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GROUND WATER ISOTOPIC INVESTIGATION IN THE AREA OF THE VILLAGE OF MREŽIČKO, KOŽUF MOUNTAIN, REPUBLIC OF MACEDONIA

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A b s t r a c t: This paper represents the results of isotopic investigation conducted on ground water (mineral) in the area of the village of Mrežičko (Kožuf Mountain). A measurement has been made on the water from the spring source of the ground water "Kožufčanka" and on the water from the spring source of the ground water "Izvorska" regarding the presence of tritium (^{3}H), isotopes of oxygen (δ^{18}O) and hydrogen (δ^2H), and the radioisotopes of carbon (^{14}C). The obtained values regarding the presence of isotopes of oxygen and hydrogen indicate that the ground water originates from precipitation. The obtained values regarding the presence of tritium indicate that the water is more than 63 years old, and the obtained values regarding the isotopes of carbon indicate that the spring sources of the ground water date back to the Paleolithic age.

Key words: isotope; hydrogen; tritium; oxygen; carbon

INTRODUCTION

In the investigation regarding the origin and the age of two ground waters as well as their spring sources, radioisotopes of hydrogen, tritium ^{3}H, stable isotopes of oxygen and hydrogen δ^{18}O and δ^2H and radioisotopes of carbon ^{14}C were used.

Tritium (^{3}H) is a radioactive isotope of hydrogen, produced by the interaction of cosmic rays and nitrogen in the layers of the atmosphere. It decays by beta decay reaction releasing low energy E_{max} = 18.6 keV (Theodorson P., 1996). Tritium has a half-life of 4500 ± 8 days (Lucas and Unterweger, 2000). It forms chemical bonds with other elements the same way as hydrogen does. Water as a form of tritium is called tritiated water, symbol $^1H^3HO$ or HTO. The tritium measured today does not fully have cosmic origin. Great amount of this isotope is produced as a result of human impact, during nuclear weapon testing, thus releasing tritium. Nowadays, it is not possible to determine the age of ground water due to the increased amount of tritium. However, this method of dating the age is good for determining the age of ground water. If the ground water does not contain tritium, it is younger than 100 years. If it does not recharge, therefore the spring source is likely to dry up quickly. However, if the water contains certain amount of tritium, that water tank is old and recharging.

Nowadays, tritium is used as tracer for determination of ground water origin and for determination of the mean residence time (MRT) in the underground up to 40 years.

Methods based on the study of this isotope are used in hydrogeology for determination of:

– the mean residence time of water in the underground in the last 40 years, using isotopic-geological models;

– the recharge intensity of the ground water through the zone of aeration;

– ground water recharge by surface accumulation;

– studying the storing and draining of the aquiclude;

– the direction and speed of ground water.

It is very important to know the data for time allocation of tritium in the atmosphere for certain area, as well as the hydrological data (amount of rain, yield of spring sources, effective infiltration,

and rate of evaporation). International Atomic Energy Agency (IAEA) in Vienna regularly publishes data regarding the activity of tritium in precipitation in all the regions world-wide where they have monitoring stations.

Stable isotopes of oxygen and hydrogen $\delta^{18}O$ and $\delta^{2}H$

Stable isotopes of oxygen and hydrogen $\delta^{18}O$ and $\delta^{2}H$ are often used to determine the origin of water. The content of these isotopes is variable due to the processes of fractioning (isotopic separation) caused by the change of their aggregate state (water – condensation or evaporation). The value of $\delta^{18}O$ and $\delta^{2}H$ in precipitation depends on:

– altitude (by increasing the altitude it increases the impact of the light isotopes in precipitation – temperature and pressure effect);

– latitude (by increasing the latitude it increases the impact of the light isotopes in precipitation);

– distance from the sea (so called continental effect), by increasing the distance from the sea it increases the impact of the light isotopes in precipitation;

– season (summer rains are enriched with heavy isotopes compared to the light rains);

– the amount of precipitation (the greater the amount of precipitation, the greater the amount of light isotopes in precipitation);

– evaporation (it increases the amount of heavy isotopes in precipitation).

