Natural Lead Isotope Variations in the Atmosphere

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ABSTRACT

Stable lead (Pb) isotope data from pre-contamination peat sections has the potential to contribute to our understanding of earth system processes (e.g., atmospheric circulation, erosion, volcanic activity) in the past. Key questions arise however. Can the Pb isotopes archived in peat records be used for assessing aerosol dynamics on a hemispheric scale or do they mainly reflect inputs from local soils? What natural Pb sources are important and do contributions vary over time? In order to answer these questions we have synthesized all available Pb isotope data from pre-contamination peat sections in Europe, Australia, North America and South America. We specifically examine the spatial and temporal variability of the Pb isotope records and identify regionally important trends and Pb sources.

A pooling of all available pre-contamination peat data generated an average natural $^{206}\text{Pb}/^{207}\text{Pb}$ background ratio of 1.21 ± 0.05 (2σ , $n=300$) ($^{206}\text{Pb}/^{204}\text{Pb} = 18.90 \pm 0.86$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.66 \pm 0.10$ and $^{208}\text{Pb}/^{204}\text{Pb} = 38.74 \pm 0.57$, $n=207$). The majority of the records showed limited temporal and compositional agreement, suggesting that the peat record receives mainly inputs from local (<10 km) and/or regional (10-500 km) sources. Three-isotope plots also support local and regional control and evidence a wide natural spread at some sites, particularly those located in radiogenic geological settings. A temporally synchronous isotope excursion to values between 1.16-1.18 at sites across Europe ca 4000-3000 B.C. was detected, however. While usually associated with anthropogenic sources, there are indeed natural aerosols having $^{206}\text{Pb}/^{207}\text{Pb}$ signatures as low as 1.16 as evidenced in several peat and ice core records globally. Three-isotope plots suggest that this unlikely to be a signal of mineral dust contributions, which tend to

38 have $^{206}\text{Pb}/^{207}\text{Pb}$ ratios ≥ 1.19 , but rather sourced to volcanic emissions. These results
39 stress caution when using estimates of the upper continental crust to constrain natural Pb
40 sources in, e.g., mixing equations. Considering the strong influence from local and
41 regional sources on Pb-containing aerosols in the peat record, the assessment of aerosol
42 dynamics at lower latitudes is likely best achieved using a compliment of archives rather
43 than just polar ice cores, for example.

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45 Key words: Pb isotopes; atmospheric deposition; natural; mineral dust; volcano; aerosol

1. Introduction

Lead isotopes (^{204}Pb , ^{206}Pb , ^{207}Pb and ^{208}Pb) are a powerful tool in geochemistry having been successfully applied in the fields of, e.g., geochronology (e.g., Allegre et al., 1995; Dickin, 2009) and mantle-crust dynamics (e.g., Hofmann, 1997; Allegre et al., 2008). In the atmospheric sciences Pb isotopes have been especially effective in tracing the spatial dimensions of atmospheric fallout through the analysis of forest mosses (Rosman et al., 1998), lichens (e.g., Carignan et al., 2002; Spiro et al., 2004) and direct measurements of atmospheric plumes (Simonetti et al., 2004). The temporal dimensions of atmospheric Pb contamination have been established through the analysis of peat and glacial ice (e.g., papers cited in Table 1) as well as lake sediments (e.g., Shirahata et al., 1980; Brännvall et al., 1999). To date the primary application of Pb isotopes in these records has been for reconstructing the chronology and sources of atmospheric Pb contamination.

There is, however, further potential to use Pb isotope data as a tracer of aerosol provenance to provide insight into atmospheric circulation patterns and source area conditions. This type of information is best derived from environmental archives such as ice deposits, which capture a purely atmospheric signal. Ice cores have been used to identify the Iberian Peninsula as the source of Pb contamination atmospherically transported to, and deposited on, the summit of the Greenland ice sheet during ancient times (Rosman et al., 1997). Similarly, Biscaye et al. (1997) used Pb isotopes, in combination with clay mineralogy and Nd and Sr isotopes, to show that the main source of soil dust deposited at the Greenland summit during the Pleistocene originated from Asian desert areas. Unfortunately, the ice record from Greenland gives limited information about conditions between 8000 to 3000 years ago due to low ice-quality

(Rosman, et al., 1997). Furthermore, as many long-term ice core records are restricted to polar areas and high altitude locations, these (mainly) record aerosols transported in the upper troposphere rather than in the boundary layer (lower 1–2 km of the troposphere) and are more likely to represent an integrated hemispheric signal. Ombrotrophic peat is hydrologically isolated and therefore, like ice, records atmospheric deposition alone. In contrast however, these deposits have a more widespread occurrence, particularly in formerly glaciated regions. In many of these areas peat presents a continuous archive of atmospheric fallout covering the past 8000–10,000 years, and in some cases even longer.

