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THE CHEMICAL BEHAVIOR OF SEDIMENTARY URANIUM IN AUTHIE BAY (FRANCE)

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A general study on uranium present at trace levels in anoxic sediments derived from Authie Bay (in northern France) has been undertaken. For that purpose, concentrations of various uranium species in pore waters and recovered solutions (after mineralization of sediments) were determined by ICP-AES and ICP-MS. To access the extent of early diagenesis occurring in these sediments, reduced solid sulfur species were determined after their conversion into H₂S gas following sequential extraction procedures. Our preliminary findings reveal that dissolved U(VI) precipitates rapidly with depth in pore waters certainly in the form of insoluble U(IV). Under stronger reducing conditions, new aqueous species [mostly U(OH)₅⁻ and U(HPO₄)₄⁴⁻] in which uranium is in oxidation state IV are formed in the pore water. Valuable interpretation of these particular properties of sedimentary U has necessitated a global examination of sediment biochemistry because of the influence of bacterial activities on the chemistry of Fe, Mn, S and more particularly U by metal-reducing bacteria.

Keywords: Diagenesis; Sediment; Uranium; Iron; Manganese; Speciation

INTRODUCTION

Previous reports on the behavior of uranium in estuarine and marine environments have generally argued for the importance of particulate matter, colloids and sediments as a sink or regulator for this metal [1–9]. Investigations on the fate of uranium in sediments show a valence change from soluble U(VI) (mostly as uranyl-carbonate complexes in carbonated seawaters) to particulate U(IV) in oxygen-depleted pore waters [8]. Previously, it was shown that some bacteria have a pronounced action on the overall geochemical properties of certain metallic species, particularly Fe(III),

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Mn(III and/or IV), Cr(VI) and U(VI) [8,10–13] by reducing them, thus enabling their removal and/or deposition in the particulate and sedimentary material [8,10].

In this context, it is appropriate to review the behavior of U in recent sediments which were sampled in a site not disturbed by industrial activities. We focused our attention particularly on the variable reducing conditions with depth. In this report, chemical analyses of sediments collected at two stations downstream and upstream in Authie Bay (northern France) are presented. The variations versus depth of dissolved sulfate, iron(II), manganese(II), uranium(VI) and metal sulphide precipitates are discussed in terms of biogeochemical mechanisms involving sulfate-reducing bacteria and metal-reducing bacteria. Finally, a simple calculation with the Mineql⁺ program was applied to our sedimentary system to classify the probable existence of some U species and their depth distribution in pore waters.

EXPERIMENTAL

Location and Sampling

The location of Authie Bay (northern France) is shown in Fig. 1. Sediment samplings were carried out at low tide during November 1998 and November 1999, downstream

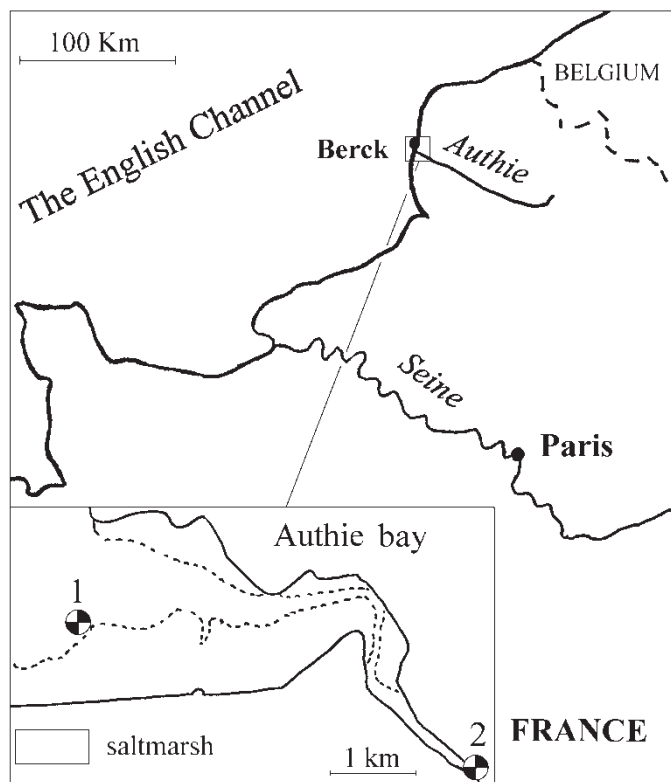


FIGURE 1 Location of Authie Bay (in northern France) where sediment samplings were performed. Stations 1 and 2 correspond to the downstream and upstream sites, respectively.

