

# Can boron and boron isotopes be used as a sedimentary marker for fire events? A case study from a historic urban fire event in W Finland

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## Abstract

The aim of this study was to seek the origin of a B peak found in two sediment profiles from a small lake close to a small-sized town in Finland. The peak was found by chance when an environmental multielement study was performed. Altogether 51 chemical elements were determined with ICP-MS, after aqua regia digestion. None of the other determined elements were enriched or depleted in the B rich layer, including elements derived from sea-salt inclusions (Na and Sr) and anthropogenic sources (Pb, Cu, Cd, Hg, etc.). Boron stable isotopes, dating of the sediment cores, and the B concentrations found in possible source materials suggest that the B rich layer is the result of leaching of wood ash produced in a fire that destroyed half of the nearby wooden town in the early 19th century. The results imply that the concentrations and isotopic signatures of B in lacustrine environments (sediments) can be used to detect historic fires.

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## 1. Introduction

Lake sediments are useful for investigating the past and present pollution load of a specific area that receives (has received) inputs from one or several sources, which may include local, regional and global natural and anthropogenic emitters. The focus of the research within this vast field can broadly be divided into two main categories. First, studies focusing on the source and increase–

decrease through time, of specific pollutants (for example Pb) for which the scientific or environmental questions concern a single element (Renberg et al., 2002). Second, studies focusing on a large number of elements that are simultaneously determined in order to solve for example paleolimnological problems (Meriläinen et al., 2003). The latter “multielement” approach has been made easier and convenient with the development of inductively coupled plasma–mass spectrometry methods for simultaneous and rapid multielement determinations on very small sample volumes. Hence, this approach has become much more common over recent times. With this approach, researchers are able to follow simultaneously many deposited

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contaminants, which undoubtedly gives a more complete picture of historic pollution and answers to questions regarding the overall and specific elemental behaviour in sediments (Virkanen, 1998; Chillrud et al., 1999). When using multielement methods, however, the analyses often contain elements for which there is no immediate research need. Consideration of such elements, may reveal interesting and previously unknown geochemical features. The explanation of such features is often a greater and more time consuming, challenge but there are possibilities for novel findings.

In this study two sediment profiles from a small lake close to a small urban centre were sampled and analyzed with multielement methods for tracking past and present pollution by chemical elements. In both profiles there was a distinct concentration peak of B that did not follow the pattern of any other determinants. The purpose of this paper is to present an explanation of this B enrichment.

## 2. Methods

### 2.1. Area description

A pond-like lake, situated ca. 2 km east of the town of Jakobstad (20,000 in., Fig. 1) and having spatial dimensions of ca. 130 m (E–W) × 220 m (N–S) and a maximum depth of 1.5 m, called the “Permoflada lake”, was studied. This lake was cut off from the Gulf of Bothnia (Baltic sea) by isostatical land uplift, which at present is ca. 8 mm/a, ca. 250–300 a ago, and is thus classified as a glo-lake. Because of the land uplift the lake was previously part of a strait that at its narrowest part crossed through Jakobstad and was called “the channel”. In Fig. 1C it can be seen that in the beginning of the 19th century the channel was very narrow, constantly shrinking due to the land uplift and also due to the input of urban waste. In the early 20th century the channel had