Past climatic conditions, inferred from environmental archives worldwide, have revealed a dynamic global climate with periods of rapidly changing oceanic- and atmospheric-circulation patterns during the mid-Holocene (Wanner et al., 2008). Previous studies have already linked changes in atmospheric Pb isotopes in pre-contamination (i.e., before the start of human Pb pollution) peat sections to climatic events (Shotyk, et al., 2001; Klaminder et al., 2003; Kylander et al., 2005) but to what extent peat records are able to identify hemispheric, and even global, atmospheric processes has not been thoroughly evaluated. Does the Pb isotope composition of peat cores exposed to the same air masses record similar events? Do individual peat archives reflect local (<10 km), regional (10–500 km) or even continental and global atmospheric conditions? If the latter is true than these records could be used as archives of large-scale atmospheric circulation patterns; if the former is true, information about small-scale variability could be acquired. What natural Pb sources are important and do contributions vary over time?

To answer these questions we have synthesized all available Pb isotope data from pre-contamination peat sections in Europe, North America, South America and Australia

with supporting data acquired from ice core records. The objectives of this work are to (i) examine the spatial and temporal variability of natural Pb aerosols; (ii) establish the geographic scale covered by peat bog records and their applicability to studying global changes; and (iii) examine natural sources of Pb to the atmosphere.

2. Data Selection

In this synthesis we focus mainly on Pb isotope records from ombrotrophic peat bogs, supported by records from ice deposits, as both of these archives directly reflect atmospheric deposition. In order to improve on the spatial coverage of the current records three minerotrophic peat bogs have also been included. Lake sediments have been excluded because the natural Pb entering a lake in the pre-contaminant environment is expected to be dominated by catchment sources. As we focus on aerosols composed of naturally derived Pb solely, we have only selected records where the authors have been able to unequivocally establish that no human Pb contribution to the recorded atmospheric signals occurred.

The geographic distribution of the sites selected for this synthesis are shown in Figure 1 and include ombrotrophic peat deposits from Sweden (Brännvall et al., 1997; Klaminder et al., 2003), Spain (Kylander et al., 2005), Switzerland (Shotyk et al., 2001), Chile (Bindler and Biester, unpublished) and Canada (Kylander et al., 2009). The minerotrophic sites are located in France (Monna et al., 2004) and Australia (Kylander et al., 2007a). It is believed that the majority of the Pb signal recorded at these sites is atmospheric in origin. In France this is based on the faithful record of European Pb pollution history, despite the possibility of non-atmospheric contributions, while at the

Australian site the ash contents are low, suggesting an atmospheric origin of mineral matter. Details of the location, temporal coverage of the cores, geological setting and instrumentation used in Pb isotope measurement for each site are given Table 1. The ice core records are from the summit of the Greenland ice sheet (GRIP) (Rosman, et al., 1997; Burton et al., 2007), Devon Island (DI), Canada (Zheng et al., 2007) and Antarctica (DC)(Vallelonga et al., 2005) and provide independent records at polar areas. The ice core from Sajama Mountain (Saj), Bolivia (Rosman et al., 2003) is represented by only 2 samples dated to 19 and 3 ky B.P. but is included due to the already sparse nature of the data. Age-depth models and the average natural Pb isotopic background are all taken as established in the original manuscripts.

3. The uncertainties in the peat record

Before interpreting spatial and temporal variations in the peat Pb isotope records, a brief discussion relating to the uncertainties associated with the analytical methods used for Pb isotope determination and age dating is necessary.

3.1 Uncertainties when measuring Pb isotopes

Lead isotopes are commonly measured using quadrupole (Q-) or multi-collector (MC-) ICP-MS and TIMS. Q-ICP-MS analyses of Pb isotopes routinely achieve precisions of 0.2-2.0% (Begley and Sharp, 1997; Quétel et al., 1997; Becker, 2002), while MC-ICP-MS and TIMS can routinely achieve precisions of 0.002-0.001% (Walder et al., 1993; Rehkamper and Halliday, 1998; Becker, 2002; Thirlwall, 2002; Weiss et al., 2004; Kylander, et al., 2009). In terms of accuracy, the performance of Q-ICP-MS and MC-ICP-MS for Pb isotope determination of environmental samples, as quantified against

TIMS measurements, can achieve levels <1.2% (Begley and Sharp, 1997; Aung et al., 2004) and <0.2% (Belshaw et al., 1998; White et al., 2000; Weiss, et al., 2004; Cocherie and Robert, 2007; Kylander et al., 2007b; Kylander, et al., 2009), respectively. Table 1 provides details of the measurement methods employed at each site. Note that cores measured by Q-ICP-MS do not produce precise ^{204}Pb data. The total $^{206}\text{Pb}/^{207}\text{Pb}$ ratio variation observed in the pre-contamination portions of the selected records is, however, greater than the analytical precision reported for each individual site (SM: 5.0%, TM: 7.1%, OM: 4.4%, DM: 3.2%, AM: 5.8%, TrM: 7.7%, EGR: 1.3%, PVO: 11.0%, PeW: 0.9%, PbR2: 2.5%, Sky1: 2.7%, LyC: 3.9%, PE: 1.5%, CG: 0.5%).

