Brief communication: Tritium concentration and age of firn accumulation in ~~an~~ an ice ~~caves~~cave of Mt. ~~Olympos~~Olympus (Greece)

Georgios Lazaridis[1,*], Konstantinos Stamoulis[2,*], Despina Dora[1], Iraklis Kalogeropoulos[3], Konstantinos P. Trimmis[4]

[1]School of Geology, Aristotle University of Thessaloniki, Thessaloniki 54124, Greece
[2]Physics Department, University of Ioannina, Ioannina, 45221, Greece
[3]Hellenic Speleological Society, Thessaloniki, 54124, Greece
[4]Department of Anthropology and Archaeology, University of Bristol, Bristol, BS8 1TH, England
*These authors contributed equally to this work

Correspondence to: Georgios Lazaridis (geolaz@geo.auth.gr)

Abstract. Firn from an ice cave in the highest mountain of Greece, Mt. ~~Olympos~~Olympus, was sampled and analysed to determine the tritium content in order to estimate rates of accumulation and to date the ice plug. The presence of a sharp ~~raise of~~ tritium peak content ~~because of~~indicating the nuclear testing era was expected to be preserved into ice beds. Tritium concentrations were found to vary from 0.9 to 11 TU. This peak did not appear in the analysed samples providing an upper age ~~estimation~~limit of less than 50 years. for the oldest sampled layer. It is suggested that the rate of melting is responsible for the absence of older firn layers.

1 Introduction

Ice caves or caves hosting perennial ice accumulations ~~(Persoiu and Lauritzen, 2017)~~(Persoiu and Lauritzen, 2018) in Greece are scattered throughout the country's latitude. In total, 76 records of ice caves in Greece have been processed according to ~~Luetscher and Jeannin (2004)~~Luetscher and Jeannin (2004) classification scheme and examined according to ~~their morphology and distribution by Lazaridis et al. (2018)~~climatological criteria and particularly the prevailing air dynamics and glaciological characteristics, such as the type of ice, by Lazaridis et al. (2018). In Mt. ~~Olympos~~Olympus, which is the highest mountain of the country, all the ice caves are classified as 'static with firn', where 'static' is interpreted as single entrance caves that form single down-sloping conduits. Ice of these caves, particularly the ones on the Eastern slopes of Olympus, ~~have~~has been exploited for years between the end of the 19th ~~centuries~~Century and the ~~post WWII years~~1950s, to provide ice ~~columns~~ to villages and ~~town at~~towns in the foothills of the mountain and across the southwestern Greek Macedonia.

In order to determine how old is the firn accumulation in these caves, measurements of the concentration of tritium in the ice were ~~applied~~carried out at the Christaki Pothole in Mt. ~~Olympos~~Olympus. Tritium is a hydrogen isotope that decays emitting beta particles of very low energy (Emax ~18.6 keV) with a half-life of ~~12.33 y.~~4500 ± 8 days (Lucas ~~&~~and Unterweger, 2000; Ehhalt et al., 2002). Tritium is produced in the upper atmosphere by the interaction of cosmic rays with the atoms of the atmosphere. This mechanism introduces tritium into the water cycle by the form of tritiated water and the normal concentration of tritium in precipitation is found to be 5-10 TU (Tritium Units, 1TU = 0.~~118~~11919 Bq/L, Terzer-Wassmuth et al., 2022).

During late '50s and early '60s nuclear era, hydrogen bomb detonations introduced huge amounts of tritium into the atmosphere, resulting in a sharp peak of tritium concentration in precipitation all over the world (Martell, 1963), especially in the northern hemisphere where tritium concentrations were increased up to 6,000 TU in Canada and Austria, reached in 1963, respectively (Cauquoin et al., 2016). In Greece, a maximum of 3,550 TU was observed also in 1963. The tritium peaks in precipitation of these years (the early 1960s, are expected to be preserved in ice sections, if they have not melted since then. Previous studies have dated ice deposits by using the tritium peak, which was either present (Kern et al., 2009) or absent (Kern et al., 2011).

