

Sedimentary Mo isotope record across the Holocene fresh–brackish water transition of the Black Sea

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Received 4 June 2004; received in revised form 4 February 2005; accepted 7 March 2005

Abstract

Mo isotope data on Black Sea sediments spanning the transition from Pleistocene oxic–limnic conditions to the prevailing anoxic marine conditions are presented. Samples were taken from a gravity core collected at a water depth of 396 m. Samples deposited under oxic bottom water conditions range from $\delta^{98/95}\text{Mo}_{\text{MOMO}} - 2.2\%$ to -1.95% (MOMO=Mean Ocean Molybdenum) while samples deposited under anoxic bottom water conditions range from $\delta^{98/95}\text{Mo}_{\text{MOMO}} - 1\%$ to -0.54% . The change of sedimentary environment is also recorded in the Mo contents increasing from oxic to anoxic sediments. The Mo isotopic composition and invariably low Mo content of the oxic sediments deposited under oxic bottom water conditions are compatible with a pure detrital origin of the Mo, irrespective of whether the deposits are of limnic or brackish origin. Mo content and isotopic compositions are identical above and below a sulfidisation front, which originates from the diffusion of sulfur species and in-situ microbial activity after establishment of brackish bottom water conditions. Further, no signal of the overlying sapropels is seen in the underlying sediments. Thus, transport of sulfur species has not mobilised Mo during diagenesis.

The $\delta^{98/95}\text{Mo}_{\text{MOMO}}$ values of anoxic samples indicate seawater as the dominant source of Mo. However, even the heaviest Mo value of the anoxic period recorded in this core is $\delta^{98/95}\text{Mo}_{\text{MOMO}} = -0.5\%$, with an average of -0.7% for all anoxic sediments, i.e. 0.7% lighter than seawater.

All samples can be explained qualitatively as three component mixtures of detrital, dissolved riverine and marine Mo. For the lower units a mass balance model can be successfully applied. For the youngest unit mixing models do not yield satisfactory results given present day water fluxes. It is therefore likely that additional Mo isotope fractionation effects are involved. First order modelling suggests that the lighter $\delta^{98/95}\text{Mo}_{\text{MOMO}}$ values of the most recent samples reflect the presence of some Mo remaining dissolved as MoO_4^{2-} in a larger part of water column above the core depth, thus allowing for a preservation of a net fractionation between MoO_4^{2-} and MoS_4^{2-} . This hypothesis is supported by the fact that the H_2S concentration critical for the $\text{MoO}_4^{2-} \leftrightarrow \text{MoS}_4^{2-}$ chemical switch is found at about 400 m water depth in the present Black Sea, close to the depth at the sampling site. At greater depth, increased H_2S concentrations lead to almost complete Mo removal, erasing the fractionation

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signal. Difference between Unit I samples from this study, and those from earlier publications (with samples taken at greater depth) may thus merely reflect the fraction of Mo scavenged at different depths. The degree of Mo scavenging in fossil black shales and the continental Mo contribution are both difficult to constrain. Therefore, black shales from restricted semi-enclosed basins may not document the Mo isotopic composition of coeval ocean waters. However, oceanic Mo is a dominant Mo source in these basins, and anoxic sediments give reliable minimum values for coeval ocean water Mo isotopic compositions.

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Keywords: Black sea; Mo isotopes; Black shales; Anoxic sediments; Redox proxy

1. Introduction

Molybdenum (Mo) isotope systematics are a natural choice for exploration as a biogeochemical tool, given its isotopic range (mass 92–100), the potential for redox shifts in the marine environment and its participation in biological processes. Because of its low (lithogenic) background concentration in marine sediments and its relatively high authigenic concentrations in reducing marine settings, Mo has attracted significant attention as a paleochemical tool (e.g., Bertine and Turekian, 1973; Brumsack and Gieskes, 1983; Brumsack, 1986; Emerson and Huested, 1991; Calvert and Pedersen, 1993; Colodner et al., 1995; Piper and Isaacs, 1995; Crusius et al., 1996; Dean et al., 1999; Morford and Emerson, 1999; Werne et al., 2002; Wilde et al., 2004 and others).

Mo exists in the oceans dominantly in the form of the tetrahedral molybdate ion (MoO_4^{2-}) which has a high solubility and a low chemical reactivity. Consequently, Mo is a nearly conservative trace element in the oceans with a long residence time (ca. 800 ka, Emerson and Huested, 1991; Colodner et al., 1995). Mo is removed very efficiently into reducing sediments in the presence of H_2S (e.g., Bertine, 1972; Shimmield and Price, 1986; Shaw et al., 1990; Emerson and Huested, 1991; Calvert and Pedersen, 1993 and references therein). Under this condition, Mo becomes particle reactive, with a particular affinity for transition metals and possibly organic matter (Helz et al., 1996; Vorlicek and Helz, 2002).