(which corresponds to a marine zone with a high salinity: ≥ 20) and upstream (which corresponds to a riverine zone with a low salinity: ≤ 0.3) in Authie Bay (see the map shown in Fig. 1), respectively. Two sediment cores were taken in the field with a 30-cm long Perspex tube. These cores were immediately isolated from the atmosphere (so as to prevent any oxidation reactions in the sediment) inside a plastic bag previously purged with nitrogen. They were afterwards sliced into 2-cm layers under a N_2 atmosphere inside a glove box; these sliced sediment samples were put separately into plastic containers previously purged with nitrogen gas, and stored in an icebox. In laboratory, sliced sediment samples were centrifuged at room temperature using an X340 Prolabo centrifuge (with a rotation speed of 4000 rpm). Anoxic pore waters were afterwards recovered under a nitrogen atmosphere in a glove box, filtered with 0.45 μm Alltech filters (cellulose acetate membrane) and immediately acidified (except for reduced sulfur analyses) with ultra-pure nitric acid (Merk, Germany) by taking 100 μL in 10 mL of pore water before elemental analyses.

Analytical Procedures

Pore water analyses

The pH and the redox potential E_h of sediment were determined in the field at various depths (every centimetre) just after sampling with a combined glass electrode (Ingold, Germany) for pH and with a combined platinum electrode (Mettler Toledo, Switzerland) for E_h (note that these electrodes were introduced directly in the sediment core).

Inorganic carbon (i.e., H_2CO_3 , HCO_3^- and CO_3^{2-}) was analyzed in pore waters using an automatic pH titrator (Metrohm; model Titrino 736 GP, Switzerland); pH analyses of interstitial fluids were carried out with a titrated $5 \times 10^{-3} \text{ mol dm}^{-3}$ solution of HCl.

Sulfate in interstitial waters was detected at 650 nm using a spectrophotometer (Kontron Instruments; model UVIKON 860, UK), as described previously [14].

Concentrations of sulfides in pore waters were determined using cathodic stripping voltammetry [15–21]. The apparatus consisted of an Autolab microprocessor equipped with an IME 663 Metrohm module element; voltammetric parameters (such as deposition potential, accumulation time and frequency) have already been described in a previous work [22].

Fluoride was determined in the interstitial fluid by potentiometry using a fluoride-specific electrode (Orion, USA) [23]. Moreover, to avoid artefacts due to some species present in pore water that can interact with the electrode membrane, such as organic matter, the standard addition method was applied (NaF solution).

Concentrations of various elements (Ca, Fe, Mg, Mn, Na, P and Sr) in pore waters and estuarine oxic waters were determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES; Liberty Serie II, axial view, Varian, Australia).

Concentrations of uranium in these waters were determined using two quadrupole ICP-MS systems: Ultra Mass 700 (Varian, Australia) or an Elan 6000 (Perkin Elmer Sciex, USA).

The equilibrium speciation of numerous dissolved components of pore waters extracted from sediments was investigated by using the Mineql⁺ computer program [24] which calculates the equilibrium state in these aqueous systems. For this purpose,

we have considered for calculation the following aqueous species: (i) cations: Ca^{2+} , Fe^{2+} , Mg^{2+} , Mn^{2+} , Na^+ , Sr^{2+} , UO_2^{2+} and U^{4+} ; (ii) anions: HCO_3^- , Cl^- , F^- , PO_4^{3-} , SO_4^{2-} and HS^- . A compilation of stability constants for equilibria involving these compounds was used. Thus, the free species concentrations for relevant components (mainly U, Fe, Mn, carbonate, phosphate) were determined by an iterative computation.

Sedimentary solid-phase analyses

Total concentration of elements in sediments were determined after their total acid digestion using a mixture of $\text{HF} + \text{HCl} + \text{HNO}_3$ (5:3:1 v:v:v) carried out in Teflon flasks. Reduced sulfur species [i.e., Acid Volatile Sulfides (denoted AVS) and Chromium Reducible Sulfur (denoted CRS)] present in raw sediments were determined after their conversion into H_2S gas by following sequential extraction procedures previously described by Canfield *et al.* [25], Cornwell and Morse [26], and more recently by Billon *et al.* [22,27,28].

