Marine and Petroleum Geology 68 (2015) 520–535

Contents lists available at ScienceDirect

Marine and Petroleum Geology

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

Research paper

Pyritization induced by anaerobic oxidation of methane (AOM) – An example from the upper devonian shale succession, western New York, USA

Gary G. Lash

Department of Geosciences, State University of New York – Fredonia, Fredonia, NY 14063, USA

A R T I C L E I N F O

Article history:
Received 25 February 2015
Received in revised form
15 August 2015
Accepted 2 October 2015
Available online 8 October 2015

Keywords:
Anaerobic oxidation of methane
Pyrite
Carbonate concretions
Sulfur isotopes
Rhinestreet shale
Upper Devonian

A B S T R A C T

The diagenetic history of the Upper Devonian Rhinestreet Shale of the western New York region of the Appalachian basin appears to reflect the upward diffusion of methane through these deposits shortly after their accumulation. The most obvious diagenetic signature of this process is numerous horizons of authigenic calcium carbonate concretions interpreted to reflect mineralization induced by the anaerobic oxidation of methane (AOM) focused along the sulfate-methane transition (SMT) zone. Additionally, a 2-m-thick section of the lower Rhinestreet preserves a diagenetic record consistent with AOM in the form of two pyritiferous stratigraphic horizons. The stratigraphically lowest horizon is a 2-cm-thick layer containing abundant ^{34}S-enriched (11.8 and 18.4‰ V-CDT) coarsely crystalline pyrite. The thinness of this interval suggests that AOM-related diagenesis remained fixed at this stratigraphic position for a brief period of time before these deposits were buried below the SMT or the SMT shifted position within the sediment column. A second paleo-SMT appears to have stabilized 60 to 80 cm above the 2-cm-thick pyritiferous horizon, meter-scale carbonate concretions being the most obvious evidence of this episode of AOM. More than this, though, the apparently Fe-limited nature of the host black shale induced the downward diffusion of ^{34}S-enriched hydrogen sulfide produced by AOM resulting in the precipitation of ^{34}S-enriched (23.1 to 27.3‰ V-CDT) pyrite below the SMT. The maximum depth of diffusion of the sulfidization front was limited by the amount of hydrogen sulfide produced within and near the SMT as well as by the availability of reactive iron in underlying deposits. The focusing of AOM-related diagenesis at the two stratigraphic positions was likely caused by non-steady-state sedimentation. However, it is impossible to decipher relative timing of formation of the two paleo-SMTs.

1. Introduction

Burial of organic-rich sediment may be accompanied by several microbially catalyzed diagenetic processes that influence sediment mineralogy (Fig. 1). Soon after accumulation, organic matter serves as a metabolic substrate for microbial dissimilatory or organoclastic sulfate reduction per the following reaction:

$$2CH_2O + SO_4{}^{2-} \rightarrow 2HCO_3{}^{-} + H_2S. \qquad (1)$$

The remaining fraction of organic matter in underlying sulfate-depleted deposits is further decomposed by microbial methanogenesis, the principal products being ^{13}C-depleted methane and ^{13}C-enriched bicarbonate or dissolved inorganic carbon (DIC) (Fig. 1; Conrad, 2005), both of which diffuse upward toward the sediment-water interface (SWI) (Chatterjee et al., 2011). At shallow depth, however, generally within the upper 25 m of the sediment column (Riedinger et al., 2006; Snyder et al., 2007a), downward diffusing seawater sulfate meets upward migrating methane along the sulfate-methane transition (SMT) zone, a thin (generally less than 2 m) fundamental biogeochemical boundary separating microbial sulfate reducers above from methanogens below (Fig. 1; Barnes and Goldberg, 1976; Reeburgh, 1976; Alperin et al., 1988; Borowski et al., 1997, 1999, 2013; Aloisi et al., 2000; Rodriguez et al., 2000; Dickens, 2001; Niemann et al., 2006; Knittel and Boetius, 2009). Within the SMT, a consortium of sulfate-reducing bacteria and methanotrophic archea consumes the sulfate and methane per the following net reaction:

E-mail address: Lash@fredonia.edu.

