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GEOSCIENCES

Elemental and mineralogical characterization of marine sediments and their relationship to sedimentary and oceanographic processes in Central Bransfield Basin

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Abstract: This work consists of the sedimentological, mineralogical, and geochemical characterization of eight marine sediment cores collected in the Central Bransfield Basin, along a transect between the South Shetland Islands to the Antarctic Peninsula and its correlation to the sedimentary and oceanographic processes of the area. A chemical characterization based on X-ray fluorescence dispersive spectrometry was implemented to obtain geochemical data of the marine sediment while the minerals were identified by X-ray diffraction. The study allowed to classify the cores into three groups according to their sediment source and chemical and mineralogical characteristics. The joint assessment of the geochemical and mineralogical signature of the sediment has confirmed that the elemental ratios Ti/Ca and Fe/Ca can be applied as proxies in the reconstitution of the terrigenous contribution to the Central Bransfield Basin if we consider the sedimentary contribution of the volcanic edifices present in the region. The Fe/K ratio associated with the Chemical Index of Alteration reinforced an increase in the degree of weathering near South Shetland Island, which is also pointed out by other authors in studies on climate change mainly in the subantarctic islands. The trend of temperature increase implies the importance of monitoring the region.

Key words: Antarctic, geochemistry, mineralogy, Sediments, oceanographic processes.

INTRODUCTION

The Bransfield Basin (BB) is one of the most studied oceanic areas in Antarctica due to its location, climatic conditions, and seasonal ice cover, and it's considered a highly productive and very dynamic region under the influence of the Weddell and Bellingshausen seas (Tokarczyk 1987, Zhou et al. 2006).

The geochemical composition of terrigenous sediment deposited in marine environments may reflect tectonic and weathering processes, while also reflecting the transport path of such sediment to the ocean (Liu et al. 2016), helping to understand the climatic history of the region. The behavior of the main chemical elements and even trace elements, work as paleoclimate proxies (indicators) and may reveal changes in bioproductivity, volcanism, water masses, the origin of source rocks, advance and retreat of glaciers, reducing conditions and diagenesis (Domack 2001).

The studies about sedimentation on continental margins reveal significant variability in the texture, mineralogy, and geochemical characteristics of sediment (Anderson 1999); however, geochemical investigations in this field are scarce or restricted. Previous studies have focused on the reconstruction of the sedimentary record and the processes associated with its physiographic configuration, from fjords to the ocean basin.

Understanding the sedimentary processes in BB is essential for a good environmental interpretation, as the sediment reflects a particular mineralogical and geochemical signature related to the climatic conditions during its deposition. Therefore, multiproxy studies are necessary to reconstitute changes in terrigenous sediment input and the influence of marine productivity over time (Lee et al. 2012).

Study area

The Bransfield Basin is located in the circumpolar low-pressure region, where the climate is determined by the successive passages of cyclonic systems, mostly originating in the southeastern sector of the Pacific Ocean (Aquino 2012). These systems transport warm and humid air, producing a maritime climate with small temperature variations, high relative humidity, summer rains, and constant cloud coverage throughout the year (Bremer 1998). This is part of the southern polar region that is most vulnerable to climate change due to its geographical position and because it is on the edge of seasonal sea ice cover (Duarte 2006). The region is also affected by cyclones from the Amundsen and Bellingshausen seas and is struck by cold air masses from the Weddell Sea and the Antarctic Peninsula (AP) that act as a barrier against the circulation of the lower atmosphere. The Central Bransfield Basin (CBB) is 30-38 km wide, approximately 230 km long, and has a maximum depth of 1950 m, being highly asymmetrical, with a narrow bank and steep slope at the South Shetland Islands (SSI) to the northwest, and, to the southeast, a wider margin with a less steep slope in the form of bathymetric steps (horst) associated with the Antarctic Peninsula (Gràcia et al. 1996, Lawver et al. 1996, García et al. 2008, 2009). Both margins contain a continental shelf dissected by numerous glacial troughs that facilitate the advance and withdrawal of sediments, a key factor in the widespread occurrence of glacial and glaciomarine processes (Prieto et al. 1999). The CBB is marked by the presence of a chain of volcanic buildings; a linear system oriented to SW-NE (Gràcia et al. 1996, Lawver et al. 1996, García et al. 2009), which separates the Western and Eastern basins by the morpho-tectonic structures of Deception and Bridgeman Islands, respectively (Lawver et al. 1996).

