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# Determination of the Isotopic Composition of Molybdenum in the Bottom Sediments of Freshwater Basins

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**Abstract**—This paper presents the results of measurements of the Mo isotopic composition in the bottom sediments (BS) of freshwater basins. Mo isotopic ratios were measured using a multicollector inductively coupled plasma mass spectrometer (MC ICP MS). Efficient methods were used in this study for Mo separation from the elements of the sample matrix and correction for instrumental mass discrimination. This allowed us to achieve a high accuracy of 0.06, 0.08, and 0.14‰ (2 σ) for the measurement of $^{97}Mo/^{95}Mo$, $^{98}Mo/^{95}Mo$, and $^{100}Mo/^{95}Mo$, respectively. The range of variations in Mo isotope ratios observed in the collected BS columns was ~2.2‰ in terms of $\delta^{97}Mo/^{95}Mo$. The results obtained here suggest that geochemical processes occurring during Mo migration with land water can change the isotopic composition of Mo. It is pointed out that the potential use of Mo isotopic systematics for reconstructions of redox conditions in seawater over the geologic past requires the quantification of isotopic effects of Mo accompanying its migration on land and the extent of possible variations in the isotopic composition of Mo entering the ocean.

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## INTRODUCTION

The sensitivity of modern mass spectrometers provides an opportunity to determine with great accuracy natural variations in isotopic ratios of a number of heavy stable elements, including molybdenum. There are seven stable Mo isotopes: $^{92}Mo$, $^{94}Mo$, $^{95}Mo$, $^{96}Mo$, $^{97}Mo$, $^{98}Mo$, and $^{100}Mo$, the relative percentages of which range from 9 to 25% [1]. Variations in Mo isotopic ratios can be caused by various processes: (1) anomalous isotopic compositions related to processes of stellar nucleosynthesis and generation of the primordial terrestrial materials [2], (2) spontaneous fission of $^{238}U$ [3], (3) double β-decay of $^{96}Zr$ to $^{96}Mo$ [3], and (4) mass fractionation during physical and chemical processes [4]. The latter process of mass fractionation has been extensively studied over the past years.

Among the attractive features of studying stable Mo isotopes is their unique geochemical properties, including their traditional use as an indicator of anoxic conditions in paleobasins [4–7]. Mo is a relatively rare element occurring in natural waters in three oxidation states: 4+, 5+, and 6+ [8]. In oxygen-saturated water, Mo shows a conservative behavior and weakly reacts with suspended matter [4, 6, 8]. Owing to this, Mo is the most abundant transition metal in seawater (~10 ppb) [4]. The geochemical behavior of Mo is sharply different under anoxic conditions. Mo species with an oxidation state of 4+ are thermodynamically stable in anoxic waters. In the presence of $H_2S$, Mo (IV) readily forms sulfur compounds, which actively react with mineral surfaces and precipitate in BS [9]. The precipitation of Mo under such conditions is so intense that marine BS forming under anoxic waters accumulates, according to some estimates, up to 50% of the annual amount of precipitated Mo in the ocean, despite the fact that the area of BS beneath anoxic waters is less than 0.5% of the seafloor area [4]. Taking into account the low concentration of Mo in the Earth's crust, the authigenic Mo concentration in sedimentary columns is used as an indicator of anoxic conditions in bottom water [5–7].

Recent isotopic studies showed that stable Mo isotopes can be efficiently used together with the data on the Mo concentration [4, 10–12]. It was shown that marine BS generated under different redox conditions have different isotopic compositions. The Mo isotopic composition of pelagic clays and Fe–Mn nodules forming under oxidizing conditions is ~2.1‰ lighter (in $\delta^{97/95}Mo$) than that of parent seawater [11, 12]. The Mo isotopic composition of BS forming beneath anoxic waters in the presence of $H_2S$ is similar to that of seawater.

Precise measurements of Mo isotope ratios were carried out by thermal ionization mass spectrometry (TIMS) [13] and MC ICP MS [14, 15]. MC ICP MS has become increasingly popular for obtaining highly accurate isotopic data. Its obvious advantages are the high degree of ionization, relatively stable instrumental

mass discrimination, and high productivity of the devices. In recent studies, the method of double-spike isotope dilution [11, 14] and normalization of the measured Mo isotope ratios to the isotope ratio of an external element (Zr or Ru) [10, 12, 15] have been used to correct for instrumental mass discrimination. Both approaches have their own shortcomings. The method of double-spike isotope dilution imposes less stringent requirements to the extent of Mo purification from the accompanying matrix, but it is very laborious, because it includes a necessary procedure of careful addition to the samples of appropriate amounts of an isotope standard. The use of Zr or Ru as external standard elements reduces the number of Mo isotope ratios free of spectral interferences (Zr has three isotopes, $^{92}$Zr, $^{94}$Zr, and $^{96}$Zr, overlapping the signals of corresponding Mo isotopes during detection; and Ru has two such isotopes, $^{98}$Ru and $^{100}$Ru). Furthermore, it was found during our study that the previous methods of Mo separation [10, 16] did not always provide the desired relationships between the degree of Mo purification and extraction for Fe-rich samples.

In this study, a new method was proposed for the measurement of Mo isotope ratios by MC ICP MS using an improved procedure for Mo purification, correction for instrumental mass discrimination of Mo isotopes, and normalization to the $^{105}$Pd/$^{104}$Pd ratio. This method was used to measure the Mo isotopic composition of BS columns collected from lakes with different redox conditions of bottom waters. The observed variations in Mo isotopic composition are interpreted in light of potential use of Mo isotopic systematics for the paleoreconstructions of the redox conditions of seawater.

