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Geochemistry of the Lake Sediments on Robert Island, South Shetland Islands, Antarctica: implications for weathering processes in Polar areas

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Abstract: The preliminary results of geochemical analyses of the surface sediments from 4 lakes on Robert Island, South Shetland, Antarctica, are presented herein. The samples were collected during the Turkish Antarctic Expedition (TAE-II) in 2018. Sediment samples were obtained from the littoral zone (approximately 20 cm) of 4 different lakes exposed on the glacier-free land area on Robert Island. The lake sediments predominantly consist of fine-grained sand, clay, and silt particles. These particles include Fe-shale and graywacke geochemical characteristics. Their plagioclase index of alteration, chemical index of weathering, chemical index of alteration, and other weathering index values, suggest that the studied sediments have likely undergone low to moderate weathering and alteration processes. The Th/U ratios generally indicated a lower distribution relatively to the upper continental crust, and they displayed slight enrichment in alkali elements, indicating a low degree of chemical weathering that has slightly influenced the sediment chemistry. Moreover, the Gd/Yb, Zr/Y, and La/Yb ratios exhibited similarities with the surrounding volcanic rocks on Robert Island. Additionally, their chondrite-normalized rare earth element (REE) patterns exhibited a similar trend, implying that the REE composition of the sediments is predominantly controlled by the local source rocks. Nevertheless, there were slight differences in the Y/Ho ratios and heavy REE (HREE) contents, suggesting the presence of additional sources contributing to the REE supply in the lake basins. The Co/Th, La/Sc, Th/Sc, and Zr/Sc ratios mostly resembled those of basic volcanic rocks, while the Rb, K, HREE, and Ni values dominantly indicated basic rocks with a minor input from felsic magmatic or quartzose sedimentary rocks. Considering the geomorphology and location of the basins, which are mostly situated along the coast where foehn winds have a limited influence over ice-free areas, it is likely that locally resuspended materials have had a significant impact. This factor may mask any potential signals of modern dust fallout and accumulation. However, possible dust sources include nearby or distant areas, such as exposed rock and sediment within the immediate vicinity of the lakes, including dry lakebeds, glacial outwash plains, or exposed moraines. Based on multiproxy element analyses, including REEs, high field strength elements, and lithophile elements, the geochemistry of the studied sediments, the overall geochemical characteristics cannot be fully explained by the local sources, suggesting that weathering processes and minor contributions from dust materials have played a nonnegligible role in shaping their chemistry.

Key words: Antarctic Peninsula, Robert Island, lake sediments, REE, trace element

1. Introduction

Continental weathering is a significant geological process that has a significant role in shaping the Earth's surface (Berner and Cochran, 1998; Singh and Rajamani, 2001). It involves the chemical and physical alteration of rocks, which in turn affects the cycling of elements in the environment. The severity of weathering is controlled by various climate factors such as temperature, runoff, precipitation, other environmental conditions, and erosion rates (Limmer et al., 2012; Liu et al., 2020). The rates of weathering and erosion are strongly influenced by climate, as they tend to be higher in warm and humid environments. In regions with low and moderate latitudes, intensified chemical weathering is connected to increased sediment discharge and substantial physical alteration and erosion during warmer interglacial periods (Xu et al., 2018). Conversely, decreased chemical weathering is associated with reduced sediment discharge and milder physical alteration and erosion during colder glacial periods (Hu et al., 2013).

In polar areas, the rate and intensity of physical weathering processes are affected by the characteristics of the bedrock and the severity of the climate (Pereira et al., 2018; Ruiz-Pereira et al., 2022). These processes, including

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subcritical cracking, can lead to increased mechanical weathering rates under changing climates. For instance, studies have shown that microclimatic conditions, such as frost shattering and thermal stress, play a dominant role in controlling weathering in polar regions (Eppes et al., 2018). In contrast, it was initially believed that chemical weathering was not an active process in extremely cold and dry polar environments. In the past, chemical weathering was not considered a significant factor in causing substantial changes in the overall composition of rocks and sediment (Kelly and Zumberge, 1961). Numerous researchers have provided advancements in our knowledge of subglacial and glacial landscapes (Tranter, 2004; Keller et al., 2007; Wadham et al., 2010; Deuerling et al., 2018). It has been proposed that chemical weathering in Arctic regions with permafrost is seasonal but regnant (Tranter, 2004; Keller et al., 2007; Tang et al., 2012). The freezing and thawing of host rocks in permafrost regions contribute to mechanical breakdown, contributing to their disintegration, and mineral alteration. These sedimentary processes may indirectly affect the release of chemical constituents through mineral dissolution and alter the geochemical characteristics of the host rocks. The emphasized chemical weathering models that rely on temperature as the main driving factor significantly underestimate the number of dissolved compounds and elements (Hartman et al., 2018). Thus, our understanding of weathering processes in polar regions has evolved over the last two decades (Shrivastava et al., 2012; Deuerling et al., 2018; Kumar et al., 2021; Lyons et al., 2021).

Antarctic lakes and their catchments exhibit unique characteristics, including extremely low temperatures, frequent freeze-thaw cycles, and excessive seasonality (Choudhary et al., 2018). In comparison to freshwater lakes in other regions, Antarctic lakes undergo distinct physical, chemical, and biological processes due to the prolonged duration of polar days and nights (Elliott, 2006; Alfonso et al., 2015). These factors make them highly sensitive to microclimate and environmental changes, as well as good archives for sedimentary processes (Phartiyal et al., 2011; Oliva and Ruiz-Fernández, 2015). As a result, these lake sediments have the potential to serve as valuable paleo archives for weathering processes that sediment experiences and their source rock lithology (Phartiyal et al., 2011; Mahesh et al., 2015; Hernández et al., 2018).

Lake sediments situated on Robert Island, within the South Shetland Islands, were studied for their geochemical characteristics (Antarctica, Figure 1a). The recent sediment accumulated in the lakes may provide important implications for source-to-sink processes under extremely cold and arid conditions. Thus, the aims of this study were to 1) investigate the chemical characteristics of the lake sediments on Robert Island, 2) examine the degree of weathering/alteration processes that these sediments might probably experience, 3) determine the source rock lithology (or lithologies), and 4) discuss the sedimentary factors controlling the general chemistry of the lake sediments on Robert Island.

2. Geological background

The South Shetland Archipelago extends approximately 300 km in a northeast direction parallel to the northern Antarctic Peninsula. It is segregated from the Antarctic Peninsula by the Bransfield backarc marginal basin to the east (Haase et al., 2012; Figure 1a). These islands are located on a crustal plate and are limited to the west by an oceanic trench zone where subduction has ceased (Barker and Griffiths, 1972). Barker (1982) also indicated that subduction of the Pacific oceanic lithosphere beneath the Antarctic Peninsula began approximately 200 million years ago.

The South Shetland Islands are predominantly composed of Mesozoic to Cenozoic volcanic rocks and associated volcanoclastics (Figure 1b). These volcanic rocks are underlain by a sialic basement consisting of schist and deformed sedimentary rocks (Smellie et al., 1984; Leat et al., 1995; Haase et al., 2012). Robert Island, a part of the South Shetland Archipelago, hosts a wide range of volcanoclastic rocks in its glacier-free zone, initially identified as the Coppermine Formation (Machado et al., 2005). These rocks include basaltic andesites, olivine-bearing basalt, polymict lapillistones, and agglomerates intercalated by andesite and basaltic andesite (Machado et al., 2005) (Figure 1b). Additionally, younger basaltic rocks have been reported in the area (Smellie et al., 1984; Machado et al., 2005; Haase et al., 2012).

