THE 1996 FLOOD EVENT: DISRUPTION OF THE ONGOING DIAGENESIS OF SAGUENAY FJORD SEDIMENTS

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ABSTRACT   As a result of the flash flood of July 1996, several million tons of sediments were eroded and rapidly transported to the Saguenay Fjord, disturbing the normal pattern of sedimentation and the associated diagenetic regime. In this paper, we present an overview of how the chemistry of the sediment evolved since this event and revealed diagenetic processes which are not readily observed under steady state conditions. The flood material contained less organic carbon, more inorganic carbon, and more Mn-oxyhydroxides than the indigenous sediments. In response to the establishment of suboxic-anoxic conditions in the flood deposit, Mn^{2+} was released to porewater by reduction of Mn-oxides present at the original sediment-water interface and in the flood material. Most of the Mn^{2+} diffused towards the new sediment-water interface, where it was mainly oxidised by IO_3^- and NO_3^-. The authigenic Mn-oxyhydroxides present at the original sediment-water interface appears to react with NH_4^+ generated in-situ or diffusing from below, producing NO_3^- anaerobically at about 12 cm depth.

RÉSUMÉ Suite à la crue éclair de juillet 1996, plusieurs millions de tonnes de sédiments ont été érodés et rapidement transportés dans le Fjord du Saguenay, perturbant le régime normal de sédimentation et le système diagénétique en place. Une vue d'ensemble de l'évolution des propriétés géochimiques des sédiments depuis la crue éclair et la description de processus diagénétiques difficiles à observer dans un système à l'état stationnaire sont présentées dans cet article. Le sédiment déposé lors de la crue contient moins de carbone organique mais plus de carbone inorganique et d'oxyhydroxydes de Mn que le sédiment indigène. Suite au rétablissement des conditions sub-oxiques/anoxiques dans la couche de sédiments déposée lors de la crue, la dissolution réductrice de ces oxydes de Mn a libéré du Mn^{2+} dans l'eau interstitielle. La plupart de ce Mn^{2+} a diffusé vers la nouvelle interface eau-sédiment où il a été principalement oxydé par IO_3^- et NO_3^-. Les oxydes de Mn authigènes présents à l'ancienne interface eau-sédiment semblent réagir avec le NH_4^+ produit in situ ou issu des couches profondes, produisant du NO_3^- à 12 cm de profondeur en milieu anoxique.

1. INTRODUCTION

In July 1996, exceptional rainfall over the Saguenay region caused a catastrophic flood that affected the upper reaches of the fjord (Figure 1). An estimated 6-9 million tons of post-glacial sediments were eroded and carried to the fjord in less than two days. The event was reviewed by Lapointe et al. (1998). Some of the most dramatic results of the flood occurred in the Baie des Ha! Ha! and the Bras Nord (Figure 1) where several tens of centimetres of new sedimentary material were rapidly deposited over the indigenous sediments (Pelletier et al., 1999). This perturbed the normal pattern of sedimentation and the associated diagenetic regime (Deflandre et al., 2000a). This disruption provided a unique opportunity to study how the chemistry of the sediment would evolve after such an event and revealed diagenetic processes which are not readily observed under steady state conditions.