## MATERIALS AND METHODS

### *Sampling*

Samples of BS were collected from ice in the deep parts of lakes Vettasjarvi and Kutsasjarvi in northern Sweden in the spring of 2003 and 2005. The surface area of Lake Vettasjarvi is ~7.8 km$^2$, and its maximum depth is 19 m. The surface area of Lake Kutsasjarvi is ~3 km$^2$, and its maximum depth if 35 m. BS samples were recovered using a gravity-type sampler equipped with a Plexiglas tube with an inner diameter of 50 mm and a hydraulic valve. The total length of the columns was 26 cm in Lake Kutsasjarvi and 12 cm in Lake Vettasjarvi. The BS columns were separated into 1-cm layers immediately after sampling.

Simultaneously with the BS sampling, the hydrochemical parameters of the water were determined in situ at the sampling sites, including the concentration of dissolved $O_2$, the pH, and the electrical conductivity using a Hydrolab Survey hydrochemical probe (Hydrolab Corp., Austin, USA). The procedure of dissolved $O_2$ measurement and water sampling for the determination of the metal abundances and speciation was described in detail elsewhere [17]. The discrimination of the chemical forms of metals into conditionally dissolved and suspended components was performed in situ by filtration through membrane filters with a pore diameter of 0.22 μm (Millipore) using a peristaltic pump.

### *Sample Preparation for Analysis*

The samples of BS were dried in a drying oven at a temperature of 50°C and then crushed in an agate mortar. Aliquots of ~0.5 g were used for the analysis. The organic matter of the samples was decomposed by annealing at 550°C for ~16 h. Then, the samples were carefully loaded into Teflon beakers, and molybdenum was extracted by 20 ml ~4 M HCl with the addition of 20 mg hydroxylamine hydrochloride ($NH_2OH \cdot HCl$). The samples were placed on an electric heater with a temperature controller, and the extraction lasted for 3 h at a temperature of 50°C. Such an extraction procedure is widely used for the dissolution of Fe and Mn oxides [18]. Taking into account that the organic matter was decomposed by annealing before the extraction, the molybdenum occurring in the solution obtained after the extraction includes fractions that were initially incorporated in Fe and Mn oxides and the organic matter. The silicate residue of BS was separated by centrifuging. The obtained Mo solutions were evaporated in a Teflon beaker. The mineral residue was again dissolved in 0.3 M $HNO_3$ and subjected to the ion exchange purification of Mo from the elements of the accompanying matrix.

### *Ion Exchange Chromatography for the Separation of Mo from the Accompanying Matrix*

Mo must be separated from the accompanying matrix elements to eliminate spectral interferences and minimize the difference between the matrix of the samples and standards. Ion exchange chromatography was conducted using chelating resin Chelex-100 and 200–400 mesh (Bio-Rad Co.). Ion exchange columns were composed of 10-ml plastic tips of dosing pipettes. Pieces of cotton wool placed in the lower parts of the ends fixed the lower position of the ion exchange resin. About 3–4 ml of resin was put into the column. Before loading the resin was washed with a 6 M $NH_4OH$ solution and then rinsed with distilled water. This operation aimed at eliminating the potential admixtures of Mo and some other elements (Si, P, and W) in the resin, because Mo elution during subsequent separation was performed using the 6 M $NH_4OH$ solution. The loading of resin into the column was followed by the sequential operations of additional resin purification, conditioning, sample loading, and Mo elution. The details of these operations are given in Table 1. After completion of these procedures (Table 1), the Mo-bearing 6 M $NH_4OH$ solution purified from the major fraction of accompanying elements was evaporated on an electric heater, and the mineral residue was again dissolved in 0.3 M $HNO_3$. The obtained solutions were ready for isotopic analysis by MC ICP MS after appropriate dilution.

The recovery of Mo and the degree of purification from Zr, Ru, Fe, Mn, Cu, Zn, and other elements were checked using aliquots of solutions collected before and after the ion exchange separation for each sample. The Mo recovery approached 100% (±5% as one standard deviation) in the all samples.

### *Mass Spectrometry*

The concentrations of Mo and 60 other elements were determined in our samples by ICP MS on an Element instrument (Thermo Finnigan, Bremen, Germany). The instrumental parameters used to obtain accurate concentration data were described in [19]. Mo isotope ratios were determined on a Neptun instrument (Thermo Finnigan, Bremen, Germany). The detection of Mo ions was conducted using nine Faraday collectors. Samples and standards were prepared in 0.3 M $HNO_3$ and were introduced to the plasma at a rate of ~0.25 ml/min through a microconcentric nebulizer and a system of two spray chambers providing introduction to the plasma of an aerosol consisting of uniform aqueous particles. A low mass resolution of $\Delta m/m \approx 400$ was used for the measurement of the Mo isotope ratios.

The Faraday cups were arranged in the following sequence: $^{94}$Mo, $^{95}$Mo, $^{96}$Mo, $^{97}$Mo, $^{98}$Mo, $^{100}$Mo, $^{104}$Pd, and $^{105}$Pd were registered by the detectors Low 4, Low 3, Low 2, Low 1, Central, High 1, High 3, and High 4, respectively. The static mode of detection was employed. All the measurements were carried out in the following sequence: isotope standard—sample—isotope standard, etc. The concentrations of Mo and nitric acid in the matrix of the standards corresponded to those of the samples; the concentrations of Mo in the solutions were 1–2 mg/l. The $^{98}$Mo signal from the solution containing 1 mg/l Mo was ~7.5 V.

Palladium was used as an internal standard to correct for the instrumental mass discrimination of Mo isotopes. Correspondingly, before performing the isotopic analyses, palladium was added to the samples and the standards such that its concentration was half that of Mo. The correction was applied using the exponential model [20] by normalizing the Mo isotope ratios to $^{105}$Pd/$^{104}$Pd. The precision of the Mo isotope ratios was ±0.06‰ for $^{97}$Mo/$^{95}$Mo, ±0.08‰ for $^{98}$Mo/$^{95}$Mo, and ±0.14‰ for $^{100}$Mo/$^{95}$Mo (two standard deviations of independent measurements). Since there is still no certified standard for Mo isotopes, the Mo concentration standard provided by High-Purity Standards (lot # 320304, Charleston, SC 29423, USA) was used as an isotopic standard in this study.

