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## Treatment protocol for using tree-ring Zn isotopes for environmental studies

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### Abstract

Zinc isotopes ( $\delta^{66}\text{Zn}$ ) are promising indicators for understanding biogeochemical processes and tracing sources in environmental geochemistry. This study, the first of its kind, proposes a treatment protocol for determining white spruce tree-ring Zn concentration and  $\delta^{66}\text{Zn}$  values. By pooling year-equivalent tree rings of four individual trees (total of 45 samples), the protocol produces reliable tree-ring Zn concentration and  $\delta^{66}\text{Zn}$  values. In the end, comparing the pooled and mean values with the individual trees shows an excellent match. It suggests that the protocol has the potential to be applied in future environmental studies.

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### 1. Introduction

Trees live at the interface between the atmosphere, hydrosphere and pedosphere, and are sensitive to multiple environmental conditions. During their growth, most trees in temperate climates produce one ring per year, allowing an absolute dating of wood<sup>1</sup>. The main uptake pathway of elements through roots and subsequent fixation in wood

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can be combined with the tree-ring chronology as a yearly record of the elements in the local soil<sup>2</sup>. Such dendrogeochemical records have proven to be powerful environmental archives<sup>3</sup>. The use of tree rings as a temporal record of elemental concentration fluctuations has been extended to metal stable isotopic systems. This is particularly true for Pb stable isotopes (whose tree-ring records have been demonstrated to be a sensitive fingerprint of Pb sources in a local area) and their changes through time<sup>4,5</sup>. The strategy for tree-ring  $\delta^{66}\text{Zn}$  analysis may perhaps similarly provide a chronological record of tree-ring  $\delta^{66}\text{Zn}$  variations through time. However, to the best of our knowledge Zn isotopes have not previously been measured in tree rings to produce a temporal  $\delta^{66}\text{Zn}$  series, and therefore there is not a pre-existing body of knowledge or robust interpretive framework. This study aims at determining a treatment protocol whereby the utility of tree-ring  $\delta^{66}\text{Zn}$  analysis to environmental geochemistry can be assessed. Previous studies have demonstrated that tree-ring pooling is an efficient sub-sampling method for light stable isotopic analysis (e.g.  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values), an approach that saves analytical time and delivers reliable isotopic results<sup>6</sup>. Therefore, we evaluate if pooling tree rings constitute an appropriate protocol to analyze tree-ring  $\delta^{66}\text{Zn}$  values of white spruce trees.

## 2. Materiel and methods

### 2.1. Tree-ring preparation

The selected site is located in the Boreal Plains ecozone<sup>7</sup>; 44 km north north-east from the main oil sands mining area of Fort McMurray, Alberta in Canada. From seventeen selected dominant and co-dominant white spruce trees (*Picea glauca* [Moench] Voss), four were sampled at 1.5 m height for dendrogeochemical analyses. Tree rings were dated and measured with standard dendrochronological methods and a statistical analysis was performed to confirm dating with the COFECHA program at GSC-Québec<sup>8</sup> (mean age of 171 years).

To evaluate the reliability of pooled versus individual trees, each tree stem cross section was cut into four equal-angle radial sections that encompassed the full suite of orientations. The time periods 1906 to 1914, 1964 to 1968, and 1978 to 1982 were selected with a 4-, 2-, and 2-years resolution, respectively (for a total of 45 analyses and a pooled versus individual tree comparative dataset of  $n = 9$ ). For each of the four trees, 0.5 g of wood of the year-equivalent tree rings were combined into pooled samples for the three test periods. For the individual samples, 2 g were collected from the respective time periods from each tree. Moreover, radial sections were sub-sampled using a clean stainless-steel electric band saw. The tree rings from each radial section were manually separated with a stainless-steel blade on a Teflon® cutting board. The blade and cutting board were pre-cleaned with ethanol and rinsed with Milli-Q water. Finally, tree-ring sub-samples were stored in Milli-Q-rinsed containers.

### 2.2. Zn concentration and isotope measurements

The 2.0 g of composite tree-ring subsample was initially weighed and then dried at 60 °C overnight. After drying it was weighed again to estimate the moisture content, and transferred into porcelain crucibles for ashing using a step-wise heating procedure (ambient temperature to 250 °C, 250 to 450 °C, and 450 °C, for 45 min, 80 min and 16 h, respectively). The ashed sample was transferred using weighing paper to Teflon® PTFE beakers pre-cleaned with aqua regia and rinsed with Milli-Q water. For maximum recovery, residual ash was transferred by rinsing the crucible with a small amount of Milli-Q water. The rinse water was evaporated at 200°C for 20 minutes, after adding 1 ml of concentrated  $\text{HNO}_3$  (TraceMetal™ Grade, Fisher Chemical). The ash was digested at 200°C by adding 1 ml of  $\text{HNO}_3$ , 1 ml of  $\text{HCl}$  (both TraceMetal™ Grade, Fisher Chemical) and 1 ml of  $\text{HF}$  (Optima™, Fisher Chemical). After evaporation to incipient dryness at 200°C, the digest was taken up in 40 ml of 2.5%  $\text{HNO}_3$ . The solution was split in two aliquots for Zn concentration (Thermo X Series 2 quadrupole ICP-MS) and isotopic ratio analyses (Nu Plasma MC-ICP-MS).

