

## Aerobic methanotrophs drive the formation of a seasonal anoxic benthic nepheloid layer in a monomictic lake

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Monomictic lakes experience thermal stratification throughout most of the warmer seasons. Often this leads to seasonal bottom water anoxia, particularly if monomixis is paired with eutrophic conditions. The southern extension of Lake Lugano is a warm, monomictic basin with bottom water anoxia, and formation of a dense benthic nepheloid layer (BNL) during summer and fall. A sharp redox gradient marks the upper boundary of the BNL, which extends to up to 15m from the sediment into the water column. Previous work has revealed that the bulk organic matter in the BNL is strongly depleted in <sup>13</sup>C ( $\delta^{13}\text{C} < -60\text{‰}$ ), indicating that the BNL in the Lake Lugano South Basin is largely composed of methanotrophic bacteria. In this study we present radio-label rate measurement and compound specific C isotope data that confirm i) high rates of aerobic methane oxidation (MOx) at the redoxcline (i.e. just above the BNL) and ii) the dominance of bacterial methanotrophic biomass in the BNL of Lake Lugano's southern basin. MOx is restricted to a narrow zone at the top of the BNL reaching maximum rates of up to 1.8  $\mu\text{M}/\text{day}$ . MOx activity leads to the formation of a sharp CH<sub>4</sub> concentration gradient (80  $\mu\text{M}$  at 92 m; 100 nM at 82 m). The C kinetic isotope effect of methane consumption is strongly suppressed at the community level ( $\epsilon = -2.4\text{‰}$ ), highlighting the near perfect methane sink at the oxycline, where > 99.9% of the CH<sub>4</sub> diffusing from the sediment is oxidised. Fatty acids (FAs) indicative of type I aerobic methanotrophs are depleted in <sup>13</sup>C ( $\delta^{13}\text{C} = -65$  to  $-80\text{‰}$ ) and are the dominant lipids in the FA fraction. In addition, preliminary molecular analysis of the microbial community provides further evidence that the formation of the BNL is driven by aerobic methanotrophs rather than by resuspension of sediments or accumulation of organic matter from the epilimnion, as is often observed in other lakes. Prior to water column mixing, these methanotrophs greatly limit the emission of accumulated methane to the atmosphere.

## Hf isotope evidence for depleted and enriched reservoirs in the Hadean

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Chase and Patchett [1] and Galer and Goldstein [2] argued for the existence of a hidden enriched reservoir in the early mantle, a perspective that has since received strong support from Hf isotope [3] and <sup>142</sup>Nd [4] evidence. The geochemistry of the earliest magmatic minerals is critical in this context. The Jack Hills zircons (JHZ) have been analyzed for Pb and Hf isotopes by several groups using either *in situ* [5-7] or solution chemistry [5,8,9] techniques. The data support the presence of normal continental crust at 4.1±0.1 Ga, with Hf model ages and inferred Lu/Hf characteristics further suggesting a 4.35 Ga protocrust formed from KREEPy upper mantle [7,9]. Whereas all studies find the same predominantly enriched signature indicating apparently massive crustal recycling and reworking during the Hadean and the Archean, only the solution chemistry studies [5,9] see evidence for a depleted reservoir in the Hadean mantle. Statistical analysis of the *in situ* data sets strongly suggests that zircons with the most radiogenic Hf were mistaken for analytical artifacts such that the high- $\epsilon_{\text{Hf}}$  end of the distribution became unduly trimmed. We therefore conclude that, although the JHZ protolith seems to have been largely enriched, it also contained undifferentiated and depleted components. Hf and Nd isotopes in komatiites [10] likewise suggest that the Archean and Hadean mantle comprised long-term depleted sources, identical in terms of time-integrated lithophile trace element characteristics to the Early Depleted Reservoir [11] deduced from <sup>146,147</sup>Sm-<sup>142,143</sup>Nd and Lu-Hf isotope studies of modern mantle material and chondrites. The uppermost KREEPy mantle likely held enough radioactive elements and water to have outlasted the crystallization of the magma ocean for 100s of Ma. If embedded within and between magma ocean cumulates and a thin hydrous lithosphere, such material may have jump-started early plate tectonics.

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