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Key Points:

- $\text{Ln}(\text{Zr}/\text{Rb})$ co-varies with the iceberg rafted debris-corrected mean grain-size of glaciomarine sediments from the Southern Ocean
- $\text{Ln}(\text{Zr}/\text{Rb})$ reflects changes in bottom current strength if the sediment is bottom current-sorted
- Constant gradients observed in plots of $\text{Ln}(\text{Zr}/\text{Rb})$ versus $\text{SS}\%$, and $\text{Ln}(\text{Zr}/\text{Rb})$ versus SS

Supporting Information:

- Data Set S1
- Data Set S2
- Data Set S3
- Data Set S4
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- Data Set S6
- Data Set S7
- Data Set S8
- Data Set S9
- Data Set S10

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Evaluating Zr/Rb Ratio From XRF Scanning as an Indicator of Grain-Size Variations of Glaciomarine Sediments in the Southern Ocean

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Abstract The $\text{Ln}(\text{Zr}/\text{Rb})$ count ratio derived from X-ray fluorescence (XRF) core scanning holds potential as a high-resolution tracer for grain-size variations of glaciomarine sediments, and hence current strength. To evaluate this approach, we conducted high-resolution grain-size measurements, together with Rb and Zr measurements by XRF core scanning and inductively coupled plasma-mass spectrometry (ICP-MS), on a series of sediment cores from different regions of the Southern Ocean. Downcore changes of the $\text{Ln}(\text{Zr}/\text{Rb})$ count ratio from XRF core scanning are consistent with Zr/Rb concentration ratios derived from ICP-MS analyses, even though Rb and Zr counts deviate significantly from concentrations due to specimen and matrix effects. The $\text{Ln}(\text{Zr}/\text{Rb})$ count ratio displays discrepancies with the bulk mean grain-size, but correlates well with the mean grain-size of the sediment fractions that do not include unsorted sand delivered by ice-rafting. These observations are supported by evidence from a grain-size separation experiment, which indicates that Zr and Rb are concentrated in different grain-size fractions. Consistent with its lack of sensitivity to coarse grain-size fractions derived from ice-rafting, the $\text{Ln}(\text{Zr}/\text{Rb})$ ratio records similar trends to the sortable silt percent ($\text{SS}\%$) and sortable silt mean (SS) grain-size. Universal gradients exist in plots of $\text{SS}\%$ versus $\text{Ln}(\text{Zr}/\text{Rb})$, and SS versus $\text{Ln}(\text{Zr}/\text{Rb})$, such that the $\text{Ln}(\text{Zr}/\text{Rb})$ ratio provides a convenient way to estimate the magnitude of changes in $\text{SS}\%$ and SS . Overall, our results support the use of the $\text{Ln}(\text{Zr}/\text{Rb})$ ratio as an indicator of bottom current strength in cases where the sediment is current-sorted.

1. Introduction

Sediment grain-size distributions contain rich information on sedimentary provenance, transport dynamics, and postdepositional modification (e.g., J. Chen et al., 2006; I. McCave and Andrews, 2019; I. McCave et al., 2006; Wu et al., 2020). A range of techniques has been developed for fine sediment grain-size measurements, including Laser Particle Sizer, Sedigraph, and Coulter counter (Konert & Vandenberghe, 1997; I. McCave et al., 2006), enabling quantitative grain-size distribution data to be obtained. However, studies on marine sediment cores usually require analyses on large sample sets, such that an ability to obtain reliable sediment grain-size information more rapidly and conveniently would be of great interest to marine sedimentologists (e.g., D. Liu et al., 2019). Such a capability would open up the potential for targeting long high-resolution records, as well as improving spatial coverage, leading to new insights on past sediment transport and climate dynamics over a range of timescales.

It is widely recognized that chemical elements can be preferentially enriched or depleted in specific grain-size fractions within sediments or sedimentary rocks, which is referred to as the “grain-size effect” (Bouchez et al., 2011; Jin et al., 2006; Yang et al., 2002). In most cases, this effect is considered unfavorable for geochemical data interpretation and needs to be excluded or corrected (Guo et al., 2018; Jin et al., 2006; Jung et al., 2016; Wilson et al., 2018; Yang et al., 2002). However, it also indicates a potential for developing proxies of sediment grain-size based on measurements of elemental geochemistry. In recent decades, X-ray fluorescence (XRF) scanning technology has enabled rapid, nondestructive, and near-continuous measurements to be made of many chemical elements in sediment cores, not only in the laboratory but also on board

ships and in the field (Jansen et al., 1998; Richter et al., 2006; Ziegler et al., 2008). Although results from XRF core scanning (“element counts”) are semi-quantitative (Q. Chen et al., 2016; Dunlea et al., 2020; Lyle et al., 2012; G. J. Weltje and Tjallingii, 2008; G. Weltje et al., 2015), the technique has been successfully applied to provide high-resolution geological tracers for multiple sediment components and processes, including siliceous (Jaccard et al., 2010, 2013; Wu et al., 2017) and calcareous productivity (S. Jaccard et al., 2010; Lyle & Backman, 2013), marine organic carbon content (Ziegler et al., 2008), and silicate rock weathering intensity (Tian et al., 2011). In light of the “grain-size effect,” this technique also holds the potential to provide useful information on sediment grain-size composition (Cuven et al., 2010; D. Liu et al., 2019).

Two elements that are known to carry sediment grain-size information are zirconium (Zr) and rubidium (Rb; Dypvik & Harris, 2001). Zirconium is mainly enriched in heavy mineral species, particularly zircon (ZrSiO_4), which is formed by various magmatic and metamorphic processes (Fralick & Kronberg, 1997). Zircon is widely distributed in natural sediments and usually has a relatively coarse grain-size, because it is hard, stable, and resistant to physical and chemical weathering (Pettijohn, 1941). In contrast, Rb is a typical dispersed element species, and with no Rb-dominated minerals in the natural environment (Fralick & Kronberg, 1997; Taylor, 1965), it is found mainly in K-rich minerals, such as mica, illite, and K-feldspar (Dypvik & Harris, 2001). Both Zr-rich and Rb-bearing minerals are transported and sorted together with other mineral grains, and consequently the Zr/Rb ratio in sediments can potentially be related to bulk grain-size variations (Dypvik & Harris, 2001).

The zirconium/rubidium (Zr/Rb) ratio has been widely used in studies on loess-paleosol sequences, where it indicates mean depositional grain-size variations, thereby providing a proxy for the East Asian winter monsoon strength (J. Chen et al., 2006; L. Liu et al., 2004). However, the association between sedimentary Zr/Rb ratio and grain-size is not yet well established in marine sediments, especially in glaciomarine sediments, where sedimentation is influenced by multiple provenance sources and transport processes including wind, ocean currents, sea ice, and icebergs (Lamy et al., 2014, 2015; I. N. McCave et al., 2014; Weber et al., 2012, 2014). With the Southern Ocean increasingly viewed as a key area for understanding past and future global climate evolution (e.g., DeConto & Pollard, 2016; S. L. Jaccard et al., 2016; Schloesser et al., 2019; Sigman et al., 2010; Wilson et al., 2020), the development of new and convenient sedimentary proxies that can be applied in this region is an important target (e.g., Wu et al., 2019). In a few recent studies, the Zr/Rb ratio has been used as a proxy for past changes in sediment grain-size, and hence bottom current speeds, in the vicinity of the Drake Passage (Lamy et al., 2015; Toyos et al., 2020) and offshore George V Land, East Antarctica (Campagne et al., 2015). A better understanding of its quantitative link with grain-size and flow speed in the Southern Ocean is thus of great interest.

In this study, we report high-resolution Zr/Rb ratios, measured by both inductively coupled plasma-mass spectrometry (ICP-MS) and XRF scanning techniques, and conventional grain-size data from a series of sediment cores collected from the Prydz Bay and Ross Sea regions of the Southern Ocean. In combination with published data from cores in the Drake Passage, we evaluate the potential of the Zr/Rb count ratio from XRF scanning as a proxy for grain-size variations in glaciomarine sediments. This study is arranged as follows. First, since previous studies on sedimentary Zr/Rb ratios were mainly based on quantitative geochemical analyses (e.g., J. Chen et al., 2006; L. Liu et al., 2004), the robustness of Zr/Rb count ratio data from XRF scanning is tested by comparison to concentration data measured by ICP-MS. Second, the grain-size information carried in the Zr/Rb count ratio is identified by comparison to the measured grain-size spectra, with support from the results of grain-size separation experiments. Finally, the strengths and potential limitations of using the XRF scanning derived Zr/Rb count ratio as a proxy for sediment grain-size variations and ocean current strength are discussed.

