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# Variations in the isotopic composition of molybdenum in freshwater lake systems

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## Abstract

Variations in molybdenum isotopic composition, spanning the range of ~2.3‰ in the terms of $^{97}$Mo/$^{95}$Mo ratio, have been measured in sediment cores from three lakes in northern Sweden and north-western Russia. These variations have been produced by both isotopically variable input of Mo into the lakes due to Mo isotopic heterogeneity of bedrock in the drainage basins and fractionation in the lake systems due to temporal variations in limnological conditions. Mo isotope abundances of bedrock in the lake drainage basins have been documented by analysis of Mo isotope ratios of a suite of molybdenite occurrences collected in the studied area and of detrital fractions of the lake sediment cores. The median $\delta^{97}$Mo value of the investigated molybdenites is 0.26‰ with standard deviation of 0.43‰ ($n=19$), whereas the median $\delta^{97}$Mo value of detrital sediment fractions from two lakes is −0.40‰ with standard deviation of 0.36‰ ($n=15$).

The isotopic composition of Mo in the sediment cores has been found to be dependent on redox conditions of the water columns and the dominant type of scavenging phases. Hydrous Fe oxides have been shown to be an efficient scavenger of Mo from porewater under oxic conditions. Oxidative precipitation of Fe(II) in the sediments resulted in co-precipitation of Mo and significant authigenic enrichment at the redox boundary. In spite of a pronounced increase in Mo concentration associated with Fe oxides at the redox boundary the isotopic composition of Mo in this zone varies insignificantly, suggesting little or no isotope fractionation during scavenging of Mo by hydrous Fe oxides. In a lake with anoxic bottom water a chironomid-inferred reconstruction of $O_2$ conditions in the bottom water through the Holocene indicates that increased $O_2$ concentrations are generally associated with low $\delta^{97}$Mo/$^{95}$Mo values of the sediments, whereas lowered $O_2$ contents of the bottom water are accompanied by relatively high $\delta^{97}$Mo/$^{95}$Mo values, thus confirming the potential of Mo isotope data to be a proxy for redox conditions of overlying waters. However, it is pointed out that other processes including input of isotopically heterogeneous Mo and Mn cycling in the redox-stratified water column can be a primary cause of variations in Mo isotopic compositions of lake sediments.

*Keywords:* Mo stable isotopes; Fractionation; MC-ICPMS; Molybdenite; Lake sediments; Deposition

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## 1. Introduction

Due to conservative behaviour of Mo in oxygenated waters and the ability to enrich authigenically in sediments under anoxic conditions with presence of sulphide species, Mo has attracted significant attention as a paleo-redox proxy (see e.g. Emerson and Huested, 1991; Crusius et al., 1996; Anbar, 2004 and references therein). It has been shown that the concomitant Mo isotope fractionation recorded in sediments can be used efficiently to complement its concentration data in reconstructions of oxygen concentrations of oceanic waters over the geological past (Siebert et al., 2001; Barling et al., 2001; Siebert et al., 2003; Barling and Anbar, 2004; Anbar, 2004; Arnold et al., 2004; Nägler et al., 2005). The current status of Mo stable isotopes in paleooceanographic research has been overviewed by Anbar (2004). According to the suggested first-order model of the Mo isotope balance in the oceans, Mo entering the oceans from continental sources is isotopically fractionated during removal from seawater into two major sedimentary sinks — oxic sediments and anoxic sediments. Because these two sinks have distinct Mo isotopic compositions, the Mo isotope signature in sediment columns has been suggested to reflect the fraction of ocean reducing waters over the geological past (Siebert et al., 2006). Based on limited Mo isotope data for basalts and granitic rocks, the riverine input of Mo has been assumed to exhibit little variations in the isotopic composition of Mo relative to those occurring in marine systems (Siebert et al., 2003; Anbar, 2004).

Data obtained in this study indicate significant heterogeneity of the Mo isotopic composition of molybdenites, the major mineral of the element, and provide evidence for a large range of variations in Mo isotopic composition of lake sediments. Our first observations of Mo isotopic fractionation in molybdenites have prompted a study aimed at evaluating the extent of Mo isotope variations in molybdenites collected from a limited area in northern Sweden and at testing the hypothesis that Mo isotopic heterogeneity of bedrock can be an important cause of Mo isotopic fractionation in lake sediments. This involves measurements of Mo isotope abundances for two sediment cores from lakes with drainage basins dominated by granite bedrock and for a suite of molybdenite occurrences collected within or close to the drainage basins of the lakes. The lakes are located in northern Sweden in the close vicinity to the largest Scandinavian Cu–Mo deposits. As a consequence, Mo concentrations in the lake sediments are strongly enriched relative to the average crustal abundance of 1–2 ppm (Taylor and McLennan, 1985). This allows determination of the isotopic composition of Mo separately for the reactive, non-detrital, fraction of the sediments and for the poorly reactive, detrital, fraction. A third sediment core in this study was acquired from a lake located on the Kola Peninsula, north-western Russia. This core provides a continuous sedimentation sequence through the Holocene. A previous study has characterized midge records of the sediment and made inferences on past hypolimnetic oxygen contents and temperatures in the lake (Ilyashuk et al., 2005). Insights into evolution of oxygen conditions in the bottom water of the lake from the midge records have facilitated interpretations of measured variations in Mo isotopic composition of the sediments.

This study shows a variable sedimentary Mo isotope signature in the lake systems, which reflects both heterogeneity of the Mo isotopic composition of crystalline bedrock and Mo isotope fractionation related to ambient limnological properties, particularly redox conditions. Although some specific fractionation mechanisms remain unresolved, adsorption of Mo by hydrous Fe oxides has been ruled out as the important mechanism of Mo isotope fractionation at circumneutral pH.

## 2. Site descriptions

Nineteen molybdenite samples from different localities in Sweden, Russia and China have been selected for this study. A description of these samples and the hosting geological settings is given in Table 1. Sediment cores have been collected from Lake Vettasjärvi and Lake Kutsasjärvi located within the Kalix River watershed, northern Sweden, and from Lake Berkut located in the southern part of the Kola Peninsula, north-western Russia (Fig. 1). Lakes Vettasjärvi and Kutsasjärvi are located in similar geomorphologic settings, neither having any significant sources of inflowing stream water. The bedrock of their drainage basins consists of granitic rocks older than 1.5 Ga. The surface area of Lake Vettasjärvi is ~7.8 km$^2$, the depth on the sampling station was 16 m, whereas the maximum depth of the lake is 19 m. The surface area of Lake Kutsasjärvi is ~3 km$^2$, the sampling depth is 26 m, and the maximum depth of the lake is 35 m.

Lake Berkut is located at *ca* 25 m above sea level, 8 km from the White Sea coast, about midway along the southern coastline of the Kola Peninsula. The lake is small and elongated (*ca.* 150 m × 75 m) with a maximum depth of about 6 m. It lacks well-developed inflows and outflows, and its catchment is limited (~0.2 km$^2$). The dominant source of recharge for the lake is atmospheric precipitation. Lake-level

Table 1
The Mo isotopic composition and geological description of molybdenites analyzed in this study

| Localities where molybdenites have been collected | $\delta^{97}Mo$, ‰ | Geological description |
|---|---|---|
| Storträsket W-deposit, Sweden | 1.51±0.1 | Greisenized albitic leucogranite with quartz veins containing wolframite, molybdenite, scheelite, arsenopyrite, pyrite, fluorite and tourmaline (Öhlander, 1986). |
| Aitik Cu–Au deposit, Gällivare, Sweden | 0.81±0.1 | Biotite rock with some quartz and coarse-grained aggregates of molybdenite in a shear zone in the Aitik ore. Hosted by 1.9 Ga metavolcanic rocks (Wanhainen et al., 2005). |
| Ferrum Cu–Au deposit, Gällivare, Sweden | 0.76±0.1 | Disseminated molybdenite in a quartz–pyroxene vein in association to quartz–tourmaline alteration with disseminated chalcopyrite and bornite. Hosted by 1.9 Ga metavolcanic rocks (Wanhainen et al., 2005). |
| Bispberg Fe-deposit, Säter, Sweden | 0.70±0.1 | Foliated chlorite rock with disseminated molybdenite flakes and magnetite. Molybdenite mainly along foliation planes. Sample from the footwall contact to the Bispber iron ore. Hosted by 1.9 Ga metavolcanic rocks (Wanhainen et al., 2005). Re–Os age of the molybdenite is 1742±17 Ma (Bergman et al., 2001). |
| Kirunavara Fe-deposit, Kiruna, Sweden | 0.59±0.1 | Anhydrite with talc and disseminated molybdenite brecciating magnetite ore. Hosted by 1.9 Ga metavolcanic rocks (Wanhainen et al., 2005). |
| Pegmatite, the Kola peninsula, Russia | 0.56±0.1 | Re–Os age of the molybdenite 1780±20 Ma* |
| Pikkujärvi Cu-deposit, Kiruna, Sweden | 0.52±0.1 | Coarse-grained aggregate of molybdenite with some chalcopyrite in association to mineralization of disseminated chalcopyrite and scapolite–microcline–tourmaline alteration. Hosted by 1.9 Ga quartzmonzonite (Wanhainen et al., 2005). |
| Allebuoda granites, Sweden | 0.40±0.1 | Molybdenite-bearing quartz veins are related to ~1.8 Ga aplitic granite. The sample was located at the contact zone between the granite and metasupracrustals. The molybdenite-mineralised aplite is very quartz-rich and potassic. Re–Os age of the molybdenite is 1829±6 Ma ** |
| Vähävaara pegmatite, Gällivare, Sweden | 0.33±0.1 | Narrow pegmatite dykes with disseminated and coarse-grained molybdenite and some bornite. Intrudes 1.9 Ga metavolcanic rocks. |
| Bratt Cu–Au deposit, Gällivare, Sweden | 0.26±0.08 | Magnetite ore with pyroxene and some calcite with small amounts of disseminated molybdenite and chalcopyrite in association to Cu–Au–Fe mineralization. Hosted by 1.9 Ga metavolcanic rocks (Wanhainen et al., 2005). |
| Kåtaberget granites, Sweden | 0.21±0.08 | Molybdenite occurs as irregularly distributed coarse aggregates in aplites, which is situated in central parts of ~1.9 Ga granite intrusions. Re–Os age of the molybdenite is 1875±6 Ma ** |
| Lietchsavo granites, Sweden | 0.19±0.08 | Quartz–tourmaline vein with aggregates of bornite and chalcopyrite and disseminated molybdenite. Hosted by 1.9 Ga metavolcanic rocks (Wanhainen et al., 2005). |
| Nunasvaara Mo-deposit, Gällivare, Sweden | 0.18±0.08 | Molybdenite and some pyrite, chalcopyrite, magnetite and apatite in orthogneiss with scapolite, hornblende and epidote. Molybdenite as coarse-grained aggregates along foliation and disseminated. Hosted by 1.8–1.9 Ga gabbro (Geijer, 1924). |
| Särkivaara Cu-deposit, Svappavaara, Sweden | 0.14±0.08 | Scapolite–garnet–pyroxene-epidote skarn with chalcopyrite, pyrrhotite, pyrite and molybdenite. Sample with aggregates of molybdenite in pyrite-rich skarn of epidote, pyroxene and garnet (Geijer, 1924). |
| JDC, porphyry Cu deposit, China | 0.12±0.08 | The sample was from Tuwu–Yandong porphyry Cu deposit. The sample was acquired as molybdenite powder from Geological Survey of China. Re–Os age of the molybdenite is 141±2 Ma (Grip and Frietsch, 1973). |
| Ahmavuoma Cu–Co–Au deposit, Sweden | −0.11±0.08 | Microcline rich granite–pegmatite with disseminated and fine-grained molybdenite. Intrudes 1.9 Ga metavolcanic rocks with pyrite–chalcopyrite mineralization. |
| Granitic rock, the Kola peninsula, Russia | −0.18±0.08 | Re–Os age of the molybdenite 1787±7 Ma * |
| HLP-5,carbonate type Mo–Pb deposit, China | −0.20±0.08 | The sample was from a carbonate vein-type Mo–Pb deposit in the Jinduicheng–Huanglongpu area of Shaanxi province on the southern margin of the north China platform. The sample was acquired as molybdenite powder from Geological Survey of China. Re–Os age of the molybdenite 223±2 Ma (Grip and Frietsch, 1973). |
| Aggojavre granite, northern Sweden | −0.25±0.1 | Aplitic granite with disseminated molybdenite, pyrite and fluorite. Also narrow quartz veins with molybdenite, pyrite and fluorite. Intrudes 2.8 Ga gneisses (Wanhainen et al., 2005). |

