Differences in properties and Cm(III) complexation behavior of isolated humic and fulvic acid derived from Opalinus clay and Callovo-Oxfordian argillite

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Abstract

Fulvic acids from deep clay formations have been isolated by the International Humic Substances Society (IHSS) standard protocol and analyzed. Near edge X-ray absorption fine structure (NEXAFS) spectroscopy reveals, that the basic structural features relating to the origin of the clay organic matter (i.e., terrestrial or marine) are preserved even after the around 150 Ma since deposition (Jurassic sediment). Analysis by asymmetrical flow field flow fractionation (AFFFF) shows the size distribution peak found for typical fulvic acids. In addition, a second larger size peak is found for the fulvic acids influenced by marine deposition. These fulvic acids also have a considerable content of organic material which does not absorb in the visible range. The Cm(III) complexation behavior has been studied by time-resolved laser fluorescence spectroscopy (TRLFS). Despite considerable fluorescence quenching, the complexation constant is shown to be in the same range as published values found for different typical fulvic acids.
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1. Introduction

The purpose of the present study is to characterize humic substances extracted from Opalinus clay and Callovo-Oxfordian argillite with respect to complexing properties. As these two geological formations are under investigation as potential host rocks for a nuclear waste repository (Thury, 2002; Lebon and Mouroux, 1999; Jorda, 2000), physico-chemical perturbations induced by the storage concept (i.e., Multi Barrier System) and potential consequences for the host rock retention capacity should be taken into account and investigated. Cement may be present in a nuclear waste repository as a waste form or as part of engineered structures. In the case of water intrusion, cement alteration will generate highly alkaline solutions (initial pH ∼ 13) that can influence clay reactivity via mineral dissolution and/or transformation (Chermak, 1992, 1993; Eberl et al., 1993; Bauer and Velde, 1999). Recently, Claret et al. (2002) and Schäfer et al. (2003b) showed that the clay dissolution expected under the above conditions was strongly influenced by the presence of natural organic matter present in the starting clay sediment (total organic

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carbon (TOC), 0.4–1.4 wt%). Furthermore, these studies demonstrated that a high concentration (~300 mg L^{-1}) of humic substances can be generated. The latter are widely recognized as important complexing agents towards inorganic and organic pollutants in the geosphere and therefore can play a major role in radionuclide migration in natural aquifers systems (Choppin, 1992; Moulin and Ouzounian, 1992; Vilks et al., 1998; Artinger et al., 2002; Schäfer et al., 2003a).

On a short time scale, a minor fraction (a few percent) of the clay organic matter is dissolved. With prolonged alkaline solution contact time a large portion (up to around 50% after about 1.5 a) of the hydrophobic clay associated organic matter becomes chemically converted into hydrophilic humic and fulvic acids (HAs and FAs) (Claret et al., 2003).

In the present paper, HAs and FAs extracted and isolated from Callovo-Oxfordian and Opalinus Clay using a slightly modified International Humic Substance Society (IHSS) protocol were investigated by UV/Vis spectroscopy, asymmetrical flow field-flow fractionation (AFFFF) and near edge X-ray absorption fine structure (NEXAFS) spectroscopy. The latter technique can offer practically the same level of information as nuclear magnetic resonance (NMR) (Scheinost et al., 2002; Schäfer et al., 2003c) but requires a very small amount of sample (~10^{-3} mg). The complexation behavior with trivalent actinides (Cm^{3+}) is studied by time resolved fluorescence spectroscopy (TRFLS).

2. Experimental

2.1. Sample origin and HAs and FAs extraction protocol

Callovo-Oxfordian clay samples from the Meuse Haute Marne site (MHM) and the Opalinus shale were investigated. The Opalinus clay sample is from 579.45 m depth of the investigation borehole Benken. Three samples from different depths of the MHM site were studied, representative for the full mineralogical sequence. These samples are from the borehole EST 104 at 447, 494 and 516 m depth (Claret et al., 2002, 2004). The TOC content in the MHM argillite clay fraction is depth independent at around 1.3 wt%. The TOC content in the Opalinus clay fraction is lower (around 0.4 wt%, Schäfer et al., 2003b). In the Callovo-Oxfordian sediments, biomarker analysis showed that the sedimentation environment in the upper stratigraphic layer (Oxfordian, sample 447) is mainly terrestrial (type III kerogen), whereas the lower stratigraphic layer (Callovian, sample 494 and 516) is mainly of marine influence (type II kerogen) (Landais and Elie, 1999). For the Opalinus clay the deposited sediments are of mixed terrestrial and marine origin (Mazurek et al., 2002; Nagra, 2002).

