



Geochemical response to pulsed sedimentation: Implications for the use of Mo as a paleo-proxy



J.L. McKay^{a,*}, T.F. Pedersen^{a,b}

^a Department of Earth, Ocean, and Atmospheric Sciences, The University of British Columbia, 2207 Main Mall, Vancouver, British Columbia V6T 1Z4, Canada

^b School of Earth and Ocean Sciences, University of Victoria, Victoria, British Columbia V8W 3P6, Canada

ARTICLE INFO

Article history:

Received 5 September 2013

Received in revised form 1 May 2014

Accepted 2 May 2014

Available online 21 May 2014

Editor: Michael E. Böttcher

Keywords:

Molybdenum

Paleoceanography

Rhenium

Sedimentary redox

Trace metals

Turbidites

ABSTRACT

Deglacial sediments in piston core JT96-02 from the continental slope off western Canada contain numerous centimeter-thick, iron sulfide-rich layers. Major and minor element chemistry, as well as C and N isotopic data suggest that these layers represent background hemipelagic sedimentation. Intervening gray silty clay layers, each of which exhibits a fining-upward trend, are distal turbidites. The iron sulfides precipitated in response to the emplacement of each turbidite, which slowed oxygen diffusion into the sediment allowing anoxic conditions to develop in the underlying relatively organic-rich deposits. Resulting sulfate reduction and precipitation of Fe-sulfide fostered Mo enrichment ($>2 \mu\text{g/g}$). It may also explain Ni, Cr, V, and Co enrichments, although differences in detrital mineralogy cannot be ruled out, particularly for Ni and Cr. Rhenium is also enriched, albeit slightly, within the sulfide layers, but low Re/Mo ratios ($\sim 0.78 \text{ ng/g}/\mu\text{g/g}$) suggest that anoxic conditions developed very rapidly. Metals with high lithogenic concentrations (Cd and U) are not obviously enriched in the sulfide layers because there was insufficient time for noticeable authigenic accumulation before deposition of the next turbidite which severed diffusive communication with overlying seawater, the primary source of metals. Silver is also slightly higher in the sulfide layers, possibly linked to higher marine organic matter content. In summary, the pulsed character of sedimentation during the deglaciation led to episodic enrichment of Mo and occurred independently of changes in bottom water oxygen or organic carbon content. This observation potentially complicates the use of Mo as a paleo-proxy in some continental margin environments.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Organic-rich marine sediments are typically characterized by high concentrations of various minor and trace metals that are commonly used as paleo-redox (e.g., Mo and Re) and/or paleoproductivity (e.g., Cd and Ni) proxies (Tribovillard et al., 2006; Calvert and Pedersen, 2007). However, the redox conditions under which these metals accumulate and the mechanisms responsible for their accumulation differ greatly. In addition, other factors such as the nature of the depositional environment (e.g., open marine versus semi-isolated basin), the degree to which a metal is bio-accumulated, variations in lithogenic flux, and post-depositional remobilization can also affect metal concentrations.

Under strongly suboxic conditions (i.e., no free oxygen and negligible dissolved sulfide), similar to those required for Fe reduction (Morford et al., 2012), Re and U enrichments ($>10 \text{ ng/g}$ and $>5 \mu\text{g/g}$, respectively) can develop. Such accumulation is assumed to be the

