Focusing patterns of transition metals in lake sediments - indicators for the reconstruction of deep-water mixing in the past?

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Introduction

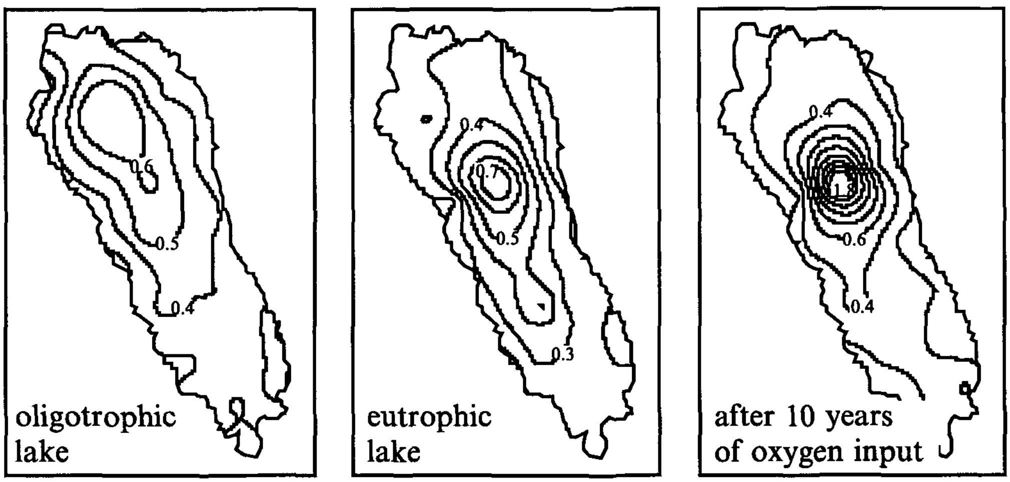
Transition metals in lake sediments show characteristic focusing patterns according to their mobility, which is strongly influenced by the redox conditions in the deep water. Oxygen concentrations in deep lakes depend on two factors: The mineralization of organic matter and deep-water mixing. Under conditions of constant nutrient input the wind-induced mixing during the cold season determines whether deep waters remain anoxic during longer periods of time or if the oxygen reservoir is replenished during winter. Different transition metals such as V, Cr, Mn, Fe, Co, Mo show a broad range of behaviour with respect to adsorption, complexation and solubility depending on the redox conditions. Their concentration and distribution in lake sediments offers some potential as proxy indicators for deep water mixing and the frequency and magnitude of strong wind events. Varved lake sediments covering the last 100 years offer an opportunity to test and calibrate focusing patterns of transition metals with limnological and meteorological time series.

Methods

Sediment cores have been analyzed from two eutrophic Swiss lakes, L. Baldegg and L. Zug. The mean hydraulic residence time of lake Baldegg is 4 years, maximum depth is 66m. The morphometry is very even: From the shore the lake bottom falls off in a gentle slope towards the center of the lake. Since the end of the last century the deepest part of the lake is seasonally anoxic. Since 1982 the lake is artificially aerated. This drastic change in deep-water oxygen concentrations offers an ideal test case to study the distribution of transition metals in a changing redox environment.

In October 1992 38 sediment cores have been taken. Three samples from each core were analyzed: The first 2cm represent the actual situation with an oxic hypolimnion, one sample

manganese in the sediments of L. Baldegg



manganese concentration in [mg/g]

from the top of the varved section of the cores characterizes the anoxic conditions until 1982 and the third sample from the end of the last century is used as reference for the more oligotrophic lake with oxic deep water. All samples have been dried and dissolved in HNO_3/H_2O_2 by microwave digestion. The concentrations of Fe, Mn, Ca, have been measured by Flame-AAS, V and Cr by GF-AAS.

In July of the following year two transects of cores have been taken in each basin of lake Zug. This lake is also highly eutrophic. It has a long hydraulic residence time of 14 years. The lake is separated into two basins. From the relatively shallow northern basin the lake bottom falls off continuously to the 200m deep southern basin. The lowest 40m in the hypolimnion are stabilized by dissolved ions from the sediment. This results in a rather permanent anoxic layer in the deepest part of the lake.

The cores were sampled every half centimeter until 15cm and from there to 40cm every centimeter. Sedimentation rates were established by ^{137}Cs dating. Samples have been dried and dissolved in HNO_3/H_2O_2. The concentrations of Ca, Mg, Fe, Mn, Zn, Cu, K have been measured on ICP-AES and V, Cr, Mo, As, Sb, W, Cd, Ba on ICP-MS.

Results and discussion

The Figures compare the two dimensional distribution of Mn in lake Baldegg in the recent, 'eutrophic' and 'oligotrophic' samples. There is a clear change in focusing patterns as a function of the redox conditions in the deep water. The more homogeneous distribution in the older sediments is in marked contrast with an intense Mn focusing in the present situation, where the hypolimnion is oxic but the sediments are strongly anoxic due to the high productivity. In an oligotrophic lake with oxic hypolimnion Mn-oxide particles will settle to the sediment surface where they are buried. When the sediment and the hypolimnion are anoxic, the settled Mn will be reduced and Mn(II) accumulates in the deep water. Reduced Mn is transported towards the redox boundary by eddy diffusion, where it is oxidized. Settling particles are produced in a well defined horizon without important focusing effects. In the case of an anoxic sediment in contact with an oxic hypolimnion, dissolved Mn from the sediment is oxidized close to the sediment surface. Since horizontal transport by eddy diffusion is fast the Mn colloids are transported towards the center of the lake before they settle out. This leads to a depletion of Mn in the near shore zones of the sediment and to an enrichment in the deeper part of the lake. The concentration profiles of Mn in sediments of the southern basin of L. Zug confirm the findings from L. Baldegg. The focusing stops at the core in 160m depth. No focusing is found in this completely anoxic zone.

Conclusions

The distribution patterns of Mn in deep lakes are promising redox indicators for the reconstruction of deep-water mixing from the sedimentary record. Other transition metals such as V, Cr, Mo and Fe also show focusing effects. Work is in progress to analyze trace metal concentrations in varved sediments of L. Baldegg at a yearly resolution and correlate the metal profiles with time series of oxygen and wind data.