

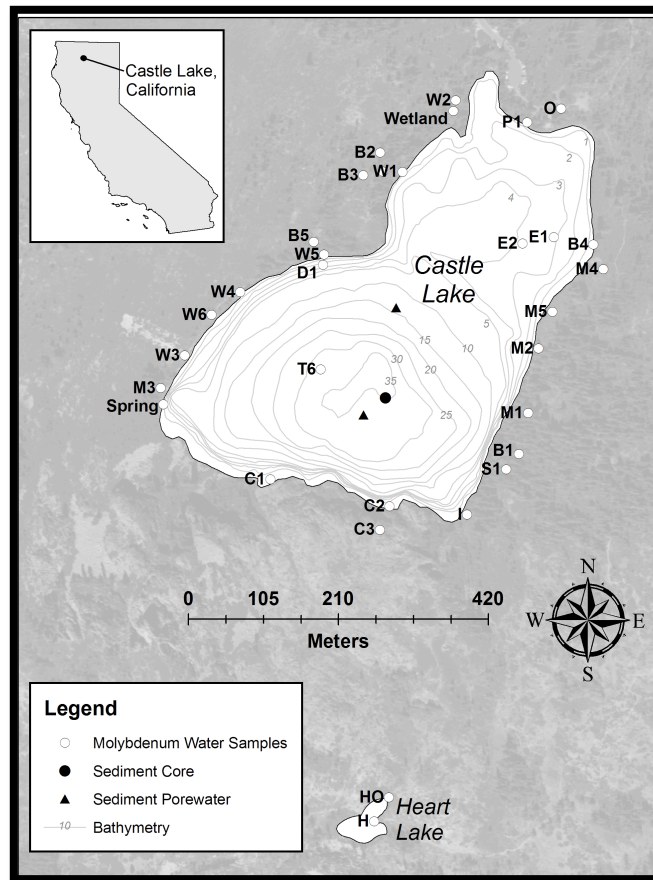
Project Report

1. Project Goals

The goal of this project was evaluation of molybdenum (Mo) flux from and diagenesis within the sediments of Castle Lake, California through sampling and analysis of sediment porewaters for Mo, Fe, Mn, sulfide and pH. Our aim was to combine this porewater data with sediment solid phase samples collected in 2008 in order to model the flux of Mo to the water column, the diagenetic influence on Mo enrichments in the sediment and the importance of anthropogenic inputs of Mo to Castle Lake sediments. Currently (early June 2010), Jennifer Glass (Arizona State U., hereafter ASU) and Anthony Chappaz (U. C. Riverside, hereafter UCR), along with colleagues from U. Nevada Reno (hereafter UNR), U. C. Davis and the Desert Research Institute Reno, are in the process of writing up our results in a manuscript for submission to *Geochimica et Cosmochimica Acta* (Glass et al. in preparation).