RESULTS AND DISCUSSION

Down-core Distribution of Iron and Manganese

The pore water profiles versus depth of Authie-Bay sediments (at stations 1 and 2 in Fig. 1) show a clear increase of Fe^{2+} and Mn^{2+} ions near the sediment–water interface (see Fig. 2). This phenomenon is related to bacterial activities in these sediments which lead to the reduction of Mn(III,IV) and Fe(III) oxides/oxyhydroxides including poorly crystalline and crystalline phases such as ferrihydrite, goethite, hematite and magnetite [29]. This increase of Fe^{2+} and Mn^{2+} concentrations is immediately followed by a strong decrease of these ions in pore waters at greater depths (Fig. 2). This depletion results from the formation of dissolved hydrogen sulfide (during bacterially reduced sulfate reduction) which reacts rapidly with pore water Fe(II) and Mn(II) to give iron and manganese monosulphides [30,31]. The fixation of H_2S through the generation of metal sulfides (MnS, FeS, FeS_2 ...) has indeed been recognized as the dominant pathway for the permanent removal of S, Fe, Mn and certain trace and toxic elements, and thus as a relevant detoxifying process in estuarine/riverine environments [32–35]. It is worth noting that although the concentration of sulfate at the sediment–water interface in the downstream site is very high, the content of solid sulfides generated during early diagenesis is found to be low. This can be explained by strong renewals and mixings in these sediments, which are induced by the effects of seawater on this bay during certain periods when tidal coefficients are high. Furthermore, limiting kinetic and reactions factors should be taken into account, especially bacterial activities, biodegradable organic carbon, the reactivity of iron...

Immobilization of dissolved sulfide within the sediment can be assessed by examining the variable accumulation/deposition of metal sulfides. For that purpose, specific chemical treatments were performed sequentially on the sedimentary material in order to determine the contents of two types of reduced sulfur solids at different depths: (i) Acid Volatile Sulphides (denoted AVS), i.e., amorphous FeS, mackinawite