3.2 Dating of pre-contamination peat

In contrast to varved lake sediments and ice core records, the chronology of the peat archives relies on indirect dating methods, such as ^{14}C -dating or chronological markers (pollen, tephra, etc.), instead of annual varve counting. Consequently, the dating precision of the former is not as good. The uncertainty of the age-depth modeling used to infer past atmospheric fluxes of Pb at an age interval of 6000-1000 B.C., which represents the time-window of many of the sites included in this study, may reach ± 1000 years. This uncertainty is generated by a typical uncertainty of about ± 500 years for the ^{14}C calibration curve (Stuiver and Reimer, 1993) and an additional uncertainty of <500 years relating to the within bulk-sample variation in ^{14}C -age (Nilsson et al., 2001). The precision of the dating can be improved by dating each sample several times, but this is rarely done and instead non-linear age-depth functions derived through fitting of several

dates are used to constrain the age of the peat. In this review, we therefore do not attempt to separate between events if the time difference is <1000 years.

4. Isotopic composition of Pb Aerosol in Pre-contamination Peat

4.1 Spatial and Temporal Variability

The pollution history at most of the sites included here has been discussed in the original papers, and in some cases synthesized as in Renberg et al. (2001) and Cloy et al. (2008). We direct readers interested in Pb pollution history to these papers. The time span of the pre-contamination peats discussed here is between 6000 and 1500 B.C. in Europe, from the early 16th century to the mid 17th century A.D. in North America, 20 kyr B.P. and 1900 A.D. in South America and 52 kyr B.P. in Australia.

Modern Pb containing aerosols are mainly anthropogenic in origin. This is seen in the peat record where $^{206}\text{Pb}/^{207}\text{Pb}$ isotope ratios in Europe, for example, converge at values around 1.14–1.18 in the surface peat (Figure 2), which is a range similar to that reported for anthropogenic aerosols (Bollhöfer and Rosman, 2002) and evidences the use of leaded petrol. In contrast to the modern, pollution-dominated atmosphere, the pre-contamination atmosphere has an average $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of 1.21 ± 0.05 (2σ , $n=300$) as calculated by pooling all pre-contamination peat analyses (Table 2). This average $^{206}\text{Pb}/^{207}\text{Pb}$ ratio is the same as that from the pooled ice core estimate of 1.21 ± 0.05 (2σ , $n=75$) and is close to the estimated Holocene $^{206}\text{Pb}/^{207}\text{Pb}$ background ratio of ~ 1.20 from Greenland ice from 150 kyr to 7 kyr (Rosman, et al., 1997; Burton et al., 2007) and ~ 1.21 from the 220,000 year Antarctic ice core record (Vallelonga, et al., 2005), but diverges

from the values of ~1.23 recorded in the Canadian Arctic (Zheng, et al., 2007) and 1.15 and 1.16 from Sajama Mountain in Bolivia (Rosman et al., 2003)(Figure 1).

Although the data are sparse, no strong geographic trend in average natural $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in the pre-contamination peat is apparent (Figure 1). On the three-isotope plots in Figures 3 and 4 many sites plot into a narrow, well-defined range and some degree of regional agreement in behavior does seem to exist. The Swedish and Spanish sites show a wider scatter than the Central European/Canadian and Southern Hemisphere fields. The scatter in the Swedish and Spanish fields could reflect the fact that these sites are surrounded by more radiogenic soils, generating more diverse ratios when local soil dust mixes with non-local sources having lower $^{206}\text{Pb}/^{207}\text{Pb}$ signatures (Table 2). The majority of Central European/Canadian and Southern Hemisphere sites sit in areas dominated by sedimentary rocks which might explain the tightness of these fields where the dusts deposited on the peat bogs from local sources are relatively well mixed and/or depleted in U and Th containing minerals. While the GRIP records plot into a tight field that overlaps with Central European/Canadian and Southern Hemisphere sites in $^{206}\text{Pb}/^{207}\text{Pb}$ vs. $^{208}\text{Pb}/^{206}\text{Pb}$ space (Figure 3), GRIP samples shows somewhat more scatter, but still less than that observed in the Sajama Mountain and Dome C records, in $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{208}\text{Pb}/^{204}\text{Pb}$ space (Figure 3).

The fact that many of the polar ice and peat core records have an average background $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of ~1.20 could be interpreted as evidence for common hemispheric Pb sources and/or effective homogenization of Pb signatures in the atmosphere. The temporal trends in $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in the pre-contamination peat however, show few similarities. This is exemplified in Figure 2, which plots together all

European records and shows significant variation in $^{206}\text{Pb}/^{207}\text{Pb}$ ratios, and hence source, across the continent. In fact, the only indication of possible synchronicity in the records at a long-distance or continental-scale occurs around 4000-3000 B.C. when $^{206}\text{Pb}/^{207}\text{Pb}$ ratios decrease to values between 1.16 and 1.18 in Sweden, France and Spain (Figure 2a). This event is weakly, if at all, expressed in Switzerland, although this could be a function of the sampling resolution (Figure 2b). Given the large amount of samples involved, this apparent decrease in $^{206}\text{Pb}/^{207}\text{Pb}$ ratios is unlikely to stem from analytical errors but rather, as discussed later, from a common Pb aerosol event/period in Europe. It is unclear if this event occurred in Greenland due to the poor sample integrity of the ice covering the period from 5295 to 962 B.C. (Rosman et al., 1997).