3. Materials and methods

A geological and limnological study was conducted as part of the second Turkish Antarctic Expedition (TAE-II) in March–April 2018. Samples were collected from litoral sediments of lakes in the glacier-free land area on Robert Island, South Shetland Islands (Figure 2). The studied lake environments included a glacier lake (L1) and 3 coastal lakes (L2, L3, and L4) (Figures 2a–2d). The lakes exhibited a range of physical parameters that have contributed to their unique characteristics. L1, the largest among them, boasts a depth of 1.5 m and spans an area of 11,961 m^2 (Figure 2b). L2, in contrast, is relatively shallow at 0.3 m but covers a significant area of 8431 m^2 (Figure 2c). L3, another notable lake, has a depth of 0.8 m and occupies 6379 m^2 (Figure 2d). Finally, L4 stands out with its depth of 1.1 m and an expansive surface area of 11,578 m^2 (Figure 2d). Instead of sampling from the bottom surface of the lakes, the surface sediment samples (0–10 cm) were taken from the littoral zone (water depth of ca. 20 cm), a specific depth below

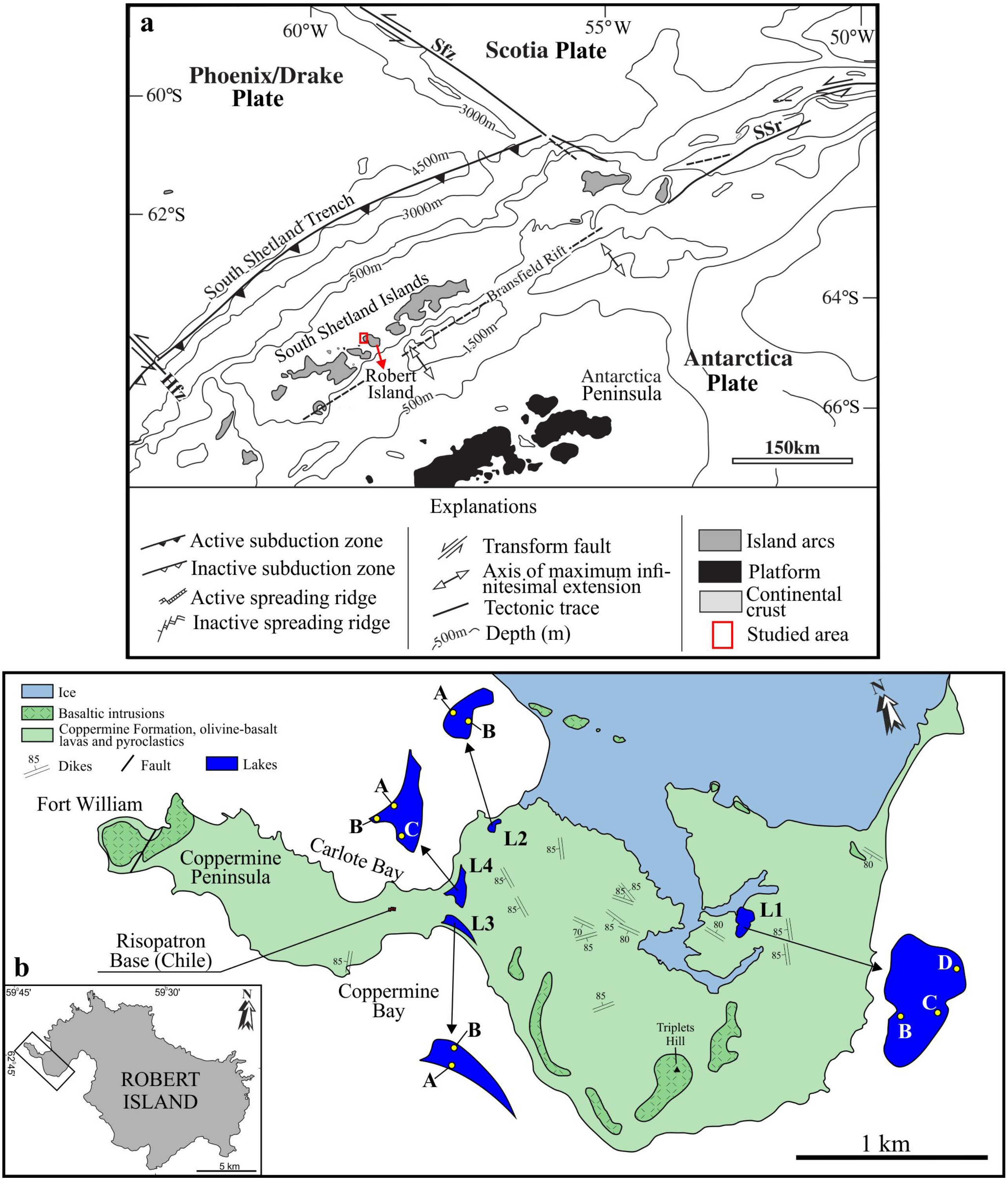

Figure 1. a) Tectonic setting of the South Shetland Islands (Machado et al., 2005), b) geological map of the area around the studied lakes on Robert Island (modified from Smellie et al., 1984 and Machado et al., 2005) and sample locations on the lakes.

