Solid Earth Discuss., 6, 761–792, 2014
www.solid-earth-discuss.net/6/761/2014/
doi:10.5194/sed-6-761-2014

Solid Earth Discussions
Open Access

Factors controlling the geochemical composition of Limnopolar lake sediments (Byers Peninsula, South Shetland Island, Livingston Island, Antarctica) during the last ~ 1600 years

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Received: 31 January 2014 – Accepted: 25 February 2014 – Published: 11 March 2014

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Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

We sampled a short (57 cm) sediment core in Limnopolar Lake (Byers Peninsula, Livingston Island, South Shetlands Islands), which spans the last ~ 1600 years. The core was sectioned at high resolution and analyzed for elemental and mineralogical composition, and SEM-EDS analysis of glass mineral particles in selected samples. The chemical record was characterized by a contrasted pattern of layers with high Ca, Ti, Zr, and Sr concentrations and layers with higher concentrations of K and Rb. The first also enriched in plagioclase and, occasionally, in zeolites, while the later were relatively enriched in 2 : 1 phyllosilicates and quartz. This was interpreted as reflecting the abundance of volcaniclastic material (Ca-rich) vs. Jurassic-Lower Cretaceous marine sediments (K-rich) – the dominant geological material in the lake catchment. SEM-EDS analysis revealed the presence of abundant volcanic shards in the Ca-rich layers, pointing to tephras most probably related to the activity of Deception Island volcano (located 30 km to the SE). The ages of the four main peaks of volcanic-rich material (AD ~ 1840–1860 for L1, AD ~ 1570–1650 for L2, AD ~ 1450–1470 for L3, and AD ~ 1300 for L4) matched reasonably well the age of tephra layers (AP1 to AP3) previously identified in lakes of Byers Peninsula. Some of the analyzed metals (Fe, Mn, Cu and Cr) showed enrichments in the most recent tephra layer (L1), suggesting relative changes in the composition of the tephras as found in previous investigations. No evidence of significant human impact on the cycles of most trace metals (Cu, Zn, Pb) was found, probably due to the remote location of Livingston Island and the modest research infrastructures – local contamination was found by other researchers in soils, waters and marine sediments on areas with large, permanent, research stations. Chromium is the only metal showing a steady enrichment in the last 200 years that could be interpreted as recent anthropogenic contamination. At the same time, some features of the chemical record suggest that climate may have also played a role in the cycling of the elements, but further research is needed to identify the underlying mechanisms.

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1 Introduction

Because of its remoteness location and isolation Antarctica is a highly sensitive area to global change. Of particular concern are the effects of global warming because of the rapid responses that may undergo ecosystems in circumpolar areas, and because of the mounting evidence of recent major changes in polar regions (Pienitz et al., 2004; Convey et al., 2009). But to put present global change into context there is a need for long-term records of environmental changes. For this purpose, lake sediments are amongst the most used archives as they host a suite of abiotic (elemental composition, isotopic records, mineral composition, etc.) and biotic (pollen, testate amoebas, diatoms, charcoal, organic compounds, etc.) proxies which can potentially shed light into environmental changes (see for example Smol and Last, 2001; Smol et al., 2001a, b).

In contrast to the Arctic and temperate zones, fewer studies have used sediment cores from lakes from Antarctica (Muir and Rose, 2004) to track environmental change, despite the large abundance of lakes in some areas like Byers Peninsula (Livingston Island, South Shetlands) (Toro et al., 2007). Most of the investigations are based on sedimentological, elemental and mineralogical analyses (Aceto et al., 1994; Bishop et al., 1996; Doran et al., 2000; Abollino et al., 2004; Webster-Brown and Webster, 2007; Malandrino et al., 2009), but also on the isotopic ($\delta^{13}C$, $\delta^{15}N$, $\delta^{34}S$) composition (Bishop et al., 2001), or the content of organic pigments (Squier et al., 2005) of the sediments. The aim was to investigate into the geochemistry of the lakes and to reconstruct climate changes. The identification and characterization of tephra layers also has received much attention (Björck et al., 1991; Björck and Zale, 1996b; Hodgson et al., 1998), pursuing the identification of their sources and to stablish a tephrochronology for the Antarctic Peninsula. Of particular interest for our study is the chronostratigraphic investigation made by Toro et al. (2013) on a composite core sampled in Limnopolar Lake.

A second major line of research is that oriented to the reconstruction of pollution. It includes the determination, in lake sediments, of the concentrations of organic pollutants (Sarkar et al., 1994; Fuoco et al., 1996), trace metals (Yin et al., 2006; Bargagli et al., 2007) and spheroidal (fly ash) particles (Rose et al., 2012). These investigations demonstrate that the level of contamination in Antarctica is much lower than in the polar regions of the Northern Hemisphere. Despite the long-range transport of some contaminants (as Pb, Hg, or organic pollutants) most of the impacts due to human activities are local (Tin et al., 2009) and mainly related to the presence of large, permanent, research infrastructures (Claridge et al., 1995; Crokett, 1998; Sheppard et al., 2000; Crockett and White, 2003; Webster et al., 2003; Santos et al., 2006; Chaparro et al., 2007).

In this paper we present the results of a study on a short sediment core sampled in Limnopolar Lake in 2003. The objective of our research was to perform a detailed, i.e. high-resolution, investigation of the geochemistry of the lake sediments, by a combination of XRF, DRX, and SEM-EDS analyses, supported by age dating and multivariate statistics, with the aim of identifying the main factors involved in the observed chemical-mineralogical changes and their timing during the last ~ 1600 years.

2 Material and methods

2.1 Study area

Limnopolar Lake (62°38′15″ S, 61°06′30″ W) is located in Byers Peninsula, the westernmost part of Livingston Island (South Shetland Islands, Fig. 1) and designated at present as an Antarctic Specially Protected Area (ASPA No. 6), limiting the human presence in the past 46 years to scientific activities, keeping it free of human impacts, far from any Antarctic Base (Benayas et al., 2013). Livingston Island hosts modets research infrastructures: a non-permanent Research Camp in Byers Penisula since

2001, and the Spanish and Bulgarian Antarctic Bases Juan Carlos I and St. Kliment Ohridski, located about 30 km to the east, since 1988.

