Using Environmental Isotopes and Krypton-81 to Characterize and Date Continental Intercalaire Paleogroundwater (Southern Tunisia)

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Abstract

In a semi-arid to arid climate region, socio-economic development is mainly dependent on deep groundwater resources. This is the case of the Continental Intercalaire (CI) groundwater which is one of the most important aquifers in the North Western Sahara in Africa. This aquifer system, extending over more than a million of km^2, is mainly confined, poorly recharged but intensely abstracted in Southern Tunisia. Efficient management of this resource relies on accurate data such as recharge/discharge rate and groundwater dynamics. In this study, environmental isotopes (^{2}H, ^{18}O, ^{13}C, and ^{14}C) were combined with long time lived radio-nuclide (^{81}Kr) to give greater constraint on the groundwater residence time in the CI. Stable isotope signature is depleted compared to the modern rainwater of Sfax station with very low deuterium excess suggesting a paleoclimatic effect. This finding is strongly supported by ^{14}C measurements where most of the analyzed samples are below the detection limit. The used carbon-14 correction models indicate residence times greater than 35 ka. However, the estimated ages range using ^{81}Kr contents are from 150 to 600 kyr, and are clearly much older than the ^{14}C ages, confirming that this method is not suitable for dating CI groundwater.

Keywords

Krypton 81 (^{81}Kr) • Carbon-14 • Noble gas Paleogroundwater • CI Tunisia

1 Introduction

Climate variability and human activity have critical impacts on the sustainability of natural water resources which may lead to the over-abstraction and deterioration of water quality. In the context of climate change and an increasing demand for water, it is essential to understand the origin, the groundwater flow dynamics and the mean residence times for the assessment of the reliability and potential of these resources as a major source of water supply over the medium and long-terms. Radio-isotopes dating of fossil groundwater could further improve the understanding of present and past flow patterns. However, dating of groundwater, particularly on time scales greater than few decades poses problems due to the heterogeneity of the geological and hydrological properties of most aquifers [1, 2]. Under these conditions, the application of inert tracers such as noble gases and radionuclide as Krypton-81, present in very old groundwater are excellent tools to estimate groundwater ages and dynamics [3]. In fact, these radiogenic noble gas isotopes are characterized by long half-life and lack of geochemical interactions.

This paper focused on one of the most important and intensive exploited aquifers in North Western Sahara Aquifer System (NWSAS): the continental Intercalaire extending over large areas of Algeria, Tunisia and also parts of Libyan Desert. The main focus of this investigation was the use of the recently available long-lived radio-nuclides and isotope age tracers for the assessment of groundwater dynamics and age of the Continental Intercalaire aquifer of southern Tunisia.

2 Settings, Sampling and Analysis

The investigated area is located in southern Tunisia and covers Kebili and Tozeur regions. It is limited to the west by the Algerian frontier, to the east by Dahar uplift, to the north

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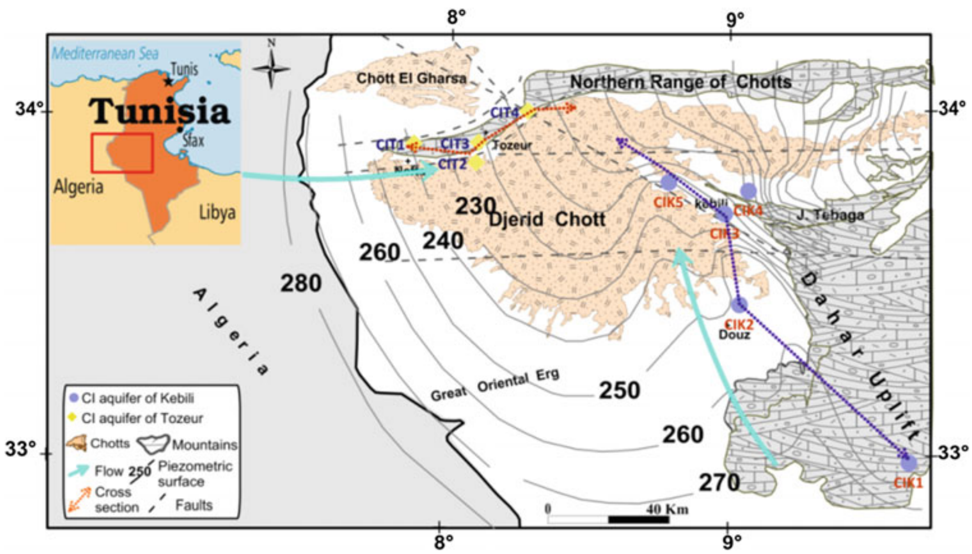