Before extracting the <2 μm size-fraction by centrifugation, carbonates were removed using the acetic acid–acetate buffer method described by Moore and Reynolds (1989). Thereafter, the humic substances were extracted using a slightly modified IHSS protocol (Swift, 1996). This extraction was done with 0.5 N NaOH under Ar and was repeated (7 times) in order to increase the extraction rate. After pH adjustment to 1 using purified 1 M HCl, the humic acid (HA) flocculate was separated by centrifugation (4300 rpm). The HA was re-dissolved in 0.1 M NaOH and NaF added. The sample was acidified again and left over night. The dissolution with NaOH was then repeated, followed by flocculation at pH 1. Finally, the flocculate was washed twice with 0.1 M HCl and freeze dried (Buckau, 1991).

After separation of the HA by flocculation from the original alkaline extract, the fulvic acid (FA) in the supernatant solution was isolated by sorption on a XAD-8 column. It was purified by two cycles of sorption on a XAD-8 column followed by alkaline elution (NaOH). Due to the small total amounts, the purified FA samples were used as the final concentrate solutions. The yield of HA from the MHM samples is between 5.2% and 7.1% TOC. The yield of FA from the MHM and Opalinus samples is between 0.5% and 1.3%. No HA was found or detectable in the Opalinus sample. The original content of TOC in the clay fraction and the yields of HAs and FAs from the different samples are given in Table 1. As the total amount of sample was in the μg range for the FAs and the HAs, NEXAFS was chosen according to its high sensitivity in this concentration range.

2.2. UV/Vis spectroscopy

UV/Vis spectroscopy was performed with a Cary 5 spectrophotometer (Cary Co., USA). UV/Vis absorption of humic substances strongly depends on the chemical conditions, namely pH, ionic strength, and the degree of complexation with metal ions (MacCarthy and Rice, 1985; Buckau, 1991). Consequently, compari-

Table 1
Total organic carbon (TOC) in the starting clay fraction samples and the fraction of TOC extracted as humic acid (HA) and fulvic acid (FA)

Sample	TOC (wt%)	HA (% of TOC)	FA (% of TOC)
447 HA/FA	1.4	5.2	1.3
494 HA/FA	1.4	5.2	1.2
516 HA/FA	1.4	7.1	0.5
OPA FA	0.4	≈0.0	1.1

*447, 494 and 516: respective depths of samples from the MHM site.
"OPA FA": fulvic acid extracted from Opalinus clay.

son of spectra from different samples requires well-defined measurement conditions. Therefore, in the present study a background electrolyte of 0.1 M $NaClO_4$ was used with solutions buffered at pH 8.5 by 10^{-3} mol/L TRIS (tris(hydroxomethyl)aminomethane). In addition, 10^{-3} M EDTA was added to avoid the possible influence of higher valent metal ions complexing with humic substances. For HA measurement, Milli-Q water was used as a blank solution. For FA, NaOH passed through the XAD-8 column prior to the FA concentration/purification was used.

2.3. NEXAFS

NEXAFS carbon K-edge spectra were measured at the scanning transmission X-ray microscopy (STXM) beamline X1A1 (NSLS), operated by the State University of New York at Stony Brook. The principle of the method is described in detail elsewhere (Jacobsen et al., 1991). The absorption by different C structures follows the Lambert–Beer Law, i.e., the absorption is directly proportional to the different mass absorption coefficients of different C functionalities as a function of the X-ray wavelength. Images are recorded between 280 and 305 eV, using the image stack option (Jacobsen et al., 2000). Image alignment of the stack sequence is used for correcting small sample stage displacement during the scan. NEXAFS spectra are then extracted from the region of interest, setting the $I_o(E)$ in a region free of sample.

STXM sample preparation was performed by drying 1 μL of HA or FA solution on a Si_3N_4 window (100 nm thick). Energy calibration of the spherical grating monochromator was achieved by using the photon energy of the CO_2 gas adsorption band at 290.74 eV (Ma et al., 1991; Hitchcock and Mancini, 1994). The X-ray absorption double feature at 297.3 eV (L_3-edge) and 300 eV (L_2-edge) of potassium (Henke et al., 1993) was used for the identification of inorganic clay constituents (e.g., illite).

For the comparison of NEXAFS spectra, a baseline correction and normalization to 1 at 295 eV prior to peak fitting was performed. The spectra were then deconvoluted following the protocol used by (Schäfer et al., 2003c):

(i) an arctangent function for the ionization potential at 290.5 eV of aromatic/aliphatic C (Hitchcock and Ishii, 1987; Hitchcock et al., 1992),

(ii) six Gaussian functions (284.4, 285.0, 286.6, 287.4, 288.6 and 289.4 with a FWHM of 0.4 eV) for the 5 π* transitions below the ionization energy. The 287.4 eV band also fitted using a gaussian function is a mixed Rydberg/valence state transition. Additionally two second, higher transition (1s–2π* for aromatic C bonded to either H or C and for aromatic C bonded to O approximately 4 eV

above the energy of the 1s–π* transition with a quarter of the 1s–π* intensity were implemented. (Francis and Hitchcock, 1992),

(iii) and two additional Gaussian functions for the σ*-transitions.