Climate is less extreme than in Continental Antarctica, characterized by a high interannual variability of temperature and precipitation (annual mean values of 700–1000 mm), with summer temperatures mostly above 0 °C (mean range from 1–3 °C) and frequent liquid water precipitation, and winter colder than 0 °C with lower record of −27 °C (Rochera et al., 2010; Bañón et al., 2013). The region is snow-covered for at least eight months of the year, and the snow cover distribution and depth is dominated by topographic variables related to wind (Fassnacht et al., 2013). In the lake catchment there is a permafrost table below an active layer of thickness up to 90–130 cm, with a thawing season of about 75 days between late December to late February (De Pablo et al., 2013).

This peninsula is the largest ice-free area of Maritime Antarctica, and contains a large number of lakes (Toro et al., 2007). Limnopolar lake catchment has a surface area of 0.58 km^2 and a water body area of 0.022 km^2. The lake is ultraoligotrophic and it is ice-covered except for 2–3 months during the summer. Although it has a main inlet, surface runoff significantly contributes to the lake volume during snow pack melt and the period of thawing of the active layer of permafrost. The lake bottom is covered by a patchy carpet of the moss *Drepanocladus longifolius* (Mitt.) Paris (Toro et al., 2013).

Vegetation in the catchment is only composed of scattered patches of mosses, lichens and microbial mats (Velazquez et al., 2013). The superficial formations are represented by a lithosol originated from the fragmentation by periglacial processes, weathering and erosion of Upper Jurassic-Lower Cretaceous marine sediments, volcanic and volcaniclastic rocks (López-Martínez et al., 1996).

2.2 Sediment sampling

The LIM03/1 sediment core was collected in December 2003 using a Glew-type gravity corer at the deepest part of the lake (5.5 m, Fig. 1) when it was iced covered, retrieving the uppermost 57 cm of its sedimentary infill. It showed a centimeter to millimeter alternation of light brownish massive clays and silty clay layers, and dark brownish moss layers. A number of more discrete, millimeter-centimeter scale darker, silty layers, made up of volcanic material, were also found.

The core was sectioned (in situ) into 0.2 cm slices for the upper 10 cm, and 0.5 cm slices below this depth. Samples were transferred to Whirl-Pak bags, sealed, and stored in darkness at low temperature (4 °C) until analysis. For the present study we selected 57 samples covering the whole core.

2.3 Elemental and mineralogical analyses

Before analysis, sub-samples were dried at 105 °C until constant weight, finely milled and homogenized. The elemental composition (Si, Al, Fe, Ti, Ca, K, Mn, Rb, Sr, Zr, Cr, Cu, Zn, and Pb) of the sediment was determined by X-ray fluorescence dispersive EMMA-XRF analysis (Cheburkin and Shotyk, 1996, 1999; Weiss et al., 1998). Standard reference materials were used for the calibration of the instruments. Quantification limits were 10 $g\,kg^{-1}$ for Si, Al, Fe, and Ti, 4 $g\,kg^{-1}$ for Ca and K, 30 $\mu g\,g^{-1}$ for Mn, 10 $\mu g\,g^{-1}$ for Cu, 5 $\mu g\,g^{-1}$ for Zn, 2 $\mu g\,g^{-1}$ for Cr, 1 $\mu g\,g^{-1}$ for Rb, Sr, Zr and 0.5 $\mu g\,g^{-1}$ Pb. Reproducibility was assessed by replicate measurements every three samples; all replicates agreed within a 5 %.

The mineralogical composition was determined by X-ray diffraction using a Philips PW1710 diffractometer (CuKα radiation and graphite monochromator). Quantification of the mineral phases was done using Match! 1.11e software.

Five dried, but otherwise unmodified, sediment samples, from 30.5, 24, 18, 16 and 6.8 cm depths, were selected for SEM-EDS analysis (LEO 435 VP). Four of them corresponded to sediment sections with high Ca concentrations and one (16 cm) to sediment located between Ca-rich and K-rich sections. The aim was to determine the presence of material of volcanic origin and the possible sedimentary processes responsible for its transport to the lake.

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The analytical instruments used are hosted in the RIAIDT (Infrastructure Network for the Support of Research and Technological Development) facility of the University of Santiago de Compostela.

2.4 Core chronology

The chronology of the core LIM03/1 was constructed using ^{210}Pb, ^{226}Ra and ^{137}Cs measurements and radiocarbon dating of two moss samples. This chronnology was overlapped with radiocarbon dating of moss samples of another long core collected in 2008 at the same lake location. The Bacon script for R (Blaauw and Christen, 2011) was used to construct the age model of the composite core. The details can be found in Toro et al. (2013).

2.5 Statistical analysis

Principal components analysis (PCA) was performed on the geochemical data to extract the main chemical signatures of the sediment elemental composition and investigate into the factors controlling them. Since compositional data are a case of closed data (Aitchinson et al., 2002; Baxter et al., 2008), a centred log ratio (CLR) transformation was applied prior to the statistical analysis (Aitchinson, 2003; Baxter and Freestone, 2006). A varimax rotation was chosen for the final PCA model. This type of rotation maximizes the loadings of the variables on the components. In the particular case of depth records, it results in the allocation into the same component of variables sharing a large proportion of their variance, i.e. chemical elements showing very similar records, enabling an easier identification and interpretation of the underlying factors (Kylander et al., 2013).

Correlation analysis was used to stablish the relation between the elemental composition and the mineralogy. Both PCA and correlation analysis were performed using the statistical software SPSS 20.0.

3 Results

3.1 Elemental composition

The concentration records of the analyzed elements can be found in Fig. 2. To summarize the geochemical composition and investigate into the underlying factors, as already indicated in the Methods section, we have applied principal components analysis to the CLR transformed data. Seven components explained almost 96 % of the total variance (Table 1). The first component (Cp1, 40.6 % of the variance) shows large positive loadings of Ca, Sr, Ti and Zr and large negative loadings of K and Rb (Table 1). The record of Cp1 scores (Fig. 3) is characterized by a see-saw pattern, particularly in the upper 35 cm, with four well defined peaks of positive scores (i.e. high concentrations of Ca, Sr, Ti, and Zr and low concentrations of K and Rb) centred at 30.5 (L4), 24.0 (L3), 18.0 (L2), and 6.7 cm (L1) depths. The sediment section below 35 cm shows almost constant negative scores (i.e. high concentrations of K and Rb and low concentrations of Ca, Sr, Ti, and Zr).

