



## Abstract

A 5.28 m long ice core was extracted from the major cave ice block of the Mammuthöhle cave system. Tritium concentration in eight samples from the upper 1.2 m of the core was measured. Electrical conductivity measurements were achieved on molten water samples and stable oxygen and hydrogen isotopic compositions were also analysed. The upper ~1.2 m of ice has been deposited from precipitation fallen before the 1960s (based on tritium <8.5 TU). The Saarahalle ice block is build from atmospheric precipitation and the water perfectly preserved the isotopic composition; however the mean  $^{18}\text{O}/^{16}\text{O}$  ratio of the ice is less depleted compared to the long-term (1973–1983)  $^{18}\text{O}/^{16}\text{O}$  ratio of precipitation at Feuerkogel the nearest (~32 km) reference station situated in the same elevation like Mammuthöhle cave. Characteristic fluctuation was observed in the conductivity along the studied cave ice profile. The conductivity oscillations seem to mirror the changing partition of karstic water and surface meltwater in the water supply of the ice accumulation. The ice layers with low conductivity seem to archive past events when more meltwater-like water have been drained and frozen onto the ice block.

## 1 Introduction

Mid-latitude glaciers are well known archives of past environmental conditions (e.g. Wagenbach, 1989; Schwikowski, 2004). Traditional methodological protocols favours glaciated terrains located in the dry firn or cold percolation zones with relatively high accumulation rates. Due to the basic glaciological constraints the available time span of these mid-latitude records proved to be severely limited and recently the research interest of ice core studies are to explore previously avoided low-accumulation environments (Wagenbach and Spötl, 2010) like miniature ice caps (Haeberli et al., 2004) or perennial cave ice accumulations (Claussen et al., 2007; Holmlund et al., 2005; Turri

TCD

4, 1449–1465, 2010

## Isotope hydrological studies on the perennial ice deposit of Saarahalle

Z. Kern et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

et al., 2009; May et al., 2010). Mammuthöhle is one of those Alpine ice caves where significant well laminated perennial ice accumulations exist.

The length of all passages in Mammuthöhle amounts to more than 65 km, and the vertical extension is 1207 m (HOEHLE 2010) which makes it the third longest and fifth deepest cave in Austria. The host rock is Upper Triassic Dachstein Limestone Formation. The genesis of Mammuthöhle cave system seems to be very complex (Plan and Xaver, 2010), but the large phreatic parts (rooms and tunnels) are believed to have formed ~10 Ma ago (Frisch et al., 2002).

Two chambers host major ice deposits, namely, Feenpalast and Saarahalle. Saarahalle ice block is the larger one with an estimated maximum ice depth of ~6–7 m (Behm and Hausmann, 2008). The ice level shows steady decrease since 1996 by a roughly constant rate of 7 cm yr<sup>-1</sup> (Mais and Pavuza, 2000). Following the process based classification of alpine ice caves (Luetscher and Jeannin, 2004) this cave ice system can be classified as dynamic cave with congelation ice.

The main scopes of this short paper are:

- To find explanation of the reflector horizons detected in Saarahalle ground penetrating radar (GPR) sections (Behm and Hausmann, 2008). Our hypothesis was that clay or cryogenic calcite layers cause the reflection.
- To explore the origin of the water formed the Saarahalle perennial cave ice deposition.
- To evaluate the potential of this cave ice deposit in palaeoclimatological/palaeoenvironmental studies.

## Isotope hydrological studies on the perennial ice deposit of Saarahalle

Z. Kern et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## 2 Materials and methods

### 2.1 Ice drilling

We have extracted a shallow ice core from the ice block of Saarahalle, using a manual drilling equipment, on the 1 September 2009. The location of the drill site was chosen by the aid of Ground Penetrating Radar (GPR). Several profiles were measured prior to drilling and the place with the maximum thickness of the ice cover was chosen. The drilling sites were positioned on the flat surface of the ice block where GPR sounding suggested 6 m ice thickness and interesting internal structure (i.e. characteristic reflection horizon) (Hausmann and Behm, 2010). The 5.28 m long core ( $\text{\O} = 3$  cm) was sectioned into 105 subsamples labelled from MH1 to MH105, starting from the surface of the ice body, each subsample's length being  $\sim 5$  cm. Each subsample was put into a dry, clean and sterile 120 ml plastic bag sealed and collected into insulated box and kept frozen until transported to the laboratory. In the laboratory all samples were left to melt completely to affirm the isotopic homogeneity of the samples, and then 12 ml water was pipetted into glass vials and stored in refrigerator for stable isotope analysis. The rest of the sample was transported to tritium concentration and electrical conductivity measurement. The level of the ice was anchored before the coring procedure and all depth data is referred, uniformly, as depth below the 1 September 2009 ice surface.

