On the Potential Joint Use of Uranium and Carbon Isotopes for Groundwater Dating

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Abstract

The well-investigated aquifer in southern Tunisia have been selected from the literature to test the potential use of uranium isotopic compositions as a groundwater dating method. This is the Senonian carbonate aquifer of the Nefzaoua basin (https://doi.org/10.1016/j.quaint.2020.01.024). For the this aquifer, an increase in U concentrations along the generalized flow path is observed in proportion to an increase in total dissolved solids, which may indicate the predominance of dissolution processes over alpha-recoil processes under oxidizing conditions for uranium. There is also an increase in U concentrations with a decrease in 14C values. For this aquifer, positive results were obtained on uranium-isotope dating. It was found that the groundwater residence time in the aquifer increases from 440 to 11,300 years from the recharge area along the generalized flow path (Figure). Uranium age correction model under oxidizing conditions in the aquifer is given in "Malov, 2018. Evolution of the groundwater chemistry in the coastal aquifers of the south-eastern White Sea area (NW Russia) using 14C and 234U-238U dating. Science of the Total Environment. https://doi.org/10.1016/j.scitotenv.2017.10.197" It is shown that for uranium-isotope dating of groundwater, three main conditions must be met: i) oxidizing conditions for uranium in the aquifer, ii) an increase in uranium concentrations with a decrease in 14C activities, and iii) the homogeneity of the aquifer in terms of hydraulic conductivity and lithological composition. The author understands the reality of the fact that groundwater dating methods are under development and improvement. Nevertheless, analysis of the evolution of the chemical and isotopic composition of groundwater, analysis of the geological and hydrogeological history of the region, hydraulic estimates of groundwater velocities in aquifers, hydrodynamic and balance justifications for the formation of groundwater, and analysis of the composition of stable isotopes can increase the reliability of dating. In the future, it is necessary to continue studies to assess the retardation factor and recoil loss factor in order to improve the uranium-isotope method for dating groundwater under oxidizing conditions for uranium. This work was supported by the RFBR (project no. 20-05-00045_A)

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On the potential joint use of uranium and carbon isotopes for groundwater dating

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Abstract The well-investigated aquifers have been selected from the literature to test the potential use of uranium isotopic compositions as a groundwater dating method. These are the Senonian carbonate aquifer of the Nefzaoua basin and Mio-Pliocene sandy aquifer of the Redjime Mâatoug, Tozeur, and Chott El Charsa Plain basins. For the Senonian aquifer, an increase in uranium concentrations along the generalized flow path is observed in proportion to an increase in total dissolved solids, which may indicate the predominance of dissolution processes over alpha-recoil processes under oxidizing conditions for uranium. There is also an increase in uranium concentrations with a decrease in ^{14}C values, although three determinations of ^{14}C are not enough. At the same time, for this aquifer, positive results were obtained on uranium-isotope dating. It was found that the groundwater residence time in the aquifer increases from 443 to 11281 years from the recharge area along the generalized flow path. In Mio-Pliocene multi-layer sandy aquifers, groundwater sampling was carried out in a very wide interval of depths from 40 to 1174 meters, in connection with which a very wide range of distribution of values of the redox potential of groundwater, retardation factor and recoil loss factor is assumed. That is, the necessary requirements for using the proposed method of uranium-isotope dating of groundwater, namely: i) oxidizing conditions for uranium in the aquifer, ii) an increase in uranium concentrations with a decrease in ^{14}C activities and iii) the homogeneity of the aquifer in terms of hydraulic conductivity and lithological composition are not met.