2. Environmental Setting of the Southern Ocean

The Southern Ocean is the marine territory surrounding Antarctica, and its ocean currents transport heat, salt, and nutrients between the Pacific, Atlantic, and Indian Oceans (Bostock et al., 2013; Rintoul et al., 2010). It is also influenced by the major upwelling branch of the Meridional Overturning Circulation (J. Marshall and Speer, 2012) and is recognized as a key region for atmospheric and oceanic CO_2 exchange (Anderson et al., 2009; Jaccard et al., 2013, 2016; J. Marshall and Speer, 2012; Sigman et al., 2010).

Figure 1. Environmental setting of the study area. (a) The Southern Ocean and the studied core sites. The ocean frontal system is after Orsi et al. (1995) and Bostock et al. (2013). SACCF, Southern Antarctic Circumpolar Current Front; PF, Polar Front; SAF, Subantarctic Front; STF, Subtropical Front. (b) The Prydz Bay area. LGAISS, Lambert Glacier-Amery Ice Shelf system. (c) The Ross Sea area. See Table 1 for locations of the core sites. Figure plotted in Ocean data view (Schlitzer, 2009).

The surface of the Southern Ocean contains a series of oceanic fronts, defined by gradients in water properties including temperature, salinity, and nutrient concentrations (Orsi & Whitworth, 2005; Orsi et al., 1995, Figure 1a). From south to north, they are the Southern Antarctic Circumpolar Current Front (SACCF), Polar Front (PF), Subantarctic Front (SAF), and Subtropical Front (STF; Orsi et al., 1995). These fronts divide the surface of the Southern Ocean into several zones, including the Antarctic Zone south of the PF, the Polar Frontal Zone between the PF and SAF, and the Subantarctic Zone between the SAF and STF.

Table 1
Information on Sediment Cores Used and Referred to in This Study

Site	Label	Longitude (°E)	Latitude (°S)	Water depth (m)	Core length (cm)	Data source
ANT30/P1-02	P1-2	72.94	65.01	2,860	624	This study; Wu et al. (2017, 2018, 2019)
ANT30/P1-03	P1-3	73.02	65.99	2,542	599	This study; Wu et al. (2017); Tang et al. (2016)
ANT29/P4-01	P4-1	70.69	64.94	3,162	421	This study; Wu et al. (2017)
ANT31/JB06	JB06	173.91	74.47	567.5	299	This study
MD07-3,128	3,128	−75.57	52.66	1,032	-	Lamy et al. (2015)
PS97/093-2	93-2	−70.37	57.5	3,781	-	Toyos et al. (2020)

There are two major branches of oceanic currents in the Southern Ocean, namely the Antarctic Circumpolar Current (ACC) and the Antarctic Slope Current (ASC; Orsi et al., 1995). The ACC reaches from the surface to the seafloor and flows eastwards, driven by the Southern Westerly Winds and bounded by the SACCF and the STF (Orsi et al., 1995). The ASC is driven by the Southern Easterly Winds and flows westwards over the Antarctic continental shelf and slope (Mathiot et al., 2011). Between the ACC and ASC is the cyclonic Antarctic Divergence Zone (ADZ), which is represented by a series of mesoscale eddies forming under the shear stress of the Southern Westerly Winds and the Southern Easterly Winds (Meijers et al., 2010). The ADZ can intrude onto the Antarctic continental shelf, thereby supplying relatively warm and salty Circumpolar Deep Water (Yabuki et al., 2006). Additionally, over broad Antarctic continental shelf regions such as those of the Weddell Sea, Ross Sea, and Prydz Bay, cyclonic gyres dominate the oceanic transport.

Because of the cold climate conditions, the Southern Ocean is influenced by the presence of sea ice and icebergs. Satellite observations show that the maximum sea ice cover occurs in austral winter, with an area of ca. 18.3×10^6 km² during September forming a continuous ring around Antarctica, while minimum sea ice cover occurs in austral summer, with an area of ca. 3×10^6 km² in February (Comiso, 2010). Icebergs in the Southern Ocean are mainly distributed along the pathway of the ASC and in gyres over the Antarctic continental shelf and slope, but they can also be transported further northwards (Budge & Long, 2018), leading to the discharge of Iceberg Rafted Debris (IRD) across the entire Southern Ocean.

3. Materials

Materials used in this study were obtained from four sediment gravity cores ANT30/P1-02 (P1-2), ANT30/P1-03 (P1-3), ANT29/P4-01 (P4-1), and ANT31/JB06 (JB06) retrieved during the 29th, 30th, and 31st Chinese Antarctic Research Expeditions onboard *R/V Xuelong* in 2012–2013, 2013–2014, and 2014–2015, respectively (Figure 1, Table 1). Our major focus is on cores P1-2 and JB06.

Cores P1-2 (624 cm in length), P1-3 (599 cm), and P4-1 (421 cm) were retrieved from the lower continental slope and continental rise near Prydz Bay, East Antarctica in water depths of 2,542–3,162 m (Figure 1b, Table 1). The color of these cores varies cyclically between olive, brown, and gray. The core sediment principally consists of structureless clayey silt and silty clay, with a minor proportion of sand (63–2,000 μ m) and a few randomly distributed dropstones (>2 mm). Age models for these cores were established previously (Wu et al., 2017) by tuning their export production records to the LR04 benthic $\delta^{18}\text{O}$ stack (Lisiecki & Raymo, 2005), because extremely poor carbonate preservation prevents the application of oxygen isotope stratigraphy.

Core JB06 (299 cm in length) was collected from the JOIDES Trough on the western outer continental shelf of the Ross Sea, East Antarctica in a water depth of 568 m (Figure 1c, Table 1). The color of the core changes from light and dark gray at the bottom to olive at the top. The core sediments are coarser than in core P1-2 and are mainly composed of clayey silt and sandy clayey silt. Sand (>63 μ m) fractions mostly occur in the depth interval from 70 to 230 cm, with a few randomly distributed dropstones. Carbonates are rare in the core sediments, except toward the bottom between 240 and 270 cm core depth, where benthic foraminifera are common. No age model has been established for this core yet. However, previous studies from the Ross Sea indicate that such benthic foraminifera-rich sediments were deposited in a subice shelf environment during the last glacial period (<36 ka ¹⁴C age, Taviani et al., 1993; Yokoyama et al., 2016).

In addition to these four cores, we also refer to two other cores from previous studies in the vicinity of the Drake Passage (Figure 1, Table 1).

4. Methods

The experimental methods used in this study include geochemical analyses by XRF core scanning and ICP-MS, grain-size measurements, and water content measurements. All measurements on core JB06 are reported here for the first time. Grain-size measurements on core P1-2 (Wu et al., 2018) and XRF core scanning on cores P1-2, P1-3, and P4-1 (Wu et al., 2017) have been conducted previously, but Zr and Rb counts of these cores are reported and discussed here for the first time. Down core ICP-MS measurements were only conducted on core P1-2. Water content was only measured on core JB06. We also conducted Rb and Zr concentration measurements by ICP-MS on separated grain-size fractions from cores P1-2 and JB06 (see Section 4.3). All measurements were carried out at the State Key Laboratory of Marine Geology, Tongji University, Shanghai, China, except for the grain-size separation experiment, which was carried out at Qingdao Sparta Analysis & Test Co. Ltd., Qingdao, China.

4.1. XRF Core Scanning

XRF core scanning measurements were obtained directly on the split core surface of the archive half of each core using an AVAATECH XRF core scanner at 1 cm intervals. The split core surface was covered with a spex certiprep 3532 Ultralene foil (4 μm thick) to protect the probe of the scanner from contamination and to prevent desiccation of the sediment. A Pd filter was placed in front of the incoming X-ray beam and measurements were taken at 1 cm resolution with a size of 1×1 cm. Each core was triple-scanned for elements from Al to Ba at 1 mA at different tube voltages (10, 30, and 50 kV) with 30 s counting time. Further technical details relating to the XRF core scanner are described in Richter et al. (2006).

