ARTICLE IN PRESS

Chemical Geology xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Puzzling Zn isotopes in spruce tree-ring series

L. Dinis[a,*], P. Gammon[b], M.M. Savard[a], C. Bégin[a], I. Girard[b], J. Vaive[b]

[a] Geological Survey of Canada, Natural Resources Canada, 490 rue de la Couronne, Québec G1K 9A9, Canada
[b] Geological Survey of Canada, Natural Resources Canada, 601 Booth Street, Ottawa K1A0E8, Canada

ARTICLE INFO

Editor: K Johannesson

Keywords:
Zn isotope ratios
Tree rings
Translocation
Oil sands region

ABSTRACT

Zinc (Zn) isotopes have shown promise for investigating biogeochemical processes and tracing sources of Zn for environmental studies. This study, the first in its kind, investigates Zn isotopic ratios in tree rings and soils of two sites in the Northern Athabasca Oil Sands Region (NAOSR) of Alberta, Canada. To this end, we have developed an appropriate protocol to analyze tree-ring δ^{66}Zn values by pooling year-equivalent tree rings of four individual trees for both sites. The results of combined tree-ring Zn concentrations show minimal variation in heartwood, with a statistically significant decrease after 1979 and 1986 for site 1 and site 2, respectively. For site 1, tree-ring $\delta^{66}Zn_{JMC\ Lyon}$ ratios vary between 0.83 ± 0.08 to 0.54 ± 0.07‰ with a statistically significant decrease from 1877 to 2008. For site 2, $\delta^{66}Zn_{JMC\ Lyon}$ ratios range from 0.78 ± 0.02 to 0.59 ± 0.07‰ with the lowest values obtained for the outermost ring closest to the bark. However, this site does not display statistically significant long-term trend. In comparison to the tree rings, adsorbed Zn within soil organic horizons is relatively enriched in heavy isotopes ($\delta^{66}Zn_{JMC\ Lyon}$ of 1.00 ± 0.20 to 1.12 ± 0.10 and 0.81 ± 0.10 to 0.86 ± 0.06‰ for sites 1 and 2, respectively). Tree-ring and soil organic horizons δ^{66}Zn values are also substantially heavier than the value reported for adsorbed Zn in NAOSR tailing sands ($\delta^{66}Zn_{JMC\ Lyon}$ = 0.35 ± 0.06‰). The heavy signature in the organic horizons may be a product of Zn biogeochemical cycling through soil processes and uptake by trees, although Zn atmospheric deposition from the NAOSR cannot be discounted. On the other hand, tree physiological processes, particularly radial translocation, could have potentially influenced the studied tree-ring Zn concentration and isotopic characteristics. However, this mechanism has not received substantial research. The δ^{66}Zn analyses in different wood components are required before its influence on δ^{66}Zn values can be properly assessed and tree-ring δ^{66}Zn can be used as environmental indicators.

1. Introduction

Trees live at the interface between the atmosphere, hydrosphere and pedosphere, and are sensitive to multiple environmental conditions. During their development, most trees in temperate climates produce one ring per year, enabling an absolute dating of wood (Fritts, 1976). The absorption of elements through roots, leaves and bark and their subsequent fixation in wood can be combined with the tree-ring chronology as a yearly record of the elements present in soil and atmosphere (Amato, 1988; Lepp, 1975). Boreal trees such as white spruce can be as old as 300 years in areas protected from fire, or even up to 1000 years above the Arctic Circle (Giddings, 1962). Thus, tree-ring carbon and oxygen isotopes provide temporal environmental information that can be translated into climatic reconstruction (e.g., Flower and Smith, 2011; McCarroll and Loader, 2004; Porter et al., 2014; St. George et al., 2009; Tardif et al., 2008) and atmospheric emission records (e.g., Bukata and Kyser, 2007; Doucet et al., 2012; Savard et al., 2004; Savard et al., 2014), which extend further back in time than shorter-term instrumental records. The development of dendrogeochemistry has now extended to metal isotopes such as Pb, which has been demonstrated to be a sensitive fingerprint of Pb sources (e.g., Mihaljevič et al., 2011; Novak et al., 2010; Saint-Laurent et al., 2010; Savard et al., 2006). Such records have therefore proven to be powerful environmental archives. With the analytical development of the multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS), tree-ring metal stable approach can now be extended to non-traditional isotopic systems such as Zn.