The ratio of isotopes in water is expressed in correlation to the standard isotopic composition of ocean water at >40 m (SMOW – Standard Mean Ocean Water) of depth.

There is a linear line between $\delta^{2}H$ and $\delta^{18}O$ in precipitation world-wide called Global Meteoric (GMWL – Global Meteoric Water Line).

Radioactive isotopes of carbon ^{14}C (radiocarbon)

There are three isotopes of carbon in nature, ^{12}C (common and stable), ^{13}C (rare and stable) and ^{14}C (very rare and radioactive), which decays into ^{14}N with the β-particle emission. The half-life of the decay is 5.370 years. Isotopes of carbon ^{14}C are formed in higher parts of the atmosphere under the influence of thermal neutrons on the atoms of nitrogen.

Atoms of ^{14}C oxidize to carbon dioxide (CO_2), which is mixed with the existing atmospheric CO_2 afterwards. It is incorporated into living organisms by assimilation. ^{14}C appears in waters as diluted carbon dioxide in hydrocarbonates (HCO_3^-) and in waters with pH > 9 as diluted ion (CO_3^-) in TIC (total inorganic carbon). The carbon in TIC may be determined up to 40.000 years of age. Also, although rainwater contains diluted atmospheric CO_2, thus contains ^{14}C as well, the radioactive carbon in ground water does not originate from atmospheric carbon only. Infiltrated rainwater passing through the layers of the earth dilutes the CO_2 which has biogenic origin and which is formed by organic substances decay in the soil or by assimilation of the roots of plants and microorganisms. Theoretically, the specific activity of the diluted biogenic carbon is 100%, as well as the carbon of the other living things and the atmosphere.

GEOGRAPHICAL AND GEOLOGICAL SETTING

The spring sources of ground water that are subject of this investigation are located near the village of Mrežičko in the volcanic area of Kožuf Mountain. Kožuf area is a big volcanic complex in the southern part of the Republic of Macedonia on the area of the mountain range of Kožuf. According to the geotectonic regionalization of this part of the Balkan Peninsula this complex is in the area of the Vardar zone (Arsovski, 1962).

The Kožuf area, roughly speaking, in the east is divided by the fault zone, which is also the western border of the gabbro-diabase ophiolite complex Demir Kapija–Gevgelija, and in the west is divided by faults structure dividing the Pelagonian massif from the Vardar zone (Janković, et al., 1997) (Figure 1).

The location of this volcanic complex at the transversal zone Kožuf–Kukuš (Arsovski et al., 1984) with the intersection of the Vardar zone indicates central type of volcanism, activated on the tectonic knot, and formed by the reactivated fault structures from the Vardar direction (NW–SI, N–S) and the newly formed fault zone Kožuf–Kukuš (I–W) during the neotectonic period (Figure 1).

