

Molybdenum isotopic composition of modern and Carboniferous carbonates

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We investigate the redox-sensitive isotope system of molybdenum (Mo) in marine carbonates to evaluate their potential as archive of the Mo isotopic composition of coeval seawater. We present Mo isotope data ($\delta^{98/95}\text{Mo}$) of modern skeletal and non-skeletal carbonates as well as a variety of precipitates from the mid and late Carboniferous. The external reproducibility is determined by repeated analyses of two commercially available carbonate standards. The resulting uncertainty of the low concentration samples is $\pm 0.1\%$ (2σ). Analysis of modern ooid sands from the Bahamas shows a consistently heavy Mo isotopic composition ($\delta^{98/95}\text{Mo}$ between 2 and 2.2‰), approaching modern mean seawater values ($\delta^{98/95}\text{Mo} = 2.3\% \pm 0.1\%$ (2σ)). This suggests that isotope fractionation during Mo uptake into non-skeletal carbonate precipitates is small. In contrast, modern skeletal carbonates show variable isotopic compositions (0.1 to 2.2‰) which suggests a biologically controlled fractionation process. The varying Mo signatures found in Carboniferous cement phases point to a strong response to local changes in fluid composition from which they precipitated. Overall, we recognized three important factors to cause an offset relative to ocean water: Mo derived from skeletal components, input of detrital Mo and admixture of light, hydroxide derived Mo via diagenetic fluids. All of these factors cause a lighter Mo isotopic composition relative to seawater. Due to the apparent small isotope fractionation during Mo uptake into non-skeletal carbonates, their $\delta^{98/95}\text{Mo}$ closely reflects the ambient fluid composition. From these results we conclude that carbonates represent a promising new tool to characterize the water mass Mo isotopic composition of marine paleo-environments.

1. Introduction

In recent years molybdenum (Mo) isotopes have been used to investigate the paleo-redox conditions of Earth's atmosphere and oceans. Precise Mo isotope analyses, performed on various rock types and seawater, have revealed large and systematic variations in the marine environment (Barling et al., 2001; Siebert et al., 2003; Arnold et al., 2004; Siebert et al., 2006). All of these studies particularly focused on anoxic sediments and/or oxic manganese crusts, two of the major marine Mo sinks. Oxic seawater contains Mo as the stable oxyanion molybdate (MoO_4^{2-}) with a molar concentration of ca. 0.11 μM (Collier, 1985). Measurements of five seawater samples of different locations and water depths revealed a homogenous seawater $\delta^{98/95}\text{Mo}$ composition of $2.3 \pm 0.1\%$ (2σ) (Siebert et al., 2003). The low chemical reactivity of MoO_4^{2-} results in a relatively long residence time of ca. 800 ka (Emerson and Husted, 1991; Colodner et al., 1995). The transformation from chemically unreactive molybdate to highly reactive thiomolybdate under enhanced levels of dissolved sulphide

has been proposed to be the prime reason for authigenic Mo enrichment in euxinic sediments (Helz et al., 1996; Erickson and Helz, 2000; Barling et al., 2001; Neubert et al., 2008). The use of black shales as archives of Mo isotope signatures of coeval ocean water is a first order approach based on the assumption of an almost complete Mo scavenging under sulphidic conditions, where potential fractionation effects are eliminated. However, below the critical $\text{H}_2\text{S}_{\text{aq}}$ concentration of 11 μM ("Action Point of Switch"; Erickson and Helz, 2000) Mo isotope fractionation is as significant as in oxic sediments (Neubert et al., 2008). In other words, reducing sediments do not per se archive the Mo isotopic composition of coeval seawater, even under euxinic conditions. Thus, additional independent constraints are needed to determine the paleo-ocean water Mo isotopic composition. Marine carbonates are a potential archive, but their Mo isotopic signature has not yet been investigated. This is partly due to analytical difficulties related to their low Mo content ($\ll 1$ ppm). However, it is precisely these low concentrations that make the Mo isotopic composition of carbonates attractive. High concentration deposits, such as suboxic and anoxic sediments, are archive and major Mo sink at the same time. Increased rates of authigenic Mo enrichment in the respective environments can trigger changes in the global Mo reservoir and alter the isotopic composition of seawater. Carbonates, on the other hand, are a minor sink, accounting for $\leq 1\%$

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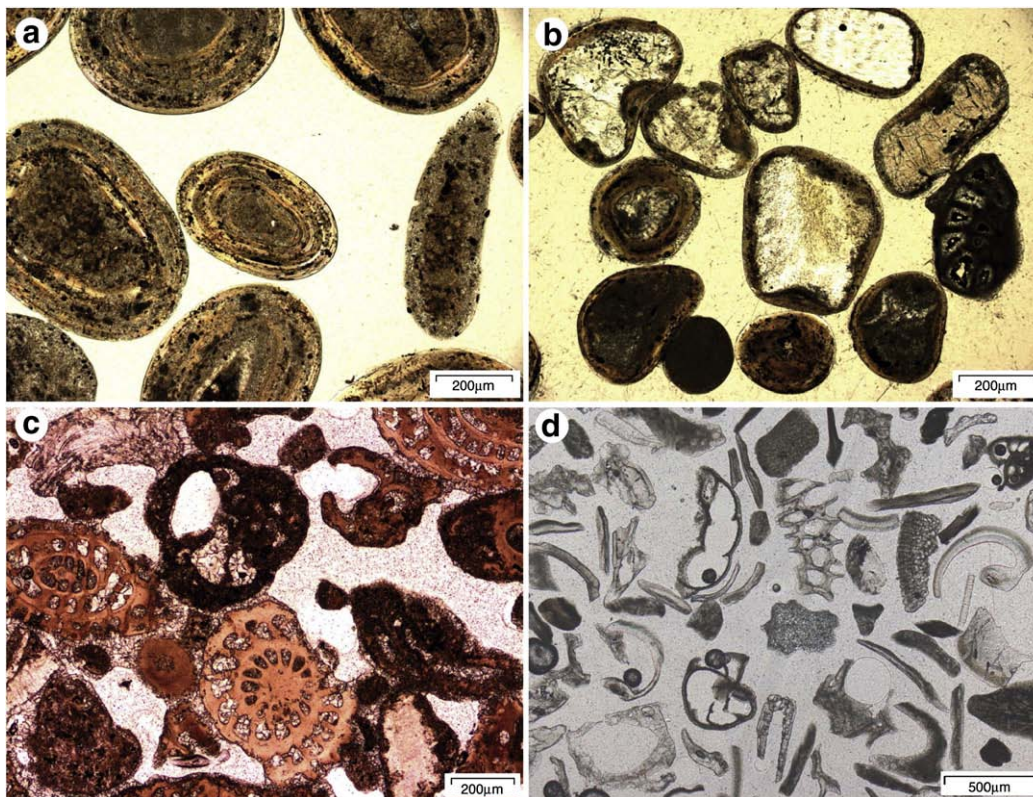


Fig. 1. Photomicrographs of carbonate sands from four different locations. a: Ooid sand from the Bahamas, typically dominated by thick aragonitic cortices surrounding the small nuclei. b: Ooid sand from Abu Dhabi (Persian Gulf) with abundant large nuclei consisting of detrital grains and skeletal components coated by single to few aragonitic laminae. c: Loosely cemented skeletal sand from Florida. The sample is mainly composed of foraminifera and shell debris. The bladed cement fringes on carbonate grains are typical for the marine-phreatic zone of shallow marine settings. d: Carbonate sand from Scotland composed of a wide variety of skeletal debris.

the global marine Mo (see Section 5.2). As a result, changes in the carbonate $\delta^{98/95}\text{Mo}$ do not affect the global oceanic Mo inventory due to mass balance reasons. Compared to the Mo sinks mentioned previously, carbonate rocks could provide a more continuous archive of the Mo isotopic composition of coeval seawater because they were formed throughout most of Earth's history. Their occurrence in a wide variety of sedimentary environments and their diverse composition, from entirely skeletal to non-skeletal, however, complicate their applicability as geochemical proxy. Because the reconstruction of the $\delta^{98/95}\text{Mo}$ evolution of paleo-oceans depends on the identification of seawater archives, such a diversity makes the characterization of carbonates of different origin and kind particularly important. It is thus the purpose of this pilot study to provide a first set of Mo isotope and concentration data on precipitates from modern marine settings in order to assess the range of isotopic signatures, to explore fractionation patterns and to identify possible archives of coeval ocean water. To test whether

carbonates from the geological record hold the potential to preserve the pristine ocean water $\delta^{98/95}\text{Mo}$, Carboniferous samples from two different paleo-geographical settings were analyzed additionally. These samples provide the opportunity to compare trends with those found in the modern ocean and to identify Mo sources which cause diagenetic overprinting.

