

Molybdenum geochemistry in a seasonally dysoxic Mo-limited lacustrine ecosystem

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Abstract

Lakes are important for storage of the essential micronutrient molybdenum (Mo) during its transfer from the continents to the oceans, but little is known about the major sources and sinks for Mo in lacustrine ecosystems. We studied Mo cycling in Castle Lake, a small subalpine lake in the Klamath-Siskiyou Mountains of Northern California underlain primarily by mafic and ultramafic rocks where primary productivity is limited by Mo bioavailability. The deeper water of the lake becomes dysoxic (9–90 μM dissolved oxygen) during the summer. This study was undertaken to identify the sources of Mo to Castle Lake and establish a Mo budget. We measured Mo concentrations in a suite of bulk solids (lake sediments, soils and bedrock) and aqueous samples (sediment porewaters, soil runoff, spring waters, snow and ice) from Castle Lake and its watershed. Lake sediments have elevated Mo (7–36 ppm) compared to soils and bedrock (0.2–2 ppm) and Mo/Al values were nearly two orders of magnitude higher than the crustal abundance. Sediment porewaters had higher Mo (4–15 nM) than lake water (2–4 nM), soil runoff (0.1–6.2 nM), snowmelt (≤ 0.1 nM), lake ice (0.3–2.2 nM) and local spring waters (0.03–2.72 nM). Bulk lake sediments had negative $\delta^{98/95}\text{Mo}$ values, ranging from -0.5 to -1.0‰ (± 0.1). We used the numerical model PROFILE to estimate the net reaction rate of Mo in the porewater. Model calculations ruled out diagenesis as a source of Mo to lake sediments; diagenetic Mo always represented $\leq 5\%$ of the total Mo content in sediment. We also ruled out dissolved Mo inputs from groundwater and watershed inflow as important sources of Mo. Two whole-lake experimental Mo additions in the 1960's could have contributed a sizeable amount of Mo to the lake sediments, but only over a short period. Atmospheric deposition of anthropogenic Mo from extensive copper smelting that occurred south of Castle Lake from 1896 to 1919 and from major Californian urban centers today were negligible Mo sources. Mo flux from the sediments ($0.4\text{--}0.5 \text{ nmol cm}^{-2} \text{ yr}^{-1}$) was roughly equal to Mo fluxes from surface inflow and outflow, whereas Mo burial fluxes were significantly higher ($11.5 \text{ nmol cm}^{-2} \text{ yr}^{-1}$). Because dissolved Mo fluxes were minimal, and atmospheric Mo deposition was estimated to be a minor source of Mo ($< 1 \text{ nmol cm}^{-2} \text{ yr}^{-1}$), the largest source of Mo is non-detrital particulate matter ($\sim 12 \text{ nmol cm}^{-2} \text{ yr}^{-1}$), likely a mixture of organic matter and Fe–Mn oxyhydroxides as supported by Mo isotopic data.

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1. INTRODUCTION

Molybdenum (Mo) is an important biological micronutrient and paleoredox proxy (e.g., Arnold et al., 2004; Scott et al., 2008). Because the riverine supply of Mo to the ocean is controlled by atmospheric O₂ concentrations, Mo in seawater was scarce (~10 nM; Anbar et al., 2007; Scott et al., 2008; Reinhard et al., 2013) before atmospheric O₂ rose to modern levels. Presently, marine Mo concentrations are high (105 nM; Collier, 1985) and Mo displays conservative behavior in seawater because (a) it is present as the soluble chemical species molybdate (Mo(VI)O₄²⁻) under oxic conditions, (b) it has a long residence time (130,000–440,000 years; Miller et al., 2011), and (c) biological requirements for Mo are small relative to the amount of Mo available. In freshwater systems, Mo concentrations are generally much lower (<20 nM; Glass et al., 2012 and references therein, although notable exceptions exist, such as terminal saline lakes (Marino et al., 1990; Johannesson et al., 2000)), and Mo scarcity has been shown to limit primary productivity in oligotrophic lakes (Goldman, 1960; Glass et al., 2012; Romero et al., 2013).