The source of glacial sediments is directly related to the physiography of the CBB and partially controls the spatial distribution of sediments (García et al. 2009). Sediments are mainly derived from the glacial and proglacial activity, turbidite currents, debris flows, and marine currents from the Weddell and Bellingshausen seas. In this complex geological setting, glacial, glaciomarine, and marine processes have been interacting since the Last Glacial Maximum. (Prieto et al. 1999).

MATERIALS AND METHODS

We collected eight marine gravity-cores along an NW-SE transect in the CBB, with approximately 230 km in length, connecting the Antarctic Peninsula to the South Shetland Islands, and ranging from 300 to 1463 meters in depth (Fig. 1).

X-ray fluorescence analysis (XRF) was performed to determine the chemical composition of the elements contained in the samples. More specifically, in this process, the energy of the fluorescence radiation identifies the element, while its intensity allows its concentration in the analyzed sample to be measured (Ferretti 2009). Through this analysis, the levels of oxides of each element were obtained. 172 samples were analyzed using an

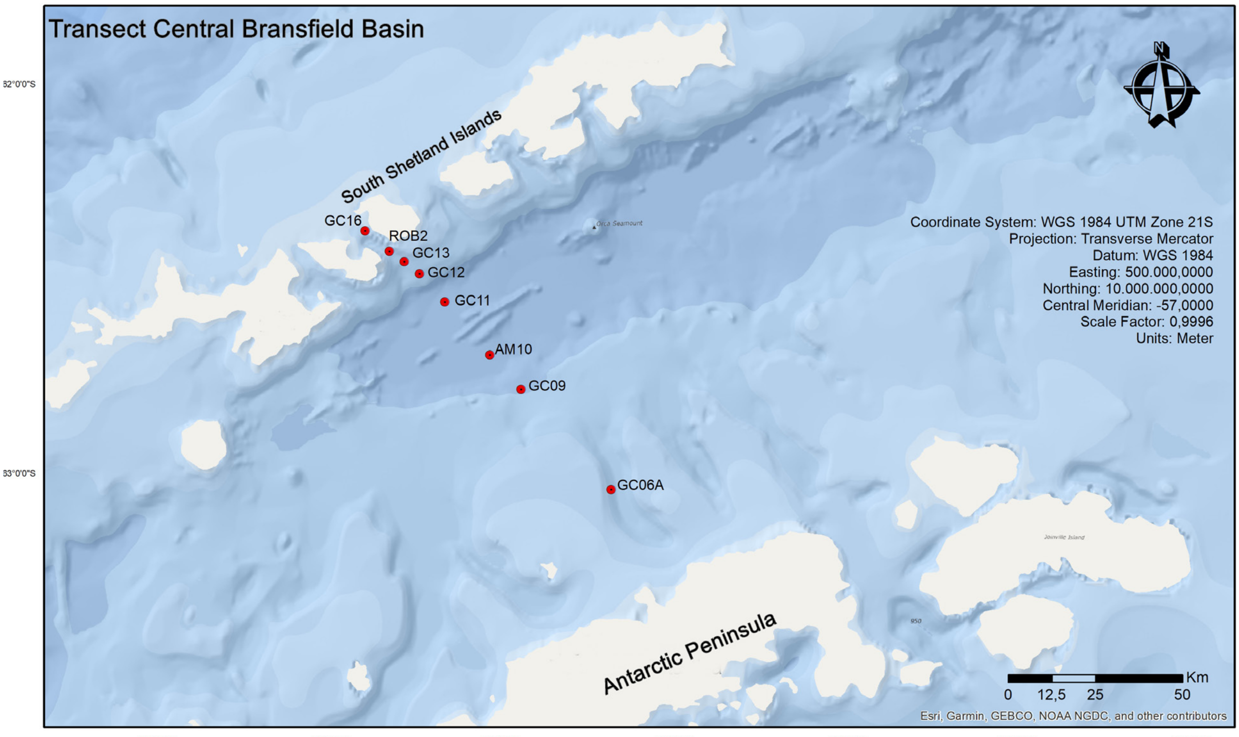

Figure 1. Map with eight marine cores collected in the CBB.

Epsilon 1 MalvernPANalytical (Supplementary Material - Figure S1).

