## Holocene climate history and watershed dynamics of the crow wing watershed, North Central Minnesota as interpreted from $\delta^{18}$ O and $\delta$ D in lake sediments

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Two lakes located at opposite ends of the Crow Wing watershed in central Minnesota are being investigated to determine the control of watershed dynamics on preserved climate records. Lake Mina is located near the drainage divide, and Moody Lake is near the outlet of the Crow Wing River into the Mississippi River. Pollen analysis and <sup>14</sup>C dates on a core from the center of Lake Mina indicate a complete Holocene sediment record with a basal age of approximately 10,800 BP calendar years.  $\delta^{18}$ O of the authigenic carbonates in Lake Mina varies between -1.17 ‰ and -6.91 ‰ representing fluctuations in the temperature/aridity of the region and/or hydrology of the lake system/watershed throughout the Holocene. Modern sediments in Moody Lake contain no authigenic carbonates, although lower sections of the core contain 5-10% Total Inorganic Carbon (TIC). Total Organic Carbon (TOC) in the same core ravaries between 10-35%. The lack of any authigenic carbonates in the upper sediments of the core precludes comparison of  $\delta^{18}$ O between Lake Mina and Moody Lake. However, compound specific analysis of the palmitic acid  $[CH_3(CH_2)_{14}COOH]$   $\delta D$  in the TOC of Moody Lake provides a record of changing temperature/aridity in the lake. The Moody Lake  $\delta D$  values range from approximately -200 ‰ in the basal portion to -180 ‰ in the most recent sediments, with a peak of -165 ‰ in the mid-section of the core. This pattern is interpreted as reflecting initially cooler conditions in the early Holocene, a gradual warming to a mid-Holocene maximum followed by a recent cooling. Comparison of the  $\delta D$  profile and lake level history derived from stratigraphic correlation of sand layers in shoreline transects can be used to help distinguish between an isotopic shift due to temperature and one due to changes in aridity.

## Isotope fractionation during subduction: The case for Li and B

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Li and B isotopes have been used extensively in the last few years to constrain mass fluxes in subduction zones. Compared to pristine mantle sources, components entering subduction zones (low-temperature altered basalts, pelagic sediments) are predominantly enriched and isotopically heavier in Li and B. However, it has yet to be evaluated how these characteristics of subducting crust are influenced by processes operating on these rocks during subduction.

One important process that must be taken into account is isotope fractionation during dehydration. Both B and Li isotopes are known to fractionate between minerals and fluids at low temperature conditions, with the heavier isotope (<sup>7</sup>Li and <sup>11</sup>B) being typically enriched in the fluid. Both elements are very fluid-mobile and since large fluid fluxes occur during early stages of subduction (by clay diagenesis and breakdown of other hydrous silicates), this leads to an isotopically heavy fluid leaving the subducting slab, and an isotopically light residue being subducted to great depth.

Here we present two extreme examples from rocks having escaped the subduction factory that show direct evidence of strong fractionation of both Li and B isotopes. The first example are Alpine eclogites having been subjected to conditions of ca. 6500C/2.0 GPa and corresponding to metabasaltic material having passed the forearc in subduction zones. Clean omphacite separates that are a proxy of the whole rock Li isotopic composition during high pressure conditions have some of the lowest  $\delta^7$ Li values recorded to date (as low as -11 ‰; Zack et al., 2003, EPSL 208, p. 279-290).

The second example from Syros, Greece are metasomatic rinds between eclogite knockers and surrounding matrix (serpentinite and metasedimentary schist). The metasomatic rinds are tourmaline-rich and are interpreted to be crystallized from B-rich fluids that were mobilized during dehydration at high pressure (ca. 470°C/1.5 GPa). These tourmalines have extreme d11B values as high as +28 ‰and are evidence for isotopic heavy subduction-related fluids at depth of ca. 45 km.

Although isotope fractionation seems to operate efficiently during prograde metamorphism of subducting slabs, the overall importance of this process depends on several factors, e.g. the amount of fluid released at low temperature (the effect of isotope fractionation decreases with increasing temperature). In an extreme endmember case, mica-rich sediments can retain almost all their water to a depth of >100 km (Schmidt & Poli, 1998), hence limiting isotope fractionation in these rocks.