4.2. ICP-MS

For quantitative Rb and Zr analyses on core P1-2, dry bulk sediment was sampled at 2 cm intervals, finely ground and ashed at 600°C for 2 h to measure the loss on ignition, and digested in a concentrated HF and HNO₃ mixture, together with a series of Chinese and USGS rock and sediment reference materials, before analysis by ICP-MS (IRIS advantage) (Wei et al., 2003). The relative standard deviation (RSD), as calculated from the reference materials, is generally better than 5% for Rb and Zr. Duplicate measurements on randomly selected samples also indicate a very good reproducibility (RSD <5%).

4.3. Grain-Size Separation Experiment

To evaluate the relationship between grain-size and Zr and Rb concentrations, we conducted a grain-size separation experiment. Previous such experiments on loess have typically divided the sediment into <2, 2–8, 8–20, 20–32, and >32 μm fractions, because loess is mainly composed of clay- and silt-sized sediment (e.g., J. Chen et al., 2006; L. Liu et al., 2002). Because our samples contain significant proportions of sand, we followed the above divisions, but further divided the >32 μm fraction into 32–63, 63–150, 150–250, and >250 μm fractions. Briefly, a sample from each of cores P1-2 and JB06 was leached with 30% H₂O₂ and 1 mol/L acetic acid to remove organic matter and carbonate, respectively. The residues were then separated based on Stokes' settling velocity law into <2, 2–8, 8–32, and >32 μm fractions using a centrifuge, according to J. Chen et al. (2006). The >32 μm fractions were further separated into 32–63, 63–150, 150–250, and >250 μm fractions by sieving. The separated fractions were digested and measured by ICP-MS for Rb and Zr concentrations, following the procedures described in Section 4.2.

4.4. Sediment Grain-Size

Grain-size measurements were conducted at 2 cm intervals. For this analysis, 0.15 g of dry bulk sediment from each sample was successively treated with 10% H₂O₂, 1.0 N HCl, and 2.0 N NaOH in a water bath at 85°C to remove organic carbon, carbonate, and biogenic silica. After confirming the successful removal of

all biogenic components by microscope inspection, the samples were soaked in 20 ml distilled water and dispersed by an ultrasonicator for 2 min, followed by analysis using an Automatic Laser Analyzer (Beckman Coulter LS230; Wu et al., 2018). Such a particle size analyzer can be used for grain-size analysis in the range of 0.375–2,000 μm . The analytical reproducibility was assessed using the Normalized Euclidian Distance (ND), according to Jonkers et al. (2015). Measurements on 10 randomly selected duplicate samples indicate NDs that are all less than 0.02 (2%), indicating good reproducibility.

To investigate if the core sediments were subject to significant bottom current sorting, sortable silt mean grain-size (SS, defined as the geometric mean grain-size of the 10–63 μm fraction) and sortable silt percent (SS%, defined as the 10–63 μm fraction relative to the <63 μm fraction) were calculated after I. N. McCave et al. (1995). These parameters have previously been calculated for core P1-2 (I. McCave and Andrews, 2019).

It should be noted that our grain-size data was measured by laser particle sizer. Previously, I. McCave et al. (2006) criticized this approach for the determination of fine particle sizes on the grounds that shape effects could lead to slow-sinking platy particles below 10 μm in diameter leaking into the >10 μm range. However, such shape effects appear to be insignificant for glacial sediments from high latitude oceans because glacial grinding produces equant grains (Konert & Vandenberghe, 1997; N. Marshall et al., 2014). Overall, the reliability of laser sizer derived grain-size data has been confirmed by recent studies (Li & Piper, 2015; Mao et al., 2018; N. Marshall et al., 2014; I. McCave and Andrews, 2019).

To further explore the association between the Zr/Rb geochemistry and grain-size composition, we also defined a new variable, partial mean grain-size (PMG), which is defined as the mean grain-size of the interval from the finest grain-size bin (0.375 μm) to a coarser grain-size bin, as follows:

$$\text{PMG}_{g_m} = \frac{\sum_i^m g_i f_i}{\sum_i^m f_i} \quad (1)$$

where m is the serial number of a specified grain-size (μm); g_i and f_i represent the grain-size of the i -th grain-size bin and the volume percent of the i -th grain-size bin, respectively; and PMG_{g_m} means the PMG of the < g_m μm fractions. For instance, PMG_{63} represents the PMG of the <63 μm fraction ($m = 56$, $g_{56} = 63$).

4.5. Water Content

Water content was measured at 2 cm intervals in core JB06. 25–35 g freshly split samples were weighed, then dried at 55°C for 72 h and re-weighed. Water content was calculated as follows (Wu et al., 2019):

$$\text{WatCon} = \frac{(M_w - M_d)}{M_w} \times 100\%, \quad (2)$$

where WatCon represents water content (wt.%), and M_w and M_d refer to the weights of wet and dried samples, respectively.

5. Results

5.1. Core ANT30/P1-02

Downcore distributions of Rb and Zr in core P1-2 from both XRF core scanning and ICP-MS measurements show consistent glacial-interglacial variations (Figures 2a and 2b). In the Rb records, higher/lower values mainly coincide with cold/warm periods respectively, except during glacial marine isotope stage (MIS) 12, in which the values are as low as during the subsequent interglacial MIS 11. In contrast, the Zr records usually show higher values during interglacial periods and lower values during glacial periods. In the Zr/Rb ratio records (Figure 2c), the glacial-interglacial variation is even clearer than in the Rb and Zr records, with higher values during interglacial periods and lower values during glacial periods (including glacial MIS 12). The XRF scanning derived and ICP-MS derived Zr/Rb records display better consistency than the individual

Figure 2. Downcore records from Prydz Bay core P1-2 plotted versus age. (a) Rb counts and concentration. (b) Zr counts and concentration. (c) Zr/Rb count ratio from X-ray fluorescence (XRF) core scanning and Zr/Rb concentration ratio from inductively coupled plasma-mass spectrometry (ICP-MS). (d) Mean grain-size (samples with extremely high grain-size plotted in red). (e) SS and SS%. (f) Spectrum of grain-size compositions. Glacial intervals are shaded gray and labeled with MIS numbers according to Lisiecki and Raymo (2005).

Rb and Zr records, consistent with previous observations of major element counts and count ratios by XRF scanning (Dunlea et al., 2020).

The grain-size of the core sediment is dominated by the 1–20 μm fraction (Figure 2f), with the exception of two intervals with high sand content at ~ 365 ka and ~ 465 ka. Changes in mean grain-size generally exhibit a similar pattern to the Zr/Rb ratio (Figure 2c cf. Figure 2d). Despite the visual similarity, the correlation coefficient between the two records is only 0.07 ($N = 309$). However, after removing the extreme samples with high sand content (colored red in Figure 2d), the correlation between the records of Zr/Rb ratio and mean grain-size improves significantly to 0.55 ($N = 300$).

The $\overline{\text{SS}}$ varies between 14 and 25 μm , with an average of 20 μm , and the SS% varies between 8% and 49%, with an average of 25% (Figure 2e). The SS and SS% show significant glacial-interglacial fluctuations, but the temporal patterns of the two records differ during some intervals. Interestingly, the $\overline{\text{SS}}$ record shows a temporal pattern rather similar to the mean grain-size record (Figure 2d), while the temporal pattern of the SS% is more similar to changes in the Zr/Rb ratio (Figure 2c).

5.2. Core ANT31/JB06

In core JB06, the water content ranges from 20 to 80 wt.% (Figure 3a). It varies irregularly between 20 and 50 wt.% around an average value of ~ 30 wt.% in the lower 150 cm of the core, and then increases irregularly toward the core top. Rubidium (Figure 3b) and Zr (Figure 3c) counts show co-varying downcore changes in the upper 210 cm, whereas an inverse pattern emerges in the lower part of the core. The downcore pattern of the Zr/Rb count ratio (Figure 3d) mostly follows that of the Zr counts, with significant variability in the lower ~ 90 cm and a decreasing trend toward the core top. Generally, these records exhibit significant negative correlations with the water content (Figure 3a), with correlation coefficients between the water content and Rb and Zr counts of -0.81 and -0.78 ($N = 148$), respectively. The correlation coefficient between the water content and the Zr/Rb count ratio is much lower, at -0.44 ($N = 148$).

