

No effect of thermal maturity on the Mo, U, Cd, and Zn isotope compositions of Lower Jurassic organic-rich sediments

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ABSTRACT

The isotope ratios of redox-sensitive metals in organic-rich rocks are critical tools for quantifying the timing and severity of deoxygenation and nutrient cycling in Earth's past. The resilience of isotopic data to thermal alteration of the host sediments over millions of years of burial is, however, largely unknown. We present molybdenum, uranium, cadmium, and zinc stable-isotope data from two stratigraphic successions of the same Lower Jurassic Posidonienschiefer unit in the Lower Saxony Basin of northern Germany that were affected by different burial histories. We show that thermal maturity had no effect on the isotopic compositions of these elements but does appear to have increased their concentrations in the rock. The data corroborate the results of laboratory-based maturation studies and provide constraints on the Mo, U, Cd, and Zn isotopic compositions of ca. 182 Ma seawater in the Lower Saxony Basin.

INTRODUCTION

Isotopic measurements of metallic elements are widely employed as a means to elucidate the redox history of the oceans. Some elements, such as molybdenum (Mo) and uranium (U), have been used to trace the development of oxygenated conditions on Earth, and to quantify the expansion and contraction of deoxygenated zones in the oceans (Dickson, 2017; Clarkson et al., 2018). The isotopic compositions of several other metals, including zinc (Zn) and cadmium (Cd), might also record redox conditions or productivity, due to their strong affinity for burial in organic-rich sediments (Little et al., 2016; Vance et al., 2016; Isson et al., 2018; Bryan et al., 2021). However, the application of these latter two isotope systems to disentangle paleochemical changes in the oceans is still in its infancy (e.g., Georgiev et al., 2015; Sweere et al., 2020).

An important prerequisite for the robust application of any paleoenvironmental proxy is that the mineral or sedimentary archive used to

infer past chemical conditions was unaffected by diagenetic or metamorphic processes, or at least that the effect of such processes on the measured chemical composition can be quantified (Eroglu et al., 2021). Catagenesis (thermal maturation of organic matter) may have a central role to play in altering the geochemical signature of metals at high burial temperatures due to metal adsorption onto, and incorporation into, organic molecules (Lewan and Maynard, 1982; Chappaz et al., 2014; Dahl et al., 2017). However, the effect of catagenesis on metal isotopes in a widely employed paleochemical archive, namely, organic-rich shales, is not well understood.

GEOLOGIC SETTING

The Lower Saxony Basin (LSB) in northern Germany (Fig. 1) preserves a ca. 182 Ma organic-rich unit called the Posidonienschiefer unit. Since its formation in the Early Jurassic, this unit has been buried to a variety of depths within the LSB due to locally variable basin subsidence, followed by inversion during the Paleogene (Betz et al., 1987; Bruns et al., 2013). The

organic matter contained within the Posidonienschiefer unit has therefore been exposed to vastly different degrees of heating over horizontal distances of tens of kilometers. These characteristics of the Posidonienschiefer deposits in the LSB offer the ideal opportunity to test whether thermal maturation can alter the isotopic composition and concentration of metals contained within organic-rich sedimentary rocks.

Two drilled exploration cores recovered from different parts of the LSB contain ~30-m-thick, stratigraphically equivalent sections of the Posidonienschiefer unit. These units can be readily correlated to each other via their distinctive enrichments in total organic carbon (TOC), which stand in contrast to the underlying and overlying organic-poor mudrocks of Pliensbachian–early Toarcian and late Toarcian age, respectively (Fig. 2). The units postdate the early Toarcian oceanic anoxic event in the LSB. One of the Posidonienschiefer successions, in core A, contains labile organic matter with hydrogen indices >700 mg hydrocarbon (HC)/g TOC. By contrast, the organic matter in core B has hydrogen indices of ~0 mg HC/g TOC, demonstrating a substantially greater maximum burial depth, with consequent thermal alteration of organic matter and loss of hydrogen-rich moieties through expulsion of petroleum fluids. The different burial histories of each core are confirmed by reflectance measurements of terrestrial organic macerals (vitrinite, %R_o) of ~0.5 for core A (immature) and ~3.5 for core B (overmature).