2.4. AFFFF

AFFFF was carried out with a system from Wyatt Technology (USA) using a fractionation channel from ConSenxus (Germany) and regenerated cellulose membrane from Wyatt Technology (USA) with a nominal cut-off of 1 kDa (the nominal cut-off size related to the mass of 1000 Dalton of globular proteins). The asymmetrical channel has a length of 286 mm and a spacer thickness of 0.54 mm. As mobile phase, 5 mM Tris buffer (pH ∼ 9.1, Thang et al., 2001) was used at a channel flow of 0.6 mL min^{-1} and a cross-flow of 3 mL min^{-1}. The absorbance of the effluent was recorded with an UV/Vis detector (K-2500, Knauer, Germany) at 210 nm. A detection wavelength of 210 nm was chosen because of the low sample concentrations and in order to monitor also constituents that, contrary to HAs and FAs do not show significant absorption in the visible range. The fractionated sample volume was 20 μL. For calibration of the AFFFF system, polyacrylic acid (PAA) standards were used from American Polymer Standards Corp. (USA) and Polymer Laboratories, Germany (Hoque et al., 2003; Wolf et al., 2005).

2.5. TRFLS

TRFLS measurements were performed using a pulsed Nd:YAG-pumped dye laser system (Continuum, Powerlite 9030, ND 6000). An optical multichannel analyzer consisting of a polychromator (Chromex 250) with a 1200 lines/nm grating was used for detection of the fluorescence emission. To fade out any light scattering and background fluorescence, the emission spectra of Cm(III) were recorded 1 ms after the exciting laser pulse (laser dye: Exalite 396.6 nm) in the wavelength range of 580–620 nm in a time window of 1 ms. For lifetime measurement, the delay time between laser pulse and camera gating was scanned with time intervals of 20 μs. Samples were prepared in a glove box under Ar atmosphere by adding 2×10^{-7} mol/L of Cm^{3+} to the 3 different HA solutions ([HA] = 10 mg DOC/L; DOC = Dissolved Organic Carbon), and 1×10^{-7} mol/L to the 4 different FA solutions (6.6 < [FA] < 10 mg DOC/L; see Table 3). Investigations were conducted at pH 5.7–6.0. In this range hydrolysis is negligible and only two species are formed in significant concentrations. These species are the Cm FA complex and the non-complexed Cm^{3+} ion. Thereby, spectral evaluation is straightforward.

Furthermore, the results can be readily compared with published data.

3. Results and discussion

3.1. UV/Vis spectroscopy

UV/Vis adsorption spectra of HA and FA are featureless over the whole UV/Vis wavelength range showing only a strong absorption increase with decreasing wavelength linked to aromatic and other organic chromophores (Traina et al., 1990; Chen et al., 2002). Evaluation of UV/Vis spectra is either achieved by comparing absorption measurement at a specific wavelength or absorption ratios at two different wavelengths. The UV absorptivity at 260 nm is commonly used to determine the relative abundance of aromatic C═C content (Traina et al., 1990; Chin et al., 1994). However, the sharp increase below 300 nm can be considerably biased by salt presence or limited sample amount, as in the case of this study. For characterization/classification of HAs and FAs, a frequently used absorption ratio is E_4/E_6 (absorption at 465 over 665 nm, Chen et al., 1977). This ratio can presumably be used for estimating the degree of humification. Due to the low absorption at 665 nm, however, the results become strongly influenced by the quality of the background compensation. In samples of limited concentration, reproducibility suffers under this background compensation problem. Given that the relative shape of HA and FA spectra are similar, any absorption ratios can be used for classification of HAs and FAs. A ratio that is not sensitive to background compensation and is not affected by high absorption of salt and contaminants in the UV range is E_3/E_4 (absorption at 300 nm over the absorption at 400 nm, Artinger et al., 2000).

The UV/Vis spectra of the samples are shown in Fig. 1. The absorption is normalized to the DOC content. The large differences in this "specific absorption" reflect differences in the humic substances. It also, however, reflects the presence of low-absorbing organic compounds.