*Determined in the lab of Luleå University of Technology using the method described in (Malinovsky et al., 2002).

**Determined in the lab of Holly Stein at Colorado University, USA.

The isotopic composition is relative to our in-house Mo standard. Uncertainty terms given are reproducibilities of separately prepared subsamples at 2 $\sigma$ level.

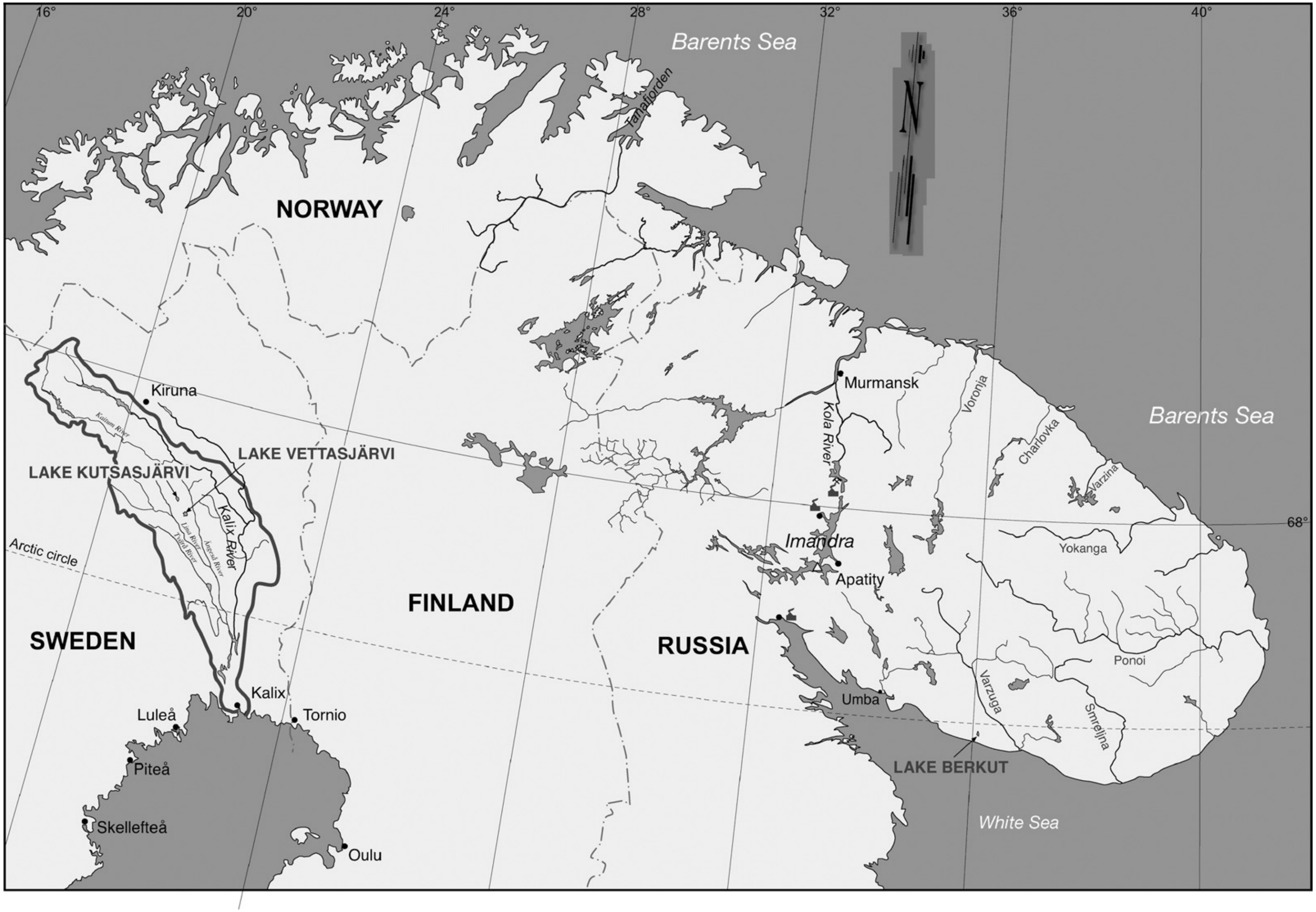

Fig. 1. Study area. Thick solid line gives outlines of Kalix River drainage area where Lake Kutsasjärvi and Lake Vettasjärvi are situated in. Most of molybdenites measured in this study have been collected within Kalix River drainage area.

fluctuations are also determined by local groundwater conditions. The site is surrounded by boreal coniferous forest with approximately equal proportions of spruce and Scots pine. The bedrock is composed of Achaean and Proterozoic gneiss and amphibolites, which are overlain by glaciofluvial sands of presumably similar mineralogical composition. The deglaciation of the area probably occurred around or slightly after 12,000 cal. years BP (Svendsen et al., 2004). The lake water is acidic with a pH of 4.4. A small mire is situated on the eastern side of the lake. Pictures of Lake Berkut can be found in (Ilyashuk et al., 2005).

## 3. Sample collection

Molybdenites have been accurately picked up from pieces of the hosting rocks by hand. Collection of the sediment cores in Lakes Vettasjärvi and Kutsasjärvi was performed from the ice during April 2003 and May 2005. Apart from the sediment cores, three other types of samples were obtained during the sampling — suspended particulate matter (SPM), filtered bottom water and porewaters. The sampling started from *in-situ* measurements of the depths and vertical profiles of dissolved $O_2$, pH and conductivity of water columns at each sampling station at the lakes, in order to determine the location of the oxic–anoxic transition zone. Dissolved $O_2$, pH and conductivity values were determined using a Hydrolab Survey II water quality probe (Hydrolab Corp., Austin, TX, USA).

No significant dissolved $O_2$ depletion relative to surface water was found in the water column of Lake Kutsasjärvi. A sediment core was acquired from the lake using a gravity corer. Sectioning of this core into 1 cm thick layers was carried out immediately after sampling under oxic atmosphere. The total length of the sampled sediment core was ~26 cm.

At Lake Vettasjärvi anoxic conditions prevail in the lowermost 25 cm of the water column. SPM and filtered waters were sampled successively across the oxic–anoxic transition zone from depths of 15.0 m, 15.2 m, 15.4 m, 15.6 m and 15.8 m at a location with 16.0 m water depth. The samples were collected by *in-situ* filtration using the method described by Ödman et al. (1999). Briefly, silicon tubing was lowered to each selected depth and water was then pumped by means of a portable Masterflex peristaltic pump (Cole-Palmer International, Chicago, IL, USA) and filtered on-line through a Millipore membrane filter. The filters (Millipore, 142-mm external diameter) are composed of cellulose acetate and cellulose nitrate fibers woven into a matrix with a nominal pore size of 0.22 μm. They were mounted in metal-free polycarbonate filter holders (Geotech Environmental Equipment Inc., Denver, CO, USA). The filtered water samples were collected into 1 l low-density polyethylene bottles. Within 24 h after sampling the water samples were acidified to 0.1 M $HNO_3$ concentration in the laboratory. Filtering equipment and all plastic labware used in the sampling were acid-washed in 1 M $HNO_3$ before use. For cleaning purposes, the filters were leached in 5% (v/v) acetic acid for 72 h and then soaked several times in deionized water until no smell of acetic acid was appreciable.

In another day a sediment core was withdrawn at the same sampling station at Lake Vettasjärvi using a gravity corer. The core tube was immediately transferred into an argon-filled glove bag. Under argon atmosphere the core was sliced into contiguous 1 cm thick sections. The porewaters were pressed out of these sections using 10 ml syringes with 0.45 μm membrane filters. Only a fraction of the porewaters from the sediment sections was collected because the filters were clogged rapidly by fine sediment particles. An additional sediment core was therefore acquired at the same sampling site at Lake Kutsasjärvi and sectioned into contiguous 1 cm thick layers under oxic atmosphere, i.e., no separation of the porewaters was performed. The total length of the sampled sediment core was ~12 cm. The porewater samples were acidified to 0.2 M HCl concentration in the laboratory within 24 h after sampling.