Keywords: groundwater, dating, radiocarbon, uranium isotopes, southern Tunisia

1. Introduction

Groundwater is better protected from anthropogenic pollution compared to surface water, and therefore their use is more preferable. However, they are hidden underground and require special research methods to substantiate the possibility of operation for a given period while maintaining the required quality. In particular, there is an urgent need for reliable methods for determining the groundwater residence time (groundwater dating) in an aquifer. If this time is very short, then there is a danger of penetration of surface pollution, if it is very long, then it is possible to pull up deep substandard waters. Radiocarbon dating is most actively used; attempts are made to use ^{3}H, ^{3}He, ^{36}Cl, ^{39}Ar, ^{81}Kr, ^{129}I

and other isotopes and geochemical tracers (Bascaran et al., 2011; Mook et al., 2000). Methods for radiocarbon dating of groundwater have been developed in the most detail (Han et al., 2012, 2014; Han and Plummer, 2013, 2016). However, despite the widespread use of ^{14}C, the interpretation of the radiocarbon age is still limited by many uncertainties in estimating the initial radiocarbon content in recharge areas (^{14}C$_0$) and accounting for important chemical and physical processes that alter its activity as it moves in the groundwater flow. Additional sources of carbon in water can be, for example, soil CO_2, oxidizing organic matter, oxidizing methane, dissolving carbonate rocks. Carbon can also be removed from water by exchange reactions and precipitation. Therefore, to assess the calculated value of ^{14}C$_0$, taking into account all these processes, many models and approaches have been proposed, which are inappropriate to consider in detail in this article. An overview is available in Han and Plummer (2016).

At the same time, it is obvious that the combination of dating methods for different isotopes allows a more objective approach to assessing the time of groundwater residence time in aquifers. Therefore, we support the idea of joint use of radiocarbon and uranium isotope methods (Rogojin et al., 1998; Fröhlich, 2013; Malov, 2016). Unlike cosmogenic radiocarbon, uranium isotopes are almost completely transferred into groundwater from water-bearing rocks, that is, uranium-isotope dating is an independent method in relation to radiocarbon dating. In addition, the range of the time interval of uranium-isotope dating is much wider.

The uranium-isotope method was actively used in the second half of the last century. Due to the long half-life of ^{234}U (2.46×10^5 years), many attempts have been made to apply the uranium isotope ratio ^{234}U/^{238}U to the dating of old groundwater up to hundreds of thousands of years old (Osmond et al., 1974; Andrews et al., 1982; Andrews and Kay, 1983; Fröhlich and Gellermann, 1987; Ivanovitch et al., 1991; Bonotto, 2000; Deschamps et al., 2004; Maher et al., 2006; Porcelli, 2008). However, in a number of cases, it was suggested that changes in the activities of uranium isotopes may not correspond to the residence time of groundwater in the aquifer, but rather characterize the redistribution of uranium between the water-bearing rocks and the aqueous phase. The reasons for this are very different. Thus, Andrews et al. (1982) assumed the ^{238}U content in the solution is constant with an increase in ^{234}U due to the recoil loss factor, which showed the possibility of an increase in the ^{234}U/^{238}U ratio to incredible values instead of its decrease in the reducing conditions of the aquifer; the specific surface area, on which the recoil loss factor depends, was taken from 7 cm^2/g (Andrews and Kay, 1983) to 12 m^2/g (Maher et al., 2006) etc. Consequently, to obtain reliable values of the groundwater residence time, the method requires a more reliable knowledge of the characteristics of the aquifer, for example, such as the retardation factor R and the probability of ^{234}U transition into water during the radioactive decay of ^{238}U in the rock (recoil loss factor p). These parameters are determined by the granulometric and mineralogical composition and sorption properties of aquifers rocks, as well as by the redox potential of groundwater and the degree of their non-equilibrium

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with respect to rock-forming minerals (saturation index). The number of works in this direction is still small, they are mainly related to laboratory studies of uranium leachability from sediments (Wang et al., 2017; Malov, Zykov, 2020), its lag behind the solution during filtration in a porous medium (Dangelmayr et al., 2017). Under natural conditions, the uranium dissolution rate, retardation factor, and recoil loss factor were studied by Luo et al. (2000); Maher et al. (2004).