http://dx.doi.org/10.1016/j.marpetgeo.2015.10.002

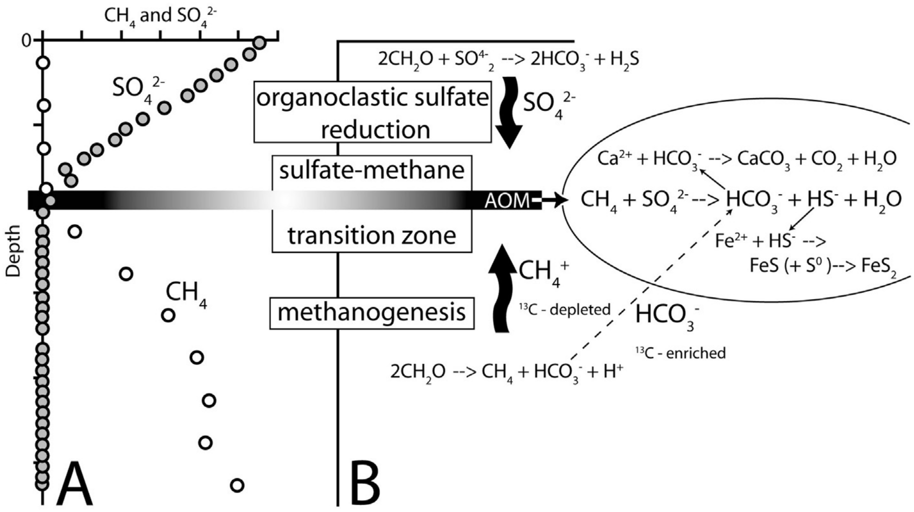

Fig. 1. (A and B) Typical pore fluid profile produced by the dominant biogeochemical processes occurring in the upper part of continental margin sedimentary sections, including organoclastic sulfate reduction and microbially mediated anaerobic oxidation of methane (AOM) focused at the sulfate methane transition zone (SMT). Heavy arrows show upward migration of methane and downward diffusion of seawater sulfate. The dashed arrow highlights the potential delivery of ^{13}C-enriched dissolved inorganic carbon (bicarbonate) to the SMT from deeper in the sedimentary section (Chatterjee et al., 2011). Reactions at right illustrate principal processes occurring within and close to the SMT. The profiles are patterened after data from Borowski (2004) and Snyder et al. (2007b).

$$CH_4 + SO_4^{-2} \rightarrow HCO_3^- + HS^- + H_2O, \qquad (2)$$

a process known as anaerobic oxidation of methane (AOM) (Fig. 1; Reeburgh, 1976; Boetius et al., 2000; Fossing et al., 2000; Chatterjee et al., 2011; Regnier et al., 2011).

The depth of the SMT below the SWI is controlled by multiple factors, including the accumulation rate of sedimentary organic matter, the sedimentation/burial rate of the sediment column, and the degradation kinetics and age of the organic matter (Dean and Schreiber, 1978; Bréhéret and Brumsack, 2000; Borowski et al., 2013; Meister et al., 2013). Under certain conditions, SMT depth is regulated by methane flux and consequent seawater sulfate flux, both expressed as gradients (Borowski et al., 1996; Niewöhner et al., 1998; Fossing et al., 2000; Arndt et al., 2006; Riedinger et al., 2006; Chatterjee et al., 2011). Under steady-state conditions of constant methane and sulfate flux, the SMT remains at a fixed depth relative to the SWI (Borowski et al., 2013). However, the onset of non-steady-state conditions, including variations in methane flux, will induce a change in the position of the SMT relative to the ocean floor until steady-state conditions are re-established and the SMT is once again stabilized relative to the SMT (Borowski et al., 1996, 2013).

A volume of sediment experiencing steady-state burial passes through the SMT acquiring minor or trace amounts of ^{34}S-enriched pyrite and authigenic calcite (Raiswell and Fisher, 2004; Borowski et al., 2013). However, a marked reduction of sedimentation rate (i.e., depositional hiatus) stabilizes a thin stratigraphic horizon of the sediment column along the SMT for a protracted period of time resulting in the enhanced formation ^{34}S-enriched pyrite and authigenic calcium carbonate along this stratigraphic position (Fig. 1; Kasten et al., 1998; Adler et al., 2000; Jørgensen et al., 2004; Borowski et al., 2013). This relatively straightforward process can be complicated by the availability of aqueous iron in the diagenetic environment, the SMT. If the sediment within or near the SMT contains low concentrations of aqueous iron, as has been described from some deposits that accumulated under strongly reducing, even euxinic, conditions (Middleburg, 1991; Lyons et al., 2003; Jørgensen et al., 2004), excess sulfide produced by AOM will diffuse upward, perhaps to the SWI, and deeper into the sediment column where it may form sulfide minerals upon encountering dissolved iron. Jørgenson et al. (2004) and Neretin et al. (2004), for example, attributed the formation of ^{34}S-enriched pyrite in freshwater deposits of the Black Sea sediment column to methane-driven sulfate reduction in overlying euxinic deposits that had accumulated during the Pleistocene/Holocene sea level rise.

It is becoming increasingly obvious that AOM is a widespread diagenetic reaction in fine-grained marine sediment along many modern continental margins (Reeburgh, 2007). Further, it is estimated that as much as 90% of the methane produced in these deposits globally is consumed by AOM before migrating to the seafloor (Regnier et al., 2011). In spite of its obvious importance to Earth's carbon cycle and atmosphere, however, AOM has generally been unrecognized in the ancient rock record, especially Paleozoic successions. This paper presents data suggesting that AOM coupled with organoclastic sulfate reduction and methanogenesis within the organic-rich Upper Devonian Rhinestreet Shale of the western New York region of the Appalachian basin created a diagenetic environment that (1) resulted in the precipitation of ^{34}S-enriched pyrite and authigenic calcium carbonate and (2) induced the diffusion of AOM-produced hydrogen sulfide into underlying organic-lean gray shale causing the precipitation of μm-to cm-scale masses of ^{34}S-enriched pyrite in these otherwise pyrite-deficient deposits. The investigated Upper Devonian interval, arguably one of the best preserved ancient examples of diagenesis produced by sulfide diffusion, illustrates the interconnection of the depositional history of a sediment interval, non-steady-state sedimentation/burial, and AOM as a mechanism of generating ^{34}S-enriched hydrogen sulfide that is eventually preserved as pyrite.

2. Stratigraphic framework

The Upper Devonian clastic succession of western New York comprises part of an eastward-thickening body of marine shale and scattered siltstone beds that passes upward into shallow marine or brackish-water deposits (Friedman and Johnson, 1966; Woodrow et al., 1973; Baird and Lash, 1990) thus recording progradation of