Leaching experiments on aquifer rocks of the Aquitaine Basin (France): uranium concentrations and activity ratios, preliminary results.

Christophe Innocent\textsuperscript{a*}, Eline Malcuit\textsuperscript{b}, Philippe Négrel\textsuperscript{a}, Emmanuelle Petelet-Giraud\textsuperscript{a}

\textsuperscript{a}BRGM, 3 avenue Claude Guillemin BP 6009, 45060 Orléans cedex 2, France
\textsuperscript{b}CFG Services, 3 avenue Claude Guillemin BP 6429, 45064 Orléans cedex 2, France

Abstract

Long-term leaching experiments were done using aquifer rocks of the Aquitaine Basin, ranging in age from Santonian to upper Eocene. Leachates were sampled after one hour, one day, one week, and one month, and were analyzed for U concentrations and activity ratios. Overall, U contents in the leachate decreased with increasing time. U activity ratios were characteristic of each aquifer rock. Only slight variations, when present, were found between the one-week and the one-month leachates. In most cases, the short-lived leachates (one hour, one day) displayed U activity ratios closer to the equilibrium value.

Keywords: leaching experiments; uranium; U-series; aquifer rocks; Aquitanian Basin; Eocene.

1. General background

The Eocene sands aquifer of the Aquitaine Basin (southwestern France) constitutes a critical groundwater resource, as it is extensively exploited for drinking water use, especially in the Bordeaux area. It is composed of sandy Tertiary sediments alternating with carbonate deposits, thus including a large variety of aquifer lithologies. It has been extensively studied for its hydrology, hydrochemistry and isotope geochemistry [1-5].

In this context, it is critical to constrain as precisely as possible the residence times of these groundwaters in their aquifer. Uranium isotopes potentially constitute a powerful tool for such
investigations, especially in the case of “old” groundwaters (i.e.; for residence times longer than the “limit” of $^{14}$C dating) [6]. However, this requires considering water/rock interaction processes, since the evolution of the ($^{234}\text{U}/^{238}\text{U}$) ratio corresponds in many cases to an open system.

$^{234}\text{U}$ activity ratios exhibit very high ($^{234}\text{U}/^{238}\text{U}$) ratios in some Eocene groundwaters, as high as 13.5 [7]. These very high $^{234}$U activity ratios correlate positively with previously obtained $^{14}$C ages [1], indicating that the enrichment in $^{234}$U due to water/rock interaction increases with time. This precludes the application of a simple down-flow model for radioactive decay of excess $^{234}$U [6]. However, alternative processes have been suggested to explain the high ($^{234}\text{U}/^{238}\text{U}$) ratios measured in some aquifers, for which these ratios, like in the case of the Eocene groundwaters, are expected to increase with time [8].

Thus, leaching experiments have been carried out in order to better understand the origin of such $^{234}$U enrichments in natural groundwaters by investigating $^{238}$U in the solid phase of the different aquifers. Cuttings recovered from 8 different aquifer rocks were selected. They include 4 lithological facies of Mid-Eocene sedimentary rocks: lignite-bearing sands and limestones, calcarenites and marls. In addition, two lithologies from lower Eocene (clays and lignite-bearing sands), one from upper Eocene (marly limestone) and finally one from Upper Cretaceous (Santonian limestone) were also leached.

2. Experimental

Approximately 2.5 grams of aquifer sample were placed in a closed bottle filled with 250 ml of water acidified with 50 µl of 6N HCl, which resulted in a pH value slightly lower than 3. Bottles were placed in an oven at 50°C. Once leaching time was reached, 20 ml of water were sampled. Then the bottle was re-filled with 20 ml of “new” acidified water, and put back in the oven. Leachates were sampled after 1 hour, then 24 hours, one week and finally one month. We are aware that such leaching experiments over a long period of time imply high water/rock ratios. As fine size fractions were present in the aquifer cuttings, the 1 hour leachates were centrifuged immediately after collection, in order to remove the fine fractions that were still not deposited at the bottom of the bottle. Leachates were spiked with a $^{233}\text{U}-^{236}\text{U}$ double spike and evaporated. $^{238}$U was extracted using a UTEVA resin [9] and run on a Neptune MC-ICP-MS equipped with a RPQ filter. Detailed analytical techniques on mass spectrometry have been published elsewhere [10].

3. Results and discussion

$^{238}$U concentrations in leachates vary from 7 pg/g to 1 ng/g, and are found to decrease with time, especially during the early stages (Fig. 1), except for the calcarenite of Mid-Eocene, for which $^{238}$U contents decrease regularly from the 1 hour to the 1 month leachate, and for the lignite-bearing sands of Lower Eocene, which displays the lowest $^{238}$U content in the 1 hour leachate.