The specific absorptions at 300 and 400 nm, and the absorption ratio E_3/E_4 of the samples are shown in Fig. 2. In this figure also the correlation regions are shown for a large number of HAs and FAs from 4 different aquifer systems and some HAs and FAs isolated from deep and near surface groundwater sediments (Artinger et al., 2000). The results show, that both the HAs and FAs from the present study fall in a range rather typical for HAs (high specific absorption and high absorption ratio). The specific absorption of 447 HA is somewhat high. The data for the other two HAs and the FA 447 FA fall within the typical range. The FAs 494 FA, 516 FA and OPA FA, however, show very low specific absorptions. Given that the relative absorption curve shapes are so similar for all FAs of the present study (cf. Fig. 1, lower part), the low specific absorption may indicate the presence of low UV/Vis absorbing organic constituents.

3.2. AFFFF

The size distribution of the different FAs is determined using AFFFF. The data are presented in Fig. 3.
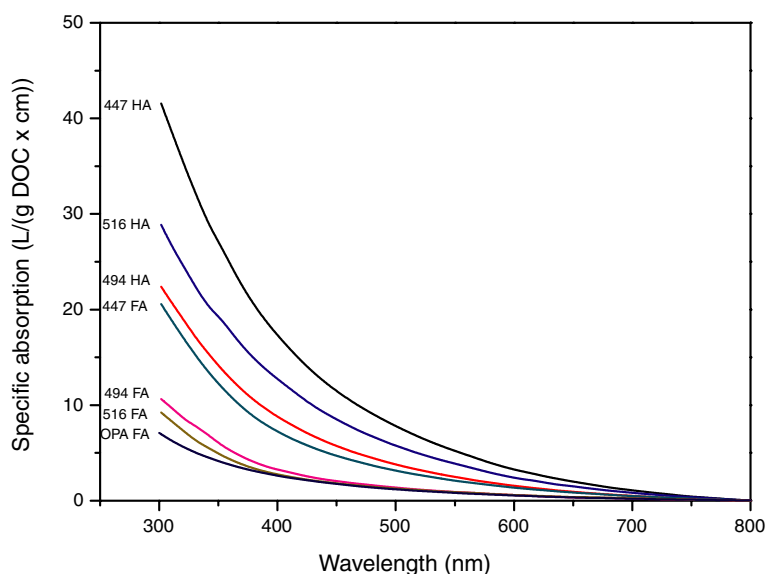

Fig. 1. UV/Vis spectra of humic and fulvic acid samples, normalized to the DOC concentration.
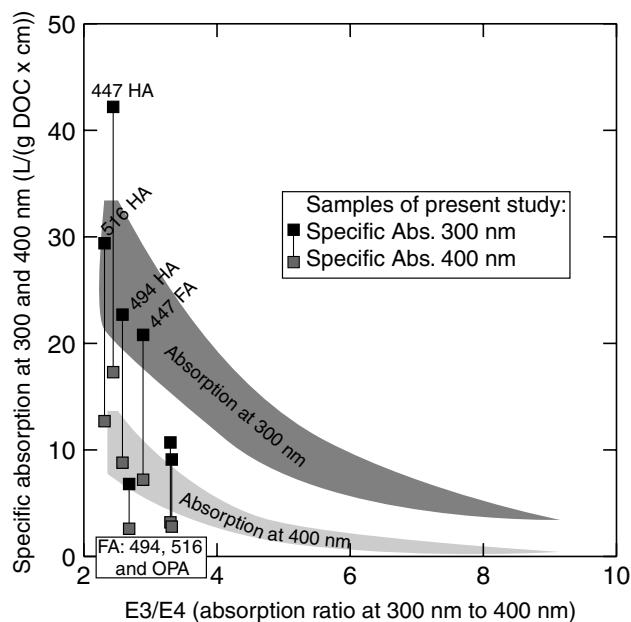
Fig. 2. UV/Vis absorption properties (specific absorption at 300 and 400 nm, as well as absorption ratio E_3/E_4) of a large number of groundwater and sediment humic and fulvic acid samples from 4 aquifer systems (shaded areas from Artinger et al., 2000) and samples from the present investigation.
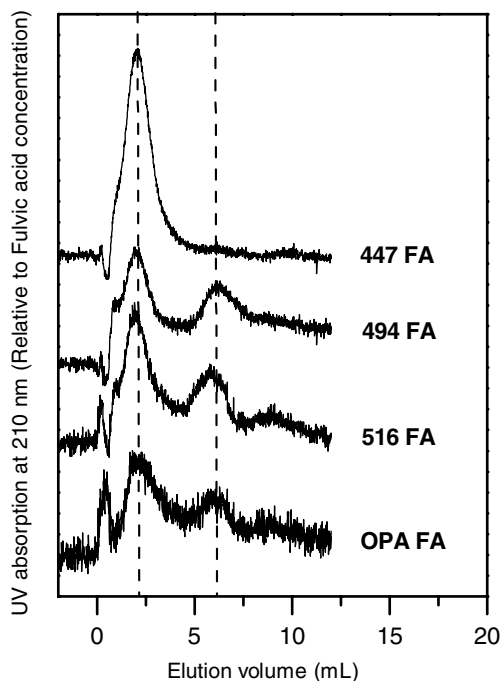

Fig. 3. AFFFF of fulvic acid samples recorded at pH 9.1 in 0.005 mol/L Tris buffer.