The drilling penetrated the characteristic reflector zone but no any major clay or cryogenic calcite horizon has been observed in the core. So we had to reject the above mentioned hypothesis about the potential origin of the reflection in the GPR profile.

### 2.2 Tritium measurements

Tritium activities were measured on water melted from eight non-neighbouring samples (MH1, MH4, MH8, MH10, MH13, MH16, MH19, MH22) using liquid scintillation counting (LSC) technique. Water samples were distilled before LSC measurements to minimize quenching (Svetlik and Budska, 2001). 10 mL of distilled water sample was

TCD

4, 1449–1465, 2010

## Isotope hydrological studies on the perennial ice deposit of Saarahalle

Z. Kern et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



mixed with 10 mL of Ultima Gold LLT cocktail in a low-diffusion PE-vial and measured by a Wallac 1220 Quantulus (Perkin Elmer) ultra low level liquid scintillation spectrometer at the Institute of Nuclear Research HAS. Measuring time was 750 min per sample, resulting a critical level (LC) of 8.5 TU (tritium unit, 1 TU is  $0.1183 \text{ Bq L}^{-1}$ ) (Curie, 1995).

5 The LC was fairly high as there was not possible to apply electrolytic enrichment due to the small sample amount.

### 2.3 Electrical conductivity

Specific electrical conductivity (EC) was measured on melted water samples at the Institute of Nuclear Research, HAS at a constant  $24.5^\circ\text{C}$  temperature using LABCOR  
10 Consort C533 instrument. Results are reported in  $\mu\text{S cm}^{-1}$ .

### 2.4 Stable isotope analysis

Stable oxygen and hydrogen isotope measurements were carried out according to the ideas of  $\text{CO}_2\text{-H}_2\text{O}$  equilibration (Epstein and Mayeda, 1953) and  $\text{H}_2\text{-H}_2\text{O}$  equilibration by Pt-catalyst (Posser and Scrimgeour, 1995). The equilibrated  $\text{CO}_2$  and  $\text{H}_2$  gases  
15 were measured by a Finnigan delta plus XP mass spectrometer in continuous flow mode at the Institute for Geochemical Research, HAS.

Stable isotope compositions are expressed in the conventional delta notation (McKinney et al., 1950):

$$\delta = (R - R_{\text{std}}) / R_{\text{std}} \times 1000 \text{ [‰] VSMOW,}$$

20 where  $R$  and  $R_{\text{std}}$  are  $^{18}\text{O}/^{16}\text{O}$  or  $^2\text{H}/^1\text{H}$  ratios in the sample and the standard (Vienna Standard Mean Sea Water = VSMOW), respectively. Two-point linear normalization was applied to determine the final results (Paul et al., 2007). The uncertainties of the stable isotope data are  $\pm 0.2\text{‰}$  and  $\pm 2.0\text{‰}$  for oxygen and hydrogen, respectively.

## Isotope hydrological studies on the perennial ice deposit of Saarlhalle

Z. Kern et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## 2.5 Isotopes in precipitation

Data of nearby stations of the ANIP (Austrian Network of Isotopes in Precipitation) (Humer et al., 1995) have been used as reference for the isotopic characteristics ( $\delta D$ ,  $\delta^{18}O$ ,  $^3H$ ) of the local/regional precipitation. Selected stations were Salzburg, Feuerkogel and Golling (Fig. 1). In addition, the monthly mean tritium concentration of past precipitation at Vienna was extracted from the ISOHIS database (IAEA, 2004). Decayed tritium activity was calculated for the date of measurement of cave ice samples using the half-life as 12.32 years (Lucas and Unterweger, 2000).

