Geochemical Perspectives Letters

Pyrite: an authigenic host phase for tungsten in sulfidic sediments

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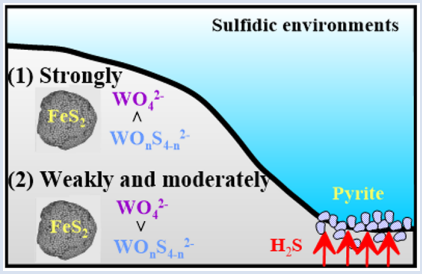
Abstract



Tungsten (W) has recently gained recognition as a potentially powerful tool for reconstructing palaeo-oceanic conditions, yet its enrichment mechanisms in sulfidic environments remain poorly constrained. Here, we investigate W cycling in sulfidic sediments from the Haima Cold Seep (South China Sea), revealing a paradoxical decoupling of low W concentrations and high enrichment factors (W_{EF}), which we attribute to pyrite-mediated W sequestration. Sulfidation promotes pyrite formation and Fe-Mn (hydrogen)oxides dissolution. Inadequate W uptake by pyrite causes low bulk W content, yet the high $(W_{py})_{EF}$ can elevate the bulk sediment W_{EF}, thereby producing the decoupling between low W content and high W_{EF} in the sediment. Furthermore, varying environmental sulfidic levels drive aqueous W speciation, affecting subsequent pyrite adsorption and leading to differences in pyrite W content and W_{EF}. This study significantly enhances our understanding of the W cycle in sulfidic marine environments.

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Introduction

Tungsten (W), a redox-sensitive transition metal, has gained prominence as a tracer for reconstructing redox evolution in marine systems (Cui *et al.*, 2021; Kurzweil *et al.*, 2021, 2022; Yang *et al.*, 2022, 2023). Under oxic conditions, dissolved tungstate (WO_4^{2-}) stabilises in seawater and becomes enriched in sediments through adsorption onto Fe-Mn (hydrogen)oxides (Kashiwabara *et al.*, 2013; Mohajerin *et al.*, 2014; Cui *et al.*, 2021). In sulfidic conditions, however, W transitions to soluble thiotungstate species ($WO_nS_{4-n}^{2-}$) (Cui *et al.*, 2021), which conventional models associate with limited authigenic enrichment due to the absence of stable mineral hosts, resulting in either detrital-dominated signals or W-depleted anomalies (Cui *et al.*, 2020, 2021; Miao *et al.*, 2024a). Leveraging this principle, previous studies compared W contents between methane-seep and non-seep sediments (Miao *et al.*, 2024a). The research revealed that methane-seep sediments exhibit lower W contents (avg. 1.5 mg/kg) than non-seep sediments (avg. 2.1 mg/kg), attributable to localised sulfidic conditions induced by sulfate-driven anaerobic oxidation of methane (SD-AOM) (Miao *et al.*, 2024a). However, these seep sediments ($1.2 < W_{EF} < 1.9$) display a higher W enrichment factor (W_{EF}) compared to non-seep sediments ($1.2 < W_{EF} < 1.5$) (Miao *et al.*, 2024a), indicating that authigenic W enrichment persists even within sulfidic settings. This finding stands in contrast to the prevailing paradigm of W depletion in sulfidic sediments. Moreover, if this holds true, the assignment of authigenic W host phases in sulfidic sediments remains an unresolved scientific enigma. Crucially, this ambiguity significantly hinders the reliable reconstruction of palaeo-marine redox conditions using W enrichment patterns.

Kurzweil *et al.* (2022) proposed that iron sulfides might be the primary host phase for authigenic W in sulfidic sediments, but this remains unverified. Methane seeps, ubiquitous along continental margins (Peckmann and Thiel, 2004; Guan *et al.*, 2013; Skarke *et al.*, 2014), create sulfidic environments through SD-AOM—a process generating hydrogen sulfide and enriching pyrite in sediments (Jørgensen *et al.*, 2004; Miao *et al.*, 2022; Chen *et al.*, 2023; Smrzka *et al.*, 2024). Therefore, sulfidic sediments within seep environments can be used to investigate the cause of the decoupling between W content and W_{EF}, and to determine whether pyrite is the primary host phase for authigenic W in these sediments. The Haima Cold Seep (South China Sea; Fig. 1b), China's largest active methane seep, features sulfide-rich seafloor deposits (Miao *et al.*, 2021, 2024b). Previous analyses of Q6 and QDN-MS6 site sediments within this system revealed sulfidation markers, including elevated pyrite content, $\delta^{34}S$ values, $(Mo/U)_{EF}$ ratios and TS/TOC ratios (Fig. 1c), confirming that methane-derived fluids drive sustained sulfidic conditions (Miao *et al.*, 2021, 2022, 2024b). Leveraging this framework, we present high-resolution W geochemical data from Haima Cold Seep sediments to address two unresolved queries: (1) the identification of authigenic W host phases under sulfidic sediments, and (2) the apparent contradiction between W enrichment patterns in sulfidic settings.