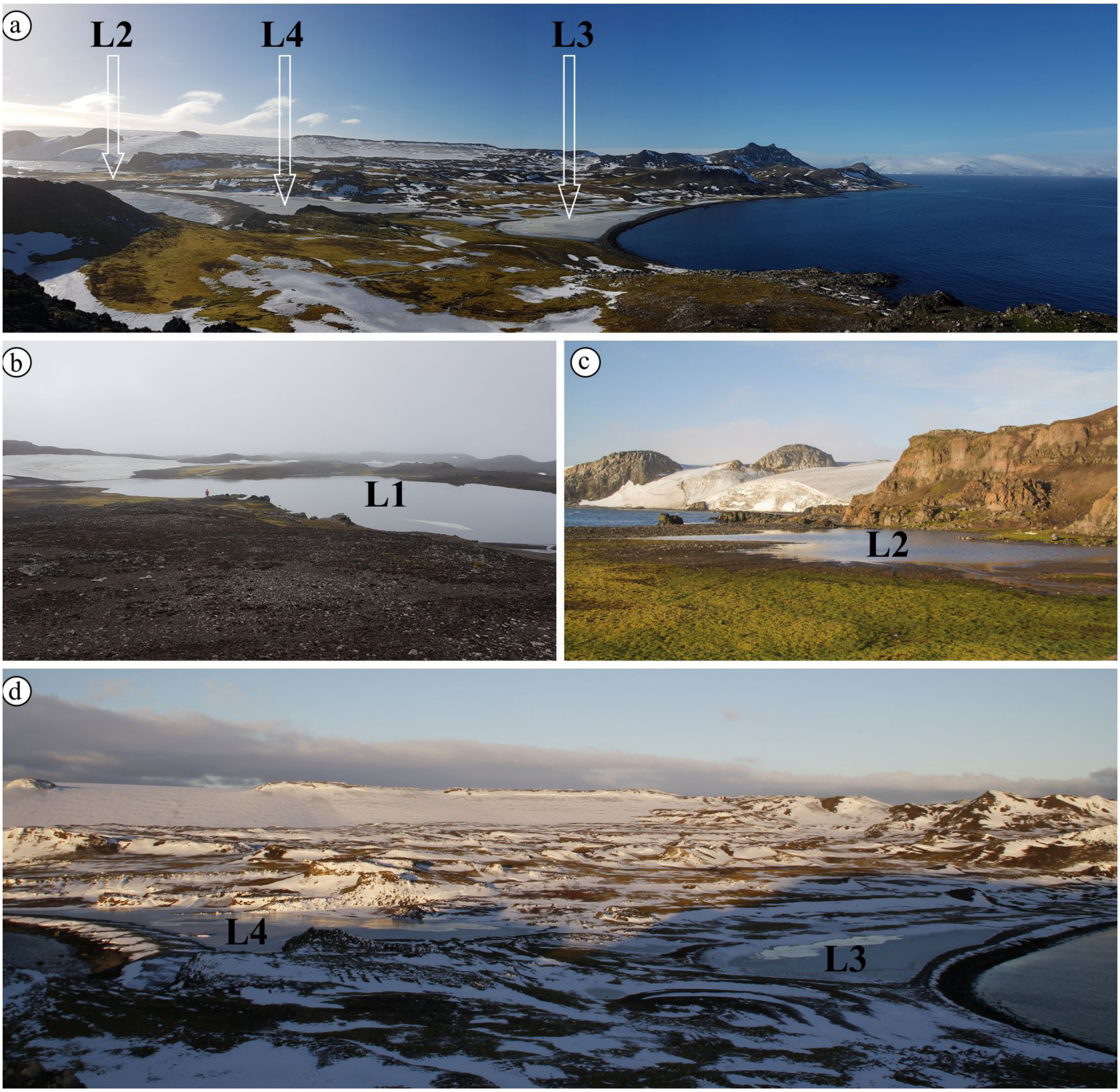

Figure 2. Field images of the studied lakes (L1, L2, L3, and L4: numbers for the sampled lakes), a) general view of the Coppermine Peninsula and L2, L3, and L4 lakes, b) view of the L1 glacier lake, c) close view of the L2 lake, d) general view of the L3 and L4 coastal lakes.

the surface, using a sterile plastic sampling spoon. The glacial lake, L1 had ultraoligotrophic conditions (< 1 μg/L PO_4 and < 50 μg/L total inorganic nitrogen) and very low specific conductivity (115 μS/cm). Coastal lakes (L2–L4) had more elevated nutrient concentrations (8–19 μg/L PO_4 and 120–635 μg/L total inorganic nitrogen) and specific conductivities (238–735 μS/cm), reflecting the effect of the sea. Detailed information on the physicochemical characteristics of the lakes was reported previously by Özkan (2023). Special measures were taken to preserve the cold-chain during the transportation of the samples. The samples primarily consisted of fine-grained sand, clay, and silt-sized particles with diverse petrographic compositions.

Ten samples were selected to analyze the major, trace, and rare earth elements (REEs) at the Applied Conservation Macro Ecology analytical laboratory in Vancouver, Canada. The major elements in the samples were analyzed using inductively coupled plasma (ICP) optical emission spectroscopy. For this analysis, 0.2 g of powder, crushed to a grain size smaller than 200 mesh, was fused with 0.5 g of $LiBO_2$. The trace elements and REEs were analyzed using ICP mass spectrometry after dissolving 0.2 g of powder through a 4-acid digestion process. Analytical precision was determined based on replicated analyses, and the detection limits were found to be 0.001 wt% for the major oxides, 1 ppm for trace elements, and 0.5 ppm for REEs.

The chemical index of alteration (CIA), plagioclase index of alteration (PIA), and chemical index of weathering (CIW) were calculated using Eqs. (1)–(3) below (Nesbitt and Young, 1984; Harnois, 1988; Fedo et al., 1995):

$$CIA = (100)\ [Al_2O_3 / (Al_2O_3 + CaO^* + Na_2O + K_2O)] \quad (1)$$

$$PIA = (100)\ [(Al_2O_3 - K_2O) / (Al_2O_3 + CaO^* + Na_2O + K_2O)] \quad (2)$$

$$CIW = (100)\ [Al_2O_3 / (Al_2O_3 + CaO^* + Na_2O)] \quad (3)$$

Here, CaO* is the amount of CaO incorporated in the silicate fraction of the rock (after Taylor and McLennan 1985).

The normalization values were chondrite and the upper continental crust (UCC) (after Taylor and McLennan 1985).

The discrimination functions (after Roser and Korsch, 1988) are given in Eqs. (4) and (5) below:

$$F1\ (F1 = -1.773TiO_2 + 0.607Al_2O_3 + 0.76Fe_2O_3(total) -1.5MgO + 0.616CaO + 0.509Na_2O - 1.224K_2O - 9.09). \quad (4)$$

$$F2\ (F2 = 0.445TiO_2 + 0.07Al_2O_3 - 0.25Fe_2O_3(total) + 1.142MgO + 0.438CaO + 1.47Na_2O + 1.426K_2O - 6.861). \quad (5)$$

The La/La*, Pr/Pr*, Ce/Ce* and Eu/Eu* values were calculated using Eqs. (6)–(9) below:

$$La/La^* = LaN / (3PrN - 2NdN), \quad (6)$$

$$Pr/Pr^* = PrN / (0.5CeN + 0.5NdN), \quad (7)$$

$$Ce/Ce^* = 3CeN / (2LaN + NdN), \quad (8)$$

$$Eu/Eu^*\ ratio = EuN / (SmN + GdN)^{0.5}. \quad (9)$$

4. Results

The geochemical data are illustrated in the Table. The studied samples comprised SiO_2 (47.42 to 48.98 wt%; ave. 48.07 wt%), Al_2O_3 (13.06 to 16.70 wt%; ave. 15.62), Fe_2O_3 (7.75 to 9.21 wt%; ave. 8.51), CaO (7.71 to 11.68 wt%; ave. 8.61), MgO (6.31 to 9.45 wt%; ave. 7.33), Na_2O (1.97 to 2.87 wt%; ave. 2.37), and K_2O (0.50 to 0.90 wt%; ave. 0.64). They fell within the graywacke and Fe-shale range in the chemical classification diagram (Figures 3a and 3b) and

Table. Geochemical results of the studied lake sediments.

	Unit	MDL	L1-B	L1-C	L1-D	L2-A	L2-B	L3-A	L3-B	L4-A	L4-B	L4-C
SiO_2	%	0.01	48.8	48.2	47.42	47.46	47.5	48.43	48.98	47.72	47.71	48.49
Al_2O_3	%	0.01	16.14	16.16	16.03	16.7	16.41	15.07	13.06	15.76	15.77	15.07
Fe_2O_3	%	0.04	8.75	8.86	9.03	9.21	9.18	7.92	8.12	8.1	8.2	7.75
MgO	%	0.01	6.31	6.83	6.87	6.62	6.82	6.82	9.45	7.58	7.94	8.02
CaO	%	0.01	7.91	8.46	7.71	7.92	7.85	8.46	11.68	8.4	8.92	8.74
Na_2O	%	0.01	2.87	2.7	2.34	2.41	2.28	2.47	1.97	2.25	2.22	2.15
K_2O	%	0.01	0.57	0.6	0.54	0.5	0.51	0.62	0.5	0.85	0.9	0.78
TiO_2	%	0.01	1.09	1.02	1.05	1.14	1.12	1.02	0.81	0.82	0.77	0.78
P_2O_5	%	0.01	0.35	0.34	0.33	0.36	0.35	0.28	0.21	0.26	0.22	0.22
MnO	%	0.01	0.15	0.15	0.15	0.14	0.14	0.12	0.14	0.13	0.14	0.12
Cr_2O_3	%	0.002	0.03	0.037	0.03	0.027	0.03	0.045	0.101	0.036	0.044	0.053
LOI	%	- 5.1	6.8	6.4	8.2	7.2	7.5	8.5	4.7	7.8	6.8	7.5
Sum	%	0.01	99.75	99.74	99.74	99.74	99.74	99.75	99.72	99.71	99.71	99.73
Ba	ppm	1	171	187	158	193	192	168	130	263	263	224
Ni	ppm	20	75	79	80	73	78	68	86	69	67	80
Sc	ppm	1	28	30	29	29	30	33	50	32	36	35
Be	ppm	1	2	< 1	< 1	< 1	2	< 1	2	< 1	2	2
Co	ppm	0.2	34.9	35.1	35.3	33.1	35.7	36.5	35.5	31.3	31.2	29.2
Cs	ppm	0.1	0.7	0.5	0.4	0.4	0.4	0.4	0.3	0.3	0.4	0.3
Ga	ppm	0.5	16.9	17.5	16.9	16.3	16.1	15	12.4	14.7	14.3	13.2
Hf	ppm	0.1	2.6	2.3	2.3	2.7	2.5	2.3	1.8	1.8	1.7	1.7

Table. (Continued).

