

Natural organic matter (NOM)-clay association and impact on Callovo-Oxfordian clay stability in high alkaline solution: Spectromicroscopic evidence

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Abstract. The understanding of chemical association between natural organic matter (NOM) and clay minerals is of paramount importance to predict the long term stability of host rock formations for deep geological nuclear waste repositories. Synchrotron-based soft X-ray spectromicroscopy demonstrates a strong association between K-rich clay phases (illite) and NOM in the Callovo-Oxfordian argillite (Meuse-Haute Marne, or MHM site, France) and a weaker association in the Opalinus clay (Benken, Switzerland). C(1s) spectra show no significant depth dependent variation in the MHM site (447-516m). Alteration experiments under oxidizing conditions and high pH of the Callovo-Oxfordian clay indicate a passivation of chemically reactive sites by NOM that is responsible for the kinetic hindered clay dissolution/transformation. These experiments lead to a significant release of humic/fulvic acid colloids in the alkaline solution with time dependent variation in size and functional group content.

1. INTRODUCTION

Host rocks considered for deep geological storage of nuclear waste include clay-rich formations as (e.g.) the Callovo-Oxfordian argillite (MHM site, France) and the Opalinus shale (Zürcher Weinland, Switzerland). However, there are concerns that the mineralogical composition of these clay formations will not be stable under alkaline pore fluid conditions (pH > 12) typical for initial cement alteration. To assess this stability, the impact of the Solid Young Fluid (SYF) [1] on the clay mineralogy of the Callovo-Oxfordian argillite has been studied experimentally under oxidizing conditions which are expected to occur in the excavation disturbed zone (EDZ) during the installation of the repository shafts and galleries. Indeed, in the alteration experiments performed by [2], the clay mineralogy is little affected as compared to analogue studies with pure smectite systems [3] even though the pH is still high after long reaction times. This low reactivity of clay minerals has been attributed to the presence of organic matter in the samples [2], and an important release of organic colloids has been observed. Because the marine/terrestrial deposition of argillite and shale generally occurs in the presence of organic material [4] and because the P/T evolution during burial diagenesis/catagenesis can change drastically the organic composition in these systems [5], reliable clay stability predictions can only be drawn if the NOM-clay association is precisely characterized. As a consequence, the present study focuses on (1) the C(1s) and K(L_{2,3}) NEXAFS (Near Edge X-ray Absorption Fine Structure) spectromicroscopic characterization of the initial clay-NOM association in the Callovo-Oxfordian argillite and Opalinus shale, (2) investigation of the role of NOM on clay dissolution kinetics and (3) the critical evaluation of NOM as a potential source for humic & fulvic acid colloids in solution under oxidizing conditions.

2. EXPERIMENTAL

The clay fraction (< 2 µm) of four MHM samples (447, 490, 494, 516 m below surface - borehole EST 104) and one Opalinus shale sample (579.19-579.45m - borehole Benken) were selected as representative of the two mineralogical sequences. For details on clay fraction preparation, mineralogical characterization and batch experimental setup under alkaline conditions it is referred to [2, 6]. The TOC concentration in the Bure argillite is depth independent ~1.3 wt% and < 0.4 wt% in the Opalinus clay [2, 6]. Scanning transmission X-ray microscopy (STXM) investigations were performed at the beamline X1A (NSLS) op-

erated by the State University of New York at Stony Brook. The principle of the method and the sample preparation using a wet cell assembly is described in [7,8]. STXM images of clay suspensions were recorded at the carbon K-edge and potassium L-edge. In the NEXAFS spectra illitic clays are identified using the X-ray absorption double feature at 297.3 eV (L₃-edge) and 300 eV (L₂-edge) of interlayer potassium. STXM investigations on alkaline treated samples are limited to sample 447. For C(1s) NEXAFS spectra deconvolution ionization threshold (IP) was set to 290.5 eV and a single arctangent function was used to generate the continuum spectrum up to 295 eV. FWHM of Gaussian peaks was set to 0.4 eV and 7 Gaussian functions representing the main π^* transitions were used (Fig. 1A). Two additional σ^* -transitions were simulated by simplified Gaussian shape function with a FWHM of 0.6 eV and 0.8 eV, respectively.

3. RESULTS & DISCUSSION

3.1 Untreated clay

The simultaneous measurement of the C(1s) NEXAFS and the potassium L-edge in the same pixel area clearly indicates an association of NOM with K-rich clay phases (illite) in the Callovo-Oxfordian argillite (Fig. 1A). Furthermore no significant depth dependent C(1s) variations in the average spectra are noticeable after deconvolution of the spectra (Tab.1). The observed clay-NOM association can be interpreted as a so-called sorptive protection mechanism preventing diagenetic degradation of NOM via sorption on clays [9]. The microscopy of the clay-NOM associates (Fig. 1B) shows no homogeneous clay coverage in form of a monolayer coating as proposed by [10], but rather a blurred patchy distribution [11]. The noted association implies that NOM sequestration may be more closely related to patterns of continental weathering and clay mineralogy than to ocean water chemistry or marine productivity as already pointed out by Kennedy and co-workers [12]. Isolated organic areas with high aromatic content known as amorphous organic matter (AOM) typical for Type II kerogen [13] were also observed (Fig. 1B). This discrete AOM constitutes usually only a minor portion (<10%) of the total organic carbon [12] in which oxidized organic compounds (benzoquinone type groups) are detectable.