2. Materials

Pulverized carbonate standards BCS-CRM, 393 limestone and ECRM, 782-1 dolomite were obtained from the Bureau of Analysed Samples, Ltd., Middlesborough, England. Ooid sands from 4 different locations on the Bahamas and two from the Persian Gulf (Abu Dhabi) were chosen to represent non-skeletal precipitates (Fig. 1, Table 1). Skeletal samples include a variety of single specimens as well as two skeletal carbonate sands of different geographical provenance, of

Table 1
Mo isotopic compositions and element data of modern marine sands.

Sample	Description	Coordinates ^a	$\delta^{98/95}\text{Mo}$ (‰)	2σ	$\delta^{98/95}\text{Mo}$ corr. (‰) ^b	$\delta^{98/95}\text{Mo}$ corr. (‰) ^c	Mo (ppm)	Al (ppm)	Ti (ppm)
<i>Sands</i>									
Rz9225e	Ooid sand, Lee Stocking, Bahamas	26°45'N, 76°04'W	2.05	0.05	2.07	2.08	0.038	32	2
TPS1044	Ooid sand, Great Bahama Bank, Bahamas	23°15'N, 78°00'W	1.93	0.06	2.01	2.02	0.026	79	4
RzJC182	Ooid sand, Joulter's Cay, Bahamas	25°30'N, 78°13'W	1.98	0.06	2.18	2.19	0.018	125	6
RzO	Ooid sand, Schooner Cay, Bahamas	24°56'N, 76°26'W	1.87	0.04	2.03	2.01	0.025	146	6
RzAD381	Ooid sand, Abu Dhabi, Persian Gulf	24°28'N, 54°19'E	1.09	0.02	1.54	1.43	0.068	1483	56
RzAD383	Ooid sand, Abu Dhabi, Persian Gulf	24°28'N, 54°19'E	0.95	0.06	1.32	1.10	0.060	1130	25
FLB1A	Carbonate sand, Florida	24°35'N, 81°34'W	1.60	0.05	1.66	1.66	0.043	127	5
Ach-SAND	Carbonate sand, Scotland	58°10'N, 05°18'W	1.57	0.04	-	1.87	0.054	2758	30

^a Determined using Google Earth.

^b Correction based on Al concentrations (see Section 4.2).

^c Correction based on Ti concentrations (see Section 4.2).

temperate as well as tropical regions (Fig. 1, Table 2). The sampled specimens are fresh and very well preserved and show no optical signs of recrystallization or ferromanganese (oxyhydr)oxide coatings. The most prominent evidence for lack of diagenetic alteration is the preservation of their original color. The three investigated corals have retained their original aragonitic mineralogy. In analogy to the modern samples, we produced a dataset of various carbonate materials from the mid and late Carboniferous of two different locations. Detrital micrites, microbial micrites and a number of diagenetic cement phases (= non-skeletal carbonate) to complement the modern ooid sands were analyzed (Fig. 2). Cements and microbial carbonates relate to ooids inasmuch as their precipitation is inorganic or microbially induced and hence not associated with biologically controlled mineral formation. At the same time these non-skeletal phases are more homogenous than oolitic limestones because admixture of skeletal components and detrital grains is avoided.

Carboniferous platform carbonate samples of the late Pennsylvanian (Gzelian) were sampled from outcrops in South Guizhou, China. The hand specimen contains detrital micrite followed by a succession of calcified algal mats and early marine radiaxial fibrous calcite. A second dataset was established on Carboniferous samples from northern Spain. It comprises carbonates from the paleo-slope of a high-rising, microbial boundstone dominated platform of the Sierra del Cuera domain. It nucleated during the early/middle Pennsylvanian (Bashkirian/Moscovian) in a marine foreland basin of the Cantabrian Zone (Bahamonde et al., 2007). Samples include a detrital micrite as well as botryoidal cement, early marine radiaxial fibrous calcite and shallow-burial cement phases (blocky calcite and saddle dolomite). From the more southerly Picos de Europa domain two microbial boundstones consisting of a grey microbial matrix with abundant, massive vug-filling early marine botryoidal cement were analyzed. According to Bahamonde et al. (2007) this lithofacies is characterized by in-situ microbial carbonate mud and microspar which exhibits a clotted peloidal microfabric.

Table 2
Results of Mo analysis of modern, biologically precipitated carbonate samples.

Sample	Description/origin	Coordinates ^a	$\delta^{98/95}\text{Mo}$ (‰)	2 σ	Mo (ppm)
<i>Bivalves</i>					
Flo 116	Florida	24°35'N, 81°34'W	1.36	0.05	0.016
RzAD-1	Oyster, Abu Dhabi, Persian Gulf	24°28'N, 54°19'E	1.39	0.03	0.057
Inv-1	Scotland	58°07'N, 05°15'W	1.59	0.05	0.010
Ach-1	<i>Mytilus</i> , Scotland	58°10'N, 05°18'W	0.93	0.05	0.010
Ach-2	<i>Ensis</i> , Scotland	58°10'N, 05°18'W	2.06	0.04	0.013
Inv-2	<i>Ensis</i> , Scotland	58°07'N, 05°15'W	1.45	0.04	0.018
MCD-3	Indo-Pacific realm	29°57'S, 31°03'E	1.19	0.03	0.072
<i>Gastropods</i>					
Inv-3	Scotland	58°07'N, 05°15'W	0.67	0.06	0.005
Ach-3	<i>Patella</i> , Scotland	58°10'N, 05°18'W	1.54	0.07	0.004
RW-Con	<i>Conus</i> , Indo-Pacific realm	unknown	1.87	0.05	0.026
RW-Nat	<i>Natica</i> , Indo-Pacific realm	unknown	1.54	0.05	0.020
<i>Other</i>					
BA-1	<i>Halimeda</i> , Barbados	13°12'N, 59°30'W	1.79	0.04	0.075
RzB	Brachiopods (<i>T. septentrionalis</i>), Canada	44°45'N, 65°49'W	0.07	0.10	0.117
Serp-305	Serpulid tubes, Abu Dhabi, Persian Gulf	24°28'N, 54°19'E	0.90	0.04	0.120
<i>Corals</i>					
ES-1	Bahamas	22°21'N, 72°57'W	2.02	0.04	0.015
AW-1	Bahamas	23°45'N, 76°04'W	2.19	0.04	0.017
ES-2	Florida	24°35'N, 81°34'W	2.00	0.04	0.028

^a Determined using Google Earth.