METHODS

Element concentrations of samples from cores A and B were measured by first dissolving

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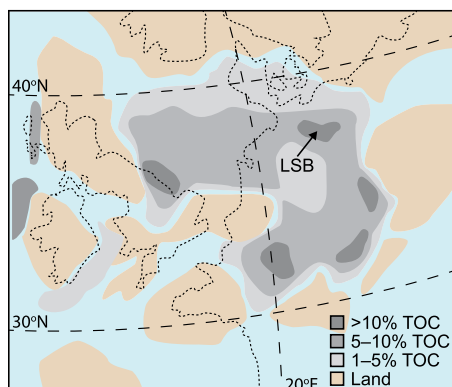


Figure 1. Location of the Lower Saxony Basin (LSB) in the Early Jurassic (ca. 182 Ma). Modern shorelines are shown as dashed lines. TOC—total organic carbon.

sample aliquots in a 3:1 mixture of concentrated HNO_3 and HCl at 150–180 °C to oxidize organic matter, followed by a 2:1 mixture of HNO_3 and HF at 120 °C to dissolve silicates. Measurements were made on sample aliquots diluted in 3% HNO_3 by inductively coupled plasma–mass spectrometry (ICP-MS). Reported concentrations have uncertainties of $\pm 10\%$, based on replicates of samples and certified reference solutions and materials (U.S. Geological Survey [USGS] SDO-1 shale).

For stable Mo, Zn, Cd, and U isotopes, sample powders were similarly digested

completely, after the addition of double-spike solutions (^{100}Mo – ^{97}Mo , ^{67}Zn – ^{64}Zn , ^{113}Cd – ^{111}Cd , ^{236}U – ^{235}U). Each element was purified using established anion-exchange methods (Weyer et al., 2008; Dickson et al., 2020; Sweere et al., 2020). Mo, Zn, Cd, and U isotope ratios were measured on a Nu Plasma multicollector ICP-MS at the University of Oxford (UK). Isotope ratios are expressed according to the following equation:

$$\left(\left[\frac{(R_{\text{sample}} - R_x)}{R_x} \right] \right) \times 1000, \quad (1)$$

where R_{sample} is $^{98}\text{Mo}/^{95}\text{Mo}$, $^{66}\text{Zn}/^{64}\text{Zn}$, $^{114}\text{Cd}/^{110}\text{Cd}$, or $^{238}\text{U}/^{235}\text{U}$, and R_x is the U.S. National Institute for Standards and Technology (NIST) standard 3134 for Mo, Institute for Reference Materials and Measurements (IRMM) standard 3702 for Zn, NIST standard 3108 for Cd, and certified reference material CRM145 standard for U. Delta values for Mo and Zn were corrected by 0.25‰ and 0.28‰, respectively, to place them on their zero-delta scales (Näglér et al., 2014; Archer et al., 2017). External reproducibilities of $\pm 0.08\%$, $\pm 0.07\%$, and $\pm 0.06\%$ (all 2 standard deviations [SD]) were determined for Mo, Zn, and Cd by processing multiple aliquots of USGS SDO-1 through the full analytical procedure. For U, reproducibility was determined from sample replicates and repeated analyses of standard reference material SRM 950a, giving a

value of $\pm 0.1\%$. Procedural blanks were ~ 2 ng for Mo, 3 ng for Zn, and < 1 ng for Cd and U.

Hydrogen index (HI) values were measured using Rock-Eval 6 (Behar et al., 2001). The TOC data were previously reported by Hooker et al. (2020). Accuracy and precision of the measurements were quantified with an internal shale standard (St. Audries Bay Shale) as $\pm 0.2\%$ for %TOC and ± 15 mg HC/g TOC for HI. Highly reactive Fe species (Fe_{HR}) were determined with established techniques (Poulton and Canfield, 2005). Replicate atomic absorption spectrometry (AAS) analyses gave a relative standard deviation of $< 5\%$ for all extraction steps. Total Fe concentrations (Fe_{T}) used to calculate $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$ ratios were determined by X-ray fluorescence, with uncertainties of $< 1\%$ determined from replicate standards.

