shell of pectindes and of brachiopods are suitable for paleoclimatic reconstruction as they secret their skeleton in oxygen isotopic equilibrium with seawater. As pectinides are supporting little salinity variation they are particularly suitable in reconstructing water paleo-temperatures.
A geochronological age from a tuff intercalation from the studied outcrop made possible to correlate the evaluated Middle Miocene temperatures and seasonally variations with the interpreted oceanographic changes at that time, which occurred world-wide. The $^{39}Ar/^{40}Ar$ age of the fresh volcanic biotites from the tuff intercalations shows a value of 14.2 ± 0.1 Ma
Moreover the $\delta^{18}O$ profiles measured on molluscs have been used to evaluate growth rates and to determine the relationship between growth interruption and seasonal variation.

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Recharge Area of mineral springs in Jezersko area (N Slovenia)

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The geological conditions in the Karavanke mountains are strongly related to Periadriatic lineament. In the geological sense the lineament divides Karavanke into northern and southern part. This tectonic structure of first order has also big influence on hydrogeology of the area. In the central part of Southern Karavanke, along Slovenian and Austrian border, extensive Košuta unit of dachstein carbonate rocks is present. In the Southern Karavanke mountains springs from carbonate rocks prevail, however in the central part of the mountain ridge some other interesting springs can be found, among them mineral springs are very important. Mineral springs are positioned in the area between Jezersko to Solčava in Slovenia and between Vellach and Eisenkappel in Austria. Heterogeneous chemical composition is significant for them and in mainly all springs free CO_2 is present.

In the area of Zgornje and Spodnje Jezersko in Slovenia three springs that are very likely to be from mineral origin were studied. The first spring Ankova slatina is situated in a valley northern from farm Anko (Zgornje Jezersko). The altitude of the spring is 985 m above sea level. In the past the spring was captured by small water capture that is nowadays abandoned. Above the capture site two boreholes were drilled. Usually water flows out from boreholes under the pressure but it sometimes happens that water completely dries up. Due to the presence of CO_2 gas water outflow from the borehole mouth pulsate. Few meters below boreholes the spring occurs. During the research period it was established that the spring is intermittent. The outflow from spring and boreholes varies between 0 to 8 l/s.

In the area of Spodnje Jezersko famous tufa quarry is positioned. The deposits of tufa are very big and thick. In the western part of the quarry the relatively strong spring is present. The altitude of the spring is 860 m above sea level. Water flows out from fissures in limestones that are likely to be of Carboniferous age. Bellow the spring very strong and fast precipitation of recent tufa is present. The capacity of spring was estimated to be between 26 and 45 l/s.

The third spring is situated bellow Virnikova planina on the left bank of the creek. The altitude of the spring is 1200 m above sea level. On the both side of the creek channel tufa deposit are present. On the basis of high specific conductivity values in the creek water the spring was found during the hydrogeological mapping. The capacity of the spring is between 2 to 4 l/s.

On the monthly basis during the investigation period 14 samples were taken for each spring, except for Ankova slatina that dries up two times. The rudimentary chemistry (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, NO_3^{2-}, SO_4^{2-}, HCO_3^{-}) and $\delta^{18}O$ and $\delta^{13}C$ were measured. On the basis of field parameters and analytical results basic chemical equilibrium parameters were calculated by PHREEQE computer code. The mean altitude of spring recharge areas were calculated with altitude effect 0,2‰/100m obtained in the Košuta region that is in the vicinity of investigated area.

For Ankova slatina the average of $\delta^{18}O$ value is –10,00 ‰ with the amplitude of 0,64 ‰. From the chemical point water can be determined as Ca^{2+} - Mg^{2+} – Na^{+} - HCO_3^{-} - SO_4^{2-} type. The average of $\delta^{13}C$ value is –6,12 ‰ with the amplitude of 3,39 ‰. The calculated values of pCO_2 in spring water are between –1,66 and –0,77 and saturation indexes of calcite are between –1,03 and 0,38.