Nb	ppm	0.1	3.8	3.3	3.2	3.9	3.7	3.2	2.1	2.1	1.8	2.1
Rb	ppm	0.1	6.4	6	6.7	5.2	5.3	8	6.4	10.4	11.8	8.8
Sn	ppm	1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Sr	ppm	0.5	536.4	570.5	589.6	622.3	584.2	487.3	383.7	697.3	674	607.4
Ta	ppm	0.1	0.3	0.2	0.2	0.2	0.3	0.2	0.1	0.1	< 0.1	< 0.1
Th	ppm	0.2	1.6	1.6	1.5	1.5	1.5	1.3	1.4	2.2	2.3	1.7
U	ppm	0.1	0.4	0.5	0.4	0.4	0.3	0.7	0.3	0.7	0.6	0.7
V	ppm	8	218	229	209	210	210	203	220	212	230	195
W	ppm	0.5	64.9	41	35.7	32	40.1	61	51.2	47.4	37.3	35.6
Zr	ppm	0.1	104.8	92.7	95.2	108.8	104.7	99.6	68.5	70.1	64	65.9
Y	ppm	0.1	18.7	18.1	17.6	21.3	19.4	18.2	14.8	14	13.2	12.9
La	ppm	0.1	12.2	12.7	12.6	13.9	14	10.5	8.1	10.6	10.7	9.4
Ce	ppm	0.1	25.9	27.7	26.7	29.2	29	21.6	16.4	23.2	22.5	20.2
Pr	ppm	0.02	3.65	3.82	3.67	4.08	4.07	3.06	2.53	3.18	3.1	2.82
Nd	ppm	0.3	16.6	16.8	16.7	18.3	17.9	13.8	11.5	14	13.1	13.2
Sm	ppm	0.05	3.84	3.86	3.75	4.02	4.21	3.14	2.75	3	2.95	2.9
Eu	ppm	0.02	1.18	1.18	1.17	1.32	1.33	1.06	0.94	0.97	0.96	0.95
Gd	ppm	0.05	3.82	3.74	3.74	4.22	4.15	3.49	3.19	3.22	2.96	2.8
Tb	ppm	0.01	0.58	0.57	0.56	0.62	0.59	0.51	0.45	0.44	0.42	0.39
Dy	ppm	0.05	3.42	3.34	3.25	3.67	3.7	3.22	2.75	2.71	2.6	2.43
Ho	ppm	0.02	0.72	0.67	0.67	0.77	0.76	0.63	0.56	0.51	0.5	0.48
Er	ppm	0.03	1.92	1.97	1.96	2.21	2.16	1.93	1.62	1.48	1.4	1.42
Tm	ppm	0.01	0.28	0.26	0.27	0.29	0.28	0.27	0.19	0.2	0.18	0.18
Yb	ppm	0.05	1.72	1.61	1.65	1.86	1.82	1.66	1.37	1.34	1.3	1.33
Lu	ppm	0.01	0.27	0.26	0.24	0.26	0.26	0.24	0.2	0.19	0.17	0.18
CIA			58.71	57.88	60.22	60.66	60.67	56.61	48.00	57.81	56.71	56.36
PIA			80.12	78.22	89.27	88.61	90.12	70.81	57.95	73.98	71.29	68.94
CIW			59.96	59.15	61.46	61.78	61.83	57.96	48.90	59.67	58.60	58.05

in the quartz-rich range (Figure 3c). The intensity of the weathering and chemical alteration was expressed using the formula for CIA proposed by Nesbitt and Young (1984). The formula for the PIA suggested by Fedo et al. (1995), and that for the CIW given by Harnois (1988) were also used. The PIA, CIA, and CIW weathering indices varied between 71.89–76.40, 81.90–85.07, and 73.77–78.25, respectively. They were plotted as low to slightly moderate weathering and alteration in the ternary diagrams (Figure 4). They have a narrow range of Ni (67.00–86.00 ppm), Th (1.30–2.30 ppm), Hf (2 1.70–2.70 ppm), Th/U (1.86–5.00), La/Sc (0.16–0.48), Co/Th (13.57–28.08), Zr/Sc (1.37–3.75), and Th/Sc (0.03–0.07). The large-ion lithophile elements (LILEs, such as Cs, Rb, K, Ba, Sr, and Eu) and high field strength elements (HFSEs; Ti, Zr, Hf, and Nb) were normalized to the UCC (Taylor and McLennan, 1985). The REEs (La to Lu) were normalized to chondrite (Taylor and McLennan 1985). Their distribution is shown in Figures 5a and 5b. The REE patterns were represented mainly by an enrichment in light REEs (LREEs) over mixed REEs and heavy REEs (HREEs), presenting a uniform pattern in the REE distribution diagram. The distribution of REEs in the sediment samples exhibited a similar pattern to that of the local host rocks, showing an enrichment of LREEs over HREEs. In addition, the studied samples consisted of a wide range of average REEs (∑REEs) (67.35–106.02 ppm), Sc (28.00–50.00), and Y (12.90–21.30) contents. Their ∑REE contents were lower than those of the Post-Archean Australian Shale (PAAS) (183.0 ppm) and UCC (146.4 ppm) (Taylor and McLennan 1985). Their