3. Analytical methods

3.1. Mo purification and MC-ICPMS analyses

Carboniferous samples were drilled from polished slabs. Prior to dissolution modern skeletal carbonate was cleaned with deionized water. Mo was purified using the separation procedure described in Siebert et al. (2001) and Wille et al. (2007), modified to suit the carbonate matrix and to make the processing of larger amounts of sample possible. Between 0.4 and 6.5 g of material were weighed into screw-top PTFE beakers. To account for Mo isotope fractionation during column separation (Anbar et al., 2001; Siebert et al., 2001) and to resolve instrumental mass bias, a $^{100}\text{Mo} + ^{97}\text{Mo}$ double spike was added prior to dissolution and chemical purification. For a detailed description of the double spike design applied see Siebert et al. (2001). The sample-spike mixture was dissolved in 6.4 M HCl with the addition of H_2O_2 to keep Mo in its highly soluble Mo^{6+} oxygenation state. Once the sample was dissolved, the beaker was closed and placed on a hot plate at 120 °C for 24 h. Subsequently, organic and detrital material was separated from solution by centrifugation. The solution was transferred into another PTFE vial. To ensure complete leaching of Mo, the residue was again boiled in 6.4 M HCl at 120 °C for 24 h. After renewed centrifugation the aliquots were combined and dried on a hot plate. Leaching experiments conducted by Siebert et al. (2003) showed that Mo is extremely soluble even at low acid strength. We therefore refrained from separately extracting the Mo bound to the carbonate fraction from Mo bound to the detrital silicate components and/or organic matter by stepwise leaching. Rather, we ensured total removal of Mo from all constituents, which is particularly important in the context of sample normalization to Al or Ti concentrations, which we used as a proxy of the lithogenic Mo contribution. Complete extraction was tested on leachates as well as residues. The organic and detrital residues of three carbonate rock samples were attacked with 48% HF + 14.4 M HNO_3 (4:1). ICP measurements after repeated column chemistry revealed Mo-intensities below background level. Additionally, the chemistry was tested on Carboniferous matrix micrite DS-A (see Section 4.3) which exhibits the largest detrital contribution of all samples investigated in this study. Analysis of sample splits revealed identical results within error (concentrations and isotopic compositions) after both, HCl and HF/ HNO_3 digestion (Table 3). Thus, the application of the proposed HCl + H_2O_2 digestion is sufficiently effective for the total leaching of Mo from carbonate rocks. The dried sample solutions were redissolved in 6 ml 4 M HCl followed by stepwise loading onto anion exchange columns (1 ml Dowex™ 1X8 resin, 200–400 mesh). Each ml of sample solution is allowed to settle completely into the resin before adding the next fraction. Once loaded, 5 ml 4 M HCl + 0.3% H_2O_2 solution is added for washing and cleaning. Elution of Mo is accomplished with a change in acid from HCl to HNO_3 . First, 2 ml 2 M HNO_3 is used for Fe and Zr elution. Subsequently, 6 ml 2 M HNO_3 is added to extract the Mo fraction, which is collected in PTFE beakers and left to dry on a hot plate. Additionally, a cation exchange column (2 ml Dowex 50WX8™ resin, 200–400 mesh) was used to remove any residual iron. The dried Mo fraction, obtained from anion chemistry, is redissolved in a solution of 2 ml 0.5 M HCl + 0.1% H_2O_2 and loaded onto the column in two steps of 1 ml each which are both collected in PTFE beakers. The remaining Mo is eluted with a solution of 4 ml 0.5 M HCl + 0.1% H_2O_2 and collected in the same beaker. Finally, the dried down purified Mo fraction is taken up in 0.5 M HNO_3 for ICPMS measurement. All data were produced on a double-focusing MC-ICPMS as described in the protocol of Siebert et al. (2001) except for the sample introduction which was done using an Apex™ desolvating nebulizer. The isotopic composition is measured relative to a standard solution (Johnson Matthews, 1000 $\mu\text{g}/\text{ml}$ ($\pm 0.3\%$) ICP standard solution, lot 602332B). Final Mo isotopic data are reported as $\delta^{98/95}\text{Mo} = [({}^{98}\text{Mo}/{}^{95}\text{Mo})_{\text{Sample}} / ({}^{98}\text{Mo}/{}^{95}\text{Mo})_{\text{Standard}} - 1] \times 10^3$. Data presented were acquired with a preferred

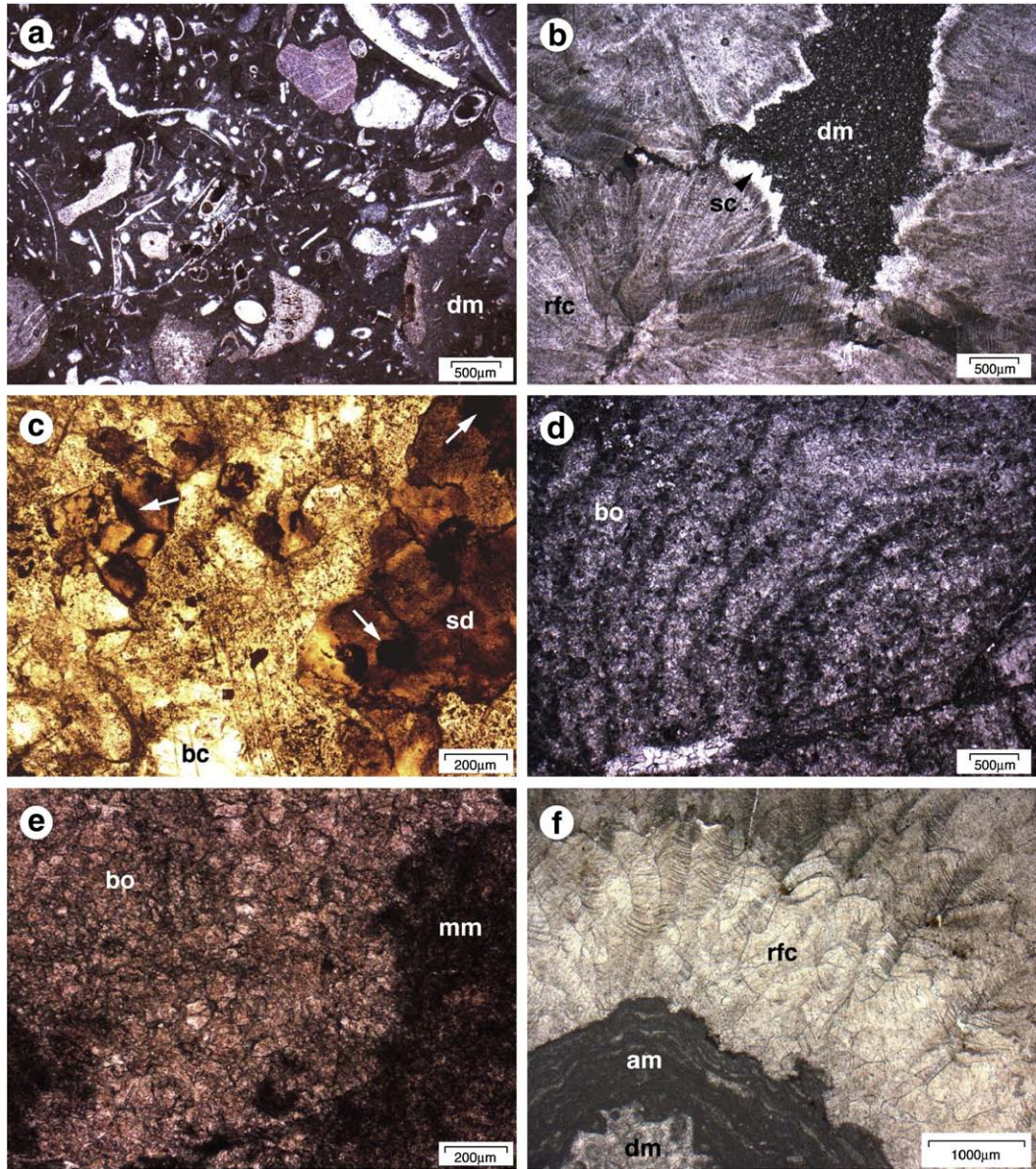


Fig. 2. Photomicrographs of Carboniferous cement and matrix samples from Spain (a–e) and China (f). Samples a–c belong to the red stained facies of the Sierra del Cuera domain. a: Red stained detrital biomicritic matrix (dm, sample DS-A). b: Cavities within the red stained micrite (dm) are filled with fluid inclusion-rich, early marine radial fibrous calcite cement (rfc, sample DS-B). The syntaxial encrustations of scalenohedral calcite (sc) are interpreted to reflect a change from marine to shallow-burial diagenesis (Van der Kooij et al., 2007). c: The burial diagenetic blocky calcite (bc) is partly replaced by fluid inclusion-rich (arrows) saddle dolomite (sd). These two cement phases are combined in sample DS-D and DS-D3. d: Botryoidal cement (bo) from the Sierra del Cuera platform (sample SA3A). e: Botryoidal cement (bo) and microbial micrite (mm) of the Picos de Europa domain. f: Photomicrograph showing the detrital and non-skeletal phases of sample ZSG-2. The detrital matrix micrite (dm) is succeeded by calcified algal mats (am) and multiple layers of well preserved early marine radial fibrous calcite.

quantity of ≥ 60 ng and a minimum of 20 ng of Mo in solution. A blank sample was run with every separation chemistry. Total Mo-blank of the procedure is < 2 ng with occasional outliers at < 3 ng.