result of Re and U reduction and subsequent precipitation (Koide et al., 1986; Barnes and Cochran, 1990; Klinkhammer and Palmer, 1991; Crusius et al., 1996; Morford et al., 2005, 2009, 2012), although the exact mechanism(s) are poorly understood. Seawater is the primary source of both elements, although in some situations particulate non-lithogenic U may be important (Zheng et al., 2002). Chromium and V are also reduced under suboxic conditions, forming compounds that are highly particle reactive (Emerson et al., 1979; Emerson and Husted, 1991), although over the long-term surface adsorption may not be an effective trapping mechanism (Tribovillard et al., 2006). Reduction can also lead to the precipitation of more stable Cr and V hydroxides and oxides (e.g., $\text{Cr}(\text{OH})_3$ and $\text{VO}(\text{OH})_2$, $\text{V}(\text{OH})_3$ and/or V_2O_3 ; references in Calvert and Pedersen, 2007). Once dissolved sulfide is present in the porewater many elements will be enriched in the solid phase due to the formation of insoluble sulfides (e.g., Cd, Zn) while others (e.g., Ni, Co) are incorporated into pyrite (Morse and Luther, 1999). For example Cd, which has a single stable redox state, is known to form an insoluble sulfide (CdS) when trace amounts of H_2S are available (Pedersen et al., 1989; Rosenthal et al., 1995). This can lead to small Cd enrichments ($<1 \mu\text{g/g}$) in suboxic sediments associated with sulfate reduction in organic-rich microenvironments and larger enrichments ($>8 \mu\text{g/g}$) in anoxic sediments that contain abundant dissolved sulfide. The source of Cd is commonly assumed to be the

* Corresponding author at: College of Earth, Ocean, and Atmospheric Sciences, 104 CEOAS Admin. Building, Oregon State University, Corvallis, OR 97331, USA. Tel.: +1 541 737 4054; fax: +1 541 737 2064.

E-mail addresses: mckay@coas.oregonstate.edu, mckay_jen@yahoo.ca (J.L. McKay), tfp@uvic.ca (T.F. Pedersen).

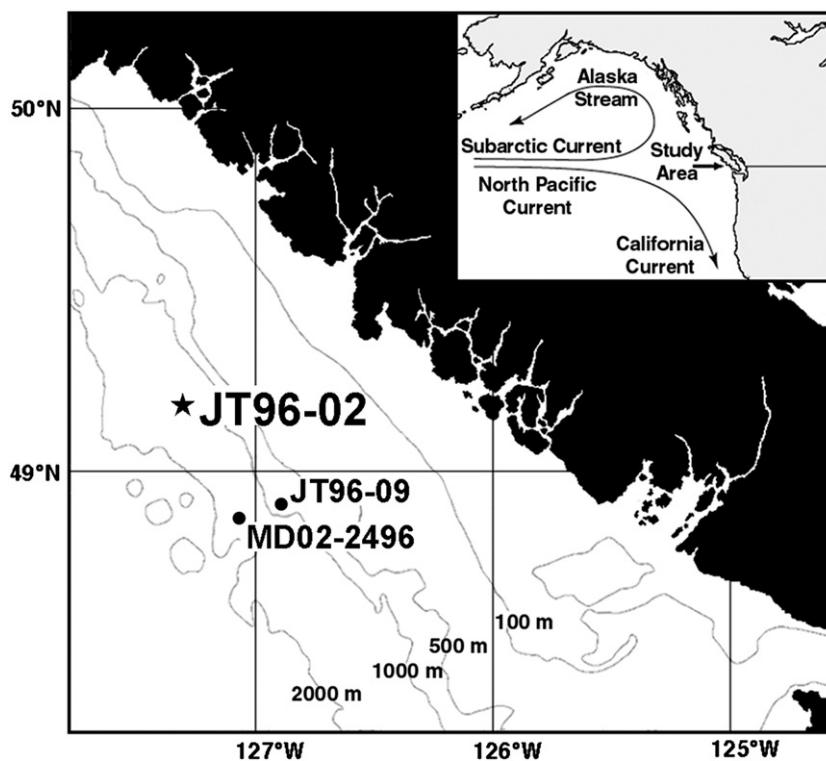


Fig. 1. The study area, located in the Northeast Pacific Ocean off the west coast of Vancouver Island, Canada. Piston core JT96-02 (49° 12.8'N and 127° 18.6'W) was collected from a water depth of 1340 m. The locations of two nearby cores (JT96-09 and MD02-5496) are also shown.

