Cheng, H.: Increased autumn and winter precipitation during the Last Glacial Maximum in the European Alps, Nat. Commun., 12, 1839, https://doi.org/10.1038/s41467-021-22090-7, 2021.

cave geometry and the associated ventilation pattern. Their ice deposits 97 represent sporadic permafrost occurrences and do not inform about the wider 98 thermal environment. In contrast, at high altitudes and high latitudes subsurface 99 100 ice deposits are still preserved by the presence of permafrost under the current climate- conditionschange. There, mountain permafrost is limited to areas where 101 a periglacial belt is present, with MAAT  $\leq 0^{\circ}$  C. For example, in the European 102 Alps, discontinuous mountain permafrost is observed between above 2600 and 103 to 3000 m a.s.l. (Boeckli et al., 2012), while in southern Europe permafrost is 104 generally absent (i.e. not observed even on the highest massif of the Iberian 105 Peninsula, Gómez-Ortiz et al., 2019). In the Central Pyrenees few studies 106 suggest the possible presence of permafrost above 2750 m a.s.l. (Serrano et al., 107 2019, 2020; Rico et al., 2021), and the presence of a few ice caves has only 108 109 recently been documented (e.g. Sancho et al., 2018a; Serrano et al., 2018) informing about the occurrence of sporadic permafrost.-110

The aim of this study is to characterize the permafrost conditions in Devaux cave, a high-altitude ice cave in the Central Pyrenees. We monitored air, water and rock temperatures and used cryogenic cave deposits to i) document the distribution of permafrost within this cave, and ii) to study the processes that resulted in perennial cave ice bodies and associated cryogenic mineral occurrences.

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## 118 2. Study site

Devaux cave opens at ~2838 m a.s.l. in the NE cliff of Gavarnie cirgue (France) 119 of the Monte Perdido massif (MPm) in the Central Pyrenees (Fig. 1a). The cave 120 is located between the Parc National des Pyrénées (France) and the Parque 121 Nacional de Ordesa y Monte Perdido (Spain). Named after Joseph Devaux who 122 discovered and explored it in 1928, the cave was later investigated with respect 123 to its hydrogeology and microclimatology and preliminary descriptions of its 124 deposits were reported (e.g., Devaux, 1929; 1933; Rösch and Rösch, 1935; 125 126 Rösch, 1949; dDu Cailar and Dubois, 1953; Requirand, 2014). 127

## Comentado [M8]: Reviewer #2

In contrast, at high altitudes and high latitudes ice deposits are still preserved under the current climate change may be in relation to the permafrost presence.

Done

A)190-91

#### Comentado [M9]: Reviewer #2 198-99: (T) the presence of a few ice caves has only recently been documented

Done

Comentado [M10]: Reviewer #2 B) 198-99:

), informing about sporadic permafrost

Done

The area is dominated by limestones and dolostones ranging from the Upper 128 Cretaceous to the Eocene-Paleocene. MPm is the highest limestone karst area 129 in Europe reaching up to 3355 m a.s.l. (Monte Perdido peak) (Fig. 1b). The 130 nearest peaks to Devaux cave are Marboré (3248 m a.s.l.) and the three Cascada 131 peaks (3164 m, 3111 m, and 3098 m a.s.l.). The limestone thickness above the 132 cave varies between ~200 and 250 m (Fig. 2a). In Devaux, the galleries follow 133 the axis of a NW-SE striking syncline (Fig. 1b). A river runs along the cave (Fig. 134 135 2a, b). The cave has two known entrances: the lower one corresponds to the main outlet of the cave river (Brulle spring, North 1, ~2821 m a.s.l.), while the 136 upper entrance is known as the "Porche" (South, ~2836 m a.s.l.) (Figs. 1c and 137 2b). Between these two entrances, a small gallery (Spring North 2) opens +1.2 m 138 above Brulle spring (Fig. 1c). Brulle is one of the main springs in the Gavarnie 139 cirque. This spring drains a catchment of ~2.6 km<sup>2</sup> (polje) located on the southern 140 face of MPm between ~2850 and 3355 m a.s.l. (Figs. 1b and, 1d). Major water 141 flow is observed during late spring and early summer when snowmelt recharges 142 occurs in a catchment characterised by shafts, sinkholes and small closed 143 144 depressions (Fig. 1d). The water of Brulle spring feeds, together with some other springs located a few hundred meters below, the Gavarnie waterfall (Fig. 1b). A 145 tracer experiment (du Cailar et al., 1953) indicated that part of the water of the 146 Gavarnie waterfall, and thus likely also from Brulle spring, comes from a ponor in 147 148 the Lago helado (lake, Fig. 1e), located  $\sim 2.3$  km to the east of Devaux cave (Figs. 1b and 2a). The Gavarnie waterfall (Fig. 1b) turned green within ~21 hours after 149 injection of the tracer but the water at Brulle spring was not directly checked (du 150 Cailar et al., 1953). During the colder months, the spring water as well as the 151 152 Gavarnie waterfall freeze.

The geomorphology of the area is dominated by karst, glacial and periglacial 153 landforms. The area was strongly glaciated during the last glacial period on both 154 155 sides of the massif (e.g., Reille and Andrieu, 1995; Sancho et al., 2018b; Bartolomé et al., 2021). Today, only two glacier relicts covered by scree deposits 156 are present in the Gavarnie cirque (Fig. 1b): 1) the Cascada dead-ice which is 157 located several hundred meters below Devaux cave, and 2) a dead-ice 158 accumulation in the NE wall of the cirque. Till present close to Brulle spring, on 159 the access to Devaux and in the Cascada glacier, point to a much larger glacier 160

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161 extent in the past, maybe corresponding to the Little Ice Age or even the

Neoglacial advance recognized in the nearby Tucarroya (Fig. 1b) and Troumouse
cirques (Gellatly et al., 1992; González Trueba et al., 2008; García-Ruiz et al.,
2014, 2020).

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The study area lies at the transition between Atlantic and Mediterranean climate, 165 with generally cold and dry winters and warm and dry summers. In MPm, the 166 annual zero-0°C isotherm is located at ~ 2900 m a.s.l. (López-Moreno et al., 2016; 167 168 Serrano et al., 2019). The wet seasons are fall and spring. The annual precipitation at the Góriz meteorological station (2150 m a.s.l. and 3 km SE of the 169 170 cave) averages 1650 mm. However, mass balance calculations of the nearby Monte Perdido glacier, where more than 3 m of snow (density(p 450 Kkg/m<sup>3</sup>) 171 172 accumulates between November to April, indicates a minimum amount of 1500 173 mm w.e (water equivalent), therefore the total annual precipitation in elevatehigh areasparts of the massif exceedsss 2500 mm However, mass balance 174 175 calculations of the nearby Monte Perdido glacier suggest that annual precipitation 176 next to the cave may exceed 2500 mm, as the snow depth measured in early 177 May exceeds on average 3 m (López-Moreno et al., 2019). In the MPm, discontinuous permafrost is present between ~2750 and ~2900 m a.s.l. and 178 becomes more frequent above ~2900 m a.s.l. on the northern side (Serrano et 179 al., 2019). Periglacial activity is characterized by rock glaciers, solifluction lobes 180 181 and patterned ground (Feuillet, 2011).

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# 183 3. Material and methods

# 184 **3.1 Cave survey and mapping**

A survey of Devaux cave was conducted using a compass and clinometer as well as a laser distometer (Disto-X, Heeb, 2014). In addition to cave ice, chemical and clastic deposits were mapped inside the cave<u>- These features were overlain onto</u> the cave survey to produce a geomorphological cave map (Fig. 2b). The labelling of the cave chambers (A to K) follows the nomenclature introduced by Devaux (1929) and Rösch and Rösch (1935). A map of potential solar radiation (RAD) of the MPm was obtained using an algorithm which considers the effects of the surrounding topography on shadowing considering the position of the sun. RAD was calculated for every month of the year and was then averaged to obtain an annual mean. Details of this computation can be found in Pons and Ninyerola (2008).