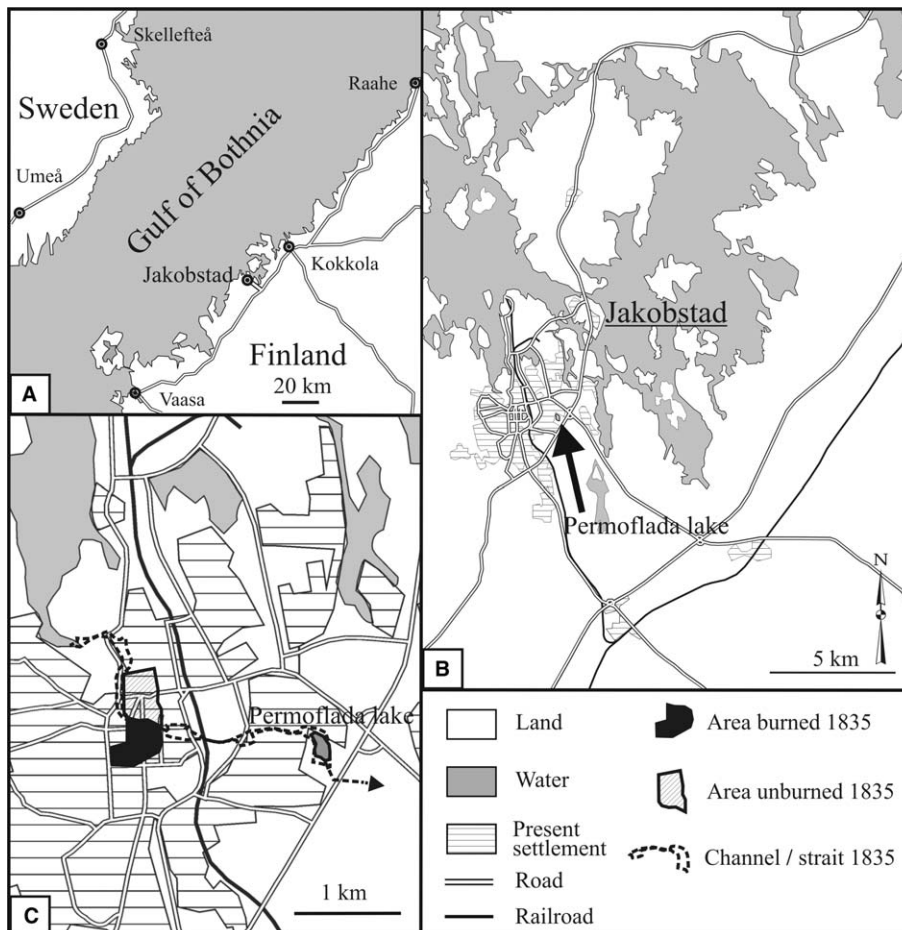


Fig. 1. The location of the city of Jakobstad (A), the Permoflada lake (B), and the historical sites/waters discussed in the text (C).

almost dried out, as seen from a photograph (Nikula, 1952). The overgrowth of the channel had already been noted by surveyor Hans Henric Aspegren (1763), who wrote in 1763: “*It would be easier to reach the town [from the east]... if the channel through the town was dredged, which could be performed without high costs, it would thus be possible to pass it comfortable with boats... and it is not many years since that [the passing with boats] still occurred, due to lack of maintenance it is fairly overgrown*” (authors’ translation). This describes the, possibly very rapid, overgrowth of the channel that was never dredged. Hence, according to this the lake was finally cut off in the mid-18th century after which it is unlikely that any greater water flow occurred and the only outlet was towards the east, which today exists as a ditch. Today Permoflada has no major inlets, and during sampling or afterwards no major surface inflow of water has been noted in the surrounding ditches. The pH of the lake water is not known but all natural lake waters in the area are acidic and weakly buffered with a pH range of 4.5–6.5. Earlier the higher portion of brackish water probably held the pH at a higher level than today.

## 2.2. Sampling

In the spring of 2001 a 138 cm long sediment profile (P1) was collected with a Russian sampler with an inner diameter of 50 mm. The profile was subsampled into 2 cm sections. The thickness of the soft sediment was approximately that of the core since further down a distinct sand/silt layer, not penetrable with the sampler, occurred. A second profile (P2) was collected in December 2002 with a plastic pipe with an inner diameter of 50 mm. The pipe was left to stand in upright position until completely frozen (−25 °C) and later subsampled into 1–6 cm sections. The profiles were taken from the deepest part (1.5 m) with a distance of 15 m apart. Both profiles can be characterized as watery (gel like) black, fine grained, sulphide muck with a gradually increasing grey colour from ca. 65 cm downwards.

