An experimentalist call to theoreticians about XANES spectra theoretical simulation at the C K-edge, Ca and Fe $L_{2,3}$ edges

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Scanning transmission x-ray microscopy (STXM) is increasingly used in geobiology and more generally in Earth sciences [1-5]. It is a transmission microscopy providing images with 25-nm spatial resolution and a x-ray absorption near-edge structure (XANES) spectrum for each pixel of this image. The few beamlines that are available worldwide (e.g., 11.0.2 at the ALS or 10ID-1 at the CLS) give the opportunity to scan over a large energy range (e.g. 70-2200 eV) with high energy resolution enabling the study of elements such as C, N, O, Mg (using K-edges), or P, Ca, Fe or As (using L-edges). XANES spectra coupled with high spatial resolution can thus provide unique information on the speciation of diverse elements which is a 1st order interest for a variety of applications. However, very often, the use of the spectroscopic information is limited to a fingerprinting approach. We believe that theoretical developments would help retrieving significantly more information from these spectra. Here we will review some of the experimental work that we have done over the last few years in order to identify some key needs that we have and that might be adressed by theoreticians. In particular, we will discuss the use of XANES spectroscopy at the C K-edge to study the chemical composition and structure of organic carbon in (ancient) rocks and mention the implications for the study of metamorphism and/or search for ancient traces of life. Absorption variations due to linear dichroism in particular will be presented. The use of XANES spectroscopy at the Fe $L_{2,3}$ edges and difficulties to retrieve Fe redox state values will be adressed.

[1] Lepot *et al*. (2009) *Geochim. Cosmochim. Acta* 73, 6579-6599. [2] Bernard *et al*. (2010) *Carbon* 48, 2506-2516. [3] Carlut, *et al*. (2010), J. Geophys. Res. 115, G00G11. [4] Benzerara *et al*. (2011) *Ultramicroscopy*, in press. [5] Miot *et al*. (2009) *Geobiology* 7, 373-384.

Arsenic contamination of groundwater in Vietnam: Delta-wide survey and 3D geospatial modelling

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Arsenic contamination of shallow groundwater is among the biggest health threats in the developing world. The Red River Delta was recognized to be affected in 1998, but the spatial extension remained unknown [1]. Here we present the results of a groundwater survey of the entire Red River Delta combined with a unique probability model based on 3-dimensional (3D) Quaternary geology. Our investigations reveal that ~7 million delta inhabitants use groundwater that contains unsafe levels of As, Mn, Se, and Ba.

Global and sub-continental arsenic risk maps based on surface geology were recently shown to be a successful tool to initiate mitigation measures [2,3]. For the Red River delta we now established a 3D model based on stratigraphy of Quaternary geology, which visualizes As hot-spots at depths and identifies safe regions for drinking water production.

This 3D model further reveiled anomalities of As enrichment in the aquifers. Particularly in the Hanoi area, depth-resolved probabilities and As concentrations indicate drawdown of As-enriched water from Holocene aquifers to naturally As-safe Pleistocene aquifers, most likely as a result of more than 100 years of groundwater abstraction. Vertical As migration induced by large-scale pumping from deep aquifers has been discussed to occur elsewhere, but has never been shown to occur at the scale seen here. The present situation in the Red River Delta is hence a warning for other As-affected regions where groundwater is extensively pumped from uncontaminated aquifers.

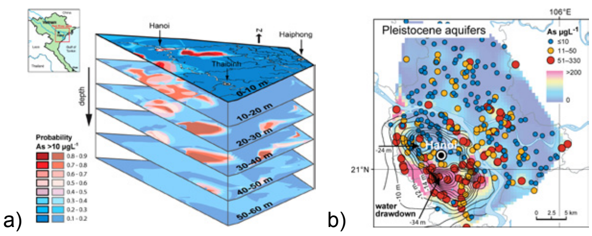

Figure 1: a) As risk map (3D), Red River Delta. b) As levels in the Pleistocene aquifers, and water drawdown in Hanoi [4].

[1] Berg *et al*. (2001) *Environ. Sci. Technol.* **35**, 2621-2626. [2] Winkel *et al*. (2008) *Nature Geosci.* **1**, 536-542. [3] Amini *et al*. (2008) *Eviron. Sci. Technol.* **42**, 3669-3675. [4] Winkel *et al*. (2011) *Proc. Natl. Acad. Sci. USA*. **108**, 1246-1251.