## RESULTS AND DISCUSSION

The isotopic compositions of Mo are given in delta notations as [4]:

$$\delta^{X/95}\mathrm{Mo} = \left[\frac{(^{x}\mathrm{Mo}/^{95}\mathrm{Mo})_{\mathrm{sample}}}{(^{x}\mathrm{Mo}/^{95}\mathrm{Mo})_{\mathrm{standard}}} - 1\right]1000, ‰, \quad (1)$$

**Table 1.** Sequence of operations for Mo separation by ion exchange chromatography using 3 ml Chelex 100 resin and 200–400 mesh

| Eluent | Volume, ml | Purpose |
|---|---|---|
| 8 M $HNO_3$ | 15 | Resin purification |
| Distilled water | 5 | Resin purification |
| 0.3 M $HNO_3$ | 10 | Resin conditioning |
| 0.3 M $HNO_3$ | 12 | Sample loading |
| 0.07 M HCl | 10 | Matrix elution |
| 0.1 M HF | 50 | Matrix elution |
| 6 M $NH_4OH$ | 12 | Mo elution |

where $^{x}$Mo/$^{95}$Mo are the isotopic ratios $^{97}$Mo/$^{95}$Mo, $^{98}$Mo/$^{95}$Mo, and $^{100}$Mo/$^{95}$Mo for the sample and isotope standard, respectively, after correction for instrumental mass fractionation. The isotopic compositions of Mo obtained in this study are represented by these three isotopic ratios, which show the minimum number of spectral interferences during MC ICP MS measurements.

The Mo isotopic compositions of BS from lakes Vettasjarvi and Kutsasjarvi are given in Table 2. Before discussing the geochemical applications of these results, analytical aspects of this study will be briefly discussed.

### *Potential Spectral Interferences during the Determination of the Mo Isotopic Compositions*

Spectral interferences for Mo isotopes can be related to the overlap of Mo and signals from isobaric isotopes of Zr ($^{92}$Zr, $^{94}$Zr, and $^{96}$Zr) and Ru ($^{98}$Ru and $^{100}$Ru) and formation of polyatomic and two-charged ions in the plasma. The most important spectral interferences for Mo isotopes are listed in Table 3. As can be seen from Table 3, Fe, Mn, Cu, Zn, and Ni are donor elements during the formation of many polyatomic ions. Most of the spectral interferences due to these elements cannot be discriminated from the signals of Mo isotopes even using the high-resolution functions of the mass spectrometer. The concentrations of these elements in geological samples are usually higher than the concentration of Mo, which emphasizes the need for careful preliminary purification of Mo from the accompanying matrix elements.

### *Degree of Mo Separation from the Accompanying Matrix*

An important prerequisite of Mo separation from the accompanying matrix elements is that Mo must be quantitatively recovered after the purification procedure. This is necessary to prevent the possible fractionation of Mo isotopes as a result of incomplete recovery. The fractionation of Mo isotopes as a result of incom-

**Table 2.** Results of the Mo isotopic analysis of the bottom sediments of freshwater lakes in northern Sweden; *h* is the depth of the layer in the BS column relative to the surface in cm. The error of the measurement corresponds to one standard deviation

| Sample | $\delta^{97/95}$Mo, ‰ | $\delta^{98/95}$Mo, ‰ | $\delta^{100/95}$Mo, ‰ |
|---|---|---|---|
| *h*, cm | *Lake Vettasjarvi* | | |
| 1 | –0.62 ± 0.03 | –0.91 ± 0.04 | –1.44 ± 0.08 |
| 2 | –0.48 ± 0.03 | –0.72 ± 0.03 | –1.14 ± 0.05 |
| 3 | –0.46 ± 0.03 | –0.69 ± 0.03 | –1.12 ± 0.05 |
| 4 | –0.26 ± 0.03 | –0.39 ± 0.03 | –0.57 ± 0.05 |
| 5 | –0.63 ± 0.03 | –0.91 ± 0.03 | –1.45 ± 0.05 |
| 6 | –0.81 ± 0.03 | –1.22 ± 0.03 | –1.96 ± 0.05 |
| 7 | –0.61 ± 0.03 | –0.90 ± 0.03 | –1.48 ± 0.05 |
| 8 | –0.49 ± 0.03 | –0.74 ± 0.03 | –1.19 ± 0.09 |
| 9 | –0.70 ± 0.03 | –1.04 ± 0.03 | –1.69 ± 0.05 |
| 10 | –0.67 ± 0.03 | –1.01 ± 0.03 | –1.62 ± 0.05 |
| 11 | –0.82 ± 0.03 | –1.21 ± 0.06 | –1.94 ± 0.07 |
| 12 | –0.92 ± 0.03 | –1.35 ± 0.04 | –2.17 ± 0.06 |
| *h*, cm | *Lake Kutsasjarvi* | | |
| 1 | 1.01 ± 0.03 | 1.48 ± 0.04 | 2.43 ± 0.06 |
| 2 | 1.10 ± 0.04 | 1.65 ± 0.05 | 2.70 ± 0.06 |
| 3 | 0.96 ± 0.03 | 1.40 ± 0.03 | 2.31 ± 0.05 |
| 4 | 1.26 ± 0.04 | 1.89 ± 0.04 | 3.10 ± 0.06 |
| 5 | 0.92 ± 0.04 | 1.37 ± 0.07 | 2.26 ± 0.1 |
| 7 | 0.56 ± 0.03 | 0.83 ± 0.03 | 1.35 ± 0.05 |
| 8 | 0.62 ± 0.04 | 0.96 ± 0.04 | 1.61 ± 0.06 |
| 9 | 0.55 ± 0.05 | 0.84 ± 0.04 | 1.36 ± 0.08 |
| 10 | 0.71 ± 0.03 | 1.05 ± 0.03 | 1.71 ± 0.05 |
| 11 | 0.83 ± 0.03 | 1.21 ± 0.04 | 1.98 ± 0.09 |
| 12 | 0.81 ± 0.07 | 1.21 ± 0.08 | 1.95 ± 0.10 |
| 13 | 0.40 ± 0.03 | 0.60 ± 0.03 | 0.98 ± 0.05 |
| 14 | 0.52 ± 0.03 | 0.78 ± 0.04 | 1.30 ± 0.06 |
| 15 | 0.64 ± 0.03 | 0.96 ± 0.04 | 1.56 ± 0.06 |
| 16 | 0.17 ± 0.04 | 0.24 ± 0.04 | 0.46 ± 0.06 |
| 25 | 0.08 ± 0.04 | 0.12 ± 0.04 | 0.26 ± 0.06 |