For Zn concentrations, certified reference materials NIST SRM 1575a (pine needles), BCR-CRM 482 (lichen), and uncertified AGBS (in-house black spruce trunk wood) were included as full protocol standards (i.e. these samples followed all sample preparation steps). The average measured Zn concentrations for SRM 1575a was  $37 \pm 1$  ppm ( $n = 7$ ; certified value  $38.0 \pm 2.0$  ppm), and for BCR 482 the measured Zn concentration was  $98.10 \pm 2.70$

ppm ( $n = 8$ ; certified value  $100.60 \pm 2.20$  ppm). Therefore both standards yielded identical accuracies and precisions of 2% and 3% respectively. The average measured Zn concentrations for AGBS was  $9.10 \pm 0.20$  ppm ( $n = 27$ ).

The Zn isotopic analyses used standard ion-exchange purification step<sup>9</sup> thus avoiding matrix interferences and maximizing Zn ionization<sup>10</sup>. The resin type (AG MP-1; Bio-Rad Laboratories, CA, USA) used can release organic components that generate non-spectral interferences during analyses<sup>11</sup>. Therefore, post ion-exchange samples were refluxed overnight with a concentrated  $\text{HNO}_3$  in PFA<sup>®</sup> closed jars. Each solution was subsequently diluted to 400 ppb and 200 ppb of NIST 976 Cu was added as an internal standard. The latter was combined with the standard sample-standard bracketing (SSB) method using the NIST-SRM 683 reference standard to correct for instrumental mass bias<sup>12</sup>. The slope of the  $\ln (^x\text{Zn}/^{64}\text{Zn})$  (where  $x = 66$  or  $68$ ) versus  $\ln (^{65}\text{Cu}/^{63}\text{Cu})$  fractionation line was used to correct the raw ratios of Zn. The slope and corresponding coefficient of determination, plus inserted international standards, were used to reject or accept the daily batch (i.e. determination of instrument stability – if rejected the whole batch was rerun). Monitoring  $^{62}\text{Ni}$  demonstrated no  $^{64}\text{Ni}$  isobaric interference on  $^{64}\text{Zn}$ . The Zn isotope ratios are expressed in conventional delta ( $\delta$ ) notation in per mil (‰), relative to NIST-SRM 683 and analytical error is reported as  $2\sigma$  (2 S.D.). International Zn standards BCR-CRM 482, IRMM 3702 and “Lyon-JMC” were included into each batch and their  $\delta^{66}\text{Zn}$  values are in accordance with what has been found in the literature (Table 1). The total procedural blank was  $< 5$  ng, which is considered insignificant to bias the results.

Table 1. Summary of reference materials analyzed for Zn isotopic ratios\*.

Standards	n	$\delta^{66}\text{Zn}$ (‰)	$\delta^{68}\text{Zn}$ (‰)	Authors
BCR-CRM 482	17	$-0.05 \pm 0.11$	$-0.02 \pm 0.17$	Our study
	8	$0.07 \pm 0.03$		<sup>13</sup>
	3	$-0.07 \pm 0.10$	$-0.09 \pm 0.18$	<sup>14</sup>
IRMM 3702	12	$0.15 \pm 0.05$	$0.32 \pm 0.07$	Our study
	2	$0.25 \pm 0.16$	$0.52 \pm 0.33$	<sup>14</sup>
	24	$0.20 \pm 0.07$		<sup>15</sup>
Lyon-JMC	19	$-0.12 \pm 0.04$	$-0.24 \pm 0.07$	Our study
	4	$-0.07 \pm 0.01$	$-0.10 \pm 0.01$	<sup>16</sup>

\* Values ( $\pm 2\sigma$ ) are reported to the NIST-SRM 683 solution  
*n* = number of aliquot measurements