2. Description of Field Research, Summer 2009

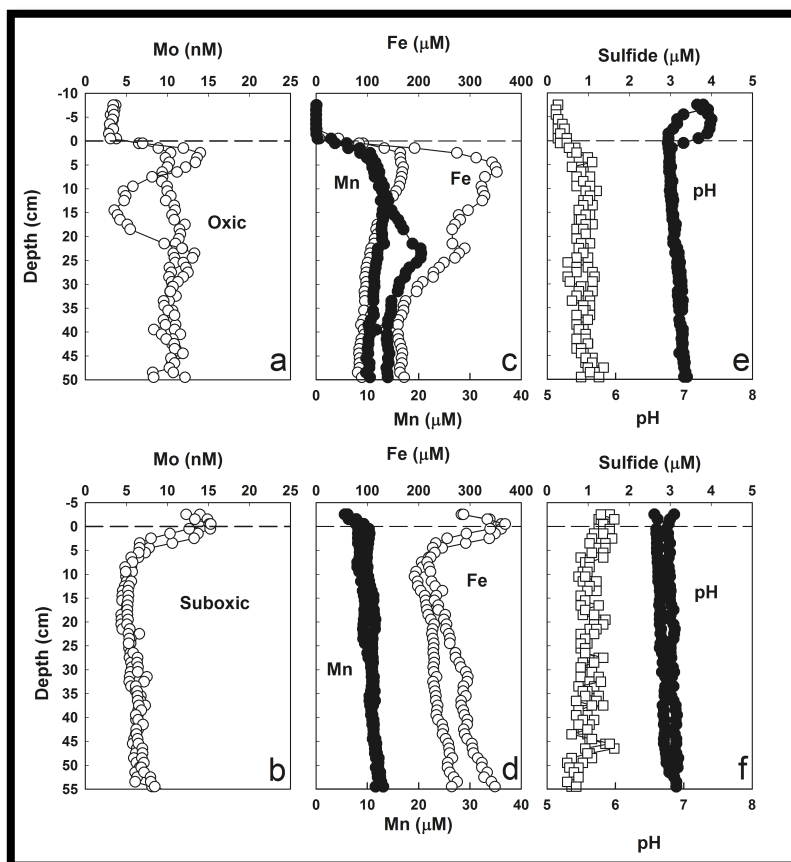
The Lewis & Clark Field Scholarship funded a field trip for two researchers (Glass & Chappaz) and three SCUBA divers to Castle Lake, California (GPS coordinates: 41°13'39"N 122°23'01"W) in mid-June 2009. All participants camped at the site and utilized the Castle Lake Limnological Laboratory for necessary preparations. Porewater sampling devices (called "peepers") 60-cm in length with 1-cm depth sampling resolution were deployed at two sites in Castle Lake sediments on 19 June 2009 (see black triangle symbols on map). SCUBA divers installed four peepers into the sediments at the shallow site (12m) with oxic bottom water and another four peepers at the deep site (35m) with suboxic bottom water. Deep-water peepers were installed as close as possible to the location where the sediment core was taken in 2008 (see black circle symbol on the map). Three weeks later, peepers were retrieved and sampled for pH, metals, sulfide, organic carbon and major anions. Whereas pH was measured immediately after sampling in the field, the rest of the samples were transported to ASU and UCR for processing and analysis. Porewater metal analyses were performed at ASU using a Thermo-Scientific X-Series inductively-coupled plasma mass spectrometer and sulfide analyses were performed at UCR using the Cline method. Organic carbon and major anion analyses were also performed at ASU.



3. Preliminary Results

In both the oxic and suboxic sites, Mo concentrations ranged from ~4-15 nM (see panels a & b in figure), whereas lake water Mo was 2-4 nM. The shape of the Mo profiles was very different between the two sites.

In the oxic site, the Mo maximum was ~1-2 cm below the sediment-water interface (dotted horizontal line), whereas in the suboxic site, the Mo maximum was at the sediment-water interface. In both sites, maximum Mo coincided with maximum Fe (see panels c & d in figure). In the oxic site, one of the peeper Mo profiles stayed constant (~10 nM) below the Mo maximum. The other profile declined to a minimum of ~4 nM at 10-15 cm and then increased so that below ~23 cm, Mo was constant at ~10 nM (see panel a). Both Mo profiles for the suboxic site declined to a constant concentration of ~5 nM below the sediment-water interface to the bottom of the profile (panel b). Sulfide increased from undetectable levels to ~1 μM between 10-15 cm in the oxic site (see panel e), whereas in the suboxic site sulfide was >1 μM above the sediment-water interface (see panel f).



Sulfide increased from undetectable levels to ~1 μM between 10-15 cm in the oxic site (see panel e), whereas in the suboxic site sulfide was >1 μM above the sediment-water interface (see panel f).