After the elemental analysis in XRF, the Chemical Index of Alteration (CIA) (Nesbitt & Young 1982) and the Plagioclase Index of Alteration (PIA) (Fedo et al. 1995) were calculated according to the equations below. The PIA is a modification of the CIA and is used where plagioclase is susceptible to alteration (Fedo et al. 1995). Values of 100 indicate the presence of intense weathering while values between 55 and 50 indicate low weathering action and values between 45 and 50 indicate the absence of alteration processes (Goldeberg & Humayun 2010):

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

$$PIA = [Al_2O_3 - K_2O) / (Al_2O_3 + CaO + Na2O - K_2O)] \times 100: (2)$$

Where the oxides are expressed as molar proportions (Fedo et al. 2012): moles Al_2O_3 = % Al_2O_3 / 101.96 moles CaO = % CaO / 56.08 moles NaO = % NaO / 61.98 moles K_2O = % K_2O / 94.20.

In addition, indicators capable of reflecting changes in sedimentary input were considered. High-resolution XRF scans of Fe, Ti, K and Ca help to define the sedimentological parameters (Govin et al. 2012).

Mineralogy provides the investigation of small structures of matter and the conditions under which they diffract, allowing the knowledge of crystalline substances and the identification of the main minerals in the sediments which will indicate the differences in the behavior of the material due to the degree of alterability (Silva 2013). The diffractograms are the results of this process that present excess peaks that appear in the magnetic separation of the minerals. This analysis was performed using an X-ray diffraction instrument (XRD), the Bruker D8 Advance equipment (Figure S2).

The study of mineralogy contributes significantly to the classification of sediments, as it makes it possible to discriminate the minerals present which will indicate the differences in the behaviour of the material due to the degree of alterability. The interaction between mineralogical analyses and other tests is very important, since the characterisation of the material becomes difficult when methods are carried out that focus on the same analysis, that do not cover the behaviour of the material in physical, chemical and mineralogical terms, among others (Neumann et al. 2004). These analyses provide a more concrete identification of the constituents of the samples, as they show their behaviour.

Minerals were identified from their characteristic peaks with the MATCH! software, which uses COD (Crystallography Open Database – Cambridge University) as a reference.

RESULTS

To verify if there is any pattern in the distribution of the chemical composition of the cores along the transect, a graph was made with the average values of the main chemical elements of each core (Figure S3). It is possible to notice that Fe and Si are the elements in greater abundance in almost all samples. The Fe's percentage gradually drops from the SSI continental shelf (represented by GC16 core) to the lower slope (represented by GC09 core), with a sharp drop in the upper slope of the AP (represented by the GC06A core). The Fe percentage decreased as the AP approached, and the opposite occurred with Cl, which increased as it approached the AP. The Si presented higher values in the cores that were close to the volcanic buildings (cores GC11, AM10, and GC09).

The elemental ratios Ti/Ca and Fe/Ca showed similar behavior in all cores. The Fe/K ratio (Table I and Fig. 2) has been used as an indicator of chemical weathering, in the figure 5 it is showed a decreasing trend, with higher values close to SSI and lower values close to AP, which may suggest more intense weathering in nearby ISS.

To analyze the degree of weathering suggested by the Fe/K ratio, the Chemical Index Alteration, proposed by Nesbitt & Young (1982), and the Plagioclase Index Alteration, proposed by Fedo et al. (2012) In these indices, values of 100 indicate intense chemical weathering and between 40 and 55 indicate the default or incipiency of this process.

Were calculated since both indexes use elements in oxides to indicate the degree of this process. The CIA values of the cores ranged from 24 to 40, while the PIA values ranged from 7.7

Table I. Elemental ratios.

Cores	Ti/Ca	Fe/K	Fe/Ca
GC16	0,22	8,19	2,79
ROB2	0,22	7,73	2,77
GC13	0,23	7,06	2,78
GC12	0,24	6,75	2,61
GC11	0,29	4,36	3,33
AM10	0,32	4,08	4,02
GC09	0,31	4,52	3,14
GC06A	0,22	2,45	2,26

to 34.6, which infers that these sediments are relatively immature (Srivastava et al. 2013), that is, the minerals of the cores that form the ISS-PA transect show, supposedly, little or no chemical alteration (Fig. 3).

The main minerals identified by X-ray diffraction in the cores close to the SSI are part of the pyroxene and plagioclase groups (feldspars), found mainly (Figure S4), while in the cores near the volcanic buildings, minerals from the sulfate family are predominant (Fig. 4). In the core closest to the AP (GC06A) chloride minerals, especially halite, were found along the entire core (Fig. 5).