The limited temporal synchronicity and different Pb isotopic composition of the pre-contamination peat sections suggests that peat bogs capture aerosol Pb mainly from local and regional sources. The importance of local soil dust is further indicated by higher $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in peat bogs surrounded by soils having high $^{206}\text{Pb}/^{207}\text{Pb}$ ratios as in Sweden and Spain (Brännvall et al., 1999; Klaminder et al., 2003; Kylander et al., 2005). In general, these regions also show the widest variability in $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of 3-8% (average across six sites is 5.5%) and 11% (6% if excluding the two large excursions), respectively. This wide range is indicative of periodic mixing of local sources with more distant regional sources which generally have lower $^{206}\text{Pb}/^{207}\text{Pb}$ ratios (Table 2). Peat records appear to capture regional atmospheric Pb cycles as indicated by similar $^{206}\text{Pb}/^{207}\text{Pb}$ ratio trends in both the pre- and post-contamination peat (i.e., more than and less than 3500 years ago, respectively) from southern Sweden (n=6) (Figure 2). Evidence for the importance of local and regional contributions to atmospheric records was also

found by Thompson et al. (1998) in their 22,000 year ice core record from Sajama Mountain in Bolivia. In this case however, soil and crustal contributions were gauged through the measurement of insoluble particulates (dust) rather than Pb isotopes.

We note that decreasing $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in the Swedish peat bogs appear in ~1000 years cycles, i.e., ~4200 B.C., 3100 B.C., 1900 B.C. and 1000 B.C. Bond cycles operate on 1500-year-long climatic cycles in the North Atlantic and are known to have occurred during the Holocene (Bond et al., 1997). Considering that periods with decreasing $^{206}\text{Pb}/^{207}\text{Pb}$ ratios occur in a partly cyclical manner it seems plausible that there is a link between the temporal changes in the isotopic composition of the peat and climate change in the North Atlantic, possibly through greater dune building/soil erosion during cold periods.

Australia and North America are only represented by a single peat core each, while South America is represented by three cores, making it difficult to interpret these records in the context of regional atmospheric fallout. The pre-contamination period covered by each of these records is variable as well, dating between 19,000 yr B.P. and 1900 A.D. at South American sites, from the early 16th century to the mid 17th century A.D. in North America and from 52 kyr B.P. in Australia. Given the fact that several of these records are much longer than those from Europe, the isotopic variability of the pre-contamination sections at these sites is surprisingly low with 3%, 1% and 4% variability observed in South America, North America and Australia, respectively. (The low variability observed at the North American site is surely a product of the short temporal span of this core). Many of these records also comfortably over-lap in time with the post-contamination

period in Europe, but no evidence of the large scale Pb activities occurring on this continent exist; rather, each record seems to reflect its own local/regional history.

The records from GRIP, Antarctica and Australia cover one or more glacial periods, where significant changes in atmospheric aerosol loading occurred (Petit et al., 1990; Steffensen, 1997; Delmonte, et al., 2004). The relatively limited variation in the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of the Australian peat (4%) and Antarctic (5%) ice, despite the fact that changes in aerosol source undoubtedly occurred during these large climatic shifts, suggest that the captured aerosols are derived from a few and/or isotopically homogenous sources. In the case of the Australian record local and regional contributions are easy to envisage while in Antarctica long range sources are likely to dominate due to the paucity of local and regional sources. The record from Greenland shows greater variability (7%) in $^{206}\text{Pb}/^{207}\text{Pb}$ ratios between 150 kyr and 7 kyr which could reflect the fact that there are more potential sources (i.e., land masses) in the Northern Hemisphere compared to the Southern Hemisphere.

4.2 Possible Natural Sources

Natural sources of Pb in aerosols include mineral dusts, volcanoes, sea salt spray, forest fires and biogenic particulates, where the latter three redistribute Pb ultimately derived from the former (Nriagu, 1989; Freydier et al., 1999). The importance of volcanic and soil dust-derived Pb in the atmosphere has been debated (e.g., Hong et al., 1996; Hinkley et al., 1999; Hong et al., 2003; Hinkley, 2007). Lead isotopes have been an important tool in separating volcanic and soil-derived Pb in polar ice-core records (Van de Velde et al., 2005). Soil-derived Pb generally has a $^{206}\text{Pb}/^{207}\text{Pb}$ ratio ≥ 1.19 . For example, the major

soil dust emitting areas on a global scale, including the Sahara-Sahel area (Sun, 1980; Abouchami and Zabel, 2003), Saharan Holocene loess (Grousset et al., 1994), Gobi desert (Biscaye, et al., 1997) and European loess soils (Klaminder, et al., 2003; Sterckeman et al., 2006), have $^{206}\text{Pb}/^{207}\text{Pb}$ ratios varying between 1.19 and 1.25. Volcanic Pb on the other hand, may show a larger variation depending on the proportional mixing between mantle sources and the crust.

