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THEMATIC ISSUE

Hydrological systems from the Antarctic Peninsula under climate change: James Ross archipelago as study case

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Abstract Hydrological systems of the ice-free areas of the James Ross archipelago (NE Antarctic Peninsula) provide a unique opportunity for studying recent environmental changes associated with the current Global Warming. Geochemical, hydrological, sedimentological, and magnetic studies were carried out on different lake systems and ephemeral ponds from post-Holocene periglacial environments to characterize their natural variability. Significant differences between the lakes were observed based on physicochemical analyses, and can be attributed to several characteristics and processes taking place (geochemical, diagenetic, biological, etc.) in individual lake catchments. Seymour-Marambio Island's lakes exhibit high total dissolved solids (~ 3.300 mg L^{-1}) due to the high rate of evaporation in the region, whereas trace elements show differences in the lithological source. Lakes from Vega and James Ross islands are comparatively diluted, with the highest pH values up to 10.2. Within Vega Island, trace elements discriminate lakes into sectors which show statistical differences due to variations in lithological sources. Dissolved sources can be divided according to their kinetics into: high-rate processes which occur during summer months (evaporation, salt precipitation, atmospheric precipitation, melting processes) and low-rate processes (mineral weathering, giving a long-term signature). The present multidisciplinary study contributes to a better understanding of Antarctic lake systems, and can be used as a baseline dataset for further studies investigating the impact of recent climate changes on the biological and geochemical characteristics of these pristine ecosystems in the future.

Keywords Freshwater ecosystems · Limnology · Sediment · Geochemistry · Magnetism · Antarctic Peninsula

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Introduction

Antarctica is one of the most pristine remaining places in the world, where most human activities take place at permanent settlements (Antarctic Stations) having environmental impacts at varying levels (Claridge et al. 1995; Sheppard et al. 2000; Webster et al. 2003; Santos et al. 2005; Chaparro et al. 2007). As presented in Meybeck (2005), few areas of the world still exhibit comparably pristine water geochemistry, enhancing the worth of this locality for the investigation of various topics, especially those related to natural processes occurring in the environment. The knowledge of different Antarctic environments is critical for understanding a wide variety of modern environmental processes in order to better estimate causes and effects of future environmental changes associated with the current Global Warming.

In a global framework of climate change, the Antarctic Peninsula is one of the fastest-warming regions on Earth, where the mean annual air temperature warmed by around 2.8 °C during the last 50 years (Vaughan et al. 2003; King et al. 2004; Meredith and King 2005; Turner et al. 2005; Hodgson et al. 2013). The consequences of this dramatic climate change on different ecosystems (e.g., lakes, glaciers), have been poorly documented and studied (e.g., Hawes et al. 2014). This region, the most deglaciated area on the Antarctic continent (e.g., 20 % in James Ross Island, Ingólfsson et al. 1992), provides a unique opportunity for studying recent and past environmental changes. The current meteorological conditions of the NE Antarctic Peninsula make this region very sensitive to recent climatic changes, taking into account their thermal proximity to the freezing point, as well as its rapid warming, producing modifications to the landscape (e.g., increasing or decreasing of glaciers' size), and hydrochemical processes (e.g., Quayle et al. 2002; Vaughan et al. 2003; King et al. 2004; Turner et al. 2005; Mulvaney et al. 2012; Hodgson et al. 2013; Nedbalová et al. 2013; Silva Busso et al. 2013). The Antarctic Peninsula forms an effective barrier for the westerly winds (Engel et al. 2012), creating a precipitation shadow resulting in a more arid outlook to the east, compared with those in the Maritime Antarctic Region (such as South Shetland Islands).

The climatic and geomorphological conditions allow the development of diverse and abundant freshwater systems during the austral summer. Most of the studied water bodies are formed by glacial erosion and deposition on ice-free areas after ice cap retreat during the Holocene (Ingólfsson et al. 1998; Carrivick et al. 2012). The particular characteristics of a given system result from the interaction of geological, chemical, and biological factors, known as the "critical area" (Brantley et al. 2007). The terrestrial vegetation is limited mainly to lichens and bryophytes, whereas aquatic life is formed by rich microbial benthic mats (composed of algae and cyanobacteria) and several crustaceans (*Branchinecta gaini* Daday and *Boeckella poppei* Mrázek). Although a geochemical characterization of these water bodies is scarce (e.g., Silva Busso et al. 2013; Chaparro et al. 2014; Vignoni et al. 2014), significant progress has been made during the last decade respect to the knowledge and influence of climate change in the region (e.g., Zale and Karlen 1989; Skvarca et al. 2004; Mulvaney et al. 2012; Nedbalová et al. 2013), together with the diversity and taxonomy of the aquatic and limno-terrestrial flora (e.g., Kopalová et al. 2012, 2013, 2014).

This paper provides a multidisciplinary study of several unknown lakes and ponds from Seymour-Marambio Island (SMI, Fig. 1C1), James Ross Island (JRI, Fig. 1C2) and Vega Island (VI, Fig. 1C3), in the Antarctic Peninsula region. These systems are characterized using geochemical, sedimentological, and magnetic approaches that provide baseline information for comparison with other limnological, paleoecological, or environmental studies in the region. The great sensitivity of these lacustrine systems and the rapid climate changes undergoing in the region, enhance the importance of these studies in high latitudes.

Geological and climatic settings

Studied lakes are located in three different islands (Seymour-Marambio, James Ross Island and Vega Island) in the James Ross Archipelago (JRA) in the northwestern Weddell Sea, East of the northern tip of the Antarctic Peninsula (63°40′–64°20′S and 57°00′–58°00′W; Fig. 1).

The climate in the JRA is 'semi-arid' (Laity 2008) with annual snowfall ranging from 200 mm to 500 mm yr^{-1} w.e. (water equivalent of precipitation; Strelin and Sone 1998; Van Lipzig et al. 2004). Moreover, climate is characterized by short summers (December–February), with mean temperatures for the warmest and coldest months at Marambio Station (64°14′S, 56°38′W) of −3.3 and −14.5 °C, respectively. The terrestrial vegetation on the islands is limited to non-vascular plants and composed of a predominantly bryophyte and lichen tundra.

Most of the studied lakes are endorreic, developed on glacial valleys carved on marine sedimentary rocks and volcanic rocks. Three types of hydrologic basins can be recognized in JRA considering the water source: fed by glaciers ablation, the active layer of permafrost, or by snow melting. Normally, hydrologic basins are of mixed character, prevailing one type or another according to the geomorphological lake position. The dominance of one type over the others also varies temporarily. During winter

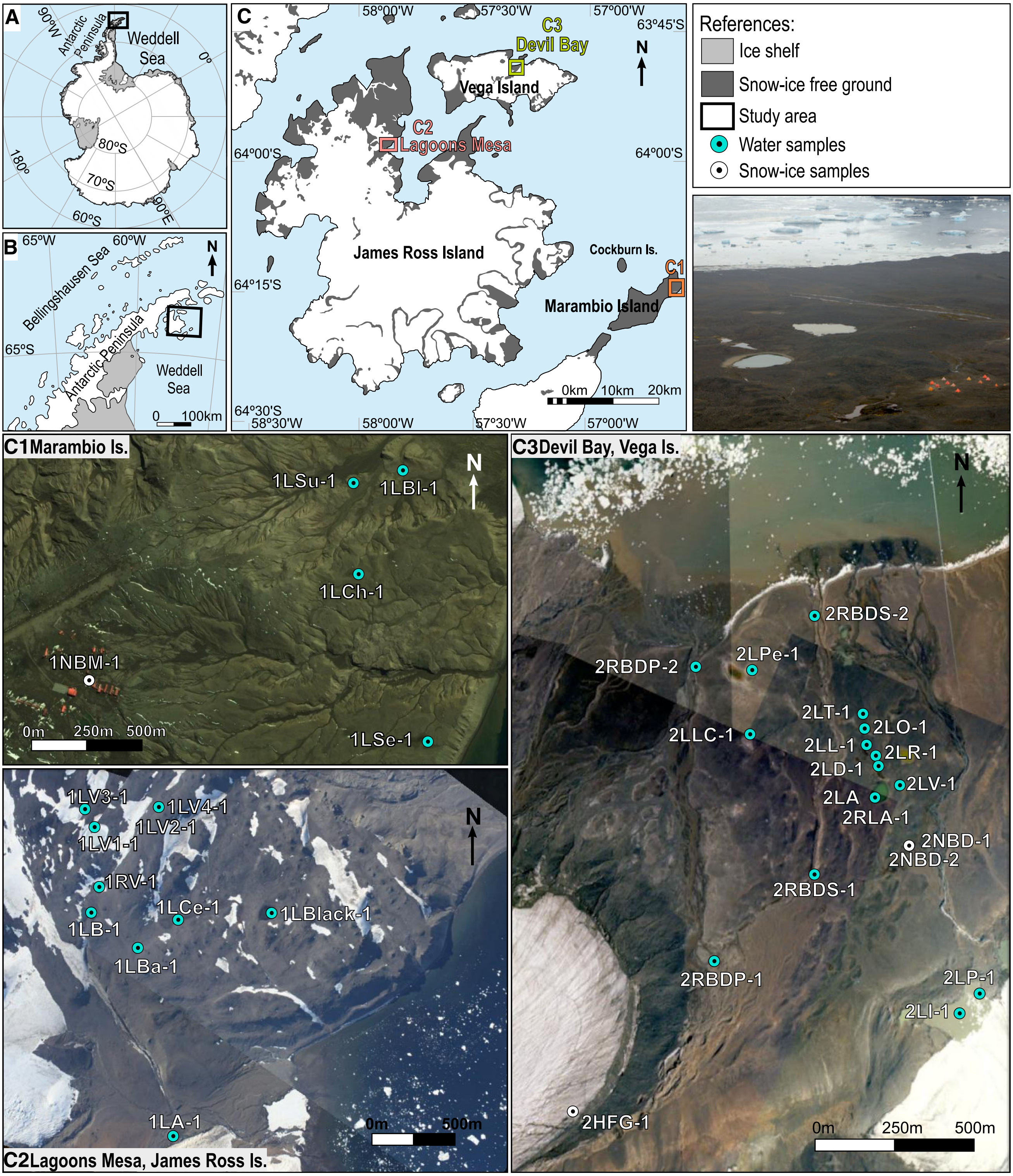

Fig. 1 Study area and location of sampling points. **a** Antarctic Continent; **b** Antarctic Peninsula; **c** sampling localities marked with a square (*C1*, *C2*, *C3*) in SMI, JRI and VI, respectively

the whole system is paralyzed because of the freezing of liquid water bodies, except from snowfall that accumulates on the surface. With the increase of temperature in late spring and early summer, snow melting occurs first, followed by thawing of the active layer as well as activation of the glacial rivers. When mean temperature is high enough, the permafrost develops the active layer, and at this time is put into operation the complete water cycle. Lakes, depending on their nature, collect surface runoff and can drain underground into surface streams and these to the sea.