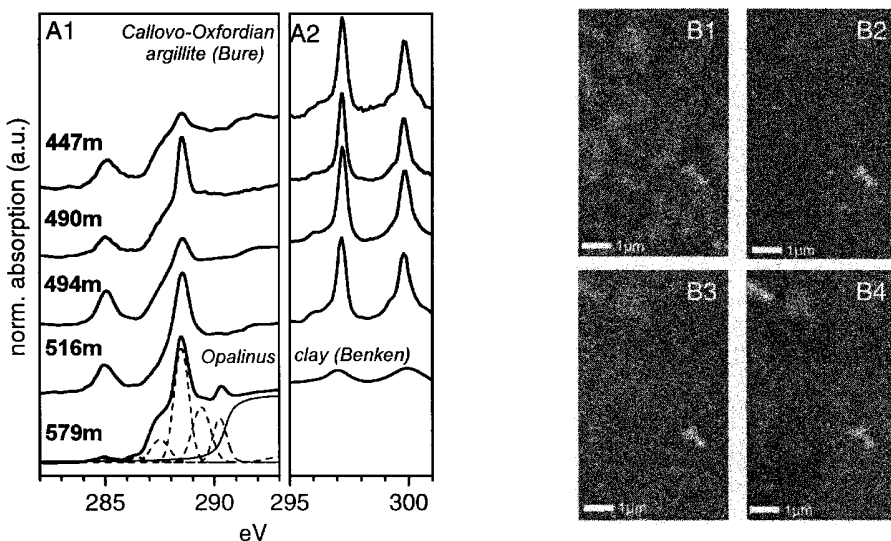


Figure 1: A1: C K-edge spectra of the Bure and Opalinus untreated clay fraction and Gaussian functions used for deconvolution. A2: Potassium L_{2,3} edges of the samples. B: Ratio images ($-\log [I/I_0]$; $I_0 = \Sigma(280-283\text{eV})$) of sample 490m. B1: Potassium distribution, $I=297.2\text{eV}$; B2: aromatics, $I=285\text{eV}$; B3: aliphatics, $I=287.6\text{eV}$; B4: carboxyl, $I=288.4\text{eV}$.

In addition, enrichment in carboxyl groups has been observed in the K-rich areas (thick illite platelets) in samples of the MHM site. In comparison, the untreated Opalinus clay (Fig. 1A) shows lower potassium L-edges absorption in the C-edge normalized spectra, therefore indicating a weaker association of NOM

with K-rich illite. This might point to a preferential association with other clay mineral phases (kaolinite, chlorite) as indicated by additional FT-IR measurements. Furthermore Opalinus clay is significantly depleted on aromatic functional groups in comparison with the samples from the MHM site. The ratio of the $1s-\pi^*$ transition at 285eV and of aromatic carbon bonded to oxygen (286.6eV; phenol type groups) in Opalinus clay is similar to values reported for hydroquinone and implies an average degree of hydroxylation close to 2OH/ring and lower than reported values for phenol indicating an average hydroxylation $\sim 1\text{OH}/\text{ring}$ in the Bure argillite [14, 15]. A possible explanation for the significant lower aromatic band intensities (285 eV) in the Opalinus shale might be the polycondensation associated relative increase of carboxyl and aliphatics according to the P/T history of the sediment. In addition, oxidation of the Callovo-Oxfordian argillite increases the content of triaromatic steroids (phenanthrene) in the total aromatic fraction [16].

Table 1: Semiquantitative analysis of the average Carbon K-edge by spectra de-convolution in the energy range 280-295eV. Values given are proportion in % of the sum of the seven π^* Gaussian peaks used.

Sample	$\frac{C_{\text{arom}}-C_{\text{arom}}}{C_{\text{arom}}-H}$, phenol type	CH_2, CH_3 carboxyl	carbonyl	carbonate	$\Sigma(I_{\text{fit}}-I_{\text{meas}})^2$		
Opalinus	1.6	3.0	18.4	38.8	23.1	15.2	0.03297
Bure 447m	12.0	4.1	18.9	31.4	21.4	12.1	0.26007
Bure 490m	10.1	3.3	19.7	36.3	23.6	7.0	0.04825
Bure 494m	12.4	2.4	15.2	35.6	23.0	11.4	0.04678
Bure 516m	11.9	3.2	17.6	35.0	22.1	10.2	0.16874

