## PALAEOENVIRONMENTAL RECORDS FROM ICE CAVES OF VELEBIT MOUNTAINS - LEDENA PIT AND VUKUŠIĆ ICE CAVE, CROATIA

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Abstract: Perennial ice is a common deposit in the caves of north Velebit Mts, Croatia. On the basis of historical cave maps ice level subsidence were estimated to 9 m and 0.2 m between 1962 and 2007 in Ledena Pit and Vukušić Ice Cave, respectively. The ice loss trend in Ledena Pit has seemed to slow down since the mid-1990s. Reassessment of the 1995-year tritium measurement suggests that the ice formed from the precipitation of the '63-bomb-peak might be at 3.75 m below the 1995 ice surface. Mean ice accumulation ( $r_{acc}$ ) and basal melting ( $r_{bm}$ ) rates were calculated for the 1963-1995 period as 18 cm/yr and 38 cm/yr, respectively. The lowermost ice layer (-40 m) can be dated to 333 year-old applying  $r_{acc}$  or 105 year-old by  $r_{bm}$ . The large difference can be interpreted as  $r_{acc}$  presents ice accumulation especially for the 1963-95 period, while the long-term mean accumulation rate is better approximated by the  $r_{bm}$ .

Comparison of stable isotopic composition of nine cave ice samples and the local precipitation suggests that the precipitation of the winter half year exerts major role in the ice formation overriding the importance of the rain from summer half year.

Key words: ice loss, basal melting, tritium, stable oxygen isotopes, stable hydrogen isotopes

#### **1. INTRODUCTION**

Cave ice deposits are worldwide reported to show pronounced shrinkage over the past decades (Rachlewicz & Szczucinski 2004, Luetscher et al. 2005, Trofimova 2007). This widely observed process threaten cave ice deposits with tremendous volume loss or ultimately total disappearance. The ice loss phenomenon call urgent need to investigate the probably unique palaeoenvironmental information stored in cave ice deposit.

In the present paper ice surface evolution is studied in two Croatian ice caves on the base of cave maps prepared during the past half-century. In addition authors are to re-evaluate the radio- and stable water isotopic data derived from cave ice samples during the mid-90s (Horvatinčić 1996). The reason of this reevaluation is that new data have become available about the local precipitation from Zavižan (44.82N, 14.98E, 1594 m a.s.l.) meteorological station since 2000 (IAEA, 2004, Horvatinčić et al. 2005, Vreca et al. 2006) giving a more appropriate reference for a cave ice/precipitation comparison.

#### **1.1 SITE DESCRIPTION**

Velebit Mts stretch in NW-SE direction along the Adriatic coast, in Croatia (Fig. 1). Geomorphologic research studies have shown that the Pleistocene glaciation spread over a large part of the mountain range. Various types of glaciers were differentiated, and morphologic proofs (denudation and accumulation) of their expansion were found (Bognar et al. 1991, Bognar & Faivre 2006).

Ledena Pit in Lomska duliba (Ledena jama u Lomskoj dulibi) and Vukušić Ice Cave (Vukušić snježnica) are located in the northern part of the Velebit Mts (Fig. 1).

Entrance of Ledena Pit (44.74N, 15.03E,

1235 m a.s.l.) is situated in Lomska duliba glacier valley, so genesis and morphology of the cave is closely connected with spreading and dynamics of the past glacier of Lomska duliba. Ledena Pit is a knee-shaped, 536 m deep karst pit. A part of the entrance of the pit preserves a vast ice block. It spreads from -50 m depth to -90 m depth, and takes 20-30 m in diameter (Fig. 2a).



Fig. 1. Location of the caves Ledena Pit (1) and Vukušić Ice Cave (2). Zavižan station for local precipitation is close to the site 2.

During the speleological and morphological explorations of the pit, the isotope analysis of cave ice, wood branch from ice and speleothems also were done. The estimated age of ice deposit based on tritium (<sup>3</sup>H)

activity in ice and radiocarbon (<sup>14</sup>C) dating of wood branch in the ice was cca 500 years. In addition, the age of flowstone (from -60 m depth) dated by the  $^{230}$ Th/ $^{234}$ U method was estimated to be cca 300 000 years (Horvatinčić 1996, Jelenić et al. 2001).

Vukušić Ice Cave (44.8N, 14.98E, 1490 m a.s.l.) is located near the Zavižan Peak. Thickness of its ice deposit is estimated to be more than 10 m (Fig. 2b).

### 2. MATERIALS AND METHODS

#### **2.1 MASS BALANCE**

Detailed maps about the ice surface are available from 1962, 1977, 1993 and 1996. Present conditions were also surveyed. To quantify the changes between the dated levels two representative profiles were chosen for both caves and difference between historical ice levels were determined along these profiles (Fig. 2).