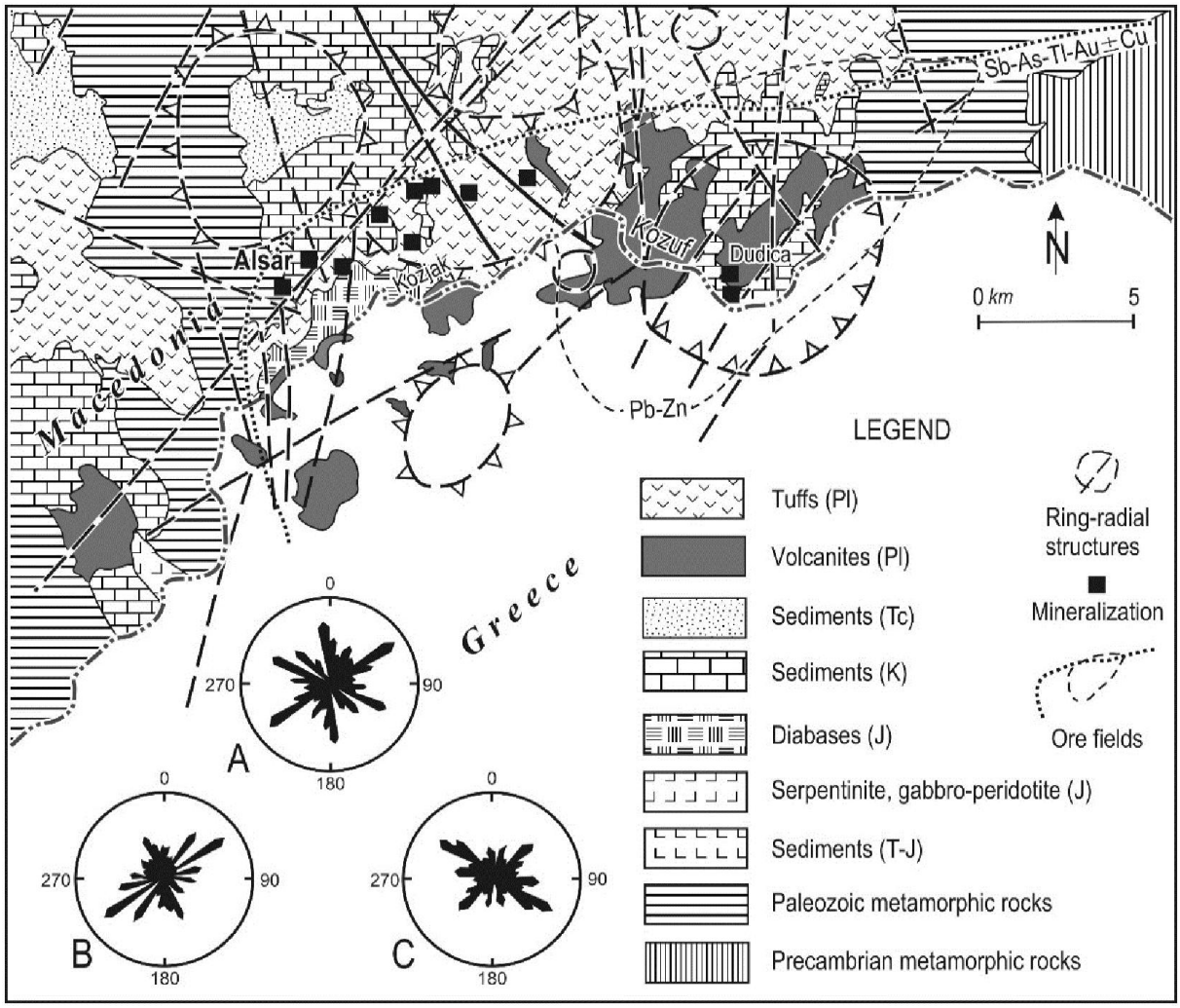

Fig. 1. Morphostructural map of Kožuf Mountain (Boev, 1988; modified Boev and Jelenković, 2012)

The ring structures typical for the area of this complex also point to this type of volcanism (Boev et al., 1990) (Figure 1).

Geologically speaking, Kožuf area was built by several geological formations represented in several stratigraphic complexes, namely (Figure 2):

– complex of Precambrian metamorphic rocks;

– complex of Paleozoic metamorphic rocks;

– complex of Triassic-Jurassic sedimentary rocks;

– complex of Upper Cretaceous sedimentary rocks;

– complex of Upper Eocene sedimentary rocks;

– complex of Pliocene sediments and pyroclastics;

– complex of Quarter sediments.

Also, the geological structure includes the complexes of magmatic rocks represented in:

– complex of metamorphic rhyolites and pyroclastites;

– complex of serpentinized ultrabasic rocks;

– complex of basic magmatic rocks;

– complex of volcanic rocks.

All the above mentioned stratigraphic complexes add to the complexity of the geological structure of Kožuf Mountain, with the Tertiary volcanic activity (6.5 to 1.8 MA, Boev, 1988) as the most dominant position of all, to which the numerous mineralization and ground water appearances are connected.