3.2 High alkaline solution reaction of Callovo-Oxfordian argillite

After 2 years reaction in SYF the NOM is still partly associated with clay and covers clay particle edge Si, Al functional groups (Fig. 2C), whereas basal surfaces appear to be depleted of their initial organic coverage [2]. Spectra of the clay associated NOM after SYF reaction show features similar to that observed for the untreated clay material (Fig. 2A). After two years reaction time bonding of organic ligands to crystal edges is still effective, and the limited increase of carboxyl groups in released DOC (Fig. 2B)

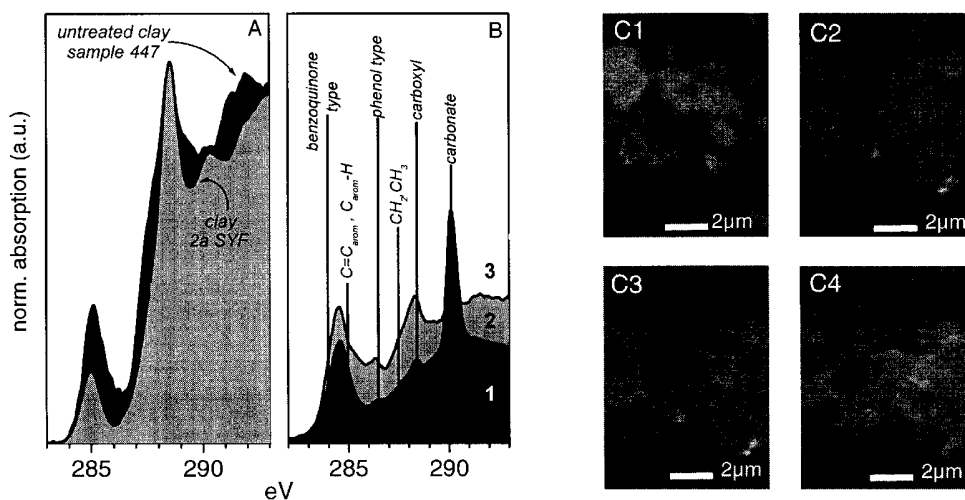


Figure 2: Clay sample 447 m (MHM site) after alkaline alteration. A: C K-edge spectra of the untreated clay fraction and after two years reaction time in SYF solution. B: Carbon functional group characterization in reaction solution (DOC), 1: 3d in SYF; 7.1% of TOC released. 2: 74d in SYF (25.8%) 3: 350d in SYF (40.9 %). All absorption spectra initially normalized to 1 at 295 eV and spectra in B are weighted on the relative amount of DOC released. C: Ratio images ($-\log [I/I_0]$; $I_0 = \Sigma(280-283\text{eV})$) of sample 490m 2a treated in SYF. C1: Potassium distribution, $I=297.2\text{eV}$; C2: aromatics, $I=285\text{eV}$; C3: aliphatics, $I=287.6\text{eV}$; C4: carboxyl, $I=288.4\text{eV}$.

suggests a carboxyl mediated strong NOM surface complexation. The observed passivation of these reactive clay edge sites is likely responsible for the very limited mineralogical transformation in SYF as discussed by [2]. In addition, enrichment in carboxyl groups has been observed in the K-rich areas (thick illite platelets) in samples of the MHM site. The organic matter (DOC) released from clay after one year reaction in SYF represents ~40% of the total C_{org} content. Under high alkaline conditions expected in the near-field of a nuclear-waste repository with cement waste packages, such high concentrations of hydrophilic organic substances are generated by conversion of initially clay associated mainly hydrophobic natural organic matter. This DOC is quantitatively HA & FA and shows a continuous decrease in colloid size to $80\% < 1\text{kDa}$ after one year reaction time [2]. The released HA/FA C(1s) spectra differ significantly from the clay associated NOM and shows benzoquinone type (284 eV) functional groups indicative for oxidative processes (photodegradation). Additional fluorescence spectroscopy studies reveal a significant red shift of the isolated HA to 520 nm in the emission spectra with a excitation wavelength of 260 nm [17]. This red shift can be related to a significant contribution of quinone type groups to the overall HA fluorescence as pointed out by [18]. These results together with the above mentioned observation of benzoquinone type groups on AOM support the sorptive protection mechanism of NOM via clay association proposed by [9]. Furthermore a pronounced increase of phenol type groups (286.6 eV) and, to a lesser extent, of carboxyl groups (288.6 eV) with time is observable. FT-IR investigations showed comparable spectra independent of sampling depth for the HA isolates after one year SYF reaction [17]. However, a decrease in released DOC concentration can be observed with sediment depth [2] leading to two possible explanations: (a) Diagenetic differences in the Callovo-Oxfordian formation resulting in a stronger polycondensation and insolubilization (humins) of HA/FA in the lower sediments or (b) considerable land derived organic matter in the upper part of the formation, where HA and FA can still amount from 5-70% after complete diagenetic insolubilization.

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