Owing to analytical limitations, little work has been done on Mo isotopes (e.g. Murthy, 1963; Wetherill, 1964; Giussani et al., 1995; see review in Wieser and De Laeter, 2000) until recently. New

MC-ICPMS-techniques, however, offer high analytical precision and sensitivity combined with more rapid sample analysis. Data produced within the last three years have already gone some way towards establishing the basis of Mo isotope systematics: Dauphas et al. (2001) showed, that Mo isotope anomalies other than mass dependent fractionation appear to be absent in Earth materials, even though they are present in extraterrestrial matter (Yin et al., 2002; Dauphas et al., 2002). Isotope fractionation of Mo by anion exchange chromatography in the laboratory has been reported (Anbar et al., 2001; Siebert et al., 2001), as has Mo isotope fractionation in nature (Siebert et al., 2001; Barling et al., 2001; McManus et al., 2002; Siebert et al., 2003). In their pilot study on terrestrial Mo isotope fractionation, Barling et al. (2001) observed a significant offset between ferromanganese nodules and anoxic sediments (deposited in the presence of H_2S), the latter being isotopically heavier. Further, these authors reported the Mo isotopic composition of a Pacific Ocean seawater sample being within the range of values for anoxic sediments, closest to modern Black Sea anoxic sediments. Consequently they suggested that the Mo isotopic composition of seawater may reflect changes in the relative proportions of anoxic and oxic sedimentation in the oceans through time, and that this variation may be archived in anoxic sediments. In a more recent study Arnold et al. (2004) reported a narrow range of Mo isotopic compositions in eight (sub) recent anoxic sediments from the Black Sea and the Cariaco basin, two of which were identical within error to recent ocean water. Siebert et al. (2003) confirmed the offset between ocean water and ferromanganese crusts as well as pelagic sediments (1 per mil per mass unit) and found virtually identical values over the entire

depth profiles of two Fe–Mn crusts representing 60 Ma. They also demonstrated that the isotopic composition of dissolved Mo in the ocean is homogeneous irrespective of location or depth, as expected from the long residence time of Mo. However, open ocean reducing sediments with low bottom water oxygen ($<10 \mu\text{M}$), were found to vary significantly but within the range intermediate between ocean water composition and oxic sediments (Siebert et al., 2003).

Further, pore waters from Santa Monica basin sediments (bottom water oxygen $<5 \mu\text{M}$, McManus et al., 2002, 2003, low to undetectable levels of sulfide in pore waters ($<1 \mu\text{M}$), McManus pers. com.) were found to vary significantly: the study of McManus et al. (2002) showed that during authigenic uptake of Mo within these sediments the lighter Mo isotopes are preferred, leaving behind a heavier Mo isotope pool in pore waters, in some cases even heavier than seawater.

Hence the stage is set for Mo isotope investigations for paleoredox reconstructions by a well defined offset between (homogeneous) ocean water and oxic sediments.

With regards to black shales, the potential of Mo isotope fractionation as diagnostic tool for depositional environment is not yet well defined, due to many variables and variations observed. In particular, the following questions need to be answered:

- 1) Is the deposited Mo signal preserved under anoxic diagenetic conditions or is there a post-depositional mobility?
- 2) Is there a Mo isotope fractionation between dissolved Mo and Mo precipitated in the presence of H_2S ? If so, black shales would only record coeval water if all Mo is precipitated, while incomplete removal would allow some isotope fractionation to be preserved.
- 3) If the isotopic composition of Mo in anoxic sediments is not identical to ocean water, is it possible to distinguish between fractionation effects and inputs from sources other than ocean water?

In an effort to address these questions we have analysed samples from a section spanning the transition from oxic–limnic to marine reducing conditions at the start of the Holocene in the Black Sea.

2. Sampling area, methods and material

The Black Sea is the largest anoxic basin on earth and the modern analogue for the formation of organic-matter rich sediments in the geological past. Current knowledge of the ecology and oceanography of the Black Sea system has been reviewed recently by Neretin et al. (2001), Sorokin (2002) and Jørgensen et al. (2004) and is, therefore, only briefly summarised here. The sediments at the study area in the NW part of the Black Sea have been described in detail by Jørgensen et al. (2004) and Neretin et al. (2004). The Black Sea water column is stratified due to restricted influx of seawater via the narrow Dardanelles straits and the $<40 \text{ m}$ deep sill of the Bosphorus pathway. Surface waters are oxygenated but below 100 m the water column is permanently devoid of oxygen. The surface water (salinity 17.5‰ – 18.5‰ , Murray et al., 1991) shows significant influence from riverine inflow. The Danube river contributes about 35% of this fresh water inflow and half of the total terrestrial sediment load. Significant riverine contributions to the northern Black Sea also stem from the Prut, Dnestr, Bug and Dnepr rivers, principally draining the low-relief Russian platform. The replacement time of the whole upper layer is of the order of two decades. The deep water with a salinity of 22.3‰ (Murray et al., 1991) is evidently dominated by marine water and denser than the upper layer. Its replacement time is estimated to be several hundred years (Top and Clarke, 1983; Falkner et al., 1991; Murray et al., 1991).

The Black Sea is the type system for sediment formation under euxinic conditions and sedimentary changes in response to changes in the global seawater level. Besides being an archetype of recent marine anoxic environments, the Black Sea provides an important archive in its sediments. Its stratigraphy consists of Pleistocene limnic sediment (Unit III), Holocene marine sediments (Unit II) and the modern coccolith ooze (Unit I) (Ross and Degens, 1974; Arthur and Dean, 1998). Unit III was deposited during the last glaciation when the Black Sea basin hosted an oxic freshwater lake due to the sea level low stand. The first seawater intrusions have been shown to appear at about 9.8 ka b.p. (Jones and Gagnon, 1994; Arthur and Dean, 1998) (brackish oxic sediments, Unit IIb). Anoxic deep water conditions were estab-