Fluxes of Mo from the sediments to the overlying water column were calculated using the simplified formula: $\text{Flux} = -D_s(\partial[\text{Mo}]/\partial x)$. D_s is given by $\phi^2 D_w$ where ϕ is the sediment porosity (0.935 (Sanders et al. 2008)) and D_w is the tracer diffusion coefficient of MoO_4^{2-} at 4°C ($5.2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (Chappaz et al. 2008)). Fluxes were found to be $7-8 \times 10^{-18} \text{ mol Mo cm}^{-2} \text{ s}^{-1}$ for the oxic site. Suboxic fluxes were more difficult to calculate due to limited samples available above the sediment-water interface, but we estimated that Mo flux ranged from $2-7 \times 10^{-18} \text{ mol Mo cm}^{-2} \text{ s}^{-1}$. These fluxes are roughly equal in magnitude to those calculated for inflowing springs and soil runoff based on our analysis of over 100 snowmelt, spring and runoff samples collected throughout 2008 to 2009 by B. Eustis (Master's Student, UNR).

Preliminary porewater modeling results indicated that diagenesis is a minor source of Mo to the lake sediments, which are highly enriched in Mo (up to 40 ppm) compared to average crustal rocks. We ruled out watershed Mo inputs by analyzing a range of soils and bedrock from the Castle Lake basin, which were all < 2ppm Mo. We are now analyzing stable Mo isotopes in the sediment core to search for evidence of anthropogenic Mo isotopic signatures. Based on sedimentation rates calculated previously for Castle Lake (Sanders et al. 2008), we estimated that the base of the sediment core dates back to the mid-late 1800's.

4. *Significance of the Preliminary Results*

This study contributes two major findings to the field of trace metal geochemistry in lake ecosystems. First, our finding that sediments – especially when they are oxic – contribute a Mo flux roughly equal to that of all the Mo inputs from the watershed is significant because it suggests that lakes in watersheds that meet two conditions – (1) low bedrock Mo and (2) bottom waters that are anoxic or suboxic for much of the year – will likely have extremely low Mo concentrations (<1 nM) and may be Mo-limited for biological activity.

Secondly, our results suggest that high levels of Mo in Castle Lake sediments are not diagenetic in origin, nor are they a result of high Mo levels in watershed bedrock. The origin of this Mo is currently under investigation. Previous studies have shown that atmospheric deposition is the major source of anthropogenic Mo (Chappaz et al., 2008). Since the wind direction at Castle Lake is primarily from the S-SW, we hypothesize that mining and especially smelting activities in local massive sulfidic ore deposits (especially the Iron Mountain-Richmond Mine near Redmond, CA ~60 km S-SW of Castle Lake) may have been a major source of Mo to Castle Lake from the mid-1800's to the early-mid 1900's. The fact that Mo levels remain elevated in the top of the sediment core suggests that delivery of Mo to the lake remained steady throughout the rest of the 1900's and early 2000's (despite the closure of mines and smelters in the mid-1900's) perhaps due to increased fossil fuel combustion in Northern California throughout that time period. Similar findings have been reported for mercury concentrations in the sediments of Castle Lake (Sanders et al. 2008).

5. *Photographs of Field Research*

Please find photographs of the field research on these web albums:

<http://picasaweb.google.com/jenniglass/ScubaDiversCastleLake#>
<http://picasaweb.google.com/brennecka/CastleLakeCA#>

If you would like high-resolution versions of any of the photographs, please download them from this website: <http://www.dropbox.com/gallery/7713969/1/Castle%20Lake?h=20683f>

References

Chappaz A, Gobeil C, Tessier A (2008) Geochemical and anthropogenic enrichments of Mo in sediments from perennially oxic and seasonally anoxic lakes in Eastern Canada. *Geochim. Cosmochim. Acta* 72(1):170-184

Glass JB, Chappaz A, Eustis B, Heyvaert AC, Waetjen D, Anbar AD (in preparation) Anthropogenic vs. natural sources of molybdenum to Castle Lake, California *Geochim. Cosmochim. Acta*

Sanders RD, Coale KH, Gill GA, Andrews AH, Stephenson M (2008) Recent increase in atmospheric deposition of mercury to California aquatic systems inferred from a 300-year geochronological assessment of lake sediments. *Appl. Geochem.* 23(3):399-407