

## Water Rock Interaction [WRI 14]

# Water-rock interaction and residence time of groundwater inferred by $^{234}\text{U}/^{238}\text{U}$ disequilibria in the Tunisian Continental Intercalaire aquifer system

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### Abstract

The uranium content and  $^{234}\text{U}/^{238}\text{U}$  ratios have been measured in more than thirty groundwater samples over the Tunisian part of the Continental Intercalaire (CI) aquifer. In this large artesian aquifer, uranium behavior is mainly controlled by redox front systems. The uranium concentrations vary by 5 orders of magnitude from  $10^{-4}$  to 20 ppb and the ( $^{234}\text{U}/^{238}\text{U}$ ) activity ratio from 1 to 10. Close to CI outcrops in the Dahar Mountains, the stepwise decrease in U concentrations combined with a significant increase of the ( $^{234}\text{U}/^{238}\text{U}$ ) ratio up to 10 ("augmenting regime") is followed, downflow by a ( $^{234}\text{U}/^{238}\text{U}$ ) decrease up to 3 ("decaying regime"), clearly indicating the occurrence of a redox front. We will discuss the significance of  $^{234}\text{U}$ - $^{238}\text{U}$  disequilibria in terms of water residence times and its potential to trace water-rock interaction mechanisms.

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### 1. Introduction

The distribution of naturally occurring radionuclides in groundwater can provide important insights into water-rock interaction processes and residence time of fluids in geological systems. Processes occurring during water-rock interaction induce significant fractionation between U series nuclides that reflect their contrasting chemical behavior during their release into the fluid phase. This generally leads to

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pronounced radioactive disequilibria (i.e. departure of the parent/daughter activity ratio from unity) in fluid phase, whereas host rocks show only tiny disequilibria or, in most cases, secular equilibrium state even if this ultimately depends on the analytical precision. Due to their various half-lives, the U-series nuclides are powerful allies in the quest to investigate water-rock interaction processes over a large range of time-scales [1, 2]. Owing to the half-life of  $^{234}\text{U}$  ( $T_{1/2} = 245\,250$  yr) and the specific mechanisms that generate radioactive disequilibrium between the two isotopes of a same element, the ( $^{234}\text{U}/^{238}\text{U}$ ) activity ratio (AR) has attracted geochemists and hydrogeologists because of its potential use to trace groundwater flow pattern and characterize old groundwater [3]. ( $^{234}\text{U}/^{238}\text{U}$ ) disequilibrium systematically occurs in groundwater with ARs commonly in the range 0.5-6.0 [3], with in most cases, ratios  $>1$ . The  $^{234}\text{U}$  excess in solution results from either  $\alpha$ -particle recoil ejection of the  $^{234}\text{U}$  precursor,  $^{234}\text{Th}$ , into solution [4]; from enhanced mobility of  $^{234}\text{U}$  due to potential  $^{234}\text{U}$  oxidation during recoil [2]; or from preferential leaching of  $^{234}\text{U}$  from crystal lattices damaged by decay of the parent  $^{238}\text{U}$  [5].

Osmond and Cowart [1] developed a general model of AR evolution in confined aquifers that takes into consideration both the redox-dependent behavior of uranium and its impact on the alpha-recoiled  $^{234}\text{U}$  production and  $^{234}\text{U}$  excess in solution (see Fig 1). Under oxidizing conditions, uranium is in hexavalent state (U(VI+)) and highly soluble while in reducing conditions, it is reduced to its tetravalent state and characterized by very low solubility. Where oxidizing water enters the aquifer, uranium concentrations are relatively high and show a pattern of increasing concentration. ARs show near-equilibrium value or small  $^{234}\text{U}$  excess that may increase with residence time with AR up to 2-3 ("augmenting regime"). Where waters enter reducing zones, uranium concentration drastically decreases due to precipitation of uranium. Conversely, ARs increase due to enhanced  $^{234}\text{U}$  recoil production related to precipitated uranium on the host rock. Further downflow of the reducing zone, the U concentration remains relatively constant whereas the ARs decrease ("decaying regime") until they attain pseudo equilibrium with the rock matrix.

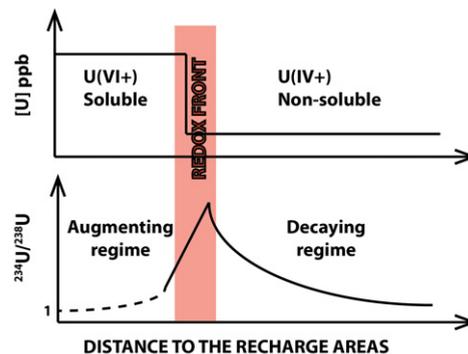


Fig. 1. General model of uranium concentration and  $^{234}\text{U}/^{238}\text{U}$  evolution in aquifers (Osmond & Cowart [1])

It results from this general model that  $^{234}\text{U}$  distribution in solution should be related to the residence time of the fluid. Therefore, numerous studies attempted to use the AR for groundwater dating [6]. However, in most studied aquifers, no clear relationship between groundwater ages and ARs was evidenced, casting doubt on the reliability of this method to date groundwater.

Here we report uranium isotope analyses from groundwater samples of the Tunisian part of the Continental Intercalaire (CI) aquifer. This study is part of large-scale work undertaken to constrain ages of groundwater in the North Western Sahara Aquifer System (NWSAS), using integrated geochemical and isotopic methods. This will allow us to discuss the relationship of the AR and groundwater residence time as constrained by others chronometers ( $^{14}\text{C}$ ,  $^{36}\text{Cl}$ ,  $^4\text{He}$ ).