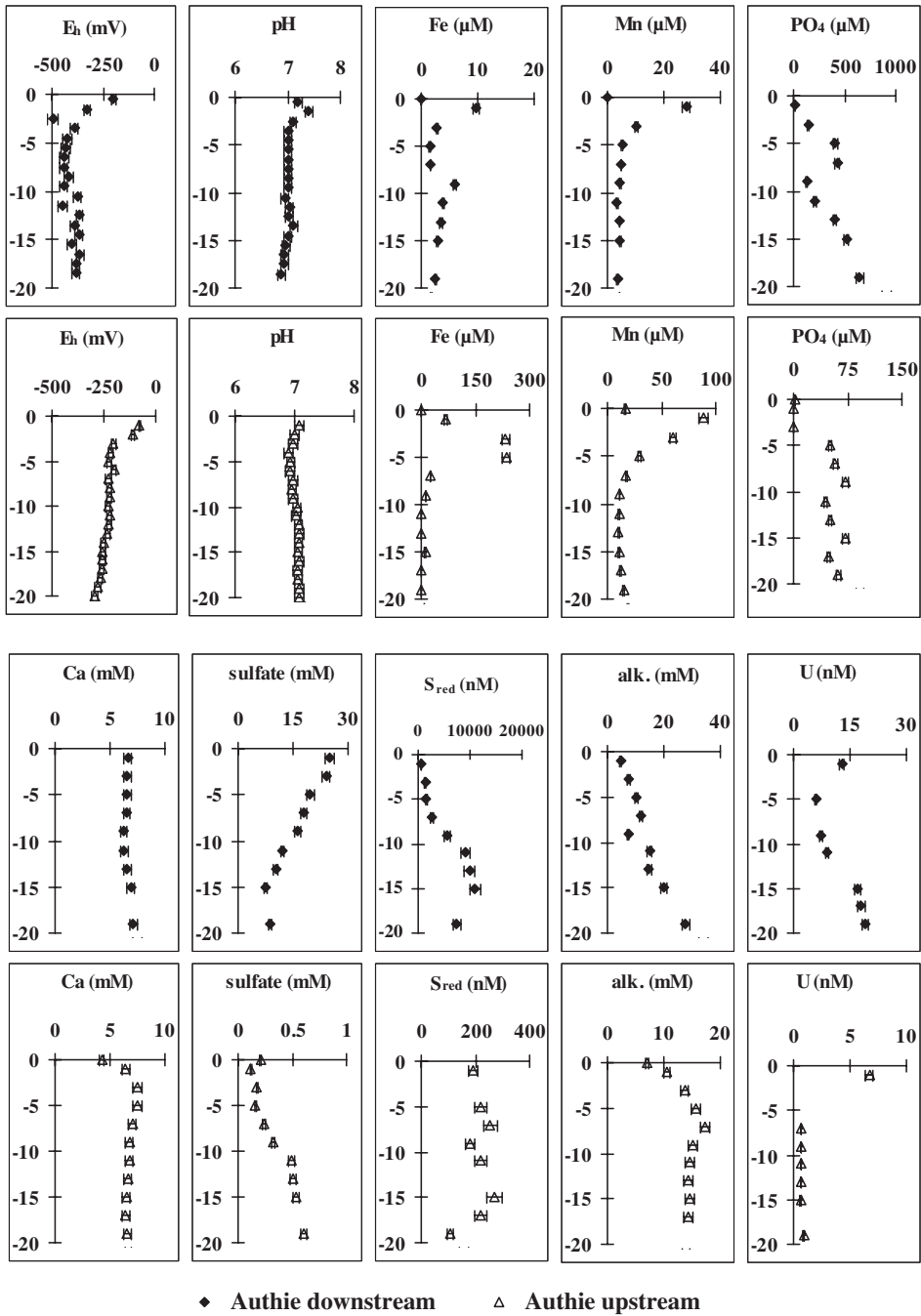


FIGURE 2 Concentration profiles (versus depth) of redox potential (versus Ag/AgCl), pH, Fe, Mn, PO₄, SO₄, reduced sulfur (denoted S_{red} in the figure), alkalinity (denoted alk. in the figure) and U in Authie-Bay pore waters.

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and greigite; and (ii) Chromium Reducible Sulfur (denoted CRS), i.e., sedimentary pyrite and elemental sulfur. Sedimentary sulfurs (AVS-S, CRS-S and total S) profiles obtained with depths for anoxic sediments collected downstream and upstream in Authie Bay are represented in Fig. 3. In both cases, AVS-sulfur profiles display a progressive increase with some fluctuations to a depth of 20–25 cm, whereas the CRS-sulphur profiles exhibit an abrupt increase to a depth range of ~ 5 –7 cm, while at greater depths the CRS-S contents fluctuate, remaining nearly constant. It should be noticed that the total-S profile found for downstream sediments (at station 1, see Fig. 1) increases more abruptly with depth than for the upstream ones (at station 2, see Fig. 1). This observation is a consequence of a higher microbial activity in buried sediments derived from station 1 and is confirmed by a strong depletion with depth of sulfate ions observed in pore waters extracted from station-1 sediments (Fig. 2), probably as a result of a stronger degradation of organic matter by sulfate-reducing bacteria [30,31]. Indeed, significant variations in the concentration profile of particulate organic matter from downstream sediments are detected (in comparison with that observed for upstream sediments in which “old” terrestrial organics are more abundant and therefore less reactive), suggesting a stronger biochemical reactivity in the sedimentary medium (see Fig. 4).

Down-core Distribution of Uranium

In the uppermost sediment cores (between 0 and 4 cm depths), dissolved uranium profiles found in pore waters extracted from Authie-Bay sediments (at stations 1 and 2;

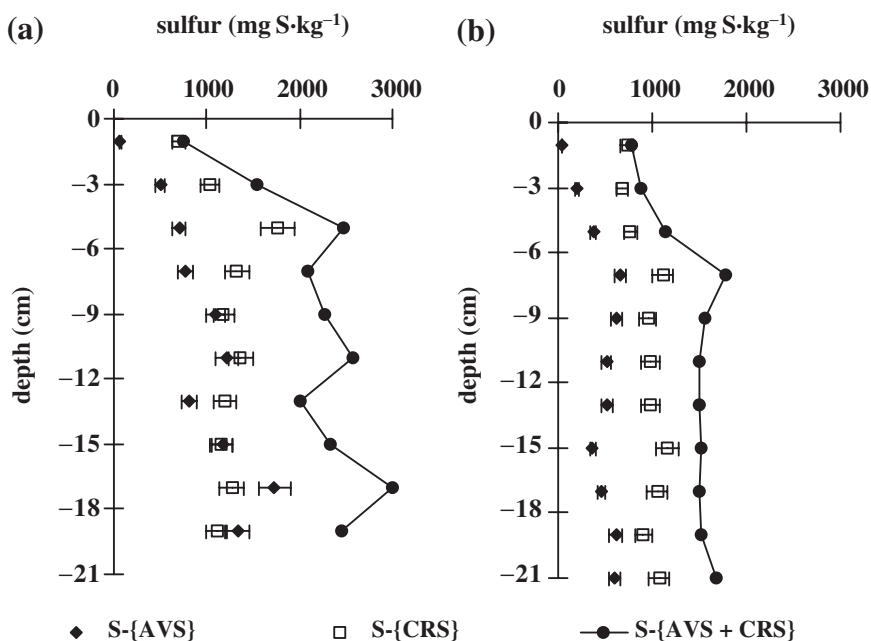


FIGURE 3 Content profiles (versus depth) of AVS, CRS and AVS + CRS in the sedimentary cores sampled at station 1 [graph (a)] and station 2 [graph (b)].