#### **2.2 ISOTOPIC DATA**

Nine samples were collected from the ice block of Ledena Pit alongside a vertical ice profile in 1995. Tritium concentration and stable isotope composition of the samples were analysed. Regarding their tritium activity samples from -30 and -40 m were determined as inactive and the highest activity was found at 3m depth (Horvatinčić 1996, Horvatinčić & Krajcar-Bronić 1998).

Stable oxygen and hydrogen isotopic ratios were also measured in the collected cave ice samples. Stable isotope data ranged from -6.74‰ to -10.25‰ and from -50.3‰ to -67.9‰ (vs. VSMOW), for  $\delta^{18}$ O and  $\delta$ D, respectively (Horvatinčić 1996).



Fig. 2. a) Vertical profile of Ledena Pit (Ledena jama) and b) Vukušić Ice Cave (Vukušić snježnica). Colour lines represent the ice level in different dates (see legend). Characteristic profile where ice level change is determined (results are in Fig. 4) is indicated by the vertical line.

# **2.3 ESTIMATED TRITIUM SERIES OF LOCAL PRECIPITATION AND FITTING TRIALS**

To refine the <sup>3</sup>H-based age scale past tritium concentration of local precipitation was estimated from long-lasting series of near GNIP stations (IAEA 2004).

When monthly values were available for the stations Genoa, Zagreb and Belgrade the weighted average was computed for the location of Ledena Pit. Weights were calculated from the stations' geographical coordinates. Each derived value was involved into a linear regression against the

corresponding measured monthly data of the longest European series for Valentia (Ireland) (Fig. 3a). Applying the regression equation another estimation of precipitation's tritium content for Ledena Pit was calculated (Fig. 3b). The final estimation was derived as completed the interpolated series by the regressed data from Valentia record. Estimated series, finally, covers the period of 1957-1995. Over this period only 8 month missed estimated data we are convinced that these gaps hardly have any significant effect on the further analysis. Subannual variability was filtered by 13-month moving average.

As original descriptions had not reported about melt related stratigraphic marks (e.g.: mud layer) from the ice profile (Horvatinčić 1996, Jelenić et al. 2001) continuous deposition was assumed. Three different trials were calculated assuming constant ice growth and locating the 1963-peak at i) 3.25 m ii) 3.5 m and iii) 3.75 m below the 1995 ice surface.



Fig. 3. Estimated past tritium concentration of the atmospheric precipitation at Ledena Pit. a) Linear regression between corresponding monthly data of interpolated (in the Genoa-Zagreb-Belgrade triangle) tritium concentration of precipitation at Ledena Pit (Tritium GZB) and Valentia from 1976-1995 period. b) Time series of estimated tritium concentration of precipitation at Ledena Pit.

#### **3. RESULTS AND DISCUSSION**

#### 3.1 ICE LEVEL CHANGES IN VUKUŠIĆ ICE CAVE AND LEDENA PIT

Cave map of Vukušić Ice Cave presents higher ice level from 1996 than the ones were recorded before and after this date (Fig. 2b). However this condition is probably biased due to the intra-annual variability of cave ice dynamics. The well-marked snow slope at the entrance evidences that the 1996-survey must conducted at an early stage of the annual cycle of cave ice evolution, so this level is presented (Fig. 2b) but not regarded when the long-term change was determined (Fig 4).

Morphological evidences and archive data from previous surveys suggest that both ice blocks have shrunken over the past decades. Ice surface decreased by  $\sim$ 0.2 m in Vukušić Ice Cave and by  $\sim$ 9 m in Ledena Pit since 1962. However the ice loss trend was not constant during this time. It seems to become more moderate over the last decade in Ledena Pit (Fig. 4).



Fig. 4. Decrement history of ice in the two studied Croatian ice caves between 1962 and 2007. Data are presented on different y-axes due to the large difference in the range of ice level changes between the two caves.

#### **3.2 TRITIUM OF ICE DEPOSIT IN LEDENA PIT**

For evaluation we used tritium data of ice deposit in Ledena Pit (Horvatinčić 1996, Jelinić et al. 2001). Similarly to previous evaluation we applied 1963 as the date of <sup>3</sup>H bomb-peak the Northern Hemispheric precipitation (see recent review by Fourré et al. 2006).

The age of each sample was estimated in each trial by assuming a constant growth rate (Fig. 5).