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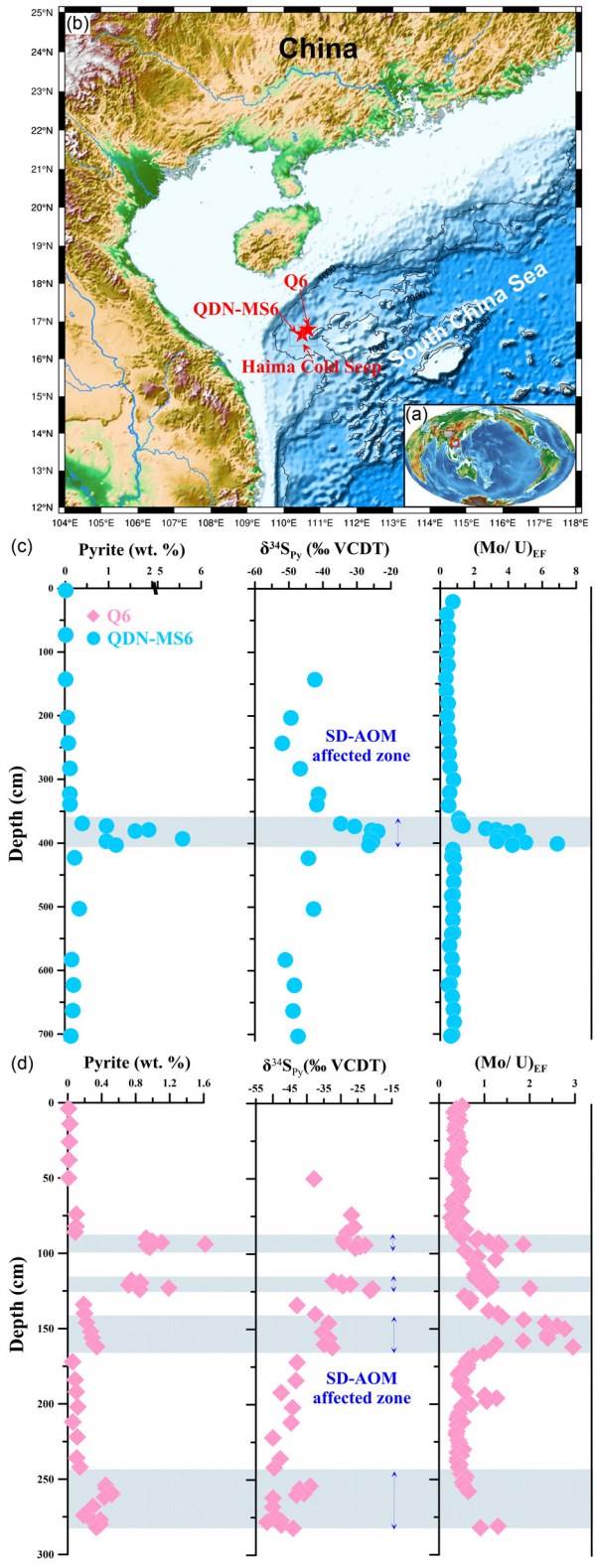

Figure 1 **(a)** Map of the World. The red rectangle represents the study area **(b)**. **(b)** The red stars represent the sampling locations. **(c, d)** Down core variations of pyrite, $\delta^{34}S_{Py}$, $(Mo/U)_{EF}$ and TS/TOC ratios in sediments of Q6 (based on Miao *et al.*, 2021, 2022) and QDN-MS6 (based on Miao *et al.*, 2024b), respectively. $\delta^{34}S_{Py}$ = sulfur isotope of pyrite; $(Mo/U)_{EF}$ = (Mo/U) enrichment factor ratios; TS/TOC = total sulfur/total organic carbon.