## 3 Results and discussion

### 3.1 Tritium data

Serial  $^3H$  measurement is a powerful tool to date cave ice deposited from precipitation of the past ~60 years (Horvatinčić, 1996; Horvatinčić and Krajcar-Bronić, 1998; Kern et al., 2009a). However in the present case tritium activity of each measured sample was below the detection limit (8.5 TU) of the applied method. Keeping in mind that Saarlhalle ice block has suffered continuously negative mass balance since 1996 by  $\sim -7 \text{ cm yr}^{-1}$  rate (Mais and Pavuza, 2000). This fact not only excludes the existence of recent deposits at the ice surface but the cumulated erosion takes 91 cm thick ice loss through the past 13 years. At this point two theories can be tested. Assuming that the average accumulation rate was relatively low, for instance  $1 \text{ cm yr}^{-1}$ , in the period before the recently observed erosion, it means that 91 annual cycles have been erased by the recent melting. Therefore the uppermost layer cannot be younger than 1905(=1996–91). We must take into account that anthropogenic tritium appeared in the European precipitation from ~1953 (Eriksson, 1965) and before that event the natural level of tritium in the precipitation in Central Europe was around 5 TU (Roether, 1967); which have decayed to  $\sim 0.1$  TU level. This model suggests that there is hardly

## Isotope hydrological studies on the perennial ice deposit of Saarlhalle

Z. Kern et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



found any ice with  $^3\text{H}$  activity exceeding the 8.5 TU level and the measurement results agree this model.

Alternatively, we can assume that the average accumulation rate was high, for instance ten times higher ( $10\text{ cm yr}^{-1}$ ) than in the first theoretical experiment. In this case only 9–10 annual layers should have been eroded since 1996. Thus the top-most layer might be  $\sim 1986 (= 1996 - 10)$  and the upper 1.2 m of the record should reach back to  $\sim 1974$ . Compared the inferred limit (8.5 TU) of actual cave ice activity to the decay-corrected time series of past precipitation of Salzburg, Feuerkogel and Vienna it is evident that all precipitation fallen between  $\sim 1961$  and 1981 should still exceed the 8.5 TU activity level (Fig. 2). So each sample between MH10 and MH22 should have contained tritium above the actual detection limit. The obvious contradiction gives credence to the first theory and we reckon that the uppermost ice layer of the core has been deposited from precipitation fallen before the 1960s.

### 3.2 Stable water isotopes

Data for stable water isotopes are available of 84 samples for  $\delta^{18}\text{O}$  and of 79 samples for  $\delta D$ . Stable isotopic data of the cave ice samples ranged from  $-12.95\text{‰}$  to  $-9.50\text{‰}$  and from  $-92.8\text{‰}$  to  $-66.2\text{‰}$  (vs. VSMOW) for  $\delta^{18}\text{O}$  and  $\delta D$ , respectively. The  $\delta^{18}\text{O}$ - $\delta D$  plot mirrors the well known strong correlation as a distinctive feature of atmospheric precipitation (Craig, 1961). In addition the equation of the fitted regression line (so-called water line) is almost identical with precipitation collected at the nearby Golling (Fig. 3). This suggests that Saarhalle ice block is build from water originated from the precipitation; in addition the water perfectly preserved the isotopic composition of local atmospheric precipitation. The close agreement between the cave ice water line and the local meteoric water line suggests an absence of any complex kinetic isotopic fractionation process affecting precipitation before it aggregated into the Saarhalle ice block. This indicates that there may be a climate signal in the cave ice isotopes (Fórizs, 2005; Perşoiu et al., 2007).

## Isotope hydrological studies on the perennial ice deposit of Saarhalle

Z. Kern et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Isotope hydrological studies on the perennial ice deposit of Saarahalle

Z. Kern et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Feuerkogel station is situated almost at the same altitude as Mammuthöhle and their distance is ~32 km hence this station can be regarded as the nearest perfect reference for Mammuthöhle site. The average stable isotopic composition of the cave ice (−10.9‰) is clearly less depleted than the long-term (1973–1983) amount-weighted annual mean  $\delta^{18}\text{O}$  value of Feuerkogel (−12‰) precipitation. Similar observations are reported from many ice caves (e.g. Claussen et al., 2007; F6r1rzs et al., 2004; May et al., 2010; Per6oiu et al., 2007) however it is not a general rule because cave ice sometimes comparable or more depleted than the mean annual precipitation (e.g. Yonge and McDonald, 2006; Luetscher et al., 2007; Kern et al., 2009b).

Two hypotheses are addressed as potential explanation for the well preserved water line and the remarkably less depleted isotopic ratios of the Saarahalle cave ice.

- (1) infiltrating precipitation might have evaporated under almost saturated conditions (i.e. Relative humidity > 95%) in the karstic fissures so the fractionation is undistinguishable from the equilibrium. The vapour probably left the system for instance as precipitated in a different part of the cave.
- (2) biased seasonality could also explain the difference, inasmuch as the winter season precipitation cannot take full part in the ice accumulation. A plausible reason could be that larger fraction of the melting snow runoff during spring. As a consequence the characteristically more depleted winter precipitation cannot contribute to the annual infiltration equally with its contribution to the annual precipitation.