The core sediment is characterized by a higher fine sand content in the lower ~ 160 cm and a higher silt fraction in the upper ~ 140 cm (Figure 3g). The mean grain-size varies between 11 and 104 μm (Figure 3e), with an average of 39 μm and a generally decreasing trend toward the core top. Intervals with higher mean grain-size values correspond to intervals with higher fine sand content. The mean grain-size is positively correlated with the Zr/Rb count ratio, but the correlation coefficient is only 0.34 ($N = 148$).

The $\overline{\text{SS}}$ varies between 19 and 40 μm , with an average of 26 μm , and the SS% varies between 32% and 88%, with an average of 53% (Figure 3f). Downcore patterns of the two records are rather consistent, and both are similar to the Zr/Rb count ratio (Figure 3d), with the closest match arising for the SS% record (e.g., compare records at ~ 290 cm).

5.3. Regional Comparison of Zr/Rb in Prydz Bay Sediment Cores

Temporal patterns of the XRF scanning derived Rb, Zr, and Zr/Rb ratios in cores P1-3 and P4-1 are consistent with those of core P1-2 (Figure 4). Hence, both the pattern and amplitude of glacial-interglacial variations appear to be reproducible across multiple cores in Prydz Bay.

5.4. Grain-Size Separation Experiment

The distributions of Rb, Zr, and Zr/Rb against grain-size are fairly consistent between the two cores (Figure 5). Rubidium concentration varies between 100 and 240 ppm in core P1-2 and between 45 and 180 ppm in core JB06, being higher in core P1-2 than core JB06 for all grain-size classes (Figure 5a). In core JB06, Rb decreases with increasing grain-size across the whole grain-size spectrum, while in core P1-2 Rb decreases with increasing grain-size in the <63 μm fraction but then slightly increases with increasing grain-size in the >63 μm fraction. In contrast, Zr concentrations are comparable in the two cores, varying between 104 and 327 ppm in core P1-2 and between 77 and 254 ppm in core JB06 (Figure 5b). In both cores, Zr content increases with increasing grain-size in the <63 μm fraction and decreases significantly with increasing grain-size in the >63 μm fraction. The Zr/Rb ratio varies between 0.5 and 3.0 in core P1-2 and 0.8–3.1 in core

Figure 3. Downcore records from Ross Sea core JB06 plotted versus depth. (a) Water content (note reversed axis). (b) Rb counts from X-ray fluorescence (XRF) scanning. (c) Zr counts from XRF scanning. (d) Zr/Rb count ratio from XRF scanning. (e) Mean grain-size. (f) SS and SS%. (g) Spectrum of grain-size compositions. Dashed lines in (d) and (e) indicate the general decreasing trends toward the core top. The yellow shading indicates a layer rich in benthic foraminifera of last glacial age (<36 ka ^{14}C age according to Taviani et al. [1993] and Yokoyama et al. [2016]).

Figure 4. Time series derived from X-ray fluorescence scanning of (a) Rb counts, (b) Zr counts, and (c) $\ln(\text{Zr}/\text{Rb})$ count ratios from Prydz Bay sediment cores P1-2, P1-3, and P4-1. Glacial intervals are shaded gray and labeled with MIS numbers according to Lisiecki and Raymo (2005).

JB06 (Figure 5c), with slightly higher values in core JB06 than in core P1-2 for all grain-size classes. We also note that the distribution of Zr/Rb approximately follows the Zr concentration: it increases with increasing grain-size in the $<63\ \mu\text{m}$ fraction and decreases with increasing grain-size in the $>63\ \mu\text{m}$ fraction.

6. Discussion

6.1. Relationship Between Zr/Rb Ratios From ICP-MS and XRF Scanning

XRF scanning data are widely regarded as semi-quantitative due to specimen and matrix effects. The specimen effect relates to the inhomogeneity and irregular measurement geometry of the specimen (Jenkins, 2012; Vries & Vrebo, 2002), which can be reduced by smoothing the split core surface to be scanned (Richter et al., 2006), while the matrix effect describes the influence of interelement interactions. The matrix effect is a nonlinear function of the concentrations of all the elements present, which can induce scattering, absorption, and enhancement effects on the intensities of the element of interest (G. J. Weltje and Tjallingii, 2008; G. Weltje et al., 2015). In particular, variability in water content linked to changes in the sedimentary phases present and/or the extent of compaction usually imparts a significant matrix effect (Q. Chen et al., 2016; Lyle & Backman, 2013; Tjallingii et al., 2007).

In our records, the minor discrepancies between Rb and Zr derived from XRF scanning and ICP-MS measurements in core P1-2 could be interpreted as a result of matrix and/or specimen effects (Figures 2a and 2b), while the Rb and Zr counts in core JB06 are clearly affected by changes in water content (Figures 3a–3c). Hence, the relationship between Zr and Rb data derived from XRF scanning and ICP-MS measurement needs to be carefully considered.

In order to convert element counts from XRF scanning into element concentrations, early studies usually applied the general linear regression technique (e.g., Jansen et al., 1998; Tjallingii et al., 2007). However, these studies did not consider the matrix and specimen effects (G. J. Weltje and Tjallingii, 2008), which can lead to considerable scatter and bias in cross-plots of intensity versus concentration, as evidenced in our

Figure 5. Results of grain-size separation experiment on cores P1-2 and JB06. Distribution of (a) Rb concentration, (b) Zr concentration, and (c) Zr/Rb concentration ratio against grain-size. All data were measured by inductively coupled plasma-mass spectrometry (ICP-MS).

Rb and Zr data (Figures 6a and 6b). More recently, studies have highlighted that corrections for interstitial water content can improve the conversion of counts to concentration (Q. Chen et al., 2016; Lyle et al., 2012). However, these studies focused mainly on long-term trends of element distributions, and were only able to reduce but not eliminate matrix effects (Q. Chen et al., 2016; Lyle et al., 2013).

In parallel, based on the theory of XRF spectroscopy and principles of compositional data analysis, G. J. Weltje and Tjallingii (2008) proposed a log-ratio calibration equation (LRCE) for relating element count ratios from XRF scanning to element concentration ratios, as follows:

$$\ln\left(\frac{W_{ij}}{W_{iD}}\right) = \alpha_{jD} \ln\left(\frac{I_{ij}}{I_{iD}}\right) + \beta_{jD}, \quad (3)$$

where W_{ij} and W_{iD} represent the concentrations (weight proportion) of elements j and D in specimen i ; I_{ij} and I_{iD} represent the net intensity of elements j and D in specimen i from XRF scanning; and the coefficients α_{jD} and β_{jD} represent the matrix effect and machine detection efficiency, respectively, for element j relative to element D . The LRCE has been further updated to a multivariate calibration equation that better accounts for the matrix effect and is able to predict bulk element concentrations (G. Weltje et al., 2015), but here we are interested in only the Zr/Rb ratio and hence consider Equation 3 to be sufficient.

For a specific elemental ratio, the specimen effect is eliminated and α_{jD} and β_{jD} in Equation 3 become constants, because two simultaneously measured elements are subject to the same specimen effect and a co-variant matrix effect (G. J. Weltje and Tjallingii, 2008). Since both Zr and Rb counts were measured at 30 kV voltage, Equation 3 is appropriate for describing the relationship between the Zr/Rb count ratio and concentration ratio, as follows:

$$\ln\left(\frac{W_{iZr}}{W_{iRb}}\right) = \alpha_{Zr-Rb} \ln\left(\frac{I_{iZr}}{I_{iRb}}\right) + \beta_{Zr-Rb}, \quad (4)$$

where W_{iZr} and W_{iRb} represent the concentrations of Zr and Rb in specimen i ; I_{iZr} and I_{iRb} represent the net intensity of Zr and Rb in specimen i from XRF scanning; and the coefficients α_{Zr-Rb} and β_{Zr-Rb} represent the matrix effect and machine detection efficiency, respectively, for Zr relative to Rb.