Samples and Methods

Sample location, analytical methods and data processing are described in the Supplementary Information.

Results and Discussion

Depletion of W content and its causes in sediments. The seep sediments (QDN-MS6: 0.9–2.5 mg/kg, avg. 1.6 mg/kg; Q6: 0.9–2.2 mg/kg, avg. 1.6 mg/kg) exhibit significantly lower W contents compared to non-seep sediments (QDN-MS6: 2.3–3.9 mg/kg, avg. 3.1 mg/kg; Q6: 1.4–2.8 mg/kg, avg. 1.9 mg/kg) (Fig. 2). This W depletion phenomenon in seep sediments is attributed to the fact that SD-AOM fundamentally alters the geochemical conditions. Under oxic environments, W accumulates through adsorption as WO_4^{2-} on Fe-Mn (hydrogen)oxides (Kashiwabara *et al.*, 2013; Dellwig *et al.*, 2019; Cui *et al.*, 2021). However, sulfidic conditions induced by methane seepage (Jørgensen *et al.*, 2004; Lin *et al.*, 2022) trigger two critical processes: (1) Inhibition of Fe-Mn (hydrogen)oxides formation and their reductive dissolution eliminates primary W adsorption sites, increasing aqueous WO_4^{2-} concentrations (Johannesson *et al.*, 2013; Mohajerin *et al.*, 2016); (2) Sulfurisation converts WO_4^{2-} to soluble $WO_nS_{4-n}^{2-}$ species, particularly complete conversion to WS_4^{2-} under strong sulfidic conditions (>1 mM H_2S) (Mohajerin *et al.*, 2014; Yang *et al.*, 2022). These metastable thiotungstates exhibit enhanced seawater solubility and reduced sedimentary retention (Mohajerin *et al.*, 2016; Dellwig *et al.*, 2019). Diagnostic geochemical signatures—elevated $(Mo\text{-}U)_{EF}$ values (Fig. 1c) and high Mo/W molar ratios (Fig. 2)—confirm persistent sulfidic conditions in the identified intervals, providing conclusive evidence for the sulfur-mediated W mobilisation mechanism in methane seep-affected sediments.

The role of pyrite in the W cycle. The W_{EF} revealed a counterintuitive pattern: instead of declining below expected thresholds, W_{EF} values in seep sediments frequently exceeded baseline levels. Notably, average W_{EF} values reached 1.3 at Q6 and 1.8 at QDN-MS6 (Fig. 3), surpassing values reported for sulfidic Black Sea sapropel (average $W_{EF} = 0.8$; Dellwig *et al.*, 2019). This apparent paradox directly challenges the established paradigm of limited authigenic W enrichment under sulfidic conditions (Dellwig *et al.*, 2019; Cui *et al.*, 2021), suggesting either unique biogeochemical processes in methane seepage environments or limitations in current geochemical proxies. Thus, our investigations will focus on uncovering the reasons behind the authigenic enrichment of W in the sulfidic environments.

Prior to related discussions, we considered whether the observed W enrichment could be attributed to the potential dilution effect by Al. To evaluate this, we calculated the W/Al ratios for each sample, as this represents a standard approach to account for potential Al dilution. The W/Al values were then compared to that of the UCC (~0.25) (Rudnick and Gao, 2014). As shown in Figure 2, the W/Al ratios in our samples are significantly higher than the UCC value. This indicates a clear relative enrichment of tungsten even after normalising to Al content, supporting the interpretation of authigenic enrichment and effectively ruling out Al dilution as a significant influencing factor.

In sediments, W is commonly associated with host phases like Fe-Mn (hydrogen)oxides, clay minerals and organic matter, leading to the expectation that sediments rich in these components would exhibit elevated W content and authigenic enrichment (Kurzweil *et al.*, 2021; Yang *et al.*, 2023, 2025). However, we