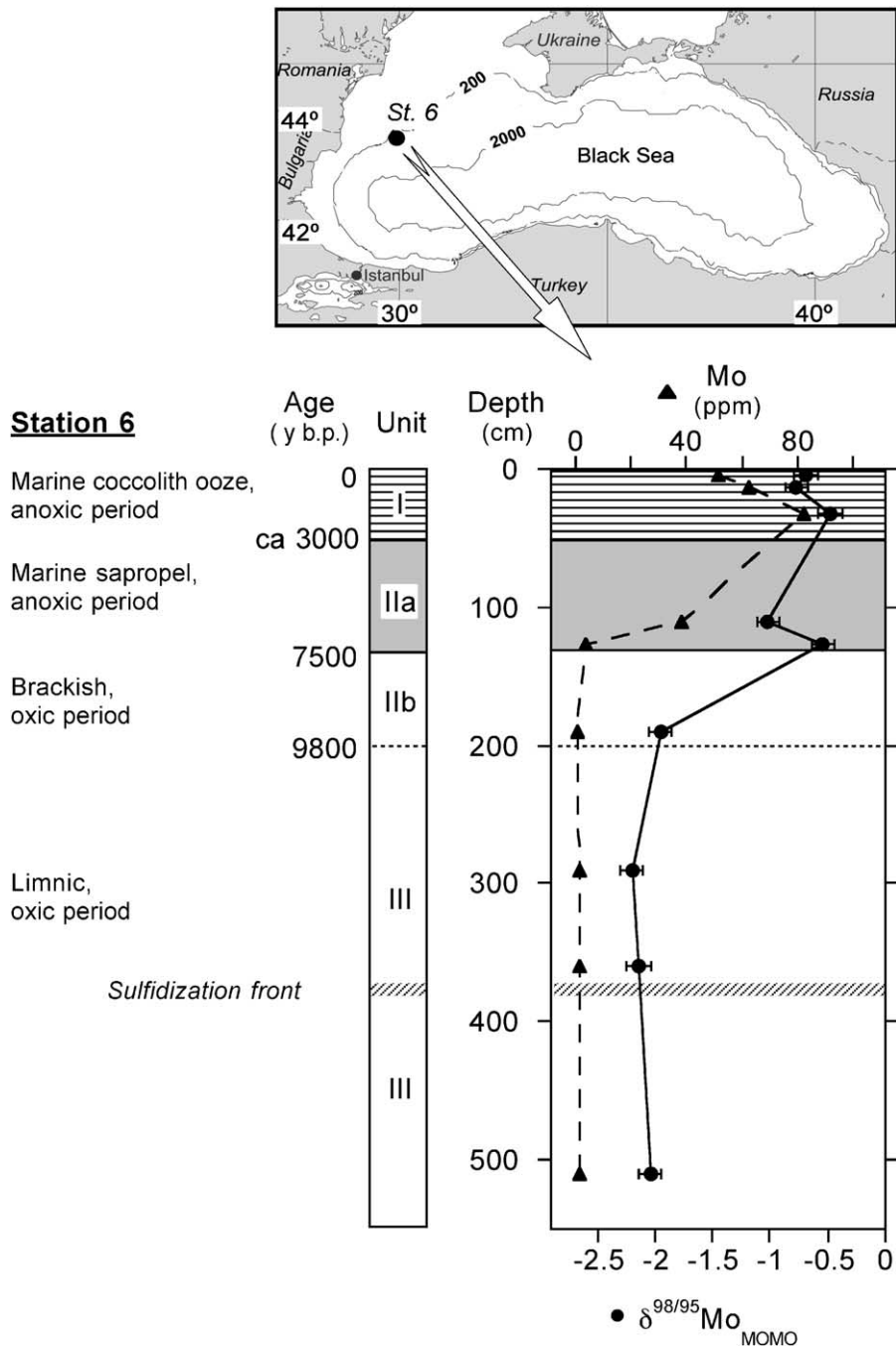


Fig. 1. Main stratigraphic sequences at station 6 (396 m water depth; after Jørgensen et al., 2004) and related Mo data. Triangles: Mo concentration, filled circles $\delta^{98/95}\text{Mo}_{\text{MOMO}}$. Mo isotope data show change in depositional environment (oxic to anoxic) and are not affected by post depositional downwards migration of H_2S .

lished about 7.5 ka ago, documented by sapropel deposition (Unit IIa), while a stable seawater influx across the Bosphorus has formed at least 7.15 ka ago (Ryan et al., 1997; Aksu et al., 1999; Görür et al., 2001). Younger varved coccolith ooze (Unit I) result from the appearance of the coccolithophorid *Emiliana huxleyi* from about 3 ka ago on (Calvert et al., 1987; Lyons, 1991; Hay et al., 1991; Arthur and Dean, 1998). This was caused by a salinity increase of the Black Sea surface waters to values permanently above 11‰, which is the minimum level required by *Emiliana huxleyi* (Bukry, 1974). One consequence of the seawater intrusion into the Black Sea and the establishment of anoxic conditions was a downward diffusion of dissolved sulfate into the underlying sediments and subsequent in-situ production of H₂S due to microbial sulfate reduction associated with anaerobic methane oxidation (Jørgensen et al., 2004; Neretin et al., 2004). This is further marked by a band coloured black by iron sulfides within Unit III indicating the present bottom of a progressing sulfidisation front (Jørgensen et al., 2004).

In the present study, samples from an 8 m long gravity core reaching down into limnic sediments were analysed. This provides an archive of the transition from oxic limnic to the prevailing anoxic marine conditions, as well as the effects of downward diffusion of dissolved species on Mo isotopic signatures. Samples were taken during a research cruise of *R/V Petr Kottsov* in the western Black Sea in September 1997 at Station 6 (43°40'47N, 030°07'54E) at a water depth of 396 m. The station is located on the broad slope region of the NW Black Sea where significant amounts of Danube sediments are deposited. (Fig. 1, see Jørgensen et al., 2004 and Neretin et al., 2004 for a detailed description). The oldest core sample was taken at a sample depth of 510 cm (\approx 15 ka), while the sulfidisation front is currently found at 310–380 cm. The sedimentation rate for the whole anoxic period was calculated to be 0.17 mm y⁻¹ (Jørgensen et al., 2004). In the oxic limnic period it was significantly higher, in the range of 0.6 mm y⁻¹ due to larger detrital input (Lüschen, 1998). Intermediate sedimentation rates of c. 0.3 mm y⁻¹ result for the brackish period (Unit IIb) if the limnic to brackish transition (defined by geochemical parameters and diatom frustules, Jørgensen et al., 2004) is considered in relation to the first seawater intrusions

about 9.8 ka b.p. (see above). Ages ascribed to samples in this paper are based on sedimentation rates following Jørgensen et al. (2004). They are intended to be used as a guide when referring to the Black Sea history outlined above.