# 196 3.2 Cave monitoring

The cave consists of large rooms (e.g., room F, or-and those located beyond 197 SCAL chatière) connected by small galleries (Fig. 2b), locally with narrow 198 passages (e.g., galleries close to SPD room or SCAL chatière, Fig. 2b). 15 199 stations were installed in the outmost ~350 m of the cave to monitor air (11 200 sensors), water (2 sensors) and rock temperature (2 sensors) (Fig. 2b). Cave air 201 temperature variations were recorded using different devices (Hobo Pro v2 U23-202 001 (accuracy ±0.25°C, resolution 0.02°C), Tinytag Talk 2 (accuracy ±0.5°C, 203 resolution, 0.04°C) and ELUSB2 (accuracy ±0.21°C, resolution 0.5°C)). The cave 204 river temperature was recorded at two points. T; the first site (W7) was located 205 close to the Brulle spring (Fig. 2b; Hobo TiDBit V2, accuracy ±0.21°C, resolution 206 0.02°C) and, the second site (W6) was located in room F (Fig. 2b; Hobo UA-001-207 08; accuracy ±0.53°C, resolution 0.4°C). Both sensors were installed at a water 208 depth of 20 cm. Finally, the rock temperature was recorded at two sites (R1 and 209 R2 in room D and K, respectively) using a Hobo U23-003 device (accuracy 210 ±0.25°C, resolution 0.02°C). Each sensor has two external temperature probes 211 212 (channels 1 and 2, Ch1-Ch2). These temperature probes were installed in two 213 horizontal drill holes of 60 cm depth, ~1.5 to 2 m from each other.

We monitored <u>sporadically</u> the cave during different <u>time</u>-intervals between 2011 and 2015, while a continuous monitoring was carried out between July 2017 and July 2021. <u>We calculated the mM</u>aximum, minimum and mean temperatures as well as the number of frost/warm days<u>were obtained</u> for each sensor and site (Fig. 2b). Changes in the ice morphology were evaluated using wall marks measured at four points since 2013 in room G and using one point during 2020-2021 in room SPD (Fig. 2b) using a digital sliding caliper.

The outside temperature was measured at two points in the MPm, at the "Porche" entrance (~2836 m a.s.l.) and on the southern face of MPM at ~2690 m a.s.l. For Comentado [M11]: Reviewer #2 C) 1183:

comparison, these temperature records were corrected assuming an adiabatic 223 lapse rate of 0.55°C 100<sup>-1</sup>5.5 °C km<sup>-1</sup> m (López-Moreno et al., 2016; Navarro-224 Serrano et al., 2018) to an elevation of ~2850 m a.s.l., corresponding 225 approximately to the lower limit of the hydrological catchment area of Devaux. In 226 both cases, the temperature was measured using Tinytag Talk 2 sensors 227 equipped with a radiation shield. These data were compared to the temperature 228 record from the Pic du Mmidi de Bigorre meteorological station (PMBS; 2011-229 230 2020) (2860 m a.s.l., ~28 km N of Devaux) obtained from Météo-France. Moreover, the homogenised MAAT dataset available since 1882 from PMBS 231 232 (Bücher and Dessens, 1991; Dessens and Bücher, 1995) was were used to 233 identify identify long-term climatic temperature trends.

# 3.3 Mineralogy, water and mineral sampling X-ray diffraction, ion chromatography and sulfur isotopes

X-ray diffraction (XRD) analyses were performed on sulfate and carbonate
crystals from rooms G, D and K, as well as on sulphide and oxidized crystals
thereof from the host rock (Fig. sS1). The analyses were performed at the
Geosciences Institute in Barcelona (GEO3-BCN-CSIC) using a Bruker-AXS
D5005 powder diffractometer configured in <u>0/20-mode</u> (e.g. (Rodríguez-Salgado
et al., 2021) theta-2 theta geometry.

Samples of cave drip<u>e\_water</u>, ice and river water were analysed for major ions by
ion chromatography (IC) at the laboratories of the Pyrenean Institute of Ecology
(Zaragoza). Carbonate alkalinity was determined by titration within 24 hours after
sampling.

Sixteen samples, including sulfate crystals, dissolved sulfate and pyrite crystals 246 were selected for sulfur isotope analysies at the Godwin Laboratory for 247 248 Paleoclimate Research of the University of Cambridge (UK), following the methodology of (Giesemann et al., (1994). For gypsum samples, ~5 mg of 249 powdered gypsum were dissolved in deionized water at 45°C overnight. Then, a 250 BaCl<sub>2</sub> solution (50 g/L) was added to induce BaSO<sub>4</sub> precipitation. In the case of 251 water samples, BaCl<sub>2</sub> was added directly to the sample. Subsequently, 6M HCl 252 was added to remove any co-precipitated carbonate mineralse and the BaSO4 253 precipitate was rinsed several times with deionized water. Finally, BaSO4 was 254

**Comentado [M12]:** Reviewer #1 line 210: I suggest expressing the lapse rate as 5.5°C km<sup>-1</sup> because the current expression is confusing. It suggests 0.55°C change by 0.01 m.

#### Comentado [M13]: Reveiwer #1

line 214: Please capitalize "Midi"

#### Comentado [M14]: Reviewer #1:

The title of sub-section 3.3 needs revision. The current title is misleading. The section is not about sampling but about the methodology of the applied mineralogical and geochemical analyses.

#### Comentado [M15]: Reviewer #1:

An additional related comment is that it is stated in section 4.4.2 that "XRD analyses yielded ...gypsum, calcite, ... pyrite and goethite," however no evidence is presented. I suggest adding some annotated diffractograms (at least in a supplementary document) in the revised version.

**Comentado [M16]:** Reviewer #1 line 244: Maybe "Bragg-Brentano geometry" or " $\theta/2\theta$ -mode" would be the appropriate expression.

#### Comentado [M17]: Reference added.

Rodríguez-Salgado, P., Oms, O., Ibáñez-Insa, J., Anadón, P., Gómez de Soler, B., Campeny, G., and Agustí, J.: Mineralogical proxies of a Pliocene maar lake recording changes in precipitation at the Camp dels Ninots (Pliocene, NE Iberia), Sedimentary Geology, 418, 105910, https://doi.org/10.1016/j.sedgeo.2021.105910, 2021.

Con formato: Color de fuente: Énfasis 1

# Código de campo cambiado

**Comentado [M18]:** Reviewer #1: It is also quite strange that there is not any reference for the applied methods. Please consider citing the proper references in the revised manuscript.

#### Comentado [M19]: Reference added:

Giesemann, A., Jaeger, H.-J., Norman, A. L., Krouse, H. R., and Brand, W. A.: Online Sulfur-Isotope Determination Using an Elemental Analyzer Coupled to a Mass Spectrometer, Anal. Chem., 66, 2816–2819, https://doi.org/10.1021/ac00090a005, 1994. dried at 45°C overnight. Sulfates dissolved in water were precipitated using the
same method.

Isotope measurements were carried out using a Flash Elemental Analyzer (Flash-257 258 EA) at 1030 °C. The samples were folded in tin capsules. After sample combustion, the generated SO<sub>2</sub> was measured by continuous-flow gas source 259 isotope ratio mass spectrometry (Thermo Scientific, Delta V Plus). Samples were 260 run in duplicate and calibration was accomplished using NBS-127. The 261 reproducibility (1 $\sigma$ ) of  $\delta^{34}$ S was better than 0.2‰, similar to the long-term 262 reproducibility of the standard over the run (0.2%).  $\delta^{34}$ S isotope values are 263 264 reported relative to VCDT (Vienna-Canyon Diablo Troilite).

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## 266 4. Results

## 267 4.1 Devaux cave description

Devaux cave is ~2500 m long and comprises three distinct levels (Fig. 2b). The 268 lower and the middle levels correspond to the Brulle spring (0 m), and the 269 270 "Porche" entrance (~+14.5 m), respectively. The third one comprises chambers and galleries +21 m to +29 m above the Brulle spring (Fig. 2b). In the inner part 271 of the cave, some unexplored vertical chimneys may connect to sinkholes in the 272 catchment above the cave (Fig. 2a). The main ice deposits are located in rooms 273 D, G, SPD and K (Fig. 2b). Except for SPD, these chambers located above the 274 Porche entrance (between ~+1 and +7 m) can be accessed via ascending 275 276 passages.

During the cold season, the cave river starts freezing at the spring and the ice 277 278 then expands backward into room F (Fig. 2b). The ice totally or partially clogs the 279 main gallery and dams the water inside the cave forming a small lake (cf. also Rösch and Rösch, 1935). This process is important for the seasonal ice extent 280 281 as the flooding of the cave depends on whether the springs (North 1 and North 2) are frozen or not (e.g., Rösch and Rösch, 1935). Webcam observations 282 (Gavarnie, Oxygène hut) suggest a possible freezing of the Brulle spring from 283 late November to mid-May simultaneous with the freezing of the Gavarnie 284 waterfall. Moreover, historical photos (e.g., Devaux, 1929; Rösch and Rösch, 285 1935) and our own observations show that snow during winter and spring can 286

reach the Brulle entrance - a situation that also favours the blocking of the 287 288 springs. As a result of such flooding events, slackwater deposits are presentformed in the cave entrance zone, but locally also further into the cave 289 290 (e.g., in rooms I, J, K and SCAL chatière, along the main gallery; Fig. 2b), while silty sediments are found at elevated positions with respect to the river level (e.g., 291 in rooms D and G). Sandy sediments dominate in the large rooms located beyond 292 the SCAL chatière. Two such successions (~1 m thick) comprising hundreds of 293 294 rhythmitic fine -sand- and silt layers are present in elevated areas with respect to the current river, witnessing major events of back-flooding. 295

Observations made during summer show a dominant air-flow direction from the inner to the outer parts of the cave, exiting through the Brulle and Porche entrances. Conversely, the opposite is expected for the cold season (chimney effect). When the Brulle spring is partially clogged by the ice during early summer forcing the stream to flow below the ice, air flows from room F to C (Fig. 2b) (e.g., summer 2021). The air flow is imperceptible in rooms D, G, and close to K located away from the main cave passages.