plete recovery from an anion exchange column was described in [15]. The main problem in Mo purification with preservation of its quantitative recovery is related to Fe separation. In this study, the conditions Fe/Mo < 1 was used as a criterion for Mo purification from Fe. Most of our samples were purified by a single-stage treatment by ion exchange chromatography as described in Table 1. However, some samples were not sufficiently purified from Fe after the first passage through the column. In such cases, the 6 M $NH_4OH$ solution containing Mo was evaporated, and the mineral residue was dissolved in 0.3 M $HNO_3$. This solution was reloaded into the same column preliminarily conditioned with 0.3 M $HNO_3$ solution. The procedure described in Table 1 was then repeated.

A specific feature of Chelex 100 ion-exchange resin is its ability to change volume depending on the ionic form of its particles [21]. The volume of the resin increases considerably during the stage of Mo elution with 6 M $NH_4OH$ solution owing to dramatic change from acidic to strongly alkalic pH. It was observed during the initial stages of this study that the undecomposed organic matter of BS may react with the resin during Mo elution and significantly hinder the passage of solution through the resin. This problem was circumvented by the practically complete decomposition of organic matter in our samples by their annealing at 550°C.

The concentrations of Ru, Zn, Cu, Mn, and other elements that can interfere with Mo isotopes were reduced to the level of trace concentrations and were, in most cases, no higher than blanks (distilled water) for the Element ICP MS.

### *Instrumental Discrimination of Mo Isotopes and Estimation of the Quality of the Isotope Ratio Measurement*

The instrumental discrimination of Mo isotopes was ~2% per atomic mass unit in favour of heavy isotopes. The procedure of correction for instrumental mass discrimination was aimed at adequately accounting for the difference between the coefficients of passage through the mass spectrometer of light and heavy Mo isotopes and for the effects of variations in the instrumental mass discrimination between the samples and standards owing to the imperfect correspondence of their matrixes and the small variations in the voltage of the electromagnetic lenses of the instrument. The exponential model described in detail in [20, 22] was used for the correction procedure. An important characteristic of the exponential law of isotope fractionation is the linear relation between the logarithms of two measured isotopic ratios. Proceeding from this feature, the correction for instrumental mass discrimination by the normalization to the isotopic ratio of an external element (Pd in our case) utilizes the proportionality between the coefficients of mass discrimination for Pd and Mo isotopes. It is also well known that the coefficients of instrumental mass discrimination for various elements are not identical, and

**Table 3.** Main spectral interferences during measurement of the isotopes $^{94}$Mo, $^{95}$Mo, $^{96}$Mo, $^{97}$Mo, $^{98}$Mo, $^{100}$Mo, $^{104}$Pd, and $^{105}$Pd by MC ICP MS. The relative contents of the compounds shown in parentheses were calculated using the recent compilation of isotope abundances of IUPAC [1]

