Marine and Petroleum Geology 27 (2010) 1262–1272

Contents lists available at ScienceDirect

Marine and Petroleum Geology

journal homepage: www.elsevier.com/locate/marpetgeo

Methane-derived authigenic carbonates from active hydrocarbon seeps of the St. Lawrence Estuary, Canada

Denis Lavoie [a,*], Nicolas Pinet [a], Mathieu Duchesne [a], Andrée Bolduc [a,b], Richard Larocque [b]

[a] Geological Survey of Canada, Quebec Division, 490 de la Couronne, Quebec City, QC G1K 9A9, Canada

[b] Fisheries and Oceans Canada, Maurice Lamontagne Institute, 850 Route de la Mer, Mont-Joli, QC G5H 3Z4, Canada

ARTICLE INFO

Article history:
Received 29 May 2009
Received in revised form
15 February 2010
Accepted 23 February 2010
Available online 3 March 2010

Keywords:
Carbonate concretions
Methane seep
Bacterial chemosynthesis
St. Lawrence River
Quaternary

ABSTRACT

Nearly 2000 pockmarks with diameters ranging from a few tens of meters up to 700 m are present on the seafloor of the St. Lawrence Estuary in eastern Canada. Coring of some pockmarks resulted in the recovery of various-sized and shaped carbonate concretions in a predominantly silty mud matrix. Petrographic and geochemical data on four authigenic carbonate concretions are reported as well as data from shell material in the unconsolidated sediment. Video observations and echo-sounder images indicate that the sampled pockmarks are actively gas venting. The video images show significant look-alike microbial mats in areas where gas is venting. The carbonate concretions are primarily made up of carbonate cements with varying percentage of shell fragments, micrite particles and fine-grained clastics. Orthorhombic crystal morphology and diagenetic fabrics including isopachous layers and botryoids characterize the aragonite cement. Oxygen isotopes ratios for the cement crusts do not record any thermal anomaly at the site of precipitation with $\delta^{18}O_{VPDB}$ ratios (+3‰) in equilibrium with cold (5 °C) deep marine waters, whereas significant negative $\delta^{13}C_{VPDB}$ ratios (−9.9 to −33.5‰) for cement and shell material within concretions indicate that the carbonates largely derive from the microbial oxidation of methane. The $\delta^{13}C_{VPDB}$ ratios of aragonite shells (−2.7 to −5.6‰) taken from unconsolidated sediments at some distance from the concretions/vents show variable dilution of HCO_3^- with negative $\delta^{13}C_{VPDB}$ ratios derived from microbial oxidation of methane with isotopically normal (0‰) marine bicarbonate. These results are in agreement with other lines of evidence suggesting that pockmarks formed through the recent and still active release of gas from a reservoir within the Paleozoic sedimentary succession.

1. Introduction

The presence of gas-charged sediments below seafloor depressions on seismic profiles has been first suspected from evidence such as wipe-out zones and high amplitude anomalies (King and MacLean, 1970; Fleischer et al., 2001). The geological importance of seabed morphological features associated with fluid leakage was increasingly acknowledged through the increased coverage of the seafloor by high-resolution bathymetry data that led to the global documentation of crater-like depressions (pockmarks) in diverse tectonic settings (Judd and Hovland, 2007). Therefore, with increased density of combined seafloor mapping and seismic profiling, the association in planar view of seafloor pockmarks at the top of vertical seismic zones with gas-related wipe-out and amplitude anomalies (or seismic "chimneys") became ubiquitous (Løseth et al., 2009; Pinet et al., in press). The interest in pockmarks peaked with the documentation of the close association between seabed methane escapes and specific ecosystems (Paull et al., 1992). The understanding of these enigmatic life oases in environments hostile to light-dependant carbon-based life forms has profound impacts on the origin and search of life on the primitive Earth and abroad (Nisbet and Sleep, 2001). Pockmark studies now include a wide range of scientific disciplines that document various aspects of seabed fluid release and the interrelationships between geochemical, physical and ecological processes.

Seeping fluids responsible for the formation of pockmarks are commonly hydrocarbons and the interest of the oil and gas industry is obvious. Major hydrocarbon offshore domains are characterized by these seeping features; e.g. the Gulf of Mexico (MacDonald et al., 1990), the North Sea (Cole et al., 2000), the offshore domains of both West Africa (Pilcher and Argent, 2007) and Brazil (Sumida et al., 2004). However, pockmarks can also form where evidence for thermogenic hydrocarbons are lacking (Kelley et al., 1994).

* Corresponding author. Tel.: +1 418 654 2571; fax: +1 418 654 2615.
E-mail address: delavoie@nrcan.gc.ca (D. Lavoie).

0264-8172/$ – see front matter
doi:10.1016/j.marpetgeo.2010.02.014

Carbonate-cemented crusts, concretions and bioaccumulations are an almost ubiquitous feature in modern methane venting pockmarks (Hovland et al., 1987; Campbell, 2006). These carbonates are the end products of microbial chemosynthesis where complex communities of opportunistic methane-oxidizing Archaea and sulphur-oxidizing Bacteria (such as *Beggiatoa*) are thriving on the methane that emanates from the seafloor (Niemann et al., 2005).

In the St. Lawrence Estuary, pockmarks were first suspected based on high-resolution seismic profiles (Syvitski and Praeg, 1989) before regional seismic and bathymetry surveys showed that they occur in profusion (Pinet et al., 2008a,b, in press).

The purpose of the present contribution it to present and discuss carbonate concretions within two pockmarks of the St. Lawrence Estuary in a context of comprehensive understanding of seep sites using a multidisciplinary approach. We report new echo-sounder, sidescan, video, core and geochemical data. The herein reported site survey allows documenting gas bubble emissions from the seabed, bacterial mats, bivalve specific communities and hardground-like pavements located in the pockmarks. Cores raised from pockmarks resulted in the sampling of some of these carbonate crusts. Sampling of unconsolidated shell-rich sediments away from the venting areas was also done for comparative purposes.