### 3. Results

Zinc concentrations from analysis of the four individual trees vary from 2.16 to 8.65 ppm. All trees, except one, depict slightly decreasing concentrations with age. The other tree has its lowest concentrations in the 1906-1914 time period with an average of 3.23 ppm, and roughly equivalent and higher concentrations in the two later time periods (average of 4.27 and 4.30 ppm from 1964 to 1968 and 1978 to 1982, respectively). Its concentrations vary from 3.07 to 4.69 ppm. The highest concentrations for an individual tree vary between 5.99 and 8.65 ppm with an average of 8.05, 7.91 and 6.42 ppm respectively for the 1906-1914, 1964-1968 and 1978-1982 time periods. The lowest concentrations observed for another individual tree vary between 2.16 and 3.07 ppm with an average of 6.96, 6.34 and 6.03 ppm within the three time periods. Concentrations of the last tree are between 5.83 and 7.31 ppm. The average values for the three time periods are 6.96, 6.34 and 6.03 ppm from the early period to the recent. Analysis of variance (ANOVA) showed that the concentration differences between trees were statistically significant at the 5% level ( $P < 0.001$ ), while there are no statistical differences between the three periods. The calculated average for the four individual trees stays the same over the three test periods (ranging from 4.56 to 5.48 ppm) with an average of 5.31, 5.21 and 4.79 ppm for 1906-1914, 1964-1968 and 1978-1982 time periods, respectively. The pooled samples values ranging from 4.64 to 5.53 ppm and has an average of 5.38, 5.28 and 4.71 ppm for 1906-1914, 1964-1968 and 1978-1982 time periods, respectively. The pooled samples values compare well with the mean of the four individual tree values ( $r = 0.66$ ;  $P < 0.05$ ).

For all tree samples, the  $\delta^{66}\text{Zn}$  values vary from  $0.51 \pm 0.08$  to  $0.74 \pm 0.06\text{‰}$ , with the greatest individual tree variability being 0.20‰, and the lowest 0.14‰. The tree showing an opposite trend in concentrations has its  $\delta^{66}\text{Zn}$  values ranging from  $0.57 \pm 0.07$  to  $0.66 \pm 0.10\text{‰}$  with an average of 0.63, 0.62 and 0.62‰ respectively for the 1906-1914, 1964-1968 and 1978-1982 time periods. For the tree showing the highest concentration values, the  $\delta^{66}\text{Zn}$  values vary between  $0.51 \pm 0.08$  and  $0.65 \pm 0.01\text{‰}$  with an average of 0.61, 0.57 and 0.63‰ respectively for the three time periods. The tree with the lowest concentration values has  $\delta^{66}\text{Zn}$  values varying between  $0.54 \pm 0.02$  and  $0.74 \pm 0.10\text{‰}$  with an average of 0.68, 0.59 and 0.60‰ within the three time periods. The  $\delta^{66}\text{Zn}$  values of the last tree are between  $0.54 \pm 0.11$  and  $0.74 \pm 0.06\text{‰}$  with an average of 0.63, 0.64 and 0.64‰ from the early period to the recent. The  $\delta^{66}\text{Zn}$  values for the 1906-1914 (from  $0.58 \pm 0.08$  to  $0.74 \pm 0.10\text{‰}$ ) and 1964-1968 periods (from  $0.51 \pm 0.08$  to  $0.74 \pm 0.06\text{‰}$ ) have greater variations than the 1978-1982 period (from  $0.57 \pm 0.07$  to  $0.66 \pm 0.06\text{‰}$ ). However, these differences are relatively small and the  $\delta^{66}\text{Zn}$  values of the four individual tree-ring series over the three test periods are all within the analytical errors. The pooled samples display  $\delta^{66}\text{Zn}$  values between  $0.58 \pm 0.04$  and  $0.66 \pm 0.05\text{‰}$  with an average of 0.62, 0.61 and 0.59‰ for the three time periods, consistent with those of the individual samples. Using the  $\delta^{66}\text{Zn}$  results of the individual trees and weighting for concentration differences between trees, the  $\delta^{66}\text{Zn}$  value that the pooled sample should have can be calculated from the relative inputs from each tree. The weighted Zn isotopic value for the pooled samples displays values from 0.53 to 0.65‰ with an average of 0.63, 0.58 and 0.63‰ respectively for the 1906-1914, 1964-1968 and 1978-1982 time periods. There is no significant difference between the values obtained by analysis of the pooled sample and the weighted-average calculated from the individual trees.

#### 4. Conclusion

The results obtained with the pooling method adequately represent the concentration of the individual series trees, which correlates well with the arithmetic mean concentration of the three test periods. Considering that the  $\delta^{66}\text{Zn}$  weighted mean values of the four individual trees and the one of the pooled samples are well within analytical error, the pooling method can be considered as an adequate technique to produce reliable tree-ring Zn isotopic series. Pooling is therefore validated as an effective protocol to treat tree-ring samples and produce Zn concentration and  $\delta^{66}\text{Zn}$  series that can be used for understanding environmental processes through time. By adjusting the sample weight it could be adapted to any Zn concentration found within tree-rings. It seems overall that this protocol may help studies aiming at differentiating Zn sources and emissions, and understanding local Zn cycling and processes of Zn uptake by trees.

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