The first group of lakes is located in Lagoons Mesa in NW JRI (Fig. 1C). It corresponds to an elevated irregular surface formed by glacial erosion on volcanic rocks of James Ross Island Volcanic Group (JRIVG), covered by glacial deposits with basaltic clasts. Numerous shallow lakes can be found in surface depressions such as Vondra 1-Vondra 4, Azul, Black, Cecil, Buena/Cyanobacteria, Roja, and Verde River (Fig. 1C2). JRI is the largest island (2600 km^2) in the western Weddell Sea, nearly 20 % of its surface is ice-free, most of which lies in the northern part of the island. The central ice cap of JRI reaches 1628 m at the ice-covered extinct volcano, Mount Haddington. From a geological point of view, JRI is formed by a thick succession of deep marine to shallow fossiliferous clastic sedimentary rocks (lower Cretaceous-Cenozoic) intruded by Tertiary volcanic rocks of basaltic composition of the JRIVG. Covering the sequence, glacial and glacial-marine sediments can be found (upper Miocene-recent).

The second group of lakes is located in the vicinity of Argentina's Marambio Station on SMI (Fig. 1C). Rocky outcrops are generally from a marine source with abundant fossil fauna; only in the plateau area there are Quaternary glacial levels. However, SMI has a particular hydrologic system due to the absence of glaciers. The contribution of water to the systems is mainly produced by melting of snow and ice contained in permafrost. For example Silva Busso et al. (2000) characterized the hydrological behavior describing an active layer up to 2.5 m depth, which forms an unconfined aquifer during the summer suprapermafrost melting over the impermeable permafrost level. The surface water system corresponds to a series of small streams with transitional regimes, active during the summer and flowing to the Weddell Sea (Silva Busso et al. 2013). The studied lakes and ponds (Seca, Chica, Blanca, and Sucia, Fig. 1C1) are located on La Meseta Formation (Eocene), where sandstones and shales with interbedded conglomerates rich in shells were deposited in a deltaic, estuarine and shallow marine environment (Marenssi et al. 2002).

The third group of lakes (Anónima, Larga, Del costado, Rugosa, Pequeña, Incierta, Verde, Olvidada, Terminal, Peinada, and La Cumpa lakes) is located on the NE of VI (Devil Bay, Fig. 1C3). Those lakes occupy small depressions on the basal moraine deposits left by Bahía del Diablo Glacier on its retreat after the Last Glacial Maximum. These deposits are mainly composed of volcanic rocks of basaltic composition (*JRIVG*).

Lake surfaces vary, in general, from 1000 to 16,000 m^2, whereas they are all shallow (<10 m depth). Marambio lakes present the shallowest depth (~20 cm depth, ephemeral ponds), while other lakes ranged between 20 and 460 cm, with a mean ~210 cm depth. According to Nedbalová et al. (2013), the studied lakes can be divided into three of the exposed groups based on their origin, geomorphological position and hydrological stability. Lagoons Mesa lakes (JRI) belong to the "stable shallow lakes on higher-lying levelled surfaces". These lakes are assumed to be among the oldest in the studied region. SMI lakes are "epehemeral shallow lakes on higher-lying leveled surfaces", whereas VI presents a variety of lakes with different origins. Lake Peinada is a "shallow coastal lake", developed mostly in the early to mid-Holocene, following relative sea level fall and/or glacier retreat in the coastal areas. The remaining lakes of VI (except from Lakes Incierta and Pequeña) are "stable lakes in old moraines", formed after degradation of local glaciers after the Holocene neoglacial. Lakes Incierta and Pequeña are "small unstable lakes in young moraines in front of retreating local glaciers". They are young and originated from the last retreat of local glaciers.

Materials and methods

Sampling

Water and sediment samples were taken from lake systems of Lagoons Mesa on JRI, Devil Bay on VI and NE of SMI during two field campaigns in the Antarctic summer 2012 and 2013. Some snow and glacier-ice samples were also collected to compare geochemical signatures of different sources: atmospheric and glacier. Twenty-five lake water, 6 river water, 3 snow, 1 ice, 25 sediments, and 12 core samples were collected. Table 1 shows samplings points' location and the material collected at each point.

An extra sediment sample was collected from Lake Blanca's margin for X Ray Diffraction (XRD). Physicochemical variables were determined in water and snow-ice samples; whereas geochemical measurements: total organic and inorganic carbon (TOC and TIC), and magnetic studies (magnetic susceptibility, magnetic hysteresis, remanent magnetization and thermomagnetic measurements) were determined in bottom lake sediments and cores.

Water analysis

Hydrochemical characterization was made on 5 samples collected from SMI (1 snow, 4 lake waters); 10 samples from JRI (1 river, 9 lake waters); and 20 samples from VI (2 snow, 1 ice, 5 river waters, and 12 lake waters).

Table 1 Location of samples collected, indicating type of sample in each point

Island	Sampling point	Date	Sample	Sample kind	Latitude (S)	Longitude (W)	Altitude (m snm)	Depth (cm)	Surface (m^2)
Marambio	Base	02/02/2012	1NBM-1	Snow	64°14′25.56″	56°37′29.36″	196	–	–
	Lake Seca	20/01/2012	1LSe-1	Water, sediments, cores	64°14′37.90″	56°35′36.50″	49	20	3000
	Lake Chica	20/01/2012	1LCh-1	Water, sediments, cores	64°14′12.60″	56°35′56.00″	64	10	1000
	Lake Blanca	22/01/2012	1LBl-1	Water, sediments, cores	64°13′57,80″	56°35′38,70″	14	20	1000
	Lake Sucia	24/01/2012	1LSu-1	Water, sediments	64°13′59.20″	56°35′55.70″	15	ND	ND
James Ross	Verde River	10/02/2012	1RV-1	Water	63°57′50.83″	57°54′18.15″	194	–	–
	Lake Vondra 1	12/02/2012	1LV1-1	Water	63°57′39.13″	57°54′18.43″	243	ND	ND
	Lake Vondra 2	12/02/2012	1LV2-1	Water	63°57′39.13″	57°54′18.43″	241	ND	ND
	Lake Vondra 3	08/02/2012	1LV3-1	Water, sediments	63°57′35.64″	57°54′22.32″	259	310	13000
	Lake Vondra 4	12/02/2012	1LV4-1	Water, sediments	63°57′35.40″	57°53′49.13″	231	ND	ND
	Lake Azul	11/02/2012	1LA-1	Water	63°58′42.60″	57°53′49.20″	26	ND	ND
	Lake Black	12/02/2012	1LBlack-1	Water	63°57′56.90″	57°52′59.20″	222	ND	ND
	Lake Cecil	12/02/2012	1LCe-1	Water	63°57′57.80″	57°53′42.90″	170	ND	ND
	Lake Buena - Cyanobacteria	10/02/2012	1LB-1	Water, sediments, cores	63°57′56.00″	57°54′22.60″	237	270	1900
	Lake Roja	12/02/2012	1LBa-1	Water, sediments, cores	63°58′03.30″	57°54′02.10″	173	5	
Vega	Camp	23/01/2013	2NBD-1	Snow	63°49′25.80″	57°19′23.95″	34	–	–
	Camp	15/02/2013	2NBD-2	Snow	63°49′25.82″	57°19′23.95″	34	–	–
	Glacier	11/02/2013	2HFG-1	Ice	63°49′48.94″	57°20′37.03″	57	–	–
	Stream 1 (upstream)	05/02/2013	2RBDP-1	Water, sediments	63°49′36.36″	57°20′07.92″	182	–	–
	Stream 1 (downstream)	05/02/2013	2RBDP-2	Water, sediments	63°49′07.46″	57°20′10.46″	31	–	–
	Stream 2 (upstream)	09/02/2013	2RBDS-1	Water	63°49′28.44″	57°19′45.48″	116	–	–
	Stream 2 (downstream)	09/02/2013	2RBDS-2	Water, sediments	63°49′02.28″	57°19′42.96″	7	–	–
	Anónima Stream	26/01/013	2RLA-1	Water, sediments	63°49′20.96″	57°19′30.86″	24	–	–
	Lake Incierta	20/01/2013	2LI-1	Water, sediments	63°49′41.82″	57°19′15.78″	187	ND	ND
	Lake Pequeña	20/01/2013	2LP-1	Water, sediments	63°49′40.08″	57°19′11.11″	66	ND	ND
	Lake La Cumpa	23/01/2013	2LLC-1	Water, sediments	63°49′14.41″	57°19′58.58″	48	ND	ND
	Lake Peinada	23/01/2013	2LPe-1	Water, sediments	63°49′07.82″	57°19′57.72″	22	ND	ND
	Lake Anónima	17/01/2013	2LA-1	Water, sediments, cores	63°49′20.96″	57°19′30.86″	24	460	2732
		12/02/2013	2LA-2	Water	63°49′20.96″	57°19′30.86″	24	460	2103
	Lake Verde	21/01/2013	2LV-1	Water, sediments	63°49′19.71″	57°19′25.03″	27	90	2830
	Lake Del Costado	19/01/2013	2LD-1	Water, sediments	63°49′17.80″	57°19′29.68″	16	130	ND
	Lake Rugosa	19/01/2013	2LR-1	Water, sediments	63°49′16.75″	57°19′30.18″	16	ND	ND
	Lake Larga	19/01/2013	2LL-1	Water, sediments	63°49′15.64″	57°19′32.12″	15	ND	ND
	Lake Olvidada	22/01/2013	2LO-1	Water, sediments	63°49′13.91″	57°19′32.38″	13	ND	ND
	Lake Terminal	22/01/2013	2LT-1	Water, sediments	63°49′12.40″	57°19′32.59″	13	ND	ND

ND not determined

Water temperature, water pH (or pH for short), redox potential, electrical conductivity, total dissolved solids (TDS), and alkalinity were measured in situ. Alkalinity was measured as $CaCO_3$, using a 0.1600 N H_2SO_4 solution until pH = 4.5. End point titration was reached in unfiltered water. For subsequent determinations, samples were vacuum-filtered in the field with 0.22 μm pore-size cellulose filters (HA-type, Millipore Corp.). An aliquot was stored in polyethylene bottles, at 4 °C for the determination of anions by chemically suppressed ion chromatography with conductivity detection. Other aliquot was acidified (pH < 2) with concentrated, redistilled and ultrapure HNO_3 (Sigma-Aldrich) for the analytical determination of major, minor, and trace elements by inductively coupled plasma-mass spectrometry (ICP-MS, Activation Laboratories Ltd., Ancaster, Ontario, Canada). Detection limits are reported in the corresponding tables. The results for major, minor, and trace elements were validated using NIST (National Institute of Standards and Technology) 1640 and Riverine Water Reference Materials for Trace Metals certified by the National Research Council of Canada (SRLS-4).