## 303 4.2 Climate setting of Devaux cave

The MAAT at the elevation of Devaux cave is ~0 °C (-0.04 °C; 2017-2021). On 304 the other hand, a positive MAAT (1.8 °C) is recorded on the southern side of the 305 MPm at a similar altitude (Fig. 3a). Maximum and minimum air temperatures 306 outside the cave vary between 24.5 °C and -17.2 °C (hourly values, 2017-2021). 307 308 The PMBS MAAT record (Fig. 3b) shows an increase warming trend of -+around 309 +1.5 °C since the beginning of the measurements in 1882. Before 1985, temperatures below 0°C dominated the annual cycle, while positive MAATs 310 became more frequent in recent years. Minimum temperatures also show an 311 312 temperature increaseing trend of ~+2.5 °C, while the maximal annual temperatures do not show a clear trend. The north-facing Gavarnie cirque is 313 associated with a clear RAD anomaly (Fig. 4). Values lower than 215 kWh/m<sup>2</sup> are 314 observed at ~2000 m and between ~2800 and 2900 m a.s.l., corresponding to 315 the cirque bottom, the area located behind La Torre peak and the surroundings 316 of Devaux cave. At the cave site entrance the RAD value is only 390 kWh/m<sup>2</sup>, in 317

Comentado [M20]: Reviewer #2

line 290: Please explain it a bit more what is "an increase of ~+1.5 °C". A trend value? or the difference between the mean of a certain period at the beginning and at the end of the record? or what?

Comentado [M21]: Reviewer #2

line 299: Please check the dimension.

stark contrast to the summit areas and surroundings where the RAD often
 exceeds 1500 kWh/m<sup>2</sup> (Fig. 4).

While the mean daily air temperature (MDAT) at the cave entrance (purple line in 320 321 Fig. 5) and the temperature series from PMBS (pink line in Fig. 5) agree in their absolute values, the variability of MDAT at the Devaux entrance is lower than at 322 the PMBS. This pattern could be related to local topographic conditions leading, 323 for instance, to less RAD, or to the position of the sensor in the cliff (less night 324 325 emissivity). Given this radiation contrast, warmer temperatures prevail on the southern side of the MPm (Fig. 4), favouring early snowmelt in spring and early 326 summer, while at the same time the temperature stays below 0 °C in the cave's 327 surroundings. 328

## 329 4.3 Devaux cave temperature variations

The cave can be separated into distinct areas depending on their thermal regime:

ventilated galleries (rooms A, B, C, F and the main gallery from SPD to SCAL
 <u>chatière</u> to K) and <u>these poorly ventilated parts</u> off the main air flow path (rooms

333 D, G<u>, K</u> - Figs. 2b, 5).

## 334 4.3.1 Well-ventilated cave parts

335 Air (T2air, T5air, T10air, T11air) and water (W6water, W7water) temperature data show large seasonal oscillations. at T2air, T5air, T10air T11air, T12air, W6water, W7water and 336 R2rock sensors. All sensors except T11air, T12air, and R2rock-show a few days with 337 of positive temperatures during summer. Sensor T2air (2011-2012, Fig.5a), which 338 is also the closest to the Porche entrance, shows the highest correlation (r) with 339 the external temperature (0.73, p<0.001). Sensor T5air (2017-2021, Fig. 5d) in 340 room B also shows a high correlation and significant correlation (0.82, p<0.0005) 341 with the outside temperature. During the major cave refrigeration cooling that 342 takes place between the end of October toand May and the correlation is 343 significatent and ranges between 0.68 to 0.84. During the summers and part of 344 the falls, the correlations decreases notably (-0.23 to 0.76). -Sensor T11air (2018-345 2021, Fig. 5d) is located in SPD room. Despite being a well-ventilated gallery, the 346 sensor is relatively protected from the air flow by the room morphology and shows 347 348 lower correlations (0.69, p<0.001) is partly protected from the air flow and shows

349 lower a correlation (0.69, p<0.001) despite being located in a well-ventilated

**Comentado [M22]:** Reviewer #2 I315: I think this could be reformulated, as the authors list water, and rock T sensors together with the air T sensors.

Con formato: Color de fuente: Automático

Con formato: Color de fuente: Automático

gallery (SPD room). Also during the refrigeration winter months, the correlations 350 are lower (0.49-0.62, p<0.001) than in T5air. -Sensor T5air (2017-2021, Fig. 5d) 351 in room B also shows a high correlation with the outside temperature from 352 353 November to May (0.82, p<0.001(2017-2018); 0.66, p<0.001(2018-2019); 0.66, 354 p<0.001(2019-2020); 0.86, p<0.001(2020-2021)), while during summer and fall correlations with external temperatures are slightly weaker (0.52, p<0.001(2017-355 2018); 0.37, p<0.001(2019-2020); 0.66 p<0.001(2020-2021)). Sensor T11<sub>air</sub> 356 357 (2017-2021, Fig. 5d) is located in SPD room. Despite being a well-ventilated gallery, the sensor is relatively protected from the air flow by the room morphology 358 359 and shows lower correlations (0.45, p<0.001(2018-2019); 0.34, p<0.001(2019-2020); 0.79 p<0.001 (2020-2021)) compared to T5air- Sensor T10 (2014-2015, 360 361 Fig. 5c) does not show any significant correlation with the external temperature. 362 Sensors T12air and R2reek are located in room K, and similar to T11air, the chamber morphology shields them from the air flow. Rock temperature sensor R2 rock 363 chows a slightly variable temperature ranging between 0.10°C and 0.28°C 364 365 (mean of 0.24 and 0.23°C for channel 1 and 2, respectively). Sensor T12air 366 shows a low correlation with the external temperature (r<sup>2</sup>=0.35, p<0.001 (2018-2021)), and the same is observed for Text R2 rock (r<sup>2</sup>=0.35, p<0.001 (2010 2021). 367 Meanwhile the correlation between T12 air and R2 rock is high but not significant 368 (r<sup>2</sup>-0.93, p>0.005 (2019-2021). 369

370 The water sSensors W6water and W7water (Figs. 5b, c) recorded water temperature variations during the years 2012-2013 and 2014-2015, respectively. Both sensors 371 record a continuous temperature decline from the end of November to mid-372 January until the water freezes. At W7<sub>water</sub>, the temperature ranges between -0.3 373 374 and -5.8 °C between the end of fall and the beginning of winter, while between 375 January and the beginning of June, the temperature stays close to 0°C between January and the beginning of June. At W6 water, the temperature reached a 376 377 minimum of -1.7 °C and shows smaller variations than at W7<sub>water</sub>. No significant correlation was found between the external air temperature and the river water 378 temperature. Only W6<sub>water</sub> shows a weak small correlation with the external 379 temperature when ice is absent (0.39 p<0.001 and 0.40 p<0.001). 380

**Comentado [M23]:** line 346: I suggest replacing "small" with "weak".

For each monitored interval, the mean annual cave temperature at the T2<sub>air</sub>, T5<sub>air</sub>
 and T11<sub>air</sub> sensors is lower than the outside mean temperature for the same

period-(by\_0.4°, 2.0°, 3.3° C-lower, respectively). The W6<sub>water</sub>, W7<sub>water</sub> and T10<sub>air</sub>
 sensors show mean temperatures higher than the external mean temperatures
 (by\_1.6°, 2.6°, 2.5° C-higher, respectively). The periods 2011-2012 and 2017-2018
 (at T2<sub>air</sub> and T5<sub>-air</sub>, respectively) represent the coldest cave years of the monitoring
 period.