## 2.3. Analyses

The samples were dried below 60 °C, and the water content determined. P1 was comminuted with an agate mortar by hand while P2 was gently com-

minuted and homogenized by hand through the sample bags. Loss on ignition (LOI) was determined by combustion of samples at 500 °C for 4 h after drying to a constant weight in 105 °C (LOI was assumed to crudely resemble the total organic material in the samples). For element analyses ca. 1 g samples were leached in 6 ml hot (95 °C) dilute aqua regia (HCl–HNO<sub>3</sub>–H<sub>2</sub>O in proportions 2–2–2) diluted to 20 ml and analysed by ICP-OES and ICP-MS. A total of 51 chemical elements were determined. The analyses were performed in a commercial accredited laboratory. Altogether 13 replicates were determined for both profiles showing only 0–3 ppm differences for B from the corresponding routine samples. The Spearman rank correlation coefficient of the duplicate replicate pairs was 0.95. Stable B isotopes were analyzed in eight samples with ICP-MS-DRC (Elan 6100 DRC) after an aqua regia leach. Certified reference material SRM-951 was used for the analyses. A <sup>11</sup>B/<sup>10</sup>B value of 4.00436 was determined for the SRM-951 standard (5 replicates determined). Each sample was run in triplicate and the mean was used. The error for each sample was calculated into δ<sup>11</sup>B comparable values from the standard deviation, divided by the mean, of each triplicate (rsd% in Fig. 5). The δ<sup>11</sup>B values were calculated using the following equation:

$$\delta^{11}\text{B} = \frac{(^{11}\text{B}/^{10}\text{B})_{\text{sample}} - (^{11}\text{B}/^{10}\text{B})_{\text{SRM951}}}{(^{11}\text{B}/^{10}\text{B})_{\text{SRM951}}} \times 1000 \quad (1)$$

The surfaces of both profiles were analyzed for enrichment peaks in <sup>137</sup>Cs activity from the Chernobyl accident (1986) and maximum atmospheric nuclear weapons testing (1963). The analyses were performed at the Department of Physics at Åbo Akademi. The counting of charcoal and spherical carbonaceous particles (SCP) was carried out on P2 as described by Rhodes (1998). Briefly, ca. 0.2000 g sediment was leached in several steps with 6% H<sub>2</sub>O<sub>2</sub>, at temperatures ranging from 20 to 45 °C, in order to remove and bleach the dark organic matter. The bleached sediment was mounted on petri dishes and the particles counted under a microscope at 630× magnification. This bleaching method was developed for the analysis of charcoal but since this bleaching is milder than methods suggested for SCP quantification it does not affect the spherules. In order to be sure of the presence of SCPs at the start of the record the whole Petri dish was thoroughly examined for the section 28–38 cm.

### 3. Results

#### 3.1. Sedimentation dynamics

Above the hard sand/silt layer, there is a ca. 40 cm thick layer (sampled only in P1 where the sediment was thicker) with stable concentrations of ash, water and LOI (Fig. 2). This layer reflects the time period when the lake was part of the strait. Above this, at ca. 93–63 cm, the concentrations of ash decreases while concomitantly those of water and LOI increases. This is caused by a gradual decrease in the deposition of minerogenic material, which is connected to the period (first half of 18th century) when the strait was ultimately cut-off and the present lake was formed. The upper 63 cm, which is thus younger than 1750, belongs to the ongoing lake stage representing a current “depositional steady state”. The deviation at the sediment–water interface in P2 is due to, as yet, poor sediment compaction (Fig. 2).

#### 3.2. Sedimentation rate of current “steady state” layer

The  $^{137}\text{Cs}$  results show two distinct peaks for P2 which are likely to represent the years 1986 (Chernobyl accident) and 1963 (maximum atmospheric nuclear weapons testing). In P1 only the 1986 peak was detected but it had the same intensity as the cor-

responding peak in P2 (Fig. 3). The absence of the 1963 peak in one of the profiles (P1) is not an uncommon phenomenon in these types of environments (Virkanen et al., 1997). In this case it could be due to small local variations in sedimentation or different sampling devices used for the two profiles. Because of this and the denser subsampling of the surface of P2, that profile was used for dating purposes (Table 1, Fig. 3). Spherical carbonaceous particles are formed in the high temperature combustion of fossil fuels (coal and oil). This is an activity which has taken place during the last ca. 150 a. Thus the presence or absence of such particles can be used as an aid for dating sediments (Rose, 2001). The SCP record started at 38 cm depth (Fig. 4). This represents, according to Rose (2001), 1850–1860 at the earliest, but may also be later. By using these time markers (Table 1) the sedimentation rate down to 63 cm was estimated (the rate from 1850/1860 downwards was directly extrapolated from the 1963–1850 rate), under which the sedimentation dynamics alter and rate estimations are impossible with the methods used.

