

# $^{234}\text{U}/^{238}\text{U}$ DISEQUILIBRIA ALONG SEDIMENTARY DISCONTINUITIES IN A DEEP FORMATION: LATE DIAGENETIC U-RELOCATION PROCESSES VS. LARGE SCALE FLUID CIRCULATION EVIDENCE ?

P. Deschamps<sup>\*1,2</sup>, C. Hillaire-Marcel<sup>1</sup>, J-L. Michelot<sup>2</sup>, R. Doucelance<sup>1,3</sup> and B. Ghaleb<sup>1</sup>,  
1: GEOTOP, UQAM-McGILL, Montréal, H3C 3P8, Canada 2 : FRE CNRS-UPS OrsayTerre, Université Paris-Sud, Bat. 504, 91 405 Orsay Cedex, France,  
3: Laboratoire 'Magmas et Volcans', Université Blaise Pascal, Observatoire de Physique du Globe de Clermont-Ferrand, France  
\* Email: m106050@er.uqam.ca

## 1. Introduction

The safety of nuclear waste disposal in deep geological formation relies on the strategy of multi-barriers that must prevent or, at least, retard radionuclide migration from the disposal to the biosphere. From this viewpoint, uranium and thorium-decay series systematic provides site-specific, natural analogue information for the assessment of in-situ, short to long-term migration of radionuclides in the far field of a nuclear waste disposal in geological formation. One of the applications of U-series systematic in hydrological and geochemical characterisation of a potential nuclear waste disposal is to determine the state of radioactive equilibrium in the host rock body. This may help to assess the chemical stability of a potential host medium for a radioactive waste repository with respect to transport of chemical species by providing information on radionuclide migration on time scale up to 1 Ma. Any disequilibrium between a daughter radionuclide and its parent implies that a chemical disturbance has affected the rock and fractionated the both radionuclides. Such a disturbance must have occurred within a period that does not exceed a few half-lives of the daughter. One generally considers that it has been linked to water/rock interactions. This approach was first investigated by Schwarzc et al. (1982) and applied to experimental sites located in magmatic bedrock (e.g. Gascoyne and Cramer, 1987; Gascoyne et al., 2002; Gascoyne and Schwarcz, 1986; Griffault et al., 1993; Smellie et al., 1986; Smellie and Stuckless, 1985). In these studies, the focus was set on the altered or fractured zones of the rock matrix where water/rock interaction may have taken place. This approach permits to investigate the time scale of such interactions and, thus, to temporally constrain groundwater circulation event, as it is understood that both phenomena are associated. Here, we present highly precise and accurate isotopic analyses of uranium ( $^{234}\text{U}/^{238}\text{U}$ ,  $T_{1/2}(^{234}\text{U}) = 245,250$  a) from deep, low permeability, sedimentary formations in order i) to document the mobility of actinides in such environment and ii) to constrain the time scale of the geological phenomena responsible for it.

## 2. Geological and hydrological setting

This work is part of the geological investigations undertaken by the French Radioactive Waste Management Agency (ANDRA) in order to study the safety of radioactive waste repository in deep geological clay layers. The French government authorised ANDRA to build a scientific Underground Research Laboratory at a depth of 500 m in a 150-million-year-old clay formation straddling the Meuse and Haute-Marne regions (Eastern France). The target formation belongs to Mesozoic sedimentary rocks of the eastern Paris basin and is a thick (130 m), 420-550 m deep, Callovo-Oxfordian argillite unit. This formation is over- and underlain by low-permeability Oxfordian and Bathonian limestones, respectively (Figure 1). These oolitic/oncholoitic shelf limestones and bioherms are characterised by several generations of cements. According to stable isotopes evidence ( $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ ), Buschaert (2001) showed that i) the late generation of euhedral calcite cement constituted the filling of all macroscopic cavities and of the remaining micro-porosity and ii) the parent fluid of recrystallised cements, goeodes and fracture infillings likely contained a component of continental origin. Moreover, sub-vertical tension gashes are filled with the same kind of sparite as those of goeodes and micro-porosity. These micro-discontinuities, which are linked to the opening of extensional fractures, crosscut sub-horizontal stylolites, indicating a co-genetic formation.