Therefore, in this article we consider it more appropriate to show R and p in the form of their ratio R/p. The main calculated equations are as follows (Malov, 2013, 2016):

$t = \ln(1/k) : D_4$, where $k = 1 - [U^{\mathrm{W}} \cdot R \cdot (AR - 1)] : (M_{\mathrm{S}} \cdot U^{\mathrm{R}} \cdot p)$ (1) where t is the groundwater residence time in oxidation conditions for uranium in sandstone aquifers; D_4 is the decay constant for ^{234}U, 2.8263 10^{-6} a^{-1}; U^{W} is the concentration of uranium in water; U^{R} is the content of uranium in the rock; AR is the U isotopes activity ratio in the water sample; M_{S} is the solid mass to fluid volume ratio. In this case, two unknown parameters remain in formula (1), which cannot be directly measured in water and rock samples: t and R/p. Therefore, in order to use equation (1), it is necessary to make several determinations of the groundwater age by other methods, for example, using isotopes of carbon. Then, we need to find out whether there is an increase in uranium concentrations in groundwater with a decrease in the concentration of radiocarbon. If this is the case, then the mean values R/p for the studied aquifers are determined. After this, uranium-isotopic dating of other groundwater samples is carried out, which is less labor-intensive and more accessible than radiocarbon dating. The average value of the retardation factor/recoil loss factor ratio (R/p) in samples from the sandstone aquifer of the upper Vendian strata and overlying horizons is assumed to be (24±4) (Malov, 2016). In the articles (Malov, 2018; Malov and Tokarev, 2019), the obtained datings were refined taking into account the mixing processes quantitatively characterized by hydrochemical and isotopic (^{2}H-^{18}O) data.

1. **Discussion of experimental results**

The well-investigated aquifers have been selected from the literature to test the potential use of uranium isotopic compositions as a groundwater dating method.

1. Senonian carbonate aquifer of the Nefzaoua basin (samples 14, 18, 5, 7, 6, 9, 4, 17,15);

2. Mio-Pliocene sandy aquifer of the Redjime Mâatoug (samples 28, 29, 31), Tozeur (samples 32, 38, 40, 43, 44, 47, 50, 51), and Chott El Charsa Plain (samples 56, 59, 60, 61, 62) basin (Hadj Ammar et al., 2020).

In the article of Hadj Ammar et al. (2020) in Fig. 4 (Conceptual hydrochemical cross-sections along the generalized flow path in Nefzaoua basins, showing some of the main U and major ions-results) shows the classical distribution of uranium concentrations in groundwater along the flow line from recharge area in Dahar

to the Djerid Chott in Senonian carbonate aquifer of the Nefzaoua basin. An increase in uranium concentrations is observed in proportion to an increase in total dissolved solids (TDS) (Fig.1a), which may indicate the predominance of dissolution processes over alpha-recoil processes under oxidizing conditions for uranium. There is also an increase in uranium concentrations with a decrease in ^{14}C values, although three determinations of ^{14}C are not enough (see Table 1).
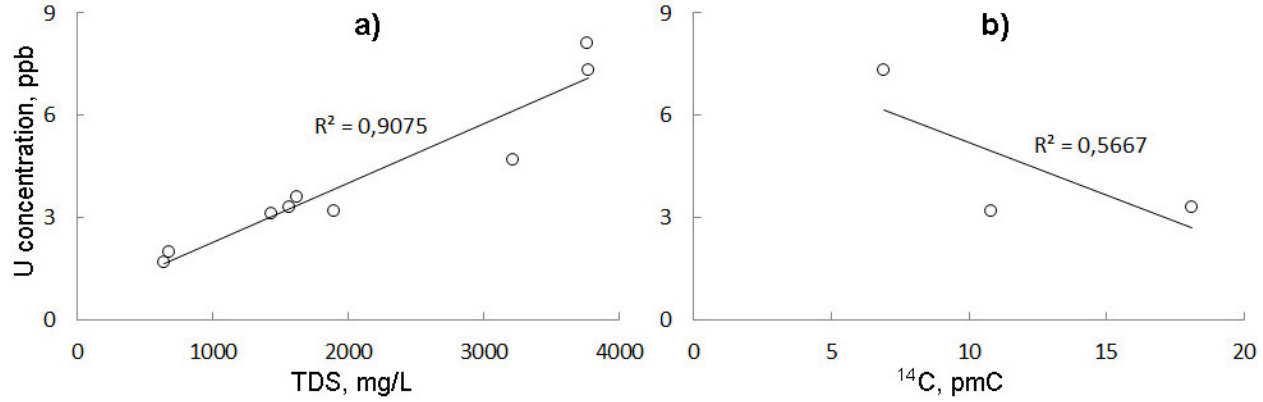