The sediment core from Lake Berkut was retrieved from a floating platform in the deepest central part of the lake in August 1999 with a Russian peat sampler which is 1 m long and 7.5 cm in diameter. The uppermost loose sediments were sampled with a gravity corer and subsampled in the field. The sediment cores were extruded and described in the field, transferred to supportive liners, wrapped in plastic film and transported to cold storage (4 °C). The 158 cm sediment sequence was divided into 71 contiguous sections, 2–4 cm thick and adjusted to lithostratigraphic boundaries. Subsamples of the contiguous sections were taken for analyses of midge remains (Ilyashuk et al., 2005), elemental and Mo isotopic analyses. The remaining parts of the sections were wet-sieved for macrofossils used for radiocarbon dating.

## 4. Analytical methods

### 4.1. Sample preparation

#### 4.1.1. Molybdenites

Aliquots of molybdenite samples with masses of *ca* 0.1 g have been brought to solution using aqua regia (3 parts of 10 M HCl:1 part of 16 M $HNO_3$) in Teflon beakers kept for hours on a hot plate at 250 °C. After complete dissolution the samples were evaporated on a hot plate to dryness and reconstituted in 0.3 M $HNO_3$.

#### 4.1.2. Sediment cores

Sediments samples were air dried and then ashed at 550 °C during ~16 h. The calculated Loss On Ignition (LOI) has been used as an indirect estimation of organic matter in the sediment cores from Lake Kutsasjärvi and Lake Vettasjärvi. No correction for potential losses of water from structure of clay minerals was applied. Total organic carbon (TOC) was determined on the sediment core from Lake Berkut using a CE Instruments NC2500 elemental analyzer.

Further decomposition of sediment samples was performed in two successive steps in order to estimate the differences in Mo concentration and isotopic composition between the non-detrital phase, associated with organic matter and Fe–Mn oxides, and the detrital silicate phase. After ashing of organic matter a reductive hydroxylamine–hydrochloride leach was used to dissolve Fe and Mn oxides by addition of 12 ml of ~3.5 M HCl/0.01 M hydroxylamine–hydrochloride ($NH_2OH{\cdot}HCl$) solution to *ca.* 0.5 g of sample aliquot in Teflon beakers (Boström et al., 1982; Kersten and Forster, 1989). These suspensions were kept during 3 h on a hot plate at 50 °C. The sample suspensions were then transferred into polypropylene tubes, centrifuged, and the aqueous phase was decanted. Aliquots of the aqueous phase were taken for concentration measurements. The sample solutions were dried down on a hot plate and reconstituted in 0.3 M $HNO_3$. The remaining detrital silica residues of the samples were transferred into Teflon microwave bombs and digested in a mixture of aqua regia (2.5 ml of 16 M $HNO_3$:7.5 ml of 10 M HCl) with addition of 1 ml of 25 M HF during 1 h in a microwave oven using 600 W power setting. After completing the microwave-assisted decomposition, aliquots of the sample solution were taken for concentration measurements. The sample solutions were dried down on a hot plate and reconstituted in 0.3 M $HNO_3$.

As Mo concentrations in the detrital phase of sediments from Lake Berkut were found to be too low for Mo isotope ratio measurements, the non-detrital and detrital fractions of Mo were combined together, dried down on a hot plate and reconstituted in 0.3 M $HNO_3$. The sample solutions in 0.3 M $HNO_3$ matrix were ready for ion-exchange purification of Mo prior to isotope ratio measurements.

Mass-specific magnetic susceptibility ($\chi$) was determined on freeze-dried and fine-ground subsamples of the sediment core from Lake Berkut using a Geofyzica Brno Kappabridge KLY-2 apparatus.

#### 4.1.3. SPM in the water column of Lake Vettasjärvi

The SPM samples were prepared for elemental analysis using a modified microwave-assisted extraction procedure described in Ödman et al. (1999). The filters were placed into 120 ml microwave digestion PFA Teflon vessels. 5 ml of 16 M $HNO_3$ and 1 ml of 10 M HCl were added. The vessels were closed and allowed to stand overnight at room temperature. The samples were then heated in a microwave oven for 60 min using a 600 W power setting.

### 4.2. Purification of Mo

Purification of Mo prior to Mo isotope ratio measurements is necessary in order to eliminate potential spectral interferences and minimize matrix effects during MC-ICPMS measurements. Molybdenum from most geological samples has to be purified because Mo is a minor or trace constituent of the sample matrix. The only major exception is molybdenite, $MoS_2$, a mineral in which Mo is the major constituent; other elements are present at negligible levels relative to Mo. Therefore, no purification has been applied after decomposition of molybdenites in this study.

The purification procedure employed in this study has been described in detail elsewhere (Malinovsky et al., 2005), and only a brief summary is presented here. Separation of Mo from concomitant elements was performed by ion-exchange chromatography using the chelating resin Chelex-100. The efficiency of purification and yield of Mo have been estimated on aliquots of each sample taken before and after ion-exchange separation and measured by single-collector inductively coupled plasma mass spectrometry (ICP-MS). The yield of Mo through the ion-exchange column was always better than 90% (the average value is 95±3%; the uncertainty is one standard deviation based on $n=46$). The sample preparation and ion exchange separation of Mo was carried out in a clean environment (class 1000). The dilution of solutions was performed using deionized “Milli-Q” water and nitric acid that was additionally purified by sub-boiling distillation in a quartz vessel. Procedural blanks were prepared for all sample manipulations and found to contain negligible quantities of Mo (<10 ng) relative to those of Mo in the samples.

### 4.3. Mass spectrometry and data processing

Mo isotope ratio measurements were performed using a Neptune MC-ICPMS (Thermo Finnigan, Germany). The typical operation conditions for the instrument and the performance of Mo isotope ratio measurement protocol are described in Malinovsky et al. (2005). Briefly, six Mo isotopes, namely $^{94}$Mo, $^{95}$Mo, $^{96}$Mo, $^{97}$Mo, $^{98}$Mo, $^{100}$Mo as well as $^{104}$Pd and $^{105}$Pd were measured. The analyses were conducted in the static mode. Samples were analyzed in a sequence of isotope standard, "unknown" sample, isotope standard and so on. Concentrations of samples and bracketing standards were matched to within 20%. All samples and standards were analyzed in duplicate, giving a total analysis time per sample of ~15 min. A low resolution mode was used in this study; typical sensitivity for $^{98}$Mo$^+$ was ~7.5 V/mg l$^{-1}$ Mo. The samples were diluted to Mo concentration of 1 or 2 mg l$^{-1}$ Mo with 0.3 M $HNO_3$ and spiked with Pd at 0.5 or 1 mg l$^{-1}$ Pd. Instrumental mass discrimination is corrected for by using Pd spiking and normalization to the $^{105}$Pd/$^{104}$Pd ratio. Under normal operating condition, mass discrimination of $^{97}$Mo/$^{95}$Mo ratio was 1.97±0.02% (±1 $\sigma$; $n=42$) and 1.98±0.03% (±1 $\sigma$; $n=36$) per mass unit for typical standards and samples, respectively. The small difference of the magnitude in mass bias between typical standards and samples provides an additional indication of suitability of Mo purification chemistry used in this study. The measured $^{97}$Mo/$^{95}$Mo, $^{98}$Mo/$^{95}$Mo and $^{100}$Mo/$^{95}$Mo ratios were consistent with mass-dependent isotope fractionation and well reproducible. However, the results for $^{96}$Mo/$^{95}$Mo and $^{94}$Mo/$^{95}$Mo ratios were erratic for most of the samples. We attribute this to interferences originating from residual matrix elements on $^{94}$Mo and $^{96}$Mo isotopes, notably $^{54}$Fe$^{40}$Ar on $^{94}$Mo and $^{56}$Fe$^{40}$Ar on $^{96}$Mo.

The on-line data processing included calculation of the ion beam intensity ratios and filtering of outliers by a 2 $\sigma$ test. Further statistical treatment of the data was performed off-line. For the presentation of results, δ-notation is utilized (Anbar, 2004; Malinovsky et al., 2005), as defined by the relationship:

$$\delta^{97}\mathrm{Mo} = \left[\frac{(^{97}\mathrm{Mo}/^{95}\mathrm{Mo})_{\mathrm{sample}}}{(^{97}\mathrm{Mo}/^{95}\mathrm{Mo})_{\mathrm{standard}}} - 1\right] \cdot 1000\% \qquad (1)$$

where $^{97}$Mo/$^{95}$Mo$_{\mathrm{sample}}$ and $^{97}$Mo/$^{95}$Mo$_{\mathrm{standard}}$ are the measured ratios for sample and in-house Mo standard (High Purity Standards, lot # 320304, Charleston, SC 29423, USA), respectively, corrected for instrumental mass discrimination using Pd. Precision of $^{97}$Mo/$^{95}$Mo ratio measurements in the terms of reproducibilities on a sample solution between runs within a single instrumental session is better than 0.1‰ at 2 $\sigma$ level. However, long-term reproducibilities of separately prepared subsamples of sediments have been found to be larger, for most samples within 0.2‰ at 2 $\sigma$ level.

In order to compare Mo isotopic data obtained in this study with the results of other works the Mo solution (Johnson Matthey, ICP standard solution, lot 602332B) used as the isotopic standard by Siebert et al. (2001, 2003) was measured against our in-house Mo standard. $\delta^{97}$Mo value of the aforementioned Johnson Matthey ICP standard solution was −0.03±0.1‰ (2 $\sigma$ level) relative to our in-house Mo standard; other isotope ratios including $^{96}$Mo, $^{98}$Mo and $^{100}$Mo were also indistinguishable between these two standards, within the limits of instrumental precision. The isotopic composition of Mo in seawater was calibrated against the Johnson Matthey Mo standard in previous studies (e.g. Siebert et al., 2003), yielding $\delta^{97}$Mo value of ~1.53±0.1‰ (recalculated from the original value given as $\delta^{98/95}$Mo by using the relation $\delta^{97/95}\mathrm{Mo} \cong 2/3 \times \delta^{98/95}\mathrm{Mo}$). The nearly identical Mo isotopic composition for our in-house Mo standard and that used by Siebert et al. (2003) allows easy comparison of Mo isotope data reported in our study with Mo in seawater.