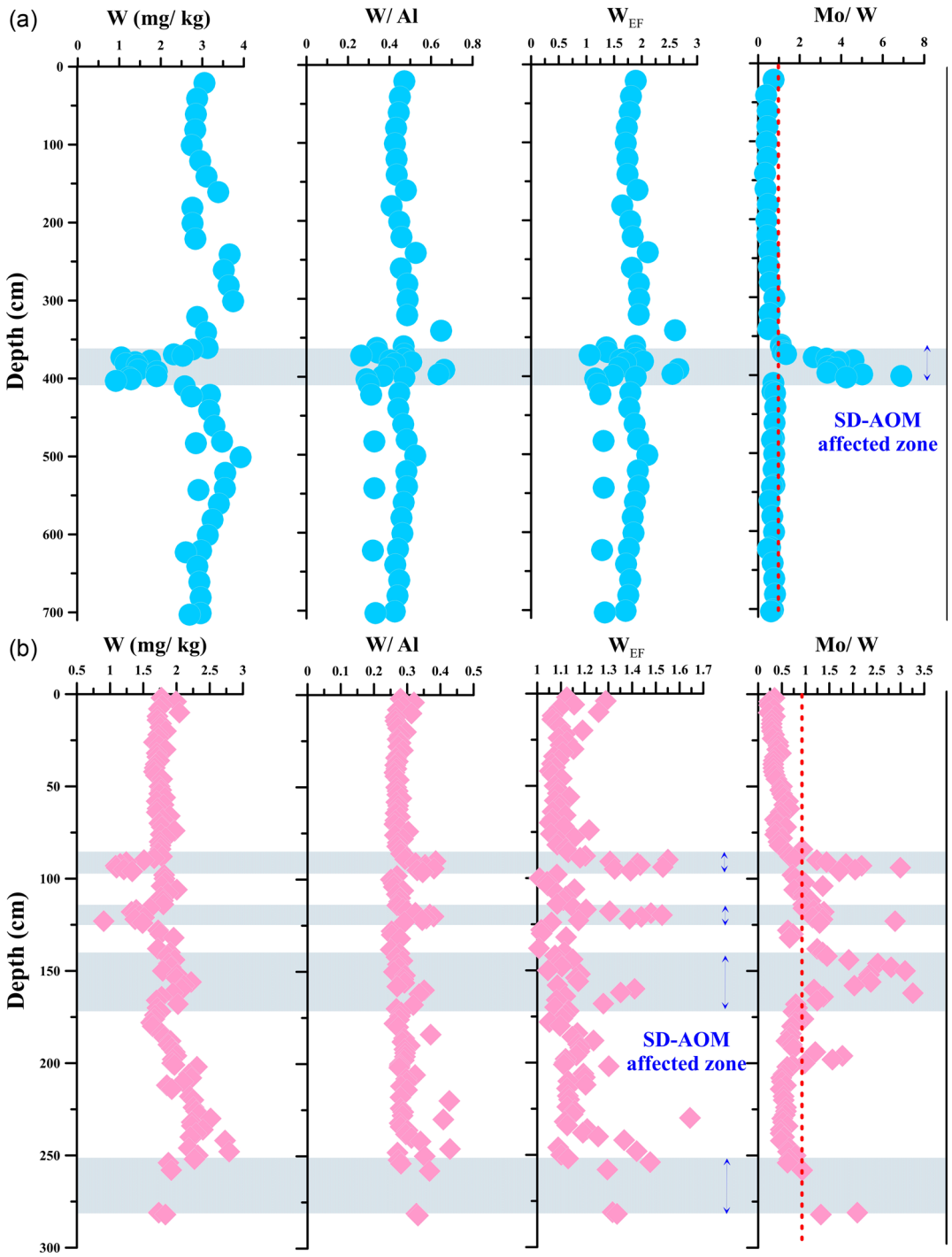

Figure 2 Geochemical characteristics of sediments in **(a)** QDN-MS6 and **(b)** Q6. The bands (blue) indicate areas affected by sulfate-driven anaerobic oxidation of methane (SD-AOM). The red dotted line represents the Mo/W molar ratio of the upper continental crust, which is 0.9 (Rudnick and Gao, 2014).

observed low W content and the absence of a correlation with these typical host phases (Fig. 4), suggesting their limited role in authigenic W enrichment in our study area. Notably, at site QDN-MS6, TOC and clay contents also decrease in the seep sediments, in addition to Mn. This suggests that TOC and clay components may also be performing a function similar to Fe-Mn (hydrogen)oxides, though perhaps not as the dominant factor. Drawing on recent findings that iron sulfide can host W in sulfidic environments (Cui and Johannesson, 2017), and considering the known importance of pyrite authigenesis in methane seepage zones, we propose that pyrite is a key host phase for W in our study area. This conclusion is supported by the substantial pyrite formation observed in methane-impacted sediments and the strong correlation between W and pyrite content ($R^2 = 0.75$ in QDN-MS6 and $R^2 = 0.58$ in Q6; Fig. 4). Therefore, these findings strongly suggest that pyrite content is a key factor for the occurrence of authigenic W in sulfidic, methane seepage sediments.

