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# Does pyrite act as an important host for molybdenum in modern and ancient euxinic sediments?

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## Abstract

Molybdenum (Mo) is a popular paleoproxy for tracking the spatiotemporal pattern of euxinic (anoxic and sulfidic) conditions in the ancient ocean, yet surprisingly little is known about the processes leading to its fixation under sulfidic conditions. Pyrite has been proposed to be the main host phase for Mo sequestration. To clarify the role played by pyrite, and thus to refine the utility of this paleoproxy, modern and ancient samples from six different study sites were analyzed, all representing euxinic conditions, using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS). Although pyrite often shows substantial enrichments relative to average crust and even matrix samples of similar size, our results show that most of the Mo in euxinic muds and shales is found in the non-pyrite matrix (80–100%) and not in the pyrite grains (0–20%)—simply because the volume of matrix dominates the bulk sediments/rocks. A relationship between the percent of Mo hosted by pyrite and the sulfur isotope composition of that pyrite is observed and can be linked to post-depositional alteration. Specifically, the oldest, typically most altered samples, show the highest $\delta^{34}S$ values because of limited sulfate availability at the time of their formation in the early ocean. In these old samples, the relatively small amount of Mo sequestered initially within pyrite is more likely to have been released to the matrix during the strong recrystallization overprints that these rocks have disproportionately suffered. Despite the universal importance of appreciable $H_2S$ availability during Mo uptake, we conclude that pyrite should be viewed as a nontrivial sink for Mo but clearly not the primary host in most euxinic shales and rather suggest that other burial pathways should be emphasized in future studies of the mechanisms of Mo sequestration in such settings.

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## 1. INTRODUCTION

Elucidating when and how oxygen concentrations rose in Earth's early atmosphere is crucial to understanding the parallel evolution of life. To explore these questions, researchers have used diverse geochemical proxies first developed in modern settings such as the Black Sea. One of the most promising indicators of past redox states is molybdenum (Mo). Generally, sedimentary Mo concentrations are much higher in anoxic/sulfidic environments compared to average crustal rocks (e.g., Crusius et al., 1996; Lyons et al., 2003; Tribovillard et al., 2004; Scott and Lyons, 2012). Recently, this property has led to important discoveries that have improved our knowledge of oxygen distributions on the early Earth (e.g., Anbar et al., 2007; Scott et al., 2008, 2011; Kendall et al., 2010; Li et al.,

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2010; Gill et al., 2011). Over the last decade, Mo isotope systematics have also emerged as a promising tool for assessing how redox conditions have evolved in both modern and ancient settings (e.g., Arnold et al., 2004; Neubert et al., 2008).

Molybdenum speciation in modern oxic seawater is dominated by the unreactive molybdate anion, $Mo^{VI}O_4{}^{2-}$, with a modern seawater concentration of about 100 nM (Collier, 1985; Emerson and Huested, 1991; Morford and Emerson, 1999). As such, it is a conservative trace element and the most abundant transition metal in the modern ocean, with a residence time of ~440,000 years (Miller et al., 2011). Molybdenum geochemistry has been studied extensively over the last three decades (e.g., Bertine and Turekian, 1973; Brumsack and Gieskes, 1983; Helz et al., 1996, 2011; Chappaz et al., 2008, 2012), and the mechanistic processes involved in its incorporation into oxic sediments are relatively well understood, but those occurring under anoxic and/or sulfidic conditions remain less clear.

Enrichments at the oxic sediment–water interface are usually attributed to Mo adsorption onto manganese and iron oxyhydroxides (e.g., Crusius et al., 1996; Zheng et al., 2000; Barling and Anbar, 2004; Chappaz et al., 2008; Goldberg et al., 2009). However, when free sulfide is present, sulfur atoms substitute progressively for the oxygen in $Mo^{VI}O_4{}^{2-}$ to form highly reactive tetrathiomolybdate, $Mo^{VI}S_4{}^{2-}$, through a series of intermediates ($Mo^{VI}O_xS_{4-x}{}^{2-}$; Helz et al., 1996; Erickson and Helz, 2000). The removal processes and ultimate fate of $Mo^{VI}S_4{}^{2-}$ under these conditions remain topics of discussion. Some argue that a reduction step from $Mo^{VI}$ to $Mo^{IV}$ is necessary for Mo fixation into sediments (François, 1988; Emerson and Huested, 1991; Calvert and Pedersen, 1993; Vorlicek et al., 2004). Other works suggest that Mo is scavenged by pyrite and/or organic matter (Huerta-Diaz and Morse, 1992; Helz et al., 1996; Bostick et al., 2003; Vorlicek et al., 2004; Tribovillard et al., 2004). A new model describing Mo removal occurring in euxinic water has been proposed and argues for a Mo–Fe–S mineral phase whose precipitation is controlled by a combination of sulfide concentration, pH, and availability of reactive iron (Helz et al., 2011). Recently, XAFS evidence has shown that Mo is present as a reduced $Mo^{IV}$–S compound in sediments from a sulfidic lake (Dahl et al., 2013).

