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LOSS ON IGNITION (LOI) PROCEDURES:

Lake sediment water content, bulk density, and organic matter and carbonate content may be estimated by weight loss measurements in core sub-samples subjected to sequential heating (Dean 1974; Heiri et al. 2001; Santisteban et al. 2004). For example, organic matter is oxidized to carbon dioxide and ash at temperatures between ~200 and 500ºC. Further evolution of carbon dioxide from carbonate mineral forms occurs at temperatures between approximately 700 and 900ºC. Weight losses associated with water and carbon dioxide evolutions are easily quantified by recording sample weights before and after controlled heating (ignition at 550 and 1000ºC) and, in turn, may be correlated to water content, and organic matter and carbonate content.

Calculations:

Water content within lake sediment is typically estimated by weight losses within core sub-samples following overnight drying at ~110ºC within low-temperature ovens. Comparable results may be obtained, however, using longer drying times (>36 hours) at significantly reduced temperatures. Internal (University of Pittsburgh) laboratory experiments have demonstrated water losses no greater than 0.015 g following additional drying at 110ºC (i.e., overnight drying at 110ºC following 36 hours of drying at 60ºC). Water loss is therefore accurately estimated as the weight difference between wet sample weight and sample weight following drying at 60ºC for thirty-six hours:

$$Water\ Loss\ (g) = [Sample\ Wet\ Weight] - [Sample\ Dry\ Weight]$$

Internal laboratory protocol (see below) estimates sample wet and dry weights according to the following equations, when utilizing pre-weighed polyethylene sampling vials:

$$Sample\ Wet\ Weight\ (g) = [Vial\ Weight\ With\ Cap + Wet\ Sample] - [Empty\ Vial\ With\ Cap]$$

$$Sample\ Dry\ Weight\ (g) = [Vial\ Weight\ With\ Cap + Dry\ Sample] - [Empty\ Vial\ With\ Cap]$$

Sample wet and dry weights (in grams) may be equated with sediment wet and dry bulk density (i.e., grams per cubic centimeter) if 1.0 cm^{-3} core sub-samples are utilized. Sediment water content (expressed as percent water by weight or volume) may be calculated readily from wet and dry bulk density values:

$$Percent\ Water\ By\ Volume = [Wet\ Bulk\ Density\ (g\ cm^{-3})] - [Dry\ Bulk\ Density\ (g\ cm^{-3})] \times 100$$

$$Weight\ Percent\ Water = ([Wet\ Bulk\ Density] - [Dry\ Bulk\ Density] / [Wet\ Bulk\ Density]) \times 100$$

Organic matter content is readily calculated then as the difference in weight between the sediment dried at 60ºC and the ash created following ignition at 550ºC within a high temperature muffle furnace:

$$\%\ Organic\ \ Matter = [Weight\ \ of\ \ Post\ 550°C\ \ Ash] / [Weight\ \ Post\ 60°C\ \ Dry\ \ Sample] \times [100]$$

Organic matter content may be multiplied by a constant to estimate the organic carbon concentration of sediment samples. Typically, sedimentary organic matter contains between 40 and 60% organic carbon. Consider the example of simple organic compound:

$$molecular\ weight\ C_n \ / \ molecular\ weight\ (CH_2O)_n = 12.011 / 30.026 = 0.40002$$

The multiplicative factor used to convert organic matter content to organic carbon content is quite arbitrary and highly speculative. Consequently, results should generally appear as losses by weight percent (Weight % LOI, 550°C).

The difference in weight between the 550 and 1000ºC ashes may (to first approximation) be assumed to result from loss of carbon dioxide during carbonate mineral break-down. However, loss on ignition techniques cannot indicate which carbonate minerals may be present within any given sample. Because calcium carbonate is (typically) the dominant form of carbonate in most lake sediments, weight losses at 1000ºC may nonetheless be used to estimate calcium carbonate content:

$$\%\ CaCO_3 = \frac{[Weight\ \ of\ \ Post\ 550°C\ \ Ash - Weight\ \ of\ \ Post\ 1000°C\ \ Ash]}{[Weight\ \ Post\ 60°C\ \ Dry\ \ Sample]} \times 2.274 \times 100$$

$$where\ 2.274 = 100.088 \ / \ 44.009 = molecular\ \ weight\ \ CaCO_3 \ / \ molecular\ \ weight\ \ of\ \ CO_2$$

It should be noted that clay minerals may contain significant quantities of lattice-bound hydroxide (as much as five percent by weight) and these ions may be liberated (as water) at high temperatures. Calcium carbonate content estimates from weight losses at 1000ºC may therefore contain errors as great as five percent and (as such) data results are most appropriately reported as losses by weight percent (Weight % LOI, 1000°C).