Interpreting a tree-ring δ^{66}Zn record requires an understanding of the Zn sources, potential isotopic fractionations and pathways in the local environment. Mattielli et al. (2009) reported heavy isotope depletion in particles emitted from the main chimney of Pb-Zn refineries, suggesting Zn isotopes can undergo significant fractionation during heavy industrial processing. This provides a basis for differentiating natural from anthropogenic Zn sources and using tree-ring Zn isotopes

* Corresponding author.
E-mail address: lauriane.dinis@canada.ca (L. Dinis).

https://doi.org/10.1016/j.chemgeo.2017.11.015
Received 29 March 2017; Received in revised form 9 November 2017; Accepted 14 November 2017

Please cite this article as: Dinis, L., Chemical Geology (2017), https://doi.org/10.1016/j.chemgeo.2017.11.015

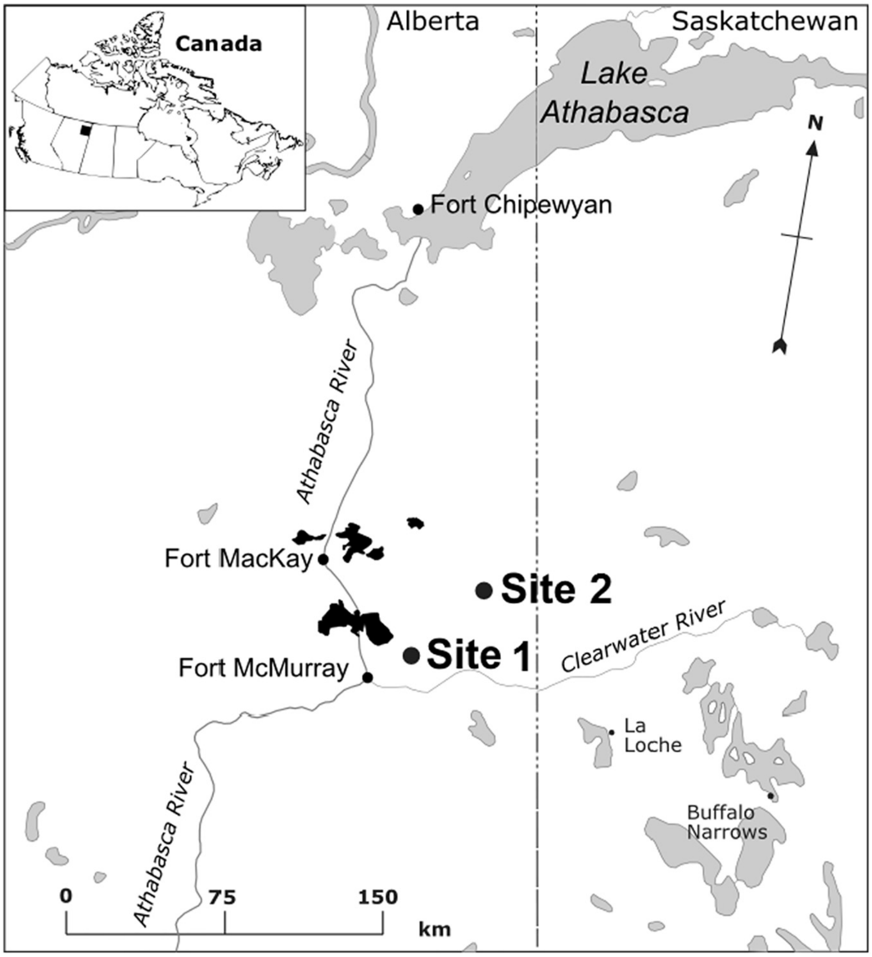

Fig. 1. Location of the studied sites relative to the main surface mining area (black surfaces) in the Northern Athabasca Oil Sands Region (NAOSR).