DISCUSSION

In this work, it is possible to classify the cores into three groups according to their chemical composition. The first group formed by cores GC16, ROB2, GC13, and GC12, contains the highest percentages of iron, calcium, aluminum, and the lowest potassium content. The presence of these elements can be explained by the recurrent physical weathering of mafic rocks that make up the South Shetland Islands (Santos et al. 2007, Peter et al. 2008). García et al. (2011), with cores from the CBB, also close to the SSI, classifies the material found as glacially eroded sediments from the archipelago meltwater, transported toward the submarine slopes and basin.

The second group is formed by the GC11, AM10, and GC09 cores, which have a high silicon content, which may be related to the proximity of volcanically active regions, such as the Three Sisters volcanic buildings and Deception Island.

Martins et al. (2022) identified black laminations in core GC09, to be, possibly, volcanic ash; these have already been identified in past works, such as that of Yonn et al. (1994), in sediments in the Bransfield Basin. In addition, felsic igneous rocks are rich in silicon and relatively poor in iron and magnesium, formed by feldspar and silica.

The GC06A core is the closest to the Antarctic Peninsula and contains the lowest iron content; on the other hand, it has the highest percentage of chlorine and sulphur, which may partially explain the yellowish coloration of the core. Leventer et al. (2006) identified laminations in cores near the Antarctic Peninsula in an orange-brown hue composed of diatoms deposited during the annual spring flowering.

The groups described at the beginning of this section remain in the elementary ratios, presenting similar behavior according to their

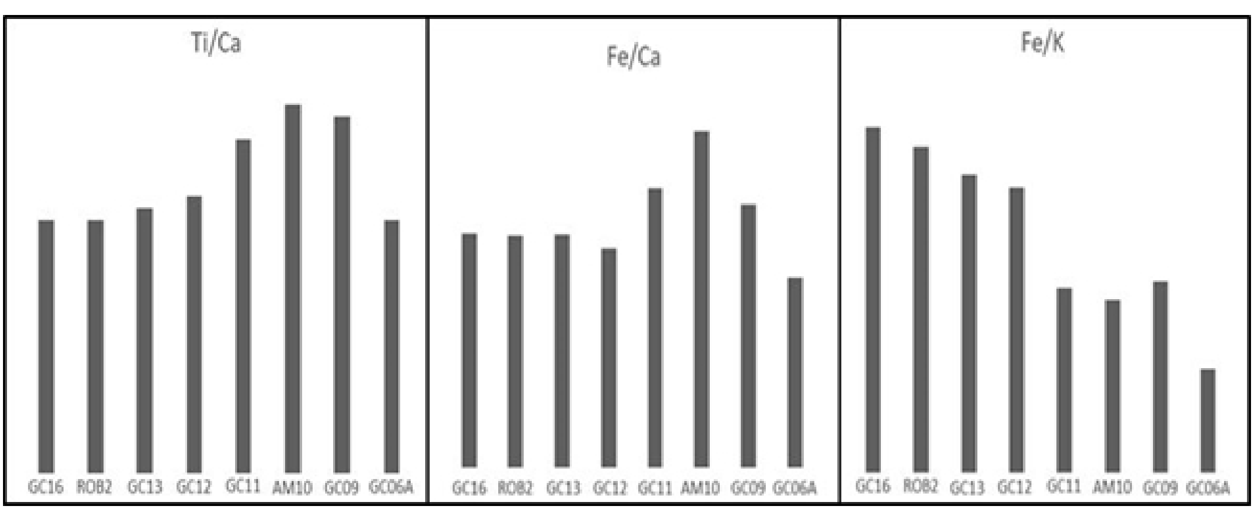

Figure 2. Elemental ratios of cores.

possible source of sediments. Analyzing the elemental ratios average values (Table I and Fig. 2), cores GC11, AM10, and GC09 showed higher proportions of terrigenous contributors. Although these cores are located close to the Oceanic Basin, iron and titanium are associated with siliciclastic components, probably due to the Three Sisters volcanic edifices.

Martins et al. (2022) observed a significant presence of biological material (siliceous leaks) in the GC06A core, demonstrating a restricted capacity for terrigenous input, and thus allowing biogenic sedimentation. This hypothesis could be corroborated by the Ti/Ca and Fe/Ca elemental ratios of the core that showed the lowest values of terrigenous contribution.