The size distribution of the sample 447 FA from the MHM site shows the typical size distribution of FA (Wolf et al., 2005). The other MHM FA isolates derived from sediments of marine origin, in contrast to the sample 447 FA isolated from terrestrial deposited sediments, show a bi-modal distribution. The first peak of the smaller size fraction fits well with FAs in general and also with the FA from the 447 FA (terrestrial origin). The second peak indicates a larger size fraction of atypical size for FAs. The same bi-modal size distribution is found for the isolated FA from the Opalinus clay. The results support the indications from UV/Vis spectroscopy, namely that, with exception for 447 FA, there are additional components in the FA samples. These components are obviously of organic nature (lowering the specific UV/Vis absorption), are larger in size and show some chemical similarities with FA (being sorbed on the XAD-8 column in the acidic range and elute in the alkaline range). Aiming at identifying the nature of the samples, they were also characterized by NEXAFS.

3.3. NEXAFS

The NEXAFS spectra of the samples are shown in Fig. 4. In this figure, the measured spectra are given together with the Gaussian functions used for different C functionalities and the arctangent function representing the ionization potential. The outcome of spectra deconvolution is shown exemplarily by sample 516 HA. The results for all the HAs and FAs are summarized in Table 2. As expected, the dominant oxygen containing functional group is of carboxyl type, more pronounced in FAs than in HAs.
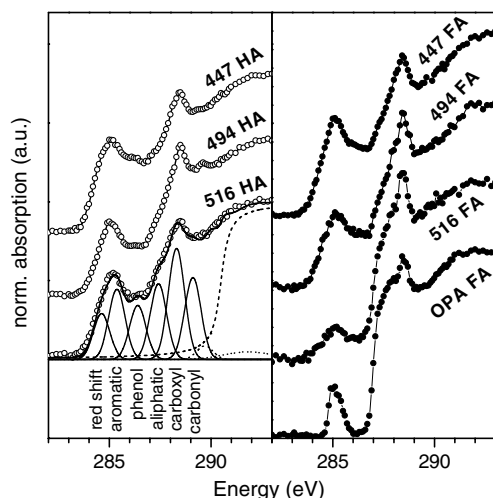
Fig. 4. NEXAFS spectra of the isolated humic and fulvic acid samples together with the peaks of individual carbon functionalities and additional transitions used for peak deconvolution on the example of 516 HA.

According to Rice and MacCarthy (1991), HAs from different sources suggest a "preferred" composition for each environment, with the aliphaticity of humic material from marine sources being higher than for those of terrestrial origin. A direct quantification of the relative composition by NEXAFS is hampered by the lower sensitivity for the mixed Valence/Rydberg state transition of methyl and methylene groups compared to intense 1s–π^* transitions of aromatics or C=C, as well as phenol or carboxyl type groups. Nevertheless, the data in Table 2 can be used to draw some important conclusions, especially trends between the different substances.

A clear trend of depositional transition from a terrestrial to marine environment is not well reflected in the Callovo-Oxfordian argillite extracted HAs. In contrast to this, the aliphaticity as well as carboxyl and carbonyl type functional groups of the MHM FAs show a clear trend with an enrichment with depth. Furthermore the red-shift area, aromatic C=C and C—H and phenol-type

functional groups show an apparent decrease. These observations are consistent with the higher H/C ratio in the case of type II kerogen. Marine organic detritus is predominantly of algal origin and therefore of highly aliphatic nature (Nissenbaum and Kaplan, 1972), whereas soil organic matter is more aromatic in nature due to the ubiquity of lignin in terrestrial plants (Flaig, 1972).

In the case of the Opalinus clay, the isolated FAs show an unexpected high aliphatic nature typical for marine derived organic material, whereas the whole sediment is of mixed terrestrial–marine origin (Nagra, 2002). The observed discrepancy could either by interpreted as a preferential release of marine-derived organic material or might be due to the thermal overprint with burial temperatures of ∼80 °C (Nagra, 2002) in comparison to the Callovo-Oxfordian argillite (approx. 40 °C, Elie et al., 2000). These higher burial temperatures can lead to the observed elevated aliphaticity and the high degree of aromatic ring condensation indicated by a near disappearance of aromatic associated oxygen containing functional groups (red shift area and phenol) in the C(1s) NEXAFS.