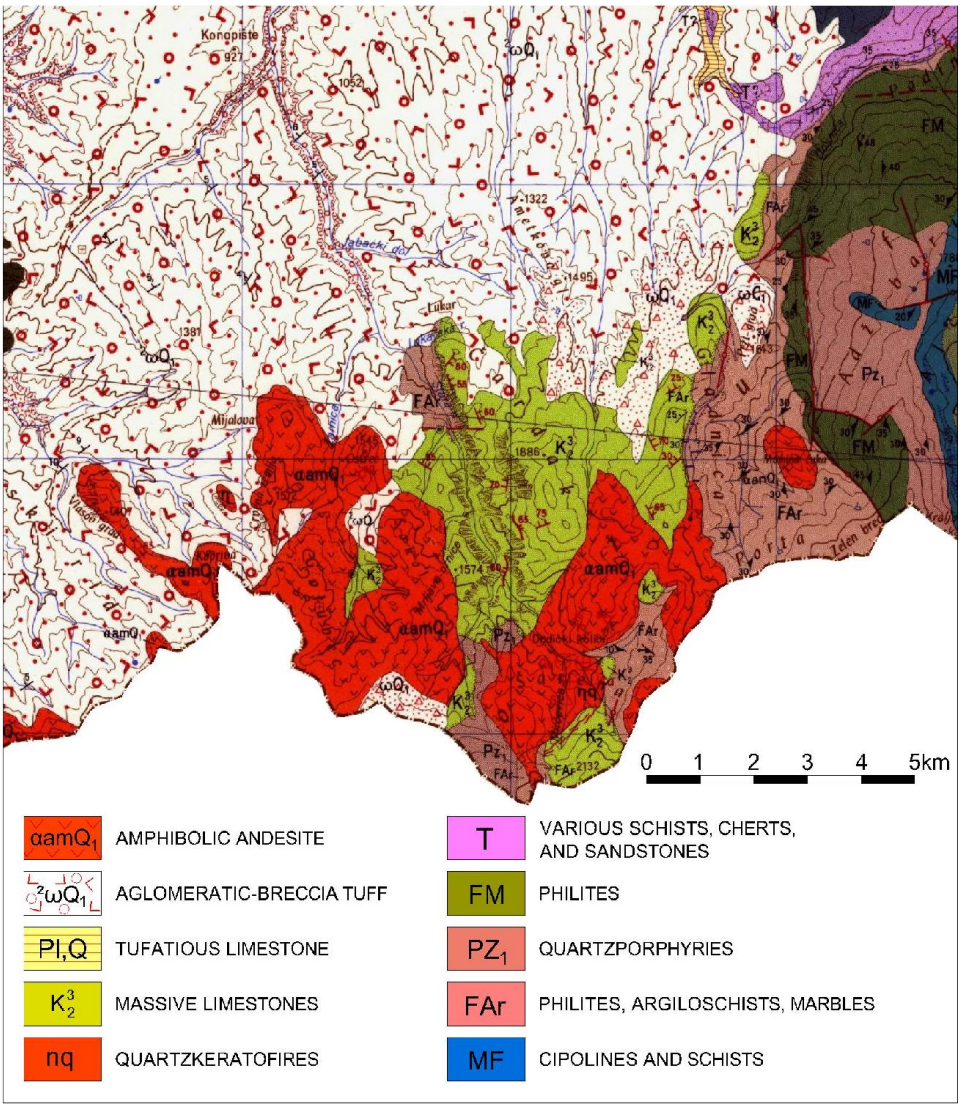

Fig. 2. Geological map of a part of Kožuf Mountain

APPLIED METHODOLOGY

Samples of ground water have been collected in Nalgene bottles and were sent to the laboratory for isotopic investigation in ANCASTER, Ontario, Canada, in order to determine the presence of isotopes of oxygen, hydrogen, tritium and isotopes of carbon. The lab tests were done according to the requirements of the standard ISO, and the determination of the isotopes of carbon was done using the MAC techniques.