#### 3.3. Boron

In both profiles a distinct B peak exists with a maximum of 45 and 34 mg/kg B (Fig. 5). The peak concentrations (P1) are up to 30 mg/kg (200%) above the “normal” for the lake. There are other B peaks in P1 at 15 and 85 cm, but these are minor and not much above the background level. The very

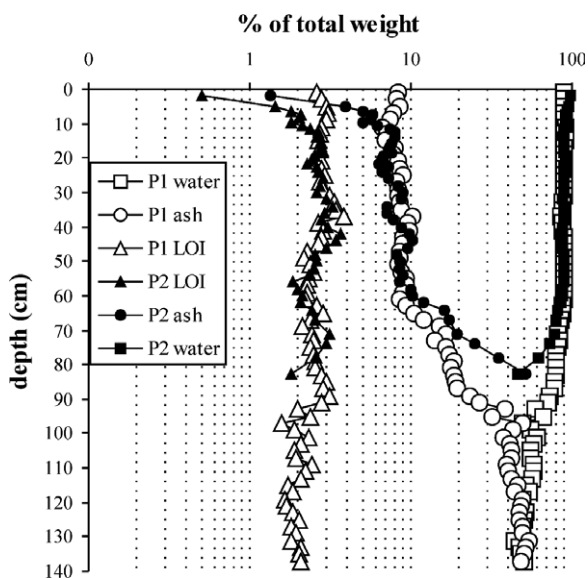


Fig. 2. Concentrations of water, loss on ignition (LOI) and ash in two profiles (P1, P2) from the Permoflada lake.

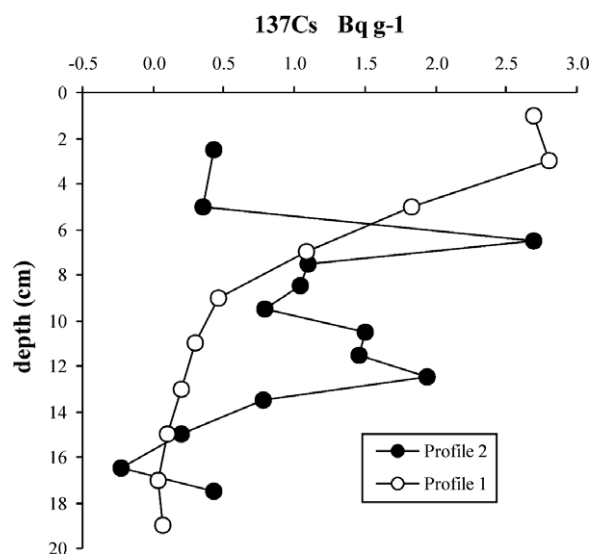


Fig. 3.  $^{137}\text{Cs}$  activity in two profiles from Permoflada lake.

Table 1  
Calculated sedimentation rates between different time markers in profile 2 in Permoflada lake

Nr	Time period	Thickness (cm)	Number of years	Event	Sedimentation rate (cm/a)	Error range (cm/a)
1	2002–1986	6.5	16	Chernobyl accident	0.41	±0.03
2	1986–1963	6.0	23	Nuclear weapons testing	0.26	±0.04
3	1963–1850	25.5	113	Start of SCP record	0.23	±0.02
4	1963–1860	25.5	103	Alt. start of SCP record	0.25	±0.02

The “Thickness” column shows the thickness between each “Event” used for dating the sediment. The last column shows the possible variation in sedimentation rates based on slice thicknesses. Two alternative dates for the start of the SCP record are given, according to Rose (2001).