3. Methods

A detailed description of the analytical techniques is given in Siebert et al. (2001). The method involves the use of a double spike (¹⁰⁰Mo, ⁹⁷Mo) to resolve analytical from natural mass dependent isotope fractionation. In addition the double spike technique provides Mo concentrations. Samples were calcinated, spiked and dissolved by HF–HNO₃ digestion, followed by chemical Mo purification. Mo isotopic compositions were determined using a Nu instruments MC-ICPMS. For isotope data presentation the ⁹⁸Mo/⁹⁵Mo ratio is used. The external standard reproducibility is at or better than \pm 0.1 per mil for this ratio (2 s.d.). In the absence of an internationally accepted standard we use the mean ocean water composition (MOMO, Siebert et al., 2003) as our standard reference.

4. Results and discussion

Results are presented in Table 1 and Figs. 1 and 2. Two main groups are observed in terms of Mo isotopic composition: a) samples deposited under oxic conditions (BS-1 to BS-4, $\delta^{98/95}\text{Mo}_{\text{MOMO}}$ from -2.2‰ to -1.95‰) with no distinction between limnic and brackish origin and b) samples deposited under anoxic conditions (BS-5 to BS-9, $\delta^{98/95}\text{Mo}_{\text{MOMO}}$ from -1 to -0.54‰). Thus the Mo isotope ratios clearly respond to the change in sedimentary environment and the difference between oxic and anoxic sedimentation is well resolved. Qualitatively, this result is in line with the findings and hypotheses on different scavenging and fractionation processes discussed in Barling et al. (2001) and Siebert et al. (2003). The change of sedimentary environment is also recorded in the Mo concentration increase from oxic (0.8–1.0 ppm) to anoxic sediments, however this signal appears to be delayed. The oldest anoxic sample is still low in Mo content (3.4 ppm)

Table 1

Lab. #	BS-1	BS-2	BS-3	BS-4	BS-5	rep.	BS-6	BS-7	BS-8	BS-9
Depth (cm)	510	360	290	190	130		110	31-33	12-13	3-4
Sedimentary Environment	Limnic	Limnic	Limnic	Marine	Marine		Marine	Marine	Marine	Marine
$\delta^{98/95}\text{Mo}_{\text{(MOMO)}}$	-2.04	-2.14	-2.20	-1.95	-0.54	-0.39	-1.02	-0.48	-0.77	-0.69
2 σ err.*	0.09	0.10	0.10	0.09	0.09	0.16	0.10	0.09	0.09	0.09
Mo (ppm)	1.0	1.0	1.0	0.8	3.4	3.5	38.2	82.4	62.3	51.8
SiO ₂ (%)	48.8	48.8	48.8	52.1	45.5		53.6	27.7	23.1	29.6
Al ₂ O ₃ (%)	12.9	12.5	12.3	10.7	9.6		9.9	9.2	7.7	8.3
TiO ₂ (%)	0.63	0.62	0.61	0.58	0.53		0.53	0.38	0.32	0.38
TIC (%)	2.67	2.66	2.66	2.63	1.11		1.81	5.9	6.21	5.9
TOC (%)	0.51	0.48	0.58	0.52	3.63		4.87	5	3.46	4

All samples are from station 6 (Jørgensen et al., 2004).

* In run precision of analyses (2 σ standard error). External reproducibility was ± 0.1 (2 SD).

while the younger ones are between 38 and 82 ppm. TiO₂ concentrations are similar in all samples indicating similar detrital contributions. This difference may be related to the transition from anoxic to anoxic sulfidic water column conditions during the development of the physio-chemical conditions of the Black Sea.

4.1. Diagenetic Mo mobility

The most obvious feature of post sedimentary alteration in these sediments is marked by a black band of amorphous iron sulfide above which distinct horizons of greigite and pyrite formation occur (Jørgensen et al., 2004).

This sulfidation front is caused by a progressing diagenetic alteration due to downward diffusion of dissolved sulfate into the older sediments and subsequent in-situ production of H₂S due to microbial sulfate reduction associated with anaerobic methane oxidation (Jørgensen et al., 2004; Neretin et al., 2004). At the sulfidation front H₂S reacts with Fe(III) and with Fe²⁺ diffusing up from below. The sulfidation front now is positioned within the limnic sediments that were deposited under oxic bottom water conditions (i.e. between samples BS-2 and BS-1). Mo content and isotopic compositions are identical above and below the black band indicating the bottom of a sulfidation front, and no signal of the high Mo content and heavy Mo isotopic composition of the overlying marine sapropels is found in the underlying previously oxic sediments. Apparently neither the downward migration of sulfate through the sapropels

nor sulfide diffusion within the previously oxic sediments did result in significant Mo mobility during diagenesis.

Likewise, Lyons et al. (2003) found no direct evidence for significant Mo enrichment via diffusion into sulfide rich pore waters of sediments from the Cariaco Basin even though they underwent a heavily sulfide overprint. Therefore, anoxic sediments bear a high potential to preserve pre-diagenetic Mo signals.