Detailed monitoring on infiltration and ice formation process surely help to find the more probable explanation.

### 3.3 Conductivity data

EC values ranged from 39.6 to 220  $\mu\text{S cm}^{-1}$ . EC showed less variability over the upper 1.3 m of the core and in the section below 3.3 m. In contrast, EC presented large fluctuation in between. It is interesting to compare this fluctuation range with some reference data of the regional stream water and cave dripwater (Fig. 4).

EC was reported to range between 15 and 95  $\mu\text{S cm}^{-1}$  at two meltwater streams from the Austrian Alps measured over two years (2001–2002) (Krainer et al., 2007). In the case of dripwater the multiannual monitoring project of the Obir Cave (Karawanken Mts) could provide a potential reference (Spötl et al., 2005). The range of fluctuation of cave dripwater monitored at three dripsites over five years (1999–2003) ranged between  $\sim 220$  and  $300 \mu\text{S cm}^{-1}$ .

EC from the cave ice generally placed between the reported conductivity range of surface waters and cave drip waters. The measured EC maxima from the cave ice are similar to the lower boundary of the range of dripwaters. The EC minima of the cave ice wander around the highest boundary of surface meltwater but occasionally enter into the range of meltwater streams. The more and less variable sections observed on the conductivity profile can be explained as more pronounced karstwater dominance at the lower part of the ice deposit, some intermittent episodes of surface water dominance over the middle section and lack of this episodes near to the surface.

Worth mentioning that the EC values obtained from a similar research from the cave ice of Eisriesenwelt (Tennengebirge Mts, Austria) (May et al., 2010) are similarly variable but characteristically lower. This suggests some discrepancy in the karst-water/surface water partition in the cave ice accumulation between the two ice cave systems.

## 4 Conclusions

Stable oxygen, hydrogen isotopic composition, tritium concentration and electrical conductivity were analysed on a 5.28 m long ice core extracted from the ice block of Saarhalle chamber in the Mammuthöhle cave, Austria.

Basic results are:

- (1) The upper  $\sim 1.2$  m of ice and the uppermost ice layer has been deposited from precipitation fallen before the 1960s (based on tritium  $< 8.5$  TU).

TCD

4, 1449–1465, 2010

## Isotope hydrological studies on the perennial ice deposit of Saarhalle

Z. Kern et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Isotope hydrological studies on the perennial ice deposit of Saarhalle

Z. Kern et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

(2) The Saarhalle ice block is build from water originated from the precipitation, in addition the water perfectly preserved the isotopic composition of local atmospheric precipitation as shown by its water line ( $\delta^{18}\text{O}$ - $\delta D$  plot), however the isotopic composition compared to the long-term (1973–1983) mean  $\delta^{18}\text{O}$  composition of precipitation at Feuerkogel is relatively enriched. This challenges the interpretation of fluctuation in this cave ice water isotope record.

(3) Electrical conductivity data presented intermediate values between surface waters and cave drip waters. The conductivity oscillations seem to mirror the changing partition of karstic water and surface meltwater in the water supply of the ice accumulation. The ice layers with low conductivity seen in middle section of the cave ice deposit seem to archive past events when more meltwater-like water have been drained and frozen onto the ice block.

The potential of this cave ice deposit for palaeoclimatological study is still a matter of debate. The age determination of the deposit and dating of the events is still a challenge. We will try tritium dating applying the  $^3\text{H}$ - $^3\text{He}$  ingrowth method (expected detection limit  $\sim 0.1$  TU) (Palcsu et al., 2010).

The correlation of GPR profile (Hausmann and Behm, 2010) with conductivity and stable isotope profiles is also an exciting future task.

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### Isotope hydrological studies on the perennial ice deposit of Saarahalle

Z. Kern et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Isotope hydrological studies on the perennial ice deposit of Saarlhalle**

Z. Kern et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Holmlund, P., Onac, B. P., Hansson, M., Holmgren, K., Mörth, M., Nyman, M. and Perşoiu, A.: Assessing the palaeoclimate potential of cave glaciers: the example of Scarişoara Ice Cave (Romania), *Geogr. Ann.*, 87A, 193–201, 2005.