Chemical data were processed with AQUACHEM software (Waterloo Hydrogeologic, Inc). PHREEQC (Parkhurst 1995) input files were constructed using the AQUACHEM PHREEQC interface. These programs were used to calculate saturation index (SI) for different mineral phases and elements speciation in the given conditions, i.e. the element distribution in all the possible dissolved chemical species that can be found in the samples. The SI is the ratio between the ion activity product for the given material and the reaction constant at a given temperature. It is a useful value to determine the degree of saturation: when $SI > 0$, it means that the solution is supersaturated with respect to the mineral phase and therefore may precipitate, whereas when $SI < 0$ it means that the solution is below saturation of the specified mineral. Moreover, the equilibrium speciation of trace elements in the lakes was also obtained using PHREEQ-C in representative samples.

Sediment analysis

Bottom sediment samples were collected from shallow lakes and streambeds using a standard scoop sampler. Particular attention was paid to the collection of the sediment/water interface. In the deepest lakes an Eckman dredge was slowly lowered to capture the uppermost sediments. Samples were skimmed from the top of the dredge (2–3 cm), stored in plastic bags, and refrigerated until analyzed.

Lake-sediment cores were collected from the deepest part of the lake systems of JRI, MI, VI (Table 1). The extraction was made from an inflatable raft with a side-filling core sampler (Russian sampler, Faegri and Iversen 1989) that allows obtaining semicylindrical cores of 7 cm diameter and 1 m long. Cores were wrapped and refrigerated until analyses. The cores were macroscopically described, photographed, sub-sampled at 1 cm intervals, dried at room temperature, sieved (2 mm) and stored. A total of 656 sub-samples were obtained.

Loss on ignition method (LOI) was used to estimate total organic and inorganic carbon contents in sediment samples (Heiri et al. 2001). Dry matter in sediments was determined by drying the samples at 105 °C to constant weight. Organic matter was measured as loss-on-ignition upon heating at 550 °C for 4 h. The carbonate content was calculated as the loss of weight after burning the LOI residue at 950 °C for 2 h (Heiri et al. 2001).

Magnetic measurements in cores were carried out in two laboratories: CGeo (Querétaro, México) and CIFICEN (Tandil, Argentina), using a Bartington MS2/3 magnetic susceptibility meter; a Molspin shielded alternating field demagnetizer; an Agico JR5 and a Molspin Minispin magnetometer; a MicroMagTM 2900 magnetometer (Alternating Gradient Magnetometer, Princeton Measurements Corporation) and a horizontal Curie balance. Different subsamples (~ 0.03 to 8 cm^3) were prepared in the laboratory for rock magnetic studies: magnetic susceptibility, anhysteretic and isothermal remanent magnetization (ARM, IRM), magnetic hysteresis and thermomagnetic measurements ($M(T)$). Several related magnetic parameters, ratios and plots were obtained and analyzed: magnetic susceptibility (κ), mass-specific magnetic susceptibility (χ), saturation magnetization (M_s), remanent magnetization (M_r), relative contribution of paramagnetic and diamagnetic minerals to the M_s (para/diamag. cont.), anhysteretic susceptibility (κ_{ARM}), κ_{ARM}/κ and remanent coercivity (Hcr).

The mineralogy of Lake Blanca sediment's sample was determined through X-ray diffraction (XRD) from randomly orientated powder of the bulk sample carried out in Philips X'Pert PRO PW3040/60 difractometer (FAMAF, UNC, Argentina). Diffraction data were analyzed using High Score program in order to identify possible salt minerals precipitated.

Statistical analysis

Multivariate analyses were performed on resulting lake data in order to: (1) determine particular features of each island and lakes; (2) explore the relationships between chemical variables of the samples; and (3) determine which variables-descriptors are significant for a lake's cluster.

The methodology applied is a combination of the principal component analysis (PCA) and the cluster analysis (CA). The PCA analysis is performed on the original dataset matrix (i.e., X matrix). Results are expressed in another matrix (i.e., X^* matrix) in order to present Euclidean distance between individuals. The CA on the X^* matrix using the Euclidean distance, is applied in order to produce statistical differentiated lake's groups.

This methodology allows eliminating those dimensions which are sure to be "noisy". A very high variability percentage is explained (above 80 %), and it should be retained by the selected components to obtain a more stable and clear hierarchy. The main use of the hierarchy obtained is therefore; simplify in order to help in interpreting the results of the PCA method.

In order to test the null hypothesis: "the average of variable X for group k is equal to the general average" (i.e., X matrix does not characterize category q); a V test for each cluster is applied. The test-value is calculated in Eq 1 as follows:

$$t_k(X) = \frac{\overline{X_k} \quad \overline{X}}{\sqrt{\frac{n \quad n_k}{(n \quad 1)n_k}}\, S_X} \qquad (1)$$

where $\overline{X_k}$is the mean of group (cluster) k, $\overline{X}$ and S_x^2 are the mean and variance overall of variable X respectively and n_k is the number of individuals carrying the category q. The t_k (X) value has a t-student distribution and it is a "standardized" deviation between the mean of those individuals with the category k and the general average.

All analyses were carried out using the FactoMineR package (Husson et al. 2007) in R (R Core Team 2014).

Results

Water geochemistry

Geochemical data is shown in Tables 2 and 3. Lakes present geochemical characteristics significantly different from each other, depending on which island they belong to. SMI lakes show particular physicochemical characteristics, with the highest TDS values, ranging between 1570 and 5190 mg L^{-1}, and pH values slightly alkaline, between 7.6 and 8.2. Lakes in JRI present diluted waters (mean $\sim$40 mg L^{-1}), more alkaline that SMI with maximum pH values of 9.8 (mean $\sim$8.2); whereas VI's waters exhibit greater variation of pH, ranging from neutral to clearly alkaline (maximum pH = 10.2, mean values $\sim$9.0). High pH values are present in those lakes with cyanobacterial and microbial mats communities (Fig. 2). These high pH values could be explained by photosynthesis reactions (Libera 1993), however more analyses are needed. The TDS show relatively low values with a mean $\sim$100 mg L^{-1} (Table 2).

Both NO_3^- and NO_2^- present concentrations below detection limit (i.e., <0.25 mg L^{-1}), except for lakes Buena and Cecil, and Anonima River which exhibit low concentrations (main $\sim$3.03 and $\sim$0.76 for NO_3^- NO_2^- respectively). The main water contributions to lake systems come from snowfall, glacial ice and permafrost melting; and from surface runoff. Ice and snow are very dilute, with low TDS, with an average value of $\sim$20 mg L^{-1}, and higher values ($\sim$87 mg L^{-1}) in fresh snow collected on SMI. These samples show slightly acidic pH values varying from 5.5 to 7.1, and low alkalinity (Table 2).

Water classification is shown in Fig. 3 with a Piper diagram (1944). Ice and snow melting are of the sulfate-mixed type in SMI, while in VI, its anionic composition is variable; VI snow samples are more calcic, whereas the ice sample is sodic-potasic. Lake waters from SMI are of the sulfate type and a mixed cationic composition with little variation between each other. However, JRI presents its lake waters of the bicarbonate-mixed type, showing again, a relatively constant classification. In contrast, the chemical classifications of water bodies in VI are chloride-sodic-potasic. There are no samples with a chloride signal, as shown in Lyons et al. (2012) for many ponds in McMurdo Dry Valley.

Trace elements in natural waters are characterized by concentration <1 mg L^{-1}. In Antarctic lakes, trace elements concentrations (Table 3) range from as low as <0.001 (detection limit)—4 µg/l for ultra-trace elements (Y, ∑REE, Ga, Th, U, As, Sb, Cs, Co, Cd, and Pb) up to 0.7–1230 µg/l for minor elements such as Fe, Mn, Zn, and Sr. There are several outliers in different elements and lakes. Most of them belong to SMI, as Sr, Li, and U (Lake Seca); Mn, Co, and ∑REE (Lake Chica); whereas outliers as Zn in Lake Black, Sr in Lake Buena and Pb in Lake Azul belong to JRI. These outliers indicate local lithology variations.

The mean major, minor, and trace metals species are clearly different in SMI comparing to JRI and VI. The most striking feature predicted by equilibrium speciation is the importance of metal-sulfate and metal-carbonate complexes in SMI, as is shown in Table 4. There is represented the mean percentage of some species (free aqueous cation; sulfate and carbonate) in the different islands. Otherwise, the equilibrium speciation of some other elements is also almost entirely dominated by free aqueous ions M^{+z} or M^{-z} (e.g., Ba^{+2}, K^+, Li^+, Na^+, Ni^{+2}, Cl^-) in all samples. A general tendency of element such as Al^{+3}, Fe^{+3}, and Cr^{+3} to be partially or fully hydrolyzed [nM^{+3}•m(OH)] in aqueous environment is observed in the area. Moreover, Pb^{+2} also exhibit $\sim$20 % as hydroxo-complex. Oxoanionic species are stable for As (mainly As^{+5} arsenate) and Sb^{+5} (SbO_3^-). Finally, Si dominates as H_4SiO_4, as is expected. This trace element behavior is usually presented in natural environments (e.g., Aiuppa et al. 2005; Mosley et al. 2015).

Dissolved concentrations of each element were normalized to a known patron (i.e., upper continental crust—UCC—McLennan 2001) and are shown in the spider-diagrams of Fig. 4, following UCC abundance in each island. Trace element concentrations are several orders (from 1 to 7) lower than the host rocks. Moreover, the world average of trace elements (Gaillardet et al. 2003) was included for comparison. The geochemical signature is comparable within samples with respect to the distribution of the more concentrated elements, as well as the elements which are more depleted. The world average geochemical signature follows the same pattern, although some elements present a relatively low concentration (e.g., Ti, Zn), while Sr and Ba exhibit higher values. Most elements are included in Antarctic samples range.