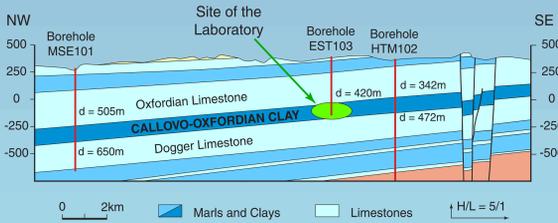


FIGURE 1: Northwest/Southeast geological cross-section of the ANDRA Eastern Site

## 3. Sampling

The sampling strategy was focussed on the Callovo-Oxfordian formation and its bounding Bathonian and Oxfordian formations, more particularly on the two interfaces between argillite and limestone units. The core samples analysed were obtained from two ANDRA prospecting boreholes located near the site where the Underground Research Laboratory is being built. The borehole HTM 102 (1101 m depth) was drilled within the whole series from Kimmeridgian to Bathonian sediments. It cross-cut the Callovo-Oxfordian argillite unit between 342.70 m and 472.16 m depth. The borehole EST 103 (526 m depth) reaches the Callovo-Oxfordian formation at 420m depth. Four argillite samples from borehole EST 103 and twelve Oxfordian and Bathonian limestone samples from the borehole HTM 102 were chosen. Samples showing homogeneous sedimentary structure (4 argillite and 5 limestone samples) were finely powdered and analysed for their uranium content and isotopic composition ( $^{234}\text{U}/^{238}\text{U}$ ). The 7 other samples are characterised by sedimentary discontinuities clearly identified as stylolites (see Photo 1 and 2). For these samples, we have sub-sampled the stylolitic joints as well as a part of the associated carbonate matrix rock close to the seam. For the HTM 02924 sample, as it showed a major sub-horizontal stylolitic joint in the middle, we have taken thirteen sub-samples, along a perpendicular transect to this discontinuity (see Figure 6). Finally, 33 sub-samples were finely powdered and analysed for their uranium content and isotopic composition. The subsamples of the HTM 02924 sample were also analysed for major and trace elements.

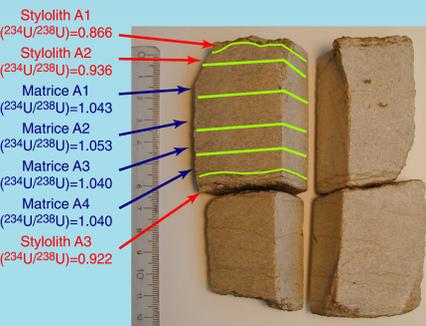


Photo 1: Sub-sampling of the HTM 02928 sample (478 m depth, Dogger Limestone)



Photo 2: Sub-sampling of the HTM 80824 sample (306 m depth, Oxfordian Limestone)

## 4. Analytical Techniques

High precision analyses are required to determine whether the system is at secular equilibrium or not. For this reason, we have developed a technique for precise measurement of uranium isotopic composition ( $^{234}\text{U}/^{238}\text{U}$  AR) as well as concentration using a Micromass IsoProbe MC-ICP-MS at the GEOTOP Research Center (Deschamps et al., 2003). Compare to the methods used by other MC-ICP-MS users for uranium analyses (e.g. Luo et al., 1997), we only use Faraday detectors in static mode. This strategy avoids the problems related to the gain calibration of the Daly-Faraday detectors. However, since we do not use a Daly detector and its associated energy filter, the high abundance sensitivity of this instrument (up to 28 ppm) becomes a major problem to solve. As a consequence, we have developed a method for tail correction, quite similar to the one proposed by Thirlwall (2001). This is based on the effective and precise quantification of tail contribution underneath each peak due to adjacent ion beams, as independently determined by measurements of mono-isotopic ion beams. We believe that this approach is of great interest for MC-ICP-MS users who will perform U as well as Th analyses. For uranium analyses, mass discrimination bias is corrected by the use of a double spike  $^{236}\text{U}$ - $^{233}\text{U}$ . Using a high efficiency desolvating microconcentric nebulizer system, the ARIDUS® MCN 6000, the amount of U consumed per  $^{234}\text{U}/^{238}\text{U}$  analysis is about 200 ng which is sufficient to obtain a  $^{234}\text{U}$  signal of 4 mV for 50 cycles of 5 seconds. This procedure takes approximately 10 minutes and allows us to obtain a precision and external reproducibility at least comparable to other laboratories (0.8‰ on the NBS 960, n = 19). Our analyses of this standard reference material are in excellent agreement with previously published values (see Figure 2). The results of duplicated measurements of a limestone sample (HTM 02924 #1) give a total reproducibility (analytical and chemical combined) of ~1.3‰ ( $2\sigma$ , n = 9) for the ANDRA samples (see Figure 3).