Based solely on the correlation diagram between W and pyrite content, it is difficult to unequivocally confirm the

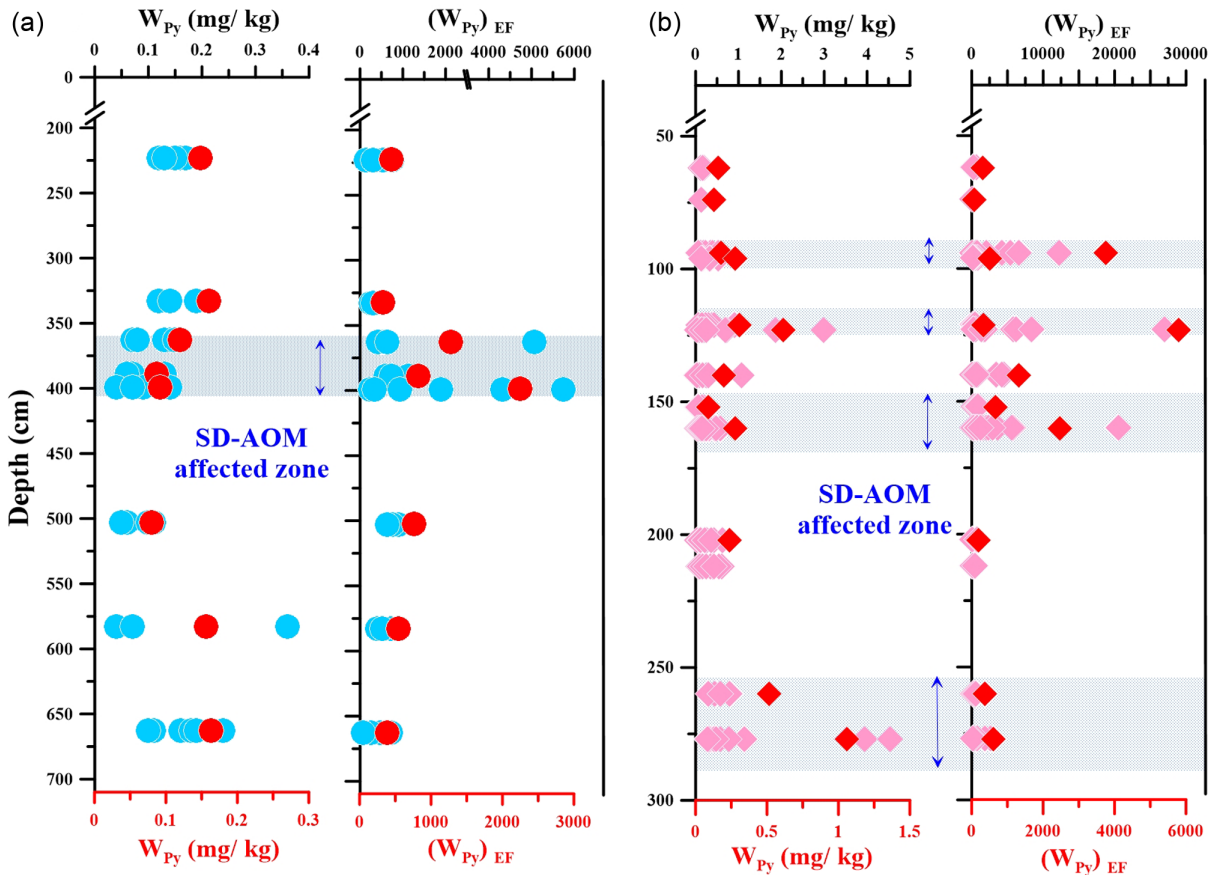

Figure 3 Down core variations of the W contents and W_{EF} in pyrite samples in cores **(a)** QDN-MS6 and **(b)** Q6. The bands (blue) indicate areas affected sulfate-driven anaerobic oxidation of methane (SD-AOM). Each blue and pink symbol corresponds to a single pyrite measurement, with red symbols showing mean values.