### 4.4. Lake Berkut sediment chronology

The chronology of the sediment sequence of Lake Berkut is based on eight calibrated AMS radiocarbon dates obtained on macroscopic remains of predominately terrestrial plants (Ilyashuk et al., 2005). Calendar-year age estimates expressed as 94.5% probability envelopes were obtained by calibration of the radiocarbon dates based on the IntCal98 calibration data set (Stuiver et al., 1998), using the OxCal3.5 radiocarbon calibration software.

## 5. Results and discussion

### 5.1. Mo isotopic composition of molybdenites

Mo isotope abundances for the molybdenite samples are shown in Table 1. An important observation is a range of ~1.7‰ in terms of $^{97}$Mo/$^{95}$Mo ratio for the isotopic composition of Mo in the measured molybdenites. This range is larger than that reported for molybdenites previously (Wieser and De Laeter, 2003; Anbar, 2004; Pietruszka et al., 2005). It is noteworthy to mention that 0.7‰ of the 1.7‰ observed range is accounted for by one sample from Storträsket W-deposit, which has $\delta^{97}$Mo value of 1.51±0.1‰. A typical $\delta^{97}$Mo value for the measured 19 molybdenite samples can be represented by median of 0.26±0.43‰, where uncertainty denotes one standard deviation.

As seen from Table 1, our data reveal no systematic correlation between Mo isotopic composition and either age of the molybdenites or temperature estimate in magmatic–hydrothermal systems. The isotopic behaviour of Mo in the ore-forming environments remains virtually unstudied. It is also unknown whether the isotopic composition of Mo is variable within a single magmatic–hydrothermal ore system. A detailed study of these issues is warranted in the light of recent findings of variations in the isotopic composition of Zn up to 0.6‰ in terms of $^{66}Zn/^{64}Zn$ ratio for Zn minerals within single volcanic-hosted massive sulphide ore deposits (Mason et al., 2005).

Mo concentrations in granites within the drainage basins of Lake Kutsasjärvi and Lake Vettasjärvi are low and range from 0.1 to 9 ppm with the average value on the order of 1–2 ppm (Öhlander, 1985). A substantial, if not dominant, fraction of Mo released during weathering of the bedrock of the studied area in northern Sweden is provided by Mo mineralization, as molybdenite occurrences are widely distributed in the area. It has been documented previously that its high susceptibility to weathering makes molybdenite the primary source of Mo for soils developing on granitic rocks (Adriano, 2001). The Mo isotope data for molybdenites in this study suggest that Mo released from the granitic bedrocks during weathering has a variable Mo isotope signature. Preliminary investigations revealed no Mo isotope fractionation associated with dissolution of granites under laboratory conditions (Siebert et al., 2003). Thus, the net isotopic composition of Mo in Lake Kutsasjärvi and Lake Vettasjärvi is presumably controlled by mixing of Mo derived from isotopically heterogeneous bedrock and by feedback processes

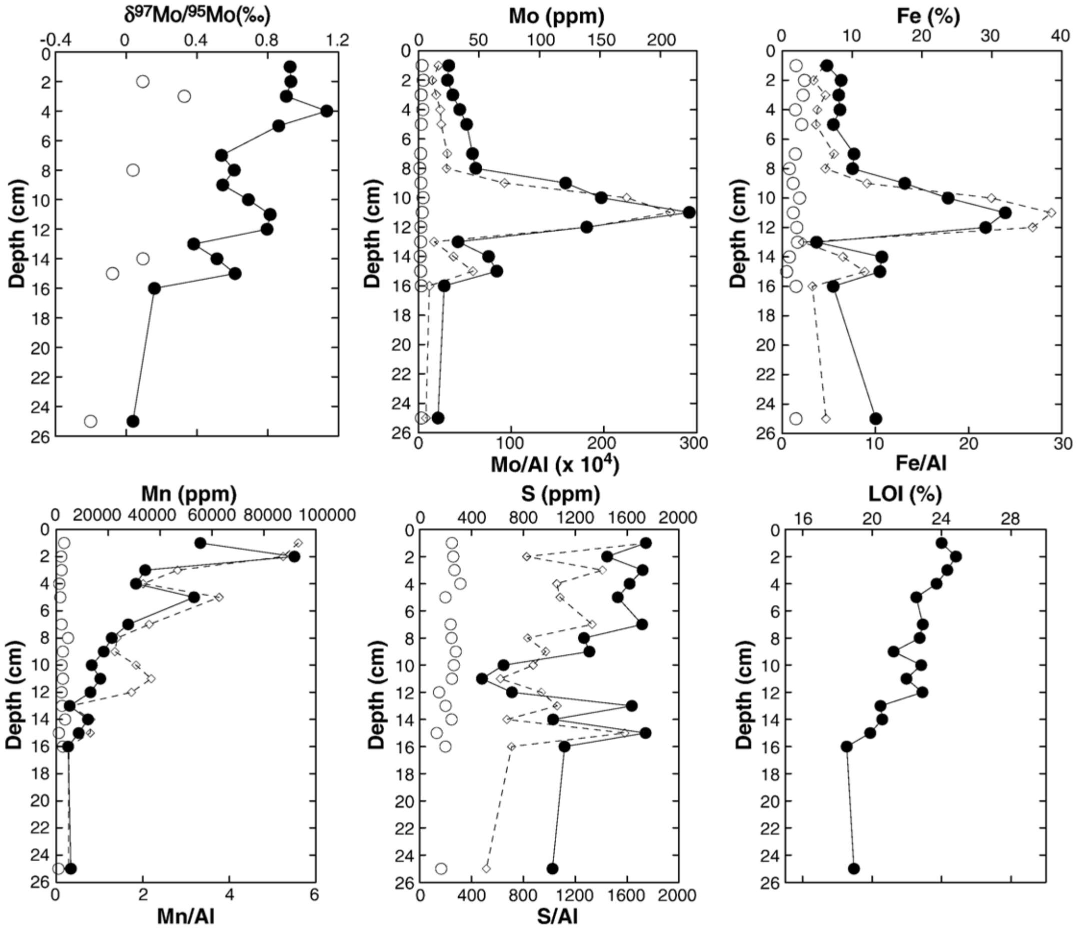

Fig. 2. Mo isotopic composition and concentrations of Mo, Mn, Fe, S and Loss On Ignition (LOI) in the sediment profile from Lake Kutsasjärvi. Filled circles represent the bulk isotopic composition and bulk element concentrations. Open circles show the Mo isotopic composition and element concentrations of the detrital fraction. Open diamonds show the bulk element concentrations normalised to Al. Reproducibilities of $^{97}Mo/^{95}Mo$ ratio measurements on separately prepared subsamples were within 0.2‰ at 2 $\sigma$ level. Reproducibilities of replicated concentration measurements were typically 5 to 7% at 2 $\sigma$ level.

operating during transport of Mo within drainage basins and in the lake systems.

### 5.2. Lake sediments

Transport of Mo within drainage basins is dominated by hydromorphic pathways, *i.e.*, surface and ground waters (Cook, 2000; Adriano, 2001). As such, lake sediments provide records of the isotopic composition of Mo transported from drainage basins. The detrital fraction of lake sediments, *i.e.*, silicate mineral phases resistant to weathering, provide a Mo isotopic signature of the bedrock within the drainage basin, whereas the non-detrital fraction may reflect Mo isotope fractionation due to immobilisation of Mo from solution onto reactive solid phases and organic matter.

Mo isotopic data and concentrations of Mo, Mn, Fe, and S as well as LOI or TOC records for the sediment cores from Lake Kutsasjärvi, Lake Vettasjärvi and Lake Berkut are shown in Figs. 2, 3 and 4, respectively. Fig. 4 also shows mass-specific magnetic susceptibility (MS) of sediments and chironomid-inferred bottom water conditions for Lake Berkut through the Holocene. Fig. 5 shows porewater concentration data for Lake Vettasjärvi. Mo isotopic and concentration data for the non-detrital and detrital fractions of Lake Kutsasjärvi and Lake Vettasjärvi are also given in Table 2.

The concentration data on the aforementioned figures are reported as concentrations both in the bulk sediments and in the detrital fractions, as well as the element/Al ratios. The latter highlight the true variability rather than changes in concentrations that result from