RESULTS AND DISCUSSION

The obtained data on the presence of isotopes of oxygen and hydrogen is presented in Table 1, and the graphical interpretation is presented in Figure 3.

The results from the investigation regarding the presence of isotopes $\delta^{18}O$ and δD shown in Figure 1 point to the fact that the position of the analyzed ground water in the area of the village of Mrežičko (Kožuf Mountain) is near the rainwater direction, which is confirmed by the fact that there is a great recharge of the ground water by current precipitation (IAEA, 1981; IAEA, 1983; IAEA, 1995).

T a b l e 1

Results from the investigation on the presence of isotopes $\delta^{18}O$ and δD

Analyte symbol	$\delta^{18}O^{-}$	δD
Unit symbol	VSMOW	VSMOW
Analysis method	ISO	ISO
K/1-1	–9,64	–62,6
R/1-1	–9,7	–62,4
T/1-1	–9,53	–60,9
MR/1-1	–9,32	–59,5
TD/1-1	–8,38	–53,5
MA/1-1	–9,46	–58,6
K/2-2	–9,85	–62,6
R/2-2	–9,76	–62,4
T/2-2	–9,54	–59,9
K/3-3	–9,74	–62,8
R/3-3	–9,78	–62,5
T/3-3	–9,54	–60,7
K/4-4	–9,82	–63,2
R/4-4	–9,75	–62,6
T/4-4	–9,52	–60,7

The data obtained for $\delta^{18}O$ and δD in water samples from formerly mentioned localities, were plotted on a summary diagram of isotope compositions of waters of different origins (see Taylor 1967; Brownlow, 1996; Misra, 2000) with a primary goal to determine the exact origin of waters of interest (Figures 3 and 4).

The plots have shown that majority of data plots are on or near the MWL indicating the meteoric origin of waters for most of the samples. This is very similar to some other findings for mineralized ground water in the Republic of Macedonia (Serafimovski et al., 2012).

The obtained values from the investigation of the presence of tritium are presented in Table 2.

The obtained values shown in Table 2 (^{3}H <8) point to the fact that the waters which are subject to the research ware formed 63 years.