Lead three-isotope plots of the pre-contamination peat sections and possible natural sources are shown in Figures 5 and 6. These natural sources are represented by sediments from the North Atlantic (Farmer et al., 2003) and North (Jones et al., 2000; Pettke et al., 2000) and Southwest Pacific (Stancin et al., 2008), which mirror mineral dust from the continents; sediments from rivers worldwide, which represents the upper continental crust (UCC)(Milot et al., 2004); loess from China (Biscaye, et al., 1997; Jones, et al., 2000), Mongolia, North America (Biscaye, et al., 1997), New Zealand (Stancin, et al., 2008), and France (Sterckeman, et al., 2006), which typifies mineral dust from the continents; volcanic rocks from Italy (Ayuso et al., 1998; De Astis et al., 2000; Viccaro and Cristofolini, 2008), Spain (Cebriá et al., 2000), France (Downes and Dupuy, 1987; Wittig et al., 2007), Iceland (Sun and Jahn, 1975; Sun et al., 1975; Thirlwall et al., 2004), Greece (Pe-Piper, 1998), Faroe Islands (Holm et al., 2001) and Canary Islands (Sun, 1980; Praegel and Holm, 2006) to constrain volcanic sources; and mid-ocean ridge basalts (MORB) are included for reference (Sun, 1980). Note that there is no documented volcanic activity on the Faroe Islands during the Holocene and we include these data only as a proxy for sub-marine volcanoes that can be expected to develop along the Icelandic-Faroe fault line.

In general, loess deposits (and Pacific sediments) overlap to a good degree with Central European/Canadian, Southern Hemisphere and GRIP fields. These source fields overlap with previous estimates of the UCC in $^{206}\text{Pb}/^{207}\text{Pb}$ vs. $^{208}\text{Pb}/^{206}\text{Pb}$ space (Figure 5), but less so in $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ space (Figure 6). The scatter in the Swedish and Spanish sites and position of the various volcanic fields suggests that at these sites volcanic additions could be more important. It is, however, difficult to separate the effects of the radiogenic backgrounds at these sites from volcanic contributions vis-à-vis defining the importance of mineral dusts.

The UCC and its estimated composition are commonly used as a reference in mixing equations when aiming to characterize Pb derived from natural sources. Kramers and Tolstikhin (1997) modelled $^{206}\text{Pb}/^{204}\text{Pb}$ values of 18.68-19.11 for the upper continental crust. Values of 19.32 (Asmerom and Jacobsen, 1993) and 19.22 (Hemming and McLennan, 2001) have been estimated based on the measurement of suspended matter in rivers and deep sea turbidites, respectively (Table 2). Estimates of the UCC made using sediments from rivers worldwide have predicted $^{206}\text{Pb}/^{204}\text{Pb}$ values of 19.07 and 18.93, using sediment flux and surface area balancing methods, respectively (Millet, et al., 2004). The global average isotopic composition of ^{204}Pb -normalized ratios in the peat cores ($^{206}\text{Pb}/^{204}\text{Pb}=18.90$, $^{207}\text{Pb}/^{204}\text{Pb}=15.66$, $^{208}\text{Pb}/^{204}\text{Pb}=38.74$), as well as the available ice core data, falls below many previous approximations of the UCC, with the main exception being the modelled data of Kramers and Tolstikhin (1997). This is also apparent on the three-isotope plots in Figures 3 and 4, where many of the pre-contamination data points do not fall into the published UCC range and vary widely around it. In fact, it is Lynch's Crater in Australia, the only site located in a volcanic

setting, which overall falls closest to these approximations (Table 2). As argued previously, the pre-contamination peat is representative of a mixture between local and regional sources. In theory the UCC should be representative of the unweathered upper crust. Contributions from crustal sources, however, are likely in the form of eroded soils. Alteration of Pb isotope signatures is known to occur during some soil and bedrock weathering processes (Harlavan et al., 1998; Harlavan and Erel, 2002; Kylander et al., 2008). As such we may not expect the isotopic composition of these two fields (pre-contamination peat/ice and UCC) to be similar, particularly when contributions from, e.g., volcanic sources to the pre-contamination peat may have occurred. The use of the UCC as a natural end-member in mixing equations should therefore be carefully assessed on a site-by-site basis and thoroughly consider the surrounding geology and all possible Pb sources.

Major natural atmospheric Pb sources generally have $^{206}\text{Pb}/^{207}\text{Pb}$ ratios ≥ 1.19 and it is often assumed that an input of Pb with a $^{206}\text{Pb}/^{207}\text{Pb}$ ratio less than 1.19 is anthropogenic in source (Klaminder, et al., 2003). However, in our data $^{206}\text{Pb}/^{207}\text{Pb}$ ratios below 1.19 are also occasionally found in the pre-contamination peat record. For example, $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios around 1.16 and 2.1, respectively, are present in both the Spanish and Swedish peat deposited between 4000-3000 B.C. Klaminder et al. (2003) and Kylander et al. (2005) hypothesized that the possible origin of this Pb was anthropogenic given that small-scale copper mines were operating at this time in Europe (Nriagu, 1983). New isotopic data from other pre-contamination peat sections, potential natural volcanic sources and polar ice-record have been published since, which suggest that natural sources are more likely. First, $^{206}\text{Pb}/^{207}\text{Pb}$ ratios as low as 1.17 are found in

peat layers deposited several thousand years prior to modern contamination in Australia and Southern Chile (Figures 3 and 4), supporting the existence of natural sources with low $^{206}\text{Pb}/^{207}\text{Pb}$ ratios. This finding is supported by ice-core data showing that Pb with a $^{206}\text{Pb}/^{207}\text{Pb}$ ratio around 1.16 has accumulated in more than 7000 year-old arctic ice from Canada (Zheng, et al., 2007) and 19,000 year old ice in Bolivia (Rosman et al., 2003) and Pb with a $^{206}\text{Pb}/^{207}\text{Pb}$ ratio around 1.18 has been recorded in more than 7000 year-old arctic ice from Greenland (Burton et al., 2007). With these new data in mind it is clear that there are important natural atmospheric Pb sources having $^{206}\text{Pb}/^{207}\text{Pb}$ ratios as low as 1.16–1.18. Furthermore, it seems that these sources were important globally in the pre-contamination environment given that Pb with a $^{206}\text{Pb}/^{207}\text{Pb}$ ratio below 1.18 occurs both in ice from the Arctic and Bolivia and in peat bogs in Europe, Australia and southern Chile.