In the first case (Fig. 5a) the lowest sample with detectable tritium content dated to 1946 and in the second case (Fig. 5b) it is dated to 1949. As the natural level of tritium in the precipitation in Central Europe was around 5 TU (Roether 1967) the absolute value of the tritium concentration of this sample  $(12.4\pm2.4 \text{ TU})$ argues for an anthropogenic origin. In addition, the first thermonuclear weapon detonation had been established in late 1952, the major deposition of anthropogenic released tritium has started only in 1953 in Europe (Eriksson 1965). These arguments suggest that first two model (Fig. 5 a,b) overestimate the age of this sample. The third model dates the lowest sample with detectable tritium content to 1952 which means still a little bit old age but agrees much better to the observations (Eriksson 1965). The other points are also best fitted to the tritium-curve in this third case, except the sample originated from the 0.05-0.25 cm depth below the surface which shows a surprisingly low value. This value is obviously lags behind the level of tritium concentration of the contemporary precipitation. To ascertain the validity of this pattern control measurement is recommended.

# **3.3 NEW ESTIMATIONS ABOUT THE AGE OF ICE IN LEDENA PIT**

Assuming that the <sup>3</sup>H-bomb-peak was at 3.75 m below the 1995 ice level we can calculate the mean ice accumulation rate ( $r_{acc}=12 \text{ cm a}^{-1}$ ). The lowermost ice layer (-40 m) can be dated to 333 year-old applying  $r_{acc}$ .

Thus we must to take into account that historical cave maps documented 8.8 m lowering of the cave ice surface over the period of 1962-1996. Determining the proportional lowering for the 1963-1995 period 8.65 m was derived.



Fig. 5. Comparison of the tritium data of cave ice samples in Ledena Pit and the series of estimated past tritium concentration of local precipitation. Thick blue line (13-months moving average) gives emphasis to the interannual variability. Constructed graphs follow three different assumption of the position of 1963bomb-peak below the 1995 ice surface: a) 3.25 m; b) 3.5 m; c) 3.75 m

These data suggest that despite the strong surface ice melt (8.65 m), which is evident from the old maps, significant ice accumulation (3.75 m) could take place between 1963 and 1995. These data are in contradiction (ice melting and ice accumulation in the same time at the same site) for the first glimpse; however a fast basal melting process can solve this contradiction. Based on these data basal melting rate is determined as  $r_{bm}=38 \text{ cm a}^{-1}$  (=(865+375)/(1995-1963)). This value is significantly higher than published basal melting values from Scărișoara Ice Cave (1.54 cm a<sup>-1</sup>: Racovița & Crăciun 1970, Perșoiu 2005) and Monlési Ice Cave (8±2 cm a<sup>-1</sup>: Luetscher et al. 2007). The large difference might be explained by the different settings of the ice block in Ledena Pit and in Monlési or Scărișoara Ice caves. The latter ones are sitting on the cave floor, so basal melting might be dominated by the geothermal heat flux. However, basal part of Ledena Pit ice deposit, in contrary, is extremely exposed to circulation processes of the cave atmosphere and the ablation might extremely amplify the basal melting rate. Collecting direct experimental evidences for magnitude of present basal melting rate is in progress (see 4. Conclusions and Future work)

Until first results from direct measurements about

basal melting in Ledena Pit become available we must rely on the above calculated  $r_{bm}$ . In possess of this estimation of  $r_{bm}$  mass turnover rate of the 40 m thick ice deposit can be determined to 105 years. Mass turnover rate is rough estimation for the age of lowest layer of cave ice deposit (Luetscher et al. 2007).

A plausible explanation for the large difference between  $r_{acc}$  and  $r_{bm}$  based estimation can be that  $r_{acc}$ presents ice accumulation exclusively for the 1963-95 period, while the lower part was deposited by a more rapid rate which is better approximated by the  $r_{bm}$ .

Presented new age estimation of the lowermost ice layer of Ledena Pit resulted in younger age than previous estimation of cca 500 years based on radiocarbon dating derived from a wood branch picked out from the ice (Horvatinčić 1996, Jelenić et al. 2001). Although, with 1 sigma error of <sup>14</sup>C result (100 yr) the difference is not significant.

# **3.4 STABLE ISOTOPES IN THE LOCAL PRECIPITATION AND THE CAVE ICE**

The  $\delta^{18}$ O and  $\delta$ D values in precipitation at Zavižan range from -16.5% to -2.82%, and -118.4% to -24.9% (Fig. 6) (Horvatinčić et al. 2005). The weighted annual  $δ^{18}$ O-δD mean values are (-9.42‰, -62.9‰) for Sep. 2000-Aug. 2001, (-9.46‰, -63.0‰) for Sep. 2001-Aug. 2002, and (-10.84‰, -69.4‰) for Sep. 2002-Aug. 2003. The mean values of the third period show significant offset from the first two periods to more negative values. This can refer to relatively high variability of annuals mean values. The weighted  $\delta^{18}$ O and  $\delta D$  mean values of the three annual mean values are -9.83‰ and -64.7‰. Because of the high interannual variations, this three-year mean has uncertainty when it is regarded as a representative mean value of a longer period of time. This uncertainty is indicated on the Fig. 6 by the error bars (light blue).