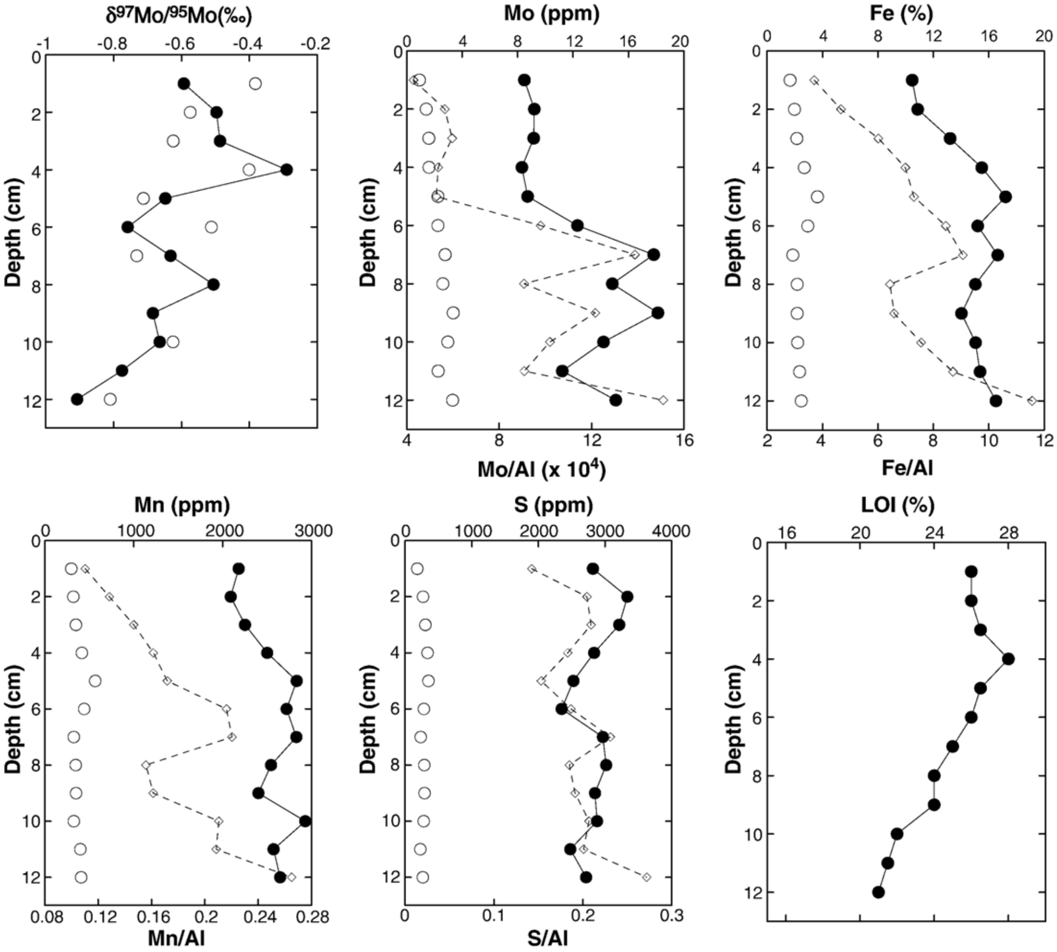

Fig. 3. Mo isotopic composition and concentrations of Mo, Mn, Fe, S and LOI in the sediment profile from Lake Vettasjärvi. Filled circles represent the bulk isotopic composition and bulk element concentrations. Open circles show the Mo isotopic composition and element concentrations of the detrital fraction. Open diamonds show the bulk element concentrations normalised to Al. A typical precision of replicated concentration measurements was 5% at 2 $\sigma$ level. Reproducibilities of $^{97}$Mo/$^{95}$Mo ratio measurements on separately prepared subsamples were within 0.2‰ at 2 $\sigma$ level. Reproducibilities of replicated concentration measurements were typically 5 to 7% at 2 $\sigma$ level.

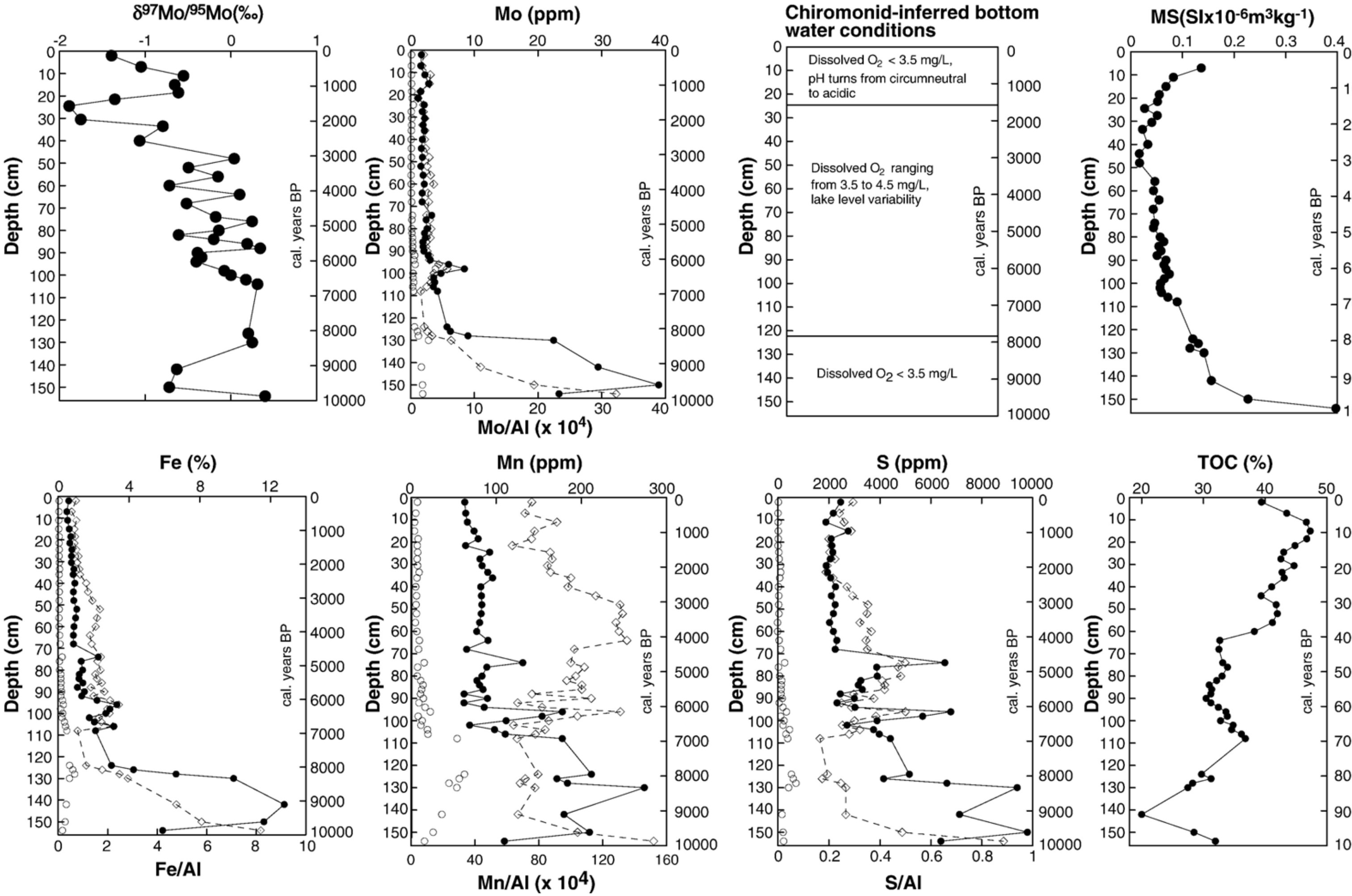

Fig. 4. Mo isotopic composition and concentrations of Mo, Mn, Fe, S, TOC, mass-specific magnetic susceptibility (MS) and chironomid-inferred bottom water conditions on sediments from Lake Berkut. Filled circles represent the bulk isotopic composition and element concentrations. Open circles show element concentrations of the detrital fraction. Open diamonds show the bulk element concentrations normalised to Al. Reproducibilities of $^{97}Mo/^{95}Mo$ ratio measurements on separately prepared subsamples were within 0.2‰ at 2 $\sigma$ level. Reproducibilities of replicated concentration measurements were typically 5 to 7% at 2 $\sigma$ level.

variable dilution, *e. g.*, by biogenic phases. Elevated element/Al ratios are assumed to reflect authigenic mineral precipitation or adsorption of the dissolved species in the porewaters.

The degree of $O_2$ saturation in bottom waters of Lake Kutsasjärvi and Lake Vettasjärvi relative to the surface water has been determined during *in-situ* dissolved $O_2$ sampling of the water columns from the ice. Concentration data for the sediment cores from Lake Kutsasjärvi and Lake Vettasjärvi show no signs of sulphidic environments, which could potentially be revealed by authigenic enrichments of S, Fe and Mo. There are no maxima in S/Al ratios downcore in any of the two lakes. The porewater concentration of total S ($0.48 \pm 0.07$ mg $l^{-1}$; $n=8$) in Lake Vettasjärvi is similar to that in the overlaying lake water ($0.42 \pm 0.01$ mg $l^{-1}$; $n=6$).

Redox conditions in the bottom water of Lake Berkut have been constrained using Mn and Fe concentrations in the sediment core, as the aerobic zone in the sediments would be reflected by subsurface authigenic enrichments of Mn and Fe concentrations. Concentrations of Mn and Fe do not exhibit any increases in the shallow sediments of Lake Berkut, which could be interpreted as authigenic enrichments at the oxic–anoxic interface. The range of Mn concentrations in the core is 50–280 ppm (Fig. 4). This is less than average crustal values, which are on the order of 600 ppm (Taylor and McLennan, 1985; Ivanochko and Pedersen, 2004). This indicates that bottom water dysoxia and/or the high organic flux to the sediments have been powerful enough to keep reducing conditions at very shallow depths in the sediments that must have impeded the accumulation of Mn and Fe at and just below the sediment–water interface. However, concomitant enrichments of Fe, Mo, Mn and S concentrations and their respective ratios to Al are evident downcore at depths of ~74 cm, ~96 cm and below 125 cm. These enrichments appear to reflect precipitations of sulphide minerals of the aforementioned metals, which might have occurred at the time of sediment formation or later during sediment diagenesis. Inferences from midge records in the core suggest a low concentration of dissolved oxygen (<1.5 mg $O_2$ $l^{-1}$) in the bottom water of Lake Berkut during the early Holocene (*ca* 10,000–8400 cal. years BP) (Ilyashuk et al., 2005), corresponding to the concentration maxima of S, Mo, Fe and Mn in the lower part of the sediment core (below ~125 cm). High organic flux and low concentration of dissolved $O_2$ in the bottom water favoured formation of sulphidic conditions at the sediment–water interface or at shallow sediment depths. The subsequent period dated *ca* 8400–1600 cal. years BP is characterized by a general increase in dissolved $O_2$ up to 4.5 mg $O_2$ $l^{-1}$ with significant variability.

