



Effect of thermal maturity on remobilization of molybdenum in black shales



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ABSTRACT

Molybdenum (Mo) concentrations in sedimentary records have been widely used as a method to assess paleo-redox conditions prevailing in the ancient oceans. However, the potential effects of post-depositional processes, such as thermal maturity and burial diagenesis, on Mo concentrations in organic-rich shales have not been addressed, compromising its use as a redox proxy. This study investigates the distribution and speciation of Mo at various thermal maturities in the Upper Ordovician Utica Shale from southern Quebec, Canada. Samples display maturities ranging from the peak oil window (VRo ~ 1%) to the dry gas zone (VRo ~ 2%). While our data show a significant correlation between total organic carbon (TOC) and Mo ($R^2 = 0.40$, $n = 28$, $P < 0.0003$) at lower thermal maturity, this correlation gradually deteriorates with increasing thermal maturity. Intervals within the thermally overmature section of the Utica Shale that contain elevated Mo levels (20–81 ppm) show petrographic and sulfur isotopic evidence of thermochemical sulfate reduction (TSR) along with formation of recrystallized pyrite. X-ray Absorption Fine Structure spectroscopy (XAFS) was used to determine Mo speciation in samples from intervals with elevated Mo contents (>30 ppm). Our results show the presence of two Mo species: molybdenite Mo(IV)S₂ (39 ± 5%) and Mo(VI)-Organic Matter (61 ± 5%). This new evidence suggests that at higher thermal maturities, TSR causes sulfate reduction coupled with oxidation of organic matter (OM). This process is associated with H₂S generation and pyrite formation and recrystallization. This in turn leads to the remobilization of Mo and co-precipitation of molybdenite with TSR-derived carbonates in the porous intervals. This could lead to alteration of the initial sedimentary signature of Mo in the affected intervals, hence challenging its use as a paleo-redox proxy in overmature black shales.

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1. Introduction

High enrichments of redox-sensitive trace elements (RSTEs) in sedimentary records, such as in black shales, have been used for identifying periods of anoxic conditions that were prevailing at the time of deposition in ancient oceans. Among these RSTEs, molybdenum (Mo) has become a recognized paleo-redox proxy to reconstruct the early Earth's oxygenation (Anbar et al., 2007; Scott et al., 2008; Lyons et al., 2014). In oxygenated seawater, Mo is a conservative element thought to be present as the molybdate

ion MoO₄²⁻ at concentrations of ~105 nM (Morford and Emerson, 1999). It is the most abundant transition element in the modern oxic ocean with a long residence time (~440–800 kyr; Miller et al., 2011). The average Mo concentration in the continental crust is 1–2 ppm (McLennan, 2001), however, it can be highly enriched in sedimentary records buried under permanently euxinic conditions (Scott and Lyons, 2012). When sulfide is present under anoxic conditions in sediments or the water column, sulfur substitutes progressively for oxygen in MoO₄²⁻, leading to the thiomolybdate species (MoO_xS_{4-x}²⁻) (Helz et al., 1996; Erickson and Helz, 2000; Vorlíček et al., 2015). The subsequent steps resulting in the formation of MoO_xS_{4-x}²⁻, which leads to Mo burial in marine sediments, remain unclear (Chappaz et al., 2014). Among the potential hosts for Mo, two appear to be important: (i) organic matter (OM) may play an important role as suggested by the strong empirical relationship between Mo and total organic carbon (TOC), found in both modern and ancient sediments deposited within euxinic waters (Algeo and Lyons, 2006; Lyons et al., 2009), (ii) pyrite was

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thought to be the main host for Mo sequestration in euxinic settings, but results from a recent study show that less than 20% of total Mo in recent euxinic sediments and black shales is sequestered in pyrite (Chappaz et al., 2014).

Molybdenum distribution in sedimentary records can only be used to reconstruct paleo-redox conditions if its concentration remains unaltered over time. Post-depositional processes, such as burial diagenesis and thermal maturation, can potentially alter primary Mo sedimentary records. It has been speculated that diagenesis in black shales may partly remobilize some RSTEs (Lev et al., 2000; Algeo and Maynard, 2004) and rare earth elements (REEs) (Abanda and Hannigan, 2006) and thus alter their original sedimentary signature.

Thermal maturity variations can modify the chemical composition of the originally deposited OM through loss of functional groups, generation of hydrocarbons, and subsequent restructuring of the molecular composition (Raiswell and Berner, 1987; Seewald, 2003). In a previous study, thermal maturation was shown to barely affect the chemical composition of black shales (Mongenot et al., 1996). Yet, these changes may alter the initial geochemical signature of redox proxies buried in black shales and lead to a misinterpretation of the original redox depositional environment. Late diagenesis takes place at elevated temperatures (~ 50 – 300 °C); generally at depths greater than 1 km and can significantly alter the chemical and textural compositions of shales due to extensive fluid–rock interaction with evolved basinal fluids (Milliken, 2003; Kharaka and Hanor, 2005). Redox reactions involving sulfate (SO_4^{2-}) and OM may occur during diagenetic processes (Machel, 2001). Among these reactions, sulfate reduction can be driven by microbial activity (microbial sulfate reduction: MSR) at low temperatures during early diagenesis (i.e., $0 < T < 60$ – 80 °C), or can occur chemically (thermochemical sulfate reduction: TSR) at higher temperatures (i.e., $80 < T < 200$ °C; Orr, 1977; Machel et al., 1995; Cross et al., 2004). Dissolved sulfate (SO_4^{2-}) sources include: buried seawater (connate water), evaporative brines (Kharaka and Hanor, 2005) and/or dissolution of calcium sulfate minerals (Machel, 2001). The major by-products of both MSR and TSR include bitumen/pyrobitumen, hydrogen sulfide, base and transition metal sulfides, and carbonates (mainly calcite and dolomite) (Machel et al., 1995; Machel, 2001; King et al., 2014).