3.2. Elements and light stable isotopes

Element concentrations of Carboniferous as well as carbonate sand samples were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) at the Laurentian University, Sudbury, Canada. 10 mg of sample was digested in PTFE beakers in a mixture of concentrated HF (0.5 ml) and HNO₃ (0.25 ml) at 140 °C during 72 h. After evaporation samples were converted twice in concentrated HNO₃, centrifuged and then diluted to 2% HNO₃ for ICP measurements. The two USGS standards BHVO-2 and BCR-2 used for standardization indicate a long-term precision better than 2%. Ooid

samples (Persian Gulf, RzO and RzJC182) were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) at the University of Strasbourg, France. 30 mg of carbonate material were digested in 4 ml 6 M HCl at 105 °C during 48 h. After evaporation samples were digested in hot (70 °C) 0.5 ml concentrated HF + 1 ml 6 M HCl during 24 h. For ICP measurement the samples are diluted in

Table 3
Results of leaching experiments on two splits of Carboniferous, detritus rich sample DS-A (red matrix micrite).

Sample	Method of digestion	$\delta^{98/95}\text{Mo}$ (‰)	2 σ	Mo (ppm)
DS-A1	Red matrix, conc. HF/HNO ₃ digestion	-0.95	0.03	0.591
DS-A2	Red matrix, conc. HCl-leach	-1.01	0.04	0.558

Table 4Results of dolomite and limestone standard measurements; $\delta^{98/95}\text{Mo}$ relative to our in-house standard (J&M standard solution, Siebert et al., 2001).

	$\delta^{98/95}\text{Mo}$ (‰)	$2\sigma^a$	Mo (ppm)		$\delta^{98/95}\text{Mo}$ (‰)	$2\sigma^a$	Mo (ppm)
Dolomite standard ECRM 782-1				Limestone standard BSC-CRM 393			
# 1	0.16	0.10	0.113	# 1	0.99	0.04	0.077
# 2	0.16	0.04	0.116	# 2	0.90	0.03	0.073
# 3	0.18	0.04	0.114	# 3	0.95	0.05	0.076
# 4	0.18	0.04	0.158	# 4	0.98	0.04	0.073
# 5	0.07	0.06	0.113	# 5	0.92	0.04	0.075
# 6	0.23	0.03	0.118	# 6	1.03	0.11	0.072
# 7	0.15	0.07	0.100	# 7	0.98	0.05	0.075
# 8	0.14	0.04	0.107	# 8	0.92	0.04	0.073
# 9	0.26	0.04	0.106				
Avg.	0.17	0.11 ^b	0.120	Avg.	0.96	0.09 ^b	0.074

^a 2 s. error of individual measurements.^b 2 σ external reproducibility.

1 N HNO₃. The analytical long-term precision of the procedure is <10% (1 σ). The stable carbon (C) and oxygen (O) isotope compositions were measured on a Finnigan Delta V Advantage mass spectrometer equipped with an automated carbonate preparation system (Gas Bench-II) at the University of Bern. Results are reported as $\delta^{18}\text{O} = [({}^{18}\text{O}/{}^{16}\text{O})_{\text{Sample}} / ({}^{18}\text{O}/{}^{16}\text{O})_{\text{Standard}} - 1] \times 10^3$ and $\delta^{13}\text{C} = [({}^{13}\text{C}/{}^{12}\text{C})_{\text{Sample}} / ({}^{13}\text{C}/{}^{12}\text{C})_{\text{Standard}} - 1] \times 10^3$ relative to the VPDB standard. Standardization was accomplished using international standards NBS 19, NBS 18 and an in-house standard. The long-term precision of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ is 0.052‰ and 0.063‰ (1 σ ; $n = 1156$) respectively.

3.3. Correction for detrital Mo contribution

Because the Mo content of carbonate rocks is well below the average continental input value of ca. 1 ppm, the dilution of the Mo signature by detritus needs to be monitored. The average input signature has been approximated by analyses of detrital sediments, volcanics and granites, which have yielded values between -0.1 and 0.3‰ (Siebert et al., 2003). The same range of values was found in oxic limnic sediments which are considered to be of detrital origin (Nägler et al., 2005). Regardless of which of these input signatures are used to perform a detrital correction the results are mostly within the measurement uncertainty. This is due to the near absence of detritus in most samples. We applied a detritus correction assuming a Mo concentration of 1.1 ppm, upper crustal Al₂O₃ and TiO₂ concentrations of 15.4 wt.% and 0.64 wt.%, respectively (all

values from Rudnick and Gao, 2004), and a Mo isotopic composition of 0.0‰. The detrital Mo concentration, Mo_{det}, is then given by Mo_{det} = [(Mo/X)_{crust} · X_{tot}], where X = Al or Ti. The authigenic Mo concentration is Mo_{auth} = [Mo_{tot} - Mo_{det}] and its isotopic composition is $\delta^{98/95}\text{Mo}_{\text{auth}} = [(\delta^{98/95}\text{Mo}_{\text{tot}} \cdot \text{Mo}_{\text{tot}} - \delta^{98/95}\text{Mo}_{\text{det}} \cdot \text{Mo}_{\text{det}}) / \text{Mo}_{\text{auth}}]$. Aluminum concentrations in carbonates can overestimate the terrigenous component of sediments if Al scavenging from seawater occurs during particle settling, a process that results in a high Al/Ti ratio (Murray and Leinen, 1996). To get good constraints on the detrital contribution to our samples we recalculated all $\delta^{98/95}\text{Mo}$ values based on both Al and Ti contents. Nearly identical values were found for most samples using either of the two element corrections. For samples with a high Al/Ti ratio the Ti content was considered to be a more accurate representation of the detrital contamination.

4. Results

4.1. Carbonate standard measurements

Considering that the Mo isotope fractionation in nature is limited to a few permil, the resolution and precision necessary to obtain paleo-oceanographically meaningful results should ideally be at $\pm 0.1\%$ or below. Compared to Fe–Mn crusts and black shales with concentrations in the order of 1–1000 ppm, carbonate rocks are very poor in Mo with concentrations mostly $\ll 1$ ppm. The reproducibility of Mo fractionation

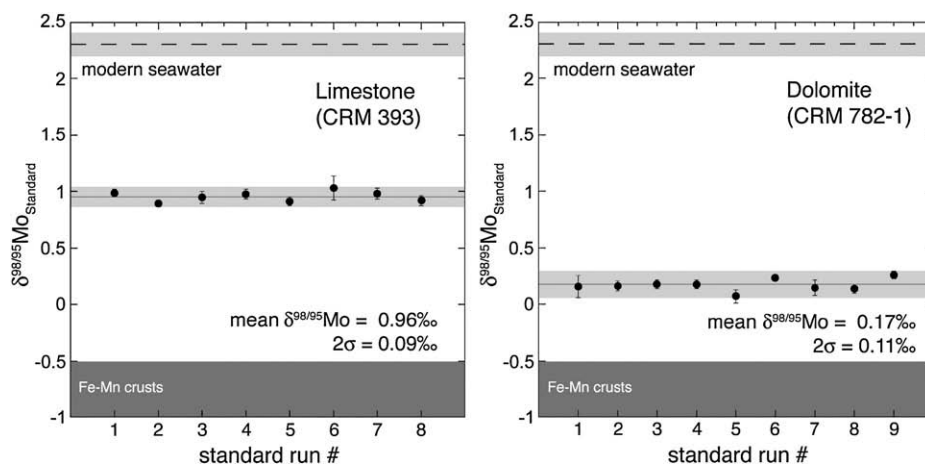


Fig. 3. Plot of the $\delta^{98/95}\text{Mo}$ ratio of the commercial dolomite and limestone standards vs. sample run. Light shaded areas: external reproducibility (2σ) of standard measurements (this study) and modern ocean water (after Siebert et al., 2003). Ocean water homogeneity was confirmed by Nakagawa et al. (2008). Their absolute value of $2.45 \pm 0.11\%$ (2σ) cannot, however, be directly compared to Siebert et al. (2003), as different standard lots were used. Dark shaded area: natural $\delta^{98/95}\text{Mo}$ variability of Cenozoic Fe–Mn crusts after Siebert et al. (2003). The range of the ordinate axes (-1.0 to 2.5‰) covers the same range as in Figs. 4, 5 and 6a.