Mo sediment geochemistry can be summarized as follows. In the presence of O₂, MoO₄²⁻ is adsorbed on Fe–Mn oxyhydroxides and accumulates in surface sediments (Chappaz et al., 2008a; Morford et al., 2007; Crusius et al., 1996, Zheng et al., 2000). Under sulfidic conditions, MoO₄²⁻ reacts with H₂S to form thiomolybdates, Mo(VI)O_{4-x}S_x²⁻ (Helz et al., 1996; Erickson and Helz, 2000) and is either scavenged by iron sulfides (Bostick et al., 2003; Helz et al., 2004; Vorliceck et al., 2004; Helz et al., 2011), sulfurized organic matter (Tribovillard et al., 2004) or reduced Mo(VI)-S compounds (Dahl et al., 2013). Sediments underlying suboxic (0–9 μM O₂; Tyson and Pearson, 1991) waters are not as enriched in Mo and are a net source of Mo to overlying waters (Crusius et al., 1996; Dalai et al., 2005). We are not aware of any studies that have investigated the geochemical behavior of Mo under dysoxic conditions (9–90 μM O₂; Tyson and Pearson, 1991).

Lakes are important mid-way reservoirs during the transfer of Mo from the continents to the oceans and display a wide diversity of geochemical conditions. Recent studies have investigated Mo systematics in permanently (Dahl et al., 2010) or near-permanently (Helz et al., 2011) stratified lakes, but such lakes are rare on a global scale. In temperate regions, dimictic lakes that mix twice a year are by far the most common type (Wetzel, 2001). These lakes experience a range of O₂ conditions from fully oxic to some level of O₂ depletion in their deep waters throughout the year. The aim of this study was to decipher the sources, sinks and the overall Mo budget in a dimictic lake with seasonal deep water dysoxia and dissolved Mo concentrations typical of freshwaters.

We chose a lake with well-characterized hydrogeological and biological parameters to study Mo cycling and isotope systematics. Castle Lake has been used as a model ecosystem to study the importance of Mo in biology since the 1960's, when it was discovered that primary productivity in the lake was limited by Mo availability (Goldman,

1960; Goldman, 1966; Glass et al., 2012). As part of these studies, two significant experimental additions of Mo to the lake were made (Goldman, 1966; Goldman, 1972). The goals of our study were to determine the sources of Mo to Castle Lake and establish a Mo budget for the lake. To accomplish these tasks, we combined high-precision Mo concentration and isotopic measurements of water, soil, and sediment samples. We also used the numerical code PROFILE (Berg et al., 1998) to estimate reaction rates in the porewater and, subsequently, to quantify the Mo flux coming out of sediments, and to determine the relative contributions of diagenetic processes, dissolved and particulate watershed and water column inputs, and anthropogenic deposition to Mo enrichments in Castle Lake sediments. Our results provide a modern context for studies using Mo as a paleoredox proxy for dysoxia and add to the scarce literature on the range of Mo isotopic compositions in lake sediments (Malinovsky et al., 2007; Dahl et al., 2010; Chappaz et al., 2012). This study also contributes a geochemical framework for studies of Mo as an important bio-limiting micronutrient in freshwater ecosystems.

2. METHODS

2.1. Site description

Castle Lake is a small, subalpine tarn lake situated at an altitude of 1706 m in a glacial cirque basin in the Klamath-Siskiyou Mountains of Northern California (Figs. 1a and b). The lake has a maximum depth of ~35 m and a mean depth of 11 m (Fig. 1a). The lake's surface area is 0.2 km² and its drainage basin is 0.8 km². The lake is composed of a deep (35 m) glacially-carved bowl and a shallow (3–5 m) littoral plain extending to the cirque lip where glacial till forms a natural dam. The basin bedrock includes gabbro, serpentinized peridotite, and granodiorite (Throckmorton, 1978; Fig. 1b). Quaternary sediments eroded from the bedrock include an assortment of boulders, cobbles, gravels, sand, and fine particles (<2 mm in diameter), with larger size fractions deposited on the northwest shore and smaller size fractions near the outflow.

Lake inflow originates from a small pond (Heart Lake) at a higher elevation to the south, and outflow is through Castle Lake Creek to the north (Fig. 1a). There is additional inflow from springs arising from faults in the bedrock (Goldman, 1961) and snowmelt in the spring. The lake's hydraulic residence time is 2–5 years (Goldman and de Amezaga, 1984). The drainage basin is uninhabited; human activity in the watershed is essentially limited to summer research and recreational activities. The watershed has not been affected by wildfires since the 1930's, or by lumbering since the 1980's. The lake sediment contains a surface flocculent layer, underlain by sediment containing 50% fine-to-medium grained sand, and 49% silt and clay (Beatty, 1968). Oxygen penetrates to a depth of ~3 cm in the shallow water sediments (Neame, 1975) when O₂ is present in bottom waters. At the deepest part of Castle Lake, the hypolimnion becomes dysoxic in the summer, whereas the shallow part of the lake remains oxic year-round.

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