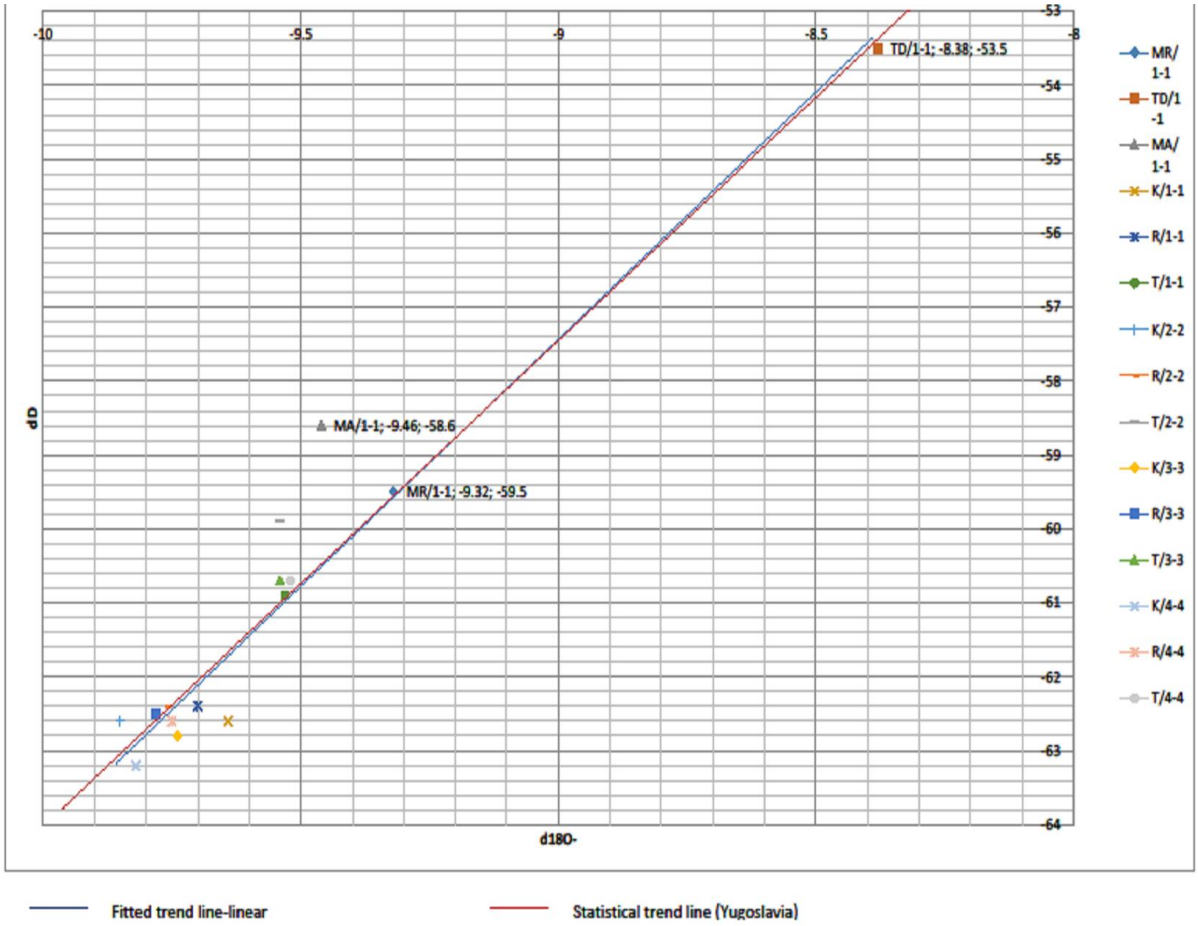

Fig. 3. Position of the obtained values of the isotopes $\delta^{18}O$ and δD regarding the global trend of the rainwater

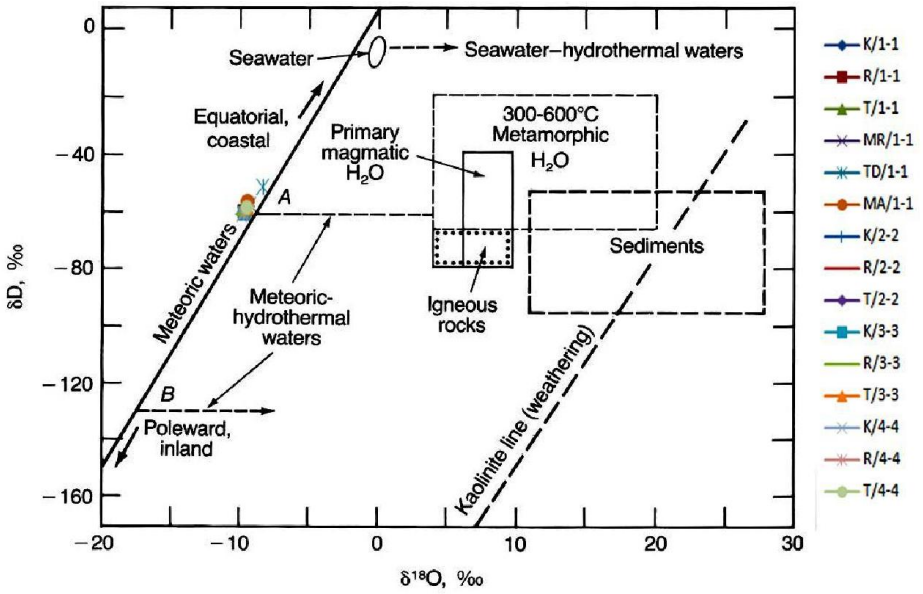

Fig. 4. Summary diagram of isotope composition of waters of different origins.
Trends of $\delta^{18}O$ shift due to water–rock interaction and exchange are shown for seawater and meteoric waters (Taylor 1967, 1974)

T a b l e 2

Presence of ^3H in ground water in the area of the village of Mrežičko

Analyte symbol	H_3
Unit symbol	TU
Analysis method	ISO
KOŽUVČANKA	< 8
IZVORSKA	< 8

The obtained values from the research on the isotopes of carbon in ground water in the area of the village of Mrežičko are shown in Figure 5 and Table 3 (spring source Kožufčanka) and in Figure 6 and Table 4 (spring source Izvorska).

