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## Earliest Eocene cold period and polar amplification - Insights from $\delta^2\text{H}$ values of lignin methoxyl groups of mummified wood

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## ABSTRACT

Three well-preserved mummified wood specimens have been excavated from three earliest Eocene (~55.5, 55.2 and 53.3 Ma) kimberlite pipes in the subarctic Northwest Territories, Canada (~64°N). Each specimen contained multi-decadal length tree-ring series and allowed measurements of stable hydrogen isotope ratios ( $\delta^2\text{H}$  values) of the lignin methoxyl groups (commonly used cellulose was largely degraded). We used these  $\delta^2\text{H}$  signatures for the reconstruction of three representative  $\delta^2\text{H}$  values of the local precipitation by applying calibrated isotope fractionations to investigate deep-time paleoclimatology. Our reconstructions indicate unprecedented low values for the subarctic early Eocene which, however, show within ~2.2 Myr an increasing trend from  $-206 \pm 17$ ,  $-202 \pm 17$  to  $-168 \pm 17\text{‰}$ . These values were interpreted along with other Arctic, subarctic and mid-latitude proxy records of that time period indicating in total a period of low stable hydrogen and oxygen isotope ratios in precipitation (onset between ~55.7 and 54.9 Ma and a recovery at  $53.3 \pm 0.6$  Ma) which is assumed to have been primarily caused by a continental cold period. An increased magnitude of this cold period was noted for our subarctic reconstructions pointing to a polar amplification where surface air temperature changes in the Arctic exceed the global trend (in response to climate forcing). In an attempt to quantify the polar amplification magnitude we estimated Arctic temperature changes using our  $\delta^2\text{H}$  results in combination with existing relationships between early Eocene temperatures and stable water isotopes. Comparing the Arctic temperature change with a global estimation proposes a polar amplification of magnitude < 4. Our estimate for the earliest Eocene shows either agreement or indicates a lower magnitude when compared to previously described Cenozoic polar amplifications commonly ranging between 2 and 4.

### 1. Introduction

Mummified wood - fossil wood that has not been petrified by secondary permineralization - is a valuable climate archive particularly for the deep-time Cenozoic where terrestrial archives become sparse (Csank et al., 2013; Jahren and Sternberg, 2003; Richter et al., 2008; Wolfe et al., 2017). Depending on the state of preservation, taxonomic determination of the fossil tree species as well as the application of climate proxies such as tree-ring width (TRW) and compound-specific stable isotope proxies at even (sub-) annual resolution are possible (Hook et al., 2015). Some of these mummified wood samples have recently been found within Eocene kimberlite host-rocks of volcanic origin (Hook et al., 2015; Wolfe et al., 2012). Kimberlite eruptions are the result of a combination of explosive devolatilisation of  $\text{CO}_2$ -rich kimberlite magma and phreatomagmatism resulting in pipe-like, volcanoclastic bodies commonly extending to projected depths of

400–600 m (Nowicki et al., 2004). In the course of post-eruptive backfills, redeposition of crater rim materials can involve the burial of ancient trees within the pipe under anoxic conditions (Cas et al., 2008; Nowicki et al., 2004; Wolfe et al., 2012).

Here, we used three mummified earliest Eocene wood samples for the measurement of stable hydrogen isotope ratios (expressed as  $\delta^2\text{H}$  values) for deep-time paleoclimate investigations. The samples were excavated during diamond mining operations in kimberlite deposits located around Lac de Gras (~64° N, 110° W) near the Arctic Circle in the Canadian Northwest Territories. The fossil coniferous tree samples of the species *Piceoxylon* Gothan 1905 and *Taxodioxyton* Hartig 1848, already introduced by Hook et al. (2015, 2015, 2013), allowed the dissection of three multi-decadal tree-ring series at annual resolution (82, 62 and 40 years). Moreover, the three mummified wood samples were found in separate kimberlite pipes including Diavik A154 ( $55.5 \pm 0.7$  Ma; Creaser et al., 2004), Diavik A418 ( $55.2 \pm 0.3$  Ma;

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**Table 1**  
Kimberlite pipes near Lac de Gras (Northwest Territories, Canada) and excavated mummified wood samples therein.