authigenic enrichment of W on pyrite. This is because pyrite content itself serves as an indicator of sulfidic conditions and reflects the intensity of the sulfidic environment. Therefore, further analytical work focusing on the W content within pyrite is required. As shown in Figure 3, W content within pyrite (0.01–4.53 mg/kg) is significantly lower compared to Fe-Mn crusts (42–134 mg/kg; Yang *et al.*, 2023), which exhibit 9–4466 times higher W concentrations. This disparity reflects pyrite's weaker adsorption capacity for W (Cui and Johannesson, 2017) and the enhanced solubility of $WO_nS_{4-n}^{2-}$ in sulfidic conditions (Kashiwabara *et al.*, 2013; Cui and Johannesson, 2017), meaning that pyrite formation, even in large amounts, cannot fully compensate for the W loss resulting from the reduction or absence of Fe-Mn (hydrogen)oxides. In addition, the pyrite at QDN-MS6 and Q6 sites in methane seepage environments showed significantly higher authigenic enrichment of W (Fig. 3). Its extraordinary W_{EF} (reaching several thousand to tens of thousands) can dramatically amplify the bulk sediment W_{EF} even at low pyrite abundance (Fig. 3). Therefore, the negative correlation arises because pyrite captures only low amounts of W compared to Fe-Mn (hydrogen)oxides. Meanwhile, this decoupling mechanism explains the paradoxical co-occurrence of low W content and high W_{EF} in seep sediments.

Pyrite tungsten enrichment patterns as indicators of sulfidation intensity. Varied methane seepage intensities at QDN-MS6 and Q6 result in differing sulfidic conditions and, consequently, distinct W enrichment patterns in pyrite. The seep sediments at QDN-MS6 display higher $(Mo/U)_{EF}$, pyrite content and Mo/W molar ratio than those at Q6 (Fig. 1c and Fig. 2). This suggests that the methane seepage activity at QDN-MS6 is more intense, leading to a stronger sulfidic environment. Q6 exhibits a greater $(W_{EF})_{Py}$ than QDN-MS6, potentially stemming from the contrasting W species present. Thiotungstate anions may have lower particle reactivity than thiopolybdate anions (Cui and Johannesson, 2017; Cui *et al.*, 2021). Stronger methane seepage at QDN-MS6 generates a more intensely sulfidic environment, favouring the dominance of $WO_nS_{4-n}^{2-}$, which exhibits limited pyrite adsorption. Conversely, weaker methane seepage at Q6 leads to a weakly sulfidic environment where WO_4^{2-}, with stronger pyrite affinity, predominates (Cui and Johannesson, 2017; Cui *et al.*, 2021). While this allows for higher W content and W_{EF} within individual pyrite grains at Q6, the overall lower pyrite abundance due to the less intense sulfidic conditions ultimately results in a lower bulk W_{EF} in Q6 sediments compared to the pyrite-rich, but less W-enriched, pyrite found at QDN-MS6 (Fig. 3).

While studies of authigenic W enrichment in marine sediments have advanced understanding of historical ocean oxygenation—typically through its link with Fe-Mn (hydrogen) oxides (Kurzweil *et al.*, 2022; Yang *et al.*, 2023)—our results reveal a distinct mechanism relevant to sulfidic periods. By demonstrating pyrite's significant role as an authigenic host for W in methane-seep environments, we therefore propose that pyrite can preserve signatures of W content from the sulfidic seawater. This finding provides a novel proxy for reconstructing marine palaeoenvironments during periods of widespread sulfide (Large *et al.*, 2014; Zheng *et al.*, 2023), advancing the interpretation of redox-sensitive metal records in Earth's biogeochemical history.

