IN SITU µ-RAMAN OBSERVATION OF URANIUM DIOXIDE WEATHERING IN CONTACT WITH WATER AND UNDER ION BEAM IRRADIATION

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Earth and space environment are sometimes the frame of extreme conditions of temperature, pression and irradiation. I*n situ* characterizations are necessary for a better understanding of the structural and chemical changes induced by such extreme environmental conditions. This paper deals with *in situ* Raman characterization of a material exposed to ionic irradiation.

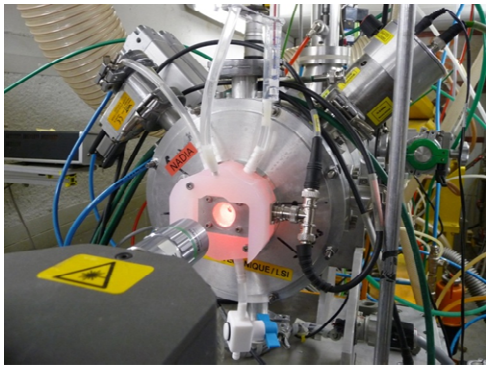

Fig.1 : In situ irradiation µ-Raman head with the cyclotron beam radiolyse cell.

One topic where the irradiation effect is a key-point is the study of the uranium mobility in the geosphere: Naturally, uranium exists in concentrations of a few ppm in soil, rock and water (more than 4 10^7 t as ore and 4.5 10^{12} t in sea water). Besides, the human activities induces a release of uranium ores and secondary weathering products to the surface environment.
It is well known that exposed to oxidizing conditions, tetravalent U(IV) present in uraninite and UO_2 spent nuclear fuel is incorporated in common alteration products as U(VI) –phases, up to form an assemblage of secondary uranyls minerals with chemical compositions indicative of the local environment. These uranyl phases are more soluble than U(IV) material and thus, this leads to an increase in mobility of uranium to groundwater and soil. For these reasons, the impact studies of the environment on the hydration-oxidation weathering of uranium minerals is of first importance.
For uranium compounds, deal with the environmental condition mean dealing with irradiation [1]: Indeed, uranium is naturaly weakly α radioactive with more than 100's million years half-life. Then, uranium products are the most often exposed to self-irradiation or irradiation from neighbouring active actinide products. Unfortunatelly, the possibilities to observe over time the effects of weak radio-activity as in the natural fission reactors of Oklo (Gabon) are infrequent. Effects of ionic irradiation can then be simulated by accelerator ionic beam, where high flux allows to simulate in a short time the dose and fluence of long time natural exposure. The sparsity of appropriate natural conditions and the experimental complexity of *in situ* ion beam characterization may explain the only few works on this topic.

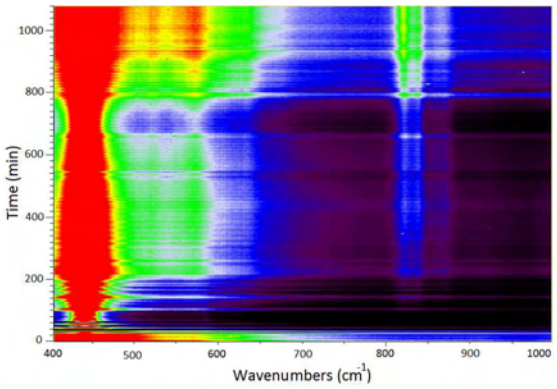

Fig.2: In situ Raman kinetic of the UO_2/water interface during and after irradiation. Colors represent Raman intensity and y-axis the time (one spectrum by 2 min).

Therefore, a significant part of this paper, is dedicated to the original *in situ* Raman spectrometer coupled with an ionic beam of a cyclotron accelerator (see figure 1). In a second part we present and discuss the Raman monitoring Uranium U(IV) dioxide / water interface under He ions irradiation. The figure 2 shows the evolution of the Raman spectra with time. One can distinguish the evolution of hydroxide and peroxide uranyl U(VI) compounds exhibiting signature in the 800-900 cm^{-1} range. Stability of these uranyl oxide hydrates versus the environmental conditions are widely discussed [2,3], and the irradiation effect clearly needs to be taken into account [4].
Our results provide, in part, a foundation for developing predictive models of U(IV) ↔ U(VI) natural cycles.

[1] Utsunomiya S. et al. (2005) *Earth planet. Sci. Lett.* , *240*, 521–528. [2] Sowder A.G. et al. (1999) *Environ. Sci. Technol.* , *33*, 3552–3557. [3] Kubatko K-A.H. et al. (2003) *Science*, *302*, 1191–1193. [4] Corbel C. et al. (2006) *J. Nucl. Mater.*, *348*, 1-17.