In Fig. 5, the aromaticity determined by C(1s) NEXAFS is plotted against the E_3/E_4 absorption ratio for the samples analyzed in this study together with HAs and FAs of different origin in the Gorleben aquifer system (Artinger et al., 2000; Schäfer et al., 2005). In the Gorleben system the E_3/E_4 absorption ratio increases from isolated HAs via FAs derived from microbiological turnover of deep brown coal sands to the highest values found in soil-derived FAs from recharge-dominated aquifer systems. The Gorleben HAs do not show a specific trend, but for the Gorleben FAs the increase in the E_3/E_4 absorption ratio is associated with a decrease in aromaticity (Fig. 5). The absorption ratios of the isolated HAs and FAs discussed in this paper are all in the range of or slightly lower than the Gorleben HAs with a low overall E_3/E_4 variation. The C(1s) NEXAFS determined aromaticity of the FAs investigated here, however, decreases with an increasing contribution of marine origin and becomes exceptionally low for the

Table 2

Distribution of carbon among the main structural groups of FA and HA as determined from their carbon K-edge spectra deconvolution

Sample	Red shift area[a]	C=C	Phenol	Aliphatic	Carboxyl	Carbonyl
447 HA	10	19	15	16	26	14
494 HA	6	17	12	18	30	17
516 HA	7	19	14	18	27	15
447 FA	8	19	14	18	28	13
494 FA	8	15	12	18	30	17
516 FA	2	7	4	27	39	21
Opa FA	0	10	0	29	39	22

[a] Red shift due to heteroatom substitution/aromatic ring destabilization or benzoquinone type functional groups.
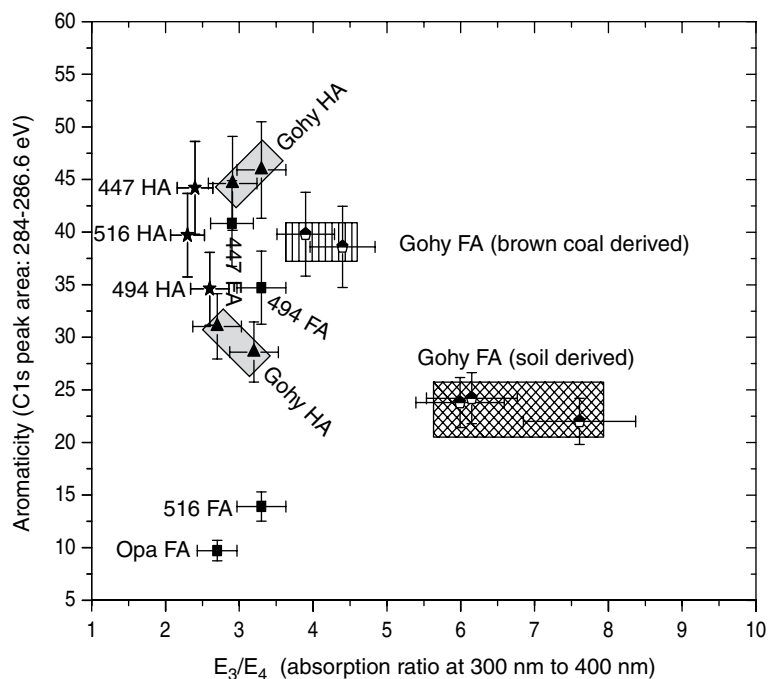
Fig. 5. Aromaticity (peak area between 284 and 286.6 eV (quinone, C=C and phenolic groups, cf. Table 2) plotted against the absorption ratio E_3/E_4 for the present samples and for comparison, samples of different origin from the Gorleben aquifer system (Artinger et al., 2000).

samples 516 FA and OPA FA. The "clustering behavior" of the sample 516 FA and OPA FA is striking. To what extent this reflects an explicit marine origin (516 FA) or a mixed effect of marine influence and higher burial temperature (OPA FA) can not be clarified at this point. Although 447 FA and 494 FA were extracted, respectively, from Oxfordian and Callovian stratigraphic layers, they also cluster together which, at first glance, does not reflect the contrasting origin of the initial organic matter input. However, Landais and Elie (1999) have shown that the transition between the two types of organic matter does not strictly coincide with the mineralogical transition (Claret et al., 2004) occurring in the Callovo-Oxfordian. The sample situated at −494 m belongs precisely to this mineralogical transition (Claret et al., 2004).

3.4. Cm(III) complexation behavior

The complexation behavior was studied using TRFLS. By this method metal ion speciation can be done with respect to excitation and emission band shapes, and fluorescence decay behavior (Kim et al., 1991a,b). In the present study, the emission spectra show the characteristic shape of humate and fulvate Cm complexes with a peak maximum around 600 nm, compared to 593.8 nm for the non-complexed Cm^{3+} ion (Fig. 6) (Buckau et al., 1992; Czerwinski et al., 1996).