The second component (Cp2, 12.7 % of the variance; Table 1) is characterized by large positive loadings for Fe and Mn. The record of Cp2 scores (Fig. 3) shows a trend of slightly increasing values from 60 to 27 cm, and a steady decrease from this depth to the surface -with three distinctive peaks at 14–16 cm, 7.6 and 3.2 cm.

The third component (Cp3, 12.2 % of variance; Table 1) shows large positive loadings for Si and Al. The scores are around zero (i.e. close to average concentrations of Si and Al) in the whole core (Fig. 3), with the exception of three negative excursions at 23.0, 20.0, and 2.7 cm depths.

Components from fourth to seventh (Cp4–Cp7) are represented by only one metallic element each: Cu, Zn, Pb and Cr, respectively, and account for 7.8–7.3 % of the total variance (Table 1). The records of Cp4 to Cp6 scores have in common an overall lower variability, no systematic change below 20 cm and a relatively higher variability in the section above this depth (Figs. 2 and 3). Cp4 (Cu) and Cp7 (Cr), as well as Cp3 (Fe and Mn), show a peak in scores coinciding with the uppermost peak in Cp1 scores (L1, Figs. 2 and 3), but not in the other sections with high Cp1 scores (L2 to L4, Fig. 3). Cp7 (Cr) is the only chemical component showing a trend of increasing values to the surface of the core (Figs. 2 and 3). The larger variability in the upper 20 cm probably responds to the higher resolution of sectioning and number of samples analyzed.

3.2 Mineralogical composition and SEM-EDS analysis

In all samples analyzed by XRD a broad band centred on 22° 2Θ indicated the presence of non-crystalline inorganic material. This effect was more evident in the samples of the upper 9 cm. The quatification provided in Fig. 4 only refers to the crystalline mineral phases identified.

Plagioclase (66 ± 11 %), 2 : 1 phyllosilicates (probably chlorite-smectites, 22 ± 10 %), and quartz (12 ± 3 %) are the main crystalline minerals. In samples at 11.7 and 44.5 cm depths traces of a zeolite (< 1 %) of the clinoptilolite group (effects and 8.9 and 3.9 nm) were also found. In some samples there are effects (0.26 nm) that may correspond to antarcticite, but most of the other effects of this mineral overlap with those of plagioclase and it is difficult to resolve its presence.

Plagioclase content varies between a minimum of 45 % at 50.5 cm and a maximum of 83 % at 16.8 cm and tends to be higher in Ca-rich samples (Fig. 4); 2 : 1 phyllosilicates range between 5 % (at 18.8 cm) and 40 % (at 40.5 cm) and tend to be higher in K-rich sections (Fig. 4); and quartz ranges between a minimum of 6 % (at 18.8 cm) and a maximum of 16 % (at 44.5 cm) and also tends to be more abundant in K-rich sections. Plagioclase is highly correlated with Cp1 (*r* 0.77; Table 2) and, consequently, with Ca, Sr, Ti and Zr (*r* 0.73–0.77; Table 2); 2 : 1 phyllosilicates are positively correlated to K and Rb (0.48 and 0.59, Table 2) but negatively correlated to Ca, Ti, Sr and Zr (−0.58 to −0.66; Table 2); quartz shows the same correlation pattern than the 2 : 1 phyllosilicates but the correlation coefficients are larger (*r* 0.71 and 0.80 with K and Rb, −0.79 to −0.88 for the other elements; Table 2).

The samples selected for SEM-EDS analysis corresponded to the four main peaks with higher Ca (and Ti, Zr, Sr) concentrations, plus one sample located at 16 cm –

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between the peak at 18 cm and the low at 12 cm. All of them had large amounts of volcanic shards with angular, sharp edges (Fig. 5). The shards had the overall composition of a plagioclase (Si, O, Al, Ca and Na), although differences were found in the Fe and Ti content (Fig. 5). Diatoms were also present, particularly in the sample at 16 cm.

4 Discussion

4.1 Elemental and mineralogical composition of the lake sediments

There are only a few studies dealing with the elemental composition of rocks, soils and lake sediments of the Byers Peninsula. Among them, it is worth mentioning that by Navas et al. (2008), which provides elemental data of soils derived from different geological materials of the area, as well as the study by Björck and Zale (1996b) on the composition of tephras found in lake sediments of the Byers Peninsula. The paper by Toro et al. (2013), on a composite sediment core sampled at Limnopolar Lake, is also of reference, but a quantitative comparison of the elemental composition cannot be made since they used a core scanner and the data is presented as counts per second. Also, here we do not present data for two of the elements included by Toro et al. (2013), Cl and Co, but provide data for other four elements (Rb, Cr, Zn, Pb), plus LIM03/1 contains the upper 10 cm that are lacked in the composite core.

For Al, Fe, Sr, Cr and Cu, the concentrations in the sediments of Limnopolar Lake (Fig. 2) are much higher than those given for the soils of the area (both, those developed on marine sediments and on volcanic materials; Navas et al., 2008), but similar to those of the tephras found in lake sediments (Björck and Zale, 1996b). For Ca, K, Mn and Zn, concentrations are within the range found for soils and tephras. Data on Si and Ti concentrations have been published only for tephra layers (Björck and Zale, 1996b), and are similar to those found by us.

Our results on the mineralogical composition of these sediments are comparable to those of studies done in sediments and soils of the area (Jeong et al., 2004; Navas et al., 2005), in particular regarding the high contents of plagioclase. The presence of zeolite was also noted by the cited investigations. The main mineralogical changes in Limnopolar Lake sediments are mostly related to the abundance of 2 : 1 phyllosilicates (mica, smectite, and interlayered minerals). The lower section of the core (> 35 cm) is the one with the highest abundance of phyllosilicates, for which the composition is similar to that of sediments of the marine platform of the South Shetlands studied by Jeong et al. (2004). The clay fraction of these sediments was found to be enriched in smectite (63 %), in comparison to chlorite (25 %) and illite (12 %), also showing high concentrations of K and Fe (Jeong et al., 2004).