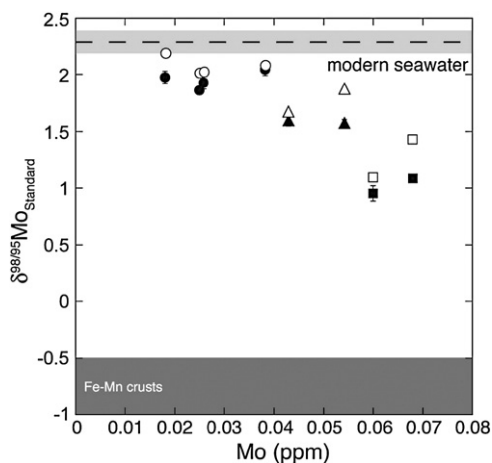


Fig. 4. Mo isotope and concentration data of modern carbonate sands. Circles = Bahamas, triangles = Scotland and Florida, squares = Abu Dhabi (Persian Gulf), open symbols = values corrected for detrital contribution based on Ti. All other labellings are as specified in Fig. 3.

and concentration data was tested by repeated analyses of two commercially available powdered carbonate standards (Table 4, Fig. 3). For these reference materials, major element analysis was available, but neither Mo concentrations nor isotopic compositions. Uncertainties of individual measurements and external reproducibilities are given as 2 standard deviation (2σ). The dolomite measurements ($n=9$) show a $\delta^{98/95}\text{Mo}$ value of $0.17\text{‰} \pm 0.11\text{‰}$ with a mean concentration of $0.17 \text{ ppm} \pm 0.04 \text{ ppm}$. The limestone standard measurements ($n=8$) resulted in a $\delta^{98/95}\text{Mo}$ value of $0.96\text{‰} \pm 0.09\text{‰}$ and a concentration of $0.074 \text{ ppm} \pm 0.004 \text{ ppm}$. The external reproducibility of the separately processed sample replicates ($\pm 0.1\text{‰}$) is the same as that of high concentrated geological samples and only slightly inferior to that of the pure Mo standard solution previously analyzed in our lab ($\pm 0.06\text{‰}$; Siebert et al., 2001, 2003).

4.2. Modern samples

4.2.1. Modern carbonate sands

Mo concentration and isotopic composition data as well as chemical data of modern sands are listed in Table 1 and shown in Fig. 4. Mo concentrations of ooid sands originating from the Bahamas are generally low with values between 0.02 ppm and 0.04 ppm. Their isotopic composition is heavy with values between 1.87 and 2.05‰. Al and Ti concentrations range from 32–146 ppm and 2–6 ppm, respectively. Mo isotopic data show an offset of roughly 1‰ between samples from the Bahamas and those from the Persian Gulf. The latter are isotopically lighter with $\delta^{98/95}\text{Mo}$ values of 1.09 and 0.95‰. Also, they are more enriched in Al (1100–1500 ppm) and Ti (25–60 ppm). All data from ooid sands referred to later on in this work are corrected for detrital Mo contamination (Section 3.3). Their corrected $\delta^{98/95}\text{Mo}$ values are up to 0.35‰ heavier. The Bahamian ooid samples are shifted to values which closely reflect modern ocean water Mo composition (2–2.2‰), with values between 1.1 and 1.6‰ the ooids from the Persian Gulf are still considerably lighter. Skeletal carbonate sands were collected from Florida and Scotland. The two samples have low Mo concentrations (0.05 and 0.04 ppm) and an identical isotopic composition of 1.6‰, intermediate between the heavy Bahamian and the lighter Persian Gulf ooid sands. Al and Ti concentrations are variable with values of 127 and 5 ppm (Florida) and 2758 and 30 ppm (Scotland).

4.2.2. Modern skeletal carbonates

Mo concentration and isotopic data are listed in Table 2 and shown in Fig. 5. Mo concentrations of a selection of modern skeletal organisms are equally low or even lower compared to those of the

carbonate sands with contents of 0.004 ppm to 0.12 ppm. Their isotopic compositions are strongly variable with values between 0.07 and 2.19‰. While bivalves and gastropods show no distinct signature, the corals show a very narrow range of $\delta^{98/95}\text{Mo}$ values between 2 and 2.2‰ coupled with a nearly uniform Mo content (0.02–0.03 ppm).

4.3. Carboniferous cements and micrites

Carboniferous samples yield strongly variable isotopic compositions (Table 5, Fig. 6). There are, however, distinct differences between the behavior of the Mo isotopic system in the late Carboniferous of China and the mid Carboniferous of Spain.

Both cement generations and the calcitized algal mats from China are isotopically heavy with $\delta^{98/95}\text{Mo}$ values of 2 to 2.3‰. The corresponding matrix micrite has a $\delta^{98/95}\text{Mo}$ signature of 0.85‰. Mo values range from 0.13 and 0.26 ppm. Al and Ti concentrations of cements and micrites from China are invariably low (30–100 ppm, <8 ppm). $\delta^{18}\text{O}$ compositions show minor variations (–2.7 to –4.4‰), $\delta^{13}\text{C}$ values scatter between –1.00 and 0.1‰. Fe and Mn concentrations are also uniform with values ranging from 1125–1194 ppm and 99–239 ppm, respectively (Table 5).

The matrix micrites and cement phases from Spain cover a much larger spectrum of $\delta^{98/95}\text{Mo}$ values. The red detrital matrix micrite from the Sierra del Cuera domain exhibits overall the lightest isotopic composition and compares well with the lightest values found in the modern marine realm, i.e. in ferromanganese crusts. Analyses on two different sample splits have revealed indistinguishable isotopic compositions of –0.91 to –1.01‰ and concentrations between 0.2 and 0.6 ppm. The closely associated, early marine radial fibrous calcite and the shallow-burial cements are heavier with isotopic compositions between –0.42 and –0.22‰ and contain less Mo (0.05 to 0.13 ppm). A botryoidal cement from the same area yields a $\delta^{98/95}\text{Mo}$ of 1.67‰ which is the heaviest value found in the Spanish sample set. Its Mo concentration is more elevated (0.26 ppm) compared to that of the other cements of this domain. Isotopic compositions of grey microbial micrites and associated cements from the nearby Picos de Europa domain overlap with those from the Sierra del Cuera domain ($\delta^{98/95}\text{Mo} = -0.56$ to 1.02‰). Mo concentrations are on average lower with values of 0.01 to 0.02 ppm (cements) and 0.06 to 0.1 ppm (micrites). Al and Ti concentrations of samples from both domains (23–305 ppm, <9 ppm) indicate a minor contribution of detrital Mo. The only exception is the red matrix micrite with a high Al concentration of around 15,000 ppm and 136 ppm Ti. $\delta^{18}\text{O}$ compositions show a large spread between –8.5‰ and 0.16‰, $\delta^{13}\text{C}$ values range

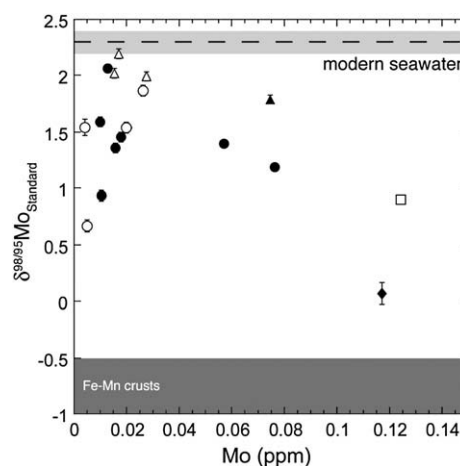


Fig. 5. Mo isotope and concentration data of modern biologically precipitated carbonates. Open circles = gastropods, filled circles = bivalves, open triangles = corals, filled triangle = calcareous algae (*Halimeda*), diamond = brachiopod (*T. septentrionalis*), open square = serpulid tubes. All other labellings are as specified in Fig. 3.

Table 5
Isotopic and chemical composition of Carboniferous samples from China and Spain.