388

## 389 4.3.2 Poorly ventilated cave parts

Air temperature sSensors located in rooms D (T3air, T4air, T8air, R1rock), and G 390 391 (T9air), K (T12air,) and rock temperature (R1rock, R2rock) show air temperatures below 0 °C during the monitoring period with small oscillations and a weak and/or 392 insignificant correlation with the external air temperature. All sensors show 393 temperatures below 0 °C during the monitoring period with small oscillations. 394 395 Sensor R1<sub>rock</sub> (Fig. 5) recorded rock temperatures consistently below 0°C during the entire monitoring period. This sensor shows constant rock temperatures (-396 1.24 °C and -1.27 °C for channels 1 and 2, respectively), similar within error to 397 the cave air temperature (T3air, T9air; 2019-2021). All sensors except for T3air 398 399 (2011-2012, Fig. 5a) show mean air and rock temperatures lower than the mean external temperature during the same period (by 0.59 °C to 2.47°C-lower). The 400 muted temperature variations in these chambers reflect reduced heat exchange 401 compared to the well-ventilated parts of the cave. Sensors T12air and R2rock are 402 403 located in room K, and similar to T11air, the chamber morphology shields them from the air flow. Rock temperature sensor R2 rock shows a slightly more variable 404 temperature ranging between -0.19°C and -0.28°C (mean of -0.24 and -0.23°C 405 for channel 1 and 2, respectively). Sensor T12air shows a low correlation with the 406 external temperature (r<sup>2</sup>=0.35, p<0.001 (2018-2021)), and the same is observed 407 408 for Text - R2 rock (r2=0.35, p<0.001 (2019-2021). Meanwhile the correlation between T12 air and R2 rock is high but not significant (r<sup>2</sup>=0.93, p>0.005 (2019-409 <u>2021).</u> 410 411

412

413 4.4 Cave deposits

**Comentado [M24]:** Reviewer #2 1357: I think R1 could be dropped from the list in parentheses, as it is not an air temperature sensor.

## 414 4.4.1 lce

Congelation ice formed by freezing of water within the cave is the most abundant type of ice, and four main ice deposits are located in chambers D, G, SPD, and K (Fig. 2b). The most relevant feature of these ice bodies is their <u>high</u> transparency and massive aspect, i.e. the lack of layering (Figs. 6a, b). Transparent ice is present on the ceiling, blocking chimneys, galleries and fractures. The local loss of transparency is related to the presence of cryogenic cave minerals and/or air inclusions (Figs. 6a, b, c, d).

A highly transparent ice deposit covers the southwest wall of room D and blocks the access to a gallery (Fig. 6a). The height of this deposit reaches ~6 m, and its base is located ~20 m above the Brulle spring. The thickness of this ice deposit ranges from 4.5 to 14.5 m (horizontal laser measurements across the ice in the gallery blocked by ice) and the estimated volume ranges from ~350 to ~710 m<sup>3</sup>. Three unconformities marked by cryogenic minerals were identified in this ice body.

In room G, an ice body (~25.8 to 29.6 m above the Brulle spring) is present on 429 the ceiling (Fig. 6b) and the estimated ice volume is ~180 m<sup>3</sup>. A comparison with 430 a historical photograph shortly before 1953 (Casteret, 1953) suggests that the ice 431 body has not changed significantly during the last ~69 years (Figs. 7a, b). Ice-432 rock distances measured at four points, however, reveal small changes at three 433 of them. The first has retreated 9.8 mm since 2014 (mean 0.9 mm a<sup>-1</sup>, n=2), the 434 second has retreated 19.2 mm since 2014 (mean 0.6 mm a<sup>-1</sup>, n=5), and the third 435 one has retreated 15.8 mm since 2013 (mean 2.2 mm a<sup>-1</sup>, n=7). At ~80 m from 436 the entrance, a small descending room (SPD) (Figs. 2b, 6c) hosts a small volume 437 of ice. Measurements between 2020 and 2021 indicate a retreat of 20 mm a<sup>-1</sup> 438 (n=1). A last major ice deposit is present ~280 m from the entrance (room K), 439 where transparent and massive ice (~15.5 m above the Brulle spring) is currently 440 fills a filling a cupula or chimney (Figs. 2b, 6d). Additional ice bodies are present 441 behind the SCAL chatière in the upper gallery (Fig. 2b), but they have not been 442 studied. 443

In contrast to these massive ice deposits, layered ice of seasonal origin is presentin small chambers adjacent to the river (E and F rooms) (Fig. 6e). This ice forms

**Comentado [M25]:** Reviewer #2 1396: (T) transparent and massive ice (~15.5 m above the Brulle spring) currently fills a cupula or chimney

sheets of around-about 10-15 cm in thickness which are present in room F and 446 nearby areas (Fig. 6f). This ice is related to the damming and freezing of water 447 inside the cave when the Brulle spring freezes. Our visits from 2017 to 2021 448 revealed that most of the damming and subsequent ice formation in room F took 449 place during winter and spring 2017-2018 corresponding with the coldest months 450 (both inside the cave and outside) of the monitoring period (Fig. 5d). These ice 451 slabs are characterized by flat surfaces on both sides and obviously record 452 453 incomplete freezing of the dammed water. The ice sheets largely disappeared during summer and fall, and only strongly degraded ice remained in elevated 454 areas of room F. 455

On the other hand, the ice sheets associated with earlier episodes of river 456 457 damming and freezing have disappeared, and only linear colour changes remained as witnesses of such events on the walls of the room E (Fig. 8d). A 458 historical photograph exemplifies these ice levels in the access between rooms 459 F and E (Fig. 8a). In August 1984 the ice was close to the ceiling and nearly 1 m 460 thick (Fig. 8a; Marc Galy, pers. comm.). This contrasts with the low ice level in 461 recent years (Fig. 8b). In total, three ice-level marks were identified in relation to 462 back-flooding and subsequent freezing of ponded water (Figs. 8c, d). They 463 appear at a lower elevation than the Porche entrance (c.+9.5, +9.2, +8.8, m with 464 respect to the Brulle spring). 465

Another important feature is the presence of hoarfrost, which is-was observed in 466 rooms <u>A</u>, B, C, E, F and along the gallery between SPD and  $\frac{\text{K}}{\text{J}}$  (Figs. 2b, 7g,  $\frac{7}{\text{h}}$ ). 467 The crystal size varies from few mm to 4 cm and appears to be upholstering some 468 469 galleries and cupolas, forming aggregates that hang from the ceiling (Fig. 6h). Finally, seasonal ice formations (e.g., icicles and ice stalagmites), as well as drips 470 are restricted to the outmost ~15 m, in the vicinity of both entrances, and in the 471 innermost part of the cave (~ 500 m from the entrance). Seasonal ice formations 472 are absent in cave sectors where transparent ice bodies and hoarfrost are 473 present. Firn deposits derived from snow are restricted to the Porche entrance. 474

475

476 4.4.2 Mineral deposits

They comprise mainly cryogenic cave minerals. XRD analyses of samples from 477 rooms D, G and K yielded gypsum and calcite, while the sulfide crystals and their 478 oxidation products present in the host rock were identified as pyrite and goethite, 479 respectively. The presence of cryogenic gypsum in Devaux was already reported 480 by du Cailar and Dubois (1953). In room D, gypsum was observed within the ice 481 and on boulders (Figs. 9a, b, c). A total of three gypsum levels (lower, middle and 482 upper, located at ~21.4, ~22.6 and ~23.9 m, respectively, with respect to the 483 Brulle spring) were identified in the ice (Fig. 9a). Due to the progressive retreat of 484 the ice body, some of these crystals are now present on the ice surface. Gypsum 485 levels comprise large single crystals (0.5-1 cm in diameter), aggregates forming 486 rafts (10 cm) up to 1 cm in thickness (Fig. 9b), as well as a fine crystalline fraction. 487 Visual eExamination of the fine fraction under using a binocular stereo 488 microscope indicates the presence of small aggregates of cryogenic cave 489 carbonates and gypsum (CCG) (<1 mm)-including globular, single and twin 490 morphologies <1 mm in diameter (Fig. 9d). 491

492

In room G, gypsum and carbonates crystals are present in the lower part of the 493 ice deposit (Fig. 10e) and on blocks. There, CCC are larger (>10 mm) than in 494 room D and include globular shapes and raft-like aggregates, similar to those 495 reported by Žák et al. (2012). Some of these CCC show gypsum overgrowths 496 (Fig. 9f). Across the ice surface, patches of globular CCC (sub-millimelitre size) 497 have been released by ice sublimation (Figs. 7a, b). In room SPD, CCC and CCG 498 (≤ 2 mm) are present within and on the ice (Figs. 2b, 7c). Finally, in room K, only 499 500 few CCC were still present within the ice, while most of them form heaps of loose 501 crystals covering blocks. Some of these CCCs exceed 5 mm in diameter. Crystal morphologies include rosettes, skeletons and rhombohedrons similar to those 502 reported by Žák et al. (2012) as well as white tapered crystal aggregates. Beyond 503 room K, regular carbonate speleothems (i.e. stalagmites, stalactites and 504 flowstones) are present. On the contrary, gGypsum crystals growing coating from 505 walls or ceilings wereas not observed. 506

507 4.5 Cave water chemistry and sulfate isotopic composition

Comentado [M26]: Reviewer #2 I452: (T, American English spelling) millilitre

Comentado [M27]: Reviewer #2 [453: (T) in room SPD. CCC and CCG

Comentado [M28]: Reviewer #2 I456: for the sake of consistency, I would drop the s at the end of CCC here.