2. METHODS

2.1 Environmental setting

The Saguenay Fjord is a long (93 km) and narrow (1-6 km) submerged valley that joins the St. Lawrence Estuary at Tadoussac (Figure 1). The Fjord branches into two shallow arms near its head, one leading south into the Baie des Ha! Ha! and the other leading north toward Chicoutimi. Hydrographic, geological and biological features of the Saguenay Fjord are described in Fortin and Pelletier (1995) and Schafer et al. (1990). Sediment accumulation rates measured prior to the flood are regionally variable: 2-7 cm yr^{-1} at the head of the fjord (station SF), ~1 cm yr^{-1} at station 05, and <0.2 cm yr^{-1} in the Baie des Ha! Ha! (stations 2, 7, 9, 13) and at stations 15 and 30 in the 275 m deep main basin (Barbeau et al., 1981; Mucci and Edenborn, 1992; Smith and Walton, 1980). The sediments that accumulate under normal sedimentation conditions, generally consist of anoxic grey-black sandy (5-10 wt%) muds with organic
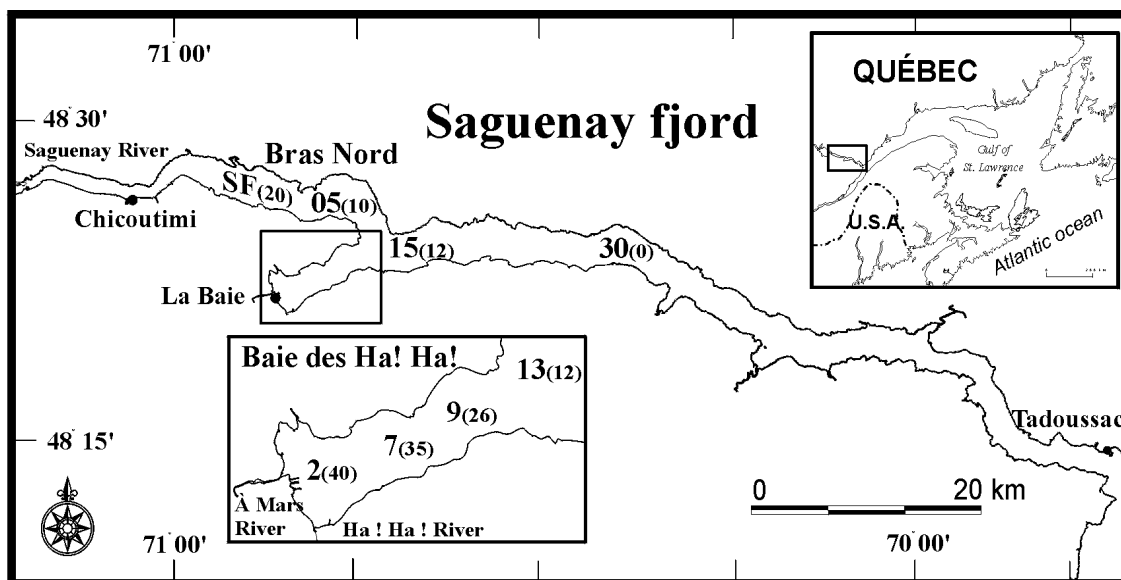
Figure 1. Map of the Saguenay Fjord showing the eight sampling sites. The number in brackets is the approximate thickness of the flood layer (in centimetre).

matter (OM) concentrations ranging from 0.5 to 3 wt%, except in the Bras Nord where more than 5 wt% OM can be found in very sandy (>30 wt%) muds (Smith and Walton, 1980).

2.2 Sampling and analytical methods

Sediments were collected at four stations along the main axis of the Fjord and at four stations in the Baie des Ha! Ha! (Figure 1) over a three-year period from 1996 to 1998. We report time-series data collected at station 05 between 1996 and 1998 in the Bras Nord and data from cores collected at station 15 in the Baie des Ha! Ha! in 1998. The sampling programs and analytical methods are described in Anschutz et al. (2000), Deflandre et al. (2000a, 2000b), Mucci et al. (2000a), and Pelletier et al. (1999).

3. RESULTS AND DISCUSSION

In the following discussion, we describe the composition of the flood deposit and how the sediment properties have evolved after the flood event.

3.1 The flood deposit

The flood material was clearly visible in cores, appearing as a lighter coloured grey-brown layer on top of the dark grey-black indigenous sediment (Figure 2). Although its thickness is variable (i.e., 10 to 50 cm; Figure 1), the composition of the flood sediments is similar throughout the affected area and is clearly different from the sediment that normally accumulates in the Saguenay Fjord. The geochemical characteristics of the flood deposit are given in Deflandre et

al. (2000a), Mucci et al. (2000a) and Pelletier et al. (1999). Briefly, it consists of grey-brown silt-muds (~10 wt% sand), except at the base of the flood deposit, where sandy-beds (up to 30 wt% sand) are often present. The organic carbon content of the flood deposit is ~1 wt%, which is 50% lower
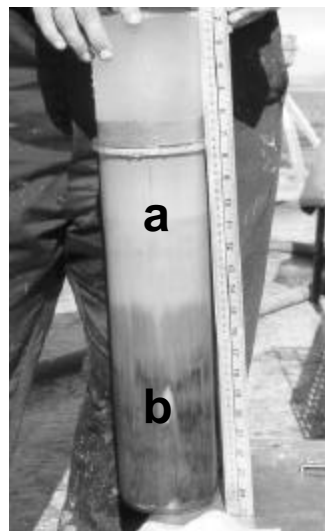

Figure 2. Photograph of a core taken in August 1996 at station SF (Bras Nord). The flood layer was ~20 cm. The top light grey-brown zone (a) is the flood sediment (suboxic portion) where both Fe- and Mn-oxides were relatively stable. The lower dark grey-black zone (b) is the anoxic portion where sulphides are present.
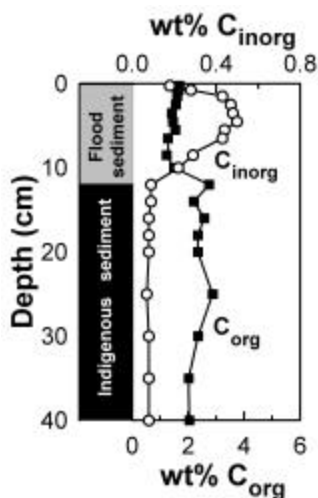
Figure 3. Vertical distributions of organic and inorganic C content in sediment collected at station 15 in 1998.