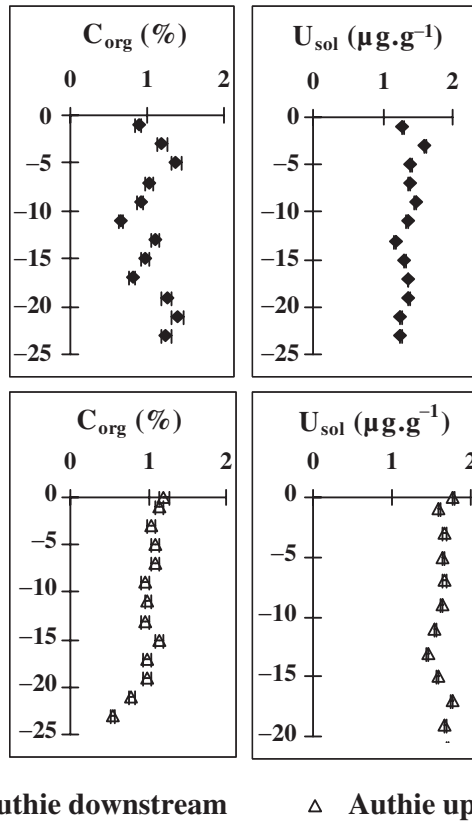


FIGURE 4 Concentration profiles versus depth of particulate organic carbon and uranium at station 1 and station 2.

see Fig. 2) show a drastic decrease in concentration from 2.5–3.0 $\mu\text{g L}^{-1}$ to 0.3 $\mu\text{g L}^{-1}$ [note that the upper values of 2.5–3.0 $\mu\text{g L}^{-1}$ (not shown in Fig. 2) correspond to dissolved U concentrations measured in bottom waters along Authie Bay]. Between 4 and 20 cm, the contents of dissolved U in pore waters derived from upstream sediments remain low and reasonably constant. This observation confirms the ability of dissolved U(VI) to be reduced to insoluble U(IV) (in the form of UO_2) in the buried sediment. The pH remains nearly constant all along the length of the core (see Fig. 2); in contrast, the redox potential (E_h) of the sediment is in the reducing range (see Fig. 2), thus strongly influencing the behavior of U. It is worth noting that direct evidence for the role of aqueous chemical/microbiological reduction of U(VI) to insoluble U(IV) in anoxic water-column and particulate materials had already been stated previously [8,10,36–38]. Thus, it has been shown that some bacteria (sulfate-reducing bacteria, e.g., *Desulfovibri* sp.; and metal-reducing bacteria, e.g., *Shewanella putrefaciens*) are capable of reducing directly or indirectly U(VI) dissolved or associated with Fe(III) and Mn(III,IV) oxides/oxyhydroxides to U(IV) [8,10].

The profile of dissolved U concentrations measured in pore waters extracted from downstream sediments differs significantly from that observed in upstream pore waters. Indeed, a high increase of U contents is detected below 4 cm, indicating a removal of U from the sedimentary material studied. Overall, this phenomenon

occurs when both the process of Fe and Mn sulfuration and the sulfate reduction take place strongly in the sedimentary medium (see Fig. 2). In this context, we believe that U in Authie-Bay sediments is intimately related to the biogeochemical cycling of Fe, Mn and S. Accordingly, in this case, changes in the behavior of U with depth under strong reducing conditions must be examined in light of the Fe–Mn–S redox cycle. In addition, the existence of such reducible solid U in Authie-Bay sediments can be explained as follows: in the oxic water column, the particulate matter consists of metal oxide coatings and biogenic particles (e.g., micro-organisms and algae) in which a component of the total U(VI) introduced to these waters can be scavenged and transported by gravitational settling towards the estuary bed. Fredrickson *et al.* [10] undertook a systematic analysis of the ability of some dissimilatory metal-reducing bacteria to reduce uranium(VI) as a crystalline U(VI) solid (metaschoepite, $\text{UO}_3 \cdot 2\text{H}_2\text{O}_{(s)}$) in the absence or presence of Fe(III) oxide minerals as an alternative electron acceptor during microbial processes. Such a mechanism should compete the involvement of U(VI) associated with the oxidised particulate matter [especially, Fe oxyhydroxides as FeOOH and Mn(III,IV) oxides] in our sediments, as pointed out previously [39,40]. Under this assumption, our experimental results seem to suggest that certain types of bacteria present in buried sediments from Authie Bay are capable of reducing “insoluble” particulate U(VI) – via a combination of direct enzymatic or indirect mechanisms [10] – to U(IV) in the presence of sedimentary metal oxides.