Kimberlite	Latitude, Longitude	Pipe	Age estimation with 95% confidence interval [Ma] <sup>c</sup>	Fossil tree species found
Ekati	64° 42′ 49″ N, 110° 37′ 10″ W	Panda	53.3 ± 0.6 (Creaser et al., 2004)	<i>Piceoxylon</i> Gothan 1905 <sup>a,b</sup>
Diavik	64° 29′ 46″ N, 110° 16′ 24″ W	A-418	55.2 ± 0.3 (Graham et al., 1999)	<i>Taxodioxyton</i> Hartig 1848 <sup>b</sup>
		A-154	55.5 ± 0.7 (Creaser et al., 2004)	<i>Taxodioxyton</i> Hartig 1848 <sup>b</sup>

<sup>a</sup> Same samples already used and described in Hook et al. (2015, 2015).

<sup>b</sup> Same samples already used and described in Hook et al. (2015).

<sup>c</sup> Derived from radiometric rubidium/strontium dating using macrocrystal phlogopite.

Graham et al., 1999) and the Ekati Panda pipe (53.3 ± 0.6 Ma; Creaser et al., 2004) representing a three-point chronology within the earliest Eocene.

Previously, cellulose extracted from mummified wood samples has been investigated for its stable isotope composition (Hook et al., 2015; Jahren and Sternberg, 2003; Wolfe et al., 2012). Mummified wood samples are, however, affected by selective degradation leading to a strong or even complete loss of cellulose leaving a lignin-rich material behind (Stacchioli et al., 2014). For the samples used here the state of preservation has previously been investigated by (Hook et al., 2015). This study indicated remnant cellulose yielding concentrations of about 5% in the youngest specimen recovered from the Ekati Panda pipe whereby the older ones found in Diavik A418 and A154 showed a complete loss of cellulose. Hence, mummified wood samples, particularly the ones of Eocene age, are dominantly or even completely composed of lignin (≥ 95%) favoring the use of a lignin based stable isotope proxy to unlock the full potential of this valuable climate archive.

Recent studies proposed the use of the  $\delta^2\text{H}$  values of the lignin methoxyl groups (expressed as  $\delta^2\text{H}_{\text{LM}}$  values) as proxy for paleoclimate investigations of tree-ring series (Anhäuser et al., 2017a,b; Anhäuser et al., 2015; Feakins et al., 2013; Keppler et al., 2007). Methoxyl groups (R-OCH<sub>3</sub>) in tree wood are predominantly ether bonded in lignin whereby the involved methyl group consists of three non-exchangeable hydrogen atoms. For modern trees at mid-latitude and low-elevation sites it has been shown that  $\delta^2\text{H}_{\text{LM}}$  reflects primarily the weighted mean annual  $\delta^2\text{H}$  values of precipitation ( $\delta^2\text{H}_{\text{precip}}$ ) modulated by a large uniform apparent fractionation (Anhäuser et al., 2017, 2017a,b). Stable isotopes in precipitation ( $\delta^2\text{H}_{\text{precip}}$  and  $\delta^{18}\text{O}_{\text{precip}}$ ) are sensitive paleoclimate-/hydrology proxies as they reflect changes in moisture source, changes during meridional vapor transport (such as water volume loss and the potential mixing with different air masses) and local temperature (Craig, 1961; Dansgaard, 1964). The dominant influence of temperature for  $\delta^2\text{H}_{\text{precip}}$  in the mid-latitudes was equivalently reflected in the  $\delta^2\text{H}_{\text{LM}}$  values measured in modern wood samples across a European North-South transect (Anhäuser et al., 2017b). This finding was also supported by a study of an annual resolution time series (time period of 1989 to 2009) of a Scots pine (*Pinus sylvestris*) where a significant  $\delta^2\text{H}_{\text{LM}}$ -temperature correlation was reported (Mischel et al., 2015). Furthermore, a field experiment investigated the potential alteration of the  $\delta^2\text{H}_{\text{LM}}$  values during biotic and abiotic degradation of organic matter (Anhäuser et al., 2015). The results clearly showed that substantial degradation of lignin did not affect the  $\delta^2\text{H}_{\text{LM}}$  values, even though that study noted a much stronger methoxyl loss (~40 to 70%) when compared to the mummified wood samples. Hence, there is not only evidence of broad insensitivity of hydrogen atom exchange but also no observable dependence between degradation and  $\delta^2\text{H}_{\text{LM}}$  giving confidence that the pristine isotope signature is preserved over geological time scales.