Fig. 1 Location map of the study area showing hydraulic head contour line and sampling points

by the Northern Range of Chotts and to the south by the great oriental Erg (Fig. 1). It is characterized by an arid climate and limited water resources with a mean annual temperature of about 21 °C and precipitation of about 150 mm $year^{-1}$.

The CI aquifer is made up of middle Jurassic to lower Cretaceous continental formations described as heterogeneous sandy and sandstone units with variable clay contents. The geological sequence of the aquifer consists of several units of detrital sediments separated by clay and gypsum rich strata. The aquifer units are confined by marl and clay layers of Cenomanian age, reaching, in some areas, a thickness of more than 600 m. The CI aquifer is the main resource for water supply. In this research work nine groundwater samples were collected along two flow paths from the main CI hydrogeological formation during February 2015 (Fig. 1) for isotopic and noble gas analyses.

3 Results

3.1 Chemical Composition

The measured conductivity of the groundwater samples ranges from 2.6 to 9.8 ms cm^{-1}. The chemical composition reveals similar water type for all the collected samples with dominance of Na^{+}–Ca^{2+} and SO_4^{2-}–Cl^{-} concentrations in both Nefzaoua (Kebili) and Tozeur basins. This chemical pattern could be explained by a water interaction process with the geological formations of the basin (dissolution/precipitation of carbonates and various evaporates) and cation exchange reactions.

3.2 Environmental Isotopes ($\delta^{18}O$, $\delta^{2}H$, ^{14}C, $\delta^{13}C$)

Stable isotopes of the water molecule of CI range from −8.4 to −7.2‰ versus SMOW for $\delta^{18}O$ with a mean value of −8‰, and from −61.5 to −50.3‰ versus SMOW for $\delta^{2}H$. The stable isotope data lie below the local meteoric water line and Global Meteoric water Line [4]. Radiocarbon activities and $\delta^{13}C$ values cover a wide range of values, from 5 to 0.25 pmc and from −10.84 to −7.9‰, respectively.

3.3 Concentration of ^{81}Kr

Concentrations of ^{81}Kr in groundwater samples are expressed in terms of the air-normalized ratio R/R_{air} = [$^{81}Kr/Kr$] sample/[$^{81}Kr/Kr$] air, where R_{air} is the modern atmospheric ratio of 1.10×10^{-12} [5]. The R/Ra ratios of present samples range from 0.16 to 0.28.

