

Evidence for micro-scale U-mobility along sedimentary discontinuities in a deep limestone formation as inferred by $^{234}\text{U}/^{238}\text{U}$ disequilibria

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This work is part of geological investigations undertaken by the French Agency for Nuclear Waste Management in order to study the safety of radioactive waste repository in deep geological clay layers. The target formation, from Mesozoic sedimentary rocks of the eastern Paris basin (France), is a thick (130-145 m), 400-500 m deep, Callovo-Oxfordian argillite unit, that is over- and underlain by Oxfordian and Bathonian limestones, respectively. Borehole core samples have been analysed for their uranium content and isotopic composition as a means to document the mobility of actinides in such deposits.

Highly precise and accurate ($^{234}\text{U}/^{238}\text{U}$) analyses (0.2%) were obtained using a Multiple Collector Inductively Coupled Plasma Mass Spectrometry. Most samples of the target formation and its bounding formations display secular equilibrium. However, in the Bathonian formation near the interface with the argillite layer, significant ($^{234}\text{U}/^{238}\text{U}$) disequilibria are observed around sub-horizontal sedimentary discontinuities, sometimes clearly identified as stylolites. Isotopic and elemental compositions of uranium have been determined along a transect, perpendicular to a major discontinuity. The results exhibit a symmetric pattern relative to this discontinuity.

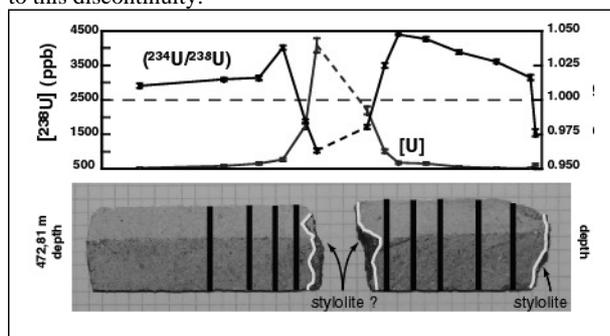


Figure 1: [U] and $^{234}\text{U}/^{238}\text{U}$ ratio in sample HTM 02924, collected 470 m downcore (the ~ 15 cm long core-sample has been rotated by 90°).

The nature and the modality of the process(es) responsible for these disequilibria (late epidiagenetic phenomenon, U-relocation from the U-rich stylolite into the U-poor embedding sediment or fluid circulation) are discussed. Whatever the process involved, it has been active during the last Ma.

Pyrite (FeS_2) oxidation at $\text{pH} < 3$

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FeS_2 oxidative dissolution in acidic media has been studied using quite every analysis technique available to scientist. We propose to use the $R = [\text{S}]_{\text{total}}/[\text{Fe}]_{\text{total}}$ aqueous ratio measured in batch dissolution experiments at $\text{pH} \approx 2$ in addition to solid characterization methods to identify the reactional mechanism. A value of $R=2$ is expected if the dissolution is thought to be stoichiometric. Aqueous S and Fe are respectively under SO_4^{2-} and Fe^{2+} forms. However a S deficit in solution was observed, leading to a ratio close to $R=1.60$. This S deficit was confirmed by complementary studies (Cf. fig. 1 and Descostes, 2001 for references and experimental procedures). We propose a mechanism based on S aqueous chemistry. $\text{S}_2\text{O}_3^{2-}$ is the first sulfoxyanion released in solution (Descostes *et al.*, 2001 and 2002). It is not stable in acidic medium (Cf. fig.2), and disproportionates into S^0 and $\text{S}_4\text{O}_6^{2-}$ before complete and rapid oxidation into SO_4^{2-} leading to $R=2n/n'$ where n and n' are the oxidation numbers of S in $\text{S}_2\text{O}_3^{2-}$ and $\text{S}_4\text{O}_6^{2-}$ respectively.

Figure 1: S/Fe ratio plotted against pH.

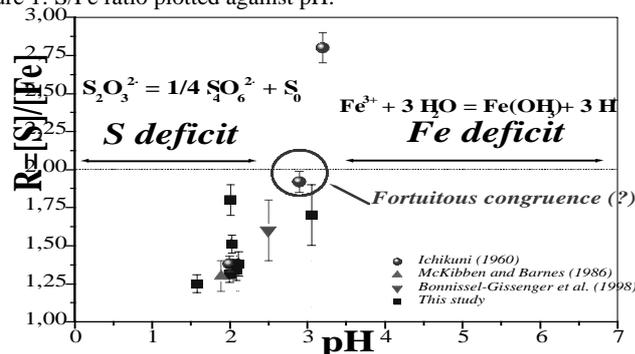
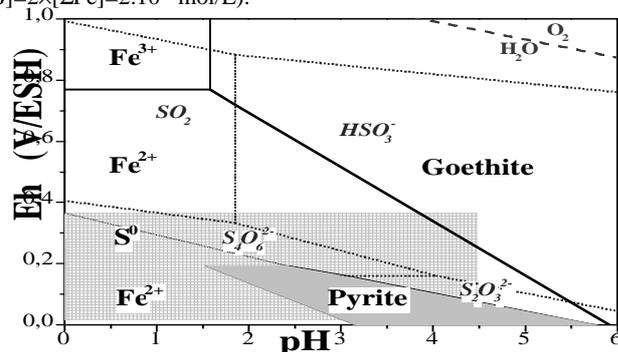


Figure 2: Fe Pourbaix diagram including S metastable species ($[\text{S}] = 2 \times [\text{Fe}] = 2 \cdot 10^{-5} \text{ mol/L}$).



References

- Descostes M., (2001), PhD Thesis, Paris VII University.
- Descostes M. et al., (2002), *Bull. Soc. géol. France*, in press.
- Descostes M., et al, (2001), *Nucl. Instr. and Meth. B*, **181**, 603-609.