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**Isotope hydrological studies on the perennial ice deposit of Saarlhale**

Z. Kern et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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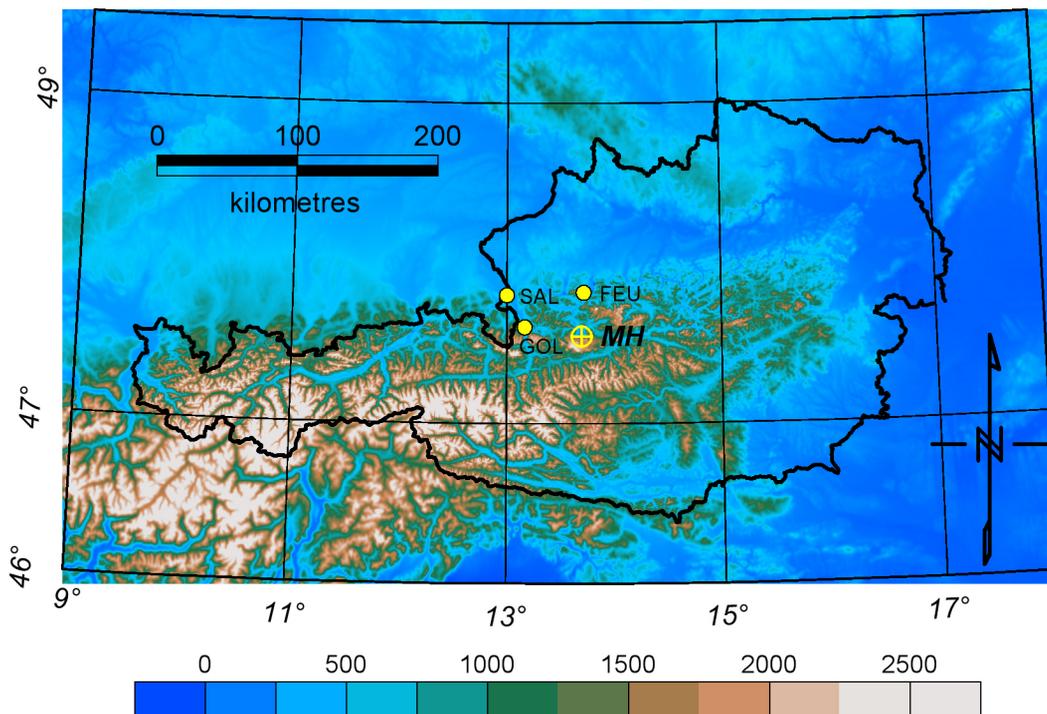
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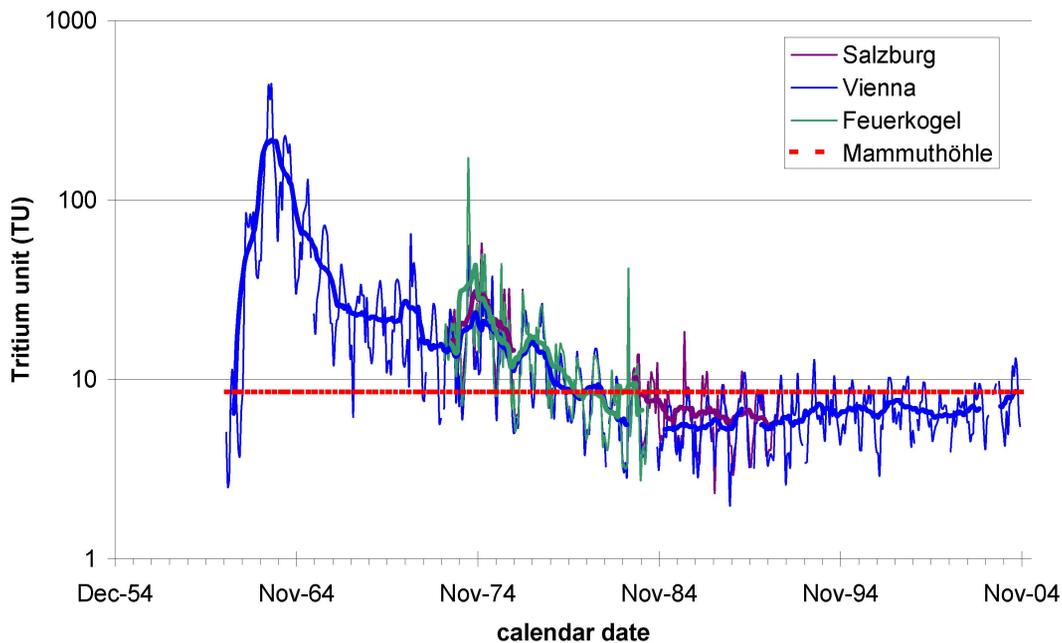


**Fig. 1.** Location of Mammuthöhle and the reference stations mentioned in the text. MH – Mammuthöhle, SAL – Salzburg, GOL – Golling, FEU – Feuerkogel.