4.2. Sediments deposited under oxic bottom water

The homogeneous Mo isotopic composition and invariably low Mo content of the limnic sediments (Unit III, BS-1 to BS-3, 510–290 cm, 15–11 ka, see Fig. 1) are compatible with a detrital origin of the Mo without significant amounts of Mo scavenged from solution. The concentrations are equal to that of average continental crust (1 ppm Wedepohl, 1995, 1.1 ppm Taylor and McLennan, 1995) and are even slightly below average upper continental crust (1.4 ppm or 1.5 ppm, same references). The Mo isotopic composition is also identical to that of the average continental crust: continental crust appears to be very homogeneous in terms of Mo isotopic composition with a $\delta^{98/95}\text{Mo}_{\text{MOMO}} = -2\text{‰}$ (Siebert et al., 2003).

Evidently the detrital fraction of the input (suspended load) dominates the sedimentary record under oxidic depositional conditions in these clastic sediments. Oxidic scavenging of dissolved Mo, dominantly present as the chemically inert MoO₄²⁻ anion, most probably was a far too inefficient process to compete with the detrital deposition of c. 0.6 mm y⁻¹.

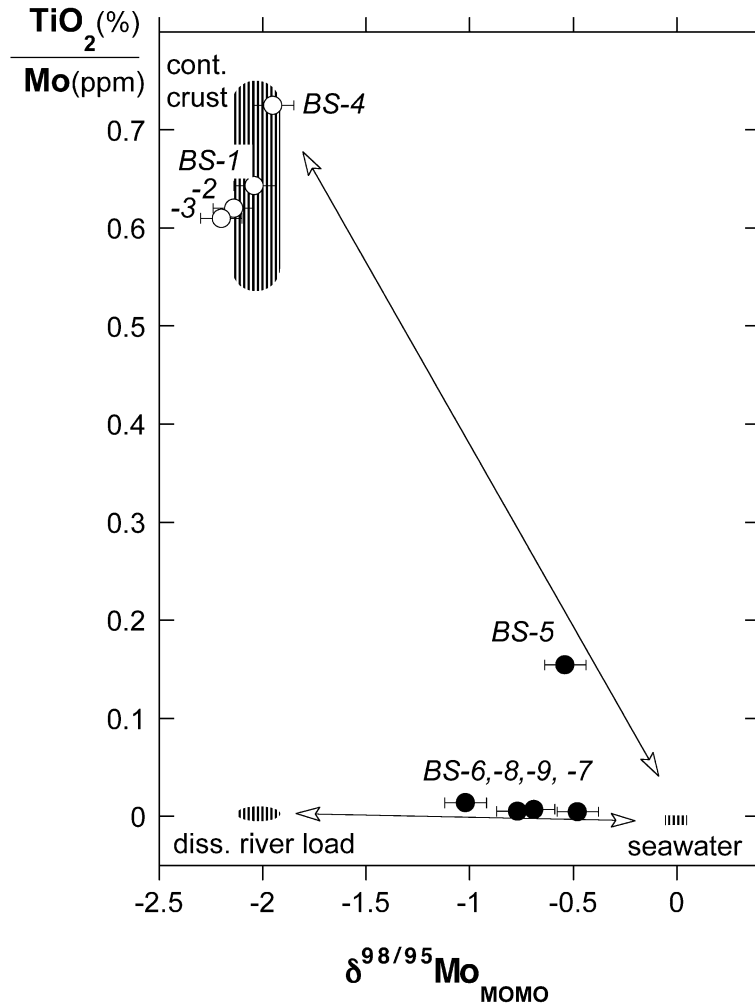


Fig. 2. $\text{TiO}_2(\%)/\text{Mo}(\text{ppm})$ vs. $\delta^{98/95}\text{Mo}_{\text{MOMO}}$: three component model for source of Mo in Black Sea sediments. Open circles: limnic and brackish, oxic sediments, filled circles: anoxic sediments. Ocean water: Mo concentration after Collier (1985), Siebert et al. (2003); Ti concentration after Quinby-Hunt and Turekian (1983), Bruland (1983). Continental crust: Mo concentration after Wedepohl (1995), Taylor and McLennan (1995), Ti concentration after Plank and Langmuir (1998), Weaver and Tarney (1984), Wedepohl (1995). Dissolved river load: Mo concentration after Manheim and Landergren (1978), Martin and Meybeck (1979); Ti concentration after Martin and Whitfield (1981). $\delta^{98/95}\text{Mo}_{\text{MOMO}}$ of all sources after Siebert et al. (2003).

Detrital Mo also appears to be dominant during the still oxic, early marine (brackish) period (sample BS-4, 190 cm; c. 9.5 ka). No significant change can be observed in either Mo content or isotopic composition (Fig. 1) even though the total amount of Mo present in solution must have been increased relative to limnic conditions. This again underscores that only an insignificant fraction of Mo was sequestered from solution per unit of time compared to particulate Mo input under oxic conditions.

4.3. Anoxic sediments

In sharp contrast, anoxic samples generally show Mo contents 1–2 orders of magnitude above crustal background and thus are clearly dominated by Mo scavenging from solution. Irrespective of the pathway of authigenic Mo formation, these high concentrations together with the very low dissolved Mo concentrations in the present day deeper waters of the Black Sea (Emerson and Husted, 1991) compared to

modern oceans, indicate that the scavenging process in this reducing environment is a highly efficient one.