The Cm(III) fluorescence decay and derived lifetimes of the different FA samples show quite similar temporal behavior as found for the Cm(III)–Aldrich HA complex (Fig. 7). The small differences are caused by different amounts of free, uncomplexed Cm^{3+} in the samples. In the HA, almost all Cm(III) is complexed, whereas for FA free Cm^{3+}_{aq} ion is still present (Fig. 6).

Determination of the Cm^{3+}_{aq} and Cm fulvate concentration is done normally by peak deconvolution. Thereby, the fluorescence intensity of the complex, relative to that of the free ion, needs to be taken into account. The fluorescence intensity of the complex depends on the excitation wavelength, but is always higher than that of the free ion. The reason is that the excitation of the complexed ion takes place by a combination of direct excitation and energy transfer via the fluorescent organic ligand. The relative fluorescence intensity of the complexed Cm ion is normally expressed by this so called fluorescence intensity factor.

Curium(III) fluorescence in the present samples is strongly quenched. As a result, fluorescence intensities of Cm complexed with brown coal derived FAs is more than one order of magnitude higher than that obtained for the FAs described in this present study. The reason for the low fluorescence intensities in the present samples may be related to structural properties and to quenching. Given the high iron contents of the present samples (up to 15%, determined by ICP-MS analysis) this is expected
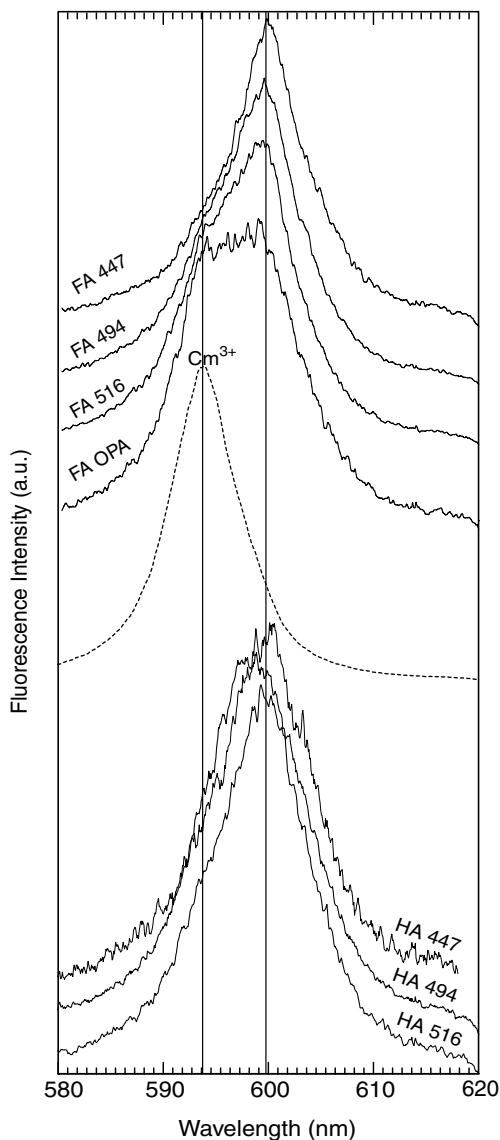
Fig. 6. Fluorescence spectra of Cm(III) with the different humic and fulvic acids. Vertical lines represent the positions of the two components humic/fulvic complex and the non-complexed Cm^{3+} ion (cf. reference spectrum).

to be the main cause. The Fe is not distributed equally over the samples, but AFFFF coupled with ICP-MS shows that it is concentrated in large particles (40–200 nm, Bouby, personal communication). It is well known that interaction with Fe oxide/hydroxide surfaces leads to the formation of non-fluorescent Cm complexes and even to the complete extinction of the fluorescence light (Stumpf, 2004). In the present case, the strong quenching is probably due to non-radiative energy transfer to the colloidal Fe(III). Quenching of Fe^{3+}-ions in fulvic acid solution is less pronounced and only relevant at very high concentrations (>10^{-4} mol/L, Stumpf, 2004).

Since the free Cm^{3+}_{aq} ion is not affected by this quench process one can estimate its concentration after peak deconvolution of the mixed spectra by comparison with the intensity of a Cm(III) standard solution containing 2×10^{-7} mol/L Cm^{3+} in 0.1 M $HClO_4$ under identical experimental conditions. Small losses of laser energy due to light scattering and absorption within the FA containing cuvettes were not taking into account. The Cm(III) fulvate concentration is then calculated from the total Cm(III) concentration and subtracting the aqueous ion concentration. The results are presented in Table 3.