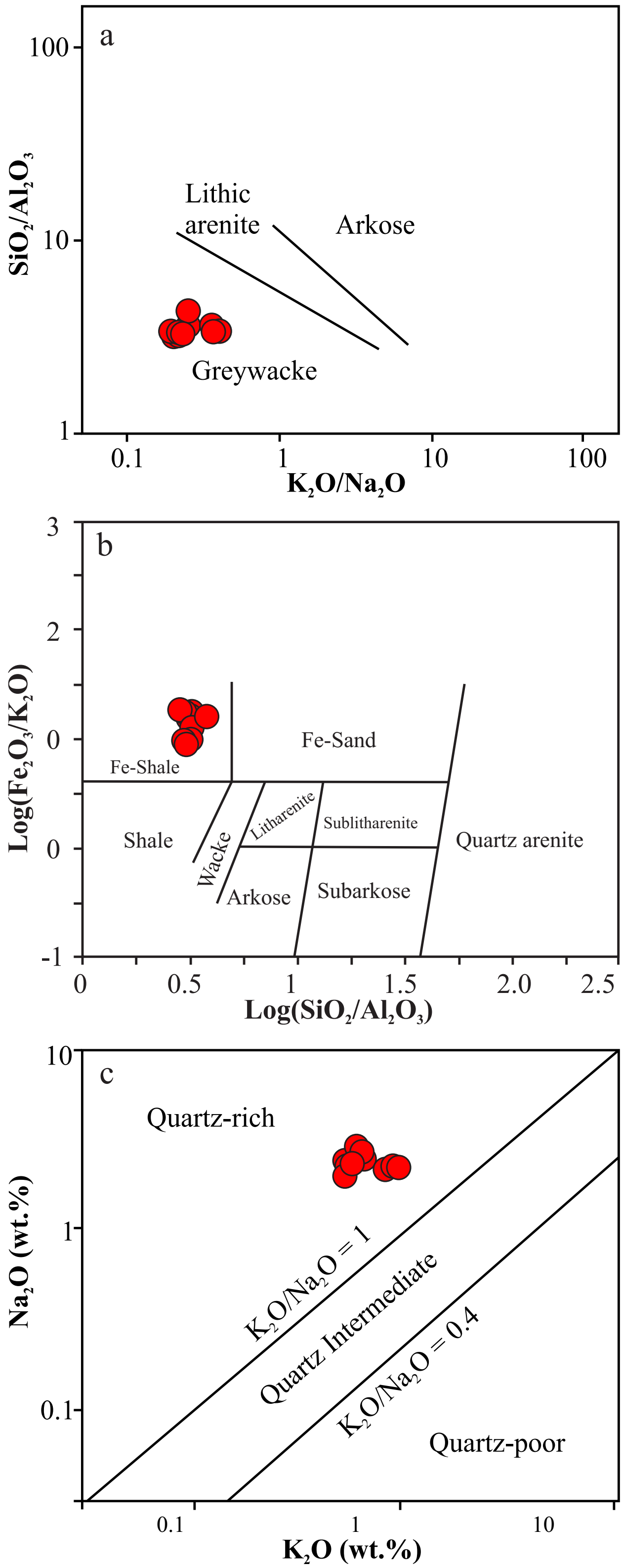

Figure 3. Geochemical classification of the sediment samples on Robert Island on the a) K_2O/Na_2O vs. SiO_2/Al_2O_3 diagram (Pettijohn et al., 1972) and b) Log(FeO/K_2O) vs. Log (SiO_2 /Al_2O_3) diagram (Herron, 1988).

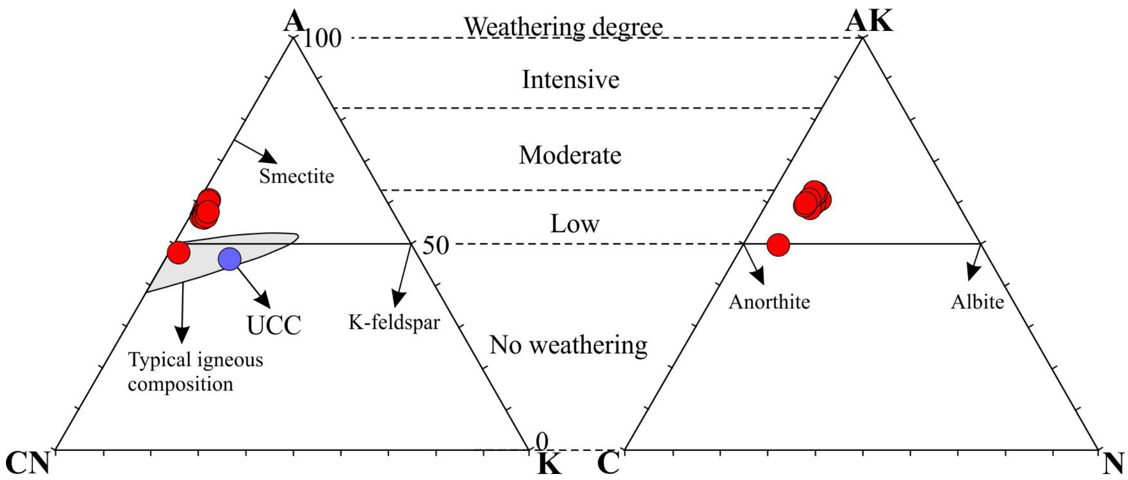

Figure 4. Ternary diagrams showing the weathering degree of host rock of the lake sediments: ($CaO + Na_2O$) - Al_2O_3 - K_2O diagram (Nesbitt and Young, 1984), and CaO - (Al_2O_3 - K_2O) - Na_2O diagram (Fedo et al., 1995; A: Al_2O_3; CN: $CaO + Na_2O$; K: K_2O; AK: Al_2O_3 - K_2O; C: CaO; N: Na_2O).

chondrite-normalized REE patterns are illustrated in Figure 5a. They displayed 1) strong enrichment LREE with high La/YbN ratios (4.02–5.59) 2) flat Eu/Eu* anomaly (0.93–1.00), and 3) relatively flat Ce/Ce* anomaly (0.87–0.96). Their La/SmN ratios were 0.46–0.56 and Nd/YbN ratios were 2.93–3.68. In the trace element diagram of the sediment samples normalized to the UCC (after Sun and McDonough, 1989), a depletion of LILEs such as Cs, Rb, and Ba is evident, while there is a slight enrichment of K and Sr. Furthermore, there is a slight enrichment in HFSEs such as Lu and Y, and significant enrichment in Ti (Figure 5b).

5. Discussion

5.1. Weathering processes

Weathering processes influence the chemical characteristics of sediments and are controlled by various geological factors, such as source rock lithologies, intensity of chemical alteration/weathering, sediment supply rate, and transportation processes (Nesbitt and Young, 1982; McLennan, 1993; McLennan et al., 1993; Cox et al., 1995). These processes result in the selective mobilization of elements like K, Na, Mg, and Ca being more easily mobilized, while several elements, such as Fe, Al, and Ti, tend to remain in the residual sediments, leading to their accumulation over time. The relative depletion of mobile elements comparatively to immobile elements during weathering/alteration processes can be quantified using different geochemical indices, as those demonstrated in numerous studies (Piper, 1974; Harnois, 1988; Perri, 2020; Kandemir et al., 2022). These indices, including the CIA, CIW, and PIA, provide quantitative measures to assess the extent of chemical weathering. Based on the calculated CIA, CIW, and PIA values, the studied sediments were likely to have undergone medium weathering and alteration processes (Figure 4). This is further supported by their positions in the low to slightly moderate areas in Figure 4.

The Th/U ratios tend to increase due to the depletion of U through weathering/alteration and other processes. The observed elevated Th/U ratios, which exceeded the UCC values, were attributed to the loss of U during weathering and the recycling of sediments (Fedo et al., 1995; Roser et al., 2002). Additionally, the oxidation of U may lead to its sedimentation or dissolution, resulting in its removal from the system (McLennan et al., 1993). In the samples herein, the Th/U ratios generally exhibited a lower distribution, falling below those of the UCC (Figure 6a). Nevertheless, a few samples (L2-B and L3-B) displayed an increasing trend, indicating the possible influence of weathering or sorting processes in enriching the Th/U ratios (Dowling et al., 2019). Their Gd/YbN ratios and LREE and HREE values were between those of the local source and PAAS (Figures 6b and 6c). When normalizing the chemical characteristics of the studied sediments and the associated local source lithology to the UCC (Figure 5b), the alkali element patterns showed enrichment relative to the volcanic rocks on Robert Island. This slight enrichment of K and Cs in the lake sediments suggests a low degree of chemical alteration/weathering processes.

On the other hand, LREEs are selectively scavenged and removed, while HREEs tend to be retained in sediments (Nesbitt, 1979; Caccia and Milero, 2007). The ratio between the LREEs and HREEs, as well as the La/Yb ratio, is important for studying the origin of sediments and the mobility of elements within the Earth's crust (Taylor