The isotopic excursions marking the European Pb event are highlighted in Figure 5 (dashed circle) and indeed plot into the fields for the Faroe Island and Icelandic volcanoes, rather than loess soils, in $^{206}\text{Pb}/^{207}\text{Pb}$ vs. $^{208}\text{Pb}/^{206}\text{Pb}$ space (only PVO is represented in the $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ plots). The provenance of Pb having $^{206}\text{Pb}/^{207}\text{Pb}$ ratios as low as 1.16–1.18 in Europe is thus likely to be volcanic. Tephra (volcanic ash) are found in peat layers deposited throughout the Holocene in western and central Europe having mainly an Icelandic origin (Van Den Bogaard and Schmincke, 2002; Blockley et al., 2007). Isotopic measurements of volcanic rocks from Iceland and the Faroe Islands also illustrate that North Atlantic volcanoes can emit Pb with $^{206}\text{Pb}/^{207}\text{Pb}$ ratios as low as 1.16 (Thirlwall, et al., 2004). We note that this volcanically derived Pb may, however, not necessarily be related to explosive terrestrial

volcanic eruptions. Rather, as suggested by Hinkley (2007), that the quiescent degassing of volcanoes could be main source of Pb containing aerosols. The period between 5000 and 1000 B.C. is known to be a period of relatively low volcanic activity on Iceland (Larsen and Eiríksson, 2008). As such, it is plausible that the archived Pb with low $^{206}\text{Pb}/^{207}\text{Pb}$ ratios is derived from passive degassing and/or sub-marine volcanic activity. That the volcanically derived Pb is not necessarily related to explosive volcanic eruptions is supported by the existence of periods with low $^{206}\text{Pb}/^{207}\text{Pb}$ ratios and increasing Pb concentrations that do not co-occur with the tephra (volcanic ash) layers (n=4) in the Patagonian profile (not shown). Measurements on volcanic rocks from the Central Volcanic Zone of the Andes have indeed found $^{206}\text{Pb}/^{207}\text{Pb}$ ratios as low as 1.15 (Bourdon et al., 2000). Using the dataset compiled here however it is not possible to do more than speculate on the importance of quiescent degassing or explosive volcanic eruptions.

Pre-contamination peat sections from South America, Australia and Antarctica have overlapping fields in $^{206}\text{Pb}/^{207}\text{Pb}$ vs. $^{208}\text{Pb}/^{206}\text{Pb}$ space (Figure 3), and to a lesser extent $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ space (Figure 4). The overlap in Australian and Antarctic fields may be significant in that the source(s) of Pb containing aerosols to the South Pole has not been unequivocally identified. To date most focus has been placed on South American sources (e.g., Delmonte et al., 2004; Vallelonga, et al., 2005), although there is a general lack of data with which to work with (Kohfeld and Harrison, 2001). The Australian record presents Pb isotope values reflecting contributions from sources across the eastern part of the country (Kylander, et al., 2007a) and given this overlap in fields, suggests that Australian aerosol sources might be worth considering as contributors to Antarctic sites. In support of this hypothesis, Revel-Rolland et al. (2006) have shown,

using Sr and Nd isotope data, that soil dust contributions to eastern Antarctica from Australia were important during interglacial, but not glacial, periods.

5. Conclusions

- The peat archive appears to consist mainly of Pb derived from atmospheric transport from local (<10 km) and regional (10-500 km) sources, as indicated by the limited co-variance in temporal trends in the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio at a long-distance/continental scale (Europe) and regional differences in the isotopic composition of the peat sections. Consequently, Pb isotope analysis of peat cores is unlikely to reveal useful information about hemispheric-scale circulation patterns and source area conditions.
- The region specific isotopic composition of the pre-contamination peat suggests that Pb isotope analysis of peat cores, in combination with other climatic proxies, could be useful when assessing regional aerosol dynamics in the past and their response to climatic events. For example, in near coastal regions, such as the studied sites in southwest Sweden where the variation in the Pb isotopic composition of the aerosols appears to be related to oceanic sources, such analyses can offer a possibility to reconstruct regional climatic changes related to oceanic and atmospheric circulation patterns.
- Natural sources having a $^{206}\text{Pb}/^{207}\text{Pb}$ ratio as low as 1.16 were active world-wide in the pre-contamination environment. Mixing calculations where natural sources are assigned a $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of ~1.20 or above, may therefore lead to an underestimation of the natural contribution to atmospheric Pb. Lead-containing

aerosols derived from volcanic sources appear to be the most likely source of this Pb having $^{206}\text{Pb}/^{207}\text{Pb}$ ratios much lower than that typically considered representative for atmospheric Pb in the pristine environment.