For spring near tufa quarry the average of $\delta^{18}O$ value is –9,35‰ with the amplitude of 0,66 ‰. From the chemical point water can be determined as Ca^{2+} - Mg^{2+} – Na^{+} - HCO_3^{-} - SO_4^{2-} type. The average of $\delta^{13}C$ value is –3,88 ‰ with the amplitude of 5,15 ‰. The calculated values of pCO_2 in spring water are between –2,45 and –1,96 and saturation indexes of calcite are between 0,16 and 0,74.

For spring bellow Virnikova planina the average of $\delta^{18}O$ value is –9,75‰ with the amplitude of 1,34 ‰. From the chemical point water can be determined as Ca^{2+} - Mg^{2+} – Na^{+} - SO_4^{2-} - HCO_3^{-} type. The average of $\delta^{13}C$ value is –6,56 ‰ with the amplitude of 5,01 ‰. The calculated values of pCO_2 in spring water are between – 0,29 and –1,08 and saturation indexes of calcite are between 0,08 and 0,52.

On the basis of hydrogeological mapping as well as hydrogeochemical and isotopic investigations it was determined that the recharge area of Ankova slatina spring is in the Devonian limestone lenses intercalated inside of Hochwipfel beds of Carboniferous age. The recharge area of tufa spring is surprisingly low in the altitude. It was determined that recharge area is in the slope materials and in the near vicinity of the spring and not in the Virnikov grintavec that is composed of Devonian limestones as we expect from the structural interpretation. The recharge area of spring below Virnikova planina is in the gypsum beds in the near vicinity.

It remains open what are the geochemical processes inside of tufa spring aquifer. From $\delta^{13}C$ data it is clear that prevailing mechanism is dissolution of limestones but it is not clear why so large deposit of tufa appear only in this place and not on the others. We suppose that additional

source of CO_2 mixing with shallow water is the reason for this and that this source is similar as for other springs in the border region of Jezersko.

Stable isotope ratios and the evolution of acidulous solutions

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In the present study 35 well and spring waters were sampled in the North of Hesse (Germany) and analysed with respect to the chemical compositions and stable isotope ratios ($\delta^{13}C$, $\delta^{34}S$, δD, $\delta^{18}O$). The solutions are used as drinking water, bottled mineral water or for medical applications. Several solutions are characterized by high concentrations of dissolved components. But most conspicuous are acidulous solutions with a high content of dissolved inorganic carbon (DIC). Although, the evolution of natural solutions is extensively studied significant gaps exist with respect to such acidulous solutions. The aim of the present study is to decipher the evolution of the solutions with respect to the sources and requirements of the catchment area.

In the acidulous solutions the source of the high amounts of dissolved inorganic carbon (DIC) and great proportions of carbonic acid is mostly vague. No recent magmatic activities are observed in the study area, but Tertiary basaltic rocks appear. If Tertiary basaltic magmas might be a primary source, CO_2 has to be stored until recent times within the underlying rocks and sediments.

The results show that the evolution of the solutions is characterized by the precipitation of meteoric water, the uptake of CO_2 and a subsequent dissolution of solids of the catchment area. Three types of solutions may be distinguished according to the chemical composition:

1: water with low concentration of dissolved ions (LOW)
2: brines dominated by Na^+ and Cl^- (BRI)
3: acidulous solutions with high concentrations of Ca^{2+}, Mg^{2+}, and DIC (CO_2)

The dissolution of carbonate minerals, essential calcite and dolomite, is closely related to the uptake of gaseous CO_2. The high Pco_2-values of the CO_2 type of about 1 atm requires a huge reservoir of CO_2-gas, which cannot be provided by soil atmospheres. From the measured $\delta^{13}C_{DIC}$-values the $^{13}C/^{12}C$-signatures of the primary CO_2 are obtained. The respective $\delta^{13}C_{CO2}$-values of the CO_2 type are either in the range of about -10 ‰ or lay between 0.8 and 3.7 ‰. The values of these two groups barely depend on the boundary conditions for the dissolution of carbonate (open and closed system with respect to the CO_2-gas).

The $^{13}C/^{12}C$-signatures of CO_2 from magmatic origin (-6 and -3 ‰) lay between the $\delta^{13}C_{CO2}$-values of above two groups. Higher and lower values may be explained by a $^{13}C/^{12}C$-