Adsorption of alkyl carbon by soil smectites

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Introduction

Placement of organic C in the stable soil organic carbon pool, characterised as that C with residence times $\geq 10^2 - 10^3$ years, remains the aim of all comprehensive C sequestration strategies, particulary those implemented to help achieve targets established within the Kyoto Protocol [1]. Alkyl C molecules constitute a significant portion of the stable organic C pool by virtue of their recalcitrance and frequent occurrence as species sorbed to the interlayer surfaces of expanding layer silicates. Here we describe the influence of humic substances on the adsorption of alkyl C molecules by a soil smectite.

Methods

Portions of <2μm, Na-saturated montmorillonite (SWy-1; CMS Source Clays) were suspended in 0.01 M $NaOCl_4$ then reacted with one of three representative alkyl C molecules in the presence or absence of FA (Elliot Soil FA II; IHSS Standards), at pH 5, 6, 7 and 8. Following 24h reaction at 25°C, the solid and solution were separated by ultrafiltration. Total organic C sorbed to the montmorillonite was measured by combustion; solution FA was quantified by UV absorption at 260 nm; adsorbed alkyl C determined by difference.

Results

We observe increased adsorption of alkyl C by montmorillonite at all pH values when FA is present. The additional alkyl C uptake varied from 1 to 2 μmol/g, decreasing with increasing pH. We propose that alkyl C forms stable associations with FA, a water-soluble humic material composed of contiguous hydrophilic and hydrophobic domains bound by van der Waals forces, π-π interactions, and H-bonds [2], and subsequently enters the interlayer space in Trojan horse fashion, concealed within the FA complex. This mechanism is consistent with the strong, positive correlation observed between FA and alkyl C abundance in soils, most notably Podzols [3].

[1] *IPCC* (2000) Cambridge University Press. 388pp. [2] Sutton *et al.* (2005) *ES&T* **39**, 9009-9015. [3] Lorenz *et al.* (2007) *Geoderma* **142**, 1-10.

Redox reactions in the reduced carbon-sulfate-uranyl system at 200-300°C: Experimental evidence and consequences for U metallogenesis

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Unconformity related uranium deposits are the world richest U deposits. They are generally rooted in graphite-bearing structure developed in graphite-bearing metasedimentary rocks in the basement. The mineralizing process is considered to occur between 150 to 200°C. [1] Reduction is a key parameter for uraninite precipitation (U^{IV}) from uranyl ions (U^{VI}) in the fluid. Graphite has been considered since a long time as non-reactive in this temperature range although alteration of graphite has been identified [2]. The aim of this paper is to investigate experimentally the role of carbon under different forms (graphite, nanocarbon and methane) for reducing uranyl sulfate solutions to precipitate uraninite.

Experiments are conducted in silica glass closed capillary [3] allowing observation under an optical microscope with *in situ* monitoring of the initial products and run products at experimental conditions.

The evolution of the concentration of the different sulfur valencies are monitored using Raman spectroscopy for each experiment. The valencies of sulfur from valency 6 to valency -2, and the carbon-bearing gas species resulting from these reactions are specifically investigated. The dissolved uranyl content is monitored combining Raman and fluorescence spectroscopy.

Experimental data are discussed in terms of the role of the carbon-bearing layers, the organisation state of graphite, and the role of methane in the precipitation of uraninite.

[1] Derome *et al.* 2005. *Economic Geology* **100**, 1529-1545. [2] Wang *et al.* (1989). *Carbon* **27**, 209-218. [3] Chou, Song & Burruss (2008). *Geochim. Cosmochim. Acta* **72**, 5217-5231.