The $\delta^{98/95}\text{Mo}_{\text{MOMO}}$ values of anoxic samples are relatively close to modern ocean water. Siebert et al. (2003) reported a homogeneous Mo isotopic composition from open ocean water samples of different oceans and depths ($\delta^{98/95}\text{Mo}_{\text{MOMO}}=0$ per definition, see above). Seawater, therefore, probably was the dominant source of Mo in these sediments. To the extent that currently available data (Siebert et al., 2003; McManus et al., 2002) allow us to draw such conclusions, continental and hydrothermal inputs are not sources of isotopically heavy Mo. However, even the heaviest Mo value of the whole anoxic period recorded in this core is $\delta^{98/95}\text{Mo}_{\text{MOMO}}=-0.5\text{‰}$, with an average of -0.7‰ for all anoxic sediments, i.e. 0.7‰ lighter than seawater. This is about 1/4 of the maximum variation found between seawater and oxic sediments (pelagic sediments and hydrogeneous Fe–Mn crusts, Siebert et al., 2003) and about 7 times analytical precision.

There are two possible explanations for the offset between ocean water and the anoxic sediments: one would be significant admixture of Mo with a lighter isotopic composition, the other would be some preservation of Mo isotope fractionation under anoxic conditions due to incomplete scavenging. These possibilities are discussed separate below, however, a combination of both would of course be possible.

4.3.1. Admixture of Mo with a lighter isotopic composition

Assuming complete Mo scavenging, or absence of Mo isotope fractionation, the Mo isotope values of the anoxic sediments can be interpreted as reflecting the Mo isotopic composition of their source (i.e. the Black Sea deep waters). Potential sources of the Mo present in Black Sea deep waters are ocean water and isotopically lighter Mo originating from continental runoff. These sources are indicated by the salinity and also supported by the stable isotope work of Özsoy et al. (2002). Recent water mass transfer to, from and within the layers of the Black sea is estimated in a number of published models (e.g. Falkner et al., 1991; Colodner et al., 1995; Özsoy and Ünlüata, 1997). However, salinity is decoupled from Mo concentration in both, the upper layer and the deep water of the Black Sea (Colodner et al., 1995): deep anoxic waters

with higher salinity show only about 3% of the Mo concentration of ocean water (Emerson and Husted, 1991) due to Mo scavenging. This decoupling propagates into the upper layer, as the latter is partly formed by an influx from the deep waters.

In Fig. 2 the potential Mo sources are plotted together with the Mo sediment data and Ti contents as monitor for detrital input. Again, the oxic sediments are indistinguishable from average continental crust, and thus represent quasi-pure detritus in terms of Mo.

The dissolved continental runoff is expected to have low TiO_2/Mo ratios due to the immobility of Ti. Its Mo isotopic composition can be assumed to mirror average continental crust, as indicated by the results of a mild leaching of granite: to get a first order assumption on the isotopic composition of the Mo released by weathering, Siebert et al. (2003) treated powdered granite with 0.05 M HCl. The dissolved Mo represents 60% of the total and its Mo isotopic composition is indistinguishable from that of the granite. The triangle defined by ocean water, continental runoff and detritus encompasses all anoxic sediment data of this study (Fig. 2). The four younger anoxic samples (BS-6 to BS-9, 3–110 cm, 6.3–0.2 ka) follow a mixing trend between marine and dissolved continental sources. Their isotope ratios ($\delta^{98/95}\text{Mo}_{\text{MOMO}}=-1.02\text{‰}$ to -0.48‰) indicate relative crustal Mo contributions of 20%–50%. Sample BS-5 plots close to the detrital-marine mixing line.

Thus the three component mixture concept allows to qualitatively explain the Mo data of all samples presented here. An important issue however is the quantitative reconciliation of these mixtures given the known fluxes of the Black Sea. Fig. 3 shows a simple box model of the present day Black Sea based on Falkner et al. (1991) and Colodner et al. (1995). According to this mixing model, the Mo flux to the sediments would have a $\delta^{98/95}\text{Mo}_{\text{MOMO}}$ value of -0.21‰ only. Özsoy and Ünlüata (1997) report significantly higher water fluxes across the Bosphorus. Applying these in the same model leads to $\delta^{98/95}\text{Mo}_{\text{MOMO}}$ value of the flux even closer to zero. To reconcile the observed Mo isotopic composition of the anoxic sediments with this model, the relative contribution of continental Mo has to be increased significantly.

Larger riverine influx is a reasonable assumption for Unit IIa (BS-6) due to the oceanographic changes