RESULTS AND DISCUSSION

Metal Geochemistry of Immature and Overmature Deposits

The mean isotopic compositions of Mo, U, Zn, and Cd in bulk-rock analyses of the Posidonienschiefer unit in cores A and B were the same within the associated uncertainties of the methods (Fig. 3). Despite the fact that the two sedimentary successions are conservatively correlated together (Fig. 2), stratigraphic profiles of the Mo, U, Zn, and Cd isotope data sets are also similar. The Student t tests of all four populations of isotope data from within the Posidonienschiefer interval do not allow the null hypothesis (namely, that the data are identical) to be rejected at $> 95\%$ significance (Table 1). Slight differences in isotopic compositions stratigraphically above and below the Posidonienschiefer unit are probably related to the lower nondetrital concentrations of the elements in these deposits.

The similarity of the isotopic compositions of Mo, U, Zn, and Cd in the immature and overmature successions of cores A and B suggests that either (1) these metals can be released during thermally induced bond reorganization and subsequently become refixed with residual kerogen/pyrobitumen, or (2) they can be incorporated into inorganic minerals (e.g., pyrite). Alternatively, they may be mostly inorganically bound within the mudrock matrix. Laboratory experiments are consistent with these mechanisms, showing that a high fraction of the metal inventory of pyrolyzed Posidonienschiefer rocks resides within a nonextractable phase (Dickson et al., 2020). The mobilization of a significant fraction of metals to organic fluids during secondary migration is not supported by either the high concentrations of Mo, U, Zn, and Cd in the overmature deposits of core B (Fig. 3) or the low abundances of these metals that have been measured in organic fluids produced during pyrolysis-induced thermal cracking and in natural oils (Odermatt and

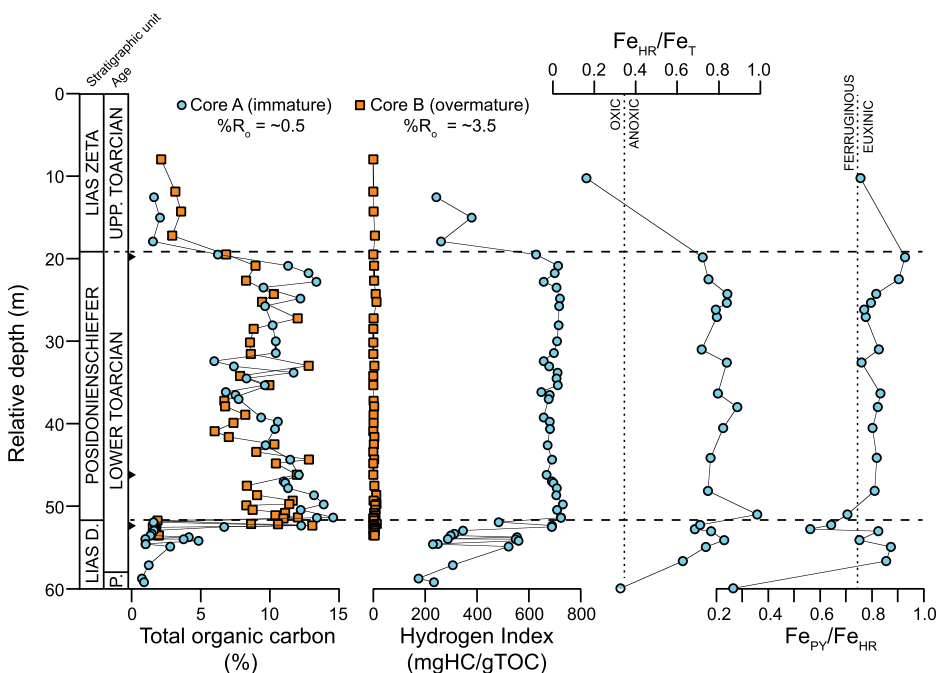


Figure 2. Stratigraphy of core A (circles) and core B (squares). Core B has been placed on the depth scale of core A by identifying tie points (arrows) at the top and bottom of the organic-rich interval and at the peak in Mo concentrations in the lower part of the unit (shown in Figure 3), and linearly interpolating depths between these tie points. Horizontal dashed lines indicate the stratigraphic position of the Posidonienschiefer unit. LIAS D.—Lias Delta; UPP.—Upper; HC—hydrocarbon; TOC—total organic carbon; P—Pliensbachian; HR—highly reactive; T—total; PY—pyrite.