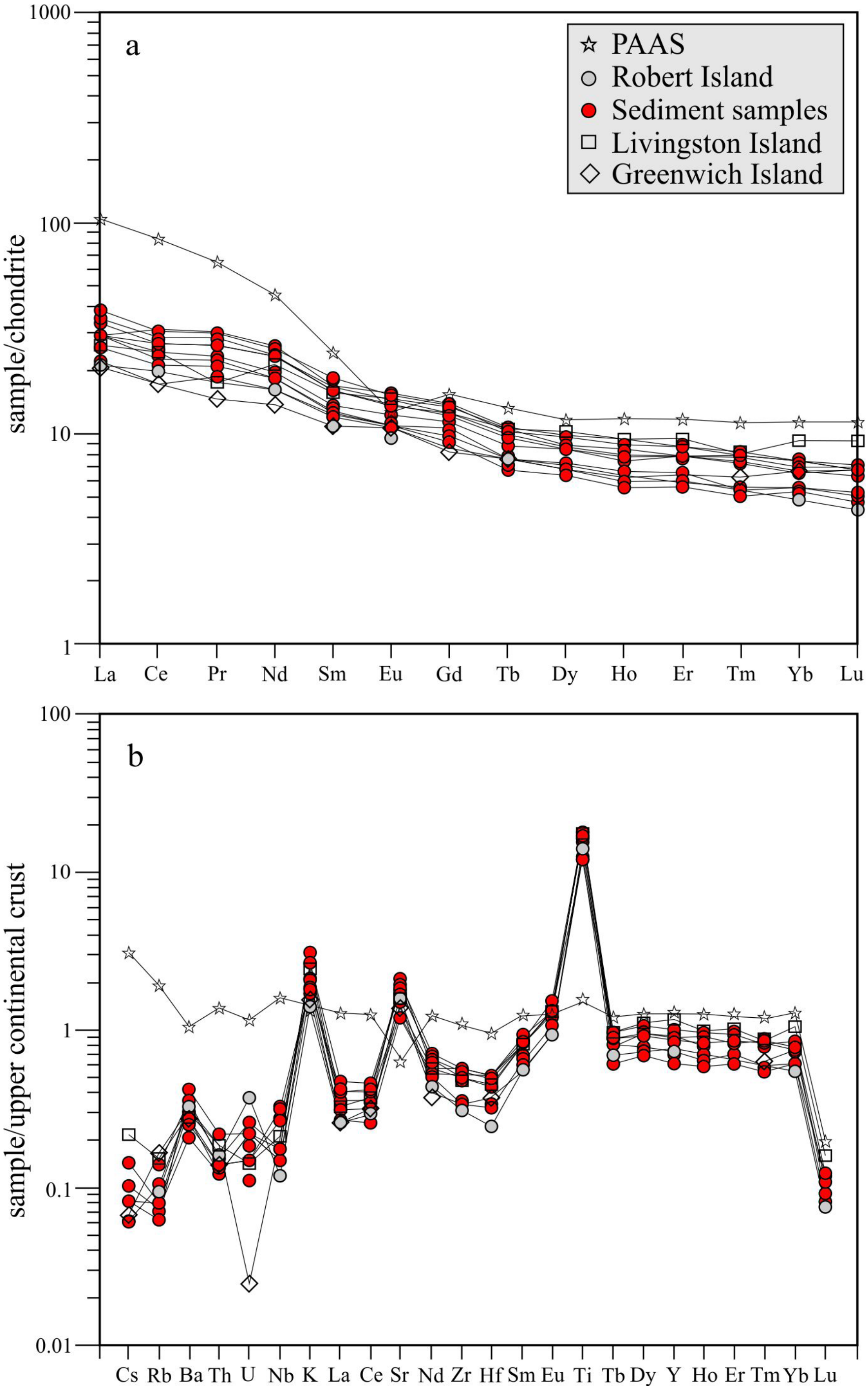

Figure 5. a) Chondrite-normalized REE diagram and b) UCC normalized trace element diagram for the studied lake sediment samples on Robert Island, volcanic rocks from the South Shetland Islands, and PAAS (data from the Livingston, Robert and Greenwich Islands are from Machado et al., 2005; PAAS from Taylor and McLennan, 1985).

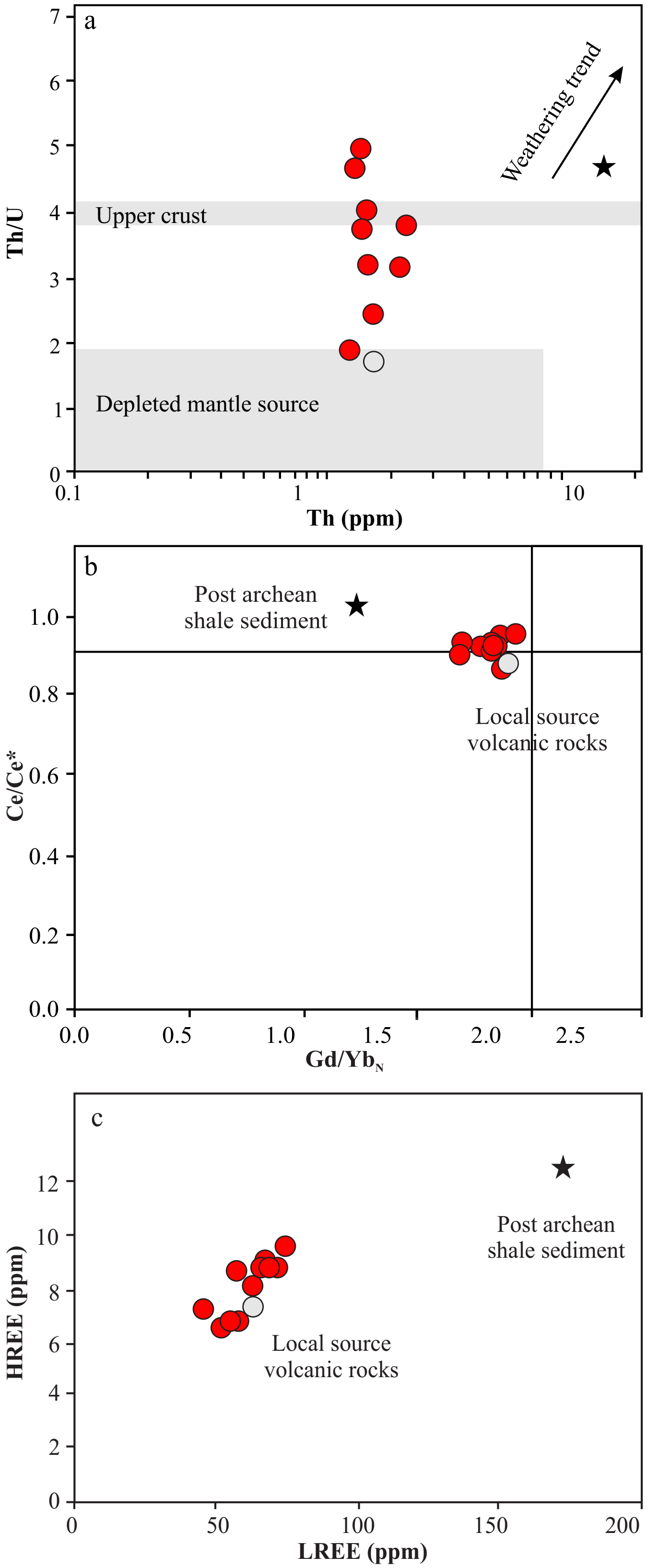

Figure 6. a) Th vs. Th/U (after Jones and Manning, 1994), b) Gd/YbN vs. Ce/Ce* (after McLennan and Taylor, 1991), and c) LREE vs. HREE.

and McLennan, 1985; Ross et al., 1995; Sholkovitz, 1995; Yang et al., 2002). When normalized to the chondrite, the studied samples were represented mainly by enrichment in the LREEs over the HREEs (Figures 5a and 5b). The La/Yb and Gd/Yb ratios exhibited similarity with the surrounding volcanic rocks on Robert Island, suggesting a limited control of chemical weathering/alteration on their REE characteristics (Figure 6b). Although they exhibited slight differences in their LREEs when compared to the local source (Figure 6c), their chondrite-normalized patterns displayed a similar trend (Figures 5a and 5b). However, the studied lake sediments showed a similar pattern to the volcanic rocks on Robert Island, indicating that their REE composition was predominantly controlled by their source rocks. The homogeneous distribution patterns of the REEs in all of the sediment samples further support the notion that the REE chemistry of the studied sediments was not significantly affected during chemical alteration/weathering processes (Piper, 1974; Su et al., 2017; Özyurt et al., 2020).