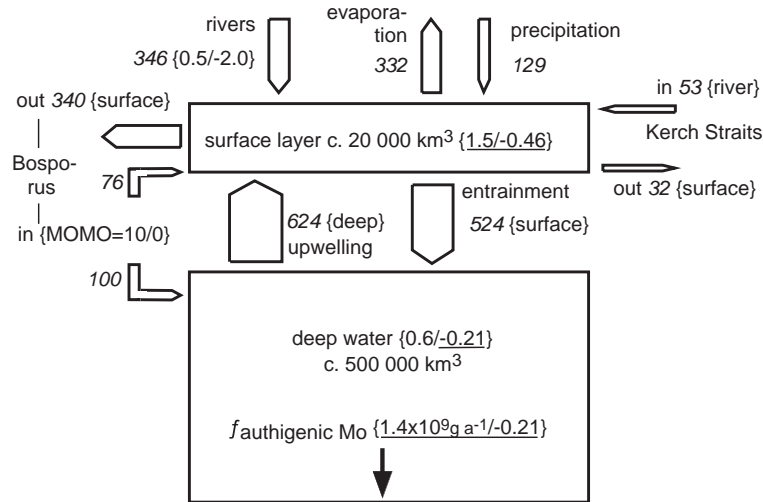


Fig. 3. Simple mixing model of the Black Sea modified after Colodner et al. (1995) and Falkner et al. (1991). Model results are underlined. Numbers in italics denote water fluxes in km³/a. In {} Mo concentration (μg/l) and $\delta^{98/95}\text{Mo}_{\text{MOMO}}$ (‰) are given or a reference to their provenance. See Fig. 2 for input data references. Refinements: average Mo concentration of the deep water box was set to 0.6 μg/l instead of 0.3 μg/l to account for higher concentrations between –100 and –500 m water depth (Emerson and Husted, 1991). Marine input via the Bosphorus was split to mix in part directly with surface water. This is observed in nature (cf. Özsoy and Ünlüata, 1997), and is necessary for the modelling due to the decoupling of salinity and Mo concentration in the deep water. It further allows the Mo flux to the anoxic sediments ($f_{\text{authigenic Mo}} = 1.4 \times 10^9 \text{ g a}^{-1}$) within the range modeled by Colodner et al., 1995 based on sedimentary data ($0.44 \times 10^9 \text{ g a}^{-1}$ to $1.44 \times 10^9 \text{ g a}^{-1}$). However the effect on the Mo isotopic composition of $f_{\text{authigenic Mo}}$ is small: without the splitting it would be $\delta^{98/95}\text{Mo}_{\text{MOMO}} = -0.12$.

recorded. In particular the absence of *Emiliania huxleyi* below Unit I indicates, that the salinity of the upper waters was far below recent values before 3 ka ago (see Introduction). This hypothesis was also mentioned by Arnold et al. (2004) for anoxic samples from Unit II.

Sample BS-5, (130 cm, 7.5 ka) taken just above the Unit IIb–Unit IIa transition has a significantly lower Mo concentration (3.4 ppm). The marine Mo contribution is thus significantly smaller than in the younger anoxic sediments, so that the $\delta^{98/95}\text{Mo}_{\text{MOMO}}$ value of -0.54‰ may result from admixture of detrital Mo alone, as indicated by the samples position in Fig. 2. A different balance of fluxes of the Black Sea occurring at the time of deposition of BS-5 may well be the reason for the lower Mo content. Until 6–7 ka ago a strong surface water outflow from the Black Sea into the Sea of Marmara is indicated (Aksu et al., 1999; Kaminski et al., 2002). Thus, the marine influx to the Black Sea might have been much smaller thus providing a lower absolute amount of Mo.

However, the results of the samples from Unit I (BS-7 to BS-9) are hard to reconcile with such

mixing models if present day water fluxes are to be adopted. The required increased continental Mo supply would have to result from a c. 5 times higher Mo concentration of the continental runoff. And indeed, the rivers of the area (see Introduction) are known to carry dissolved Mo levels in the range of 1.8–3.0 μg/l, Colodner et al., 1995, compared to the mean dissolved Mo concentration of world rivers of 0.5 μg/l (Manheim and Landergren, 1978; Martin and Meybeck, 1979). However, these high Mo levels are most probably due to anthropogenic input (Colodner et al., 1995). Following this assumption, present day upper layer water must also be considered as dominated by anthropogenic Mo, given the fact that the time scale of water exchange in that reservoir is about two decades and that high dissolved Mo levels have been observed in an early study in the sixties (cf. Colodner et al., 1995). Natural sources for anomalously high dissolved Mo river load (i.e. black shales or Mo deposits in the drainage areas) also have to be considered. According to Colodner et al. (1995), and Müller and Stoffers (1974) there are no widespread black shales in the main drainage areas. The Danube river contributing the largest sediment load drains

large loess formations, alluvia, flysh, some limestone and magmatic rocks (Garnier et al., 2002). Further, black shales would contribute a Mo isotopic composition above average continental crust. Thus they would be an unlikely source for Mo lowering the isotopic composition of dissolved Mo in the Black Sea. Mo deposits might contribute to the Mo budget of the Kuban river: Vinogradov (1957) describes Mo concentrations in ground water in Central Asia and the Caucasus region to increase from background up to 10 mg/l near molybdenite deposits. Caucasian deposits thus might contribute Mo to the Black Sea via the Rioni and Kuban rivers. However, the present day Kuban river Mo concentration 2.1 µg/l is within the range of the other rivers draining into the Black Sea. Thus, there is no clear evidence for a contribution from Mo deposits, nor could it be the unique reason for increased continental Mo.

A further possibility for additional input of Mo with continental isotopic composition is Mo leached from suspended river load in the marine environment. As the suspended Mo load in rivers draining into the Black Sea (1.2 µg/l, Volkov, 1975) is more than two times that of world average river dissolved Mo this pathway could have provided some of the excess dissolved continental Mo. Thus there is considerable uncertainty on the pre-anthropogenic continental Mo contribution. However, reconciling the Mo isotopic composition of the sub-recent samples BS-7 to BS-9 requires an amount of continental Mo not supported by the above hypotheses. Finally, the mixing model does not explain the heterogeneity of Unit I samples from different water depth: Arnold et al. (2004) report two samples from Unit I taken at a water depth of >200 m close to the centre of the Black Sea that have Mo isotope compositions indistinguishable from present day ocean water. Therefore, Mo isotopic fractionation during scavenging appears inevitable for the Unit I samples studied here. This implies that the scavenging was incomplete.