Table 2 Physicochemical characteristics and major ions of water samples

Island	Sample	pH	Eh	T	Electrical conductivity	TDS	T Alk	Mg	Ca	Na	K	Cl^-	SO_4^{-2}	TOC	TIC
	Detection limit (mg L^{-1})							0.002	0.7	0.005	0.03	0.1	0.1		
	Unit		mV	°C	μS cm^{-1}	mg L^{-1}								%	
Marambio	1NBM-1	6.37	205	–	173.10	87.10	7.32	1.58	2.20	3.28	0.09	14.24	35.15	–	–
	1LSe-1	8.31	153.5	13.00	10190.00	5190.00	167.14	786.00	707.00	1290.00	40.20	899.98	5512.65	0.49	0.09
	1LCh-1	7.63	164.8	15.50	5810.00	2650.00	31.72	286.00	540.00	319.00	10.80	309.73	3281.74	0.66	0.22
	1LBl-1	8.21	164.3	11.50	7560.00	3870.00	150.06	175.00	569.00	697.00	9.89	467.08	2760.35	0.54	0.26
	1LSu-1	7.60	149.6	8.00	3320.00	1570.00	32.94	111.00	235.00	185.00	5.69	191.55	1530.97	ND	ND
James Ross	1RV-1	7.54	218	1.90	74.70	37.50	39.04	5.09	10.90	15.60	0.73	3.88	4.19	ND	ND
	1LV1-1	7.35	212.1	5.90	51.80	25.70	15.86	0.46	1.50	2.17	0.16	2.55	1.45	ND	ND
	1LV2-1	7.30	218.1	6.40	68.80	34.30	20.74	0.70	2.00	3.40	0.24	3.10	1.52	ND	ND
	1LV3-1	8.12	170	6.90	53.80	26.90	25.62	0.95	2.40	3.99	0.37	3.18	2.15	1.69	0.61
	1LV4-1	7.23	215.1	6.50	51.20	25.60	14.64	0.26	0.90	1.01	0.06	2.41	2.93	1.28	0.49
	1LA-1	7.83	194.3	5.50	44.10	22.30	62.22	55.00	26.20	86.20	3.47	0.73	1.37	ND	ND
	1LBlack-1	8.68	209.8	9.80	103.50	55.90	38.92	2.49	6.40	6.26	0.58	11.52	2.49	ND	ND
	1LCe-1	9.15	ND	9.60	121.80	61.50	62.40	18.30	18.60	22.70	0.95	8.10	4.53	ND	ND
	1LB-1	8.50	ND	3.40	81.40	40.70	37.82	8.66	14.20	12.90	0.44	653.92	3958.17	3.41	0.59
	1LBa-1	9.80	212.7	15.60	164.40	82.40	68.62	4.07	12.50	14.40	0.81	12.28	5.24	2.57	0.63
Vega	2NBD-1	6.48	ND	6.40	18.40	9.20	1.22	0.10	<0.7	0.44	0.11	1.38	0.78	–	–
	2NBD-2	5.48	ND	6.50	27.30	13.70	3.42	0.21	<0.7	0.71	0.34	0.71	0.30	–	–
	2HFG-1	6.40	ND	8.80	28.80	14.30	6.25	0.32	0.90	3.06	0.59	2.95	0.76	–	–
	2RBDP-1	8.00	ND	1.30	71.50	36.20	8.30	0.76	2.40	11.80	0.61	16.29	4.53	0.39	0.19
	2RBDP-2	7.97	ND	4.50	81.50	40.80	14.64	0.90	3.50	11.50	0.87	11.64	6.89	0.31	0.20
	2RBDS-1	8.19	ND	9.40	149.90	75.10	25.01	2.02	4.80	21.50	0.91	18.64	5.58	ND	ND
	2RBDS-2	9.63	ND	5.10	177.10	88.80	38.02	0.93	2.60	33.10	0.90	13.58	4.29	0.79	0.31
	2RLA-1	8.24	ND	2.60	214.00	108.10	39.04	4.28	11.90	24.40	1.48	63.61	15.80	4.25	0.48
	2LI-1	8.10	ND	6.20	225.00	114.30	30.74	3.03	4.60	35.19	2.16	49.35	5.46	0.71	0.25
	2LP-1	9.24	ND	19.70	60.60	30.30	9.74	1.27	1.60	8.49	0.78	28.47	7.42	0.36	0.26
	2LLC-1	8.24	ND	7.90	483.00	240.00	32.94	11.10	20.05	83.04	2.71	83.04	40.28	5.72	0.34
	2LPe-1	8.62	ND	7.80	374.00	223.00	31.72	10.80	20.00	200.24	2.23	261.45	129.76	2.78	0.34
	2LA-1	7.56	ND	6.80	134.70	67.30	16.71	2.71	5.70	16.60	1.40	33.12	7.71	0.82	0.15
	2LA-2	8.14	ND	7.20	154.10	77.00	21.72	3.34	7.10	18.70	1.26	13.82	2.52	ND	ND
	2LV-1	9.88	ND	11.30	297.00	148.50	112.53	6.01	12.40	52.57	2.01	52.57	3.48	8.85	0.46
	2LD-1	9.43	ND	6.10	201.00	101.20	66.17	2.10	9.30	31.10	1.27	26.93	6.98	ND	ND
	2LR-1	9.64	ND	12.20	208.00	104.80	62.33	2.08	9.80	33.30	1.19	27.63	7.09	2.28	0.42
	2LL-1	10.24	ND	13.60	224.00	113.70	52.77	1.11	5.20	59.71	1.22	60.29	19.58	3.74	0.66
	2LO-1	9.32	ND	5.30	154.80	77.60	44.04	1.88	6.60	49.05	1.25	53.75	18.23	4.02	0.39
	2LT-1	8.34	ND	4.60	170.50	85.40	43.31	1.99	7.00	35.18	1.26	35.91	15.40	5.66	0.26

T Alk total alkalinity, *ND* not determined

Table 3 Dissolved trace elements determined in samples

Island	Detection limit	Si	Al	Fe	Ti	Mn	Ba	Sr	Zr	Rb	Zn	V	Cr	Cu
		200	2	10	0.1	0.1	0.1	0.04	0.01	0.005	0.5	0.1	0.5	0.2
	Sample	µg/L												
Marambio	1NBM-1	<200	44	60	1.4	10.2	20	4.07	0.02	0.157	8.5	<0.1	<0.5	1.1
	1LSe-1	<1000	49	460	2.4	43.9	2.1	>1000	0.15	10.3	21	<0.5	<3	10
	1LCh-1	400	181	370	8.7	2760	1.7	>200	0.31	4.84	21	0.3	<0.5	5.6
	1LBl-1	1300	178	140	9.4	59.6	1.1	18.6	0.1	0.333	7.5	3.7	0.9	1.6
	1LSu-1	700	54	190	2.9	425	0.6	>200	0.06	5.75	9.7	<0.1	<0.5	1.7
James Ross	1RV-1	1600	296	330	15	24.9	3.1	40.5	0.22	0.558	18	8.1	1.1	3.9
	1LV1-1	<200	25	20	1.1	4.9	0.2	1.29	<0.01	0.067	3.6	1	<0.5	0.6
	1LV2-1	900	24	20	0.9	4.4	0.3	1.61	0.01	0.095	4.3	1.9	<0.5	0.9
	1LV3-1	400	177	300	11	6.9	1.1	4.9	0.08	0.418	14	1.3	<0.5	4.6
	1LV4-1	400	13	<10	0.6	2.8	<0.1	0.99	0.01	0.045	2.1	0.7	<0.5	0.4
	1LA-1	1600	463	420	44	292	2.3	76.3	0.7	1.75	50	13	0.6	12
	1LBlack-1	2100	76	110	4.5	29.8	0.9	3.79	0.05	0.325	122	1.6	<0.5	2.8
	1LCe-1	3600	145	250	11	255	0.6	23.5	0.17	0.66	15	4.7	<0.5	4.8
	1LB-1	<1000	352	880	9.9	716	2.5	>1000	2.9	8.77	26	<0.5	<3	6.4
	1LBa-1	4800	40	60	3.4	25.3	0.3	5.91	0.03	0.214	3.5	9.6	0.7	1
Vega	2NBD-1	<200	59	40	4.2	9.9	0.6	0.92	0.01	0.136	46	0.2	<0.5	0.6
	2NBD-2	<200	143	170	9.3	5.7	0.6	1.88	0.07	0.325	56	0.3	<0.5	2.4
	2HFG-1	500	109	180	7.5	5	0.7	2.72	0.14	0.336	42	0.9	<0.5	3.4
	2RBDP-1	1900	268	290	15	7.7	0.8	8.28	0.12	0.37	11	4	<0.5	0.6
	2RBDP-2	2900	859	###	40	17.5	2.7	14.5	0.21	1.01	25	5.5	1.3	1.2
	2RBDS-1	3500	48	20	1.8	1	0.3	7.12	<0.01	0.307	11	7.1	<0.5	1.3
	2RBDS-2	3600	155	110	7.8	2.9	0.8	5.23	0.06	0.365	15	17	<0.5	0.9
	2RLA-1	5300	57	120	5.7	3.7	1.1	10.4	0.01	0.433	23	4.6	<0.5	1.7
	2LI-1	2500	187	180	15	4.2	0.7	13.2	0.25	0.53	14	7.1	0.6	1.2
	2LP-1	700	204	80	7.7	2.1	0.5	5.11	0.03	0.279	13	2.9	0.5	1.9
	2LLC-1	3500	162	260	13	13.3	2	27.5	0.1	1.22	25	0.9	<0.5	1.8
	2LPe-1	1000	122	120	8.7	9.3	1.1	42.4	0.03	0.815	14	0.5	<0.5	1.8
	2LA-1	3000	21	10	1	2.3	0.3	7.31	0.01	0.235	12	2.1	<0.5	0.9
	2LA-2	3400	147	160	11	4.9	1.7	7.95	0.06	0.554	22	3.2	<0.5	1.8
	2LV-1	5900	275	420	25	21.2	1.4	17.9	0.23	0.663	23	5.6	0.6	2.4
	2LD-1	4700	59	<10	1	0.7	0.1	5.47	<0.01	0.3	6.9	9	<0.5	0.8
	2LR-1	4800	88	50	6	2.2	0.4	7.09	0.05	0.423	14	9.9	<0.5	1.6
	2LL-1	5200	149	110	6.3	2.3	0.3	6.39	0.03	0.556	21	19	<0.5	0.9
	2LO-1	4700	383	280	18	8.6	1.1	10.4	0.04	0.527	16	24	<0.5	1.5
	2LT-1	4900	634	590	35	18.2	0.9	11.6	0.08	0.457	11	26	0.9	1.4

Island	Detection lmit	Y	Li	Ni	Pb	Ga	Th	Co	Cs	U	As	Mo	Sb	∑REE
		0.003	1	0.3	0.01	0.01	0.001	0.005	0.001	0.001	0.03	0.1	0.01	
	Sample	µg/L												
Marambio	1NBM-1	0.1	2	0.9	0.4	0	0.003	0.235	0.005	0.016	0.1	<0.1	0.01	1.441
	1LSe-1	0.1	865	35	0.6	0.1	0.005	1.09	0.06	6.55	2.1	0.9	0.2	1.07
	1LCh-1	0.5	278	29	1.2	0.2	0.021	22.1	0.033	1.03	1.4	0.3	0.08	7.088
	1LBl-1	0.1	5	1.1	1.1	0.1	0.007	0.556	0.012	0.033	0.2	0.3	<0.01	1.274
	1LSu-1	0.1	83	9.7	0.4	0	0.013	2.52	0.027	0.254	0.5	1	0.08	0.917
James Ross	1RV-1	0.1	4	1.3	2.5	0.2	0.018	0.263	0.033	0.053	0.3	0.3	<0.01	1.881
	1LV1-1	0	<1	<0.3	0.1	0	<0.001	0.034	0.001	0.005	0.1	0.2	<0.01	0.092
	1LV2-1	0	2	<0.3	0.3	0	<0.001	0.027	0.002	0.007	0.1	0.2	<0.01	0.14