## 2. Geological and hydrogeological settings

The CI aquifer is one of the largest confined aquifers in the world. It consists of a succession of several units (lower Cretaceous) of sandstone including clay-rich strata. In the central part of the basin, the facies are continental and, towards the east, lacustrine facies are progressively replaced by marine facies [7]. From south to north, the aquifer depth increases. The aquifer is considered as hydraulically continuous over the whole basin in agreement with major ions and most trace elements distributions that indicate continuous water-rock interaction, except near the Tunisian Chotts where the uniform evolution is disturbed by groundwater converging from additional flow lines [7]. Three main flowpaths from three recharge areas converge towards the main discharge area, the Gulf of Gabès (Tunisia), see Fig 2: W–E (from the Saharan Atlas), SW–NE (from southern Algeria) and S–N (from the Dahar region of Tunisia).

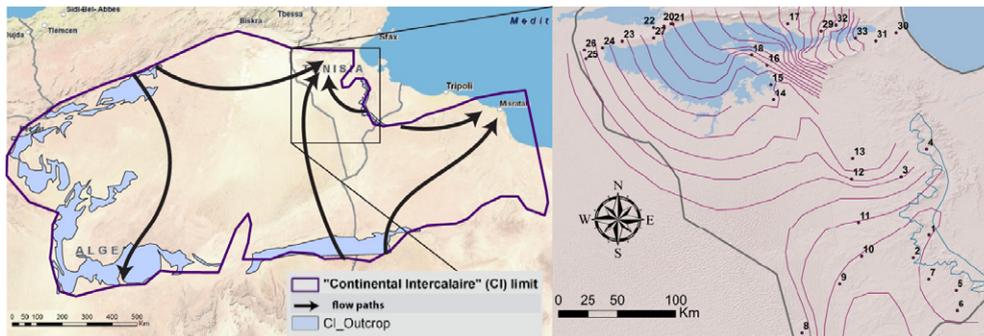


Fig. 2. Map of the CI with outcrops and main flowpaths. In the insert, the 32 sampled boreholes in the Tunisian part.

## 3. Sampling and analytical methods

Thirty-two borehole of the Tunisian part of the CI were sampled in November 2010 (Fig. 2b). One-liter samples were collected for uranium analyses in HDPE bottles and acidified with ultra-pure  $\text{HNO}_3$ . Uranium analyses were carried out on 200 ml of water. Following spiking with a  $^{236}\text{U}$ - $^{233}\text{U}$  spike and coprecipitation with iron (III) hydroxide, uranium was separated and purified using UTEVA resin. U isotope analyses were performed by Thermo Ionization Mass Spectrometry (TIMS) at CEREGE (Aix-en-Provence, France). Due to very low U content of some samples, special attention was paid to analytical blanks. Total blank procedure varies between 6 and 26 pg. This represents a significant amount (up to 60%) of uranium in some samples. Owing to the difficulty to correct for the blank contribution, these results were discarded, however they indicate that [U] of these samples is well below  $10^{-4}$  ppb.

## 4. Variations of uranium concentration and $^{234}\text{U}/^{238}\text{U}$ activity ratio (AR)

Uranium concentration widely varies from  $<10^{-4}$  to 20 ppb. Samples showing a concentration  $> 1$  ppb are located in the Dahar area, in agreement with the occurrence of oxidizing water close to CI outcrops. The remaining samples have [U] below 0,1 ppb highlighting reducing condition. Some samples have very low U concentration, below  $10^{-4}$  ppb, that are, to our knowledge, the lowest concentrations reported in the literature up to now (see [1]). These indicate that these waters are undersaturated with respect to uraninite. ARs vary from around 1 to 10. The highest ratios are located near the Dahar Mountains. This likely testifies the occurrence of a redox front in this area. Along the three main flow paths, the ARs evolution is neither continuous nor regular. However, we notice a general decreasing trend of the AR.

## 5. Evolution of $^{234}\text{U}/^{238}\text{U}$ and uranium concentration with residence time

Close to the outcrops, i.e. potential oxidizing areas, we found the highest uranium content and an increase of the  $^{234}\text{U}$  excess with the distance to the outcrops. In the reducing zones, uranium concentration dramatically decreases due to precipitation of uranium, from more than 1 ppb to 0.1 ppb. Further downflow, the AR decreases in agreement with the "decaying regime" proposed by Osmond and Cowart [1]. However, this decrease of the AR is combined with a diminution of the U concentrations in contradiction with the Osmond and Cowart model [1], which proposed a quite constant U concentration in the down dip reduced portion. This suggests that [U] decrease and its control by redox conditions may be related to residence time of U in the system. Assuming that the AR decrease downflow the redox front (from AR $\sim$ 10 to  $\sim$ 3) is only controlled by radioactive decay (i.e. the alpha recoil being negligible), we assessed a transfer time of 500 ka for U.

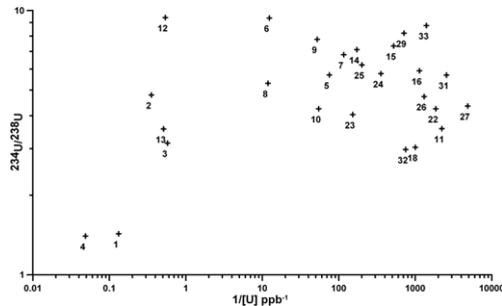


Fig. 3. ( $^{234}\text{U}/^{238}\text{U}$ ) AR versus uranium concentration in groundwater samples from the Tunisian part of the CI.

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