**Isotope hydrological studies on the perennial ice deposit of Saarhalle**

Z. Kern et al.

|                          |              |
|--------------------------|--------------|
| Title Page               |              |
| Abstract                 | Introduction |
| Conclusions              | References   |
| Tables                   | Figures      |
| ◀                        | ▶            |
| ◀                        | ▶            |
| Back                     | Close        |
| Full Screen / Esc        |              |
| Printer-friendly Version |              |
| Interactive Discussion   |              |



**Fig. 2.** Decay-corrected tritium activity of past precipitation of Feuerkogel (green), Salzburg (purple) and Vienna (blue). Thin lines show the fluctuation of monthly values, thick lines (12-month moving average) emphasize the annual variability. Dashed horizontal red line denotes the 8.5 TU level.

**Isotope hydrological studies on the perennial ice deposit of Saarhalle**

Z. Kern et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

⏪ ⏩

◀ ▶

Back Close

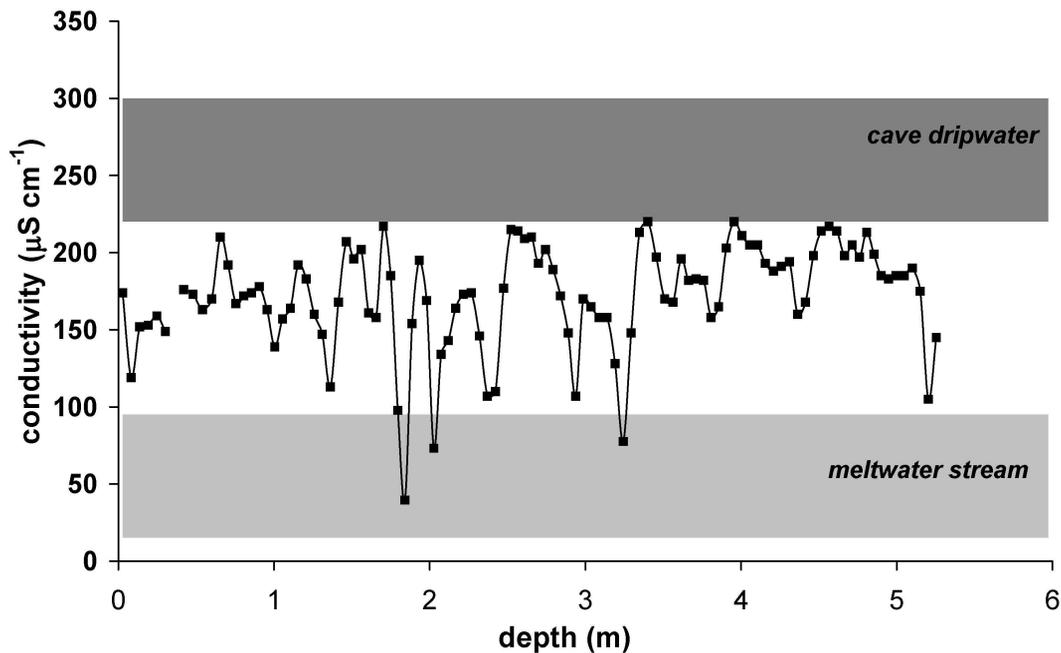
Full Screen / Esc

Printer-friendly Version

Interactive Discussion







**Fig. 4.** Electrical conductivity profile of the ice core (black line) The light gray band shows the range of fluctuation of two meltwater streams from the Austrian Alps measured over two years (2001–2002) (Krainer et al., 2007). The dark grey band shows the range of fluctuation of cave dripwater monitored at three dripping sites over five years (1999–2003) (Spötl et al., 2005).

**Isotope hydrological studies on the perennial ice deposit of Saarhalle**

Z. Kern et al.

|                          |              |
|--------------------------|--------------|
| Title Page               |              |
| Abstract                 | Introduction |
| Conclusions              | References   |
| Tables                   | Figures      |
| ⏪                        | ⏩            |
| ◀                        | ▶            |
| Back                     | Close        |
| Full Screen / Esc        |              |
| Printer-friendly Version |              |
| Interactive Discussion   |              |