Fig. 1. Uranium concentration versus TDS (a) and ^{14}C activities (b) in the Senonian carbonate aquifer of the Nefzaoua basin

In our opinion, this site is suitable for uranium-isotope dating. Substituting the values of t (^{14}C Age) and other known values of U^W, AR and D_4 in formula 1, and also conditionally taking $M_S = 9.2$, $U^R = 2220$ ppb from paper Malov (2016) (which needs clarification), we obtain the average value of $R/p = 95$. I repeat, it obtained from the available three values of the radiocarbon age and requires clarification.

Then we determine the uranium-isotope age for the rest of the groundwater samples of the Nefzaoua basin (Table 1, Fig. 2). Due to the assessment of the potential use of uranium isotopic compositions as a method for dating groundwater, the standard deviation for the ^{234}U-^{238}U age was not calculated.

Table 1. Uranium isotope age estimates in the Senonian carbonate aquifer of the Nefzaoua basin

Sample ID	$U^{W\ a}$ (ppb)	^{234}U/^{238}U[b]	^{14}C (pm)	^{14}C Age (a)	Std. Dev.	R/p	^{234}U-^{238}U Age (a)[c]
14	1.749	1.492					1383
18	1.981	1.134					443
5	4.691	1.537					4178
7	3.6	1.74					4411
6	3.204	1.669	10.8± 0.9	3508	477.4	95	3556
9	3.071	1.696					3570
4	3.334	1.732	18.1± 1.3	2531	435.4	60	4000

Sample ID	$U^{\text{W a}}$ (ppb)	^{234}U/^{238}U$^{\text{b}}$	^{14}C (pm)	^{14}C Age (a)	Std. Dev.	R/p	^{234}U-^{238}U Age (a)$^{\text{c}}$
17	7.316	1.732	6.9 ± 1.2	12157	1206.5	129	8904
15	8.121	1.833					11281
Average						95	

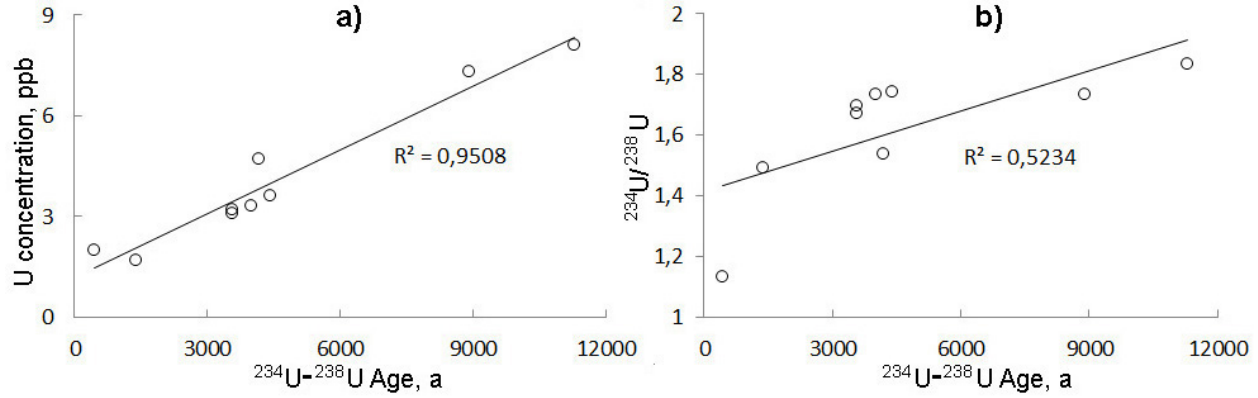$^{\text{a}}$ Error 0.1-0.2%; $^{\text{b}}$ Error 0.1-0.3%; $^{\text{c}}$ R/p = 95, Std. Dev. not calculated