Geochemical and petrographic analyses of these by-products can help differentiate between MSR and TSR (Machel et al., 1995). MSR mainly results in the formation of framboidal pyrite, whereas TSR typically results in the formation of larger cubic or prismatic pyrites (Machel et al., 1995). TSR also leads to the recrystallization of pyrite and subsequent replacement of other diagenetic minerals. Distinct sulfur isotope fractionation factors can also be used to differentiate MSR from TSR. Experiments have identified significant kinetic isotopic fractionation during microbial sulfate reduction due to initial breaking of the S–O bond in sulfate (Harrison and Thode, 1958; Cross et al., 2004). Hence, MSR is generally associated with large sulfur isotope fractionation between sulfate and H_2S ($\Delta_{\text{MSR}} = -15$ to -65 ‰ depending on the type of bacteria; Canfield, 2001; Amrani, 2014). Compared to MSR, TSR results in a much smaller degree of sulfur isotopic fractionation between sulfate and H_2S . Δ_{TSR} is temperature dependent and ranges from -15 ‰ to -10 ‰ at 150 – 200 °C (Krouse et al., 1988; Machel et al., 1995).

The effect of diagenetic processes and thermal maturity variations and their potential influence on Mo enrichment have not been previously investigated or quantified. The objective of this study is to investigate the effect of thermal maturation on possible remobilization of Mo in black shale sedimentary records. More precisely, the effects of TSR on Mo remobilization are investigated by determining Mo speciation using X-ray Absorption Fine Structure

spectroscopy (XAFS) and sulfur isotope measurements of pyrite. The study focuses on sediment intervals displaying high Mo enrichments from black shale samples affected by different levels of thermal maturation ranging from mature (peak oil window) to over-mature (dry gas zone; Haeri-Ardakani et al., 2015). Implications for the use of Mo as a paleo-redox proxy are discussed in light of these new findings.

2. Geological setting

The St. Lawrence Platform in southern Quebec consists of a thick Cambrian-Lower Ordovician siliciclastic and carbonate platform overlain by Middle-Late Ordovician foreland carbonate-clastic deposits with varying thicknesses between 1500 and 3000 m (Globensky, 1987; Lavoie, 2008; Fig. S1A and B). Along the foreland margin, the Lower Ordovician carbonate platform succession is covered by a deepening-upward succession of limestone to argillaceous limestone to black, organic-rich shale. This succession is capped by shallowing upward flysch and post-orogenic molasse (Lavoie, 2008).

The collision of the eastern continental margin of North America with a volcanic arc situated above a SE-dipping subduction zone initiated the formation of a Taconian foreland basin which consequently caused the initial collapse, subsidence, and transgression of the Middle Ordovician carbonate platform throughout the length of the Appalachian Orogen (Lavoie, 2008). Deposition of the deep open-ocean Utica Shale source rock was coincident with the final collapse of the carbonate shelf in the early Late Ordovician, in a poorly oxygenated setting that was followed by Taconian flysch (Lorraine Group) and molasse (Lavoie, 2008). The deeper water sediments of the Utica Shale were deposited during periods of rapid subsidence of the foreland basin (Globensky, 1987). The Utica Shale is progressively thicker and deeper from NW to SE and is also remobilized and imbricated in thrust stacks beneath the St. Lawrence Platform (Fig. S1C). Increase in the thickness of Utica Shale towards the east in southern Quebec as well as New York is suggested to be controlled by syndimentary faults which control the thickness and TOC richness of the unit (Smith, 2011). The Utica Shale is characteristic of early flysch-phase fill along the distal flank of the Middle to Late Ordovician Taconian foreland basin (Lavoie, 2008); it is a black, limy shale unit with thin beds of lime mudstone and siliciclastic siltstone (Globensky, 1987). The calcareous shales of the Utica Shale began to accumulate during a rapid increase in relative sea level. As a result, the carbonate-producing zone was partially shut down leaving siliciclastic muds with subordinate carbonate mud to accumulate. The source of carbonate mud in the Utica Shale has been interpreted to be related to fifth-order transgressive–regressive cycles with highstand shedding of mud from the carbonate platform which was backstepping on the Precambrian craton at that time (Lavoie, 2008; Lavoie et al., 2009). Alternation of distinct layers containing variable concentrations of benthic organisms (Lavoie et al., 2014) with thin, bioturbated, low-organic carbon shale layers suggests variation in oxygen concentration through short periods of time. Several complex tectonic wedges (e.g., Taconian, Acadian and Alleghenian) were involved in the Utica Shale burial (Lavoie, 2008). The available data indicate that the Utica Shale entered the oil window during the Late Ordovician with a southwesterly maturation increase (Lavoie, 2008; Lavoie et al., 2009).

3. Methodology

3.1. Total organic carbon and thermal maturity

A total of 279 samples were collected from cores obtained from three wells in the St. Lawrence Platform in southern Quebec at

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