- This compilation of pre-contamination records of atmospheric Pb preserved in peat bogs world-wide suggest an atmospheric Pb aerosol composition that departs from that of the polar-ice records by showing higher temporal variations in the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios and a different multi-isotope composition. Hence, inferring regional aerosol sources at lower altitudes and lower latitudes from polar ice-core records, which are more likely to represent an integrated hemispheric signal, could be problematic.

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Table 1. Name, location, geographical division and geological setting of the peat cores used in this study. Included in the description of the cores is the basal age of the core and the instrumentation used in Pb isotope and elemental determinations

Location	Core ID	Location	Calibrated Basal Age (Cal. Year)	Surrounding bedrock	Pb Isotope Measure.	Reference
Ombrotrophic deposits						
Store Mosse, Sweden	SM	57°15'N, 13°55'E	6000 B.C.	Granite, Precambrian	Q-ICP-MS	Brännvall et al, 1999
Trolls Mosse, Sweden	TM	57°40'N, 14°30'E	5782 B.C.	Granite, Precambrian	Q-ICP-MS	
Önneby Mosse, Sweden	OM	60°07'N, 13°02'E	3551 B.C.	Granite, Precambrian	Q-ICP-MS	
Dumme Mosse, Sweden	DM	57°30'N, 14°02'E	2666 B.C.	Granite, Precambrian	Q-ICP-MS	Klaminder et al., 2003
Årshultsmyren, Sweden	AM	56°45'N, 13°25'E	4789 B.C.	Gneiss, Precambrian	Q-ICP-MS	
Traneröd Mosse, Sweden	TrM	56°03'N, 13°11'E	4385 B.C.	Gneiss, Precambrian	Q-ICP-MS	
Etang de la Gruère, Switzerland	EGR	47°23'N, 7°1'E	12 508 B.C.	Carbonate sedimentary rock, Mesozoic	TIMS	Shotyk et al., 2001
Penido Vello, Spain	PVO	43°32'N, 7°35'W	6143 B.C.	Granite, Paleozoic	MC-ICP-MS	Kylander et al., 2005
Point d'Escuminac, Canada	PeW	45°55'N, 65°30'W	1635 A.D.	Sandstone, Mesozoic	MC-ICP-MS	Kylander et al., 2009
PbR2, Chile	PB	53°58'S, 70°58'W	12500 B.C.	Schists, Precambrian to Paleozoic	Q-ICP-MS	Bindler and Biester, unpublished
Sky1, Chile	SKY	52°30'S, 72°07'W	5000 B.C.	Schists, Precambrian to Paleozoic	Q-ICP-MS	
Minerotrophic deposits						
Lynch's Crater, Australia	LyC	17°37'S, 145°70'E	52 kys B.P.	Basalt, Cenozoic	MC-ICP-MS	Kylander et al., 2007
La Perge, France	PE* ¹	45°22'N, 01°06'E	3943 B.C.	Carbonate sedimentary rock, Cenozoic	Q-ICP-MS	Alfonso et al., 2001
St. Ciers-sur-Gironde, France	CG* ²	45°21'N, 00°39'E	2871 B.C.	Carbonate sedimentary rock, Cenozoic	Q-ICP-MS	

*¹Core HO 9206b in the original publication

*²Core HO 9608b in the original publication

Table 2. Summary of average Pb isotope ratios and Pb concentrations of the pre-contamination peat and ice (all errors given as 2σ). Minerotrophic sections have been removed from the base of all ombrotrophic cores. Note that n=207 for $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$, n=300 for $^{206}\text{Pb}/^{207}\text{Pb}$ average ratios while n=295 for concentration measurements in peat. Also shown are estimates of the UCC commonly used as a proxy for natural Pb.