Equation 4 indicates that the Zr/Rb count ratio should be linearly correlated with its concentration counterpart on a log-log plot. Indeed, our $\ln(\text{Zr/Rb})$ concentration data from ICP-MS and $\ln(\text{Zr/Rb})$ count ratio from XRF scanning are in good agreement with this relationship ($r = 0.83$, $N = 309$; Figure 6c). In practice, the Zr/Rb concentration ratio in a given sediment core is expected to vary over a limited range, leading to strong correlations between the Zr/Rb ratio and its logarithm, namely:

$$\ln\left(\frac{W_{iZr}}{W_{iRb}}\right) = c_1 \frac{W_{iZr}}{W_{iRb}} + c_2, \quad (5)$$

where c_1 and c_2 are constants that represent the slope and intercept, respectively, of the linear relationship. In core P1-2, the Zr/Rb concentration ratio varies between 0.6 and 1.4, and the correlation coefficient between the Zr/Rb concentration ratio and its logarithm is 0.999 ($N = 312$, Figure 6d). Consequently, $\ln(\text{Zr/Rb})$ count ratios from XRF scanning can be calibrated to derive Zr/Rb concentration ratios ($r = 0.88$, $N = 309$; Figure 6e), according to:

$$\frac{W_{iZr}}{W_{iRb}} = \alpha \ln\left(\frac{I_{iZr}}{I_{iRb}}\right) + \beta, \quad (6)$$

where

$$\alpha = \frac{\alpha_{Zr-Rb}}{c_1} \quad (7)$$

Figure 6. Scatter plots for core P1-2 of (a) Rb concentration versus Rb counts, (b) Zr concentration versus Zr counts, (c) $\ln(\text{Zr/Rb})$ concentration ratio versus $\ln(\text{Zr/Rb})$ count ratio, (d) Zr/Rb concentration ratio versus $\ln(\text{Zr/Rb})$ concentration ratio, and (e) Zr/Rb concentration ratio versus $\ln(\text{Zr/Rb})$ count ratio. The count data were derived from X-ray fluorescence core scanning and the concentration data from inductively coupled plasma-mass spectrometry (ICP-MS) measurement.

Figure 7. Bootstrap test on the robustness of the calibration between $\ln(\text{Zr/Rb})$ count ratios (from X-ray fluorescence [XRF] core scanning) and Zr/Rb concentration ratios (from ICP-MS; Figure 6e). (a and b) Probability distributions of slope α and intercept β in Equation 6. (c) Measured Zr/Rb concentrations in core P1-2 (ICP-MS data) compared to estimates based on the calibration of XRF scanning data. Glacial intervals in (c) are shaded gray and labeled with MIS numbers according to Lisiecki and Raymo (2005). ICP-MS, inductively coupled plasma-mass spectrometry.

$$\beta = \frac{\beta_{\text{Zr-Rb}} - c_2}{c_1}. \quad (8)$$

To test the robustness of the calibration, we applied a nonparametric bootstrap re-sampling algorithm to the Zr/Rb dataset of core P1-2. Ten thousand replicates were generated using a uniform distribution pseudo-random number generator, with a sample size for each replicate of 18, which is the square root of the total number of samples (309) (Efron & Tibshirani, 1994). The result shows that both α and β parameters obey normal distributions (Figures 7a and 7b). Furthermore, applying this calibration to the downcore $\ln(\text{Zr/Rb})$ count data from XRF scanning produces estimates of Zr/Rb concentration ratios that closely match the measured ICP-MS data (Figure 7c). Together, these observations support the robustness of the linear relationship between the $\ln(\text{Zr/Rb})$ count ratio and the Zr/Rb concentration ratio. In addition, the consistent

temporal variations of the $\ln(\text{Zr}/\text{Rb})$ count ratio recorded in three Prydz Bay cores (i.e., P1-2, P1-3, and P4-1; Figure 4) supports the general reliability of the $\ln(\text{Zr}/\text{Rb})$ ratio as a proxy for regional paleoenvironmental change, because these cores were retrieved from the same sedimentary environment and are expected to record a similar pattern of past changes (Wu et al., 2017, 2019).

6.2. Relationship Between Zr/Rb Ratio and Grain-Size of Southern Ocean Sediments

Our records demonstrate clear links between grain-size parameters and Zr/Rb ratios (Figures 2 and 3), but there are some discrepancies between the Zr/Rb ratio and the mean grain-size of the bulk sediment (e.g., Figure 2d cf. Figure 2c). Unlike in paleosol sequences, these differences cannot be attributed to postdepositional modifications (J. Chen et al., 2006; Liu et al., 2002, 2004), because such processes are largely restricted by the low temperatures of the Southern Ocean (Ehrmann et al., 1992) and low dissolved oxygen availability on the seafloor (Garcia et al., 2013). Hence, the relationship between the Zr/Rb ratio and the grain-size of Southern Ocean sediments requires careful consideration.

6.2.1. Relationship Between $\ln(\text{Zr}/\text{Rb})$ and Grain-Size Distributions

Grain-size separation experiments on loess show that, with increasing grain-size, decreases in Rb concentration and increases in Zr concentration are monotonous (J. Chen et al., 2006; L. Liu et al., 2002). In our samples, such a relationship appears to hold only in the $<63\ \mu\text{m}$ fraction (Figure 5), especially for Zr which peaks in the $32\text{--}63\ \mu\text{m}$ fraction and then decreases significantly with increasing grain-size in the sand fraction (Figure 5b). The enrichment of Rb in the fine sediments (Figure 5a) is consistent with its predominant association with clay minerals, although the presence of minor Rb in the coarser fractions may indicate its additional occurrence in K-feldspar or mica. For Zr, its enrichment within a limited grain-size range (i.e., $\sim 8\text{--}150\ \mu\text{m}$; Figure 5b) may indicate that zircon, as the likely major host mineral, is predominantly present in this grain-size range.

Overall, the grain-size separation experiment confirms the grain-size-dependence of the Zr/Rb ratio in both studied cores (Figure 5c), but only provides relatively low grain-size resolution. In addition, for the coarse fractions ($>32\ \mu\text{m}$) separated by sieving, the experiment does not represent a perfect analog for current sorting in the natural environment, which is influenced not only by grain-size but also by mineral density, albeit that density is a much weaker secondary control. Therefore, to explore the association between grain-size and Zr/Rb geochemistry at higher grain-size resolution and in an environmentally relevant scenario, we calculated spectra of the correlation coefficient between the downcore XRF scanning derived $\ln(\text{Zr}/\text{Rb})$ count ratio and both the volume percent of each grain-size bin (Figures 8a and 8b) and the PMG (Figures 8c and 8d).

In core P1-2 (Figure 8a), the $\ln(\text{Zr}/\text{Rb})$ ratio is negatively correlated with the $<6\ \mu\text{m}$ fractions, which include clay and fine silt, and is positively correlated with the $7\text{--}63\ \mu\text{m}$ fractions, which represent medium and coarse silt. At larger grain-sizes, the correlation with the sand ($>63\ \mu\text{m}$) fractions is generally statistically insignificant ($p > 0.01$). The $4\text{--}10\ \mu\text{m}$ interval represents a transition from negative to positive correlations, while the $50\text{--}90\ \mu\text{m}$ interval is a region where the positive correlation rapidly becomes poor.

In core JB06, the correlation spectrum shows a similar pattern to core P1-2, but with different threshold values (Figure 8b cf. Figure 8a). In this core, the $\ln(\text{Zr}/\text{Rb})$ ratio is negatively correlated with the $<23\ \mu\text{m}$ fractions, which include clay and fine to medium silt, and is positively correlated with the $30\text{--}100\ \mu\text{m}$ fractions, which include medium to coarse silt and fine sand. Its correlation with coarser sand fractions is negative or insignificant. There are also two major transitions in the correlation coefficient for core JB06, but at different grain-size intervals than in core P1-2. The first transition is from negative to positive correlations over the $20\text{--}40\ \mu\text{m}$ interval, while the second transition is over the $90\text{--}120\ \mu\text{m}$ interval, where the correlation rapidly becomes poor and/or insignificant.

Overall, while providing higher grain-size resolution, the correlation spectra (Figure 8) are consistent with the distribution of the Zr/Rb concentration ratio in our grain-size separation experiment (Figure 5c), thereby confirming the general validity of extending the experimental results to environmental applications.