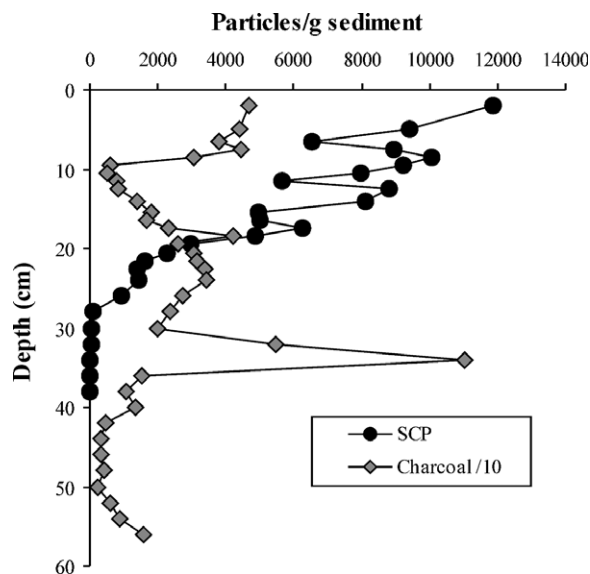


Fig. 4. The charcoal and spherical carbonaceous particle record in Permoflada lake. (Notice that the charcoal values are divided by a factor of 10).

clear B peaks indicates a unique one-time event or reaction, strongly elevating the concentrations above the normal. The peaks certainly represent the same layer since the distances from the 1986  $^{137}\text{Cs}$  peak to the B peak differ only by 0.5 cm between the profiles. This also confirms that the accumulation of sediment in both profiles has been the same.

The strongest positive correlations for B with any of the other parameters studied were with Na and Sr ( $r_s = 0.84$ , respectively, including the peak subsamples). This indicates that salt associations are dominant overall. However, at the depths where the B peaks are, no other determinant occurred in elevated concentrations, including Na and Sr (mostly sea salt), Fe, Mn, Al and S (redox indicators and hydroxide forming), Ca and Mg (carbonates) and metals such as Cd, Pb, Bi, Sb, Cu and Hg (anthropogenic input).

The  $\delta^{11}\text{B}$  values show a variation from +0.94 ( $\pm 2.40$ , rsd%) to +9.67 ( $\pm 3.53$ , rsd%) (Fig. 5). These values, which are too low for a sea-water origin, represent the isotopic signal of the brackish water mixed with the catchment input of B. The peak samples show slightly less positive  $\delta^{11}\text{B}$  values compared to the surrounding samples. Hence, the isotopic and chemical data in combination show that the detected B layer is not the result of marine-derived salt.

### 3.4. Charcoal patterns

Charcoal was present throughout the profile, but only quantified for the upper 57 cm. A slow concentration increase occurs until ca. 22.5 cm (1919), whereafter the concentration decreases until ca. 9.5 cm (1975), when a rapid increase again starts. A distinct peak was present in two consecutive samples at 32–34 cm (ca. year 1870) (Fig. 4). This peak is probably due to an unknown fire (e.g. burning of fields) very close to the lake since large charcoal pieces were present. The slow increase until 1919 is probably due to increasing population in combination with the still open landscape. The subsequent decline is probably due to the forestation of the area when free grazing ended. The post 1975 increase is most likely due to the establishment of private housing close to the lake. At the depth of the B layer, charcoal was not elevated.

## 4. Discussion

### 4.1. What is the source of the high-boron layer?

Volcanic ash is reported to contain on average smaller or similar B concentrations to that of the peak recorded here (Park and Schlesinger, 2002). However, single airborne particles of volcanic origin are known to contain variable concentrations of B,