Fig. 2. Uranium concentration (a) and U isotopes activity ratio (b) versus ^{234}U-^{238}U Age of the groundwater in the Senonian carbonate aquifer of the Nefzaoua basin

In Mio-Pliocene multi-layer sandy aquifers, groundwater sampling was carried out in a very wide interval of depths from 40 to 1174 meters, in connection with which a very wide range of distribution of values of the redox potential of groundwater, retardation factor and recoil loss factor can be assumed. According to the authors "the distribution of uranium in this complex aquifer system seems to be in agreement with the lithological variability and are ultimately a function of a number of physical and chemical factors including the uranium content of the hosting geological formation, water-rock interaction and mixing between waters having different isotopic signatures" and "suggests heterogeneous and patchy distribution of the basement lithology, and also likely irregular pathways and variable flow rates of the groundwater circulation" (Hadj Ammar et al., 2020).

That is, the requirements necessary for using the proposed method of uranium-isotope dating of groundwater are: i) oxidizing conditions for uranium in the aquifer, ii) an increase in uranium concentrations with a decrease in ^{14}C activities and iii) the homogeneity of the aquifer in terms of hydraulic conductivity and lithological composition is likely are not performed. There is a possibility of the presence of reducing conditions in the system of different aquifers, as well as the presence of sorbing minerals, which determine the increased values of the retardation factor in certain parts of the aquifers. Fig. 3c, d shows that the yellow colored samples may have underestimated uranium contents due to

the retardation factor and therefore do not fall on the trend line typical for the Vendian siltstone and sandstone aquifers (Fig. 3,a, b) (Malov, 2016), where the uranium-isotope method of groundwater dating gave positive results. If the retardation factor for these samples is 3.5 times higher than for the samples shaded with red, then these samples (yellow) will shift to the right and take the position of the samples marked in blue. In this case, the trends of ^{14}C-U and [14]C Age-U will be identical to the trends given in the work of Malov (2016).