Sample	Description	Coordinates ^a	$\delta^{98/95}\text{Mo}$ (‰)	2 σ	$\delta^{98/95}\text{Mo}$ corr. ^b (‰)	$\delta^{98/95}\text{Mo}$ corr. ^c (‰)	Mo (ppm)	Fe (ppm)	Mn (ppm)	Al (ppm)	Ti (ppm)	$\delta^{18}\text{O}$ (‰ PDB)	$\delta^{13}\text{C}$ (‰ PDB)
Gzhelian, China		25°30'N, 106°10'E											
ZS6-2-1	Grey detrital matrix micrite		0.84	0.05	0.85	0.85	0.132	1125	116	103	8	-3.45	0.84
ZS6-2-1 ^d			0.85	0.05	—	—	0.175	—	—	—	—	—	—
ZS6-2-2	Calcitized algal mats		2.03	0.04	2.04	2.04	0.262	1186	239	42	3	-2.74	0.61
ZS6-2-3	Radial fibrous calcite cement Earlier generation		2.32	0.03	2.32	2.32	0.440	1592	169	29	1	-3.55	0.23
ZS6-2-3 ^d			2.16	0.06	—	—	0.385	—	—	—	—	—	—
ZS6-2-4	Radial fibrous calcite cement Later generation		2.18	0.03	2.19	2.20	0.253	1194	99	100	7	-4.39	-1.00
Bashkirian/Moscovian, Sierra del Cuera domain, Spain		43°21'N, 04°49'W											
DS-A	Red detrital matrix micrite		-0.91	0.04	—	-1.14	0.200	5357	222	15,257	136	-0.28	5.40
DS-B	Radial fibrous calcite cement		-0.30	0.05	-0.30	-0.30	0.052	1061	208	45	1	-0.53	5.13
DS-D	Shallow-burial diagenetic cement		-0.42	0.05	-0.42	-0.42	0.127	2874	389	23	1	-4.12	6.36
DS-D3	Shallow-burial diagenetic cement		-0.22	0.04	—	—	0.065	—	—	—	—	-8.28	5.31
SA3A	Botryoidal cement		1.67	0.03	1.69	1.68	0.255	1257	207	305	9	-3.52	4.45
Picos de Europa Domain, Spain		43°11'N, 01°49'W											
NB2A-Z	Botryoidal cement		-0.56	0.04	-0.59	-0.59	0.006	1060	42	26	1	-7.29	3.69
NB2A-S	Grey microbial matrix micrite		-0.47	0.06	-0.48	-0.48	0.105	1019	41	101	4	-8.43	3.62
NB9A-Z	Botryoidal cement		1.02	0.07	—	—	0.019	—	—	—	—	-6.20	4.04
NB9A-S	Grey microbial matrix micrite		0.18	0.05	—	—	0.044	—	—	—	—	-8.37	4.04

^a Determined using Google Earth.

^b Correction based on Al concentrations (see Section 4.2).

^c Correction based on Ti concentrations (see Section 4.2).

^d 2nd analyses.

from 3.6 to 5.6‰. Most cements and matrix micrites have very similar Fe and Mn concentrations with some variations between the two domains. Fe concentrations range from 1060 to 5357 ppm, with the highest concentrations found in the red matrix micrite and the burial diagenetic cement phases. The latter also has a higher Mn concentration (ca. 400 ppm) while the remainder of the Sierra del Cuera samples yield values that are similar to those found in the Chinese

samples. Both, cements and micrites from the Picos de Europa domain are more depleted in Mn with concentrations of around 40 ppm. (Table 5).

The low Al and Ti concentrations of most analyzed cements and micrites from both China and Spain renders the detrital Mo component insignificant relative to the analytical uncertainty of the isotope analyses (calculated $\text{Mo}_{\text{det}} < 6\%$ of Mo_{tot}) and a correction was

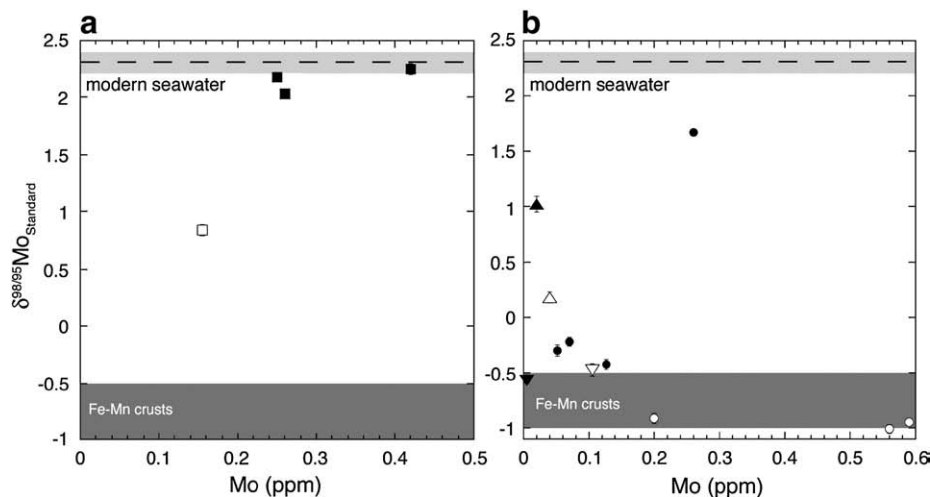


Fig. 6. Mo isotope and concentration data of Carboniferous cement and micrite samples. a: Samples from China: open square = detrital micrites, filled squares = marine cements and calcitized algal mats. b: Samples from Spain: circles = Sierra del Cuera, triangles = Picos de Europa (upright: NB2A, reversed: NB9A). Filled symbols = cements, and open symbols = matrix micrites (detrital micrite in the Sierra del Cuera domain, microbial origin in the Picos de Europa domain). Note that the two red matrix micrite analyses listed in Table 3 have been included in b. All other labellings are as specified in Fig. 3.

not applied. Red matrix micrite DS-A from Spain is the only sample where a correction is relevant due to its high Al and Ti concentrations.

5. Discussion

5.1. Modern skeletal and non-skeletal material

The consistently heavy $\delta^{98/95}\text{Mo}$ values (detritus corrected) stored in Bahamian ooid sands very closely approach modern ocean water values. Ooids typically consist of aragonite and/or calcite fibres enveloping a nucleus of calcareous or non-calcareous debris. They have been used as representative of inorganic precipitates and non-skeletal carbonates in general (e.g. Sandberg, 1983; Steuber and Buhl, 2006). In the case of the Bahamian samples, the ooids are made of thick aragonitic cortices and exhibit a minor contribution of bioclastic and detrital grains (Fig. 1). Hence, they are considered to be close representatives of pure non-skeletal carbonate. Their small to inexistent offset from ambient seawater is the first and most important observation because it implies that Mo uptake into non-skeletal carbonate is accompanied by negligible Mo fractionation. This latter process characterizes ooids (and thus carbonates precipitated without biological control, i.e. cement phases and non-skeletal carbonate in general) as potential archives of the Mo isotopic composition of coeval ocean water. Marine sediments with little or no Mo isotopic fractionation have thus been observed in two very different settings; sediments deposited under strongly euxinic conditions and oxic non-skeletal carbonates. This requires two distinct pathways of Mo uptake. On the one hand, sediments deposited under euxinic conditions with $\delta^{98/95}\text{Mo}$ values similar to seawater are generated through complete scavenging from waters with $\text{H}_2\text{S}_{\text{aq}} > 11 \mu\text{M}$ (Neubert et al., 2008). On the other hand, the small to inexistent isotope fractionation during Mo uptake into oxic, non-skeletal precipitates occurs with negligible Mo removal from the water column.