4.3.2. Mo isotope fractionation under anoxic conditions

There is extensive discussion in the literature about pathways of Mo enrichment in black shales, in particular whether water column scavenging or enrichment via diffusion across the sediment water

interface is the dominating process (cf. Lyons et al., 2003, and references therein). However a consensus exists on the importance of high concentrations of dissolved sulfide on the overall process. As for the anoxic samples discussed here enhanced dissolved sulfide concentrations exists in the water column and pore waters, the Mo isotope data cannot provide a definite answer to that problem. Considerations outlined below are however in favour of Mo scavenging from the water column to explain the Unit I Mo data of this study and their difference from those of Arnold et al. (2004). A 3-fold change in H₂S concentration results in a 100 fold change in the equilibrium ratio of MoS₄²⁻/MoO₄²⁻ (e.g. Erickson and Helz, 2000). Therefore, the transition from MoS₄²⁻<MoO₄²⁻ to MoS₄²⁻>MoO₄²⁻ is very sharp (intermediate, metastable thiomolybdates are omitted from this general discussion of the net Mo isotope fractionation effect, see Erickson and Helz, 2000). The ‘Action Point of Switch’ (APS) (Erickson and Helz, 2000) above which MoS₄²⁻ dominates over MoO₄²⁻ was found to be at a H₂Saq concentration of 11 ± 3 µM by these authors. In the present Black Sea, the depth of the APS is at about 400 m (Erickson and Helz, 2000), similar to the depth of the station 6 core analysed here (396 m). The samples discussed above (BS-6 to BS-9) may thus reflect scavenging under H₂Saq < 11 µM conditions, i.e. in the presence of some Mo remaining dissolved as MoO₄²⁻ in a larger part of water column above. Depth profiles of Mo concentrations in the Black Sea waters (Emerson and Husted, 1991) indicate 3.7 µg/l in the surface waters, about 0.8 µg/l at 400 m water depth but only 0.3 µg/l at greater depth. With the open ocean Mo concentration being 10 µg/l and the known fluxes to the deep waters (e.g. Colodner et al., 1995) the Mo concentration of the water flux to the deeper levels can be approximated as c. 5 µg/l. This value reduces to c. 3 µg/l when applying the surface water Mo concentration of 1.5 µg/l resulting from the mixing model for pre-anthropogenic riverine Mo contributions (Fig. 3). Comparing the observed deep water Mo concentration to that of the influx indicates that c. 75%–85% of the Mo is scavenged at a depth of about 400 m, but 90%–95% below 2000 m, the depth of the samples reported in Arnold et al. (2004). Incomplete scavenging, however, means that if the scavenging process frac-

tionates Mo isotopes, then this isotope fractionation will be reflected in the sediment data.

For a first order model it appears reasonable to assume that -0.5% of the offset observed between recent ocean water and the Unit I samples of this study might relate to a fractionation process, (i.e. effectively -0.5% for 85% of Mo precipitated). As the depth of the APS most probably is not stable at exactly 400 m during deposition of Unit I, it appears reasonable to attribute part of the variation of the $\delta^{98/95}\text{Mo}$ values of the respective samples to H_2Saq oscillations below 11 μM . In any case, the Mo isotopic compositions of Unit I samples indicate that the average H_2Saq concentration of the bottom water integrated over the time represented by each sample was below 11 μM .

While this is a simple model, it demonstrates that the difference between Unit I samples from this study and those from earlier publications may be related to water depth and merely reflect the fraction of Mo scavenged under variably reducing conditions.

5. Implication for reconstruction of paleo-Ocean water Mo isotopic composition

Anoxic conditions with $\text{H}_2\text{Saq} > 11 \mu\text{M}$ are difficult to constrain for fossil black shales, even more so the depth of the anoxic water column. H_2Saq below 11 μM would result in incomplete precipitation of Mo despite anoxic conditions (see above). In such cases inefficient scavenging (most probably resulting in Mo isotope fractionation) as well as mixing of Mo from different sources may play a role: mixtures of Mo derived from the formation of thiomolybdates and dissolution of Mn oxides as well as admixture of additional crustal Mo in restricted basins will all result in lighter and more variable Mo isotopic composition with respect to the coeval ocean water. Therefore black shales from restricted semi-enclosed basins may not document the exact Mo isotopic composition of coeval ocean waters, even if deposited under true anoxic conditions. This complication means that for reconstruction of paleo-anoxia the heaviest observed Mo isotopic composition of a given set of contemporaneous samples gives a minimum value for coeval seawater.

6. Conclusions

Reducing post-sedimentary fluids have not mobilised Mo or altered its isotopic composition in the sediments.

Detrital Mo dominates under oxic conditions in basins, unless purely chemical sediments are investigated. This reflects the low oxic Mo precipitation rates due to the inertness of MoO_4^{2-} .

Under anoxic conditions with $\text{H}_2\text{Saq} > 11 \mu\text{M}$ precipitated Mo carries an isotopic signature similar to that of the co-existing water mass. This Mo isotopic signature is in many cases, but not necessarily correlated with Mo concentration. Further, it is not necessarily identical to coeval open ocean water.

However, oceanic Mo is a dominant Mo source in these basins, and anoxic sediments give reliable minimum values for the Mo isotopic composition of coeval ocean water.

In the case of the Black Sea waters, continental runoff is one highly probable source of light Mo isotope excess. However for Unit I samples from station 6, an influence of Mo isotope fractionation under anoxic conditions with $\text{H}_2\text{Saq} < 11 \mu\text{M}$ appears to be present.

Acknowledgements

Crew and captain of *R/V Petr Kottsov* as well as the cruise leader B. Jørgensen and cruise co-ordinator A. Weber are thanked for all their efforts. The constructive comments of A. Anbar (on an earlier version), T. Lyons and an anonymous reviewer, as well as discussions with J.D. Kramers helped to improve the manuscript significantly. The Mo isotope work in Bern is supported by Swiss National Science Foundation (SNF-Grant 20-61933.00). MEB acknowledges the support of the Max Planck Society. [LMW]

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