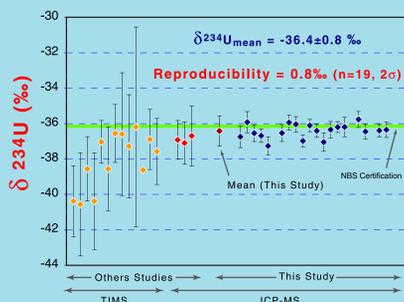


FIGURE 2: Comparison between our measurements of  $^{234}\text{U}/^{238}\text{U}$  on the NBS-960 (n=19) and data reported in the literature

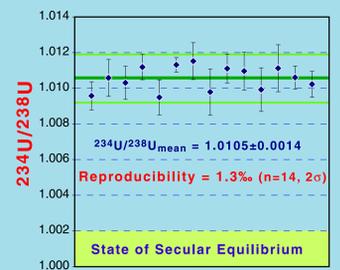


FIGURE 3: Duplicate measurements of  $^{234}\text{U}/^{238}\text{U}$  on one ANDRA sample (HTM 02924 #1, n=7)

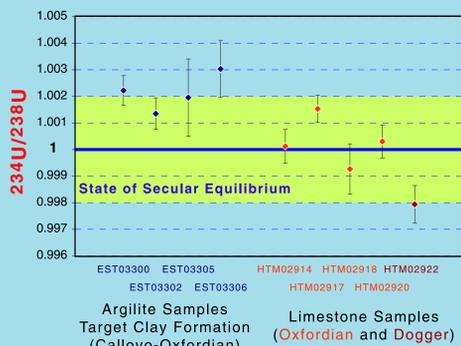


FIGURE 4:  $^{234}\text{U}/^{238}\text{U}$  measurements on whole rock argillite and limestone samples from EST 103 and HTM 102 borehole cores

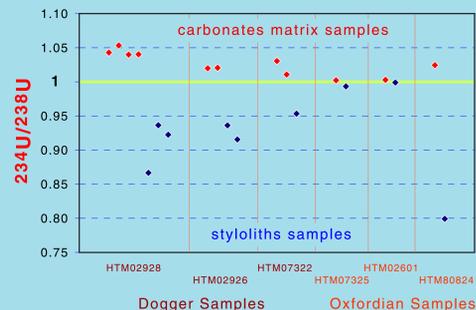


FIGURE 5:  $^{234}\text{U}/^{238}\text{U}$  measurements on styloliths (blue diamonds) and associated carbonate matrix samples (red diamonds) from HTM 102 borehole core