A common feature of all three lakes is that Mo concentrations dominate in the non-detrital fraction of the sediment cores. This is presumably accounted for by site-specific aspects of the lake drainage basins. An important site-specific aspect of Lake Kutsasjärvi and Lake Vettasjärvi is that these lakes are located in the close proximity to Cu–Au–Mo porphyry-style mineral deposits (Table 1). Quartz–molybdenite veins and their dispersed remnants are abundant in the granitic till of the area. The proximity to a molybdenite source is known as the most important factor controlling the concentration of Mo in lake sediments (Cook, 2000). Another site-specific aspect of both Lake Kutsasjärvi and Lake Vettasjärvi is that suspended matter in these lakes is enriched in non-detrital Fe and Mn compared to world rivers and the upper crust. The origin of non-detrital

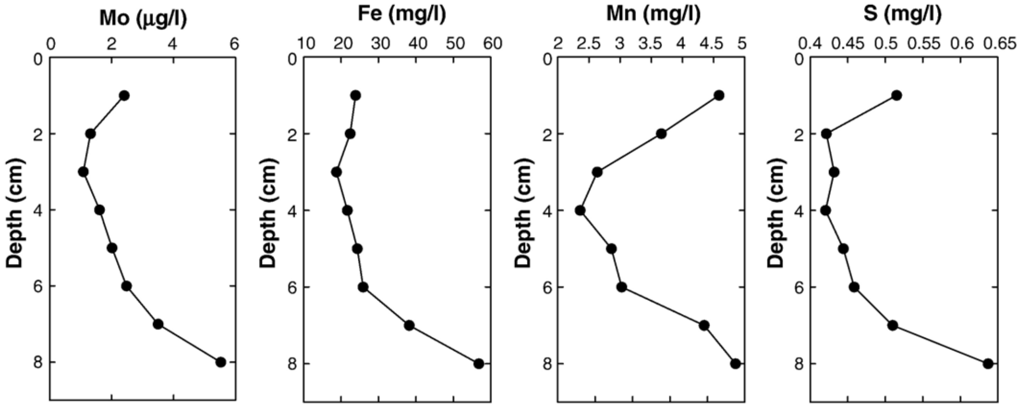

Fig. 5. Porewater profiles of Mo, Fe, Mn and S in the sediments of Lake Vettasjärvi. A typical precision of replicated concentration measurements was 5 to 7% at 2 $\sigma$ level.

Table 2
Mo concentration and isotopic data obtained on sediment cores from Lake Kutsasjärvi and Lake Vettasjärvi

| *h*, cm | Bulk Mo | | Non-detrital fraction** | | Detrital fraction | |
|---|---|---|---|---|---|---|
| | Concentration, ppm | $\delta^{97}$Mo, ‰ * | Concentration, ppm | $\delta^{97}$Mo, ‰ | Concentration, ppm | $\delta^{97}$Mo, ‰ |
| *Lake Kutsasjärvi* | | | | | | |
| 1 | 25 | 0.93 | 22 | 1.05 | 3.1 | n.d. |
| 2 | 24 | 0.93 | 20 | 1.10 | 4.1 | 0.09 |
| 3 | 29 | 0.91 | 26 | 0.96 | 2.4 | 0.33 |
| 4 | 34 | 1.13 | 30 | 1.27 | 3.7 | n.d. |
| 5 | 40 | 0.86 | 37 | 0.92 | 2.5 | n.d. |
| 7 | 45 | 0.54 | 43 | 0.56 | 2.0 | n.d. |
| 8 | 47 | 0.61 | 46 | 0.63 | 1.3 | 0.04 |
| 9 | 122 | 0.55 | 119 | 0.55 | 2.2 | n.d. |
| 10 | 151 | 0.69 | 147 | 0.71 | 4.0 | n.d. |
| 11 | 224 | 0.81 | 220 | 0.83 | 3.3 | n.d. |
| 12 | 139 | 0.80 | 137 | 0.81 | 2.1 | n.d. |
| 13 | 33 | 0.38 | 31 | 0.40 | 2.0 | n.d. |
| 14 | 58 | 0.51 | 56 | 0.52 | 1.5 | 0.10 |
| 15 | 65 | 0.62 | 63 | 0.64 | 2.0 | −0.08 |
| 16 | 21 | 0.16 | 19 | 0.17 | 2.5 | n.d. |
| 25 | 16 | 0.04 | 14 | 0.08 | 2.6 | −0.20 |
| *Lake Vettasjärvi* | | | | | | |
| 1 | 8.5 | −0.59 | 7.6 | −0.62 | 1.1 | −0.38 |
| 2 | 9.2 | −0.50 | 7.8 | −0.48 | 1.4 | −0.57 |
| 3 | 9.2 | −0.49 | 7.6 | −0.46 | 1.6 | −0.62 |
| 4 | 8.3 | −0.29 | 6.7 | −0.26 | 1.6 | −0.40 |
| 5 | 8.7 | −0.65 | 6.5 | −0.63 | 2.3 | −0.71 |
| 6 | 12.3 | −0.76 | 10.1 | −0.81 | 2.3 | −0.51 |
| 7 | 17.8 | −0.63 | 15.0 | −0.61 | 2.8 | −0.73 |
| 8 | 14.8 | −0.51 | 12.2 | −0.49 | 2.6 | n.d. |
| 9 | 18.1 | −0.68 | 14.8 | −0.70 | 3.4 | n.d. |
| 10 | 14.2 | −0.66 | 11.2 | −0.67 | 3.0 | −0.63 |
| 11 | 11.2 | −0.78 | 9.0 | −0.82 | 2.3 | n.d. |
| 12 | 15.1 | −0.91 | 11.8 | −0.92 | 3.3 | −0.81 |

n.d. — not determined.
* $\delta^{97}$Mo values are relative to the in-house Mo standard High Purity. Internal reproducibilities of MC-ICPMS measurements are better than 0.1‰ at 2 $\sigma$ level; however, long-term reproducibilities of separately prepared subsamples have been found to be within 0.2‰ at 2 $\sigma$ level. For samples where Mo isotopic measurements for the detrital phase have not been determined, the bulk Mo isotopic composition has been calculated using the average measured $\delta^{97}$Mo values for detrital phase of the appropriate sediment cores, i.e., $\delta^{97}\text{Mo}=0.05\pm0.18$‰ for Lake Kutsasjärvi sediments and $\delta^{97}\text{Mo}=-0.60\pm0.15$‰ for Lake Vettasjärvi sediments.
**Concentration and $\delta^{97}$Mo values of non-detrital fraction in these cores have also been reported by Malinovsky et al. (2005).
Both lakes are located in the Kalix River drainage basin, northern Sweden.

particles rich in Mn in the lakes and in the Kalix River watershed has been extensively studied and attributed largely to input of Fe–Mn-rich mire waters and the redox cycling in lake water columns (Pontér et al., 1990, 1992). The specific feature of Lake Berkut is that its catchment is limited (~0.2 km$^2$) and its small and relatively shallow water body sustains a high aquatic productivity and thus a high organic matter flux to the sediments. The lake water is acidic with pH of 4.4. Molybdenum has been found associated with organic matter in sediments under reducing conditions and its removal into sediments is greatly enhanced at acidic conditions (see e.g. Presley et al., 1972; Helz et al., 1996; Adriano, 2001; Ivanochko and Pedersen, 2004).

Further discussion of Mo elemental and isotopic abundances in the sediment cores is given separately for sediments deposited under oxic bottom water, *i.e.* for Lake Kutsasjärvi, and for anoxic sediments of Lake Vettasjärvi and Lake Berkut.

### *5.2.1. Sediments deposited under oxic bottom water*

The oxic–anoxic transition zone is situated below the sediment–water interface at Lake Kutsasjärvi. The location of this zone is constrained using concentration data of Mn and Fe (Fig. 2). A distinct Fe concentration maximum and an increase in the Fe/Al ratio are observed at a depth of 11 cm from the sediment–water interface, whereas Mn concentration maximum and an increase in the Mn/Al ratio are evident at a depth of 3 cm. These concentration maxima are interpreted as a result of oxidation of ferrous Fe and Mn (II), diffusing from the anoxic zone in the porewater towards the sediment–water interface, and their deposition as hydrous Fe and Mn oxides in the oxygenated sediments. The zone of Mn oxides deposition is decoupled from that of Fe oxides and located at shallower depth because oxidation of Mn (II) species requires higher redox potential than the oxidation of Fe(II) compounds (Adriano, 2001).

An interesting observation is that the elevated Fe concentration at the depth of 11 cm is coincident with the pronounced increases of Mo concentration and Mo/Al ratio (Fig. 2). This suggests that porewater Mo species co-precipitate and/or adsorb on the hydrous Fe oxides formed at the oxic–anoxic interface. In contrast, Mo concentrations and Mo/Al ratios exhibit no increases in the zone of hydrous Mn oxides deposition. Thus, it is likely that Mo migrates in the porewater from deeper sediment layers towards the sediment–water interface and is scavenged predominantly by the hydrous Fe oxides at the oxic–anoxic transition zone. A significant potential of poor-crystalline hydrous Fe oxide, ferrihydrite, for adsorption of Mo species over a broad pH range has been demonstrated by model experiments previously (Gustafsson, 2003). Coupled enrichments of Mo and Fe concentrations at a depth of 15 cm in the core can be interpreted as a relict of the former location of the oxic–anoxic interface.

The Lake Kutsasjärvi sediment sequence exhibits a general decrease in $\delta^{97}$Mo values of the non-detrital fraction from the sediment–water interface down to a depth of 13 cm (Fig 2, Table 2). However, at greater depths the Mo isotopic composition of the non-detrital fraction is nearly identical to that of the detrital fraction. $\delta^{97}$Mo values of the latter have a limited range of variations for the entire core with an average value of 0.05±0.18‰.