The total obtained values in the isotopic investigation in ground water in the area of the village of Mrežičko (spring source Kožufčanka and spring source Izvorska) are presented in Table 5.

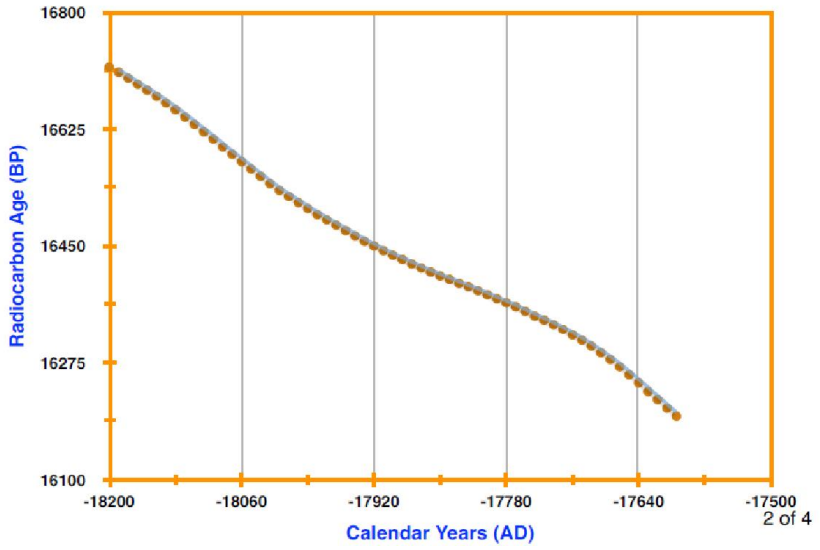

Fig. 5. Graphic interpretation of the obtained values of isotopes of carbon in ground water of the spring source Kožufcanka

T a b l e 3

Values of isotope of carbon in water in the area of the village of Mrežičko (spring source Kožufčanka)

Date received	10. 9.2015	Material type	Water
Date reported	4.11.2015	Pre-treatment	DIC-precipitate
ICA ID	15W/0907	C^{13}/C^{12}	–0.4 ‰
Submitter ID	KOŽUFČANKA	Conventional age	16480 ± 80 BP
	Calibrated age	Cal 18146 – 17688 BC	

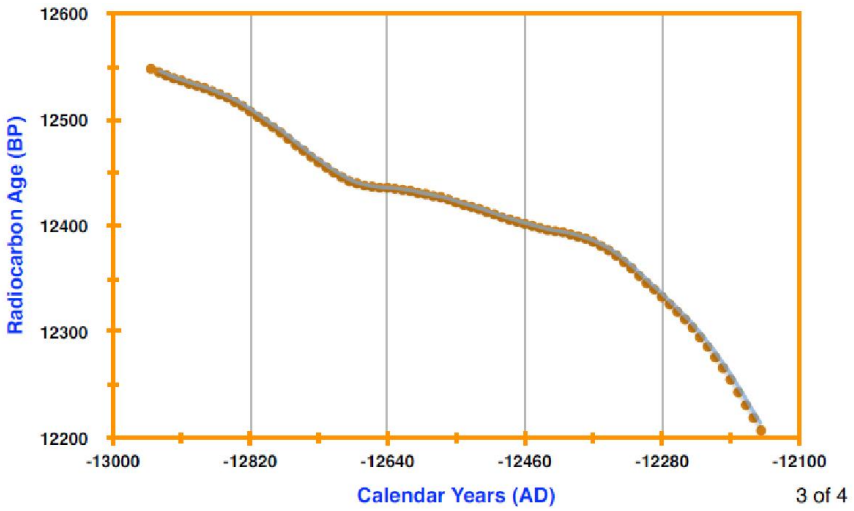

Fig. 6. Graphic interpretation of the obtained values of isotopes of carbon in ground water of the spring source Izvorska