| Mass | Oxides | Argides | Nitrides | Chlorides | Isobars | Double-charged ions |
|---|---|---|---|---|---|---|
| $^{94}$Mo | $^{78}Se^{16}O^+$ (0.24) | $^{54}Fe^{40}Ar^+$ (0.058); $^{58}Ni^{36}Ar^+$ (0.002); $^{54}Cr^{40}Ar$ (0.023) | $^{64}Zn^{14}N^{16}O^+$ (0.48); $^{63}Cu^{15}N^{16}O^+$ (0.003); | $^{59}Co^{35}Cl^+$ (0.76); $^{57}Fe^{37}Cl^+$ (0.005) | $^{94}Zr^+$ (0.17) | $^{188}Os^{++}$ (0.13) |
| $^{95}$Mo | $^{78}Se^{16}OH^+$ (0.24) | $^{55}Mn^{40}Ar^+$ (0.99); $^{59}Co^{36}Ar^+$ (0.003) | $^{65}Cu^{14}N^{16}O^+$ (0.31); $^{64}Zn^{15}N^{16}O^+$ (0.002); | $^{58}Ni^{37}Cl^+$ (0.16); | | $^{190}Os^{++}$ (0.26) |
| $^{96}$Mo | $^{80}Se^{16}O^+$ (0.49) | $^{56}Fe^{40}Ar^+$ (0.91); $^{58}Ni^{38}Ar^+$ (0.0004) | $^{65}Cu^{15}N^{16}O^+$ (0.001); $^{66}Zn^{14}N^{16}O^+$ (0.28); $^{64}Ni^{14}N^{18}O^+$ (0.00002) | $^{61}Ni^{35}Cl^+$ (0.009); $^{59}Co^{37}Cl^+$ (0.24) | $^{96}Zr^+$ (0.03); $^{96}Ru^+$ (0.06) | $^{192}Os^{++}$ (0.41); $^{192}Pt^{++}$ (0.008) |
| $^{97}$Mo | $^{80}Se^{16}OH^+$ (0.49) | $^{57}Fe^{40}Ar^+$ (0.06); $^{59}Co^{38}Ar^+$ (0.06); $^{61}Ni^{36}Ar^+$ (0.00004) | $^{65}Cu^{14}N^{18}O^+$ (0.0006) | $^{60}Ni^{37}Cl^+$ (0.063) | | $^{192}Pt^{++}$ (0.33) |
| $^{98}$Mo | $^{82}Se^{16}O^+$ (0.08) | $^{58}Ni^{40}Ar^+$ (0.68); $^{58}Fe^{40}Ar$ (0.058) | $^{68}Zn^{14}N^{16}O^+$ (0.19) | $^{63}Cu^{35}Cl^+$ (0.52); $^{61}Ni^{37}Cl^+$ (0.003) | $^{98}Ru^+$ (0.02) | $^{196}Pt^{++}$ (0.25) |
| $^{100}$Mo | $^{84}Sr^{16}O^+$ (0.006) | $^{60}Ni^{40}Ar^+$ (0.261); $^{64}Zn^{36}Ar^+$ (0.002) | $^{69}Ga^{15}N^{16}O^+$ (0.001); $^{70}Ge^{14}N^{16}O^+$ (0.21) | $^{63}Cu^{37}Cl^+$ (0.17); | $^{100}Ru^+$ (0.13) | $^{200}Hg^{++}$ (0.23) |
| $^{104}$Pd | $^{88}Sr^{16}O^+$ (0.82) | $^{64}Ni^{40}Ar^+$ (0.009); $^{64}Zn^{40}Ar^+$ (0.48); | $^{74}Ge^{14}N^{16}O^+$ (0.36) | $^{67}Zn^{37}Cl^+$ (0.01); $^{69}Ga^{35}Cl^+$ (0.45) | $^{104}Ru^+$ (0.19) | $^{208}Pb^{++}$ (0.52) |
| $^{105}$Pd | $^{89}Y^{16}O^+$ (0.99) | $^{65}Cu^{40}Ar^+$ (0.31) | $^{74}Ge^{15}N^{16}O^+$ (0.001); $^{75}As^{14}N^{16}O^+$ (0.99) | $^{68}Zn^{37}Cl^+$ (0.045) | | |

their values may vary from day to day during measurements [20, 23]. However, the effect of variations in the coefficients of the instrumental mass discrimination between measurement sessions becomes negligible if samples are intercalated with standards during the measurements and the isotopic ratios of the samples are calculated relative to the isotopic ratios of the standards. As can be seen from Fig. 1, the coefficients of instru-

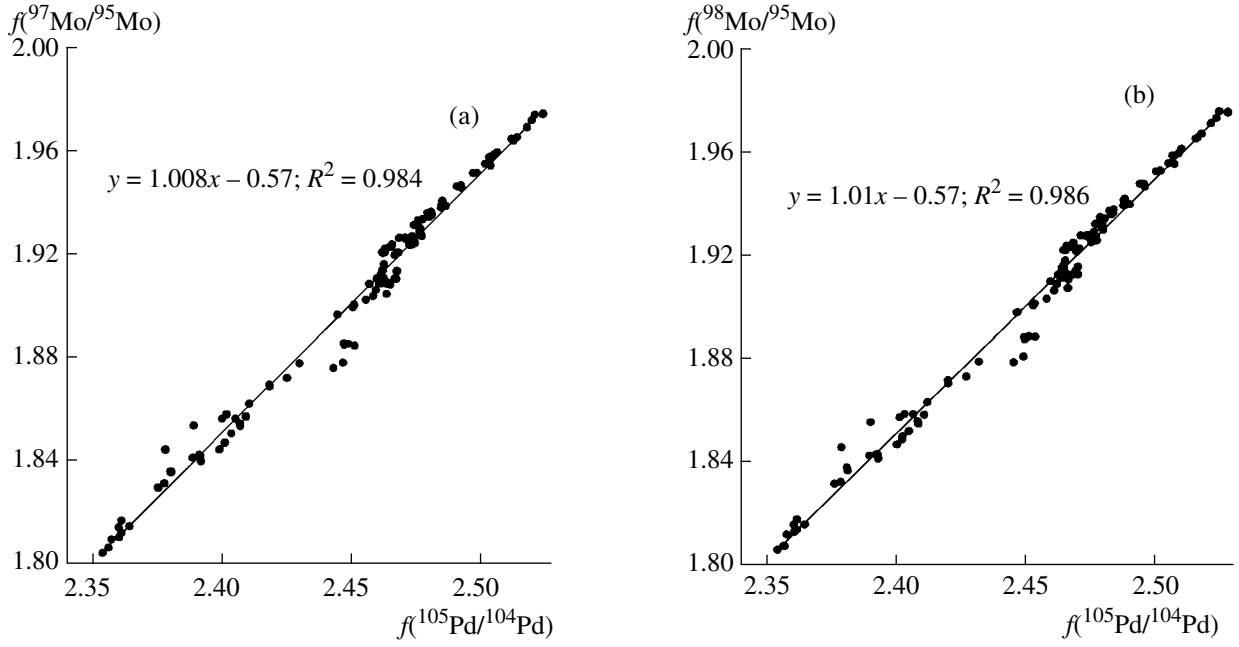


**Fig. 1.** Correlation between the coefficients of instrumental fractionation ($f$) of isotope ratios: (a) $^{97}$Mo/$^{95}$Mo and $^{105}$Pd/$^{104}$Pd and (b) $^{98}$Mo/$^{95}$Mo and $^{105}$Pd/$^{104}$Pd for the Mo isotope standard used in this study. The data were obtained during nine measurement session over five months ($n$ = 102).