The main goal of our study was specific—that is, to assess the relative role of a classically favored host for Mo—pyrite—through detailed microanalysis of modern and ancient fine-grained siliciclastic sediments that accumulated under euxinic conditions. Specifically, nine sediment and black shale samples (modern and ancient) from six different locations were analyzed using laser ablation-inductively coupled-plasma mass spectrometry (LA-ICP-MS). Results show that pyrite from these diverse locations is not the dominant host for Mo in euxinic sediments and shales. To our knowledge, few, if any, previous studies have pursued the same essential goal. It is our assertion that a full mechanistic understanding of trace metal burial, and thus the true strength of related paleoproxies, requires a tighter grasp on metal-host relationships in modern and ancient sediments. This study represents an important step in that direction.

## 2. METHODS

Table 1 provides information on the euxinic sediments and black shales we investigated. These samples were collected and characterized as part of other complementary studies focused on broad-scale paleoenvironmental interpretations. The key references are given in Table 1.

### 2.1. Sample preparation

Unconsolidated modern muds and lithified ancient sediments ranging in age from 180 to 2650 million years before present (Ma) were analyzed. The unconsolidated modern sediments were first freeze-dried. The dried samples were disaggregated by rubbing lightly with a gloved finger in a 50 mL Pyrex beaker. The resulting powders were poured into 2.5 cm diameter cylindrical molds. The molds were filled with approximately 5 ml of Struers Epofix epoxy. Lithified sediment samples were cut perpendicular to bedding and placed within 2.5 cm diameter molds, which were filled with approximately 5 ml of Struers Epofix epoxy. Both sample types were then prepared using a series of polishing compounds from coarse to fine and culminating with 1 μm diamond paste. Using a Nikon Labophot2-Pol microscope, the distributions of pyrite versus matrix were first identified for further analysis by laser ablation. Particular attention was given to select matrix zones virtually free of pyrite grains visible with the microscope and as informed by our SEM analyses (below) to enable comparison between pyrite spots and matrix. Sizes for pyrite grains ranged between 8 and 75 μm for most of the samples, and in some samples these grains formed aggregates that were further consolidated into nodules up to 5 mm in diameter or in bands up to 3 mm thick. As such, it was relatively straightforward to focus on the end-member constituents during laser ablation. Images of the samples presented in Fig. 1 were taken with a scanning electron microscope using backscattered electrons detection (SEM–BSE) at the University of Tasmania.

### 2.2. Analytical methods

The LA-ICP-MS system based at the Centre of Excellence in Ore Deposits, University of Tasmania, was used to determine trace element concentrations in the diagenetic/syngenetic pyrite and sedimentary matrix in all samples. This system employs a New Wave UP-193SS Nd:YAG Q-switched Laser Ablation System coupled to an Agilent 7500a Quadrupole ICP-MS. Samples were ablated in an ultra-high purity He atmosphere, which was mixed with Ar before flowing into the ICP-MS. The samples were analyzed in spot mode with a beam size of 10–50 μm and 10–100 μm for the pyrite and matrix, respectively. A repetition rate of 5 Hz and a laser energy of 1.8 to 2.5 J $cm^{-2}$ were used for all analyses. Data were collected over 90 s intervals, with 30 s of pre-ablation acquisition and 60 s of data acquisition with the laser on. Generally 45–50 s of data acquisition were used for the data reduction to avoid any noise associated with the first 10 s of ablation, except for pyrite grains that were small and quickly