The complexation constants (log β = 6.05 ± 0.42) are calculated from the values in Table 3 by using the charge neutralization model (Kim and Czerwinski, 1996). Values used for evaluation are 5.7 meq/g for the proton exchange capacity, a C content of 45% and a loading capacity of 60% (Kim et al., 1990; Buckau et al., 1992; Czerwinski et al., 1996). These values are typical for purified natural HAs and FAs (Kim et al., 1991b; Buckau et al., 1992), and the same is true for the resulting complexation constant.

Based on the intense quenching, one may consider the possibility that Cm(III) interacts directly with Fe colloids. The study of the influence of HA on Eu(III)/Cm(III) sorption onto hematite and γ-Al_2O_3 colloids performed by Rabung et al. (1998) and Wang et al. (2004), indicates that the formation of ternary surface complexes where HA is strongly involved in the complexation. Reiller et al. (2002) have also shown that the sorption on Fe oxides is inhibited when HA is present where there is an excess of HA sites compared

Table 3
Cm(III) complexation results with fulvic acid samples at pH 5.7–6 in 0.2 mol/L $NaClO_4$

Sample	DOC[a]	Cm^{3+}(10^{-9} mol/L)	CmFA (10^{-8} mol/L)	Log β[b] (L/mol)
447 FA	8.7	1.17	9.88	6.59
494 FA	8.7	4.18	9.58	6.02
516 FA	10.4	9.32	9.07	5.57
OPA FA	6.6	5.70	9.43	6.01

[a] DOC: dissolved organic carbon.
[b] Calculated with a proton exchange capacity of 5.7 meq/g, a loading capacity of 60% and a carbon content of 45%.
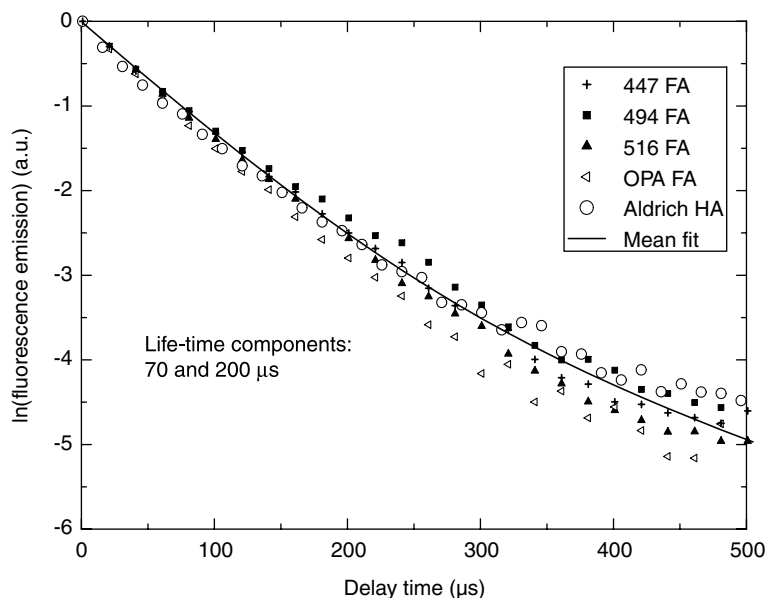
Fig. 7. Fluorescence lifetime of Cm(III) complexed with fulvic acids of the present study and for reference, Aldrich humic acid. The fluorescence decay of Cm(III) humate and fulvate complexes consists of two components with 70 and 200 μs lifetime.

to Fe oxide sites. These published observations and the agreement between the complexation constant found in the present study with that of different other humic and fulvic acids indicates the predominance of the fulvic acids in the complexation process.

4. Summary and conclusion

Up to about 8% of rapidly released clay organic matter (within about 24 h in alkaline medium) from Callovo-Oxfordian argillite or Opalinus clay is identified as hydrophilic humic and fulvic acid (standard IHSS protocol conditions). Characterization shows that especially in the Callovo-Oxfordian clay, original features of the organic matter, reflecting terrestrial and marine deposition around 150 Ma ago, are preserved in the HAs and FAs. FA influenced by marine origin shows a separate size peak, atypical for FA of terrestrial origin, and a low content of chromophoric C functionalities. Curium(III) is complexed by both the HAs and FAs. Differences in fluorescence behavior of complexed Cm(III) are most probably related to the fluorescence quenching by Fe colloids. The complexation constants $\log(\beta)$ indicate a typical complexation behavior in comparison with brown coal derived FAs. The present study is made with total FA amounts in the μg range. Further characterization and complexation studies by additional analytical methods and approaches will require larger amounts of material not presently available.

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