**Table 4.** Dissolved $O_2$; pH; electric conductivity; and concentrations of dissolved (diss) and suspended (susp) species of Mo, Fe, and Mn in the bottom layers of the water of the lakes studied. The reported errors correspond to one standard deviation

| Depth, m | $O_2$, % of saturation level | pH | Conductivity, mS/cm | $Mo_{diss}$, μg/l | $Mo_{susp}$, μg/l | $Fe_{diss}$, μg/l | $Fe_{susp}$, μg/l | $Mn_{diss}$, μg/l | $Mn_{susp}$, μg/l |
|---|---|---|---|---|---|---|---|---|---|
| *Lake Vettasjarvi, the depth at the site of the BS sampling is 16 m* | | | | | | | | | |
| 15.0 | 10 | 5.90 | 29.4 | 0.12 ± 0.02 | 0.016 ± 0.0005 | 4.4 ± 0.24 | 86 ± 1.8 | 984 ± 11 | 103 ± 1.8 |
| 15.2 | 8.3 | 5.93 | 31.2 | 0.13 ± 0.02 | 0.022 ± 0.0007 | 5.3 ± 0.1 | 116 ± 0.5 | 1350 ± 8 | 147 ± 5.7 |
| 15.4 | 4.6 | 6.02 | 35.8 | 0.19 ± 0.02 | 0.019 ± 0.0006 | 5.7 ± 0.1 | 105 ± 0.6 | 2090 ± 14 | 119 ± 0.5 |
| 15.6 | 1.2 | 6.26 | 50.4 | 0.64 ± 0.02 | 0.038 ± 0.0015 | 5.5 ± 0.19 | 325 ± 4.1 | 5780 ± 256 | 152 ± 2.7 |
| 15.8 | 0.6 | 6.90 | 73.5 | 2.25 ± 0.02 | 0.027 ± 0.0006 | 4200 ± 15 | 305 ± 0.9 | 10002 ± 218 | 30 ± 0.5 |
| *Lake Kutsasjarvi, the depth at the site of the BS sampling is 26 m* | | | | | | | | | |
| 15.0 | 80 | 6.62 | 12.9 | 0.08 ± 0.02 | 0.023 ± 0.002 | 5.7 ± 0.3 | 12 ± 0.3 | 1.06 ± 0.06 | 4.0 ± 0.4 |
| 20.0 | 80 | 6.63 | 12.8 | 0.09 ± 0.02 | 0.020 ± 0.006 | 12.9 ± 0.2 | 15 ± 0.8 | 1.24 ± 0.1 | 6.0 ± 0.4 |
| 25.8 | 65 | 6.43 | 12.0 | 0.09 ± 0.02 | 0.006 ± 0.002 | 2.4 ± 0.1 | 9.0 ± 0.3 | 1.7 ± 0.05 | 2.5 ± 0.3 |

mental mass discrimination for two isotopic ratios of Mo ($^{97}Mo/^{95}Mo$ and $^{98}Mo/^{95}Mo$) and $^{105}Pd/^{104}Pd$ are variable but their variations are mutually strictly linear.

The best way to evaluate the quality and accuracy of the isotopic analysis is to measure a sample with known isotopic composition. Unfortunately, there are no such samples for molybdenum. Because of this, the quality of measurements (i.e., the lack of spectral interferences and reproducibility) was indirectly assessed by comparing the dependencies between the measured isotopic ratios and their theoretical distribution using the method described in detail in [24, 25].

### *Variations in the Isotopic Composition of Mo in Freshwater BS*

As can be seen from Table 2, the range of variations in the Mo isotopic composition of BS from the two lakes is ~2.2‰ in terms of $\delta^{97/95}Mo$. Table 4 shows physicochemical parameters for the bottom waters of lakes Vettasjarvi and Kutsasjarvi. The concentrations of Mo, $Fe_2O_3$, and MnO in the BS are shown in Figs. 2 and 3. The BS of both lakes have low sulfur contents varying from 0.3 to 0.5% in Lake Vettsajarvi and from 0.05 to 0.2% in Lake Kutsasjarvi.

The lakes occur in similar geomorphological environments and have no significant inflowing currents. The prevailing mechanism of the formation of Fe and Mn oxides in BS is the oxidation of dissolved Fe(II) and Mn(II) species diffusing from deep BS layers upward along the concentration gradient. The main difference between the geochemical regimes of the lakes is that a bottom layer of anoxic water is formed in Lake Vettasjarvi during the winter season, whereas Lake Kutsasjarvi's waters occur under oxidizing conditions throughout the year. Owing to this, the boundary between the oxidizing and reducing conditions in Lake Kutsasjarvi is shifted into BS. The concentration peak of Fe in Fig. 3 is probably an indicator of a change in redox conditions in the column.

The $\delta^{97/95}Mo$ values of BS from Lake Vettasjarvi range from –0.26 to –0.92‰. There is a negative correlation between the Mo concentration and $\delta^{97/95}Mo$. The $\delta^{97/95}Mo$ of the BS from Lake Kutsasjarvi decreases with depth from 1.26 to 0.08‰. The variations in $\delta^{97/95}Mo$ are accompanied by variations in the concentration of Fe and Mn oxides. An interesting observation is the peak of the Mn concentration coinciding with the peak of Fe (Fig. 3). This coincidence indicates extensive Mo coprecipitation from pore waters in the course of the redox cycle of Fe.