The offset between $\delta^{97}$Mo values of the non-detrital and detrital fractions in Lake Kutsasjärvi indicates that Mo isotope fractionation operates during formation of the oxic sediments or, alternatively, that the non-detrital fraction of Mo reflects the isotopic composition of dissolved Mo in the water column, which can be different from the isotopic composition of Mo of the detrital fraction. Processes that are responsible for deposition of Mo in the non-detrital phase of the oxic sediments include its scavenging from the water column and/or porewater by Mn and Fe oxides and, to lesser extent, by organic matter. It has been demonstrated previously that light Mo isotopes are preferentially adsorbed by Mn oxides (Barling et al., 2001; Barling and Anbar, 2004). The isotopic offset between dissolved Mo and Mo absorbed onto Mn oxides was found to be ~1.8‰ in terms of $^{97}$Mo/$^{95}$Mo ratio (Barling and Anbar, 2004). Although the isotopic composition of Mo in porewater of deep sediment layers is unknown, the observed tendency of progressively lighter Mo isotopic composition of the non-detrital fraction of the sediments

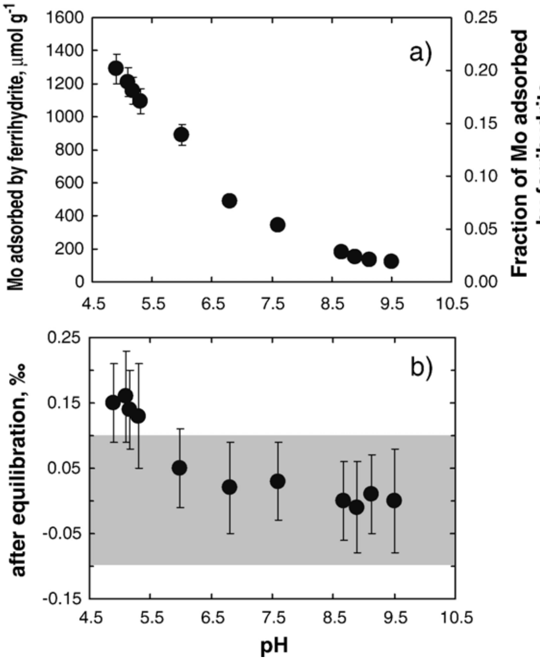

Fig. 6. Adsorption of Mo to ferrihydrite versus pH (a) and the isotopic composition of Mo in solution after equilibration (b). Approximately 0.008 g of Fe and precisely weighted aliquot of 0.1 M $KNO_3$ solution, containing 50 μmol (4800 μg) of Mo, were used in each experiment. Experimental procedure followed largely that of "pH-series" experiments described by Barling and Anbar (2004). Duration of experiments was 48 h, after that ferrihydrite was separated from the solution. The soluble Mo has been purified and its isotope ratios have been measured by MC-ICPMS. Grey band denotes a typical uncertainty of $^{97}$Mo/$^{95}$Mo isotope ratio at 2 $\sigma$ level. At pH ≥ 6 no variations in the isotopic composition of Mo are identifiable with the given level of instrumental precision. However, in acidified solutions with pH < 5.4 preferential adsorption of light Mo isotopes by ferrihydrite was observed suggesting that a change in dissolved Mo speciation from $MoO_4^{2-}$ to $HMoO_4^-$, $H_2MoO_4$ and possibly other species can account for the observation. Assuming that isotopic equilibrium in the acidified experimental suspensions is reached the fractionation faction $\alpha_{\text{solution-ferrihydrite}} = \frac{(1+\delta^{97}\text{Mo}_{\text{solution}}/1000)}{(1+\delta^{97}\text{Mo}_{\text{ferrihydite}}/1000)} = 1.0007 \pm 0.00004\,(n=4)$. It should also be noted that a more detailed study is required to verify a value of the fractionation factor in this process.

Table 3
Dissolved $O_2$ (DO), pH, conductivity and concentrations of dissolved ($_{diss}$) and suspended ($_{suspend}$) Mo, Fe and Mn species in the water of Lake Vettasjärvi

| Depth (m) | DO, % saturation | pH | Conductivity, (μS/cm) | $Mo_{diss}$ (μg/l) | $Mo_{suspend}$ (μg/l) | $Fe_{diss}$ (μg/l) | $Fe_{suspend}$ (μg/l) | $Mn_{diss}$ (μg/l) | $Mn_{suspend}$ (μg/l) |
|---|---|---|---|---|---|---|---|---|---|
| 1.5 | 96 | 6.85 | 23.3 | n. s. | n. s. | n. s. | n. s. | n. s. | n. s. |
| 11.0 | 45 | 5.97 | 24.0 | 0.08±0.01 | 0.003±0.001 | 6.7±0.3 | 24±0.3 | 9.9±0.2 | 14±0.2 |
| 15.0 | 10.0 | 5.90 | 29.4 | 0.12±0.01 | 0.02±0.001 | 4.4±0.2 | 86±2 | 984±11 | 103±2 |
| 15.2 | 8.3 | 5.93 | 31.2 | 0.13±0.01 | 0.02±0.001 | 5.3±0.1 | 116±1 | 1350±8 | 147±6 |
| 15.4 | 4.6 | 6.02 | 35.8 | 0.19±0.01 | 0.02±0.001 | 5.7±0.1 | 105±1 | 2090±14 | 119±1 |
| 15.6 | 1.2 | 6.26 | 50.4 | 0.64±0.01 | 0.04±0.001 | 5.5±0.2 | 325±4 | 5780±256 | 152±3 |
| 15.8 | 0.6 | 6.90 | 73.5 | 2.25±0.02 | 0.03±0.001 | 4200±15 | 305±1 | 10002±218 | 30±1 |
| 16.0 | 0.3 | 7.18 | 133 | n. s. | n. s. | n. s. | n. s. | n. s. | n. s. |

n.s. — not sampled.
The uncertainty term is one standard deviation. The depth at the sampling station is 16.0 m.

from the sediment–water interface down to a depth of 13 cm can be explained by upward diffusion of Mo from deeper sediments in the porewater and preferential adsorptive scavenging of light Mo isotopes by Mn oxides within the porewater system.

Hydrous Fe oxides were shown to be a dominant scavenger of Mo in fresh waters (Kaback and Runnells, 1980; Cook, 2000). As revealed by the enhanced Mo concentration coincident with Fe concentration maximum in the core, transport of Mo at the oxic–anoxic transition zone of the porewater is dominated by upward diffusion of Mo from the anoxic zone and scavenging of the element by hydrous Fe oxides (Fig. 2). However, in spite of the large increase in Mo concentration associated with Fe oxides in the sediments at the depth of 11 cm the isotopic composition of Mo in this zone does not exhibit any pronounced variations. This is suggestive of little or no Mo isotope fractionation during co-precipitation and/or adsorption of Mo by hydrous Fe oxides. It seems unlikely that quantitative removal of the element accounts for the absence of Mo isotope fractionation in this zone, because, as discussed before, a fraction of dissolved Mo appears to diffuse into the overlying oxic sediments and due to preferential adsorptive scavenging of light Mo isotopes by Mn oxides forms the observed trend of progressively heavier $\delta^{97}$Mo values towards the top of the sediment core. Our preliminary laboratory experiments carried out to simulate adsorption of Mo by ferrihydrite indicate that no Mo isotope fractionation is associated with this process at $pH \geq 6$, which is a typical pH range for most lake systems (Fig. 6).

An interesting observation is that molybdenites collected from ore deposits of Gällivare locality, i.e., at ~10–15 km distances from the lake, are characterized by $\delta^{97}$Mo values ranging from 0.18‰ to 0.81‰ and the average $\delta^{97}$Mo value of 0.47‰ ($n=5$) (Table 1). This range of $\delta^{97}$Mo values is similar to that of the non-detrital phase of Lake Kutsasjärvi sediments. As seen from Table 1, $\delta^{97}$Mo value of 1.51‰ has also been determined for molybdenites from northern Sweden, but this locality is relatively far from Lake Kutsasjärvi. Assuming that due to site-specific aspects of Lake Kutsasjärvi, i.e., abundant quartz–molybdenite veins on the lake drainage basin, molybdenites are major contributor of dissolved Mo in the water column, it is possible to interpret $\delta^{97}$Mo values of the non-detrital fraction of these oxic sediments as produced by scavenging of Mo from the water column without significant Mo isotopic fractionation. In this case minor variations of $\delta^{97}$Mo values of the oxic sediments may reflect variability of the Mo isotopic composition of dissolved Mo in the water column.

#### 5.2.2. Anoxic lake sediments

The sediment core from Lake Vettasjärvi is of limited length (12 cm). Mo concentrations in this core therefore reflect processes occurring during early diagenesis of Mo in the loose subsurface sediments. In contrast, the sediment core from Lake Berkut provides a long record of Mo deposition history. In a very general sense, processes occurring in the sediment core from Lake Vettasjärvi can be considered analogous to those in the shallow layers of the core from Lake Berkut.

*5.2.2.1. Shallow subsurface sediments from Lake Vettasjärvi.* Prior to discussing Mo isotope signatures of the sediment core from Lake Vettasjärvi the pathways for accumulation of Mo in this sediment core, and the reactive sediment phase in particular, have to be examined using the available concentration data for the bottom waters, sediments and porewaters (Figs. 3 and 5, Tables 2 and 3). The major constituents of the reactive sediment phase in the core include hydrous Fe and Mn oxides formed at the oxic–anoxic interface in the overlying bottom water, where Fe (II) and Mn (II) species diffusing from the anoxic zone are oxidized and precipitate as hydrous oxides. Data obtained by high-resolution sampling of suspended matter and co-existing water, performed across the oxic–anoxic interface in the water column of Lake Vettasjärvi, indicate a pronounced diffusive flux of Mo from the anoxic sediments into the water column (Table 3). Molybdenum in the water column is dominated by the dissolved form, referred here to as Mo that passes through a 0.22 μm membrane filter. A rapid change of the dissolved Fe concentration from 5.5 μg/l at a depth of 15.6 m to 4200 μg/l at 15.8 m shows that the interface between oxic and anoxic waters exists in this zone (Table 3). An insignificant increase in suspended Mo in the zone of oxidative precipitation of hydrous Fe and Mn oxides indicates that only a small fraction of Mo is scavenged by these oxides in the oxic–anoxic transition zone in the bottom water. In contrast, diffusive flux of Mo from the anoxic sediments appears to be a substantial contributor of dissolved Mo in the water column. This observation is in agreement with results reported recently by Dalai et al. (2005). These authors argue that input of Mo to the Chao Phraya River estuary via porewater transport from anoxic sediments is an important source of Mo in the water column.

Reductive dissolution of Fe and Mn oxides in the anoxic zone results in release of Mo from the solid phase into porewater and its migration along the concentration gradient. The porewater Mo concentration data from Lake Vettasjärvi show that a decrease in porewater Mo concentrations from the sediment–water interface down to a depth of ~3 cm is followed by an accentuated increase in porewater Mo concentration downcore (Fig. 5). The former gradient can possibly be explained by rapid reductive dissolution of Mo adsorbed by freshly precipitated Fe and Mn oxides and/or remobilisation from decomposing biogenic material. The enhanced porewater Mo concentration in the deeper subsurface sediments indicate that the overall diffusive flux of Mo is directed towards the sediment–water interface. It should be noticed that the input of dissolved Mo from anoxic sediments to the water column indicates that a sulphidic zone, where Mo is efficiently removed from the porewater, is located in deep sediment layers. The Mo concentration gradient developed in the shallow porewater of Lake Vettasjärvi suggests cycling of Mo between the water column and subsurface sediments coupled to redox cycles of Fe and Mn. Given that Lake Vettasjärvi does not have any significant inflowing and outflowing stream waters, this cycling of Mo appears to be an important control of dissolved Mo in the water column.