Procedure Details:

01. Label and weigh a requisite number of empty 20 mL polyethylene scintillation vials. ***All empty vial weights should include the weight of the cap***. Please note that vial caps should be labeled as well, with the number of the corresponding vial. Record

all weights in the working laboratory vial book. ***Vial books should not be removed from the laboratory***.

02. Obtain one (1) cubic centimeter sub-samples from the sediment cores of interest using the constant volume sampler, and transfer the sub-sampled materials to empty scintillation vials.

03. Measure and record the weight of the wet sediment and polyethylene scintillation vial (including the vial cap) using the micro-balance in the SRCC 416 laboratory. Wet sediment weights should be recorded immediately following core sampling, so as to minimize any sample weight reduction associated with water loss through the permeable walls of the scintillation vials.

04. After recording the wet sediment weight, remove all caps from the scintillation vials and place the caps beneath the corresponding vial within the cardboard flat. Transfer the entire cardboard sample flat to the low-temperature drying oven adjacent to the balance. Never place polyethylene scintillation vials in the laboratory muffle furnace. ***Be certain that the drying oven temperature is set to (and maintaining) a temperature of approximately 60ºC***. Allow the wet samples to dry in the oven at 60ºC for no less than thirty-six (36) hours.

05. While the samples dry at 60ºC, be certain to clean and dry fifty ceramic crucibles for subsequent high-temperature firings. All crucibles should be washed with soap and water, rinsed, and then dried for at least four (4) hours in the high-temperature muffle furnace. The crucibles should be dried at a temperature of ~110ºC.

06. Following the thirty-six hour drying at 60°C, remove the cardboard sample flat from the oven and record the new dry sample weight (sediment + vial + vial cap) in the working laboratory vial notebook. Return the samples to the 60ºC drying oven after recording all dry weights (see *Procedural Considerations* section below).

07. Remove the clean, dry ceramic crucibles from the muffle furnace and reset the temperature to 550ºC.

08. Record the weight of each empty crucible.

09. Transfer the post-60ºC dry sediment sub-samples to the empty crucibles and record the new weight (dry sediment + crucible).

10. When the temperature stabilizes at 550ºC, return the sample-filled crucibles and crucible trays to the muffle furnace. Seal the furnace door again, and allow the temperature to return to 550ºC. Note the time.

11. Following exactly four (4) hours of heating (ignition) at 550ºC, carefully remove the crucibles from the muffle furnace and transfer the hot samples to the 60ºC drying oven for cooling. Allow at least one hour for sample cooling.

12. Reset the muffle furnace temperature to 1000ºC.

13. When the post-550ºC ignition samples have cooled enough for safe handling, begin recording the new sediment and crucible weight. The samples must remain in the drying oven (when not in use) and therefore should be weighed "one-at-a-time".

14. After recording all post-550ºC sediment and crucible weights, the samples should be returned to the muffle furnace and subjected to the two (2) hour ignition at 1000º C. Again, timing of the two hour ignition should be measured relative to the point at which the oven achieves a 1000ºC temperature following sample placement.

15. Following exactly two (2) hours of heating at 1000ºC, carefully remove the crucibles from the muffle furnace and transfer the ignited samples to the 60ºC drying oven for at least two hours of cooling.

16. When the post-1000ºC ignition samples have cooled enough for safe handling, measure and record the final crucible and sediment weight. After recording all values, discard the remaining ignited sample and be certain to wash the crucibles for additional usage.

17. Calculate sample contents using standard equations (below) and/or the EXCEL® spreadsheet (LOI_Template.xls) stored within the laboratory computer.

Procedural Considerations:

Atmospheric humidity may influence all dry sample weights. Dried sediments as well as sample vessels (ceramic crucibles, etc.) absorb water from ambient laboratory air, providing a potentially significant source of error within calculations. Laboratory personnel should store all samples at temperatures greater than (or equal to) 60ºC throughout the loss on ignition procedure. Consequently, samples should never be left exposed on laboratory counters during weighing sessions or between high-temperature firings. Ideally, samples should be removed from the oven and weighed individually, then returned to the oven prior to additional use.

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Safety Considerations:

High oven and furnace temperatures required during analyses present an obvious laboratory hazard. Caution should therefore be exercised throughout the procedure. Tongs should be used to handle sample vessels (individual crucibles and crucible trays) heated to temperatures greater than ~70ºC. High-temperature gloves should be used when handling samples heated to temperatures between 550 and 1000ºC. Laboratory personnel should note, however, that most gloves offer protection only at temperatures less than ~350ºC. The muffle furnace door should be opened and considerable quantities of heat should be dissipated before any samples are removed. Be certain that no laboratory personnel (including the analyzer) have positioned themselves in front of the furnace when opening the door. Provide all other laboratory personnel with fair warning before opening the muffle furnace, and never leave the muffle furnace unattended when cooling.

References Cited:

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