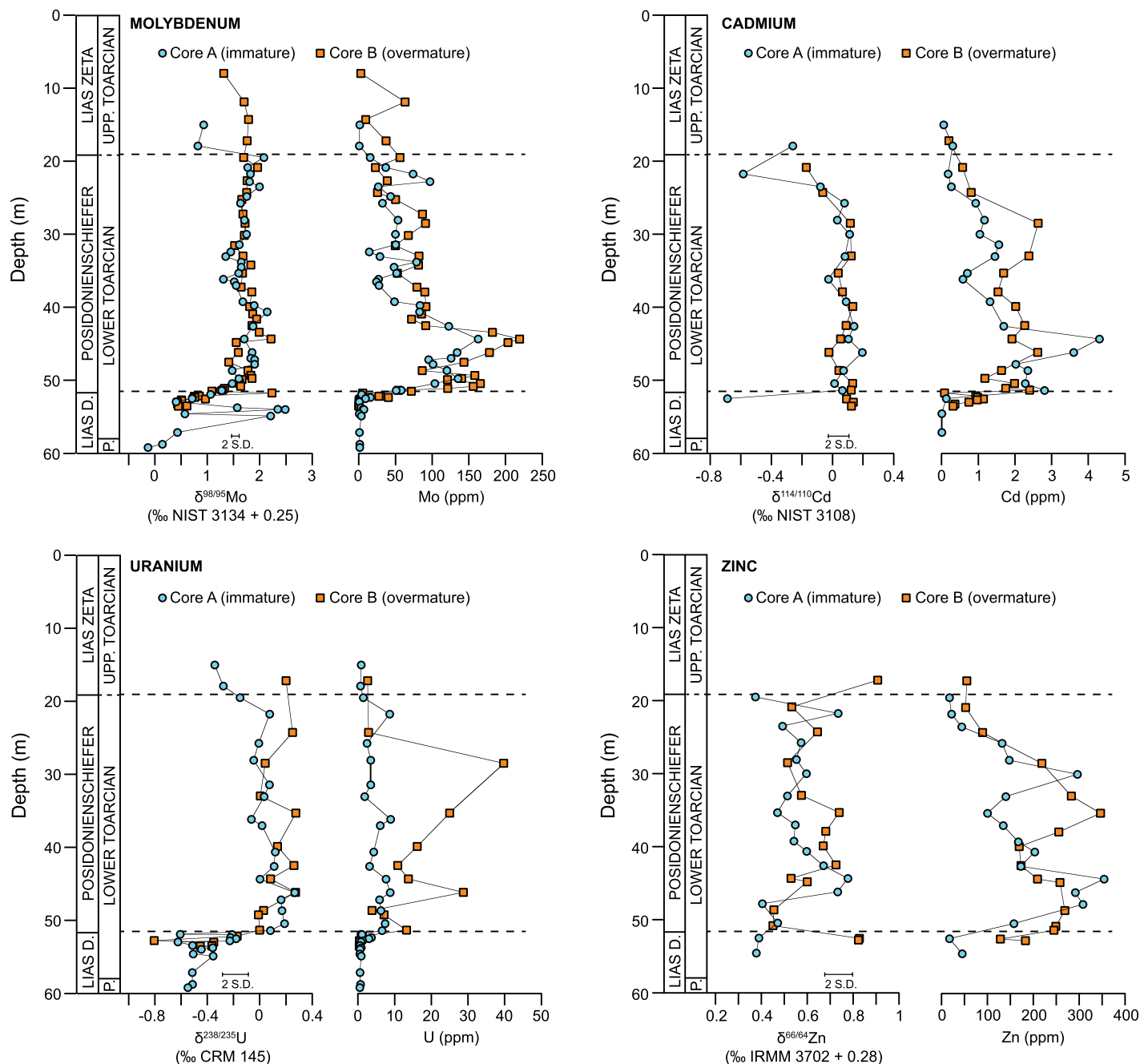


Figure 3. Metal geochemical profiles for core A (circles) and core B (squares). Core B is plotted on the core A depth scale, as defined in Figure 1, and 2 standard deviation (S.D.) external reproducibilities for each isotope system are shown by horizontal bars. LIAS D.—Lias Delta; UPP.—Upper; P—Pliensbachian.