5.2. Source rocks

The geochemical characteristics of the sediments provided valuable insights into the petrogenesis and lithologies of their provenance (e.g., Roser and Korsch, 1988; Talarico and Sandroni, 1998; Le Pera et al., 2001; Hernández et al., 2018). Certain elements, such as Al, Mn, Fe, Co, Ti, Nb, Th, Zr, Y, Sc, and REEs, are known to be relatively less sensitive to weathering and alteration processes due to their physical-chemical behavior, which makes them persistent and less prone to mobilization within the sedimentary system (e.g., Lin et al., 2019; Ocampo-Díaz et al., 2019; Özyurt et al., 2020). Various geochemical parameters, including their relative abundance, have been proposed to assess the characteristics of source rocks (Bhatia and Crook, 1986; Hayashi et al., 1997; Bellanca et al., 1998; Gore et al., 2003; Ocampo-Díaz et al., 2019; Kandemir et al., 2022, etc.).

The studied samples were clustered around the basaltic provenance area in the Co/Th vs. La/Sc diagram (Figure 7a) and the Th/Sc vs. Zr/Sc diagram (Figure 7b), suggesting that the studied samples mainly originated from mafic sources. They were predominantly plotted within mafic igneous rock sources, with a smaller proportion associated with intermediate igneous rocks (Figure 7c). Conversely, they were plotted between the PAAS and the local source rock on the Ni vs. TiO_2 diagram (Figure 8a). Similarly, based on the discriminant function diagram, most of the examined sediments indicated a trend toward basic magmatic rock provenance to quartzose sedimentary source rocks, suggesting a multigenetic source lithology (Figure 8b; Roser and Korsch, 1988). Although their Zr/Hf values (40.29) were similar to the local source rocks on Robert Island (Zr/Hf: 41.12) and the PAAS (Zr/Hf: 42.00), they were plotted between the PAAS and local source rocks, exhibiting a linear distribution from the local source rocks to the PAAS (Figures 8c and 8d). This could indicate additional sources (such as moraine deposits), contributing HREEs to the lakes. This was also supported by the enrichment in Sr, Nd, Zr, Hf, and HREEs compared to the surrounding rocks (Figure 5b).

The studied samples displayed a relatively higher concentration of LREEs and stronger Eu/Eu* ratios, implying a crustal source or more felsic magmatic source beyond their host rocks. On the other hand, lower Eu/Eu* values and higher a HREE signature pointed to a relatively low abundance of feldspar and suggested more basic magmatic rocks. Similar characteristics were recorded in the aeolian material of the McMurdo Dry Valleys, Antarctica (Diaz et al., 2020). Nevertheless, there is currently limited information regarding modern dust sources, their transport mechanisms, and their contribution to the lakes (Revel-Rolland et al., 2006; Diaz et al., 2020). These sources play an important role in the formation of recent sediments in Antarctica (Stumpf et al., 2012; Paleari et al., 2019).

Physical alteration is common, considering Antarctica's ice-free zones and their associated catchments experience low temperatures, pronounced seasonality, and frequent freezing and thawing cycles (Choudhary et al., 2018). The continent also experiences strong winds capable of eroding and transporting materials over long distances. These processes result in the deposition of fine-grained sediments derived from various sources (Diaz et al., 2018). Thus, dust can be blown into the lakes from nearby or distant sources, including exposed areas of rock and sediment within the local vicinity of the lakes, such as dry lakebeds, glacial outwash plains, or exposed moraines (Revel-Rolland et al., 2006). Local wind patterns and topography can influence these local dust sources.

Although the lakes on the Robert Island are situated at a low elevation, strong winds originating from the polar plateau at higher elevations and moving toward the coast of the South Shetland Islands have the potential to transport suspended sediment material from elevated regions beyond the lake basins. On Robert Island, hill peaks and other high-elevation morphologies can serve as significant material sources for lower-elevation surfaces, as evidenced by the resemblance in the REE patterns between the PAAS and local rock types. Although the sediment was predominantly composed of local source rocks (volcanics on Robert Island), their chemical differences, such as enrichment in HREE, Zr, Hf, and Ni, imply an additional supply from eolian sources derived through long or short-range transport of suspended materials, which rely on sediment rates and sediment. This transportation hypothesis is also supported by the presence of fungal

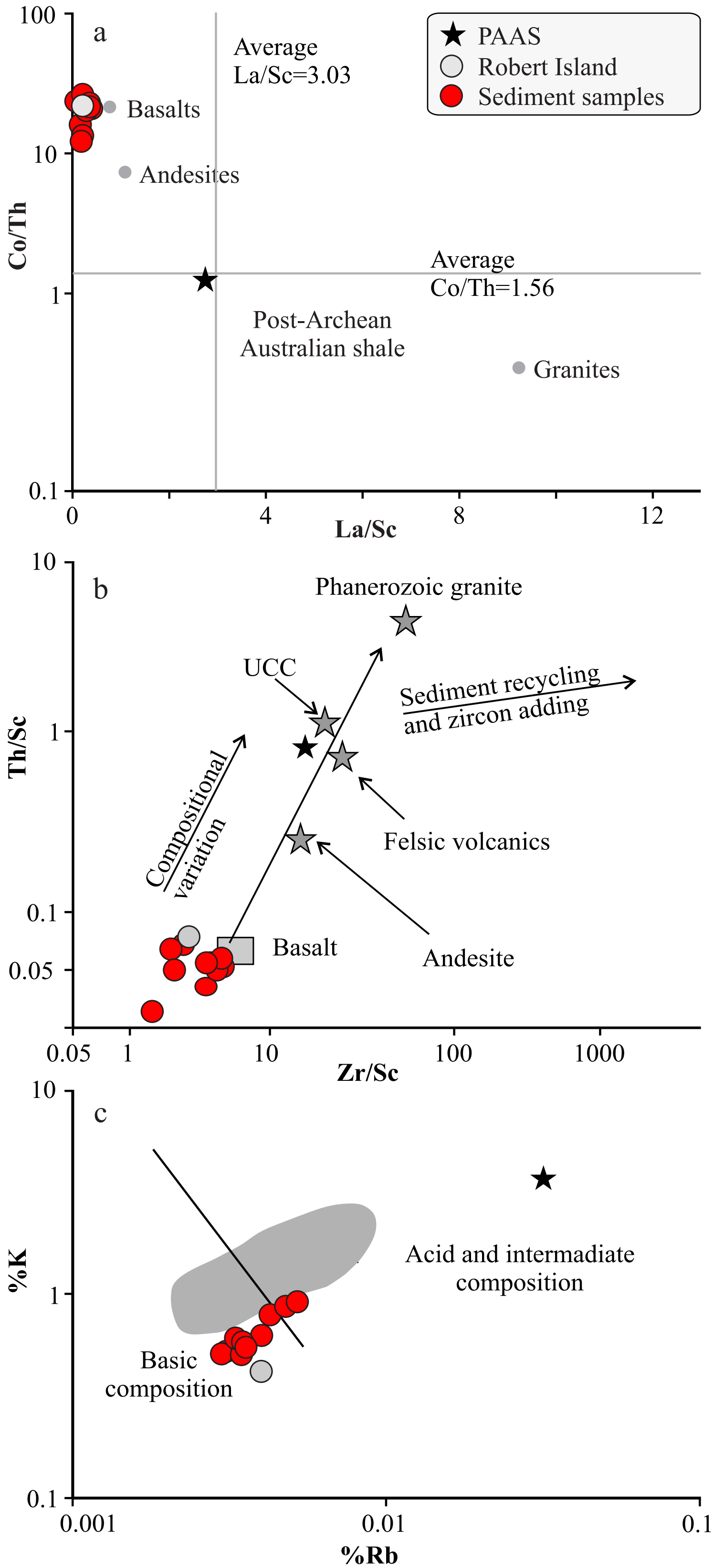

Figure 7. a) Co/Th vs. La/Sc, b) Th/Sc vs. Zr/Sc (after Roser and Korsch 1988; McLennan et al. 1993), and c) Rb vs. K (after Floyd et al., 1991).