Note that this bioreduction of U differs from that predicted on thermodynamic grounds. Indeed, microbial electron transfer is limited by complex factors such as the constraint for a direct contact of the bacterium with the metal oxide as an electron acceptor [10,41,42]. Microbial respiration and enzymatic pathways (dictating the U(VI) reduction sequence) lead to the development of a very low reductive potential on the microbial surface (as a “bio-potential” that could range from -230 to -400 mV [43,44], which permits the reduction of any electron acceptor solids such as $\text{FeOOH}_{(s)}$ in the presence of metaschoepite [10]. Bacteria are then associated with Fe–Mn–U oxide/oxyhydroxide surfaces and develop a surface bio-potential that is capable of reducing both Fe(III), Mn(III,IV) and U(VI). Note that uranium(VI) as metaschoepite also exists in the lower layers of these sediments as a consequence of its deposition with time at a sedimentation rate of about 2 cm/yr [which has been estimated from the analysis of ^{210}Pb versus depth using γ -emission spectroscopy (personal communication)]. A microbial reduction of U(VI) as metaschoepite in lower sediment layers takes place in the sedimentary medium, leading to the generation of a $\text{UO}_{2(s)}$ coating on the surface of the targeted minerals, and thereby inhibiting any subsequent reduction of insoluble U(VI) by the bacteria. This explains the very low content of dissolved U detected at depths ≤ 4 cm in anoxic sediments collected upstream in Authie Bay (with E_h varying from -80 to -291 mV versus Ag/AgCl). In contrast, this U content increases significantly in downstream pore waters as a result of the formation of the soluble U(IV)-hydroxy and U(IV)-phosphate complexes, $\text{U}(\text{OH})_5^-$ and $\text{U}(\text{HPO}_4)_4^{4-}$, respectively, which become stable under strong reducing conditions (with E_h varying from -200 to -450 mV versus Ag/AgCl). Note that the importance and fate of sedimentary phosphate in Authie Bay have already been mentioned in our recent articles [45,46].

Overall, our investigations have shown that apatite and fluoroapatite should exist in these sediments, while vivianite may be present sporadically at 4–8 upstream layers particularly because of the high iron(II) content generated in the pore waters

during early diagenesis. The release of uranium from the sedimentary particles at the water–sediment interface has also been hypothesized. Indeed, upstream the concentration of U in the topmost pore waters is about 7 nM (see Fig. 2) whereas the concentration of U in the water column is about 4 nM. These results indicate a low release of dissolved U from the upstream surface sediments. In downstream sediments, the content of U in the topmost pore water is in the range 14–15 nM (see Fig. 2), whereas the concentration of U in the water column is about 13 nM, which suggests a negligible release of dissolved sedimentary U at the water–sediment interface.