$^{238}$U activity ratios in leachates are equal or higher than the equilibrium value whatever the leaching time, except for the calcarenite (Fig. 2). In this sample, the higher the leaching time is, the lower the activity ratio is. In most samples, the 1-hour leachate value is closer to the equilibrium compared to other leachates. This could partly result from the presence of small amounts of fine size fractions, in spite of the fact that these leachates were centrifuged (see above). The other leachates (24 hours, one week, one month) display in all cases $^{238}$U activity ratios that are comparable from a leaching time to the other. The highest value is obtained for the marls of Mid-Eocene, close to 2.
Fig. 1. U concentrations vs. leaching time. The symbols reflect the aquifer lithology and the colours the stratigraphy. Black lines correspond to lignite-bearing samples.

Fig. 2. U activity ratios vs. leaching time. Same symbols as in Fig. 1.
Decreasing U concentrations indicate that, after early leaching, U should be further trapped, with the exception of the lignite-bearing sands of Lower Eocene for which U seems to be continuously leached. The fact that both U concentrations and activity ratios are comparable in the 1 week and 1 month leachates suggests that some kind of a steady state is reached. At this stage there is no longer evidence based on U concentrations and activity ratios for significant fluid/rock interaction.

Finally, in spite of the fact that the highest measured activity ratios remain by far lower than those found in natural groundwaters, the grey marls of Mid-Eocene are the only aquifer for which water/rock interaction processes result in \((^{234}\text{U}/^{238}\text{U})\) ratios in the leachates that are largely higher than the equilibrium value. As a consequence, the grey marls seem to be the best (if not the only) candidate to explain the high activity ratios in groundwaters. A working hypothesis is that leaching parameters are not “mild” enough to trigger a more drastic fractionation between \(^{234}\text{U}\) and \(^{238}\text{U}\) during fluid/rock interaction.

4. Future work

U analyses are currently underway in the bulk aquifer samples, for budget calculations to be carried out. Further leaching experiments are also planned, involving water/rock interaction using pH 7 water at room temperature.

References

[1] André L. Contribution de la géochimie à la connaissance des écoulements souterrains profonds. Application à l’aquifère des sables infra-molassiques du Bassin Aquitain. Ph.D. Thesis, University of Bordeaux III 2002, 230 p.

[2] André L, Franceschi M, Pouchan P, Atteia O. Using geochemical data and modelling to enhance the understanding of groundwater flow in a regional deep aquifer. J Hydrol 2005; 305: 40-62.

[3] Négrel P, Petelet-Giraud E, Brenot A, Millot R, Innocent C. Caractérisation isotopique et géochimique des masses d’eau dans le bassin Adour-Garonne : interconnexions et hétérogénéités – CARISMEAU. Rapport final. Tome 1 : Les outils isotopiques appliqués à la gestion des ressources en eau. Exemple de la masse d’eau des sables infra-molassiques. BRGM Report 2008, BRGM/RP-56291-FR, 192 p.

[4] Malcuit E. Origine de la minéralisation des eaux dans un aquifère multicouche profond. Exemple de la “zone minéralisée de l’Entre-Deux-Mers” (Bassin Aquitain, France). Ph.D. Thesis, University of Bordeaux III 2012, 433 p.

[5] Négrel P, Millot R, Guerrot C, Petelet-Giraud E, Brenot A, Malcuit E. Heterogeneities and interconnections in groundwaters : Coupled B, Li and stable-isotope variations in a large aquifer system (Eocene Sand aquifer, Southwestern France). Chem Geol 2012; 296-297: 83-95.

[6] Osmond J.K., Cowart J.B. The theory and uses of natural uranium isotopic variations in hydrology. Atomic Energy Rev 1976; 14: 621-679.

[7] Innocent C, Négrel P. U-series constraints on aquifer groundwater residence time: the Adour-Garonne district case (southwest France). Mineral Mag 2008; 72: 321-324.

[8] Kronfeld J., Vogel J.C., Talma A.S. A new explanation for extreme \(^{234}\text{U}/^{238}\text{U}\) disequilibria in a dolomitic aquifer. Earth Planet Sci Lett 1994; 123: 81-93.

[9] Douville E, Sallé E, Frank N, Eisele M, Pons-Branchu E, Ayrault S. Rapid and accurate U-Th dating of ancient carbonates using inductively coupled plasma-quadrupole mass spectrometry. Chem Geol 2010; 272: 1-11.

[10] Millot R, Guerrot C, Innocent C, Négrel P, Sanjuan. Chemical, multi-isotopic (Li-B-Sr-U-H-O) and thermal characterization of Triassic formation waters from the Paris Basin. Chem Geol 2011; 283: 226-241.