Table 3 continued

Island	Detection	Y	Li	Ni	Pb	Ga	Th	Co	Cs	U	As	Mo	Sb	∑REE
	lmit	0.003	1	0.3	0.01	0.01	0.001	0.005	0.001	0.001	0.03	0.1	0.01	
	Sample	µg/L												
	1LV3-1	0.1	1	1.1	1.4	0.1	<0.001	0.163	0.011	0.017	0.1	0.2	<0.01	0.786
	1LV4-1	0	<1	<0.3	0.1	0	<0.001	0.012	<0.001	0.003	0	<0.1	<0.01	0.055
	1LA-1	0.4	55	5.3	6.2	0.2	0.033	2.83	0.02	0.336	1.1	0.3	0.05	2.469
	1LBlack-1	0.1	15	0.7	0.8	0	0.008	0.118	0.006	0.008	0.2	0.2	0.02	0.593
	1LCe-1	0.2	23	3.4	1.9	0.1	0.006	1.9	0.006	0.038	0.3	0.5	0.01	1.044
	1LB-1	0.4	246	31	1.6	0.1	0.01	3.64	0.05	0.115	1.5	<0.5	<0.05	1.925
	1LBa-1	0	7	0.4	0.2	0	<0.001	0.08	0.003	0.03	0.5	1.2	0.01	0.144
Vega	2NBD-1	0	4	<0.3	0.1	0	<0.001	0.037	0.002	0.003	0.1	<0.1	<0.01	0.132
	2NBD-2	0.1	<1	0.7	0.4	0	0.001	0.137	0.003	0.006	0.1	<0.1	<0.01	0.468
	2HFG-1	0.1	<1	1	0.4	0	0.002	0.109	0.007	0.005	0.2	<0.1	<0.01	0.417
	2RBDP-1	0.1	<1	0.4	0.3	0.2	0.013	0.164	0.017	0.016	0.8	0.3	<0.01	1.06
	2RBDP-2	0.4	3	1.1	0.4	0.3	0.051	0.531	0.071	0.04	1.6	0.4	0.04	4
	2RBDS-1	0	<1	<0.3	0.3	0.1	<0.001	0.029	0.002	0.028	0.8	0.4	<0.01	0.113
	2RBDS-2	0.1	<1	0.3	0.3	0.3	0.002	0.067	0.006	0.071	2.4	0.6	0.04	0.356
	2RLA-1	0	<1	0.5	0.3	0.1	<0.001	0.118	0.004	0.045	0.7	0.6	<0.01	0.232
	2LI-1	0.1	<1	0.5	0.1	0.1	<0.001	0.11	0.006	0.158	0.6	0.3	<0.01	0.317
	2LP-1	0	<1	0.4	0.2	0.1	<0.001	0.09	0.004	0.009	0.7	0.1	<0.01	0.219
	2LLC-1	0.1	3	1	0.3	0	0.021	0.242	0.008	0.044	0.6	0.6	0.06	0.594
	2LPe-1	0.1	2	1.1	0.2	0	0.01	0.152	0.007	0.057	0.8	0.5	0.09	0.315
	2LA-1	0	<1	<0.3	0.1	0	<0.001	0.029	0.006	0.015	0.5	1	<0.01	0.078
	2LA-2	0.1	<1	0.6	0.2	0.1	0.003	0.139	0.005	0.026	0.3	0.3	<0.01	0.339
	2LV-1	0.1	4	1.1	1.1	0.1	0.013	0.384	0.009	0.071	1.2	0.5	<0.01	0.797
	2LD-1	0	1	<0.3	0.1	0.2	<0.001	0.03	0.007	0.093	2.5	0.9	0.07	0.022
	2LR-1	0	1	0.7	0.2	0.2	0.001	0.058	0.009	0.1	3.2	1.2	0.13	0.123
	2LL-1	0	<1	0.3	0.1	0.3	0.002	0.088	0.005	0.121	2.9	0.6	0.08	0.154
	2LO-1	0.2	<1	0.9	0.2	0.2	0.008	0.305	0.004	0.132	2.7	0.4	0.1	0.731
	2LT-1	0.4	<1	0.8	0.1	0.4	0.007	0.427	0.005	0.154	2.7	0.5	0.09	1.477

SMI spidergram shows the most metal concentrated samples, whereas the snow presents normalized concentration very diluted, principally alkali and alkaline cations, and ultratrace elements (e.g., Ga, Th, Co, Cs, As). Spidergram from JRI shows a wider range of variation in all the elements.

Finally, two snow and 1 ice sample from VI were analyzed showing depleted concentration in most of the elements. However, Zn, Cu, and Li exhibit greater values than lake's water. This can be attributed to atmospheric dust contamination. After reaching surface, these elements would rapidly be adsorbed into lake's sediments.

Sediment analysis

Organic matter contents (expressed as TOC) in surface sediment samples, range between 0.3 and 8.9 % with a mean value of 2.4 % (Table 2; Fig. 5a). Maximum values are recorded in lakes from VI, ranging between 0.3 and 8.9 % (mean 2.9 %) while minimum values are observed in lakes from SMI ranging from 0.5 to 0.7 % (mean 0.6 %). Intermediate TOC values are recorded in JRI (1.3–3.4 %; mean 2.2 %). In particularly, the highest TOC values correspond to the lakes Verde, Olvidada, Terminal and La Cumpa (8.9, 4.0, 5.7, and 5.7 %, respectively; Table 2). Total inorganic carbon (TIC) contents are relatively low with values <1.0 % (between 0.1 and 0.7 %; mean: 0.4 %; Table 2). This is observed in Fig. 5a, where TIC and TOC values for sediment samples of the different islands are represented in a scatter diagram. SMI has the lowest values for both TIC, and TOC, while VI samples show a wide range of variation. JRI presents in general, intermediate values, with TOC values slightly higher than TIC. The proportions of TOC and TIC were lower than 10 %, therefore it is possible assume that the siliciclastic inorganic fraction (>90 %) is the main component of the sediments.

XRD results in Lake Blanca (Fig. 5b, c) shows the presence of clastic minerals (quartz, plagioclase, feldspars,

Fig. 2 Cyanobacterial and microbial mats in Lake Roja, JRI

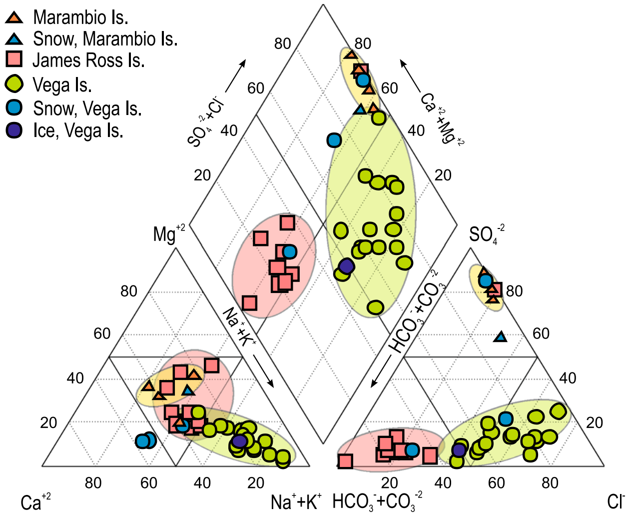

Fig. 3 Piper diagram, showing the major chemical composition of the samples, divided into different island

and micas). Moreover, Calcite ($CaCO_3$) and Thenardite (Na_2SO_4) were identified in the difractogram evidencing salt minerals precipitation.

Magnetic studies

Magnetic studies show that lake sediments from JRI and VI are dominated by ferrimagnetic minerals. In contrast, an important contribution of paramagnetic minerals is observed in lake sediments from SMI. Both kind of magnetic minerals are evident from hysteresis, IRM and thermomagnetic studies. In Fig. 6, the hysteresis curves show an important contribution of paramagnetic minerals for the SMI sample (para/diamagnetic contribution = 297 % at 1T, Lake Blanca), such paramagnetic contribution is higher than for VI sample (para/diamag. cont. = 36 % at 1T, Lake Anónima). In addition, clear differences in magnetic concentration are observed between samples, that is, $M_r = 0.4 \times 10^{-3}$ A m^2 kg^{-1} $M_s = 3.8 \times 10^{-3}$ A m^2 kg^{-1} (Lake Blanca) and $M_r = 47.8 \times 10^{-3}$ A m^2 kg^{-1}, $M_s = 154.3 \times 10^{-3}$ A m^2 kg^{-1} for VI sample (Lake Anónima).

On the other hand, the $M(T)$ curves show a similar behavior between sediments of James Ross and VI Islands: a main ferrimagnetic phase corresponding to magnetite (Tc = 580 °C) and other additional phases possibly corresponding to titanomagnetite/iron sulfides (Tc = 290 °C), goethite and hematite (Tc = 110 and 680 °C). These results are consistent with the H_{cr} values for lakes Buena, Roja, and Anónima, ranging between 38 and 82 mT.