T a b l e 4

Values of isotopes of carbon in water in the area of the village of Mrežičko (spring source Izvorska)

Date received	10. 9.2015	Material type	Water
Date reported	04.11.2015	Pre-treatment	DIC-precipitate
ICA ID	15W/0908	C^{13}/C^{12}	–14.2 ‰
Submitter ID	IZVORSKA	Conventional age	12380 ± 70 BP
	Calibrated age	Cal 12949 – 12156 BC	

T a b l e 5

Values of the calibrated age of spring sources in the area of the village of Mrežičko (Kožuf Mountain)

ICA ID	Submitter ID	Material type	Pretreatment	Conventional age	Calibrated age
15W/0907	KOŽUFČANKA	Water	DIC-precipitate	16480 ± 70 BP	Cal 18146 – 17688 BC
15W/0908	IZVORSKA	Water	Dic-precipitate	12380 ± 80 BP	Cal 12949 – 12156 BC

Date submitted	10. 9.2015	Date reported	04.11.2015
QC 1 sample ID	IAEA C7	QC 2 sample ID	NIST
QC expected value	49.35± 0.50 pMC	QC expected value	134.09 ± 0.70 pMC
QC measured value	49.0 ± 0.20 pMC	QC measured value	134.15 ± 0.40 pMC
Pass?	YES	Pass?	YES

– pMC = Percent Modern Carbon.
– IAEA = International Atomic Energy Agency.
– Calibrated ages are attained using INTCAL13: Int Cal13 and Marine13 Radiocarbon Age calibration curves 0 – 50,000 years cal BP (Reimer et al,)

The results from the isotopic investigation of carbon in ground waters in the area of the village of Mrežičko (spring source Kožufčanka and spring source Izvorska) point to the fact that these spring sources were formed during the Paleolithic age.

CONCLUSION

The investigations conducted on water from the spring source of the ground water "Kožufčanka" and water from the spring source of the ground water "Izvorska" regarding the presence of tritium (^{3}H), isotopes of oxygen ($\delta^{18}O$) and hydrogen ($\delta^{2}H$), as well as the radioactive isotopes of carbon (^{14}C), indicate that the water in the ground water originates from precipitaion. The values of tritium point to the fact that waters are more than 63 years old, and the values of the isotopes of carbon point to the fact that the spring sources of the ground water date back from the Paleolithic age.

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Р е з и м е

ИЗОТОПСКИ ИСТРАЖУВАЊА НА ПОДЗЕМНИТЕ ВОДИ ОД ОКОЛИНАТА НА СЕЛОТО МРЕЖИЧКО, КОЖУФ ПЛАНИНА (РЕПУБЛИКА МАКЕДОНИЈА)

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Клучни зборови: изотопи; водород; кислород: трициум; јаглерод

Во трудот се прикажани резултатите од изотопските испитувања на подземните води (минерални) од околината на селото Мрежичко (Кожуф Планина). Направени се испитувања на водата од изворот на подземната вода "Кожуфчанка" и на водата од изворот на подземната вода "Изворска" за изотопите на трициумот (^{3}H), кислородот (δ^{18}O) и водородот (δ^{2}H), како и за радиоактивните изотопи на јаглродот (^{14}C). Добиените вредности за изотопите на кислородот и водородот укажуваат дека водата од подземните извори води потекло од дождовниците. Вредностите на изотопите на трициумот укажуваат дека водите се постари од 63 години, а вредностите на изотпите на јаглеродот укажуваат на фактот дека изворите на подземните води датираат од времето на палеолитот.