The Mo isotope data from Lake Vettasjärvi show that $\delta^{97}$Mo values of the non-detrital fraction in the sediment core are nearly identical to those of the detritus (Fig. 3). The range of variations in $\delta^{97}$Mo values for both factions is limited with average value of $-0.60\pm0.15$‰ ($n=9$) for the detrital phase and of $-0.62\pm0.18$‰ ($n=12$) for the non-detrital one. The detritus of Lake Vettasjärvi sediments has the average $\delta^{97}$Mo value on 0.65‰ lighter than that of Lake Kutsasjärvi sediments. This relatively large shift in $\delta^{97}$Mo values between detrital phases of two lakes might be in part accounted for by not perfect separation of non-detrital phase of Mo during the reductive HCl leaching procedure and sulphide mineral occurrences in the composition of detrital phase. On the other hand, the agreement in $\delta^{97}$Mo values between non-detrital and detrital phases of Lake Vettasjärvi sediments is consistent with the explanation that granitic bedrock of the lake drainage basin is a major contributor of dissolved Mo in the water column and that an efficient removal of dissolved Mo from the water column by hydrous Fe and Mn oxides leads to formation of Mo isotope signature of the non-detrital sediment fraction that is close to that of the detrital one. This is reasonable given that Lake Vettasjärvi does not have any significant outflowing stream water and is characterized by elevated concentrations of suspended Fe and Mn in the water column.

*5.2.2.2. Mo isotope records through the Holocene for sediment core from Lake Berkut.* As seen from Fig. 4, a general tendency of decreasing Mo concentrations and Mo/Al ratios towards the sediment–water interface is evident in the core. The concentration maxima of Mo, Fe, Mn and S, as well as their respective ratios to Al, are located in the lower and middle parts of the core, at depths of ~74 cm, ~96 cm and below 125 cm from the sediment–water interface. These concentration maxima probably reflect precipitation of sulphide minerals of Mo, Fe and Mn.

The Mo isotopic composition of the sediments varies within a range of ~2.3‰ in terms of $^{97}$Mo/$^{95}$Mo ratio (Fig. 4). There is an overall trend of decreasing of $\delta^{97}$Mo values towards the top of the core. The midge records provide evidence of low oxygen concentrations in the bottom water during the early Holocene (ca 10,000–8400 cal. years BP) (Ilyashuk et al., 2005). Therefore, the heavier Mo isotopic composition in the lower part of the core can be explained by an efficient removal of Mo from solution under anoxic conditions with presence of sulphide species. However, a decrease in $\delta^{97}$Mo values is also observed at depths between 150 cm and 140 cm, concomitant with enhanced Mo and

S concentrations. This decrease in $\delta^{97}$Mo values presumably reflects redox stratification of the water column with vigorous Mn-oxide particles cycling at the redoxcline. In such a system, migrating downwards Mn oxides can scavenge Mo, preferentially adsorbing isotopically light Mo and delivering this signature to the sediments. Dilution by mineral matter having light Mo isotopic composition from the drainage basin could also contribute to the observed shift. As inferred from high values of magnetic susceptibility at the base of the core (Fig. 4), an episode of catchment erosion and deposition of mineral matter occurred at the onset of sedimentation as a result of sparse vegetation and unstable soils following the deglaciation of the area.

The Mo isotopic composition in the middle part of the core (125–30 cm), corresponding to the mid-Holocene (ca. 8400 to 2400 cal years BP), suggests dependence on variations in the lake level and the degree of $O_2$ saturation in the water column. The chironomid-inferred reconstructions suggest a lake-level fall at *ca*. 7000 years BP, resulting in weakened thermal stratification of the water column and elevated $O_2$ concentrations in the bottom waters of the lake. This process is reflected by a gradual shift of $\delta^{97}$Mo values from 0.31 to −0.08‰ (Fig. 4, at depths from ~108 to ~98 cm). Chironomid data indicate a climatic cooling, an increase in effective moisture and, as a consequence, a gradual lake-level rise at ca. 4000–2400 cal. years BP (Ilyashuk et al., 2005). Due to the cooler climate the hypolimnetic $O_2$ content remained relatively high (ca. 4 mg $O_2$/l) during this period. The Mo isotopic composition of the sediments responded by a shift towards more negative $\delta^{97}$Mo values (Fig. 4). This shift can be explained as a result of increased scavenging of Mo with preferential uptake of light Mo isotopes by Mn oxides from the water column as discussed above. Upon deposition in the anoxic sediments the Mn oxides were dissolved and released Mo which was then adsorbed to organic matter of the sediments.

The pH status of the lake water gradually turned from circumneutral to acidic after ca. 2400 cal. years BP, reflecting an increased humic acid input following paludification during this period. Depletion of dissolved $O_2$ in the hypolimnion has been inferred during this time as well. Dissolved organic acids under low pH and poor oxygen conditions are powerful complexing agents for Mo. A slight increase in Mo concentration in the uppermost part of the core confirms the enhanced removal of organically complexed Mo from the water column during the Late Holocene. $\delta^{97}$Mo values show the concomitant gradual rise of ~1.3‰. However, the most recent sediment layers are characterized by more negative $\delta^{97}$Mo values. This is probably related to increased input of mineral matter, analogous to that described for the bottom of the core. This conclusion is supported by an increase in magnetic susceptibility in the uppermost part of the core (Fig. 4), which probably reflects increased catchment erosion in response to forest clearance of and other human impact on the landscape. An additional factor is that in the acidified water of Lake Berkut scavenging of dissolved Mo species by ferrihydrite can result in preferential uptake of lighter Mo isotopes, as follows from the data presented in Fig. 6.

Thus, as evident from the Lake Berkut data, millennial-scale Mo isotope records obtained on Holocene lake sediments may vary in response to ambient limnological conditions. However, these interpretations are based on the assumption that the Mo isotope signal is preserved in anoxic sediments and left unaltered by diagenetic sedimentary processes. This assumption is supported by the recent work of Nägler et al. (2005), which suggests that reducing post-sedimentary fluids do not mobilise Mo or alter its isotopic composition. Alternatively, some post-depositional migration of Mo may have occurred in the shallow sediments of Lake Berkut during the mid-Holocene as a result of improvement of the hypolimnetic oxygen conditions. In the transition zone between poorly oxygenated sediments near the sediment–water interface and underlying anoxic sediments, Mo released to the porewater via reductive dissolution of hydrous Fe and Mn oxides can migrate along the concentration gradient. It has been demonstrated previously that the development of a concentration gradient of transition metals in water solutions drives the kinetic isotope effect in favour of light isotopes at the concentration front (Rodushkin et al., 2004). In this case the observed $\delta^{97}$Mo values of the mid-Holocene sediments may be influenced by porewater diffusion of Mo. Kracher and Shotyk (2004) have demonstrated the significance of Mo diffusion in porewater for the development of a Mo concentration profile of a peat bog.

## 6. Conclusions

The following conclusions emerge from this study. First, the Mo isotopic composition of molybdenites in granitic bedrocks exhibits considerable variations within and between the studied lake drainage basins in northern Sweden. The median $\delta^{97}$Mo value of the measured molybdenites is 0.26‰ and the standard deviation is 0.43‰ ($n = 19$). The detrital sediment fractions of two lakes exhibit narrow range of Mo isotopic variations within the cores with $\delta^{97}$Mo values of −0.6±0.15‰ ($n$=9) and 0.05±0.18‰ ($n$=6), respectively. The median $\delta^{97}$Mo value of detritus for two investigated sediment cores is −0.40‰ with standard deviation of 0.36‰ ($n$=15). This scatter is attributed to heterogeneity of Mo isotopic composition of parent crystalline bedrocks in the drainage basins of the lakes.

Second, data obtained in this study show predominant partitioning of Mo in the reactive, non-detrital, fraction of lake sediments. Hydrous Fe oxides have been shown to be an efficient scavenger of Mo under oxic conditions. In a lake with oxygenated water column the oxidative precipitation of Fe(II) in the sediment core was shown to co-precipitate with Mo and results in significant authigenic enrichment of the latter at the redox boundary. However, little or no Mo isotope fractionation during scavenging of Mo by hydrous Fe oxides in the oxic–anoxic transition zone. In a lake with anoxic bottom water the diffusive Mo flux through the sediment–water interface into the water column has been shown to be an important control of Mo distribution in the water column.

Third, data from a small lake on the Kola Peninsula suggest that Mo isotope records obtained on Holocene lake sediments may reflect temporal variations in limnological conditions related to changes in climate and vegetation. The range of Mo isotopic variations observed across the Holocene is ~2.3‰ in terms of the $^{97}$Mo/$^{95}$Mo ratio. Comparison of our Holocene $\delta^{97}$Mo record with a chironomid-based reconstruction of hypolimnetic oxygen concentration from the same core suggests a general inverse relationship between oxygenation and sediment Mo isotope composition. Although specific Mo isotope effects due to adsorption of Mo by Mn oxides, diffusion and interactions of Mo with organic matter and other solid surfaces appear to occur, these remain unresolved in this study.

These results highlight variability of the Mo isotopic composition of lake sediments deposited in areas of crystalline bedrock. The range of these variations is comparable to that documented in marine settings. Mo isotopic composition in lake sediments has displayed a potential to be a proxy for redox conditions of overlying waters; however, isotopically heterogeneous Mo transported from lake drainage basins may dominate Mo isotope records of lake sediments. Although lake waters contribute insignificantly to the water balance of major rivers, a large-scale extrapolation of the reported Mo isotopic variations suggests that dissolved Mo transported by rivers may reflect Mo isotopic heterogeneity of bedrocks in drainage basins. To what extent the Mo isotopic composition of river waters averaged over large drainage areas is influenced by this heterogeneity remains to be shown in future studies.

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