Using the monthly data the local meteoric water line (regression line) is  $\delta D=7.17*\delta^{18}O+6.74$ . But if we neglect the two outlying data (see the two red symbols on the inset graph of Fig. 6), which are rather far away from all the other data, we get a local meteoric water line of  $\delta D=8.00*\delta^{18}O+16.01$ . The difference between the two water lines is significant. The two outlying data are far under the water line and may indicate a significant evaporation effect. It can be natural (in one case the amount of precipitation was very low, 10.4 mm), or although less likely, it can be an artefact due to some evaporative enrichment of the sample before measurement. In any case these data are not characteristic, so we eliminated them and regard the second calculated meteoric water line as the Local Meteoric Water Line. It is worth noting that while the slope (8.00) of this LMWL is identical with the Global Meteoric Water Line (GMWL,  $\delta D=8*\delta^{18}O + 10$ , Craig 1961), the constant value is definitely higher, 16 vs. 10, clearly indicating the Mediterranean effect (Vreča et al. 2006).

The lower slope of ice water line ( $\delta D=5.48*\delta^{18}O$ -11.79) implies a process affecting the isotopic composition of ice in a non-equilibrium manner. This process can be partial melting (O'Neil 1968) or sublimation (or both), where the isotopically lighter fluid or gas phases leave the system, resulting in positive shift of delta values of the remaining ice. Hower the number of cave ice samples is limited (9) and further data may improve or modify the model of ice formation described above.

The intercept of LMWL and the cave ice water line ( $\delta^{18}O = -11.03\%$  and  $\delta D = -72.2\%$ ) is more negative than the multi-annual mean value of precipitation at Zavižan (Fig. 6). (This statement is valid even if we use local meteoric water line fitted to the entire data set; in this case  $\delta^{18}O = -10.96\%$  and  $\delta D = -71.7\%$ ). The difference clearly indicates that the precipitation of the winter half year plays more dominant role in the ice formation than the summer half year, as it is expected. This re-evaluation confirms prior results based on the comparison with Zagreb precipitation (Horvatinčić 1996).



Fig. 6. Black line: local meteoric water line of the Zavižan precipitation for the Sept, 2000-Dec, 2003 period (Sep, 2003 is missing). Light blue: multi-annual mean isotopic composition of the Zavižan precipitation for three complete annual cycle (Sept, 2000-Aug, 2003); error bars indicate the range of fluctuation of annual means during this period. Dark blue: water line derived from nine ice samples investigated from Ledena Pit. Inset graph shows the meteoric water line excluding the two most deviating data of Aug-Sept, 2001 (red).

As the above mentioned ice melting happens in summertime the lower amount of summer rainfall surely does not contribute to ice formation. Presumably the degree of isotopic enrichment caused by partial melting is related to the summer climate conditions.

#### 4. CONCLUSIONS AND FUTURE WORK

Reconstructed cave ice levels of two Croatian ice caves (Ledena Pit and Vukušić Ice Cave) pointed out that the ice caves of the Velebit Mts suffered similar ice volume loss over the past five decades like other ice caves around different part of the world. Ice surface decreased by ~0.2 m in Vukušić Ice Cave and by ~9 m in Ledena Pit since 1962. However some fluctuations are behind this long-term ice loss trend. Ice volume decrease seems to become more moderate over the last decade in Ledena Pit and ice accumulation was also reported in the neighbouring Lukina Pit (Lukina jama). Further research is needed to understand the controls of cave ice dynamics of the ice caves of the Velebit Mts and decide about the degree of risk in the predicted future change (IPCC 2007).

The position of the tritium peak (1963) was probably at 3.75 m (or even deeper 3.75-4 m) below the 1995 surface. The mean ice accumulation rate could be determined ( $12 \text{ cm a}^{-1}$ ) for the 1963-1995 period. The basal melting rate for the same period was estimated as  $38 \text{ cm a}^{-1}$ .

The new dataset of the local precipitation provided the re-evaluation of the stable isotopic data derived from cave ice of Ledena Pit during the mid-1990s. The relatively low slope of ice water line suggests that partial melting or sublimation affected the isotopic composition of the ice. The intercept of LMWL and the cave ice water line is more negative than the multiannual mean value of the local precipitation. This difference indicates that the winter half year precipitation plays more dominant role in the ice formation than the rain of summer half year.

To scrutinize and quantify the present dynamics of

cave ice we have installed scales into the surface of the ice block. In addition, the plastic nets were placed on the ice surface in both caves in November 2007. These equipments will serve artificial reference horizons in future monitoring of cave ice dynamics.

As a future work we plan:

- high resolution sampling alongside both ice profiles for radiochemical and stable isotopic analysis.

- tree rings based investigations (e.g., ring width, stable isotopic analysis) on samples collected from the surrounding forests (*Fagus sylvatica, Picea abies*) and from the ice deposits.

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