Comentado [M29]: Sentence added:

On the contrary, Gypsum coating walls or ceilings was not observed.

The chemical composition of water in Devaux  $\underline{cave}(n=22)$  cave is dominated by calcium and bicarbonate with relatively high Mg concentrations and locally also

elevated sulfate concentrations (Table 1). Total dissolved solids (TDS, n=7) vary

511 from 57 to 315 mg l<sup>-1</sup>. Devaux's dripwater has higher mean sulfate concentrations

512 (65 mg  $l^{-1}$ ) than the cave river (11 mg  $l^{-1}$ ) and massive and seasonal ice (2.8-18

513 mg l<sup>-1</sup>). Concerning the sulfur isotopic composition (Table 2), the The  $\delta^{34}$ S value

of dissolved sulfate in the dripwater is -14.4‰ (n=1), which is significantly higher

than in cave river water (-28.5‰ to -27.3‰, n=2; Table 2). Gypsum crystals in

room D show homogeneous  $\delta^{34}$ S values ranging from -15.1‰ to -15.8‰ (n=7),

517 while in room G they range from -12.3‰ to -11.9‰ (n=5). A pyrite sample from

518 the host rock yielded a  $\delta^{34}$ S value of -12.7‰ (n=1).

## 519 5. Discussion

520 **5.1. Processes controlling the thermal regime in Devaux cave and <u>the extent</u> 521 <u>current of permafrost extent</u>** 

A complex spatial distribution and a high degree of heterogeneity are among the main characteristics of mountain permafrost (Gruber and Haeberli, 2009). In Devaux cave the existence of permafrost can be related to a combination of two processes: i) cave atmospheric dynamics, and ii) conductive heat transfer through the rock.

527 Devaux cave is characterized by mean air and rock temperatures lower than the external mean annual temperature (Fig. 5). The low cave temperatures in winter 528 lead to an inward airflow and an associated negative thermal anomaly behind the 529 cave entrance zone. On the contrary, during summer, the cold and dense air 530 flows out of the cave due to the temperature difference between outside and 531 inside air. Also tThe heat supplied to the cave by the river can also 532 modifyinfluences the cave air temperature by exporting thermal energy . Thus, 533 this process drags cold outside air intofrom the cave during winter and on the 534 contrary during summer. Devaux cave is characterized by mean air and rock 535 temperatures lower than the external mean annual temperature (Fig. 5). The low 536 537 cave temperatures in winter lead to an inward airflow and an associated negative thermal anomaly behind the cave entrance zone. Similar seasonal ventilation 538

#### Comentado [M30]: Reviewer #2

E) I315 - figure 5d, the air temperature variations at T11 and T5 (and T2) could be discussed in additional detail (at line 481 for instance).

patterns have been observed in ice caves elsewhere (e.g., Luetscher et al., 2008;
Colucci and Guglielmin, 2019; Perşoiu et al., 2021).

On the other hand, positive temperatures are observed both in the cave river and 541 542 in the air at the cave-entrance (Fig. 5), reflecting heat advected by water (river) and the influence of the external temperature (cf. Luetscher et al., 2008; Badino, 543 2010). The lack of correlation between the external and internal temperatures 544 and the small temperature variability in rooms D, G, and K reflect their thermal 545 546 isolation from well-ventilated cave parts. There, the apparent thermal equilibrium between the rock and the cave atmosphere (Trock=Tair) supports the notion that 547 heat exchange is dominated by conduction through the bedrock. 548

The MAAT at the altitude of the cave is -0.04 °C (2017-2021) suggesting that the 549 550 0 °C isotherm is located close to the cave. Using an array of techniques (geomatic surveys, temperature monitoring, temperature at the base of the snowpack (BTS) 551 and geomorphological and thermal mapping), Serrano et al. (2019) found 552 observed mean annual ground temperatures between -1 and -2 °C on the 553 554 northern slope of the MPm suggesting that discontinuous permafrost is present between 2750-2900 m a.s.l., with more continuous permafrost startings at 2900 555 m a.s.I. The orientation of the Gavarnie cirque, as well as the high slope angle, 556 and shadow from the surrounding peaks favour the preservation of permafrost at 557 lower elevations (e.g., Gubler et al., 2011). 558

Given the high thermal inertia of the rock, the permafrost temperature at depth is 560 still under the influence of past climate conditions (e.g., Haeberli et al., 1984; 561 Noetzli and Gruber, 2009) and, therefore, part of the current permafrost in the 562 area could be inherited from previous colder times (e.g., Colucci and Guglielmin, 563 2019). In particular, the low mean annual temperatures recorded at PMBS at in 564 the late 19th century the beginning of the Industrial Era arewere favourable 565 conditions for permafrost development in the recent past. We surmise that the 566 current permafrost could be inherited from colder periods of the Little Ice Age. 567

559

In well-ventilated ice caves hoarfrost is the most dynamic ice formation on seasonal time scales. The presence of perennial hoarfrost is, however, indicative of a continuously frozen bedrock and thus representative of caves within the Comentado [M31]: Reviewer #2 I501: (T) with more continuous permafrost starting at 2900 m asl

Comentado [M32]: Reviewer #2

D) I506-513

#### Comentado [M33]: Reviewer #1.

line 511: I suggest replacing the term "beginning of the Industrial Era" with "late 19<sup>th</sup> century". As far as I know the Industrial Era begun much earlier than the PMBS record.

permafrost zone (e.g. Luetscher and Jeannin, 2018; Yonge et al., 2018). In 571 Devaux cave, perennial hoarfrost is observed in rooms where the bedrock is 572 surrounded by small ice bodies (e.g., gallery close to SPD room, Fig. 6g). Devaux 573 574 (1929) indicated the presence of ice crystals on the ceiling at the entrance of room D. In the same way, du Cailar and Dubois (1953) showed a schematic 575 cross-section of room D, where ice crystals are present at the beginning of the 576 room. These historical reports suggest these areas were probably more 577 578 ventilated in the past, which favoured the hoarfrost formation. -On the other hand, seasonal hoarfrost is present in ventilated galleries (A, B, C, F and between SPD 579 and J). Seasonal hoarfrost in room B and C, and in the area between H to J, 580 disappears at the end of summer, probably because of the heat delivered by the 581 cave river, as recorded by the T5 sensor (Fig. 5). 582

The presence of permafrost in Devaux's catchment is supported by the absence 583 of drips and/or seepage in the investigated cave passages (e.g., Luetscher and 584 Jeannin, 2018; Vaks et al., 2020). Active drips and seasonal ice formations are 585 586 limited to the first  $\sim$ 15 m of the cave as well as to the inner part (beyond room K). Mountain permafrost thus penetrates ~350 m longitudinally from the East eastern 587 cliff of the Gavarnie cirgue to the southern side of the massif, following a west-588 589 east direction. On the other hand, given the elevation of the cave and the topographic topography relief above the cave, the current maximum permafrost 590 591 thickness (without taking into account the active layer) on the southern side of the MPm is ~200 m (without taking into account the active layer). 592

593

# 594 5.2. The origin of ice in Devaux cave

The transparent and massive character of Devaux's cave ice, as well as the presence of CCC, which formation requires low congelation rates (Žák et al., (2004)), -suggests that this ice\_-formed by slow freezing of water dammed by ice at the spring. This model is consistent with the climate in of the Gavarnie cirque, cave geomorphological observations, cave air and water temperatures as well as historical reports. The cave water level can rise by several meters as indicated by slackwater deposits upstream of the Brulle spring.

## Comentado [M34]: Reviewer 2:

G) 1518 - the only place where perennial hoarfrost is indicated on figure 2B is a small recess appears to be surrounded by ventilated galleries containing seasonal hoarfrost, and as mentioned adjacent to a small ice body of room SPD. This certainly speaks to the frozen nature of the bedrock in this part of the cave, and demonstrates the clear effect of the negative thermal anomaly brought about by the ventilation pattern in the surrounding galleries. But if this is the case, could the authors comment on why there is no perennial hoarfrost in the galleries leading to room D, where such hoarfrost could also have developed?

Comentado [M35]: Reviewer #2

I535-536: massive ice is formed by slow freezing - there should perhaps be a reference here.