Chemical Speciation Modeling

We have investigated the equilibrium speciation with depth of dissolved uranium components in Authie-Bay pore waters using the pH of the solution, the equilibrium constants and the total concentrations of various ionic species and complexing agents present in the sedimentary medium. The Mineql⁺ computer program elaborated by Schecher and McAvoy [24] has been applied to determine the free ion concentrations at different sediment depths in pore waters for major components, especially HCO_3^- , CO_3^{2-} , Cl^- , F^- , HSO_4^- , SO_4^{2-} , H_2PO_4^- , HPO_4^{2-} , PO_4^{3-} , Na^+ , Ca^{2+} , and for the principal metals Fe, Mg, Mn, Sr and U. Thermodynamic calculations have subsequently been used, together with the experimental–computational data, in order to gain complementary information concerning the possible precipitation of U minerals, especially about the type and importance of U combinations with carbonates, sulfides, phosphates, fluorides and hydroxides. Note that uranium in organic complexes (such as uranyl fulvate) or adsorbed on colloidal matter are not considered in these calculations, this complexed form of U(VI) being presumed not to be available to organisms, as suggested by Markich [3]. For that purpose, the ionic activity products (IAP) corresponding to numerous natural inorganic compounds containing U at oxidation IV or VI associated with CO_3 , F, PO_4 and SO_4 have been calculated and compared with the solubility products (K_s) of these minerals. Our investigations reveal that, whatever sediment layers were studied, pore waters derived from Authie Bay are highly undersaturated with respect to these U minerals, thus indicating the total absence of such precipitates. Despite this, our analytical studies on sedimentary solids derived from Authie Bay show unequivocally the existence of U solids (see Fig. 4). This confirms our previous assumption that U precipitation along the water column in the sea is probably in the form of U oxides (e.g., schoepite) associated with Fe and Mn oxides/hydroxides. In this context, we need to explain the relative precipitation and/or release of U observed in buried sediments depending upon the redox potential of these media, as shown in Fig. 2. For that purpose, the chemical speciation modeling was done separately for Authie-Bay pore waters extracted from the uppermost layers of sediment (1–2 cm) and from the deeper ones. These two types of sediment compartment have been chosen judiciously because the behavior of sedimentary U differs significantly from one to the other. Overall, the pH profiles obtained with depth for sediments collected upstream and downstream in Authie Bay vary weakly (see Fig. 2) and are relatively close to each other. In contrast, the redox-potential (E_h) profiles vary strongly with depth, especially in deeper layers of downstream sediments (see Fig. 2). As for oxygen, its content is large enough in the upper layers of sediments (0–2 cm) to justify the high values of redox potential detected in sediment surfaces; these natural redox conditions still permit the transfer of U

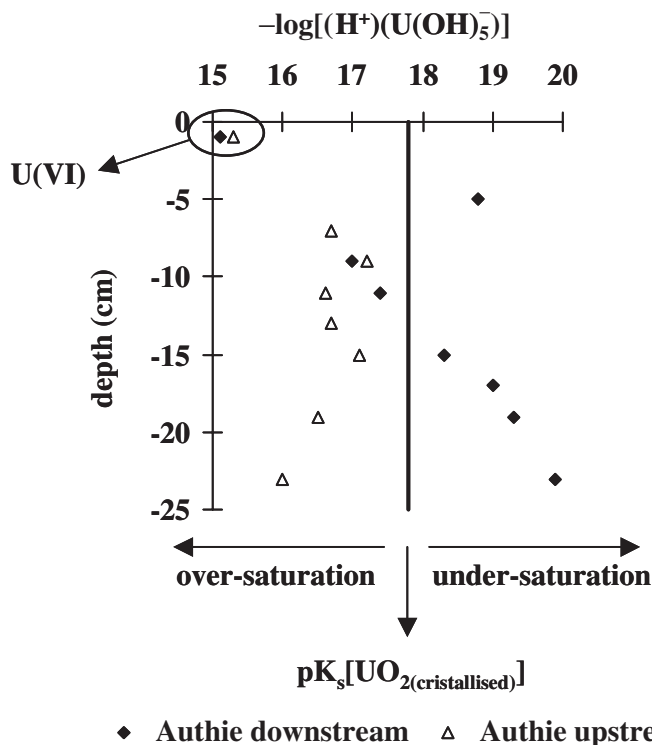
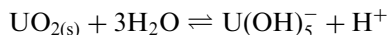
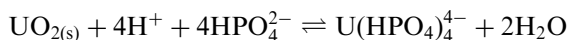


FIGURE 5 Variation of the cologarithm of the ionic activity product $[\text{H}^+][\text{U}(\text{OH})_5^-]$ as a function of depth observed for anoxic pore waters extracted from Authie-Bay sediments (note that in the first centimetres of sediments U is still in at oxidation state VI).

into its higher valence state [i.e., U(VI)], as shown in Figs. 2 and 5 (by high values of dissolved-U contents in upper layers of sediments). We further notice that the phenomenon of redox-potential decrease can also contribute to a release of sedimentary U into pore waters under strongly reducing conditions (e.g., $E_h < -350$ mV versus Ag/AgCl; see Fig. 2). To ascertain that, firstly we have hypothesized the existence of a bacterial reduction of U(VI) to U(IV) (as UO_2) and the intervention of the chemical equilibria:



and



Secondly, we have applied the Mineql⁺ computer program to pore waters extracted from deeper sediments (depths greater than 12 cm), taking account of most stability constants involving dissolved U(IV) and/or U(VI). Iterative computation has been performed without U-precipitation constraints. Our findings reveal that downstream pore waters are under saturated with respect to uraninite (a crystalline form of UO_2 ($\text{p}K_s(\text{UO}_{2\text{crystallized}}) = 17.8$) [47,48]). This indicates a release of U into pore waters in deeper layers of these sediments (see Figs. 2 and 5) in which the high phosphate