The LIM03/1 core represents the uppermost 57 cm of the composite sediment sequence studied by Toro et al. (2013) in Limnopolar Lake sediments. Although the long sequence does not include the uppermost 10 cm, the short core analyzed by us should correspond to the mineralogical Zone 3 of Unit 2, defined by these authors. The zone starts at 144 cm and extends to the top of the core, being characterized by a roughly constant mineralogy dominated by mineral phases typical of volcaniclastic material (albite, illite and quartz), its chemical alteration products (montmorillonite, saponite, talc and chlorite) and marine salt input (gypsum and antarcticite). The results for LIM03/1 are comparable -with dominance of plagioclase and 2 : 1 phyllosilicates. We were not able to corroborate the presence of minerals related to sea spray input described by Toro et al. (2013) in the composite core. Antarcticite is a highly hygroscopic mineral that may have transformed during the drying of the samples, while gypsum is only present in a few sections of Zone 3 and it is not surprising that it is absent in LIM03/1. We did not identify separately the chemical alteration products, including them in the group of 2 : 1 phyllosilicates due to the lower resolution of the XRD equipment used for this study.

4.2 Controls on sediment inorganic geochemistry

The sediments of Limnopolar Lake have a contrasted chemical and mineralogical composition, as synthesized by the first principal component (Fig. 3). Large shifts between

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layers enriched in K and Rb, with higher contents of quartz and 2 : 1 phyllosilicates, and sediments enriched in Ca, Sr, Ti, and Zr with larger abundance of plagioclase and occasional presence of zeolites, occur in the 57 cm of the analyzed core. As the SEM-EDS results demonstrate, the Ca-rich sections contain abundant volcanic shards indicating they may correspond to tephra layers with a calcalkaline composition. On the other hand, K-rich sections may correspond to sediments with a higher content of material eroded from the lake catchment, since it is dominated by marine sediments of a Jurassic-Lower Cretaceous age. Thus, during periods of low volcanic activity the geochemical signal of the sediment was controlled by the input of terrigenous material provided by the catchment, while in periods of volcanic activity it was controlled by the supply of volcanic material. This is also supported by the results obtained for quartz and 2 : 1 phyllosilicates contents, since they are negatively correlated to elements related to volcanic material and positively correlated to those related to the the marine sediments. Quartz is typically depleted in basic and ultrabasic geological materials, while it is enriched in acidic ones and in many sedimentary rocks due to its resistance to weathering.

When compared to the results obtained by Toro et al. (2013), LIM03/1 shows a more contrasted mineralogical and compositional pattern. For example, while in the short core Ca is inversely correlated to the elements characterising the terrigenous material (r −0.87 with K and −0.95 with Rb), in the composite long core Ca and K are positively correlated (r 0.67). This may be due to LIM03/1 representing a short time period with relatively more frequent volcanic events, which may result in a maximization of the differences between the two identified geochemical signals.

As for the volcanic material, it may have been directly deposited into the lake (i.e. tephra layers) but it may also have been supplied by runoff from the catchment after the volcanic eruption (reworked volcanic material). The morphology of the volcanic shards observed by SEM (Fig. 5) and the abrupt limits of three of the proposed tephra layers (L1, L3, L4), suggest that most of this volcanic material corresponds to fallout ashes deposited either directly into the lake, if the eruption occurred during ice-free

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lake periods, or on the ice-cover, if the the volcanic event took place during the winter and the material was later incoporated to the lake sediments owing to the summer ice melt. A supply from the catchment shortly after the deposition of the ashes cannot be ruled out. Support for this interpretation is found in the fact that Cp1 scores in the upper 35 cm, the section reflecting a higher volcanic activity, do not return to values similar to those of the section below, and that the peak at 18 cm (L2, Fig. 3) shows a gradual decrease in scores and not the sharp termination found for the other peaks (L1, L3, L4; Fig. 3). So, as expected, both processes may have operated through time.

Previous research developed on lake sediments and ice caps of the Byers Peninsula already demonstrated the presence of tephra layers (Björck et al., 1991; Björck and Zale, 1996b; Hodgson et al., 1998; Pallás et al., 2001), mostly attributed to the volcanic activity on Deception Island, located 30 km SE of the Peninsula. Toro et al. (2013) also found that the geochemical composition of most glass shards of the composite long core was similar to those of this volcano. The relation to the tephrochronology proposed by the mentioned investigations, and extended by Toro et al. (2013), is discussed in the next section.

The second chemical signature (Cp2) of the LIM03/1 core is related to the covariation in Fe and Mn contents, both elements which have in common their redox behaviour. The record of scores (Fig. 3) shows a moderate, and irregular, enrichment until 27 cm and a slight decrease below this depth. Post-depositional redistribution of these two elements has been shown to occur in reducing environments (Chesworth et al., 2006; Naeher et al., 2013). On the other hand, the lake is shallow and strong reducing conditions seem to be unlikely unless during periods of prolonged ice cover (inverse lake stratification) that may have resulted in a depletion of oxygen. Punctual mensurements performed under the ice cover on the 15 December 2012 revealed anoxic conditions in the lower 1.5 m of the lake water column, and methane release occurred during the extraction of long-cores in 2008. Anoxic conditions and pyrite formation was found to occur in lake-bottom sediments of deep areas of Lake Hoare, located in the Dry Valleys region of Antarctica (Bishop et al., 2001). As for the hosting Fe–Mn phases, the

SEM-EDS analyses have shown that the volcanic shards do contain variable amounts of Fe and Mn, although their concentrations show no correlation with the abundance of minerals of volcanic origin.

The third chemical signature (Cp3; Fig. 3) is the association between Si and Al, which probably represents variations in an alumino-silicate phase. This may well be a mineral present in trace amounts since no correlation was found between Cp3 scores and the abundance of any of the identified minerals, and changes in the record are minor except for the mentioned three negative excursions.