Magnetic susceptibility is a concentration-dependent parameter that evidence magnetic mineral differences among lake sediments as observed in Fig. 6, i.e. mean χ values are higher for JRI and VI (43.7–104.1 $\times 10^{-8}$ m^3 kg^{-1}) than for SMI (7.2–26.6 $\times 10^{-8}$ m^3 kg^{-1}). These sediments not only show differences in magnetic concentration (χ), but also in their magnetic grain

Table 4 Particular trace element % speciation in Anctartic lakes

Element	Free aqueous ions			SO_4^{-2}			CO_3^{-2}		
	MI	JRI	VI	MI	JRI	VI	MI	JRI	VI
Ca	**59.00**	**94.90**	**92.24**	**40.14**	0.32	1.57	0.27	4.25	5.97
Co	**70.66**	**67.52**	**49.50**	**22.59**	0.08	0.26	2.52	7.62	2.39
Cu (2)	3.29	18.08	16.84	2.17	0.04	0.17	**75.22**	**48.03**	**26.44**
Mg	**63.95**	**96.54**	**94.15**	**35.39**	0.27	1.31	0.17	2.48	3.48
Mn (2)	**77.54**	**96.90**	**92.12**	**21.46**	0.25	1.16	0.00	0.00	0.00
Pb	4.96	20.68	18.29	8.16	0.10	0.49	**57.92**	**39.82**	**19.19**
Sr	**65.24**	**97.50**	**95.90**	**34.10**	0.29	1.42	0.11	1.78	2.47
Zn	**42.72**	**63.23**	**48.09**	**27.99**	0.11	0.49	9.54	5.20	1.13

Values in bold show the dominant species of the different elements. The remaining % correspond to less concentrated species

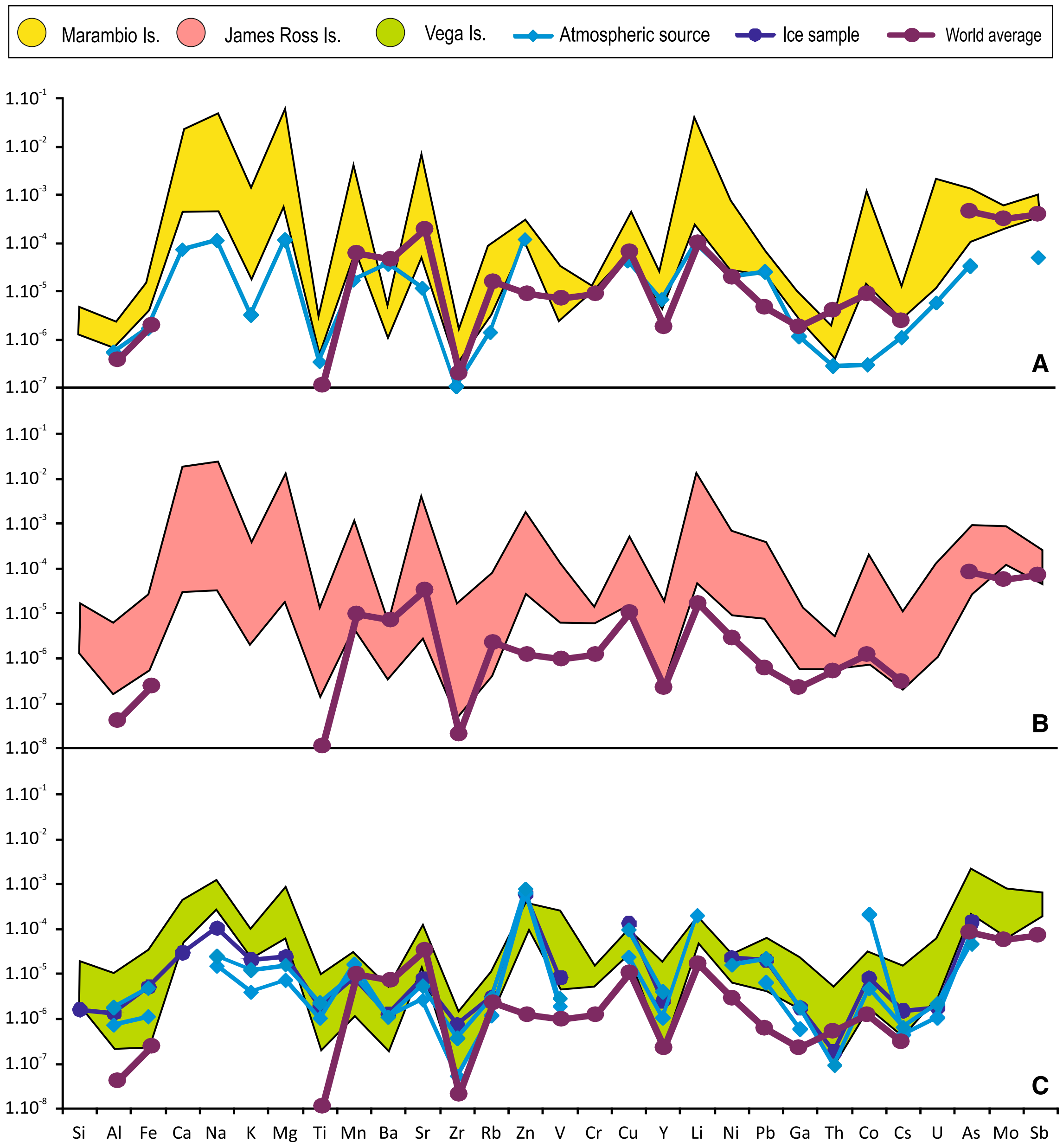

Fig. 4 Spiderdiagram showing trace dissolved composition normalized to upper continental crusts (McLennan 2001). The order of element on the *x*-axis is UCC abundance. It is included world average concentration (Gaillardet et al. 2003)

distribution (~0.1–5 μm). The κ_{ARM}/κ is a grain size dependent parameter, values about 5 and higher are indicative of the presence of very small magnetite grains (Peters and Dekkers 2003). Sediments from JRI and VI have the highest κ_{ARM}/κ values (mean values between 4.8 and 8.6, Fig. 6). Higher magnetic concentration is related to finer magnetite grains (<0.1 μm) according to the linear relationship between κ_{ARM}/κ and χ (Chaparro et al. 2014). On the contrary, an inverse linear relationship is observed for SMI where mean κ_{ARM}/κ values are below 5 (mean values between 1.7 and 3.8).

Statistical multivariate analysis

Sediment results (TIC-TOC and magnetic values) were statically analyzed, comparing them with dissolved elements and with each other. However, no statistically significant correlation was found. For that reason, multivariate statistics was applied only to water geochemical data to analyze the relationship between different variables. The PCA results show that 3 principal components (PCs) accounted for ~75 % of the total variance (Fig. 7a). The relationship between the variables was studied in relation

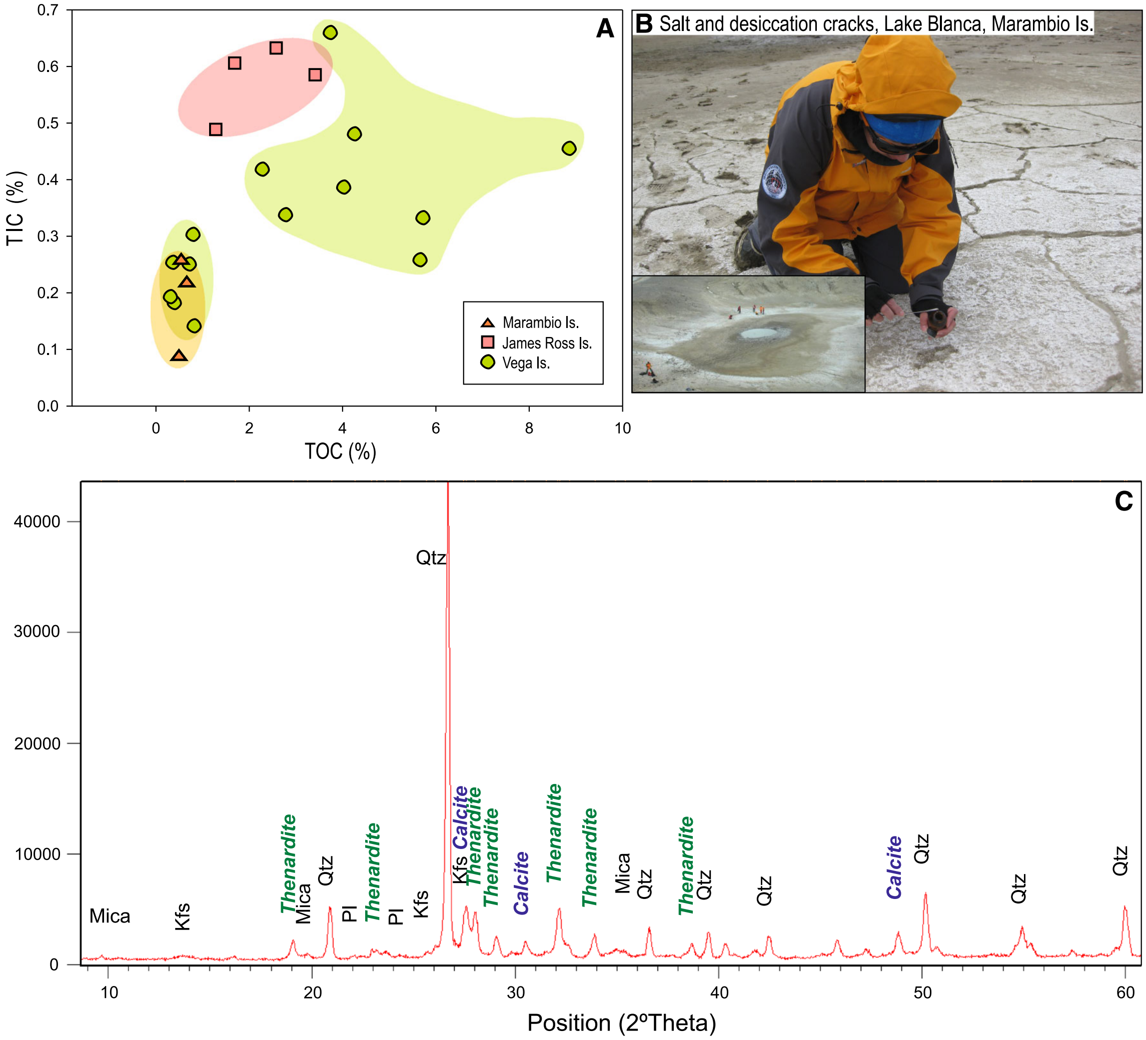

Fig. 5 **a** Total organic carbon (TOC, wt%) vs total inorganic carbon (TIC, wt%) percentages in bottom lake-sediment samples from SMI, JRI, and VI, **b** *desiccation cracks* evidencing evaporation process (*Lake Blanca*, SMI), and **c** XRD diagram showing precipitated minerals together with detrital (*Lake Blanca*, SMI)

to the values of correlation with the PC's. From these values, 3 groups of variables were observed:

1. (SO_4^{-2}+Cl^-) + Ni + Rb + (Mg+ K +Ca + Na) + Conductivity + Sr.
2. Fe + Al + Ti.
3. Mn + Co + Alkalinity + $\sum$LREE + Y + Ba + Cu.

The first group comprises those elements that are mainly controlled by seasonal actions called high-rate processes, whereas groups 2 and 3 represent trace elements from mineral weathering (low-rate process).

Based on the five PCs obtained, a CA was performed identifying 7 lake groups, shown in Table 5. Results are also shown in Fig. 7b, where samples grouped according to statistical significance in 7 groups named C1–C7. The analysis highlights that SMI lakes present outliers in major elements and the conductivity variable. These lakes, in particular, showed higher values in their measurements in relation to the global average. Blanca and Sucia lakes (C1, Fig. 7b) present values up to 5 times higher than the global mean in Ca and conductivity. Lake Seca (C4) presents outliers in every major and physicochemical variable, whereas in Lake Chica (C5) some trace and major elements were observed as outliers. These last lakes have particular characteristics that make each of them to represent an own group.