The mummified samples used here were embedded in the earliest Eocene; a period of particular (paleo-) climatologic interest as it not only had the warmest climate of the Cenozoic era but also was characterized by the most pronounced long-term warming trend culminating in the Early Eocene Climatic Optimum (EEO; Zachos et al., 2001). Superimposed onto this long-term warming trend were two

short(-term) hyperthermals including the prominent Paleocene Eocene Thermal Maximum (PETM) with an onset at ~55.9 Ma (Westerhold et al., 2015). Climate changes were accompanied by substantial shifts in greenhouse gas concentrations and, thus, the early Eocene is considered as the best available analogue of the current global warming (Hyland et al., 2016).

Here, we measured  $\delta^2\text{H}_{\text{LM}}$  values of three multi-decadal mummified tree-ring series at annual resolution to estimate representative mean  $\delta^2\text{H}_{\text{precip}}$  values of three time slices of the earliest Eocene (55.5 ± 0.7, 55.2 ± 0.3 and 53.3 ± 0.6 Ma). As the two oldest mummified wood host rocks reveal indistinguishable absolute age estimates, the three  $\delta^2\text{H}_{\text{precip}}$  reconstructions are mainly viewed as representative of two consecutive time slices. We used these  $\delta^2\text{H}_{\text{precip}}$  reconstructions for the investigation of the North American subarctic paleoclimate and discuss potential global implications of the earliest Eocene climate through comparisons with other mid-latitudinal and global proxy records.

## 2. Materials and methods

### 2.1. Lac de Gras kimberlites

Three mummified wood samples were excavated during diamond mining operations in three different kimberlite pipes (Table 1). The fossil tree species were identified as *Piceoxylon* Gothan 1905 excavated at the Ekati Panda pipe and *Taxodioxyton* Hartig 1848 excavated at the Diavik pipes A-418 and A-154 (cf. Hook et al., 2015). The kimberlite pipes are within 30 km distance of each other and located near Lac de Gras at ~64° N in the Northwest Territories (Canada) close to the Arctic Circle. Radiometric rubidium/strontium dating revealed an earliest Eocene age of 53.3 ± 0.6 Ma for the Ekati Panda pipe (Creaser et al., 2004). Both Diavik pipes A-418 and A-154 were dated as older with ages of 55.2 ± 0.3 and 55.5 ± 0.7 Ma, respectively (Creaser et al., 2004; Graham et al., 1999). This puts the oldest pipe (Diavik A-154) around the age of the Paleocene Eocene Thermal Maximum (PETM) 55.9 Ma (Westerhold et al., 2015). A potential occurrence of the Diavik A-154 *Taxodioxyton* tree within the PETM is discussed in detail in sections 3.1 and 3.5. The paleolatitude of the study site was at 65 ± 2° N indicating a nearly unchanged latitudinal location of the kimberlites for the early Eocene as compared to their present position (derived from the paleolatitude calculator [model version 2.0], van Hinsbergen et al., 2015). Present day temperature and precipitation data of the sample site was collected for the period between 1994 and 2014 from the Climate Research Unit (CRU TS 3.1; Harris et al., 2014). Seasonal temperatures fluctuate between -28 °C (January, coldest month) and 13 °C (July, warmest month) resulting in a mean annual value of -8 °C. Annual precipitation amounts to 260 mm with the majority occurring in late summer (July to September). The  $\delta^2\text{H}_{\text{precip}}$  values ranges seasonally between -244 (January) and -134‰ (July) with a weighted mean annual value of -180 ± 4‰ as derived from the Online Isotopes in Precipitation Calculator (OIPC version 3.1; available at <http://www.waterisotopes.org>; Bowen et al., 2005; Bowen and Revenaugh, 2003; Bowen and Wilkinson, 2002). This interpolated OIPC data for the kimberlite study site is in accordance with the nearest station of the Global Network of Isotopes in Precipitation (GNIP; available at [2](http://</a></p>
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