Of the metal signals, Zn and Pb (Cp5 and Cp6; Fig. 3) present irregular depth distributions with no apparent trend. Copper (Cp4), on the other hand, is high in layer L1 of volcanic material, where Fe, Mn, and Cr (Cp2, Cp7; Fig. 3) also show a more or less well defined peak. None of the other layers of volcanic material have elevated concentrations of these metals. Matthies et al. (1990) found changes in the chemical composition of tephras from Deception Island volcano, while Björck and Zale (1996b) found that the last tephra layer recorded in lake sediments of Byers Peninsula has differences in chemical composition in comparison with previous tephras (in particular, Cu concentration was higher). In the composite long core of Limnopolar Lake studied by Toro et al. (2013), Cu was found to be associated with talc, thus some of the minor changes observed in Cu concentration in LIM03/1 may have depended on the abundance of this mineral. Nevertheless, contribution from other volcanic sources cannot be ruled out. In Midge Lake, Hogdson et al. (1998) found a single acidic tephra at 2–3 cm; while Fretzdorff and Smellie (2002), in a study of thephra layers in sediments of the central Brandsfield basin, found that the composition of the uppermost layer did not match to any known Antarctic-Scotia Sea-Southern South America region source and, given its shallow stratigraphical position, concluded that the source volcano should have been active in historical times (a few hundred years at most).

Chromium (Cp7, Fig. 3) is the only metal that shows a steady increase in concentrations in the upper 10 cm, the average concentration in this section being 2 fold that of the sediments below ($115 \pm 41\,\mu g\,g^{-1}$ vs. $55 \pm 18\,\mu g\,g^{-1}$).

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Taken together, the data on metals do not point to significant effects from recent anthropogenic pollution in Byers Peninsula. This is in agreement with studies on trace metal contamination in Antarctic ecosystems (Bargagli, 2000, 2008; Sánchez-Hernández, 2000), indicating that Pb is probably the only metal whose biogeochemical cycle has been significantly affected by anthropogenic emissions (Sun and Xie, 2001; Yin et al., 2006), and that in coastal ecosystems – like the Byers Peninsula – the input of metals from anthropogenic sources and from long-range transport is negligible. Rose et al. (2012) reached the same conclusion in a study of the presence of fly ash particles in lake sediments of the Falkland Islands and Antarctica. Although detectable, the content of fly ash particles in sediments of Antarctic lakes was very low, while in the Falkland Islands the record extended back to the 19th century and showed a much higher impact of contamination.

In Antarctica, metal pollution has been found to be restricted to small areas within and the surroundings of research stations, affecting both soils, continental and marine waters (Claridge et al., 1995; Crokett, 1998; Sheppard et al., 2000; Crockett and White, 2003; Webster et al., 2003; Santos et al., 2006; Chaparro et al., 2007). Thus, the remote position of Livingston Island and the modest research infrastructures it hosts may explain the lack of pollution evidence in the sediments of Limnopolar Lake.

4.3 Chronology of the main geochemical changes

The LIM03/1 short core represents the sediment accumulation in Limnopolar Lake during the last ∼ 1600 years. The main temporal changes in sediment geochemistry are represented in Fig. 6. The record of Cp1 scores reflects the input of volcanic material (fallout ashes and reworked material) to the lake, most probably related to the activity of the Deception Island volcano. As already mentioned, previous investigations (Björck et al., 1991; Björck and Zale, 1996a; Hodgson et al., 1998; Pallés et al., 2001; Fretzdorff and Smellie, 2002) studied the chronology of tephras in the Antarctic Peninsula, that was recently extended and discussed by Toro et al. (2013). With the limitations stated above, the four peaks (L1 to L4; Fig. 3) with high positive Cp1 scores can be interpreted as events of tephra deposition to the lake, with ages of: AD ~ 1300 for L4, AD ~ 1450–1470 for L3, AD ~ 1570–1650 for L2, and AD ~ 1840–1860 for L1. The depths of these layers in LIM03/1 are somewhat shallower than those of the upper tephras of the composite Limnopolar core, probably due to differences in compaction during coring or changes in the microtopography of the sediment surface. But their timing matches quite well with those given by Toro et al. (2013): ages of ~ 650–565 cal yBP (AD ~ 1300–1385),~ 505–410 cal yBP (AD ~ 1445–1540),~ 365 cal yBP (AD ~ 1585; a peak in magnetic susceptibilty) and at ~ 135 cal yBP (AD ~ 1815). These layers were correlated to tephras AP3 to AP1 of the tephrachronology developed by Björck et al. (1991).

Most of the metals showed no consistent depth trend, so their chronologies are not considered here. As already mentioned, for Cu, the largest peak in concentrations matches the age of layer L1 (Fig. 6); while Cr shows the same peak and steadily increasing values in the last 200 years. The increase in Cr concetrations may have already started by AD ~ 1400, but the low values observed in sections corresponding to layer L2 and during the 18th century (Fig. 6) do not enable to evaluate it properly. It is interesting to note that this later minimum is also observed in Cu, Fe and Mn concentrations, as well as in the proportion of volcanic material. The systematic low values in these components may reflect the effect of other processes than those already described. Since the age of this excursion fits that of one of the coldest events of the Little Ice Age, the Maaunder minimum in solar insolation (Bard et al., 2000; Muscheler et al., 2007), climate change may have been also directly or indirectly involved in the cycling of elements in Antarctica as already propossed by other researchers (Bargagli, 2000).

5 Conclusions

The results obtained for the sediment core LIM03/1 indicate that volcanic activity has played a major role in the chemical and mineralogical composition of the sediments

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of Limnopolar Lake (Livingston Island, Antarctica) during the last ∼ 1600 years. Both, direct deposition of tephras and redistribution of volcaniclastic material by runoff from the catchment, seem to have been particularly intense since at least AD ∼ 1200. The most probable origin of the volcanic material is the Decpetion Island volcano, as found in previous investigations. Only in periods of low volcanic activity (from AD ∼ 400 to AD ∼ 1100) the composition of the sediments was controled by the Jurassic-Lower Cretaceous marine sediments which dominate in the lake catchment.