In contrast to SMI which present dissolved concentration above the global average values, there are no predominance between JRI and VI. Their values are close to the average. Most of the lakes from these two islands belong to C2 and C3, except for lakes Buena, Azul and a river sample (Stream 1, Fig. 7; Table 5). C2 samples show Ti values above-average, being the only variable that differentiates the group from the global average. C3 has

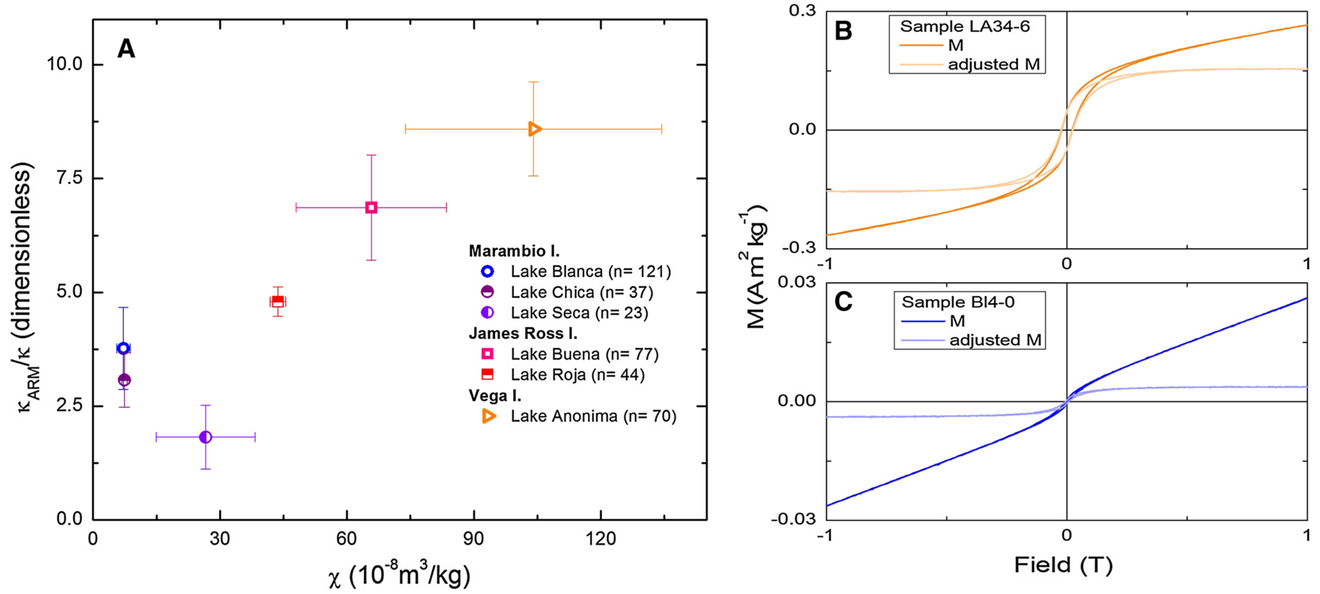

Fig. 6 **a** Biplot κ_{ARM}/κ and χ for seven lakes from *James Ross* archipelago. Mean and standard deviation (*bars*) values for each lake are represented. Hysteresis measurements of sediments from: **b** Lake Anónima (VI) and **c** *Lake Blanca* (SMI)

differences in global average from some trace elements, due to their value that is below the global average. It is noteworthy that the Lake Buena (JRI) is the only one which presents similar values to those of SMI lakes.

Discussion and interpretation

The JRA includes several hydrological systems that have developed under different conditions and diverse processes. Individual islands can be recognized by applying multivariate methods to geochemical data, showing that these systems are unique and valuable for the future monitoring of biological and hydrological responses to climate change. Therefore, the integrated analyses of water chemistry and sediment composition (TOC, TIC, and magnetic properties) of the JRA can provide important information for the interpretation of dynamics and processes on lakes.

Dissolved element sources and geochemical processes

According to kinetics, most physicochemical and biological processes occur during summer time, indicating a higher speed of development than geochemical processes (as weathering), which take place in long terms. Differences in the dissolved fraction of each island can be attributed to the sources and the kinetics of the main processes taking place in the lakes.

Lake samples are consistent in general with snow and ice collected in each island, suggesting that not only atmospheric influence, but also ice melting as hydrochemical source. In SMI, Silva Busso et al. (2000) reported similar results of pH, electrical conductivity and water classification of superficial streams as those presented here for lakes. The analyses suggest besides from the influence of the unconfined aquifer (suprapermafrost melting), marine sources on the atmospheric precipitation; dissolution of sediment salts in sedimentary rocks and significant evaporation processes. The latter process resulted in the highest major dissolved concentration and salt precipitation, which was verified in the field by desiccation cracks and also by XRD analysis (Thenardite and Calcite). Saturation index (SI) were calculated in lake samples showing the presence of supersaturated minerals (e.g., calcite, dolomite, gypsum) from lakes Seca and Blanca (SMI) with SI values up to 2, reinforcing the idea of evaporation process and high concentrated permafrost water source. Same results were predicted by Timperley (1997), whereas Healy et al. (2006) have demonstrated gypsum and thenardite precipitation from solution during winter time. In contrast, most minerals are undersaturated (SI < 1) in lakes from VI and JRI, therefore its precipitation is unexpected.

The dissolved trace elements were compared with those reported by Gaillardet et al. (2003), who reviewed the current knowledge of trace elements in rivers. Although they focused on studies of natural hydrosystems and compiled information from continents over the world, they do not include data from Antarctica. Samples show

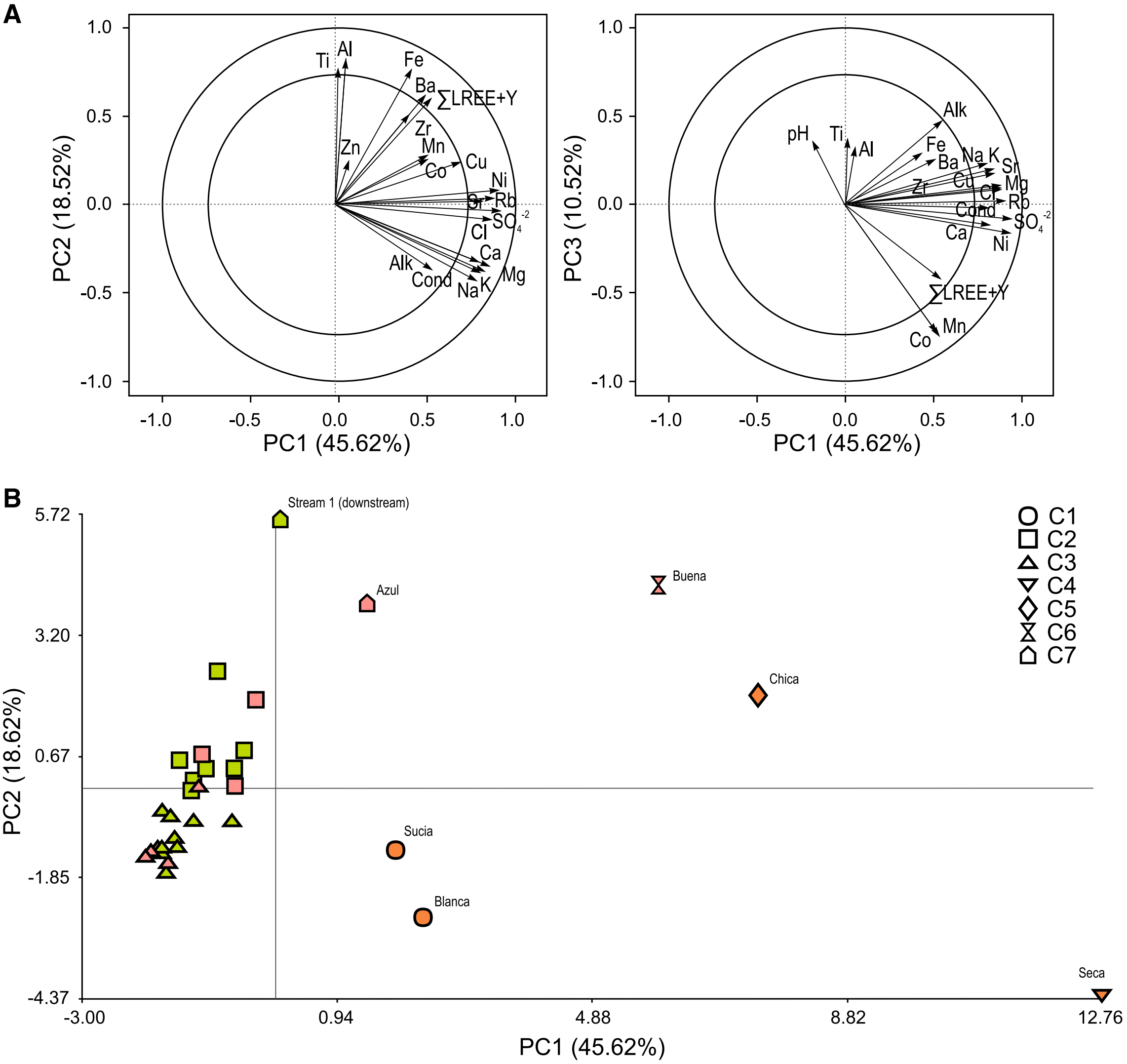

Fig. 7 Principal component analysis (PCA) of lake samples from James Ross archipelago. **a** PCA for variables, **b** PCA for individuals in the plane of the first principal components (*PC1* and *PC2*). Different groupings are observed. *Orange samples* represent SMI, *green samples* are from VI whereas *pink samples* represent JRI

concentrations in a normal range of pristine waters. However, there are several complex factors controlling the concentration of dissolved trace elements, whether natural or anthropogenic. The geochemical signals of pristine waters are similar in relation to the more concentrated element and those which present a more conservative behavior (e.g., Gaillardet et al. 2003; Lecomte 2006; Lecomte et al. 2008; Pasquini et al. 2004). Following the solubility of minerals, and also their abundance in the outcropping rocks, the trace elements that present the highest normalized concentrations in this study (i.e., $\mathrm{ppm_{sample}}$: $\mathrm{ppm_{UCC}} > 10^{-4}$) are the most labile elements in the weathering processes (such as Ca, Na, K, Mg, Sr, Li, U, As, Mo, and Sb). Some of these elements (Ca, K, Sr) are soluble large cations, known as "large ion litophile" or LIL elements (ionic potential $<40\ \mathrm{nm^{-1}}$), whereas others are transition metals and high-field strength (HFS) elements (Hofmann 1988; Patchett et al. 1984). Those that exhibit $\mathrm{ppm_{sample}}$: $\mathrm{ppm_{UCC}} < 10^{-6}$ at Antarctic systems are Al, Fe, Ti, Zr, and Th, reflecting their low mobility in the Earth's surface. Most of these elements are very insoluble, and correspond to the HFS group, which are small, highly charged cations (ionic potential $\geq 40\ \mathrm{nm^{-1}}$). All the remaining elements fall within the 10^{-6} to 10^{-4} concentration range.