overlying seawater, but settling organic matter may also deliver Cd and other bio-accumulated elements (e.g., Ag, Ni, Zn, Cu, Cr) to the sediment (Thomson et al., 2001; Nameroff et al., 2002; Böning et al., 2004; Piper and Perkins, 2004; Brumsack, 2006; Böning et al., 2009). For Ag this biogenic flux appears to dominate, obscuring any authigenic signal, thus even sulfide-poor sediments can contain large concentrations (>200 ng/g) of Ag (McKay and Pedersen, 2008). Sedimentary redox conditions only influence whether or not this particulate Ag phase is preserved; existing evidence suggests that it is not preserved in oxic sediments (McKay and Pedersen, 2008; Morford et al., 2008). Finally, Mo enrichment of up to 20 µg/g, in combination with low Mn concentrations, is indicative of anoxic sediments with sulfidic porewater, while very high Mo concentrations (>60 µg/g) indicate a euxinic depositional environment (Scott and Lyons, 2012). Experimental data suggest that Mo accumulates due to reduction and subsequent formation of thiomolybdates (Helz et al., 1996; Wang et al., 2011) that are scavenged by Fe-sulfides and organic materials (Helz et al., 1996; Vorlicek et al., 2004). Thiomolybdate formation requires a threshold H₂S concentration of ~10 µM (Erickson and Helz, 2000); hence, the link between Mo accumulation and anoxia. Direct precipitation of MoS₂ (or Mo-Fe sulfide) also occurs, but requires exceptionally high sulfide concentrations (Zheng et al., 2000; Helz et al., 2011).

In this paper we examine the distribution of minor (Mn, Ni, Cr, V, Co, Cu, Zn) and trace (Mo, Re, Cd, U, Ag) metals in piston core JT96-02 collected from a water depth of 1340 m off the west coast of Vancouver Island, Canada (Fig. 1). The lower portion of this core (90 to 211 cm) is composed of a gray clay interbedded with ~19 thin (1 to 2 cm thick) greenish-gray clay layers that occur every 5 to 10 cm (Fig. 2). These greenish layers contained abundant black material that faded within hours of opening the core indicating that the black phase was an iron monosulfide, possibly mackinawite (Holmes, 1999), which rapidly oxidizes and changes color when exposed to air. This sulfide typically

occurred as very thin laminae in the upper portion of each layer and as patches below (Fig. 2), possibly reflecting the influence of bioturbation (or lack thereof) on the distribution of organic matter, which is the locus of sulfide precipitation.

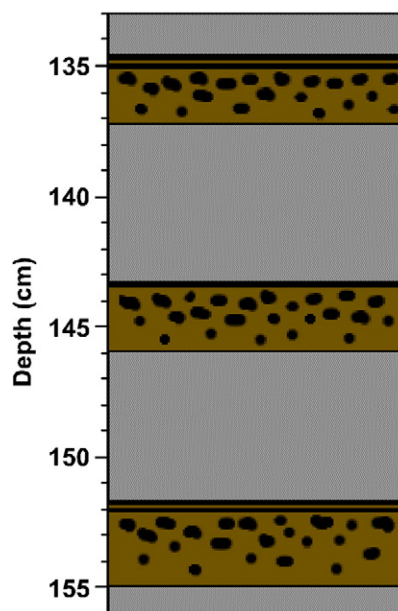


Fig. 2. Illustration of a 23 cm section of piston core JT96-02 showing three sulfide-layers (brown) and intervening gray clay layers. Near the top of each sulfide layer the sulfides (shown in black) occur as thin laminae and below this as discrete patches. No visible sulfides are observed in the gray clay layers.

Download English Version:

<https://daneshyari.com/en/article/6436550>

Download Persian Version:

<https://daneshyari.com/article/6436550>

[Daneshyari.com](https://daneshyari.com)