Previous studies have revealed the most important mechanisms of Mo precipitation in BS under oxidizing and reducing conditions in a water medium. In the case of oxidizing conditions, such a mechanism is Mo coprecipitation with Mn oxides [4, 6, 10]. In the case of reducing conditions, the predominant mechanism of Mo precipitation in BS is the formation of oxythiomolybdates ($MoO_{4-x}S_x^{2-}$) and their active interaction with mineral surfaces resulting in almost complete Mo precipitation from the water medium [4, 5, 9]. It was experimentally demonstrated that light Mo isotopes are preferentially adsorbed during the interaction of Mn

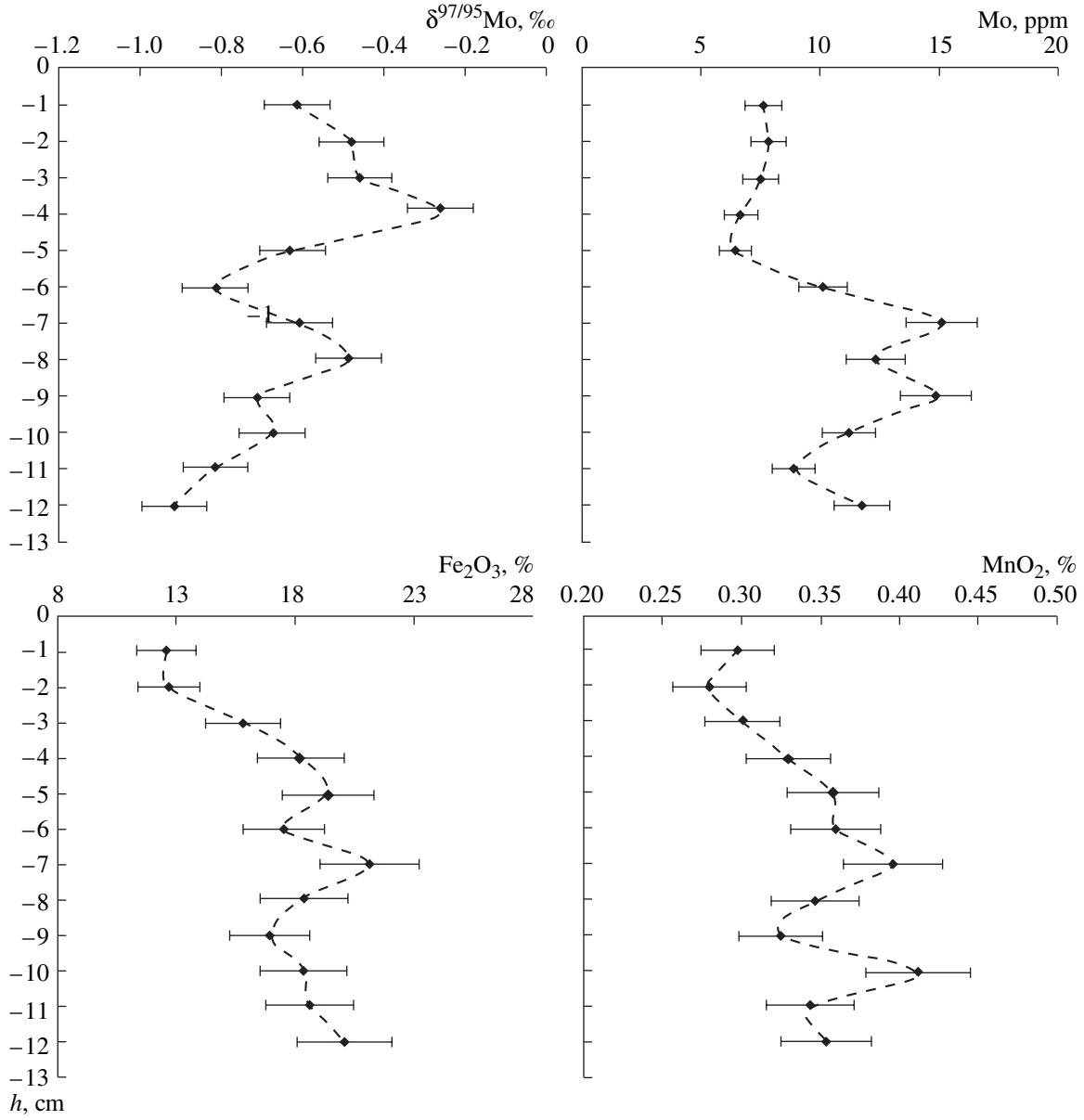


**Fig. 2.** Vertical profiles of $\delta^{97/95}$Mo and concentrations of Mo, $Fe_2O_3$, and $MnO_2$ for a BS column from Lake Vettasjarvi. The reported errors correspond to two standard deviations.

and Mo oxides [10, 26]. The $\delta^{97/95}$Mo values of Mo adsorbed on the surface of Mn oxide at near neutral pH varied from –0.5 to –1.0‰ relative to the Mo isotope standard [26]. A model was proposed for the interpretation of the geochemical behavior of Mo in BS under transitional redox conditions. According to this model, Mo precipitates from pore waters under reducing conditions in the presence of $H_2S$, whereas the transitional zone between oxidizing and reducing conditions is characterized by free Mo diffusion in a water medium without any significant chemical precipitation [4, 5]. The diffusion migration of Mo in pore waters may result in an isotopic effect owing to different diffusion coefficients of the light and heavy Mo isotopes. Rodyushkin et al. [27] showed that the diffusion of Fe and Zn ions in an aqueous solution can lead to a shift in the isotope ratios of $^{56}Fe/^{54}Fe$ and $^{66}Zn/^{64}Zn$ by more than 0.3‰ toward the light isotopes. A similar mechanism of isotope fractionation can operate in the case of Mo.