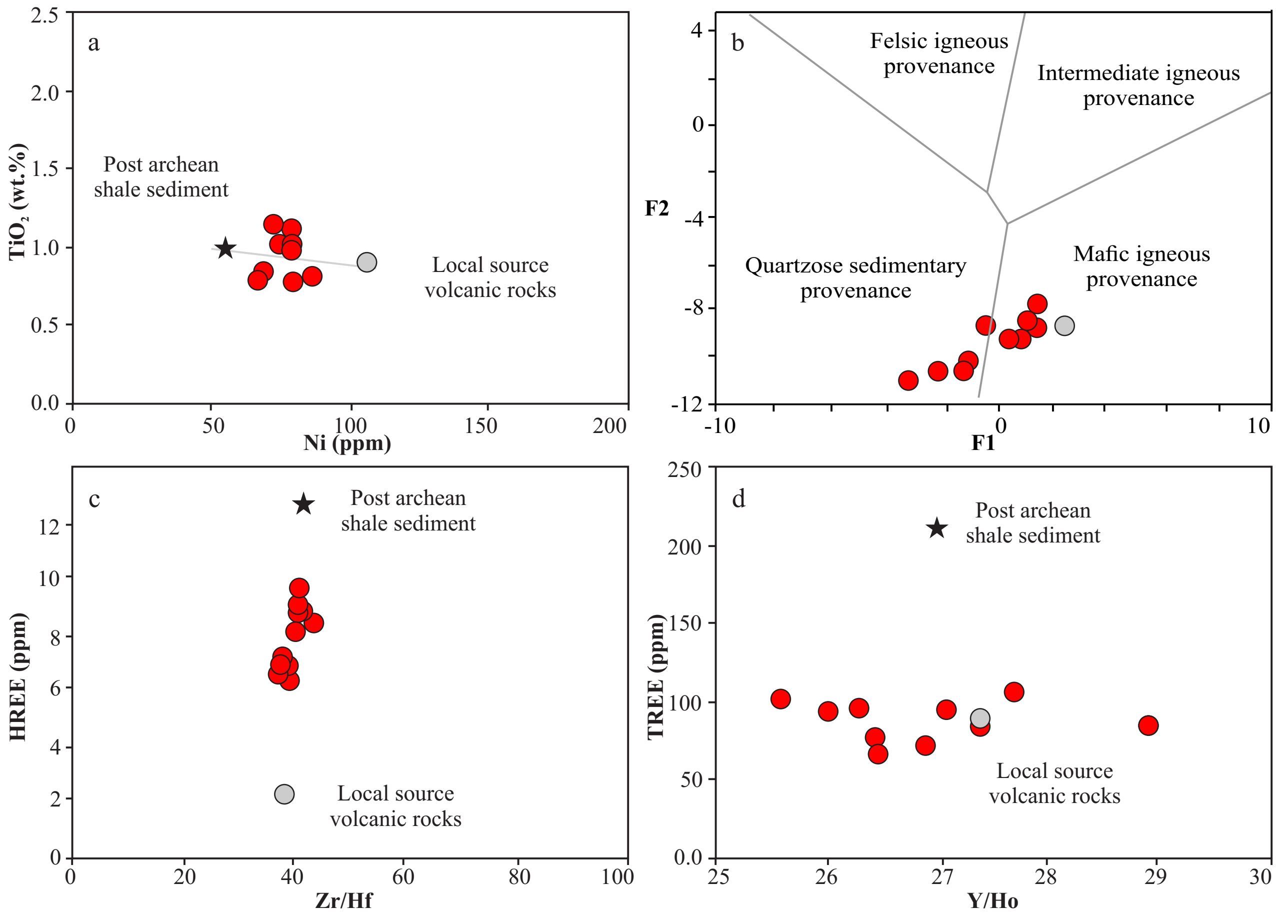

Figure 8. a) Ni vs. TiO_2, b) discrimination function of F1 vs. F2 (after Roser and Korsch 1988; McLennan et al. 1993), c) Zr/Hf vs. HREE, and d) Y/Ho vs. total REE (TREE).

remains and variations, which could potentially be attributed to long-distance transport, possibly carried along with drifted plant elements via continental winds in the Schirmacher Oasis and adjacent Nunataks, East Antarctica (Bera et al., 2012). Similarly, previous studies have shed light on the transport of pollen and spores into the Antarctic (Kappen and Straka, 1988). They proposed that the current flora in the maritime Antarctic likely originated from South America through immigration and interactions with the sub-Antarctic region (Kappen and Straka, 1988). A more recent study (Rodrigues et al., 2023) examined collected pollen samples, revealing their capability to be carried through the air for distances exceeding 3000 km. These findings support the notion of long-term transportation processes in the studied lake sediments.

In summary, it can be hypothesized that the physical and/or chemical weathering/alteration of local volcanic rocks, along with some contributions from glacier material, is the primary mechanism responsible for providing sediments in the southern depression of the lakes on the Robert Island. The glaciers and an ice stream can be responsible for transporting sediments from the surrounding volcanic rocks across the slightly or deeply eroded possible channel and consequently depositing them into the lake sediments. This process involved the movement of large volumes of ice, carrying with them a variety of sediment types and sizes. Secondary processes, such as eolian dust by the suspension transport of sediment over the lakes, which depend on the particle size and particle rates, play a less significant role in the general chemistry of the studied sediments. Dust particles can be derived from the removal of moraine material from nearby slopes or exposed rocks and transported over short or long distances.

6. Conclusions

Based on a comprehensive data set of the geology, sedimentology, and chemistry (major, trace, and REEs) of the sediments of the four Lakes on Robert Island, South Shetland, Antarctica, we propose the following important findings below:

1. The ratios of Co/Th, La/Sc, Th/Sc, and Zr/Sc in the studied samples exhibited a close similarity to those typically observed in basic volcanic rocks. This suggests that the sediments are predominantly derived from basic rock sources. Additionally, the Rb, K, F1, and F2 values indicated that the contribution from basic rocks is dominant, with minor input from felsic magmatic or quartzose sedimentary rocks. Furthermore, the HREE and Ni values fell within the range between those of the Robert basalt and the PAAS, providing further evidence of a multigenetic source for the sediments.
2. The chondrite-normalized REE patterns observed in the sediments of the lakes exhibited a trend similar to the surrounding volcanic rocks on Robert Island. However, the ratios of Zr/Hf, Ce/Ce*, Gd/YbN, and La/Ybn were also closely aligned with those of the local volcanics, indicating that the REE chemistry of the sediments was primarily influenced by the local source rocks. Slight variations can be observed in the ratios of Y/Ho, TREE, and HREE, suggesting the potential contribution of additional sources to the REE supply in the lake basins.
3. The CIA, PIA, and CIW weathering indices ranged between 71.89–76.40, 81.90–85.07, and 73.77–78.25, respectively. When plotted in the ternary diagrams of ($CaO + Na_2O$) - Al_2O_3 - K_2O and CaO - (Al_2O_3 - K_2O) - Na_2O, the sediments displayed low to medium weathering alteration processes.
4. The U/Th ratios were mostly lower than the UCC values but higher than those of the local source. They displayed a UCC normalized pattern similar to the volcanic rocks on Robert Island. Additionally, the sediments showed a slight enrichment of trace elements such as potassium (K), rubidium (Rb), and cesium (Cs), indicating a low degree of chemical weathering processes.

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