2 Cave description and geological setting

The cave under investigation (Fig. 1; and supplementary information) is located on the NW slope of Mount Olympus (N40.06898 E22.31350) at an altitude of 2,350 m, very close to the Christaki refuge. The sampling cave is included in the cadaster of ice caves in Greece under the name Christaki Pothole (Lazaridis et al., 2018). The entrance of the pit is about ten meters and continues with the floor inclining to the west. Most of the cave is covered by an ice plug that overlies limestone gravels and small blocks. The ice plug consists of accumulated firn and snow. When surveyed, it was 1.5 m thick below the entrance and progressively thickening westwards, reaching a maximal thickness of 4.5 m. The ice plug prevents any access to the westward continuation of the cave. The cave is hosted in the Cretaceous crystalline limestones with dolomite interferences (Latsoudas and Sonis, 1985). The limestone sequence has a total thickness of about 2,650 m and consists of limestones that gradually transits to dolomite. While the eastern slopes of Olympus are affected by the maritime air masses, the western slopes of Mount Olympus act as a barrier to the hot and humid westerly air masses and thus experience enhanced orographic precipitation. Ice caves in Greece are directly influenced by the prevailing climatic conditions (Perşoiu et al., 2021). The amount of precipitation in combination with the high altitude, leads to snowfalls even during summer season (Sahsamanoglou, 1989).
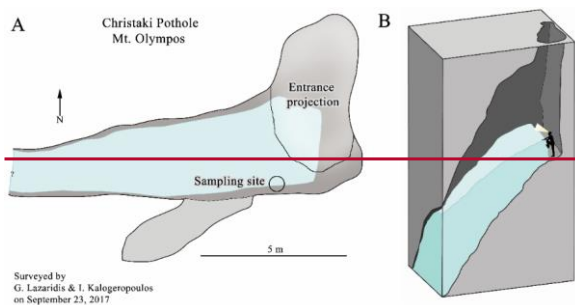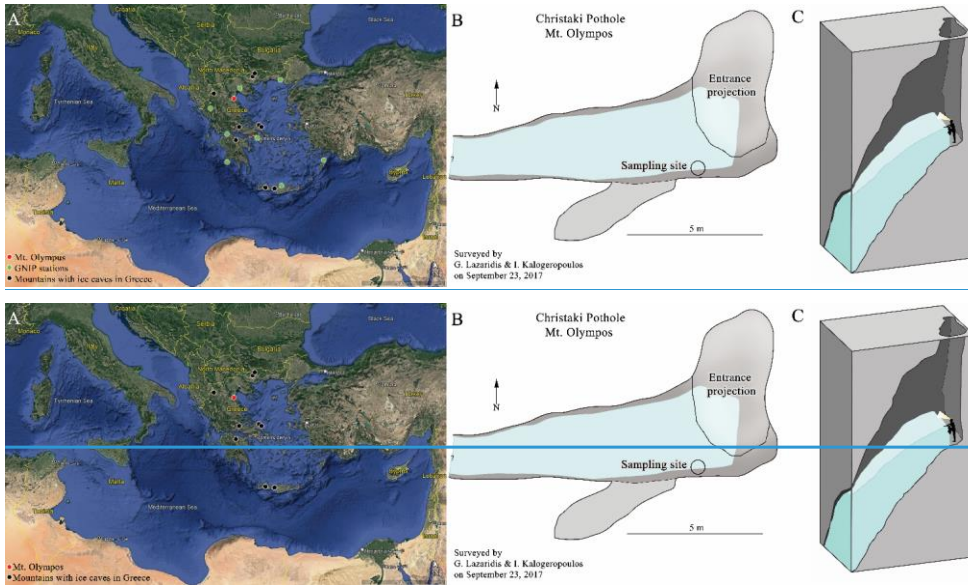
Figure 1. **A.** Location of **Mt. Olympus and** the sampled cave Christaki Pothole; ~~other mountains of Greece with ice caves; tritium~~
60   ~~monitoring stations (GNIP).~~ **B.** Ground-plan with the sampling site depicted and ~~3d~~**3D** representation of the cave. ~~Other mountains~~
~~of Greece with ice caves are depicted on A.~~

3 Sampling and methods

On 23rd of September 2017, forty-one (41) ice samples were collected from the Christaki Pothole. Each sample was collected
from a 2 m high section ~~of ~2 m high,~~(Figure 1B), with a portable cup drill of 5cm diameter and about 2-3 cm depth, resulting
65   in samples of 30 to 40 cm³, ~~in 5cm~~at 5 cm intervals and spanning from the top of the ice ~~column~~section to the cave floor.
Samples with odd numbering were ~~chosen to be measured~~selected for tritium content determination'. Measurements were
performed at the Archaeometry Center of the University of Ioannina.

Tritium measurements were conducted in a Liquid Scintillation Analyzer (TR/SL 3700 Tricarb, Perkin Elmer). ~~Eight ml of~~For
each sample, 8 mL of melted ice ~~sample,~~ without electrolytic enrichment were added in a low-potassium borosilicate glass vial
70   of 20 ml capacity and 12 ml of Ultima Gold LLT scintillation cocktail were added. The vial was closed and shaken to
homogenize the solution and was measured for 1400 min typically. Background was also recorded at the same batch of
samples. In order to establish the detection limit of the method, several background measurements were pooled and a mean
value of 1.200 ± 0.006 cpm were selected as the representative value. The detection limit was calculated using the equation

$DL = \frac{3 \cdot \sigma_B}{eff \cdot V \cdot 60 \cdot 0.11919}$ (TU), where $\sigma_B = 0.006$ cpm is the uncertainty for the background, eff = 0.26 the efficiency of the detector,

75 V= 0.008 L the volume of the sample, 60 for min to sec and 0.119919 Bq/L=1 TU. The calculated value was DL=1.~~1~~2 TU.