Polar Regions exhibit low to moderate chemical weathering (i.e., Luzon) and tend to provide sediments rich in K (derived from potassium feldspar) and illite (Yarincik et al. 2000, Govin et al. 2012). Currently, the SSI present milder temperatures and records of net precipitation during the summer, causing the melting of snow and ice, a process that results in a negative mass balance of the glaciers (Rosa et al. 2012), which creates favorable conditions for the increase of chemical weathering. However, the Fe/K ratio can also be influenced by the input of mafic material (Govin et al. 2012), since its lithology is formed by mafic volcanic rocks and still has some seismic activity. Despite the disagreement between the chemical alteration results (PIA and CIA) with the Fe/K ratio, it is still possible to indicate, however incipient, a difference between the cores close to the ISS (GC16, ROB2, GC13, and GC12), showing a low degree of weathering, from the core close to the AP (GC06A), with almost zero chemical weathering. Glaciers and ice caps located in subpolar areas of Antarctica have been retreating as a consequence of regional warming, and we know that SSI glaciers have shown large variations since the Last Glacial Maximum (Steig et al. 2009). This difference in the degree of weathering can be a consequence of this variation between the SSI, which already has net liquid precipitation, and the AP which is still frozen most of the time. The cores from the Oceanic Basin (GC11, AM10, and GC09) showed relatively high values, most likely due to hydrothermal activity, associated with volcanic buildings, which can affect the sediment's mineral composition.

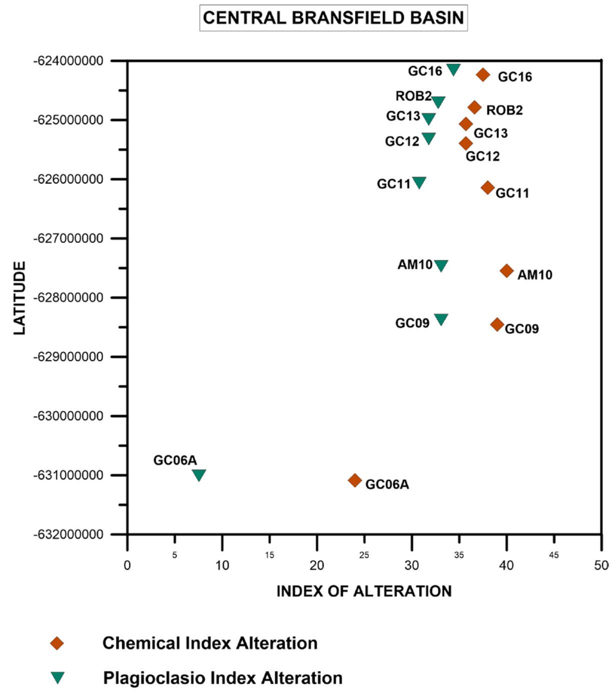

Figure 3. Index of alteration.

The mineralogy of the CBB cores is similar to the parent rock due to low rates of chemical weathering. In the cores close to the SSI (GC16, ROB2, GC13, and GC12) the main minerals found were plagioclases, clay minerals, and pyroxenes, which are common minerals in mafic rocks.

Cores collected near the volcanic buildings of the CBB (GC11, AM10, and GC09) showed laminations of black material, indicating the occurrence of volcanic ash (Martins 2020), and justified by the current geotectonic configuration, as well as by the proximity to volcanically active regions such as Three Sisters and Deception