<i>Site</i>	<i>n</i>	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{206}\text{Pb}/^{207}\text{Pb}$	(Pb) ($\mu\text{g g}^{-1}$)	<i>Available $^{206}\text{Pb}/^{207}\text{Pb}$ data for local inputs</i>
ICE	Dome C	30	18.787±1.033	15.526±0.856	38.465±2.155	1.210±0.032	0.0067±0.015
	Devon Island	14	-	-	-	1.230±0.079	0.0000273±0.0000973
	GRIP	5 ¹	18.714±0.165	15.579±0.133	38.664±0.384	1.201±0.005	0.0014±0.0058
		24 ²	18.751±0.521	15.639±0.363	38.679±0.910	1.199±0.019	0.0000347±0.0000674
	Sajama Mountain	2	18.05±0.15			1.1544±0.0030	0.000149
			18.03±0.06			1.1607±0.0019	0.000102
Mean for ice records			18.742±0.832	15.576±0.657	38.569±1.645	1.208±0.049	0.001±0.005
PEAT	PbR2, Chile	25	18.650±0.355	15.630±0.266	38.655±0.813	1.193±0.015	1.93±4.55
	Sky1, Chile	6	18.522±0.531	15.634±0.211	38.613±0.913	1.185±0.028	1.18±2.48
	Lynch's Crater, Australia	100	18.833±0.376	15.668±0.037	38.895±0.425	1.202±0.022	0.77±0.68 Soil: 1.20, 1.24 ³ Rock: 1.18-1.29 ³
	Point d'Escuminac, Canada	22	18.620±0.102	15.643±0.033	38.565±0.212	1.190±0.005	0.68±0.53
	Penido Vello, Spain ^a	27	19.803±1.007	15.714±0.067	38.444±0.386	1.260±0.059	3.2±4.7 Rock : 1.33 ⁴
	Etang de la Gruère, Switzerland	27	18.798±0.152	15.652±0.049	38.718±0.174	1.200±0.008	0.38±0.04 Soil: 1.22-1.24 ⁵
	St. Ciers-sur-Gironde, France	5	-	-	-	1.198±0.004	9.1±17.6 Soil: 1.185 ⁶
	La Perge, France	10	-	-	-	1.193±0.011	4.5±4.2
	Årshultsmyren, Sweden	23	-	-	-	1.211±0.045	0.080±0.081 Soil: 1.46 ⁷
	Traneröd Mosse, Sweden	22	-	-	-	1.196±0.047	0.24±0.049 Soil: 1.32-1.33 ⁷
	Dumme Mosse, Sweden	8	-	-	-	1.215±0.034	0.054±0.058 Soil: 1.33 ⁷
	Trolls Mosse, Sweden	5	-	-	-	1.226±0.051	0.30±0.91 Soil: 1.30-1.32 ⁸
	Store Mosse, Sweden	12	-	-	-	1.205±0.060	0.43±1.38 Soil: 1.33 ⁸
	Önneby Mosse, Sweden	8	-	-	-	1.238±0.044	0.10±0.05 Soil: 1.38 ⁸
Mean for peat records			18.90±0.86	15.66±0.10	38.74±0.57	1.21±0.05	1.2±4.5
UCC ⁹			18.93/19.07	15.71/15.74	39.03/39.35	1.205/1.212	
UCC ¹⁰			19.22	15.78	39.58	1.218	
UCC ¹¹			19.32	15.76	39.33	1.226	
UCC ¹²			18.68-19.11	15.66-15.70	38.58-39.47	1.19-1.22	
UCC ¹³							

³Kylander et al., 2007; Zhang et al., 2001; ⁴Kylander et al., 2005; ⁵Nowack et al., 2001; ⁶Semlali et al., 2001; ⁷Klaminder et al., 2003; ⁸Brännvall et al., 1999; ⁹Millot, et al., 2004; ¹⁰Hemming and McLennan, 2001; ¹¹Asmerom and Jacobsen, 1993; ¹²Kramers and Tolstikhin, 1997; ¹³Wedepohl, 1995.

^aThe definition of the natural background was changed from the original publication to include the entire pre-contamination ombrotrophic section, the two large excursion were not removed

Figure Captions

Figure 1. World map showing the geographical location of the discussed cores and the average pre-contamination $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in the aerosol. The pre-contamination period used in these calculations ranges from 150 years (PeW) to 220 kyrs (DC).

Figure 2. Temporal variations in the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in the studied peat bog archives from Europe. The six sites from southern Sweden (line) are plotted together as a five-point running mean (thick black line). Dashed line indicates a period of low $^{206}\text{Pb}/^{207}\text{Pb}$ ratios that appear to co-occur. It is unclear if this event is recorded in Switzerland.

Figure 3. Three-isotope plots of $^{206}\text{Pb}/^{207}\text{Pb}$ vs. $^{208}\text{Pb}/^{206}\text{Pb}$ using available data from the pre-contamination sections in the studied peat bogs and their generalized fields. Dashed lines represent ranges of published UCC estimates (see Table 2 for references). Symbols for each site are indicated in the right hand panel. Note that only $^{206}\text{Pb}/^{207}\text{Pb}$ data is available for three of the Swedish sites, ranges shown at the bottom of the plot.

Figure 4. Three-isotope plots of $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ (a) and $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ (b) using available data from the pre-contamination sections in the studied peat bogs and their generalized fields. Dashed lines represent ranges of published UCC estimates (see Table 2 for references). Symbols for each site are indicated in the right hand panel.

Figure 5. Three-isotope plots of $^{206}\text{Pb}/^{207}\text{Pb}$ vs. $^{208}\text{Pb}/^{206}\text{Pb}$ using available data from the pre-contamination sections in the studied peat bogs and generalized fields of possible natural Pb sources which include mineral dusts (as represented by ocean sediments and loess deposits), crustal sources (as represented by river sediments) and volcanic sources (as represented by volcanic rocks)(see text for references). Dashed lines represent ranges of published UCC estimates (see Table 2 for references). Symbols for each site are indicated in the right panel.

Figure 6. Three-isotope plots of $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ (a) and $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ (b) using available data from the pre-contamination sections in the studied peat bogs and generalized fields of possible natural Pb sources which include mineral dusts (as represented by ocean sediments and loess deposits), crustal sources (as represented by river sediments) and volcanic sources (as represented by volcanic rocks)(see text for references). Dashed lines represent ranges of published UCC estimates (see Table 2 for references). Symbols for each site are indicated in the right panel.

Kylander et al.-Fig 3

Kylander et al.-Fig 5