The observed variations in the Mo isotopic composition of BS are probably related to the combined action of the two aforementioned mechanisms: (1) preferential adsorption of light Mo isotopes on Mn oxides and (2) diffusion of dissolved Mo in pore waters. Unfortunately, any definite conclusion on the prevailing processes of Mo isotope fractionation in the BS would be premature, because many potential mechanisms of fractionation are still not studied. In particular, isotopic

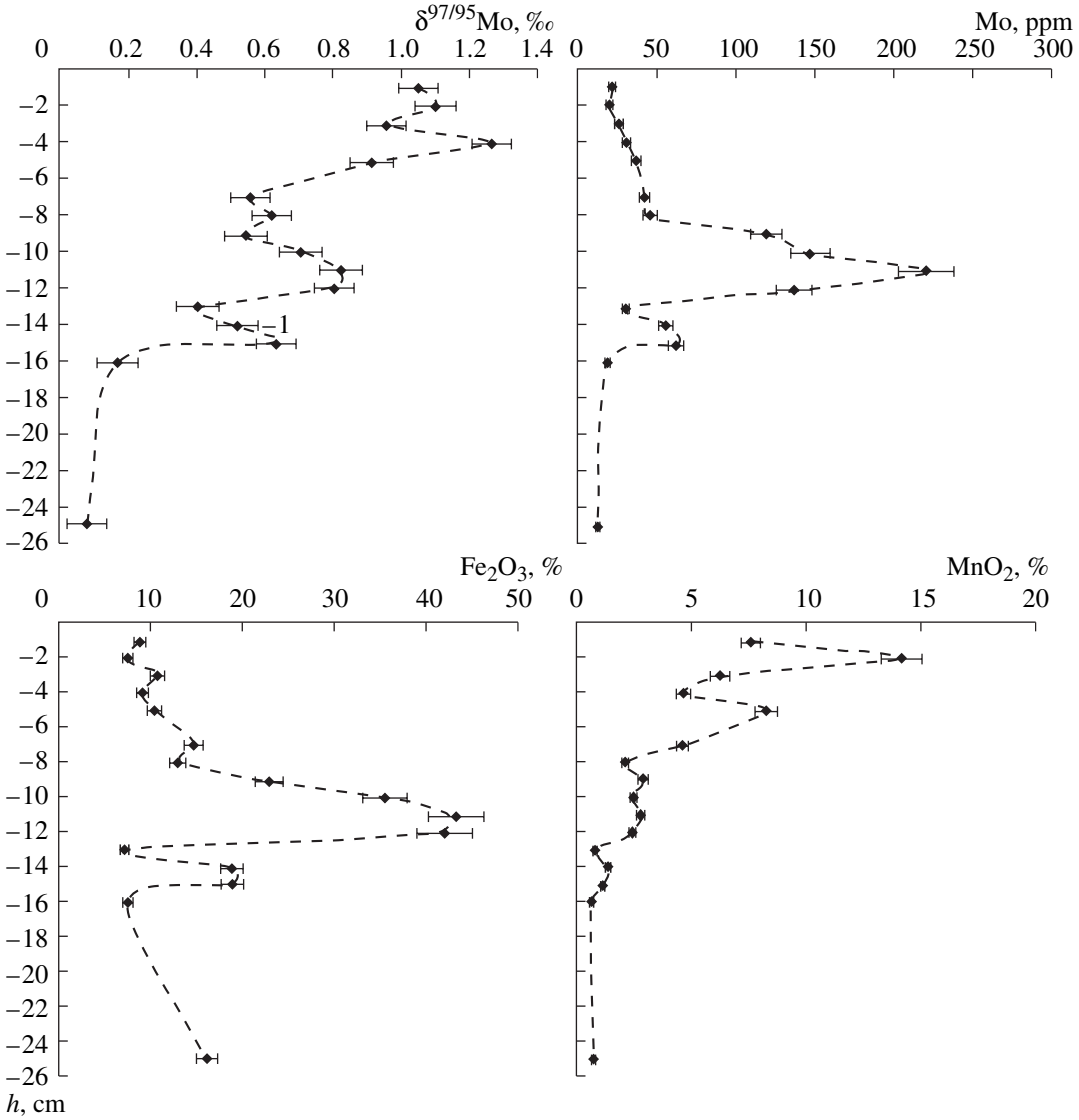


**Fig. 3.** Vertical profiles of $\delta^{97/95}$Mo and concentrations of Mo, $Fe_2O_3$, and $MnO_2$ for a BS column from Lake Kutsasjarvi. The reported errors correspond to two standard deviations.

effects related to Mo interaction with Fe oxides and organic matter are not understood.

Nonetheless, the obtained data are important, because they show that geochemical processes occurring in a catchment can modify the isotopic composition of Mo compared with the initial composition of the bedrocks. The range of variations in Mo isotopic composition in freshwater BS is comparable with that of marine sediments. It is intriguing that the first attempt to model the Mo isotope balance in the ocean suggested minor variations in the isotopic composition of Mo entering the ocean owing to continental weathering [12]. The results of our study show that mechanisms capable of changing the isotopic composition of Mo during its migration on land before introduction into the ocean must be investigated in detail.

## CONCLUSIONS

A new method was proposed for the measurement of Mo isotopic ratios by MC ICP MS. It allows accurate determination of variations in the Mo isotopic composition caused by geochemical processes. The proposed method makes use of normalization to the isotopic ratio $^{105}Pd/^{104}Pd$ as a means for correcting for instrumental mass discrimination and provides a number of advantages over previous techniques. These advantages include an improved procedure of Mo purification from the accompanying matrix elements and the possibility to measure a greater number of Mo isotopes, namely, $^{94}$Mo, $^{95}$Mo, $^{96}$Mo, $^{97}$Mo, $^{98}$Mo, and $^{100}$Mo.

The variations in Mo isotope ratios observed in the BS of freshwater basins suggest that geochemical pro-

cesses can change the isotopic composition of Mo during its water migration.

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