The distribution and characteristics of ice bodies in Devaux cave indicate that the 603 hydraulic head rose by at least ~ 15 - 29 m, which is the elevation of the ice bodies 604 in rooms G, F and K. This situation requires that all springs (including Porche) 605 are blocked for a sufficiently long time to allow for complete freezing of these cave 606 lakes. The lack of important unconformities in this massive ice (e.g., detrital 607 layers), which are usually related to seasonal ablation (e.g., {Luetscher et al., 608 2007; Stoffel et al., 2009; Hercman et al., 2010; Spötl et al., 2013), suggests that 609 the ice deposit in room G it is the result of a single flood event. On the contrary, 610 611 the small unconformities recognized in the ice body in room D suggest that several cycles of damming and subsequent ice formation cannot be discarded in 612 the formation of this ice deposit. 613

Our These observations indicate that under the current climate (both in the cave 615 and outside) only part of the water dammed in rooms F and E freezes during 616 winter and spring. This strongly suggests that the ice bodies in Devaux cave must 617 have been associated with colder and/or longer events of ponding and freezing 618 than today, when the cave was effectively sealed from the outside for prolonged 619 times. We hypothesize that the advance of a glacier on the steep slopes of 620 Devaux's surroundings could have contributed to the blockage of the spring, 621 leading to backflooding and the formation of large ice bodies in the cave. In the 622 study area, such periods of glacier growth occurred during the Little Ice Age 623 and/or the Neoglacial (González Trueba et al., 2008; García-Ruiz et al., 2014, 624 2020). 625

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614

The freezing of a flooded cave passage cannot be explained by the advection of 627 cold air alone. It is thus surmised that heat transfer through the host rock is a 628 more plausible mechanism for the complete freezing of the ponded water. The 629 cave ice bodies, just as well as the presence of cryogenic minerals, therefore 630 631 represents a record of a long cold period or of several such shorter episodes. Although the cryogenic minerals and in particular CCC<sub>coarse</sub> are typically 632 associated with permafrost thawing during warm spells (Žák et al., 2004; Richter 633 et al., 2010; Žák et al., 2012; Luetscher et al., 2013), permafrost conditions 634 prevailed during ice formation in Devaux cave. Thus, Tthe water that feeds 635

## Comentado [M36]: Reviewer #1

lines 546-552: Discordancy without visible detrital layer could also indicate unconformity. A nice example can be found in Fig5 of Hereman et al., 2010 (http://www.geochronometria.pl/pdf/geo\_36/Geo36\_05.pdf). This type of discordancy/unconformity could be also considered in this part of the discussion.

#### Comentado [M37]: Reference added:

Hercman, H., Gąsiorowski, M., Gradziński, M., and Kicińska, D.: The First Dating of Cave Ice from the Tatra Mountains, Poland and its Implication to Palaeoclimate Reconstructions, Geochronometria, 36, 31–38, https://doi.org/10.2478/v10003-010-0016-2, 2010.

## Comentado [M38]: Reviewer #1:

line 554: Maybe "These" instead of "Our"

**Comentado [M39]:** Reviewer #2 I568: (T) The cave ice bodies [...] therefore represent Devaux's springs infiltrated during late spring and summer from ponors at Lago
helado and/or surrounding poljes. (which may have acted as local taliks).
However, the heat supplied by this water may have probably not been enough to
thaw the frozen host rock. It is thus very likely that the hostrock temperature was
much-lower and/or the outlets remained closed for longer periods than today to
allow for the complete slow freezing of the ponded water.

642

# 643 5.2.1 Ice volume changes

The colour changes in the walls close to the river (room E), the historical photograph as well as speleological reports point to large changes (several meters) <u>of-in</u> the height of the seasonal ice in the flood-prone sector of the cave (Figs. 8a, b). This ice is influenced by the heat exchanged between the water and the cave.

In contrast, changes in the ice volume are almost negligible in rooms D and G 649 where the temperature is more constant and below 0°C (Figs. 7a, b). The ice 650 651 body in room G has been retreats retreating only by only ~0.6 to ~2.2 mm a<sup>-1</sup>. A similar value (3 mm a<sup>-1</sup>) was observed in Coulthard cave (Alberta, British 652 Columbia, Marshall and Brown, 1974), a cave located within permafrost (Yonge 653 654 et al., 2018). Changes in the ice body in this cave were related to slow sublimation 655 due to convective air flow inside the cave (Marshall and Brown, 1974). On the other hand, the ice in SPD room shows higher ice retreat rates (~ 20 mm a<sup>-1</sup>). 656 Similar sublimation rates have been reported in others-ice caves in the Pamir 657 Mountains and the northern part of the Russian Platform (Mavlyudov, 2008; Žák 658 et al., 2018). Overall, Devaux's cave ice deposits show a remarkable stability 659 which contrasts to-with the rapid changes observed in ice caves outside 660 permafrost areas (Kern and Perşoiu, 2013; Perşoiu et al., 2021; Wind et al., 661 2022), including other ice caves in the Pyrenees and Picos de Europa (Belmonte-662

663 Ribas et al., 2014; Gomez-Lende et al., 2014, 2016).

664

665 **5.3. Cryogenic cave minerals** 

Comentado [M40]: Reviewer #2:

lines 574-575: I suggest omitting the bracketed comment.

**Comentado [M41]:** Reviewer #2 I596: (T) which contrasts with

Con formato: Inglés (Estados Unidos)

In Devaux cave, CCC and CCG are still present within the ice (Figs. 6, a, b, c, d). 666 Worldwide, only very few in situ observations of coarse-grained cryogenic cave 667 minerals are known (e.g., Bartolomé et al., 2015; Colucci et al., 2017). du Cailar 668 and Dubois (1953) reported the presence of gypsum crystals at ~50 cm depth 669 within the ice in Devaux cave. The first evidence of in situ CCCcoarse in cave ice 670 was reported from Sarrios 6, an ice cave at 2780 m a.s.l. on the southern slope 671 of the MPm (Bartolomé et al., 2015). Colucci et al. (2017) documented the 672 673 presence of CCC<sub>coarse</sub> in a small ice cave in the Italian Alps. Recently, Munroe et al. (2021) found CCC<sub>coarse</sub> in ice of Winter Wonderland cave (Utah, USA). 674 675 Because of the abundance of cryogenic cave minerals, the size of individual crystals and aggregates thereof, and their varied-different mineralogy, Devaux 676 cave provides an additional opportunity for studying the origin of such cryogenic 677 cave minerals. 678

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The CCGs in Devaux cave represents, to our knowledge, the first occurrence of 680 its kind in a carbonate karst terrain. So far, CCGs have only been reported from 681 682 gypsum karst areas in Russia and Ukraine (Korshunov and Shavrina, 1998; Žák et al., 2018 and references therein). In those areascaves, tiny gypsum crystals 683 (gypsum powder) form during rapid freezing of water. When ice sublimates in 684 winter, this these gypsum particles powder is are released and accumulates as 685 powdery deposits on the ice surface. Eventually, they partly powder dissolves on 686 the ice surface during spring and summer due to the increase in cave air humidity, 687 and later recrystallizes forming a wide variety of delicate crystal morphologies. 688 CCGs from Devaux cave shows features that do not correspond to those 689 690 previously published from gypsum karst caves. In particular, the Devaux cave CCG<sub>5</sub> i) appears together with CCC<sub>coarse</sub> crystals (≥5 mm in some cases, in rooms 691 D and G), ii) the (raft-like) gypsum crystals are large (Fig. 9b) and, in some cases, 692 are still found within the ice (Fig. 9a) and surrounded by milky ice rich in air 693 inclusions (Fig. 9a, e), and iii) boulders are locally overgrown by gypsum (Fig. 694 9c). 695

697 Coarse-grained cryogenic cave minerals form in a semi-closed system, when the 698 water <u>freezes very slowly freezes inside the caves at low freezing rates (Žák et</u> 699 al., 2004). Once supersaturation is reached, CCM start to crystallize. The

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**Comentado [M42]:** Reviewer #2 I615: for the sake of consistency, drop s at the end of CCG here.

formation of gypsum crystals requires the presence of elevated concentrations of 700 701 dissolved sulfate which may relate to i) sedimentary gypsum deposits intercalated within carbonates (e.g., Sancho et al., 2004), ii) the presence of hydrothermal 702 703 water containing H<sub>2</sub>S in relation with related to hydrocarbons (e.g., Hill, 1987), or 704 iii) the oxidation of sulfides (e.g., pyrite) disseminated in limestones carbonate rocks (e.g., Bottrell, 1991). In the case of Devaux cave marine evaporite rocks 705 (e.g., of the Upper Triassic Keuper facies) and hydrocarbons are absent in the 706 707 catchment of the cave. The most plausible explanation for the presence of dissolved sulfate in Devaux's water is the oxidation of pyrite present in the 708 limestone (du Cailar and Dubois, 1953; Requirand, 2014). 709