Besides some minor departures, the similarity among patterns suggests concentrations in these Antarctic environments are governed by mineral solubility, with a probable second-order control imposed by sorption processes (Gaillardet et al. 2003), as well as from atmospheric

Table 5 Statistical values for each lake's cluster using CA

	V test	Mean in group	Mean overall	*p* value
C1: Blanca, Sucia				
Cond	2.68	5440.00	1002.46	<0.05
Ca	2.62	402.00	73.59	<0.05
C2: Verde River, Vondra 3, Cecil,Anónima, Incierta, Verde, Olvidada, Terminal, La Cumpa, Stream 1 (upstream)				
Ti	2.01	0.0169	0.011	<0.05
C3: Vondra 1, Vondra 2, Vondra 4, Black, Roja, Anónima, Anónima Stream, Larga, Del Costado, Rugosa, Pequeña, Peinada, Stream 2 (upstream), Stream 2 (downstream)				
Ni	−2.02	0.0004	0.004	<0.05
Rb	−2.16	0.0003	0.001	<0.05
Cu	−2.47	0.0013	0.003	<0.05
$\sum$REE+Y	−2.83	0.0002	0.001	<0.05
Al	−3.01	0.0772	0.190	<0.05
Ti	−3.18	0.0040	0.011	<0.05
Fe	−3.47	0.0607	0.245	<0.05
Ba	−3.62	0.0005	0.001	<0.05
C4: Seca				
K	5.15	40.200	3.158	<0.05
Mg	5.00	786.00	48.72	<0.05
Na	4.66	1290.00	109.20	<0.05
Cl	4.11	899.98	95.32	<0.05
SO_4^{-2}	3.88	5512.65	471.38	<0.05
Cond	3.86	10190.00	1002.46	<0.05
Sr	3.73	1.0000	0.090	<0.05
Rb	3.60	0.0103	0.001	<0.05
Ca	3.52	707.00	73.59	<0.05
Ni	3.34	0.0345	0.004	<0.05
Alk	3.32	167.40	45.73	<0.05
Cu	2.88	0.0103	0.003	<0.05
C5: Chica				
Co	5.33	0.0221	0.001	<0.05
Mn	5.22	2.7600	0.154	<0.05
$\sum$REE+Y	4.35	0.0072	0.001	<0.05
Ni	2.70	0.0287	0.004	<0.05
Ca	2.59	540.00	73.59	<0.05
SO_4^{-2}	2.16	3281.74	471.38	<0.05
Cond	2.02	5810.00	1002.46	<0.05
C6: Buena				
Zr	5.28	0.0029	0.000	<0.05
Sr	3.73	1.0000	0.090	<0.05
Rb	2.98	0.0088	0.001	<0.05
Ni	2.90	0.0305	0.004	<0.05
Cl	2.86	653.92	95.32	<0.05
SO_4^{-2}	2.68	3958.17	471.38	<0.05
Fe	2.41	0.8800	0.245	<0.05
C7: Azul, Stream 1 (downstream)				
Ti	4.05	0.0421	0.011	<0.05
Al	3.64	0.6610	0.190	<0.05

Table 5 continued

	V test	Mean in group	Mean overall	*p* value
Fe	3.16	0.8250	0.245	<0.05
Ba	2.54	0.0025	0.001	<0.05
$\sum$REE+Y	2.31	0.0033	0.001	<0.05
Cu	2.10	0.0065	0.003	<0.05

Cond conductivity, *alk* alkalinity, $\sum REE+Y$ sum of rare earth element plus *Y*

precipitation and ice/snow melting from glacier and permafrost. Here again, the elements that are more concentrated in snow and ice than in lakes and river water are from the transitional group, presenting a high affinity for colloidal particles. In the acid pH range, these elements are more concentrated in solution, which is the case for ice and snow (pH ~6), and as pH increases, these metals are adsorbed onto surfaces (e.g. colloids, organic matter, clays) decreasing their concentration in solution.

The chemical weathering of rocks results in the release of the most soluble elements. The less mobile elements remain in the regolith produced by the incongruent weathering of silicate rocks. There are some elements which evidence a clear lithological source. In SMI, lakes Seca, and Chica (statistical groups C4 and C5, respectively) present relatively high heavy metal concentration (e.g., Fe, Zn, Ni, Cu) in relation with other SMI lakes, these metals are good tracers of particular lithology influence. Some authors associate them with black shale weathering (e.g., Gaillardet et al. 2003 and references therein).

In VI, lakes Incierta and Pequeña (samples 2LI-1 and 2LP-1) are characterized by having low trace element concentration, due to the nearby glacier melting influence and insignificant rock weathering. Moreover, a group of chained-lakes (samples 2LV-1, 2LD-1, 2LR-1, 2LL-1, 2LO-1, and 2LT-1, Fig. 1C3) receive waters probably influenced by volcanic rocks' weathering due to their relatively high arsenic concentration, whereas the rest of VI lakes do not. It is evident that there is a need to study regional mineralogy to evaluate relationships between mineralogy and dissolved element concentrations.

Sediment analyses and relationships with geochemistry

A predominant composition of siliciclastic fraction (>90 %) was observed in the surface sediment samples, due to the low organic matter component (expressed as TOC) and carbonic fraction (TIC). Carbon is an important component in lake sediments, and is composed of both, organic and inorganic fractions. It is able of recording valuable environmental information, though these same characteristics can cause some additional difficulties in interpretation (e.g., autochthonous vs allochthonous sources). Allochthonous carbonates are produced by physical erosion of outcropping rocks in the drainage basin, which are then transported into the lake. Autochthonous carbonates include those materials generated from inorganic precipitation, and/or biogenic activity. The TIC analysis shows a carbonate fraction present in all sediment samples, though in low amounts (<1 %).

In SMI, inorganic carbon sources seem to be allochthonous due to sedimentary rocks and autochthonous due to salt precipitation. Whereas, in JRI and in VI the low TIC abundance for the bottom sediments is attributed to allochthonous clastic input via tributaries, but in VI, inorganic carbon could also come from carbonate shells of organisms from the fossiliferous calcareous concretions.

Organic matter constitutes a minor but important fraction of lakes bottom sediments. Samples with nitrite and nitrate content >0.25 mg L^{-1}, and also those with high pH are consistent with relatively high content of TOC in sediments as a result of high presence of microbial mats. Higher TOC values correspond to lakes with higher water residence time that allows the presence of biological communities. Something peculiar is that microbial and cyanobacterial mats in SMI seem to be inhibited, agreeing with very low TOC values.

Within VI samples, 2 groups can be indentified: <2 % TOC and >2 % TOC. The first group is composed by those river samples and lakes that are fed mostly by glacial meltwater (e.g., 2RBDP-1, 2RBDP-2, 2LI-1, 2LP-1), with low residence time and low nutrients amounts, inhibiting organic development. The second one, correspond to lakes located in an area with lower slopes, enhancing water residence time and allowing biological communities increase (e.g., 2LLC-1, 2LL-1, 2LO-1, 2LT-1).

Although significant statistical correlations between carbon contents in sediments, magnetic parameters and dissolved element concentrations were not found, the SMI chemical characteristics that were explained, are consistent with the lowest values of TOC and magnetic susceptibility (among other concentration-dependent magnetic parameters) found in the sediments. Magnetic properties reveal differences in magnetic mineralogy and concentration that can be related to the individual basin and lake's environment characteristics, and the chemical processes occurring in each lake. Different detrital (lithogenic) components are expected for each island because lakes are located on tertiary sedimentary rocks, mainly sandstones and shales (SMI) and on glacial-marine sediments with abundant volcanic rocks of basaltic composition (JRI and VI). According to the preliminary magnetic studies on rocks reported by Chaparro (2006), distinctive results between rocks showed higher magnetic susceptibility values for volcanic ($\kappa = 590 \times 10^{-5}$ SI) than for sedimentary rocks ($\kappa = 20 \times 10^{-5}$ SI). On the other hand, additional magnetic components, such as iron sulfides/oxides and fine single domain (SD, biogenic) magnetite, seem to be produced by diagenesis and the activity of algal and cyanobacterial communities, which may also explain the JRI and VI higher values of TOC, magnetic grain size and concentration-dependent parameters (i.e.: κ_{ARM}/κ and χ).

Conclusions

The present multidisciplinary study contributes to a better understanding of different lake systems located on the James Ross Archipelago, in the Antarctic Peninsula. The results allowed a characterization and examination of different lake types throughout their physical, chemical, and magnetic attributes. JRI, VI, and SMI show statistical geochemical differences. MI lakes are circumneutral and highly concentrated waters; they are shallow ponds and suffer high-rates processes as evaporation -and consequently salt precipitation- due to their position in the mesa and the absence of sunlight geomorphological barriers, increasing dissolved chemical concentrations. The deficit of biological activity was observed in the low TOC values. On the other hand, lakes from JRI and VI present alkaline and diluted waters, reflecting—in their major composition—the atmospheric signal as one of the sources.

Different rock mineralogy' sources correspond to particular magnetic and chemical properties between the islands. Trace elements are introduced in the dissolved fraction by low-rate processes (i.e., rock weathering), and high-rate processes (i.e., atmospheric dry and wet deposition and by glacier and permafrost melting). Thereby, the preferential mineral dissolution causes variations in trace-element abundances.

Antarctic hydrological systems show a particular behavior, as they are paralyzed most part of the year due to extreme low temperatures (below freezing point). During the short austral summer, they became active and different processes take place and interact between each other. Some of them act with a higher speed whereas others continue with their low kinetics. Processes such as atmospheric precipitation, glacial and permafrost melting, evaporation, salt precipitation and biological activities, can be considered high-rate processes in terms of time and intensity, while mineral weathering represent the low-rate processes. This causes modifications in the chemical composition of waters: trace elements show little variation during a summer showing a more constant behavior and local mineralogy characteristics, as low-rate mineral weathering is the main source; while major elements concentration can be greatly modified during summer, as a consequence of high-rate processes.

The results of this integrated study of James Ross Archipelago's hydrological systems provide insights into the sources and geochemical processes in pristine lakes and ponds located in high-latitudes, where recent climate changes have impacted stronger than in the rest of the world. Furthermore, these results will contribute to the base line information for the ongoing palaeolimnological studies of long sediment cores collected from these lakes, as well as contributing to the knowledge of the environmental and climatic history in the Antarctic Peninsula. Additional scrutiny and follow-up research will be required before a complete model of biogeochemical dynamics of Antarctic hydrological systems can be achieved.

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