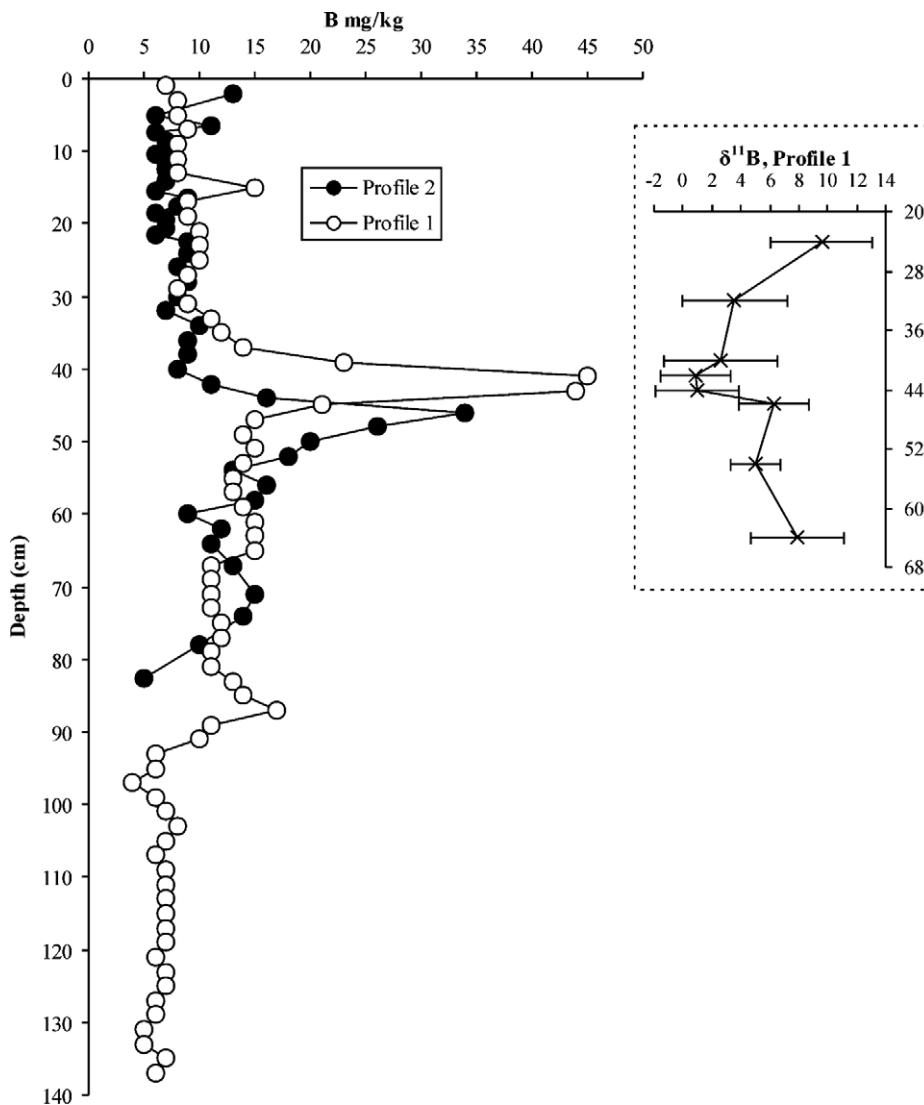


Fig. 5. The B concentration in profile 1 and 2, and the  $\delta^{11}\text{B}$  values in profile 1 (the whiskers show the rsd% error) in Permoflada lake.

ranging from 0.93 to 102 mg/kg (Eastwood et al., 1999; Pearce et al., 1999). It is thus theoretically possible, given the right meteorological conditions acting upon the “right” erupting volcano, that airborne B enriched volcanogenic particles could have been transported and ultimately deposited in the investigated area. However, this scenario is hard to believe, considering the fact that the study area is situated a long distance from active volcanoes and that B, however seldom studied in lacustrine settings, has not been reported to occur in elevated concentrations in any lake as a result of any volcanic activity.

Boron is a known micronutrient for many plants and organisms (Dembitsky et al., 2002). It is, how-

ever, very unlikely that this could be a direct source of the B because: it is impossible to envisage a mechanism which triggered organisms to enrich B, or triggered a “bloom” in B containing organisms ultimately producing a B rich layer. Also, it is unlikely that biological activity could have produced the peaks without an extra input of B. A secondary effect involving plants, algae or microorganisms cannot be excluded by using the present dataset only, but nothing points to an independent biological cause for the recorded layer.