4 Discussion

Stable isotopes composition of CI groundwater are all strongly depleted in both ^{18}O and ^{2}H compared to modern Mediterranean rainfall and the shallowest groundwaters by up to 3.5% in ^{18}O. This signature indicates a recharge at higher altitudes or a paleoclimatic effect (recharge under colder climatic conditions than at present). Based on the low ^{14}C activities, the difference between the isotopic composition of CI groundwater and that of present precipitation is caused by a paleoclimatic effect. On the other hand, longer water residence times enhance equilibration with aquifer carbonate minerals resulting in lower ^{14}C activities and more enriched $\delta^{13}C$ compositions [6]. In fact, the range of $\delta^{13}C$ values is typical of water–rock interaction by the incongruent dissolution of carbonate in recharging meteoric water ($\delta^{13}C$ −22 to −27‰). Based on the different values of pmc, together with the measured $\delta^{13}C$ values, groundwater residence time was calculated using various models [7] taking into account different geochemical processes (carbonate dissolution, soil gas CO_2 dissolution, CO_2 gas-aqueous exchange, calcite, HCO_3 exchange, gypsum dissolution or cation exchange …). These models could be subdivided into: (i) purely chemical mixing, (ii) isotopic mixing and (iii) models of chemical mixing and isotopic exchange. In the present case, only the "Fontes and Garnier Eq." model takes into account major processes occurring in the CI groundwater: gypsum dissolution and Ca/Na cation exchange reactions. The calculated residence times (26–38 ka), correspond to recharge periods of late Pleistocene and exceeds the limits of radiocarbon dating.

Krypton-81 is useful for waters age dating over 50 000 years old and up to approximately 1 Million years [3], greatly exceeding the age range of ^{14}C. The age of ^{81}Kr (t_{Kr}) is calculated by the following equation where R_{air} is the modern atmospheric ratio [5] and λ_{Kr} is 3.03×10^{-6} year^{-1}:

$$t_{Kr} = -\frac{1}{\lambda_{Kr}} \ln\left(\frac{R_{\text{Sample}}}{R_{\text{Air}}}\right)$$

The range of ages estimated for the collected samples is 150–600 kyr, and is clearly much older than the ^{14}C ages, confirming that the ^{14}C method is not suitable for dating the present samples. The lowest residence time is measured close to the aquifer outcrops in the Dahar pointing to a low recharge rate and absence of significant circulation.

5 Conclusion

The Continental Intercalaire (CI) is the largest confined aquifer of NWSAS. The use of environmental isotopes and long-lived radionuclides confirms that CI groundwater is recharged during humid periods of late Pleistocene (150–600 kyr). This information is important for evaluating groundwater dynamics and characterizing the recharge process. This will lead to identify and develop solutions for more effective groundwater management and policy.

References

1. Phillips, F.M.: Chlorine-36. In: Cook, P., Herczeg, A.L. (eds.) Environmental Tracers in Subsurface Hydrology, pp. 299–348. Kluwer Academic Publishers, Norwell, Massachusetts (2000)
2. Love, A.J., Herczeg, A.L., Sampson, L., Cresswell, R.G., Fifield, L. K.: Sources of chloride and implications for ^{36}Cl dating of old groundwater, southwestern great artesian basin, Australia. Water Resour. **36**, 1561–1574 (2000)
3. Sturchio, N.C., Du, X., Purtschert, R., Lehmann, B.E., Sultan, M., Patterson, L.J., Lu, Z.T., Müller, P., Bigler, T., Bailey, K., O'Connor, T.P., Young, L., Lorenzo, R., Becker, R., El Alfy, Z., El Kaliouby, B., Dawood, Y., Abdallah, A.M.A.: One million year old groundwater in the Sahara revealed by krypton-81 and chlorine-36. Geophys. Res. Lett. **31**, L05503 (2004)
4. Craig, H.: Isotopic variations in meteoric waters. Science **133**, 1702–1703 (1961)
5. Du, X., Purtschert, R., Bailey, K., Lehmann, B.E., Lorenzo, R., Lu, Z.-T., Mueller, P., O'Connor, T.P., Sturchio, N.C., Young, L.: A new method of measuring ^{81}Kr and ^{85}Kr abundances in environmental samples. Geophys. Res. Lett. **30**(20), 2068 (2003). https://doi.org/10.1029/2003GL018293
6. Mook, W.G., De Vries, J.J.: Environmental Isotopes in the Hydrological Cycle: Principles and Applications. IHP–V no. 39. UNESCO, Paris (2000)
7. Clark, I.D., Fritz, P.: Environmental Isotopes in Hydrogeology, 328 pp. Lewis Publishers (1997)