than in the indigenous sediment (Figure 3). The C_{org}/N molar ratio (~18; Deflandre et al., 2000a) and $^{13}\delta C_{org}$ (~-27‰; St-Onge and Hillaire-Marcel, 2000) are similar to those of the indigenous sediment, attesting to the same terrestrial origin of sediments. The flood sediment contains 0.5% inorganic carbon, which is almost undetectable in the normal fjord sediment (Figure 3). The C_{inorg} is most likely composed of calcareous materials associated with post-Wisconsinian marine clays transported during the flood event. Under the prevailing anoxic conditions, the carbonate may be preserved (Mucci et al., 2000b) and serve as a useful tracer

of this event in the future.

3.2 Post-flooding diagenetic behaviour of Mn

Preliminary observations in the Saguenay fjord sediments less than three weeks after the flash flood revealed that solid-phase Mn was already dissolving (Pelletier et al., 1999).

3.2.1 Post-depositional remobilization of Mn

As indicated in the time-series from station 05 in the Bras Nord, the authigenic Mn-oxyhydroxides had accumulated in the thin (the depth of oxygen penetration was on the order of 5 mm; L. Lefrançois, pers. comm.) oxic sediment before the flood event as expected for early diagenesis (Figure 4) fueled by the microbial degradation of the organic carbon supplied under a relatively constant sedimentation regime (~1 cm yr^{-1}; Mucci and Edenborn, 1992). The solid-phase Mn content decreased rapidly with depth and coincided with the increase in porewater Mn^{2+} concentrations. Below these sharp gradients, both the solid-phase and porewater Mn became nearly constant, reflecting an equilibrium with an authigenic mineral phase, possibly a mixed Mn-Ca carbonate (Mucci and Edenborn, 1992; Saulnier and Mucci, 2000) or adsorption onto sulphides (e.g. AVS; Arakaki and Morse, 1993).

These steady state distributions of Mn at station 05 were perturbed in July 1996 by the sudden deposition of 10 cm of flood material (Figure 4). As a result of the upward displacement of the suboxic-anoxic boundary, reactive Mn associated with the authigenic oxyhydroxides within the
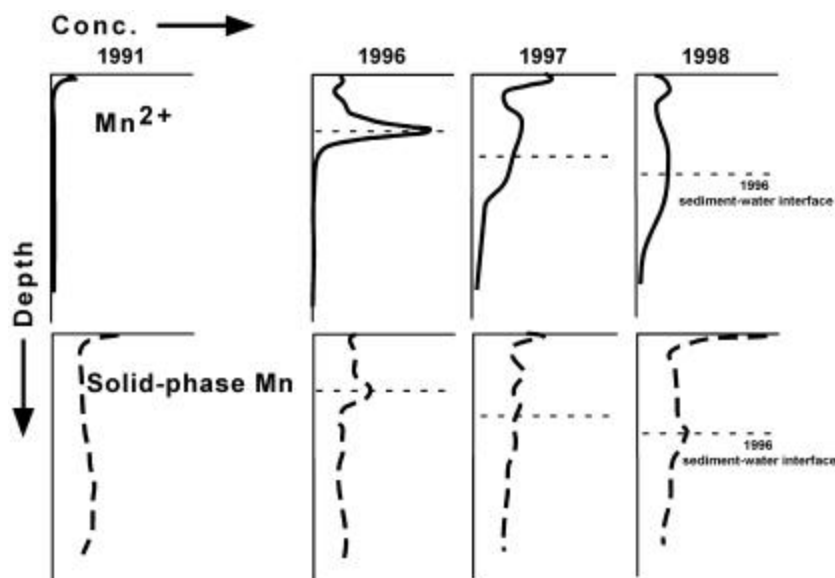