Figure 8. Correlation relationship between the $\ln(\text{Zr}/\text{Rb})$ count ratio and grain-size from sediment cores P1-2 and JB06. (a and b) Spectra of the correlation coefficient between the $\ln(\text{Zr}/\text{Rb})$ count ratio and the volume percent of sediment in each grain-size bin from cores P1-2 and JB06, respectively. (c and d) Spectra of the correlation coefficient between the $\ln(\text{Zr}/\text{Rb})$ count ratio and the partial mean grain-size in cores P1-2 and JB06, respectively. The $\ln(\text{Zr}/\text{Rb})$ count ratio was derived from X-ray fluorescence core scanning. Colored dots indicate correlation coefficients that are statistically significant (red) or insignificant (black) relative to the 1% confidence level.

In the two transition zones (Figures 8a and 8b), the correlation relationship between the $\ln(\text{Zr}/\text{Rb})$ ratio and grain-size changes dramatically. The first transition zone represents changes from Rb-dominated to Zr-dominated sediment fractions (Figure 5) and is located close to $10\ \mu\text{m}$, which represents the approximate boundary between cohesive ($<10\ \mu\text{m}$) and noncohesive ($>10\ \mu\text{m}$) sediment fractions (I. N. McCave et al., 1995). The second transition zone occurs around the grain-size of fine sand, and corresponds to significant decreases in Zr concentrations and Zr/Rb ratios (Figure 5). Comparing the spectra of correlation with the average grain-size distributions (Figures 8a and 8b, shaded areas), it is clear that the majority of the sediment in these cores comprises grain-size fractions finer than those of the second transition zone (i.e., approximately the $<63\ \mu\text{m}$ fraction in core P1-2 and the $<100\ \mu\text{m}$ fraction in core JB06).

In the spectra of correlation coefficients between the $\ln(\text{Zr}/\text{Rb})$ ratio and the PMG (Figures 8c and 8d), high positive correlation coefficients are present between the $\ln(\text{Zr}/\text{Rb})$ ratio and PMG_{63} in core P1-2, and between the $\ln(\text{Zr}/\text{Rb})$ ratio and PMG_{100} in core JB06. The correlation then decreases rapidly with the progressive inclusion of $>63\ \mu\text{m}$ fractions in core P1-2 and $>100\ \mu\text{m}$ fractions in core JB06.

In summary, the combination of the experiments and downcore analyses indicates that the $\ln(\text{Zr}/\text{Rb})$ ratio mainly reflects the grain-size composition of the relatively fine fractions (silt and fine sand) which comprise the majority of the core sediments, with only a minor influence from the relatively coarse fractions (i.e., $>63\ \mu\text{m}$ fraction in core P1-2 and $>100\ \mu\text{m}$ fraction in core JB06).

6.2.2. Limited Influence of Coarse IRD Fractions on $\ln(\text{Zr}/\text{Rb})$ Ratios

In the open Southern Ocean, coarse sediment fractions $>63\ \mu\text{m}$ or $>100\ \mu\text{m}$ are often considered to be predominantly derived from IRD, because bottom currents are typically too weak to move and sort lithic

Figure 9. Scatter plots of (a) mean grain-size versus volume percent of the $>63 \mu\text{m}$ fraction in core P1-2, (b) $\ln(\text{Zr/Rb})$ from X-ray fluorescence scanning versus volume percent of the $>63 \mu\text{m}$ fraction in core P1-2, (c) SS versus volume percent of the $>63 \mu\text{m}$ fraction in core P1-2, (d) mean grain-size versus volume percent of the $>100 \mu\text{m}$ fraction in core JB06, (e) $\ln(\text{Zr/Rb})$ from X-ray fluorescence core scanning versus volume percent of the $>100 \mu\text{m}$ fraction in core JB06, and (f) SS versus volume percent of the $>100 \mu\text{m}$ fraction in core JB06.

grains of such a diameter (Lamy et al., 2015; I. McCave and Andrews, 2019). Scatter plots between the coarse fraction percent and the bulk mean grain-size show significant positive correlations (Figures 9a and 9d), indicating that the addition of IRD to the sediment biases the mean grain-size toward coarser values (Jonkers et al., 2015; Figures 2 and 3). In contrast, the lack of correlation between the coarse fraction percent and the $\ln(\text{Zr/Rb})$ ratio (Figures 9b and 9e) suggests that IRD input does not significantly perturb the $\ln(\text{Zr/Rb})$ ratio of the bulk sediment.

Coarse IRD in the Southern Ocean is predominantly composed of quartz (e.g., Teitler et al., 2010; Williams et al., 2010) because it is abundant in Antarctic source rocks and resistant to weathering. For both studied cores, sieving and microscope inspection indicate that the $>63 \mu\text{m}$ fraction is predominantly composed of quartz ($>85\%$), with minor rock and other mineral fragments ($<10\%$), and minor biogenic fragments (e.g., foraminifera, radiolarians, and sponge spicules; 0% – 15% ; data repository [DR] Figure S1). Neither quartz nor biogenic fragments are expected to be rich in Rb or Zr, which is consistent with the low Rb and Zr concentrations in the separated $>63 \mu\text{m}$ fractions (Figures 5a and 5b). In addition, the coarse IRD fractions account for only modest proportions of the total sediment ($<50\%$, usually $<25\%$, with an average of $\sim 10\%$, see Figure 9). Together, these factors explain the lack of influence of the coarse IRD fraction on the $\ln(\text{Zr/Rb})$ ratios, and hence the potential for IRD inputs to decouple $\ln(\text{Zr/Rb})$ ratios from the bulk sediment mean grain-size (e.g., Figures 2 and 3).

6.2.3. Role of Local Hydrodynamics

The sensitivity of the Zr/Rb ratio to grain-size diminishes, and is ultimately lost, in the $>63 \mu\text{m}$ fraction in core P1-2 and in the $>100 \mu\text{m}$ fraction in core JB06 (Figure 8). Here we suggest that the different

grain-size value characterizing this second transition zone in the two cores is mainly determined by local hydrodynamics.

In core JB06, there is no correlation between the $> 100 \mu\text{m}$ fraction and the $\overline{\text{SS}}$ (Figure 9f), while down-core variations of the $\overline{\text{SS}}$ and $\text{SS}\%$ (Figure 3f) are characterized by a correlation coefficient of 0.86, which indicates that the sediment is current-sorted (I. McCave and Andrews, 2019). In the modern ocean, bottom current speeds in the Western Ross Sea range from tens of cm/s to >1 m/s, primarily composed of a tidal (barotropic) component and a benthic gravity component (Gordon et al., 2004). The $\overline{\text{SS}}$ values of core JB06 increase toward the base of the core (Figure 3f), indicating that the vigor of the local bottom current was even stronger in the past than today. Such a strong local bottom current is comparable to or stronger than those inferred from sediment cores in the Drake Passage region (Lamy et al., 2015; Toyos et al., 2020), and hence would be sufficient to sort fine sand as well as silt fractions (Lamy et al., 2015; Mao et al., 2018; I. McCave and Andrews, 2019).

In contrast, in core P1-2, the $\overline{\text{SS}}$ and $\text{SS}\%$ have different temporal patterns (Figure 2e) and a correlation coefficient of only 0.37 ($N = 312$), which implies that the bulk sediment generally lacks significant features of bottom current sorting. Since the $\overline{\text{SS}}$ and the sand percent ($>63 \mu\text{m}$) show a correlation (Figure 9c), the $\overline{\text{SS}}$ was potentially affected by the input of IRD. Nevertheless, the much finer $\overline{\text{SS}}$ values in core P1-2 than in core JB06 would tend to suggest slower flow speeds, consistent with a modern bottom current speed near the core site of <5 cm/s (Meijers et al., 2010). The average and the highest $\overline{\text{SS}}$ values in the record are 20 and $25 \mu\text{m}$, which are 2 and $7 \mu\text{m}$ higher than the core top value ($18 \mu\text{m}$). If those values are taken at face value, by applying a modern current speed of 5 cm/s (Meijers et al., 2010) and the universal flow speed versus grain-size calibration gradient (I. N. McCave et al., 2017), we estimate that the local bottom current has averaged ~ 8 cm/s and has not been above ~ 15 cm/s over the last 523 Kyr. These speeds are much slower than at site JB06, and hence would be unable to impart a current-sorting signature on the fine sand fraction (e.g., Jonkers et al., 2015).