Boron has been introduced at a late stage in societal and industrial development, and has thus commonly not been accumulated in large concentrations at urban sites. This is also seen in the city close to

the investigated lake (Jakobstad), where strongly polluted soils contain only <1–20 mg/kg of B (authors' unpublished data). Also, local "natural" materials cannot be a direct source of the high-B layer (up to 45 mg/kg), since the B concentrations: in sediments in the nearby Larsmo lake are <3–15 mg/kg (Peltola and Åström, 2002), in Holocene and recent sediments from the Baltic Sea 7–24 mg/kg (authors' unpublished data), in parent sediments of acid sulphate soils in the region 2–33 mg/kg (authors' unpublished data), in local pine needles 8–29 mg/kg, in local moss 1–11 mg/kg, in local boreal forest humus 2–15 mg/kg (Raitio and Kärkkäinen, 2002), and in common plant species (7 species of vascular plants, including trees) of Finnish and Russian forests 11–33 mg/kg (median values) (Reimann et al., 2002). The concentrations from all these reference materials were determined with similar methods to the one used in this study.

Wood ash contains hundreds of mg/kg of B largely in water-soluble form (Pohlandt and Marutzky, 1993; Khanna et al., 1994; Jönsson and Nilsson, 1996). Khanna et al. (1994) also noted that >70% of B from eucalyptus ash was water soluble. Bearing this in mind, it is intriguing that half of the nearby old wooden town (Fig. 1C), built after 1720, was catastrophically burned on the 2nd September 1835. The event took place after a long dry period and lasted for 6 h. The fire spread quickly from the SW parts to the north, aided by a strong SW wind. A total of 73 yards of which most included several wooden buildings and storage facilities were completely destroyed, leaving three people dead and 571 homeless (total population at the time was ca. 1800). The intensity of the fire is evident from the eye witness stories and by the fact that very limited amounts of goods and belongings were saved (Åhlström, 1934). Molten glass that is still found today from the ash layers indicates high temperatures (G. Björklund, pers. commun.). By using, for dating purposes, the later date of the start of the SCP record (1860), the year of the fire (1835) and that of the B peak are the same. Thus, considering all the data and information presented above, the authors propose that the B layer is caused by the catastrophic burning of the nearby town.

#### 4.2. Mechanisms of boron transport

A likely pathway of B to the lake is via ash-layer leachates, discharging to the channel waters and ultimately depositing B on the lake bottom

(Fig. 1C). It is also known that the fire remnants, including the ash, were spread out on the ground before town rebuilding (G. Björklund, pers. commun.), which could have further aided the leaching of B from the fresh ash. Since B is known to volatilize when organic materials such as coal and wood are burnt, an atmospheric pathway is theoretically possible (Clarke and Sloss, 1992; Meij, 1997). However, this pathway seems highly unlikely, e.g., due to the very low concentrations of charcoal particles in the B enriched layer.

The small shift towards the lighter B isotope in the B rich layer may be explained by a different and lighter isotope signal in the wood-ash leachates. However, the alkaline ash leachates could also, temporarily, elevate the pH in the shallow lake. At higher pH values the tetrahedral coordination ( $B(OH)_4^-$ ) in B hydroxides increases, this is more enriched in the  $^{10}B$  isotope (Vengosh et al., 1994; Hoefs, 2003). At higher pH values B adsorption to clay minerals increases and thus the clay would incorporate B with more  $^{10}B$  (Vengosh et al., 1994; Goldberg, 1997). However, it is important to note that there is far less information about stable B isotopes in terrestrial environments, including lake sediments and common tree species, compared with the large amount of literature on marine environments.

Considering, in retrospect, the solubility of B and its volatile nature it is perhaps not so strange that a B peak could be found in combination with a fire event, especially in the sediments of a small freshwater lake or pond receiving minimal input of suspended material and B rich marine waters. Although the stable isotope ratios recorded for the B in the peak would not raise any questions as such, it has to be pointed out that B isotopes have been used to successfully trace terrestrial B elsewhere in the fresh-/marine water interface (Barth, 1998), fly ash leachates in groundwater (Davidson and Basset, 1993), municipal solid waste leachates (Barth, 2000) and pollution in marine sedimentary environments (Bayless et al., 2004). Williams and Hervig (2004) also put forward the idea that the extremely light B isotope of combusted coal (volatilized B) should be traceable. The fact that no other determinants were enriched, or depleted, in the thin high-B layer in the studied pond is not only intriguing, but also opens up a possibility of tracing historic fire events with B and its isotopes. However, further studies are urgently needed in order to better understand the chemistry and physics of B during and after intensive fire events.

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