content seems to play a role in the dissolution of solid uranium IV. In contrast, upstream pore waters are over saturated with respect to the U(IV) oxide mineral, indicating the near total precipitation of U. Overall, these results are in agreement with those published by Markich [3]. These computational calculations seem to explain in part the very low levels of dissolved U in buried sediments collected upstream in Authie Bay although these must be taken with caution. Overall, we believe that the E_h values and the lower PO_4 concentrations measured in upstream sediments (compared with those found in downstream ones) are responsible for this special geochemical behavior of uranium.

Overall, general trends from our measurements indicate that both Fe and Mn oxides are reduced to Fe^{2+} and Mn^{2+} ions in buried sediments when oxygen is progressively depleted. Immediately, production of hydrogen sulphide during bacterial sulfate reduction (as SO_4^{2-} ions are consumed in pore waters) contributes to the formation of Fe and Mn sulphides and their subsequent burial, leading to an increase of AVS + CRS sulfurs with depth. These successive reactions occur at the same time as dissolved U(VI) precipitates in pore waters probably as insoluble U(IV) forms. This confirms the bioreduction of U(VI) by some metal-reducing bacteria, as suggested by Fredrickson *et al.* [10]. On the other hand, under strong reducing conditions our experimental results show the generation of new aqueous U(IV) species in pore waters from deep sediments. This observation suggests the existence of solid U(VI) (e.g., metaschoepite $UO_3 \cdot 2H_2O_{(s)}$) which is generated during the sedimentation process (sedimentation rate: $\sim 2 \text{ cm year}^{-1}$) by colloidal precipitation/complexation/coating in the water column and thereby combined with Fe(III), Mn(III,IV) oxides/oxyhydroxides as an alternative electron acceptor during the electron transfer occurring during respiration of metal-reducing bacteria (implicating a low reductive “bio-potential”) and metal oxide surface. Our E_h *in situ* measurements indicate that the detection of soluble U(IV) in pore waters necessitates redox potentials lower than about -250 mV versus Ag/AgCl. The speciation of porewater U is computed with Mineql⁺ as a function of sediment depth, and we found that in the oxic uppermost layers of sediment, uranium(VI) occurs mostly as negatively charged ions: $UO_2(CO_3)_3^{4-}$, $UO_2(CO_3)_2^{2-}$ and $UO_2(HPO_4)_2^{2-}$; whereas in deeper layers and at lower E_h values, dissolved uranium appears mostly as the $U(OH)_5^-$ and $U(HPO_4)_4^{4-}$ entities.

CONCLUSION

A close examination of the overall sedimentary process in Authie Bay was undertaken for this work in order to explain some aspects of the biogeochemical properties of uranium in connection with those of Fe, Mn and S in recent anoxic sediments for a wide range of reducing conditions in agreement with previous work [36–38]. Our investigations clearly reveal that the biogeochemical cycles of Fe, Mn and S in the sediment constitute important pathways for the interpretation of U properties. The implication of early diagenesis processes in these sediments on uranium has been confirmed by different measurements of soluble S, AVS and CRS. Generation and variability in the sedimentary medium indicate the existence of complex bioreduction phenomena which involve particularly sulfate and uranium, as evidenced by important changes observed in their concentration profiles versus depth in the pore waters of the upper part of the sediments. Hence, bacterial activity should play an important

role in these sediments. However, we cannot affirm any definite correlation between U, Mn, Fe, S and bacteria, although our findings indicate that interconnections between certain redox reactions and microbial events do exist. Thus, the biogeochemical properties of Fe, Mn, S and U are more influenced by the characteristics of the sedimentary medium at the downstream station, because bacterial activities (as suggested by Lovley *et al.* [38]) in sample sediments are higher than those observed at the upstream station as a consequence of higher sulfate concentrations in the different downstream sedimentary compartments and more biodegradable and more “young” organic matter coming from the sea. These phenomena also explain why: (i) the sedimentary medium is so anoxic in Authie-Bay sediments; and (ii) iron and manganese sulphides contents in downstream sediments are found to be about 30% more important than those found in upstream ones. Note further that the particular behavior of sedimentary uranium at the more saline station is intimately related to the lower redox potentials and higher sulfate and phosphate concentrations measured in downstream sediments than those found in upstream ones.

Acknowledgements

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