TABLE 1. STUDENT T TEST RESULTS

Variable	Core A			Core B			t value	p value
	Mean	Standard deviation	Number of observations	Mean	Standard deviation	Number of observations		
TOC (%)	10.6	2.2	31	9.5	1.9	32	2.177	0.033
HI	694	22	31	3	4	32	168.26	<0.0001
[Mo] (ppm)	70.5	39.9	31	101.9	52.3	31	-2.66	0.010
$\delta^{98/95}\text{Mo}$ (‰)	1.67	0.22	31	1.70	0.22	31	-0.608	0.545
[Zn] (ppm)	178	97	15	217	80	13	-1.165	0.255
$\delta^{66/64}\text{Zn}$ (‰)	0.58	0.11	15	0.59	0.10	12	-0.372	0.713
[Cd] (ppm)	1.7	1.1	17	1.8	0.6	15	-0.524	0.605
$\delta^{114/110}\text{Cd}$ (‰)	0.02	0.17	14	0.05	0.09	13	-0.558	0.583
[U] (ppm)	5.7	2.4	15	16.1	11.8	10	-2.777	0.021
$\delta^{238/235}\text{U}$ (‰)	0.08	0.09	15	0.12	0.12	11	-1.016	0.323

Note: Variables for which the null hypothesis (no difference between cores A and B) can be rejected at >95% significance are italicized. TOC—total organic carbon; HI—hydrogen index (mg hydrocarbon/g TOC).

Curiale, 1991; Ventura et al., 2015; Dickson et al., 2020).

The mean concentrations of Mo, U, Zn, and Cd were consistently higher in core B than in core A (Fig. 3). The magnitudes of these differences were 45% for Mo, 185% for U, 22% for Zn, and 10% for Cd, which are similar to increases in metal concentrations observed in the residues of artificially pyrolyzed rock samples (6%–57% for Mo, 21%–52% for Zn, and 15%–19% for Cd; Dickson et al., 2020). Stratigraphic variability in the down-core profiles of the metals, however, means that the populations of concentration data are only significantly different (>95%) for Mo and U (Table 1).

The LSB contains active petroleum systems, for which the Posidonienschiefer unit is a major source rock (Kockel et al., 1994). During catagenesis, source rocks with type II kerogen can lose >30%–40% of their original organic matter due to cracking and secondary migration (Raiswell and Berner, 1987), which is similar to previous estimates of organic-carbon loss from mature Posidonienschiefer successions in northern Germany (Littke et al., 1991). The differences in metal concentrations between core A and core B can be linked to the loss of substrate mass caused by the secondary migration of organic fluids, but with a smaller loss of metals. This interpretation is consistent with the limited isotopic differences between the two cores, which point to the retention of metals within the thermally altered rocks in core B.

The attribution of geochemical differences (or lack thereof) between cores A and B to contrasting thermal histories requires that the original depositional conditions at the two locations were the same. The long residence times of Mo, U, Zn, and Cd (10,000–500,000 yr in the modern ocean; Ku et al., 1977; Bruland, 1980; Miller et al., 2011; Little et al., 2013) imply that their isotopic compositions in seawater (deep ocean for Cd and Zn) would be near homogeneous. Even if the marginal marine basins of the Early Jurassic epicontinental European shelf sea experienced an ~10-fold decrease in trace-metal concentrations, similar in magnitude to estimates for Cretaceous oceanic anoxic event 2 (Owens et al., 2016), seawater values are still unlikely to have decreased by enough to cause isotopic heterogeneity within the LSB waters that would be resolvable between the two core locations.

Small differences in paleodepositional conditions may, however, have influenced trace-metal concentrations. Both cores contained similar thicknesses of the Posidonienschiefer (~30 m), which indicates a first-order similarity in accumulation rates. However, core A contained higher concentrations of detrital elements such as Al and Ti than core B, suggesting that it was deposited in a more proximal setting (Fig. S1 in the Supplemental Material¹).