In contrast, all other investigated carbonate sands show an offset between 0.5 to 1‰ from ocean water (Fig. 4). This trend can be traced back to two main factors: detrital components and admixture of skeletal debris. Considering the remarkably low Mo concentrations of the carbonate sands (0.02–0.06 ppm), the amount of lithogenic and authigenic Mo and its influence on the isotopic composition are important. With an average Mo concentration of 1 ppm the continental input is over an order of magnitude richer in Mo compared to the carbonate sands. Hence, the admixture of detrital particles introduces detectable concentrations of isotopically lighter Mo to the samples (assumed $\delta^{98/95}\text{Mo}_{\text{det}} = 0.0\%$). This is illustrated by detrital grains which form the nuclei of ooids from the Persian Gulf. This detrital component is also reflected in the Al and Ti, as well as in the Mo concentrations, the latter being roughly three times higher in the samples from the Persian Gulf compared to those from the Bahamas. A correction based on Al and Ti concentrations (Section 3.3) demonstrates, however, that the lithogenic contamination cannot be the sole source of light Mo. In addition to detrital grains, skeletal fragments make up for a large fraction of the Persian Gulf ooids, the sands from Scotland and Florida consist almost entirely of skeletal carbonate (Fig. 1). This suggests vital effects as the most likely cause for the remaining offset, because many marine organisms are known to actively control their carbonate shell precipitation (Weiner and Dove, 2003). Consequently, organisms influence the trace element and isotopic compositions of the minerals they form (Lowenstam, 1981) and ocean water values are either shifted or completely obliterated. The large scatter in $\delta^{98/95}\text{Mo}$ of modern skeletal carbonates of different origin and kind therefore suggests biologically controlled fractionation accompanied by preferential uptake of light isotopes, analogous to the isotopic systems of e.g. O and C. Due to the essential role of Mo in biological pathways, namely in the cycling of N, S and C (Howarth and Cole, 1985; Cole et al., 1993; Mendel and Bittner, 2006) such a fractionation mechanism seems plausible. Because in

most cases bulk specimens were analyzed, intra-shell variations can be excluded as possible cause. No specific $\delta^{98/95}\text{Mo}$ patterns become evident from the samples analyzed. In particular, there is no evidence for systematic changes connected to their mineralogy (aragonite vs. calcite). Corals are the only organisms investigated that show a constantly small offset from ocean water in the range of 0.1 to 0.3‰. Oxide encrustations on detrital grains and skeletal components of the carbonate sands are an additional potential source of isotopically light Mo.

We are aware that the data presented only encompass a small range of specimens from a few locations and that much more detailed investigation is necessary to understand these non-equilibrium values (e.g. species-specific and origin-specific factors). But even so, the recognition of vital effects is crucial for the use of carbonates as ocean water Mo proxy because skeletal grains add to the content of many limestones, some are entirely composed of calcifying organisms. The observed variability thus imposes limitations on the interpretation of the Mo signature stored in carbonates from paleo-environments. Unless future studies can identify species which, with respect to Mo, precipitate their skeletons in equilibrium with ocean water or at least show a constant biogenic fractionation, skeletal carbonates cannot be a reliable ocean water proxy. Insofar, corals are the only organisms identified which potentially meet the requirements to be a Mo archive of bygone oceans. However, further studies will have to investigate whether the Mo isotope ratio is preserved during recrystallization from aragonite to calcite.

5.2. Role of carbonates in the global Mo cycle, possibilities and limitations

The strikingly low concentrations emphasize a passive role of carbonate precipitates in the global Mo cycle. Changing rates of high concentration black shale sedimentation cause fluctuations in the marine Mo inventory and its Mo isotopic composition on a local to global scale. Relative to the total Mo riverine input of $1.8 \times 10^8 \text{ mol a}^{-1}$ (i.e. approximate total sink under steady state conditions) Morford and Emerson (1999) calculated that carbonate rocks (sedimented below 1000 m) host 10% of the total marine Mo. However, this value is based on the definition of carbonates as rocks with $>30\%$ CaCO_3 and an average concentration of 1.1 ppm. These authors assumed the pure carbonate Mo concentration to be close to 0.1 ppm, which is in agreement with the findings of the present study. The recalculated Mo flux then reveals a much more limited role of the (pure) carbonate sink, responsible for only ca. 1% of the total marine Mo removal. An equally low Mo incorporation into carbonates is inferred using a total carbonate accumulation rate of $18\text{--}20 \times 10^{12} \text{ mol a}^{-1}$ (Wallmann, 2001, and references therein). If CaCO_3 export and dissolution are taken into account additionally, the total (Holocene) carbonate burial becomes as low as $1 \times 10^{12} \text{ mol a}^{-1}$ (Berelson et al., 2007), suggesting that carbonates store as little as 0.1% of the total marine Mo. Thus, regarding the overall removal of Mo from the marine environment the role of the carbonate sink is insignificant and does not affect the global Mo inventory. It is the combination of low concentration and minor fractionation together with the independence from local redox conditions that creates the potential for non-skeletal carbonates to be monitors of seawater, unless diagenetically altered fluids contribute significant amounts of Mo. In the ideal case they may reflect the pristine ocean water Mo composition of paleo-oceans. These low concentrations, however, also put some analytical limits on the use of carbonates. The amount of sample needed (up to a few grams) complicates the investigation of single carbonate phases and constrains sampling resolution because inhomogeneities that potentially add Mo from a different source cannot be entirely accounted for. Consequently, a thorough petrographical and geochemical analysis of the degree of authigenic and lithogenic Mo accumulation is required because primary ocean water signatures can readily be masked.

5.3. Mo isotope patterns in Carboniferous carbonates

Carboniferous skeletal and non-skeletal samples from two different paleo-geographical settings were analyzed to test the potential of Mo isotope data of carbonates to allow reliable inferences on the coeval seawater composition. The sampled material is very well suited to explore systematics of the Mo signature and diagenetic features. They are very well preserved and sizeable, which allows the investigation of single phases rather than a mixture of detrital, skeletal and non-skeletal components. The focus of this investigation lies on characterizing fractionation patterns and identifying sources that influence the $\delta^{98/95}\text{Mo}$ of a given sample. The Mo isotopic composition of the Carboniferous ocean has not previously been investigated. Therefore, the discussion will stress the questions how closely the late Carboniferous carbonate samples preserve a seawater Mo isotope value and most importantly what the implications for the future use of the proxy are.

5.3.1. Mo isotopic composition of samples from China

The $\delta^{98/95}\text{Mo}$ values in the range of 2 to 2.3‰ of cements and calcified algal mats of China approach the isotopic composition of modern ocean water. Considering that to date no open marine Mo reservoir, particularly no carbonate, with an isotopic composition heavier than ocean water has been found, it seems reasonable to assume that the heavy signature recorded by the non-skeletal phases represents at least a reliable minimum estimate for the late Carboniferous ocean. This suggests that oxic marine sedimentation had increased considerably since the early Cambrian (Lehmann et al., 2007) and that conditions similar to today could have prevailed in the late Carboniferous. The combined results of sedimentological, petrographical and geochemical observations point to ocean water as the main fluid source for cement precipitation. The depositional setting is comparable to that of the Bahamas, where small Mo fractionation was observed between ocean water and non-skeletal carbonates. In analogy, cement precipitation and algal mat calcification in the Chinese paleo-environment is interpreted to have occurred in an open marine platform setting (Gong et al., 2007). The intense seawater circulation required for the syndimentary cement formation onto the ocean-floor substrate would have constantly replenished the Mo supply to the precipitating carbonate and thus ensured isotopically heavy ocean water as the dominant Mo source. In addition, the radial fibrous calcite cements are typically of early marine origin and thin section analysis has revealed no indication of burial diagenetic or meteoric conditions during recrystallization. The oxygen isotopic compositions are in the range of values reflecting precipitation from the Carboniferous ocean water (Popp et al., 1986) and Mn does not show elevated values typical for increasingly anoxic conditions during progressive diagenesis. The $\delta^{98/95}\text{Mo}$ offset between the heavy cements and the detrital matrix micrite can readily be understood considering the genesis of the latter. Such allochthonous sediments are a mixture of calcareous and non-calcareous debris (e.g. destruction of skeletons, erosion of lithified carbonates; Flügel, 2004). Therefore they represent a geochemical mixture of the contributing sediment sources rather than the Mo isotopic composition of the ambient fluid. Thus, Mo derived from an outside source is the straightforward explanation for the lighter signature compared to the heavy, in-situ precipitated non-skeletal phases.