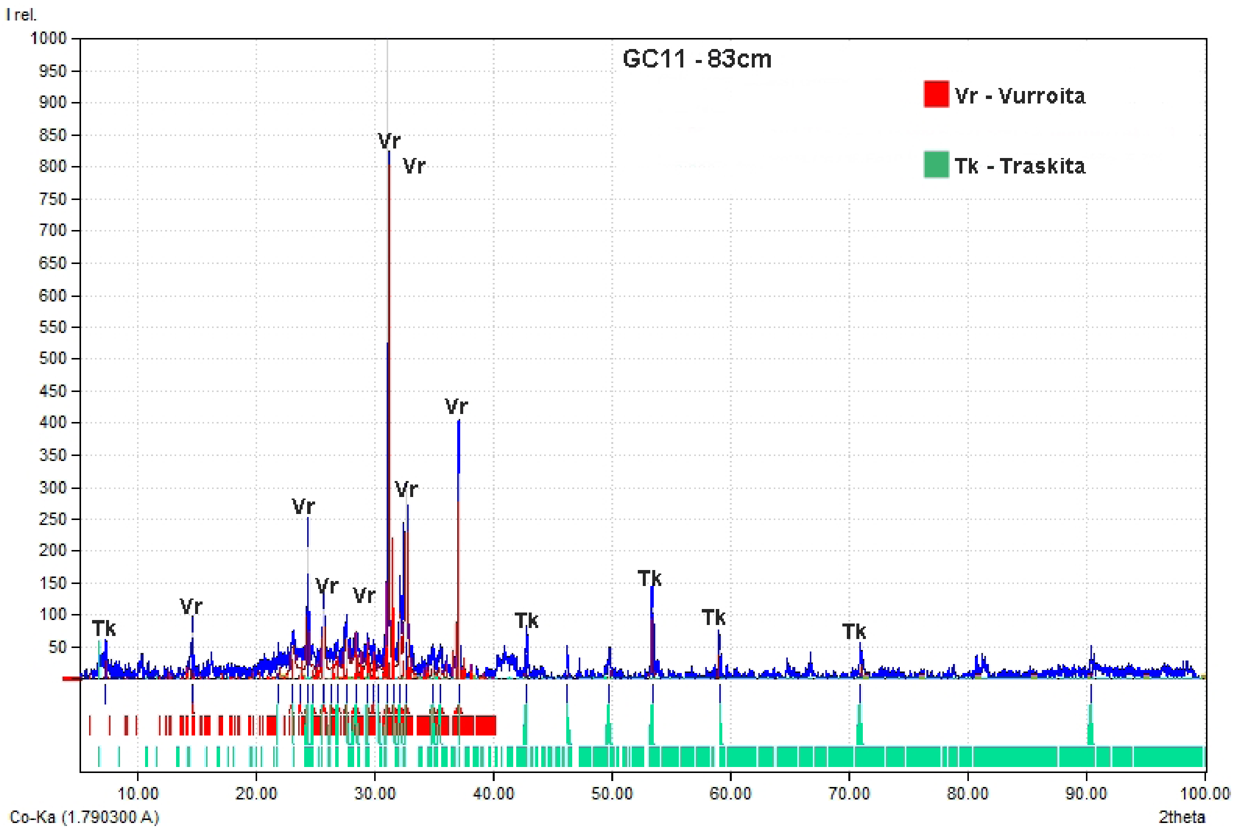

Figure 4. Main minerals identified in core GC11.

Island (Yoon et al. 1994). These cores had in common clay minerals, quartz, plagioclases, halite, and vurroite, the latter being in volcanic incrustation deposited by high-temperature fumaroles (400-600 °C).

The GC06A core, closer to the AP, showed chloride minerals (bromargyrite, and halite), quartz, and clay minerals. The presence of clay minerals is in agreement with the mineralogical analysis performed by Jung et al. (2019) on the Antarctic Peninsula platform. According to these authors, the region is characterized by low carbonate (<3%) and high biogenic opal contents (average 15%), associated with high chlorite and muscovite and low illite contents. The high chlorite values on the AP platform are due to the physical weathering of metamorphic and sedimentary rocks in cold weather conditions. Meanwhile, the constant presence of chloride minerals throughout the GC06A core, especially halite, may corroborate the importance of water currents in sediment transport in the CBB, since the waters of the Weddell Sea shelf that flow in the vicinity of the West Antarctic Peninsula, are almost entirely toward the Bransfield Basin. Deep waters cannot leave the basin due to topographic restrictions, which act as sediment traps (Wilson et al. 1999). Since the waters that arrive from the Weddell Sea are colder and saline, eventually the presence of salts such as bromargirite, and halite, detected by diffractometry, may be a consequence of the water circulation process in this region.