The four layers (L1 to L4) rich in volcanic material contain abundant shards, as found by SEM-EDS analysis, with a chemical composition of a Ca-rich plagioclase and with ages that are quite similar to tephra layers previously identified in this and other lakes of Byers Peninsula.

The volcanic activity may have also been responsible for part of the changes observed for some of the trace metals analyzed (Fe, Mn, Cu, and Cr), since they show peaks in concentrations coinciding with the tephra corresponding to layer L1. Apart from this, no evidence of enrichment has been found for the industrial period (last 300–200 years). As already suggested, the remote location of Livingston Island and the modest research infrastructures (non-permanent research Camp and only two Bases) may explain the lack of pollution evidence in the sediments of Limnopolar Lake. The only exception to this pattern is Cr, for which a steady increase in concentrations has been found in the upper 10 cm of the core (i.e. the last 200 years) as it would be expected for a chronology of anthropogenic pollution since the onset of the industrial revolution. But we do not have an explanation of why it is the only element showing this enrichment and more research is needed (analysis of stable lead isotopes, for example) before attributing it to anthropogenic emissions.

Although speculative at this stage, some features of the chemical records, as the coincidence in minima of concentrations of some elements with recent, well known, abrupt climate changes, may suggest a role of climate in the cycles of chemical elements in Antarctica. Again, more research is necessary to identify the actual mechanisms involved and support this interpretation.

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Acknowledgements. This work was partially supported by projects CGL2010-20672 and REN2000-0345-ANT (Spanish Ministerio de Ciencia e Innovación), POL2006-06635/CGL (Spanish Ministerio de Educación y Cultura), and 10PXIB200182PR (Dirección Xeral de I+D, Xunta de Galicia). A. Quesada, A. Justel and C. Rochera, members of the Limnopolar Project team, are thanked for their help with coring in 2003.

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Table 1. Loadings of the chemical elements used in the principal components analysis. Cp1 to Cp7: components; Com: communality (i.e. proportion of the variance of each element explained by the extracted components); Eigv: eigenvalue, Var: percentage of explained variance by each component.

	CP1	Cp2	Cp3	Cp4	Cp5	Cp6	Cp7	Com
Ti	**0.96**	0.06	0.04	0.14	0.02	−0.09	−0.08	0.96
Ca	**0.96**	0.06	0.02	0.07	−0.13	−0.11	0.15	0.98
Sr	**0.94**	0.23	0.02	0.06	−0.09	−0.04	0.13	0.97
Zr	**0.94**	0.11	0.03	0.19	0.04	0.05	0.08	0.97
K	**−0.89**	−0.11	0.08	−0.03	0.29	0.13	0.04	0.95
Rb	**−0.94**	−0.06	−0.05	−0.04	0.23	0.16	−0.01	0.92
Fe	0.07	**0.91**	−0.24	0.11	0.12	0.09	−0.13	0.94
Mn	0.38	**0.84**	−0.00	0.08	0.01	−0.15	−0.23	0.93
Si	0.02	−0.05	**0.95**	0.16	−0.07	0.04	−0.07	0.94
Al	0.04	−0.21	**0.84**	−0.33	0.15	0.13	−0.00	0.90
Cu	0.27	0.15	−0.05	**0.93**	0.08	−0.04	0.12	0.97
Zn	−0.32	0.12	0.04	0.08	**0.92**	−0.09	−0.01	0.97
Pb	−0.20	−0.02	0.13	−0.04	−0.07	**0.96**	−0.02	0.99
Cr	0.11	−0.29	−0.07	0.12	−0.01	−0.02	**0.94**	0.99
Eigv	5.69	1.78	1.71	1.10	1.10	1.0	1.0	
Var	40.6	12.7	12.2	7.8	7.5	7.5	7.3	

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Table 2. Correlation between mineralogy and elemental composition. Pg: palgioclase; 2 : 1 Phy: 2 : 1 phyllosilicates; Qtz: quartz; Cp1: first PCA component.

	Plag	2 : 1 Phy	Qtz
Cp1	0.77	−0.66	−0.85
Ca	0.76	−0.66	−0.79
K	−0.59	0.48	0.71
Ti	0.71	−0.58	−0.88
Rb	−0.71	0.59	0.80
Sr	0.75	−0.65	−0.79
Zr	0.73	−0.60	−0.85

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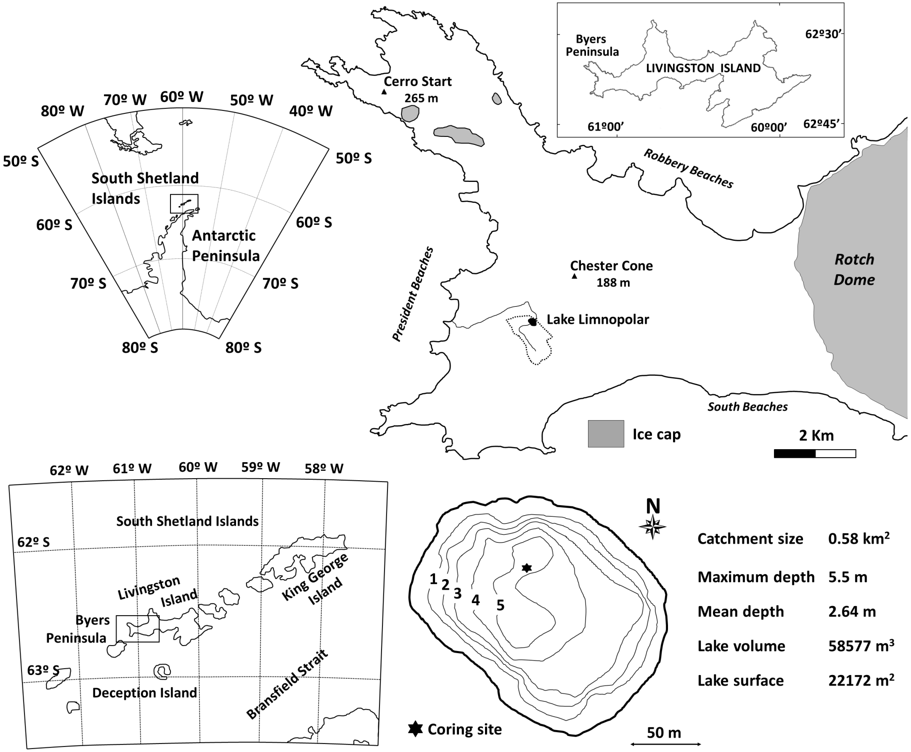

Fig. 1. Location of Limnopolar Lake on Livingston Island (South Shetaland Islands, Antarctica).