With this data set, pockmarks found on the St. Lawrence Estuary seabed become the best-documented occurrences of gas release features in a mid-latitude estuarine setting. This study impacts our knowledge and understanding of past and present-day carbonate deposition in cool water, clastic-dominated basins. Finally, the methane-driving mechanism for the formation of these carbonates has major implications for the hydrocarbon prospectivity of the marine environment of this area (Lavoie et al., 2009).

2. Oceanographic setting

The St. Lawrence Estuary is a funnel-shaped body of tide-influenced saltwater. It can be as narrow as a few kilometres near Quebec City and more than 65 km wide at its eastern edge near Pointe-des-Monts (Fig. 1). It opens to the Gulf of St. Lawrence and the Atlantic Ocean through the Laurentian channel, which is a long, continuous trough more than 350 m deep that runs 1500 km from the mouth of the Saguenay River to the shelf edge in the Atlantic ocean where it ends abruptly (Fig. 1).

The water masses have a well-developed stratification (Syvitski et al., 1983) with a temperature minimum of -1 °C in the cold intermediate layer (50–250 m) and a bottom temperature around 5 °C. The water masses are relatively well oxygenated as suggested by the presence of abundant normal marine fauna even in the deepest portion of the estuary (Syvitski et al., 1983). However, recent studies indicate that the level of oxygen concentration in bottom waters of the St. Lawrence Estuary has been steadily decreasing since the 1930s (Gilbert et al., 2005; Katsev et al., 2007) and hypoxic conditions (<62.5 mol/L) are found in the western section of the Laurentian channel (Benoit et al., 2006). Salinity in the surface layer (0–50 m) ranges from 26 to 31 psu (practical salinity unit) and steadily increases up to 34 psu on the river bottom (Syvitski et al., 1983).

The estuary carries a significant load of mud and silt-sized sediments. Below wave base, the bottom of the St. Lawrence Estuary is the site of mud accumulations. Deep currents are strong enough to locally generate large-scale migrating submarine bedforms (Syvitski et al., 1983; Bolduc and Duchesne, 2009) in coarser-grained material. These are largely restricted to the submarine deltas of major tributaries of the St. Lawrence River on its northern shore and upstream the Saguenay river mouth where the estuary drastically narrows and shallows. Core samples and seafloor photographs reveal that some areas are highly bioturbated with local shells (molluscs) and small wood fragments. In piston cores, very fine sand to fine silt millimetre-scale laminations are locally visible and sometimes affected by soft-sediment deformation (St-Onge et al., 2003). Estimates of recent sedimentation rates range from 0.70 cm/yr in the southern part of the study area to 0.22 cm/yr in the northern part (Smith and Schafer, 1999).

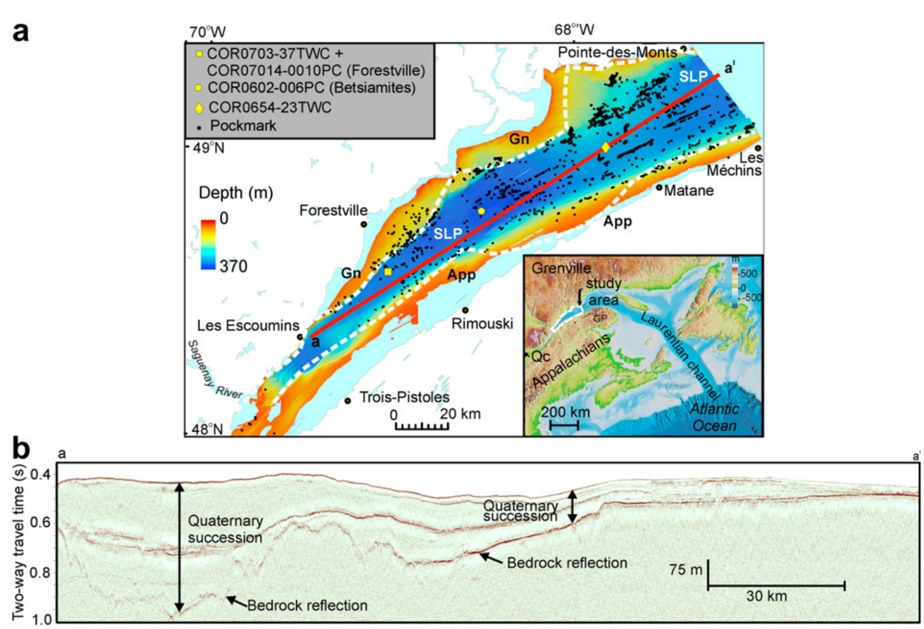

Fig. 1. (A) Multibeam bathymetric map of the St. Lawrence Estuary extending from the mouth of the Saguenay River (SW) to Pointe-des-Monts/Les Méchins (NE). The location of the cores discussed in this paper is shown as well as the abundant pockmarks marking the seafloor. The limit between the geological domains in the St. Lawrence Estuary is shown by the dashed white line (Pinet et al., 2008a). Gn is for Grenvillian, SLP is for St. Lawrence Platform and App is for Appalachians. The inset map locates the study area (outlined in white) and the connection between the St. Lawrence Estuary to the Atlantic Ocean through the Laurentian Channel, modified from Shaw et al. (2006). GP, Gaspé Peninsula; Qc, Quebec City. (B) Seismic line illustrating the along-strike variations in the bedrock topography and thickness of the Quaternary infill. The location of seismic line a–a′ is shown in (A) (orange line).