Similarly, the concentration of organic carbon in core B was only slightly less than that in core A, despite the fact that a large amount of “original” organic matter may have been lost as migrated hydrocarbons during maturation (Raiswell and Berner, 1987). A higher original %TOC for core B than core A (i.e., >15%) would account for this observation and would support the contention that core B was located in a more distal, perhaps more subsident and deeper-water, part of the LSB, where the potential for accumulation of organic matter was greater. Slightly higher metal accumulation rates, coupled with less dilution by detrital phases in the deeper parts of the LSB, may thus have contributed to the difference in metal concentrations between the two cores. The slight differences in paleodepositional conditions are supported by basin modeling (Bruns et al., 2013) and explain why metal/TOC ratios in core B overlap with metal/TOC ratios in core A (Fig. S2). Nonetheless, higher average metal/TOC ratios in core B, particularly for Mo and U, are consistent with laboratory experiments that indicate percent level increases in metal/TOC ratios with increasing maturity. These changes probably occurred due to the loss of organic matter with a low metal content during secondary migration (Dickson et al., 2020). In thermally altered mudrocks, these ratios are therefore maximum estimates of their syndepositional values.

Isotopic Constraints on the Composition of Early Jurassic Seawater

Preservation of the isotopic composition of metals in the ca. 182 Ma Posidonienschiefer unit allows the corresponding values in seawater in the LSB to be constrained. Fe-speciation data (Fig. 2) suggest that the entire shale unit was deposited under euxinic conditions. Cross-plots of Cd/Mo versus Mn*Co (Sweere et al., 2016) support a depositional environment similar to the modern Black Sea (Fig. S3), where the isotopic compositions of Cd, Zn, and Mo are similar to the global deep ocean (Neubert et al., 2008; Vance et al., 2016; Bryan, 2018). Thus, the isotopic compositions of these elements in LSB seawater were close to $\sim 0.07\text{‰} \pm 0.13\text{‰}$, $\sim 0.58\text{‰} \pm 0.20\text{‰}$, and $\sim 1.70\text{‰} \pm 0.42\text{‰}$, respectively (average and 2 SD of cores A and B). U isotopes in shales are dominated by the burial of isotopically heavy U, U(IV), which is offset from coeval seawater by $\sim +0.6\text{‰}$ (Andersen et al., 2014); the average of the Posidonienschiefer samples ($0.09\text{‰} \pm 0.23\text{‰}$)

therefore equates to an LSB seawater estimate of $\sim -0.5\text{‰}$. The reconstructed Zn isotope composition of LSB seawater overlaps with that of the modern deep ocean, unlike the Cd, Mo, and U isotope values, which are all lower.

The very low Cd isotope value is close to that of bulk silicate earth ($\sim 0\text{‰}$; Schmitt et al., 2009). Biological fractionation in the upper ocean would have increased the Cd isotope composition of water entering the LSB across a shallow sill, so such a mechanism cannot explain these low values. Likewise, there is no isotopically heavy removal sink for Cd in the oceans that could produce such low values. The large-scale burial of Cd into marine sediments globally could move the oceanic composition close to that of the weathering input fluxes, but this would require a large change in global Cd cycling that cannot be resolved from the LSB data alone. The inferred LSB seawater Mo isotope composition is probably a minimum estimate, given that sediments accumulating in some euxinic basins may be offset from coeval seawater by -0.5‰ to -0.7‰ (Dickson, 2017). Nonetheless, the LSB value is consistent with data from similar-age shales in southern Germany, the Netherlands, and Yorkshire, UK (Dickson et al., 2017). The U isotope composition of LSB seawater probably reflects a slightly greater burial flux of U into low-oxygen marine sediments in the Early Jurassic compared to the modern situation.

CONCLUSIONS

A recent study found limited isotopic variation in Mo, Zn, and Cd during laboratory pyrolysis of organic-rich rocks while finding percent-level increases in metal concentrations with maturation (Dickson et al., 2020). However, the rapid laboratory heating rates, compared to geologic conditions, make their application to natural systems uncertain. The new data from the Lower Saxony Basin confirm the relevance of these findings to natural systems, despite the significantly different time scales (millions of years versus weeks) and magnitudes (tens of degrees Celsius versus hundreds of degrees Celsius) of heating in each situation. Importantly, the new data demonstrate that metal-isotope compositions in organic-rich rocks are not significantly affected by thermal alteration of organic matter in the host substrate and thus retain primary paleochemical information. By contrast, metal concentrations may be elevated above their syndepositional values in highly mature rocks, thus giving maximum constraints on the concentrations of these elements in ancient sediments.

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¹Supplemental Material. Details of elemental relationships, non-detrital metal contents, and raw geochemical data. Please visit <https://doi.org/10.1130/GEOLOGY.18863762> to access the supplemental material, and contact editing@geosociety.org with any questions.

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