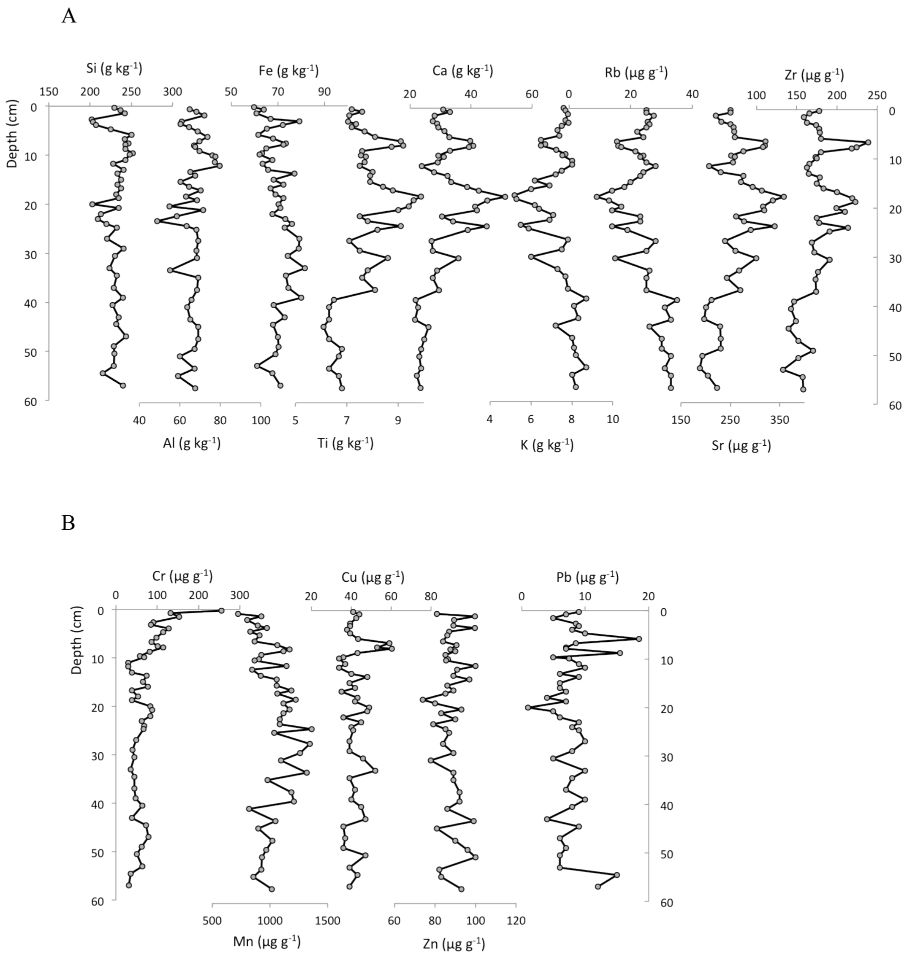

Fig. 2. Depth records of concentrations of the elements analyzed in the LIM03/1 core of Limnopolar Lake. **(A)** Major, minor and trace lithogenic elements; **(B)** metallic elements.

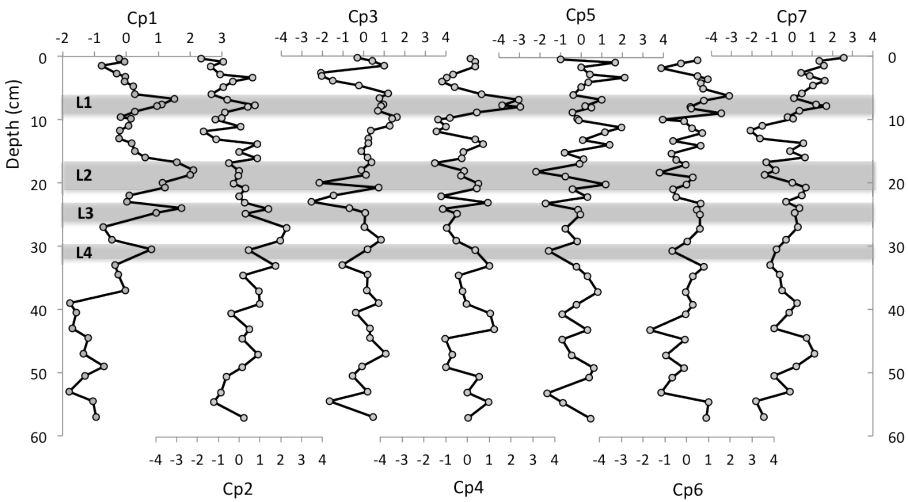

Fig. 3. Depth records of scores of the principal components extracted by PCA on the elemental composition of the sediments of the core LIM03/1 of Limnopolar Lake. L1 to L4: layers enriched in Ca, Ti, Zr and Sr, which are interpreted as tephras.