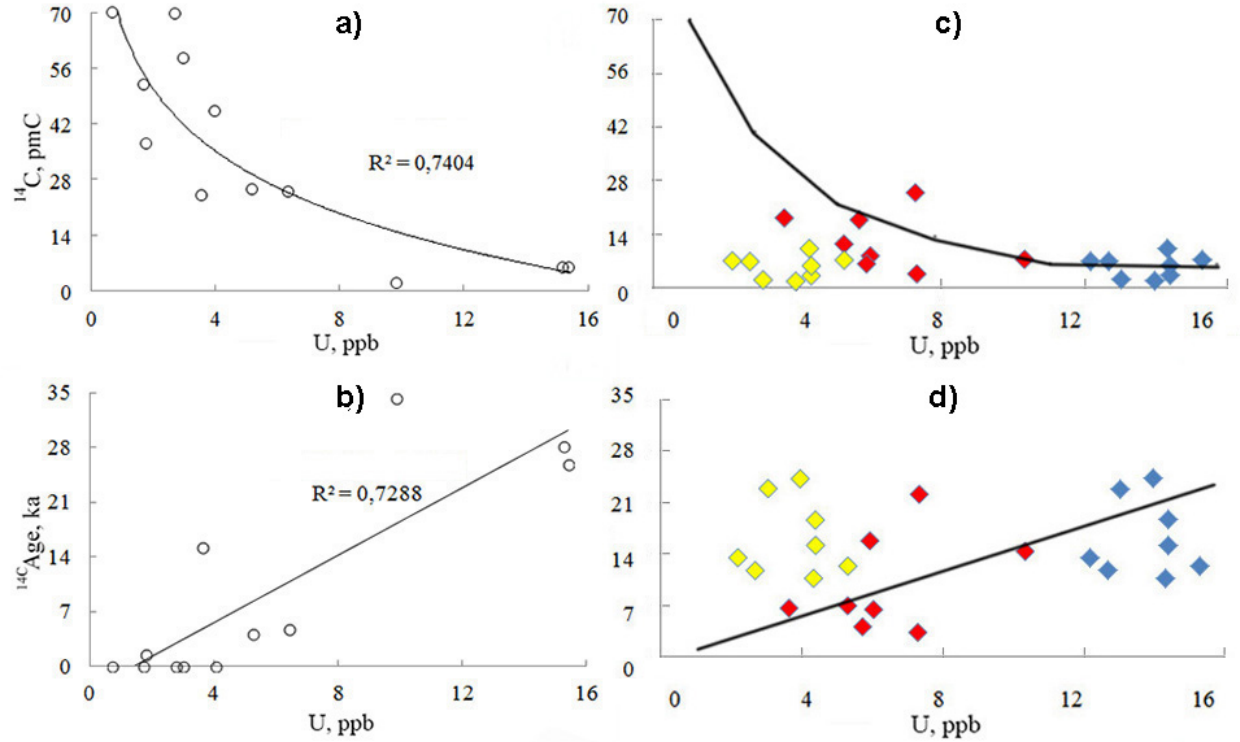Fig. 3. Changes in the U content of the groundwater under oxidizing conditions for uranium versus the measured ^{14}C activity, pmC (a) and ^{14}C age, ka (b) in the Vendian siltstone and sandstone aquifers (Malov, 2016), and same (c, d) - in the Mio-Pliocene sandy aquifer of the Redjime Mâatoug, Tozeur, and Chott El Charsa Plain basin (Hadj Ammar et al., 2020). Yellow rhombuses in Fig. 3c, d - water samples with a presumably 3.5 times higher retardation factor compared to the red rhombuses. That is, with the same calculated retardation factor values, the uranium concentrations in them would be 3.5 times higher and they would occupy the points marked with the blue rhombuses.

Of course, it cannot be categorically asserted that in this case everything is actually the case, but it must be emphasized that the proposed method of uranium-isotope dating of groundwater can be used if at least three above certain conditions are met.

1. **Conclusion**

It is shown that for uranium-isotope dating of groundwater, three main conditions must be met: i) oxidizing conditions for uranium in the aquifer, ii) an increase in uranium concentrations with a decrease in ^{14}C activities, and iii) the homogeneity of the aquifer in terms of hydraulic conductivity and lithological composition.

The author understands the reality of the fact that groundwater dating methods are under development and improvement. The dating of moving and involved in chemical processes groundwater is more difficult to carry out than the dating of immovable rocks and buried organic matter not participating in chemical processes. Nevertheless, analysis of the evolution of the chemical and isotopic composition of groundwater, analysis of the geological and hydrogeological history of the region, hydraulic estimates of groundwater velocities in aquifers, hydrodynamic and balance justifications for the formation of groundwater, and analysis of the composition of stable isotopes can increase the reliability of dating.

In the future, it is necessary to continue studies to assess the retardation factor and recoil loss factor in order to improve the uranium-isotope method for dating groundwater under oxidizing conditions for uranium.

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