to trace environmental Zn contamination histories (Aranda et al., 2012; Bigalke et al., 2010; Cloquet et al., 2006; Dolgopolova et al., 2006; Mattielli et al., 2009; Sivry et al., 2008; Sonke et al., 2008; Weiss et al., 2007). Zinc isotopes have also been used to investigate natural processes in various biological (Büchl et al., 2008; John et al., 2007a; Stenberg et al., 2005; Van Heghe et al., 2012) and geochemical systems (Fernandez and Borrok, 2009; Herzog et al., 2009; Luck et al., 2005; Paniello et al., 2012; Pons et al., 2013).

For trees, the root system is considered to be the main pathway to incorporate metals such as Zn (Lepp, 1975; Watmough et al., 1999). The processes involved, such as assimilation through root cell membrane and transport from roots to leaves, have been suggested as playing key roles in Zn cycling and isotopic fractionation (Arnold et al., 2010; Aucour et al., 2011; Caldelas et al., 2011; Moynier et al., 2009; Smolders et al., 2013; Tang et al., 2012; Viers et al., 2007; Weiss et al., 2005). While most Zn isotopic studies on trees have been conducted under controlled laboratory conditions, Viers et al. (2007) analyzed δ^{66}Zn values in roots, shoots and leaves of tropical trees growing in natural field conditions. They reported important fractionations between plant organs, with heavy isotopes becoming increasingly depleted from roots, to shoots to leaves. They also observed variations in δ^{66}Zn values between different tree species.

This study presents the first Zn isotopic dendrogeochemical record at fine resolution (4-year resolution from 1870s to 1950s and 2-year resolution until 2010s). The data have been generated from trees growing in the Northern Athabasca Oil Sands Region (NAOSR) of Northern Alberta, Canada. Since 1967, the NAOSR has hosted extensive industrial mining and processing activities for bitumen extraction that is contained within the oil sands. This industry delivered up to 2.3 million barrels/day of synthetic crude in 2014 (Alberta Energy, 2017). Airborne emissions from oil sands mining activities are reported to have low metal contents (Boutin and Carpenter, 2017; Edgerton et al., 2012; Guéguen et al., 2011; Guéguen et al., 2016; Kelly et al., 2010; Shotyk et al., 2014). However, in comparison to background values (< 10 ppm), significant Zn are found in haul road dust (31.2 ppm), overburden (18.3 ppm), tailing sands (8.3 ppm), heavy hauler fleet emissions (5147 ppm) and upgrader stack emissions (25.7 ppm; Landis et al., 2012). Savard et al. (2012) also reported Zn concentrations in fine tailings ranging from 0.70 to 4.95 and 19.1 to 49.7 ppm in adsorbed and absorbed phases, respectively. All of these sources have the potential to release mineral dust and/or aerosols to the environment. Natural dust generated by wild fires (~160 ppm; Landis et al., 2012) and aeolian processes in general could also potentially contribute to the native Zn pool in the NAOSR. At this stage, only one of those potential sources has been reported for its δ^{66}Zn values (adsorbed phase of fine tailings: 0.35 ± 0.06‰; Savard et al., 2012).

In light of the above, tree-ring Zn isotopes could be a useful tool for environmental studies. This study, as the first of its kind, initiates the evaluation of Zn isotopes of white spruce tree rings as an environmental indicator by: (1) testing a method for preparing tree-ring samples for Zn concentration and isotopic ratio measurements, and (2) producing and comparing tree-ring Zn concentration and δ^{66}Zn series from two sites.

2. Material and methods

2.1. Field characteristics and sample collection

The NAOSR is characterized by a sub-arctic semi-humid climate with contrasted seasons and a mean annual temperature of 0.7 °C (winters and summers average temperature are −13.8 and 15.0 °C,