## 5. Results and discussion

Whole rock argillite and limestone samples displayed secular equilibrium between  $^{234}\text{U}$  and  $^{238}\text{U}$  (Figure 4) indicating that there has been no significant migration of  $^{234}\text{U}$  relative to  $^{238}\text{U}$  in these samples over period as long as the last 1Ma. However, all the stylolitic and associated carbonate subsamples displayed significant ( $^{234}\text{U}/^{238}\text{U}$ ) disequilibria (see Figure 5) with a systematic feature: the stylolitic samples were always characterised by ( $^{234}\text{U}/^{238}\text{U}$ ) < 1, when all the associated matrix rock sampled showed ( $^{234}\text{U}/^{238}\text{U}$ ) > 1. For the sample HTM 02924 (Figure 6), the transect exhibited a symmetric pattern relative to the stylolitic discontinuity with: (1) an increment of the U-concentration towards the stylolitic joint and (2) a sharp transition between significant ( $^{234}\text{U}/^{238}\text{U}$ ) < 1 disequilibria in the stylolith and an excess of  $^{234}\text{U}$  ( $^{234}\text{U}/^{238}\text{U} = 1.05$ ) in the vicinity of the joint, followed by a smooth decrement of the activity ratio away from the suture zone. The uranium concentration profile is identical to the insoluble element ones (Th, Zr, Al Si, see Figure 7), indicating that, in the stylolith, uranium is likely controlled by detrital minerals. Moreover, the subsamples located outside the seam can be explained by a mixing model between a non-altered carbonate rock matrix ( $^{234}\text{U}/^{238}\text{U} = 1$ ) and an altered matrix in which secondary carbonates have precipitated (see Figure 8). This phenomenon suggested a pervasive infiltration, form the suture zone to the embedding rock matrix, of a fluid characterised by ( $^{234}\text{U}/^{238}\text{U}$ ) > 1.05 and probably inherited from the carbonate pressure dissolution.

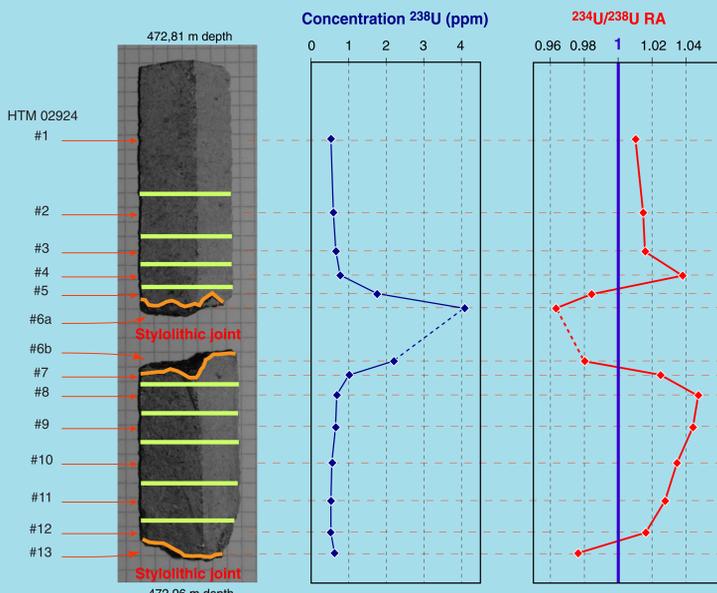


FIGURE 6: Uranium Concentration and  $^{234}\text{U}/^{238}\text{U}$  activity ratio in transect carried out on sample HTM 02924, collected 470 m downcore in HTM 102 borehole.

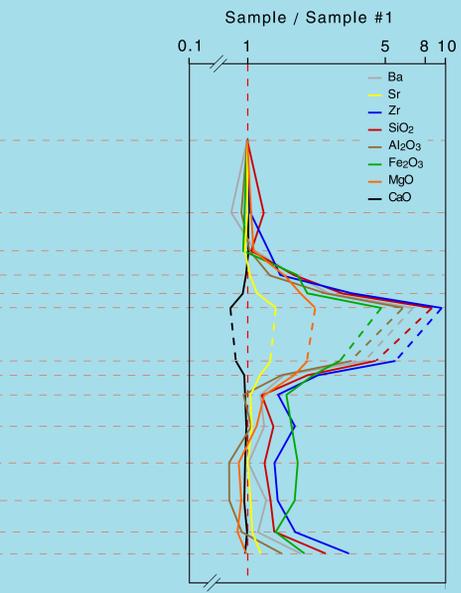


FIGURE 7: Variations of major element concentrations, normalized to sample #1, along the HTM 02924 transect.