711 Water in Devaux cave contains moderate concentrations of sulfate.  $\delta^{34}$ S values of gypsum (-11.9 to -15.8 ‰), pyrite (-12.7 ‰), and dissolved sulfate (-14.4 ‰ in 712 dripwater and -28.5 to -27.3 ‰ in Brulle spring water) are within the range of 713 biogenic pyrite and differ notably from values of marine evaporites (10-35 ‰) 714 715 (Seal, 2006). Thus, the  $\delta^{34}$ S values together with the geological setting of the cave support the hypothesis that disseminated pyrite in the host limestone is the 716 main source of dissolved sulfate and subsequently of CCG. Only the dissolved 717 sulfate  $\delta^{34}$ S values of Brulle spring are considerably more negative (-28.5‰ and 718 -27.3‰). This may be a consequence of microbially mediated redox processes 719 in the karst that discriminate against <sup>34</sup>S (Zerkle et al., 2016; Temovski et al., 720 721 2018). Further studies on the microbiology of the cave may shed light on these 722 mechanisms and how the local sulfur cycle may have changed in the recent past. 723

In gypsum caves, dissolved sulfate dominates over the bicarbonate, and the typical crystallization sequence during freezing of water with high TDS is gypsum  $\rightarrow$  carbonate (commonly calcite)  $\rightarrow$  celestine (Žák et al., 2018). In Devaux cave, however, bicarbonate dominates over sulfate, and our observations show that gypsum crystals partly nucleated on CCC<sub>coarse</sub>. Accordingly, the crystallization sequence at Devaux cave is calcite  $\rightarrow$  gypsum, taking place in a semi-closed system at low freezing rates.

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The second aspect that makes the CCG in Devaux cave unique is the size and well-developedeuhedral crystal shapes of the crystals (Fig. 9 b), which differ

**Comentado [M44]:** I666-667: (T) is the size and welldeveloped shape of the crystals

Comentado [M43]: I636: (T) related to hydrocarbons

notably from the much smaller sizes of gypsum crystals (20-200  $\mu$ m) and gypsum 734 powders (1-30 μm) found in gypsum caves in Russia and Ukraine (Žák et al., 735 2018 and references therein). Another characteristic of CCC and CCG 736 occurrences in Devaux cave is the presence of milky ice surrounding them (Fig. 737 9a, e) which seems to be related to the freezing process during the formation 738 739 cryogenic minerals in a subaqueous environment. Similar to that, CCC were 740 found within the ice and surrounded by bubbles in Sarrios 6 ice cave (Bartolomé et al., 2015). However, the scarce presence of CCC within the ice today, together 741 with the very few sites where this topic is investigated, leads to a lack of studies 742 743 about gas inclusions and CO<sub>2</sub> degassing during CCC formation.

745 Finally, the presence of gypsum aggregates overgrowing some-blocks (Fig. 9c) supports the hypothesis of subaqueous gypsum formation. On the other hand, 746 the absence of gypsum was never observed growthsinging from on the ceiling or 747 on the walls, thus allowingallows it to discard its formation from seepage water 748 followed by precipitation due to evaporation in the cave (e.g., Gázquez et al., 749 2017, 2020). In essence, all observations indicate that gypsum precipitated in a 750 751 semi-closed subaqueous environment and has been preserved from later dissolution by the exceptionally dry environment of this ice cave. Gypsum 752 precipitating from freezing waters has been also documented in the Arctic and 753 the Antarctica (Losiak et al., 2016; Wollenburg et al., 2018) and has been 754 755 proposed as a mechanisms for gypsum formation on Mars (Losiak et al., 2016).

## 757 6. Conclusions

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The investigation of Devaux ice cave, based on cave monitoring, geomorphology,
 and geochemical analyses, provides exceptional insights into the origin of
 modern and past mountain permafrost and associated processes and deposits.

Devaux cave consists of two parts characterised by different thermal regimes:
 1) the near-entrance parts and the main gallery showing large temperature
 fluctuations and cave air temperatures seasonally exceeding 0°C. These
 passages are influenced by an-advective air flow and the heat released by the
 cave river. 2) The inner sector and isolated chambers are characterized by
 muted thermal oscillations and temperatures constantly below 0°C. There, the

#### Comentado [M45]: Reviwer 2

H) Could the authors elaborate on why CCC or CCG related ice, rich in air inclusions could be related to the formation in a subaqueous environment?

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lines 676-679: I think that this info could be moved forward in the section.

cave air temperature is mainly controlled by heat conduction through thebedrock.

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Devaux cave is impacted by backflooding in late winter/early spring when the
main outlets freeze, damming the water inside the cave forming a lake. The
blocking of the outlets requires temperatures below 0°C in the Gavarnie cirque,
while on the southern side of the Monte Perdido massif, temperatures above
0°C allow water infiltration.

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- The absence of dripwater in most parts of the cave together with the presence 776 of perennial/seasonal hoarfrost, and the location of massive ice bodies on the 777 ceiling and/or filling cupulas and galleries are indicative of frozen bedrock 778 779 surrounding the cave. Permafrost at Devaux cave is attributed to a combination of rock undercooling by cave air ventilation and the local climate setting giving 780 rise to the development and/or preservation of permafrost inherited from past 781 colder periods. Currently, permafrost seems to be present above the cave 782 reaching a maximum thickness of ~200 m and a lateral extension of ~350 m 783 towards the southern face of the Monte Perdido massif. 784

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- We report the first deposits of cryogenic gypsum in a limestone-hosted ice cave. Most of the cryogenic minerals are still within the ice and surrounded by milky ice ice rich in air inclusions. Gypsum precipitation occurred subaqueously as a result of slow freezing, following CCC formation.  $\delta^{34}$ S values show that the sulfate originated from the oxidation of pyrite present in the limestone.

- Current climate conditions seem to be still favourable for the preservation of ice
 within this cave. This situation contrasts to the large ice mass loss in other ice

caves elsewhere. The ice deposits in Devaux cave allow unique insights into

processes leading to the formation of cryogenic carbonates and sulfates, and

- represents an ideala unique site to better understand the mountain permafrost
- evolution in the Monte Perdido massif and the Pyrenees in general.
- 798 Competing interests
- No competing of interest

Comentado [M47]: Reviewer #2: I718: (T) rich in air inclusions

**Comentado [M48]:** Reviewer #1 line 723: Please consider adding "ice mass" between the word large and loss to clarify the meaning of the sentence.

Comentado [M49]: Reviewer #2 1724: (T) in Devaux cave

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## 800 Authors contribution

MB conceived the project, planned fieldwork and the sampling strategy. AM 801 obtained funding for this work. MB and GC installed and maintained the sensors 802 and performed the fieldwork. GC contributed with cave monitoring data from 2011 803 804 to 2015. MB analysed monitoring, geomorphological, and geochemical data. FG performed  $\delta^{34}$ S analyses using the facilities provided by AVT. JILM created the 805 radiation map. MB designed the figures and wrote a first draft of the manuscript. 806 807 ML and CS significantly contributed to the discussion of the data. ML and AM reviewed all versions of the manuscript. All authors reviewed the manuscript and 808 contributed to the results, discussion, and final interpretation. All authors 809 approved its submission. 810

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Figure 1. (a) Location of Devaux cave in the Central Pyrenees (ASTER GDEM, NASA v3, 2019). (b) Satellite image and location of Devaux cave, main peaks, lakes, glaciers and cirques in the study area (3D ©Google Earth). The yellow arrows indicate the underground flow path from Lago helado to the Gavarnie waterfall according to the dye-tracing experiment of du Cailar et al., (1953). (c) View towards the entrances of Devaux cave. The lower entrance (~2821 m a.s.l.) corresponds to the Brulle spring (Spring North 1), while the upper one corresponds to the main entrance (Porche (South), ~2836 m a.s.l.). Spring North 2 is located between both entrances. Note person for scale (within the white circle). Remnants of ice partially blocking Brulle and Spring North 2 (July 2021). (d) Landscape view of the catchment area and approximate location of Devaux cave (in dark pink; photo: Paul Cluzon). (e) Ponor located on the southern shore of Lago Helado.



Figure 2. (a) Schematic W-E cross section from Lago helado to Devaux cave, the assumed extent of mountain permafrost, and and the interpreted underground flow path according to du Cailar et al., (1953).\_ (b) Longitudinal section and plan view of Devaux cave showing the locations of sensors and cave deposits. Labels R, W and T refer to rock, water and air temperature sensors, respectively. The enlarged area corresponds to the first ~345 m of the studied sector. Red labels correspond to the approximate location of the photographs in Fig. 76. Cave survey by Marc Galy, Groupe Spéléologique des Pyrénées (GSPY 86).



Figure 3. (a) Monthly temperature variation on the northern and southern side of the Monte Perdido massif. Red and blue triangles correspond to the 4-year means. The dashed black line indicates 0°C. Light red and blue shaded envelopes represent the maximum and minimum mean monthly temperatures, respectively. (b) Maximum, mean and minimum annual temperatures recorded at the Pic du Midi de Bigorre station since 1882. Black line indicates the general trend and dashed black line corresponds to 0°C.