In summary, when bottom currents are very strong, they can sort fine sand fractions in addition to silt, and in such a case the fine sand fractions derived from IRD would also be sorted. This scenario would enable sorting of Zr- and Rb-bearing minerals within these fractions, thereby generating significant correlations between the Zr/Rb geochemistry and the content of these grain-size fractions. Indeed, our Zr/Rb and grain-size data from the Ross Sea core JB06 (Figures 8b and 8d) may be taken as a confirmation that fine sand fractions in this region can be transported by ocean currents. This observation reiterates the importance of using a coarser grain-size diameter (e.g., >150 or $250 \mu\text{m}$) to define IRD in sedimentary records from the polar oceans (e.g., Passchier, 2011; Wilson et al., 2018).

6.2.4. Relationship Between Grain-Size Parameters and $\ln(\text{Zr/Rb})$ in the Southern Ocean

Based on the correlation analysis between $\ln(\text{Zr/Rb})$ and grain-size (Figure 8), a series of grain-size parameters would be expected to be related to downcore changes in $\ln(\text{Zr/Rb})$. For core P1-2, we plot the PMG of the $<63 \mu\text{m}$ fraction (PMG_{63} ; Figure 10a), the ratio of the volume percent in the $7\text{--}63 \mu\text{m}$ and the $<6 \mu\text{m}$ fractions (Figure 10b), the $\text{SS}\%$ (Figure 10c), and the $\overline{\text{SS}}$ (Figure 10d). For core JB06, we plot the PMG of the $<100 \mu\text{m}$ (PMG_{100}) (Figure 11a), the ratio of the volume percent in the $30\text{--}100 \mu\text{m}$ and the $<23 \mu\text{m}$ fractions (Figure 11b), the $\text{SS}\%$ (Figure 11c), and the $\overline{\text{SS}}$ (Figure 11d). Although not perfect, the parameters PMG_{63} of core P1-2 and PMG_{100} in core JB06 can be considered to provide the IRD-corrected mean grain-size (i.e., the mean grain-size of the sediment after excluding unsorted coarse fractions). Comparison to those records indicates that the $\ln(\text{Zr/Rb})$ ratio mainly reflects the grain-size composition of the IRD-corrected fractions of the sediments.

For both our studied cores, the $\text{SS}\%$ and $\ln(\text{Zr/Rb})$ have consistent downcore patterns (Figure 10c cf. Figure 10e, Figure 11c cf. Figure 11e) and are highly correlated (Figure 12b), regardless of whether the $\overline{\text{SS}}$ is well correlated with the $\text{SS}\%$ (JB06) or not correlated (P1-2; Figure 12a). The $\text{SS}\%$ and $\ln(\text{Zr/Rb})$ show a good correlation because the major enrichments of Rb and Zr overlap with the $<10 \mu\text{m}$ fraction and the $10\text{--}63 \mu\text{m}$ fraction, respectively (Figures 5a, 5b, 8a, and 8b). Therefore, if the $\text{SS}\%$ and $\overline{\text{SS}}$ are correlated, which provides

Figure 10. Time series of grain-size parameters relating to $\ln(\text{Zr/Rb})$ in core P1-2. (a) PMG_{63} . (b) Ratio of the volume percent in the 7–63 μm fraction and the <6 μm fraction. (c) $\text{SS}\%$. (d) SS . (e) $\ln(\text{Zr/Rb})$ count ratio from X-ray fluorescence core scanning. Glacial intervals are shaded gray and labeled with MIS numbers according to Lisiecki and Raymo (2005).

an indicator for current sorting (I. N. McCave and Hall, 2006), the $\ln(\text{Zr/Rb})$ and SS will also be correlated (Figure 12a cf. Figure 12c). Hence, in cases of current-sorting, temporal changes in the $\ln(\text{Zr/Rb})$ ratio will reflect relative changes of the bottom current speed. Such a scenario applies to core JB06 from the Ross Sea continental shelf, as well as to core 3128 from the southern coast of Chile (Lamy et al., 2015) and core 93-2 from the Drake Passage (Toyos et al., 2020; Figures 12a–12c).

Figure 11. Downcore record of grain-size parameters relating to $\ln(\text{Zr/Rb})$ in core JB06. (a) PMG_{100} . (b) Ratio of the volume percent in the 30–100 μm fraction and the <23 μm fraction. (c) SS%. (d) $\overline{\text{SS}}$. (e) $\ln(\text{Zr/Rb})$ count ratio from X-ray fluorescence core scanning. The yellow shading indicates a layer rich in benthic foraminifera of last glacial age (<36 ka ^{14}C age according to Taviani et al. [1993] and Yokoyama et al. [2016]).

In cases where $\overline{\text{SS}}$ data are available but not accompanied by SS% data, the robust relationship between $\ln(\text{Zr/Rb})$ and $\overline{\text{SS}}$ (Figure 12b) could potentially be useful in discriminating whether sediments were subject to bottom current sorting. For example, measurements by Coulter counter cannot provide information on SS%; in such cases, $\ln(\text{Zr/Rb})$ ratios could provide a proxy for SS% variations.

Interestingly, although the regression lines between $\ln(\text{Zr/Rb})$ and SS% differ between cores, their slopes are rather consistent (Figure 12b). For the bottom current-sorted sediments (i.e., cores JB06, 3128, and 93-2), the slopes of the regression lines between $\ln(\text{Zr/Rb})$ and $\overline{\text{SS}}$ are also similar (Figure 12c). These relationships are readily visualized when the core data are normalized by subtracting their respective mean values (Figures 12d–12f). Single values for the slopes may be derived by combining the datasets from multiple cores: 0.32 for $\overline{\text{SS}}$ versus SS%, 34.1 for SS% versus $\ln(\text{Zr/Rb})$, and 12.7 for $\overline{\text{SS}}$ versus $\ln(\text{Zr/Rb})$. Since these cores were

Figure 12. Scatter plots of (a) SS versus $SS\%$, (b) $SS\%$ versus X-ray fluorescence (XRF) $\ln(Zr/Rb)$, (c) SS versus XRF $\ln(Zr/Rb)$, (d) SS_N versus $SS\%_N$, (e) $SS\%_N$ versus XRF $\ln(Zr/Rb)_N$, (f) SS_N versus XRF $\ln(Zr/Rb)_N$. The parameters $SS\%_N$, SS_N , and XRF $\ln(Zr/Rb)_N$ are the values after subtracting their respective means. In the legends, S is the slope of regression lines and R is the correlation coefficient. In (e), the S and R values were calculated based on all core data. In (d and f), the S and R values were calculated based on data from cores JB06, 3128, and 93-2. See Table 1 for core locations and references. Note that different methods were used for grain-size measurements in different studies, that is, grain-size from cores P1-2 and JB06 was measured using an Automatic Laser Analyzer (Beckman Coulter LS230), whereas grain-size from cores 3128 and 93-2 was measured by a Micromeritics SediGraph 5100. Data from MIS 1, 5, and 11 in core 93-2 are anomalous and therefore not plotted (see Toyos et al., 2020).

retrieved from different regions of the Southern Ocean under the influence of different hydrodynamic conditions, the consistent slopes may reflect a general association between grain-size and Zr/Rb geochemistry of glaciomarine sediments from the Southern Ocean. If validated by data from additional sediment cores, these values could provide a simple means to estimate the magnitude of changes in $SS\%$ and SS based on the $\ln(Zr/Rb)$ ratio from XRF scanning. When combined with the universal grain-size-flow speed calibration gradient proposed by I. N. McCave et al. (2017), the magnitude of changes in flow speed could then be estimated in cases where the sediments are bottom current-sorted.

6.3. Scope for the Application of $\ln(Zr/Rb)$ as a Grain-Size Proxy

Our findings indicate that the $\ln(Zr/Rb)$ count ratio reflects IRD-corrected mean grain-size and can be used to indicate changes in bottom current strength if the sediment is current-sorted. Hence, long high-resolution records of bottom current strength can be obtained by calibrating the $\ln(Zr/Rb)$ ratios using a relatively small number of grain-size measurements on discrete samples (e.g., Toyos et al., 2020). Since the sediment core sites of our study and previous studies (Lamy et al., 2015; Toyos et al., 2020; Table 1) are located in different regions of the Southern Ocean with different sedimentary and hydrodynamic conditions, the consistent association between $\ln(Zr/Rb)$ ratios and grain-size variations (Figure 12) suggests a wide applicability of this approach in the Southern Ocean. In addition, the combination of these studies suggests that it

can be applied over a wide range of temporal resolution (e.g., millennial to orbital) and time periods (e.g., Holocene to >1 Ma).