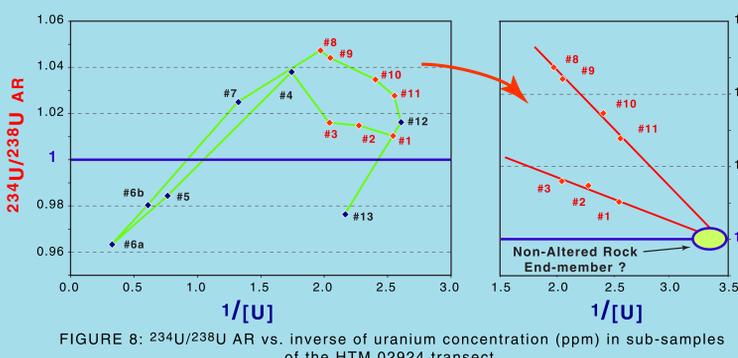


FIGURE 8:  $^{234}\text{U}/^{238}\text{U}$  AR vs. inverse of uranium concentration (ppm) in sub-samples of the HTM 02924 transect.

## 6. Conclusions

These results indicated that i) uranium migration has occurred within the last 1 Ma period and ii) styloliths play a major role in this remobilization. Such disequilibria are commonly attributed to water/rock interaction phenomenon related to fluid circulation. In this case, trace and major element data (Figure 7) rather indicated that the mechanism responsible for these disequilibria is epidiagenetic, directly associated with the presence of the stylolith, and likely due to micro-scale relocation of highly fractionated U from the stylolitic seams to the embedding carbonate matrix. Therefore, the chemical system might be seen, at a larger scale, as a closed one. However, the phenomenon responsible for the recent reactivation of the stylolitization is not determined. But, whatever is the process(es) involved, it has been active during the last Ma.

### Acknowledgements

The authors thank for constructive help and comments A. Poirier and Dr. H. Isnard. Dr. A. Simonetti's assistance for MC-ICP-MS measurement has been appreciated. ANDRA (French Nuclear Waste Management) provided drill-core samples and financial support for PD's Ph.D. RD was supported by a Lavoisier post-doctoral fellowship.

### Reference

- Buschaert S. (2001) Origine, âge et processus physico-chimiques des circulations de fluides dans les fractures: exemples de socle sous couverture (Vienne) et de formations riches en argiles (Gard, Ess). Ph. D. Université Henri Poincaré.
- Deschamps P., Doucelance R., Ghaleb B., Hillaire-Marcel C., and Michelot J. L. High-precision measurements of Uranium isotopic ratio using Multi-Collector ICP-MS: investigation of the tail correction problems. Submitted to Chemical Geology.
- Gascoyne M. and Cramer J. J. (1987) History of actinide and minor element mobility in an Archean granitic batholith in Manitoba, Canada. Isotope geochemistry of groundwater and fracture material in plutonic rock. Applied Geochemistry 2, 1, 37-53.
- Gascoyne M., Miller N. H., and Neymark L. A. (2002) Uranium-series disequilibrium in tuffs from Yucca Mountain, Nevada, as evidence of pore-fluid flow over the last million years. Applied Geochemistry 17(6), 783-792.
- Gascoyne M. and Schwarcz H. P. (1986) Radionuclide migration over Recent geologic time in a granitic pluton. Chemical Geology: Isotope Geoscience Section 59(1), 75-88.
- Griffault L. Y., Gascoyne M., Karinen C., Kerrich R., and Vandergraaf T. T. (1993) Actinide and Rare Earth Element characteristics of deep fracture zones in the Lac du Bonnet granitic batholith, Manitoba, Canada. Geochimica et Cosmochimica Acta 57(6), 1181-1202.
- Griffault L. Y., Gascoyne M., and Ford R. D. (1982) Uranium-series disequilibrium studies of granitic rocks. Geochimica et Cosmochimica Acta 46(1), 87-102.
- Smellie J. A. T., Mackenzie A. B., and Scott R. D. (1986) An analogue validation study of natural radionuclide geochemistry in crystalline rocks using uranium-series disequilibrium studies. Natural analogues to the conditions around a final repository for high-level radioactive waste. Chemical Geology 55(4), 233-254.
- Smellie J. A. T. and Stuckless J. S. (1985) Element mobility studies of two drill-cores from the Goetemar Granite (Kraakmaats test site), Southeast Sweden. Chemical Geology 51(1-2), 55-78.