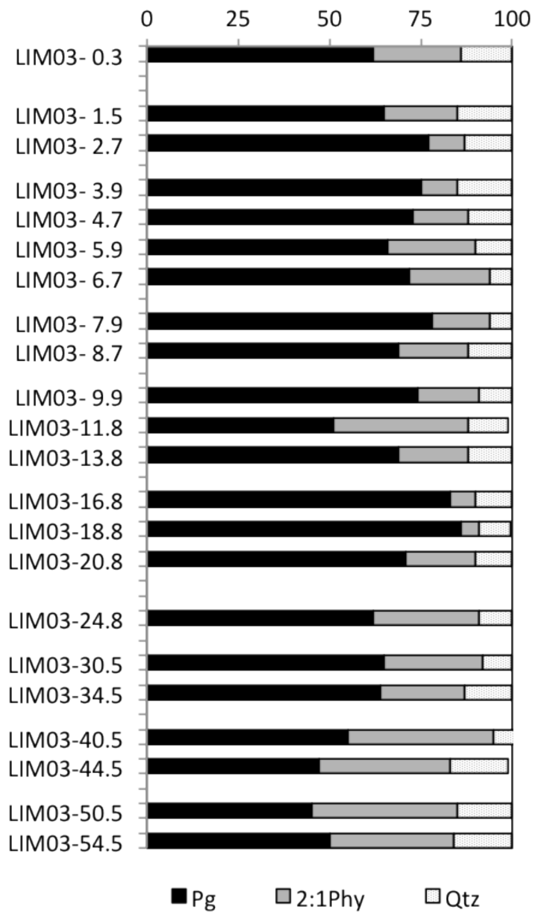

Fig. 4. Mineralogical composition of selected samples of the sediments of LIM03/1 core of Limnopolar Lake. Pg: palgioclase; 2 : 1 Phy: 2 : 1 phyllosilicates; Qtz: quartz.

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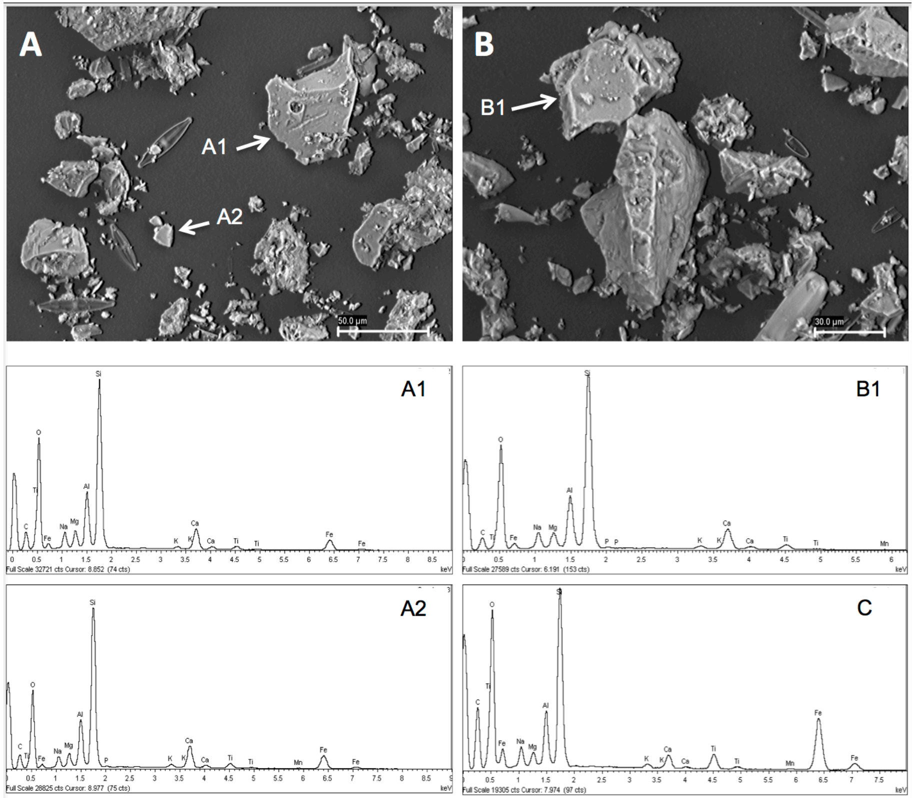

Fig. 5. Selected SEM microphotographs showing the presence of volcanic shards in Ca-rich layers of sediments of the core LIM03/1 of Limnopolar Lake, and EDS analyses of their composition. A1, A2 and B1 correspond to the shards coded in the microphotographs **(A)** (tephra at 18 cm) and **(B)** (tephra at 6.8 cm); **(C)** (tephra at 6.8 cm) is an example of a shard richer in Fe and Ti (not shown in the microphotographs).

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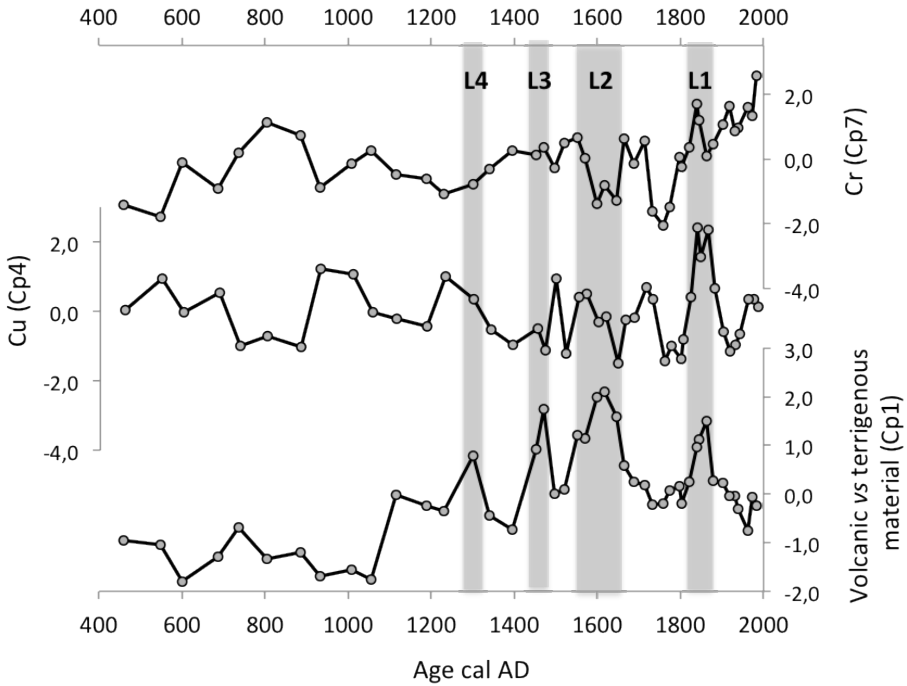

Fig. 6. Chronology of the main changes in the chemical composition of the sediments of Limnopolar Lake during the last 1600 years. L1 to L4: layers enriched in Ca, Ti, Zr and Sr, which are interpreted as tephras.

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