CONCLUSION

The study was able to classify the cores into three groups according to their sediment source

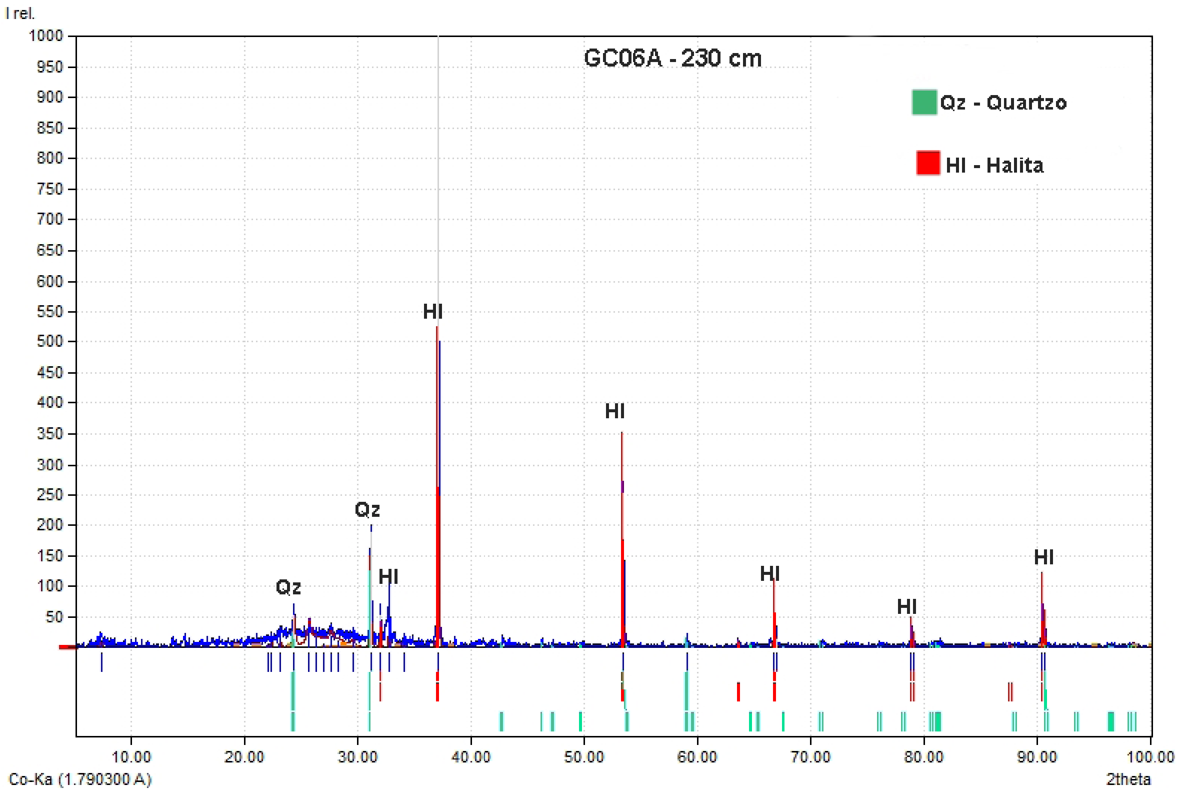

Figure 5. Main minerals identified in core GC06A.

and geochemical composition. A group with chemical and mineralogical properties similar to the rocks of the SSI; the second group related to the sedimentary contribution of volcanic buildings, and the third associated with marine processes, mainly the circulation of water in Bransfield. This indicates that the geological and oceanographical processes acting on both sides of the CBB are different.

The joint evaluation of the geochemical and mineralogical signature of the sediments allowed to confirm that the Ti/Ca and Fe/Ca elemental ratios can be applied as proxies in the reconstitution of terrigenous contribution to the CBB, if we consider the sedimentary contribution of the volcanic buildings present in the region. The Fe/K ratio associated with the chemical alteration indices reinforced, even though incipiently, an increase in the degree of weathering as the SSI approaches, in line with studies that point to more intense climate change in the subantarctic islands. However, in AP there is still a predominance of physical weathering.

Studies with marine records using geochemical multiproxies provide a window into the environmental effects of climate variation and therefore have the potential to help predict warming in the Antarctic Peninsula region. The trend of increasing temperature implies the importance of monitoring the region.

The occurrence and variation of certain minerals in marine sediments can be considered important tools in the interpretation of marine and continental processes, as well as serving as a basis for climatic inferences in future studies of paleoenvironmental reconstruction.

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SUPPLEMENTARY MATERIAL

Figures SI, SII, SIII,SIV.

How to cite

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Author contributions

Janayna Galvão is the main author, responsible for the sediment processing and analysis, discussing and writing this manuscript. The authors Arthur Ayres Neto and Rosemary Vieira actively participated in the study, with the sample planning and acquisition, data discussion, the writing processes, and the final work review. The author Jefferson Simões supported the final work review.