The basis for the association between $\ln(\text{Zr/Rb})$ ratios and sediment grain-size is that the Zr/Rb geochemistry is closely related to the grain-size of lithogenic particles. Because Zr and Rb are predominantly contained in detrital minerals, the correlation between $\ln(\text{Zr/Rb})$ and grain-size is not notably affected by processes such as biogenic deposition or authigenic mineral precipitation. Nevertheless, we caution that our studied cores were carbonate-poor, and that dilution by biogenic components could possibly affect the application of the proxy to carbonate-rich sediments (e.g., Toyos et al., 2020), which will require testing in future studies. While Si/Al ratios can also be well correlated to sediment grain-size (e.g., Bouchez et al., 2011; Guo et al., 2018; Lamy et al., 2015), interpretations of Si/Al in the Southern Ocean could be complicated by Si supplied to sediments by the biological productivity of abundant siliceous organisms (e.g., diatoms, sponge spicules, and radiolarians). In addition, if the goal is to obtain information related to current-sorting, another major benefit of using Zr/Rb ratios is their insensitivity to the input of coarse quartz-rich IRD (Figures 5 and 9), whereas such inputs would perturb Si/Al ratios.

In a recent study, D. Liu et al. (2019) developed a statistical model to predict sediment mean grain-size using multielement data from XRF scanning. However, when applying such a model to our downcore data (DR Figures S2–S5), we found that only the long-term trends of the mean grain-size time series can be predicted, whereas high frequency variability is smoothed, particularly during intervals with abundant coarse fractions (DR Figures 3 and 4). Such a scenario likely arises in part because the geochemistry can be independent of, or relatively insensitive to, the proportion and grain-size of the unsorted coarse fractions (e.g., Figures 5 and 9). In addition, the elements Mn and Fe are both used in that multielement model, but can be significantly affected by their enrichment in oxide and oxyhydroxide phases. In the Southern Ocean, Mn-oxides/hydroxides are typically authigenic in origin, and their formation may be affected by changes in abyssal ventilation (e.g., S. L. Jaccard et al., 2016; Jiménez-Espejo et al., 2019; Presti et al., 2011; Wu et al., 2018), while Fe-oxides/hydroxides can be associated with provenance changes (e.g., Wu et al., 2019). As such, these two elements may vary independent of sediment grain-size in the Southern Ocean. For the above reasons, the multielement model is considered to be unsuitable for application to glaciomarine sediments (D. Liu et al., 2019), whereas the $\ln(\text{Zr/Rb})$ ratio is insensitive to such factors, making it more suitable for characterizing grain-size variations in Southern Ocean sediments. In particular, we emphasize the strength of Zr/Rb ratios in recording grain-size in the sortable fine fraction, whereas it appears that the mean grain-size predictions from the multielement approach also contain a significant signal from unsorted coarser sand fractions (DR Figure 4).

Despite these strengths, successful application of the $\ln(\text{Zr/Rb})$ ratio as a proxy for grain-size probably relies on sediment provenance being relatively stable through time. This condition has presumably been met in the cores discussed above (Table 1), but it may not be the case in all regions, making it important to assess the sensitivity of Zr/Rb ratios to sediment provenance changes. Importantly, we have shown that the $\ln(\text{Zr/Rb})$ ratio is insensitive to quartz-dominated IRD input at levels of up to ~25% and perhaps higher (Figures 9b and 9e), leading to a specificity to the grain-size interval of interest for recording changes in current transport. Nevertheless, we caution that the correlation between $\ln(\text{Zr/Rb})$ and grain-size might be degraded if IRD accounts for a large majority of the sediment (e.g., within IRD layers) or if IRD is composed of Zr- and/or Rb-rich lithic grains. Particular care may be required for tephra-rich sediments, such as those found in the Antarctic Peninsula region (e.g., Toro et al., 2013). Tephra layers are typically characterized by high Zr (~180 ppm) and low Rb (~12 ppm) concentrations (Zhang & Liu, 1996), and hence could produce spikes in the Zr/Rb ratio and potentially decouple $\ln(\text{Zr/Rb})$ from grain-size parameters.

Some caution is required when making core-to-core comparisons, especially for cores retrieved from different regions, because the value of $\ln(\text{Zr/Rb})$ does not directly correspond to a specific value of a grain-size parameter. For example, differences in sediment provenance between regions or differences in machine detection efficiency (Equation 3) could lead to different relationships between absolute values of $\ln(\text{Zr/Rb})$ and grain-size, even though the gradients appear constant (Figures 12b and 12c). Such a scenario could also arise within a long sediment core (e.g., Toyos et al., 2020), for example, if either gradual or step changes in climate, erosion, or paleogeography led to changes in provenance. Where only

qualitative information is required, the $\ln(\text{Zr/Rb})$ ratio may provide a convenient proxy for variations of grain-size in the silt fraction of glaciomarine sediments without the need for additional measurements. However, for quantitative information and for effective comparisons between records from multiple cores, local calibrations between $\ln(\text{Zr/Rb})$ and conventional grain-size data from a subset of coupled samples will be required.

While our study has focused on sediment records from the Southern Ocean, this XRF-based approach could potentially be applied globally, either to enable better targeting of sediment cores for applying the sortable silt proxy, or to obtain proxy records of sediment grain-size in other ocean basins. However, considering the points discussed above, the approach may prove to be more suitable in some regions than others, and regional ground-truthing and calibration studies would certainly be required. We also emphasize that for any interpretations of Zr/Rb ratios in terms of bottom current speed, high-resolution records of $\ln(\text{Zr/Rb})$ must be combined with low-resolution grain-size records (specifically, SS) in order to establish that the sediment is current-sorted (I. McCave and Andrews, 2019; I. N. McCave and Hall, 2006).

7. Summary and Conclusions

We conducted a range of grain-size measurements and Rb and Zr concentration measurements using both XRF core scanning and ICP-MS on four sediment cores retrieved from the Prydz Bay and Ross Sea regions. In combination with published data from two sediment cores in the Drake Passage region, we evaluated the use of $\ln(\text{Zr/Rb})$ count ratios from XRF core scanning as a proxy for grain-size variations of glaciomarine sediment from the Southern Ocean.

Records of Rb and Zr counts from XRF core scanning are semi-quantitative due to specimen and matrix effects. However, by measuring Rb and Zr under the same conditions and using the $\ln(\text{Zr/Rb})$ ratio, these effects can be accounted for. In this case, the $\ln(\text{Zr/Rb})$ count ratio correlates well with the Zr/Rb concentration ratio measured by ICP-MS.

The $\ln(\text{Zr/Rb})$ ratio mainly reflects the grain-size dependent composition of the sediment fractions that do not include coarse unsorted IRD, and therefore provides a proxy for the IRD-corrected mean grain-size of glaciomarine sediment from the Southern Ocean. The $\ln(\text{Zr/Rb})$ ratio has a similar downcore pattern to $\text{SS}\%$ in all studied glaciomarine sediment cores, and hence can be used to indicate bottom current strength in cases where $\text{SS}\%$ and SS are highly correlated. Based on all published Southern Ocean data, the regression line for $\text{SS}\%$ versus $\ln(\text{Zr/Rb})$ appears to have a universal slope (34.1). In cases of bottom current sorting, a uniform slope also appears to exist for SS versus $\ln(\text{Zr/Rb})$ (12.7). The above correlation lines potentially provide a quick and convenient way to estimate the magnitude of changes in $\text{SS}\%$ and SS using only XRF scanning measurements of $\ln(\text{Zr/Rb})$. However, caution will be required when $\ln(\text{Zr/Rb})$ is applied to sediment that is dominated by unsorted IRD, or that is rich in Rb- and/or Zr-bearing IRD or tephra, or where major provenance changes are suspected. In addition, $\ln(\text{Zr/Rb})$ values cannot be directly compared between sediment cores from different regions, and local calibrations are required to obtain quantitative information on sediment grain-size and hence past current strength.

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Data Availability Statement

Supplementary data to this article can be found in the online supporting information and will be available in ZENODO repository via <https://zenodo.org/record/4075009#.X4A1XzOARbl>.

McCave, 2008.

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