Figure 4. Solid-phase and porewater profiles at station 05 illustrating the mobility of Mn since the 1996 flood event. The 1991 profiles represent steady state diagenesis of Mn. The solid-phase (1N HCl extraction) includes amorphous and crystalline Mn-oxyhydroxides, carbonates, and hydrous alumino-silicates. Adapted from Gagnon et al. (1995) and Deflandre et al. (2000a).
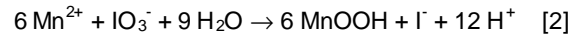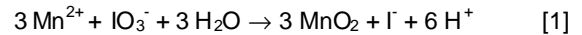
flood deposit were reduced. In contrast to iron, which was sequestered as sulphides at the original sediment-water interface (Deflandre et al., 2000a; Mucci et al., 2000a), most of the Mn^{2+} that was released to the porewater diffused to the new sediment-water interface, where it was reprecipitated as oxides (Figure 4). The amount of reactive Mn that had accumulated at or near the new sediment-water interface in 1998 exceeded the inventory at the former interface in 1991. This excess could only have been supplied by the reductive dissolution of Mn-oxyhydroxides contained in the flood deposit itself.

3.2.2 Re-oxidation of Mn^{2+} near the new sediment-water interface

The reduced Mn^{2+} diffusing to the new sediment-water interface was precipitated as oxides in the surface layer at station 15 (Figure 5b). Dissolved O_2 is generally considered to be the main oxidant for Mn^{2+}. However, our data show that the O_2 and Mn^{2+} profiles do not overlap (Figure 5a). In fact, there is a ~10 mm gap between the depths at which O_2 and Mn^{2+} are below their respective detection limits, coinciding with the zone of active Mn-oxide accumulation (Figure 5). This suggests that O_2 was not the major oxidant of Mn^{2+}.

Anschutz et al. (2000) have recently shown that Mn^{2+} can also be oxidised by iodate (IO_3^-) present in the sediment. They indicated that the production of porewater iodide (I^-) was mostly due to the oxidation of Mn^{2+} by IO_3^- according

to:.

$$3\,Mn^{2+} + IO_3^- + 3\,H_2O \rightarrow 3\,MnO_2 + I^- + 6\,H^+ \qquad [1]$$

$$6\,Mn^{2+} + IO_3^- + 9\,H_2O \rightarrow 6\,MnOOH + I^- + 12\,H^+ \quad [2]$$

Our data show that I^- was present in the layer where O_2 and Mn^{2+} could not be detected, suggesting that IO_3^- may be reduced at the same depth at which Mn^{2+} was undergoing oxidation (Figure 5). Using the same approach as Anschutz et al. (2000), we estimated how much Mn^{2+} was oxidised by iodate in this sediment, considering the magnitude of the I^- and Mn^{2+} fluxes and the stoichiometry of reactions 1 and 2. The calculations show that the reduction of iodate can account for the oxidation of 15 to 30% of the Mn^{2+} diffusing from below.

It has been proposed that Mn^{2+} may also be oxidised by nitrate (Aller, 1990; Hulth et al., 1999; Luther et al., 1997; 1998; Schultz et al., 1994; Sørensen et al., 1987) according to:
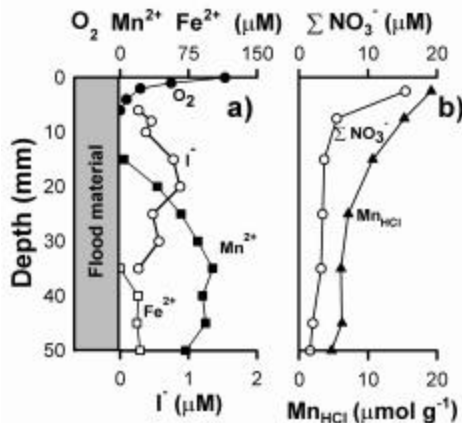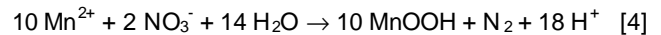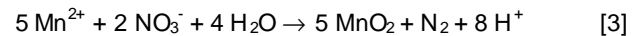
$$5\,Mn^{2+} + 2\,NO_3^- + 4\,H_2O \rightarrow 5\,MnO_2 + N_2 + 8\,H^+ \qquad [3]$$

$$10\,Mn^{2+} + 2\,NO_3^- + 14\,H_2O \rightarrow 10\,MnOOH + N_2 + 18\,H^+ \quad [4]$$

Our results show the presence of NO_3^- within the layer where microelectrode measurements indicated that Mn^{2+} was not detected (Figure 5). This suggests that NO_3^- may indeed be oxidising Mn^{2+}. Considering the stoichiometry of reactions 3 and 4, our calculations show that the oxidation of Mn^{2+} can consume as much as 65% of the vertical NO_3^- flux, suggesting that most of the upward diffusing Mn^{2+} may have been oxidised by NO_3^-.