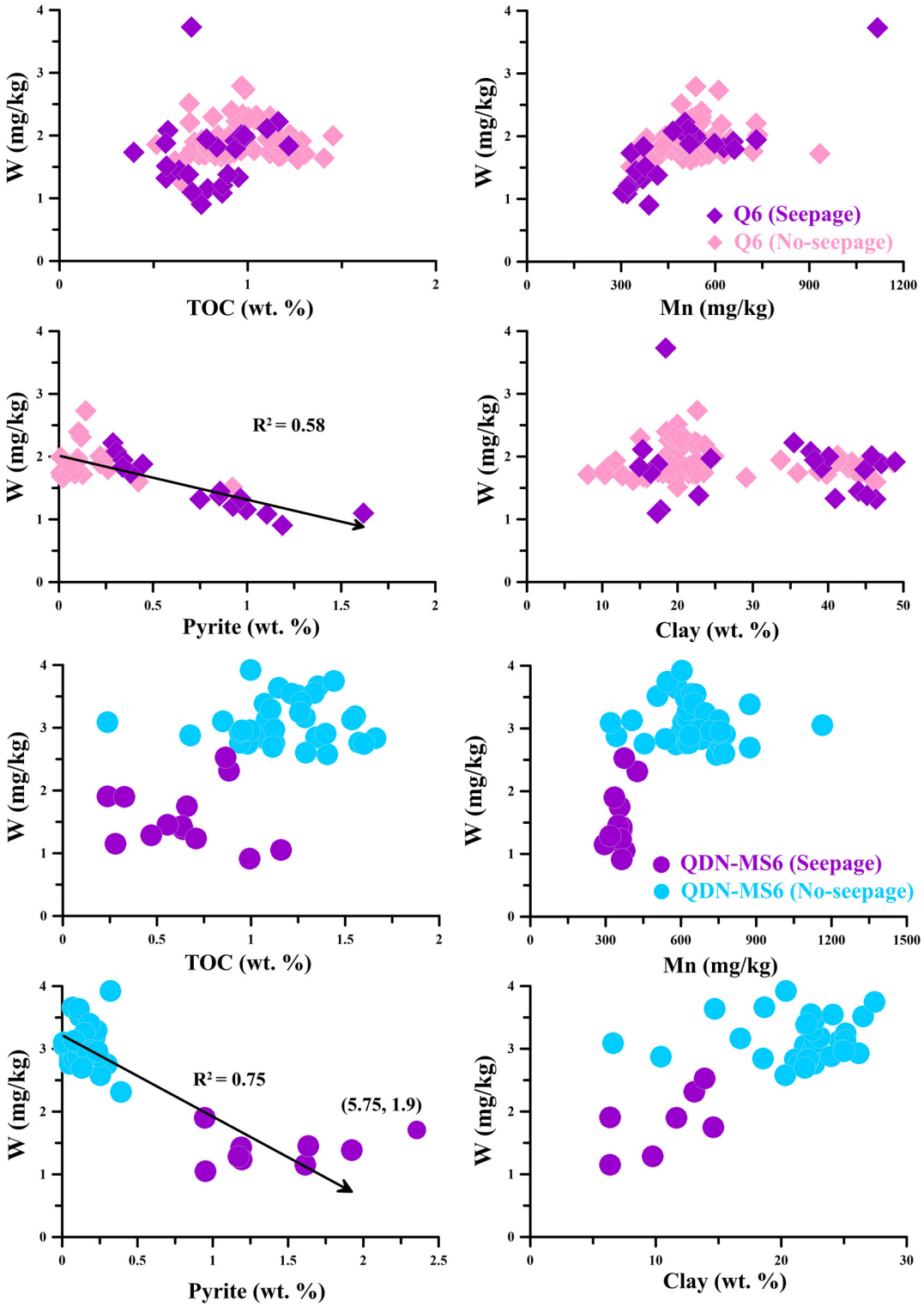

Figure 4 Relationships between W content and contents of TOC, Mn, pyrite, and clay in sediments.

Conclusions and Outlook

This study investigates the W content and enrichment characteristics in sediments and pyrite. The findings reveal that sediments experiencing methane seepage have a low W content but high W_{EF} values. Correlation analysis shows a significant correlation between sediment W content and the pyrite content. Additionally, the W_{EF} in pyrite under methane seepage is higher than in non-methane seepage environments, suggesting that pyrite plays a crucial role in the authigenic W cycle and serves as the main host phase in sulfidic environments. Moreover, the W content of pyrite varies significantly in different sulfide levels of sedimentary environments, possibly due to variations in W species. These findings position pyrite W enrichment patterns as a novel proxy for reconstructing aquatic sulfide histories, with future isotopic ($\delta^{182}W$) and microanalytical studies recommended to unravel full mechanistic details of sulfur-coupled W cycling.

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Data Availability

The data used in this study are available at PANAGEA (https://www.pangaea.de/). The data have been shared in supporting information for peer review purposes.

Additional Information

Supplementary Information accompanies this letter at https://www.geochemicalperspectivesletters.org/article2546.

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