5.3.2. Cements and matrix micrites from Spain

The diagenetic history of the Sierra del Cuera limestones has been thoroughly studied by Immenhauser et al. (2002), including light stable isotopes analysis ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) of skeletal and non-skeletal phases. The samples were interpreted to be of marine and shallow-burial origin. Their $\delta^{13}\text{C}$ values are in the range of Carboniferous open ocean seawater (Bruckschen et al., 1998), variable oxygen isotopic compositions of matrix micrites and brachiopods were mainly

attributed to a temperature gradient between basinal and platform water masses (Immenhauser et al., 2002). Our light stable isotope measurements on Mo sample splits as well as of various sub-samples are in accordance with their model. Despite the fact that these geochemical parameters identify ocean water as the dominant fluid source of cement and micrite precipitation and stabilization, the samples analyzed show a broad range of $\delta^{98/95}\text{Mo}$. Their isotopic compositions nearly cover the whole range of Mo values so far recognized in the marine environment and hence an authigenic Mo accumulation process is suggested which, to varying degrees, overprinted the pristine Mo seawater signature.

The most likely source of authigenically formed Mo in the Sierra del Cuera area is the matrix micrite DS-A. The red staining is the result of early diagenetic processes in suboxic porewaters below the sediment surface involving iron-oxidizing bacteria (Van der Kooij et al., 2007). The dispersion of submicrometric hematite was found to be responsible for the red pigmentation (Mamet and Pr eat, 2006). This, and the occurrence of a variety of Fe-(hydr)oxide encrustations (Della Porta et al., 2003; Mamet and Pr eat, 2006), link the light isotopic Mo signature of the sediment (-0.9 to -1.0%) to Mo isotope fractionation during adsorption to Fe-(hydr)oxide surfaces. Fe-(oxyhydr)oxides, in analogy to ferromanganese crusts, adsorb Mo and are associated with the preferential uptake of light isotopes (Goldberg et al., submitted for publication). The latter study shows that Mo fractionation between the solid and the dissolved phase ($\Delta^{98}\text{Mo}$) varies with mineralogy, whereby hematite exhibits the largest offset from the solution ($\Delta^{98}\text{Mo} = 2.19 \pm 0.27\%$). Consequently, our data suggest that the mid Carboniferous ocean might have had an isotopic composition of around 1.3‰. However, the uncertainty is large and the isotopic composition of the heaviest coeval, non-skeletal carbonate sample SA3A ($\delta^{98/95}\text{Mo} = 1.67\%$) is a better constraint of the minimum value of the ambient ocean water Mo composition.

The value of 1.3‰ can only be regarded as an approximation of the true seawater signature as additional factors have to be considered. The reconstruction relies on the identification of Fe-(hydr)oxides as the all-dominant Mo contributor to the red matrix micrite. Lithogenic material and the increased clay fraction as observed by Van der Kooij et al. (2007), however, are an additional source of Mo. The correction for the detrital contribution based on Ti results in a $\delta^{98/95}\text{Mo}$ of -1.14% . There are as of yet no data on the isotopic composition of clay minerals, and thus a quantitative estimate of their influence on the isotopic composition is not possible. However, in their experimental study on Mo adsorption to a variety of clays and hematite Goldberg et al. (1996) demonstrated that adsorption to hematite is much stronger and occurs over a broader pH-range. Most notably, above a pH of 7 adsorption to clays is virtually zero whereas comparably strong adsorption still occurs to hematite. As a first order approach we therefore hypothesize that the Mo adsorbed to hematite dominates over the clay bound Mo and thus authigenically formed Fe-(hydr)oxides are proposed as the main Mo source. The assumption of a single dominant source is further supported by the $\delta^{98/95}\text{Mo}$ values of the two sample aliquots DS-A and DS-A1. They exhibit identical isotopic signatures, but their Mo concentrations vary by a factor of 3 (0.2 and 0.6 ppm, respectively). This can be explained either by different modal abundances of one single source or by the presence of two sources, which need to have the same isotopic composition.

Diagenetic remobilization of authigenic Mn under changing redox conditions has been proposed to affect Mo isotope fractionation. This process has shown to generate $\delta^{98/95}\text{Mo}$ values which are even lighter than those found in modern ferromanganese oxides (Reitz et al., 2007). Consequently, we cannot exclude the possibility that a similar process involving Fe-(hydr)oxides has influenced the Mo isotopic composition of the red matrix micrite.

The Fe-(hydr)oxide derived Mo seems to not only control the isotopic composition of the red matrix, but also affect the signature of cement and microbial micrite phases of both the Sierra del Cuera as well as the Picos de Europa domain. This could be a valid explanation

for the large $\delta^{98/95}\text{Mo}$ scatter of samples from both areas and particularly for the negative signatures observed in some of the non-skeletal phases. The early marine radiaxial fibrous calcite as well as the shallow-burial diagenetic cements from the Sierra del Cuera are closely associated with red stained micrites and show negative $\delta^{98/95}\text{Mo}$ values. It can therefore be assumed that the red micrite was a local source of light Mo. Assuming a diagenetic process we hypothesize that Fe-(hydr)oxide bound Mo was transferred back into the solution. Redissolved, light Mo would then have become available in the porewater where it was subsequently incorporated into the precipitating cement phases. The offset ($\delta^{98/95}\text{Mo} = 0.6\text{--}0.8\%$) between matrix micrite and cements is then explained by mixing of locally light diagenetic fluids with heavy ocean water.

The precipitation of botryoidal cement SA3A was obviously not greatly influenced by the diagenetically altered fluids because its heavy $\delta^{98/95}\text{Mo}$ of 1.67‰ suggests ocean water as the dominant Mo contributor. The determining factor could be the position on the platform, but further investigations on rocks from various locations would be necessary to confirm this hypothesis. The same source dependent isotopic signatures were observed in microbial micrites and their associated botryoidal cements from the more southerly located Picos de Europa domain. While one sample pair has negative $\delta^{98/95}\text{Mo}$ values (-0.5 and -0.6%) similar to those observed in cements of the Sierra del Cuera, a sedimentologically identical sediment/cement pair revealed positive isotopic values of 0.2 and 1.0‰. Thin section analysis revealed no evidence of a particulate Fe-(hydr)oxide contribution to either the grey micrites or the botryoidal cements. Also, Fe concentrations of both phases are in the same order as those detected in the early marine cements of the Sierra del Cuera and the non-skeletal phases of China, where no indication (sedimentological or geochemical) for the presence of Fe-(hydr)oxides is given. A differential influence of diagenetic fluids, analogous to the Sierra del Cuera area, is therefore implied. The exact source of the light fluids in the Picos de Europa domain is speculative because the samples themselves are not closely associated with red micrites. This implies that the light diagenetic fluids would have affected the carbonates on a regional rather than just a local scale. In summary, the strongly heterogeneous Mo isotopic compositions found in Carboniferous non-skeletal precipitates of the Spanish platform environment seems to be inherited from diagenetically altered fluids. Light Mo, most likely remobilized from authigenically formed hematite, appears to exert an important control over the $\delta^{98/95}\text{Mo}$ of the non-skeletal precipitates. An inferred mixing of heavy seawater with lighter porewater Mo means that the resulting mixture was not representative for mid Carboniferous seawater. The heaviest non-skeletal sample SA3A, however, is suggested as a good minimum approximation of the ambient ocean water Mo composition.

6. Conclusions

For the first time the Mo isotopic composition of carbonates has been reported. Repeated measurements of two low Mo concentration standards by MC-ICPMS have revealed a high external reproducibility of $\pm 0.1\%$ $\delta^{98/95}\text{Mo}$ (2σ). The $\delta^{98/95}\text{Mo}$ of various modern and Carboniferous samples cover the entire range of Mo isotopic compositions so far recognized in the marine environment. With Mo contents mostly $\ll 1$ ppm carbonates are extremely depleted in comparison to the major Mo archives. The large spread in $\delta^{98/95}\text{Mo}$ values found in modern skeletal carbonates seems to be attributed to vital effects. In contrast, quasi non-skeletal ooid sands all closely approach modern ocean water Mo, which implies that the incorporation of Mo into non-skeletal carbonate is accompanied by minor isotope fractionation. Thus, their $\delta^{98/95}\text{Mo}$ is not controlled by local redox conditions as it is the case for euxinic sediments and monitors the isotopic composition of the ambient fluid. The present study has not identified any modern carbonate with a Mo isotopic composition heavier than

ocean water. Therefore, the isotopically heaviest sample can be considered a safe minimum value for the ambient ocean water composition. A thorough sedimentological, petrographical and geochemical investigation of the sedimentary environment is a prerequisite to assess possible Mo sources other than ocean water and to identify carbonate phases which provide a reliable approximation of seawater Mo.

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