Figure 4. Solar radiation map of the study area. The solar radiation anomaly observed in the Gavarnie cirque is explained by its northerly orientation and the cirque morphology. Black triangles indicate the main peaks above 3000 m. The red-white circle marks Devaux cave, while the dashed white line delineates the approximate catchment.



Figure 5. Mean daily air temperature variations at the Pic du Midi de Bigorre station (2860 m a.s.l., red), daily outside air temperature at Devaux cave (2836 m a.s.l., purple) and temperature variations in air, water and rock in the cave for the different time windows since 2011. Dark pink numbers are mean annual air temperatures (MAAT) at the Pic du Midi de Bigorre station (PMBS). Dashed lines indicate 0 °C. Black squares labelled a, b, c, and d correspond to the areas enlarged below. The black continuous line is the external temperature trend during the monitoring period.



Figure 6. (a) Upper part of the ice body in room D. (b) Ice body hanging from the ceiling and the southwest wall in room G. White <u>colours-spots at-near</u> the bottom of the deposit correspond to the <u>concentration of air</u> inclusions as well as cryogenic carbonates and gypsum in the ice. (c) Small ice body in room SPD with CCC-CCG on and within the ice. Red knife (9 cm) for scale. (d) Ice body on the ceiling of room K (Terminus Devaux, TD). (e) Brulle spring and remains of a layered ice body (September 2018). (f) Broken ice sheets in the flooded area in room F (September 2018). (g) Millimetre to centimetre size perennial hoarfrost in a blind gallery below SPD room. (h) Seasonal hoarfrost aggregates (>30 cm long size) covering a cupola close to room J.



Figure 7. (a) Photo of the ice body located in room G <u>taken shortly</u> before 1953 (Casteret, 1953). (b) Photo taken in 2017. In both pictures, white patches on the ice surface correspond to small CCC accumulations released from the ice by sublimation. Red arrows indicate common features in both images.



Figure 8. (a) Photo taken close to the river sector that connects the rooms F and E. The estimated ice level is 5 m higher than the Brulle spring. Photo by Jean Luc Bernardin (8<sup>th</sup> August 1984). (b) Similar area in 2020, and maximum extension of the seasonal lake ice formed during winter. (c) Higher ice mark level (c. +9.5 m with respect to the Brulle spring) and remnants of ice sheets from the frozen lake in 2018. (d) Two ice level marks (c. +9.2 m and +8.8 m with respect to the Brulle spring) located between the highest mark and the elevation of the ice in photo (a). In all images red arrows indicate the same rock edges, while green arrows show ice-level marks.



Figure 9. (a) Ice body in room G and three levels marked by cryogenic gypsum partially still in situ in the ice. The whitest area corresponds to milky ice with a high abundance of air inclusions. Gypsum crystals cover parts of the surface of the ice body due to ice retreat. (b) Large gypsum "raft" deposited on a block in room D. (c) Block in room D with gypsum overgrowths. (d) Microscopic image of euhedral CCG with local-cores of CCC (white arrows), globular CCC, and detail enlarged image of euhedral gypsum crystal with a core-nucleus of globular CCC. (e) CCC and CCG entrapped within milky ice in room G. (f) Detail of a CCC sample from room G covered by CCG.

		Cations					Anions								
Date	Sample	Na⁺	$\rm NH_4^+$	K⁺	Ca <sup>2+</sup>	$Mg^{2+}$	Ŀ.	C <sup>-</sup>	NO2 <sup>-</sup>	Br I	10 <sub>3</sub> -	504 <sup>2-</sup>	HCO <sub>3</sub> -	CO <sub>3</sub> <sup>2-</sup>	PO4 <sup>3-</sup>
15/09/2017	Devaux river 1	1.6	0.0	0.5	36.0	8.5	0.0	0.2	0.0	0.0	1.8	21.6	61.0	11.6	0.0
	Devaux drip 1	0.9	0.1	0.5	50.5	18.2	0.1	0.5	0.0	0.0	6.8	67.4	95.2	0.0	0.0
	Devaux drip 2	1.4	1.2	1.3	53.2	19.5	0.1	<u>+</u>	0.1	0.0	7.4	70.1	101.3	0.0	0.0
	Devaux Ice 1 (room D)	2.3	0.0	0.3	24.8	2.7	0.1	1.3	0.0	0.0	0.7	19.0	23.9	1.0	0.0
	Devaux Ice 2 (room D)	2.2	1.3	2.5	27.8	2.0	0.0	2.1	0.0	0.0	1.5	17.0	30.7	0.0	0.0
22/07/2018	Devaux river 1	0.6	0.0	0.4	32.4	4.4	0.0	0.2	0.0	0.0	0.9	5.1	53.7	4.0	0.1
	Devaux river 2	0.6	0.0	0.4	32.2	4.4	0.0	0.2	0.0	0.0	0.9	5.1	56.1	2.6	0.0
	Devaux drip 1	1.4	0.0	3.2	61.0	20.8	0.2	2.2	0.0	0.0	4.1	76.0	84.2	5.6	0.0
	Devaux drip 2	2.3	0.1	1.7	60.8	21.0	0.2	2.2	0.0	、 0.0	4.1	76.9	91.5	4.4	0.0
22/09/2018	Devaux river 1*	1.3	0.0	0.4	40.5	7.9	0.0	0.3	0.0	0.0	2.0	17.0	65.9	0.0	0.0
	Devaux drip 1*	1.6	0.0	1.2	70.6	27.2	0.2	<u>.</u>	0.0	、 0.0	9.8	116.5	90.3	0.0	0.0
28/07/2020	Devaux ice (seasonal)*	0.4	0.0	0.5	28.2	1.1	0.1	0.5	0.0	0.0	0.5	2.8	36.6	0.0	0.0
	Devaux river 1*	0.6	0.0	0.3	31.5	4.1	0.0	0.2	0.0	0.0	0.8	5.9	58.6	0.0	0.0
	Devaux drip 1*	1.1	0.2	1.1	42.3	12.5	0.1	0.5	0.0	0.0	2.9	38.4	101.3	0.0	0.0
	Devaux drip 2*	1.1	0.1	1.0	43.6	13.5	0.1	0.4	0.0	0.0	2.7	38.2	89.1	0.0	0.0
	Devaux drip 3*	1.6	0.7	1.5	47.9	13.1	0.1	<u>.</u>	0.0	0.0	2.2	36.7	107.4	0.0	0.0
26/07/2021	Devaux drip 1	2.9	0.0	1.1	83	35.9	0.3	5.9	0.6	0.1	0.2	269.3	104.9	0.0	0.0
	Devaux drip 2	3.3	0.4	2.0	73.2	29.3	0.2	6.0	0.1	0.0	28.6	212	112.2	0.0	0.0
	Devaux river 1	0.4	0.0	0.1	25.7	4.3	0.1	2.6	0.1	0.0	3.2	16.3	68.3	0.0	0.0
13/08/2021	Devaux river 1	0.7	0.0	0.2	28.6	4.9	0.1	2.6	0.0	0.0	1.5	20.4	74.4	0.0	0.0
	Devaux drip 1	7.5	2.2	5.1	49.5	15.2	0.2	10.3	0.3	0.0	6.9	77.3	130.5	0.0	0.0
	Devaux drip 2	5.1	1.3	2.8	49.3	15.6	0.2	6.5	0.1	0.0	6.5	80.5	129.3	0.0	0.0

Table 1. Chemical composition of water and ice samples from Devaux cave (in mg/l). \* Samples where TDS (total dissolved solids) was calculated.

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Location	Sample and description	$\delta^{34}$ S (‰) VCDT
Room D	Gypsum crystal (part of large raft)	-15.8
Room D	Gypsum crystal (part of large raft)	-15.5
Room D; lower gypsum level	Gypsum crystal (individual)	-15.6
Room D; middle gypsum level	Gypsum crystal (individual)	-15.0
Room D; middle gypsum level	Gypsum crystal (individual)	-15.6
Room D; upper gypsum level	Tiny gypsum crystals (aliquot)	-15.3
Room D	Gypsum crystal (individual)	-15.1
Room G	Gypsum crystal (individual)	-12.3
Room G	Gypsum overgrowth (individual)	-12.1
Room G	Gypsum overgrowth (individual)	-11.9
Room G	Gypsum overgrowth (individual)	-12.1
Room G	Gypsum overgrowth (individual)	-12.0
Limestone above cave	Pyrite crystal (individual)	-12.7
Entrance "Porche"	Drip water (1 liter)	-14.4
Brulle spring	River water 1 (1 liter)	-28.5
Brulle spring	River water 2 (1 liter)	-27.3

Table 2. Sulfur isotope values of gypsum, water and pyrite from Devaux.