These calculations suggest that redox reactions between species of iodine and manganese, and between nitrogen and manganese, can be quantitatively important during early diagenesis. Iodate and nitrate may be the main reactants that oxidised Mn^{2+} in the first 2 cm of sediment at station 15 in 1998.

3.3 An interesting aspect of the present chemistry of porewaters in the Saguenay fjord

The vertical distribution of NO_3^- in the 0-5 cm surface layer at station 15 in 1998 corresponded to what one would expect in pelagic sediments as a result of steady state diagenesis (e.g., Froelich et al., 1979). The porewater NO_3^- profile displays a high concentration below the sediment-water interface (Figure 6), where it was liberated to the porewater by oxic nitrification of organic nitrogen. Below the oxic layer, which was about 5 mm (Figure 5), nitrate is consumed by bacterial denitrification and by oxidation of the upward diffusing Mn^{2+}, with a minimum value at a depth of about 7 cm (Figure 6). However, the concentration of NO_3^- rebounded at 8 cm depth in the anaerobic sediment and a peak appeared at a depth of 12 cm. This depth corresponds

Figure 5. (a) Vertical distributions of dissolved O_2, I^-, Mn^{2+}, and Fe^{2+} in sediment porewater at station 15 in 1998. The profiles were measured simultaneously with a solid gold-amalgam microelectrode (Luther et al., 1998). (b) Vertical distributions of dissolved ΣNO_3^- (nitrate plus nitrite) and reactive Mn_{HCl} at station 15 in 1998. The concentrations have been measured from porewater squeezed and sediment of a core different that the one used for microelectrode profiling.
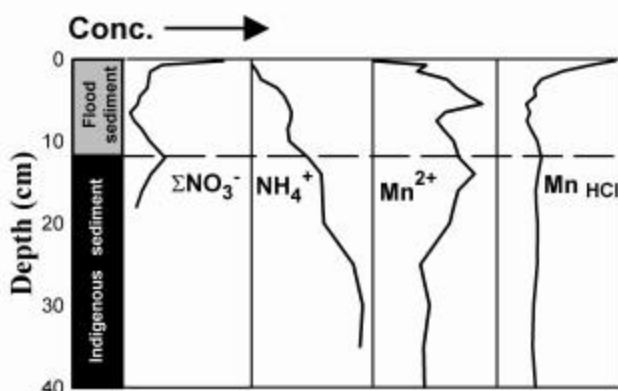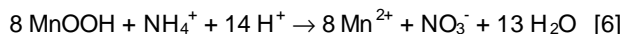
Figure 6. Vertical distributions of dissolved $\sum NO_3^-$, NH_4^+, Mn^{2+}, and reactive Mn_{HCl} in porewater and sediment at station 15 in 1998. Adapted from Deflandre et al. (2000a).

to the former sediment-water interface. Considering that bioturbation is weak at this station and limited to the first 5 cm (G. Desrosiers, pers. comm.), the high NO_3^- concentration can not be caused by the infiltration of bottom water through animal burrows. Moreover, this NO_3^- peak cannot be a remnant of the pre-flood conditions since our calculations indicate that it should be dissipated within less than three months by purely diffusional processes. The occurrence of this NO_3^- peak three years after the flood event requires local production of nitrate by in-situ diagenetic reactions. Recent laboratory and field studies (Aller et al., 1998; Anschutz et al., 2000; Hulth et al., 1999) indicate that NH_4^+ can be oxidised by Mn-oxides to NO_3^- in anaerobic sediments according to:

$$4\,MnO_2 + NH_4^+ + 6\,H^+ \rightarrow 4\,Mn^{2+} + NO_3^- + 5\,H_2O \qquad [5]$$

$$8\,MnOOH + NH_4^+ + 14\,H^+ \rightarrow 8\,Mn^{2+} + NO_3^- + 13\,H_2O \qquad [6]$$

The NO_3^- peak observed at station 15 was located precisely at the original sediment-water interface where authigenic Mn oxides were buried by the flood (Figure 6). These oxides therefore appear to be responsible for the oxidation of NH_4^+ produced in-situ or diffusing from below.

CONCLUSIONS

Following the catastrophic flood of July 1996, transport of large amounts of organic-poor post-glacial sediments into the fjord led to a non-uniform distribution of organic matter and an alteration of redox conditions that, in turn, resulted in non-steady state diagenesis. The depositional event led to the remobilization of reactive Mn but the trapping of reactive Fe at or near the former sediment-water interface. The transient state generated by the event revealed diagenetic reactions which are not readily observed under steady state

conditions such as the oxidation of Mn^{2+} by iodate and nitrate, and the anaerobic production of nitrate via the oxidation of ammonium by solid Mn-oxides.

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