4 Results and discussion

~~When extracted from the ice column the samples displayed indistinguishable ice~~The lack of well distinguished layers ~~and thus it was impossible to make a direct~~ precluded the estimation of the age of the ~~ice in the column.~~samples extracted from the ice

deposit, by layer counting. However, during the sample processing ~~the samples~~, it was revealed that almost every ice sample
80 contained remains of dust and soil~~, as a~~ which is the result of the surface debris deposited during the yearly cycle of snow accumulation during winter and partial melting during summer. ~~The ablation of the surface and the burden of each layer caused the incineration of the debris into the ice mass of each layer. Thus, it is suggested that the maximum layer thickness should not exceed that thickness corresponding to about 40 of annual firn accumulations in the ice column where the samples were collected.~~ Since the ~~ice column of the~~ cave ~~is~~ firn deposit was thought to ~~behave~~ been accumulated for many decades ~~of years~~,
85 it was ~~assumed possible to find~~hypothesized that the above-mentioned ~~peak of~~atmospheric tritium ~~raise in the atmosphere as an abrupt increase in the tritium concentration.~~peak would be found in the melted ice samples. Instead, tritium concentrations were found to vary only from 0.9 ~~-~~to 11 TU, which could be attributed to different initial tritium concentrations in ~~snow fall~~snowfall. In comparison with tritium concentrations for selected years before the sampling year (2017), most of the tritium concentrations, corrected for decay, could ~~be resulted~~result from precipitation up to 50 years before sampling year, which
90 corresponds to the calendar year 1967, when the mean annual ~~mean~~ tritium content was in the range of 130-230 TU (Fig. 2, Table S2).
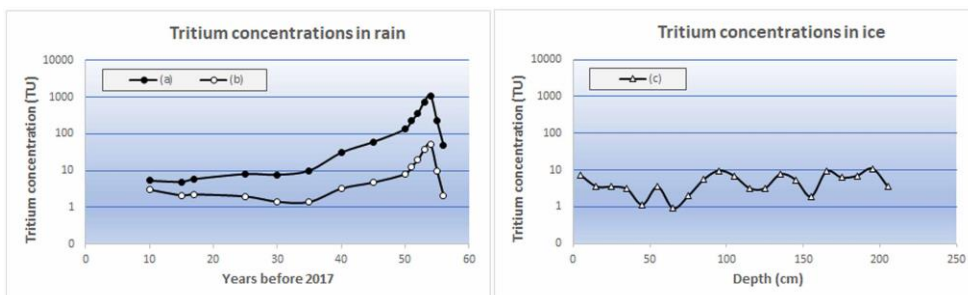
Figure 2. Tritium concentration: (a) Annual mean values of tritium in rain samples from various monitoring stations in Greece (GNIP, IAEA~~).~~, see Fig.1 for the sites of the stations and Table S3 for the coordinates and altitude). (b) Annual mean tritium values
95 **of line (a) corrected for decay at the year of ice sampling (2017). (c) Tritium content in ice samples, of odd numbering, with depth, from the Christaki pothole.**

Also, these measurements could not be attributed to ice beds deposited before the '50s, because in that case higher concentrations remaining from the high tritium concentrations during early '60s should have been preserved into some of the measured samples. This gives an upper limit of the possible age of the ice layers that were sampled during the campaign of September 2017. Considering that for this upper limit of 50 years for the base of ice layers agedeposit, the corresponding mean winter snowice layer thickness of each layer should beis at least 4 cm y^{-1}; the result is in accordance with the presence of debris in almost each sample, as well as with findings in other ice caves. In Monlesi Ice cave, Switzerland, an annual accumulation rate 7-11 cm y^{-1} was estimated based on tritium and radon^{210}Pb measurements (Luetscher et al., 2007)(Luetscher et al., 2007) and in Ledena Pit, a croatianCroatian ice cave, an average accumulation rate of up to 12 cm y^{-1} during period of 1963-1995 was also estimated (Kern et al., 2008)(Kern et al., 2008). However, these estimationsestimates do not date the time when onset of cave glaciation, nor times at which the cave started to function as anmay have been completely ice cave nor to an event of total ice melting in the meanwhile.free. The ice surface thatplug in ice caves melts when it is in contact with the cave wallsbedrock (Bella and floor is melting in non-permafrost areas such as Greece.Zelinka, 2008; Telbisz, 2019). Thus, the results are rather indicative of a melting rate that cannot support the preservation of ice that is older than 50 years. However, in deeper inaccessible parts of the cave older ice may be preserved.

5 Conclusions

The Christaki Pothole provided a two meters thick succession of ice samples that display relatively low concentration of tritium, without any pattern of an abrupt increase that could correspond to the tritium peak due to hydrogen bomb detonations in early '60s. This indicates that accumulated firn beds arewere younger than fifty years beforein 2017. The absence of earlier beds is suggested to be the result of melting rate at the bottom of the ice plug or may occur in ice beds that are not accessible due to the morphology of the Christaki potholePothole.

Data availability

All raw data are provided in the supplementary information.

Competing interests

The authors declare that they have no conflict of interest.

Author contribution

GL initiated the research; GL and KS organized field work and prepared the manuscript with inputs from all authors; KS analysedanalyzed samples; GL and IK surveyed the cave and sampled the ice; LGGL, KS, IK did the field work; DD and KSKT collected information.

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