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Trace element and isotopic evidence for temporal changes of the mantle sources in the South Shetland Islands, Antarctica

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We present Sr–Nd–Pb isotope data from the Paleocene-Eocene volcanic rocks in King George Island, South Shetland Islands, West Antarctica. The initial isotopic ratios of the analyzed samples display limited variations: $^{143}Nd/^{144}Nd$, 0.512790 to 0.512905 (εNd, +4.2 to +6.5); $^{87}Sr/^{86}Sr$, 0.703342 to 0.703877 (εSr, –15.6 to –8.0); $^{206}Pb/^{204}Pb$, 18.48 to 18.64; $^{207}Pb/^{204}Pb$, 15.50 to 15.64; $^{208}Pb/^{204}Pb$, 37.99 to 38.41. We interpret these data in combination with previously published trace and isotope data for Meso–Cenozoic volcanic rocks in the South Shetland Islands to gain a better understanding of the geochemical evolution of the mantle source region. The studied rocks are from four volcanic islands and range in age from 143 to 44 Ma. They have high abundances of large ion lithophile elements and light rare earth elements relative to high field strength elements, consistent with products of subduction related magmatism. The systematic inter-island variations are recognized from a comprehensive examination of the trace elements and isotopic compositions. The degree of enrichment of Sr–Nd–Pb isotopic compositions decreases towards younger samples, while the ratios of fluid-mobile elements/HFSE (Sr/Yb, Pb/Yb and U/Yb) gradually increase. The previous studies on these volcanic rocks concluded that the compositional variations of the South Shetland Islands volcanic suites were mainly controlled by two component mixing between altered MORB and Pacific sediments. However, we here propose that the compositional trends observed in the volcanic rocks of the South Shetland Islands can be created from the addition of a relatively constant subduction component to temporally varying heterogeneous mantle sources. The higher radiogenic Pb and Sr isotopes and lower $^{143}Nd/^{144}Nd$ ratios of the older volcanic rocks from Greenwich and Livingston islands compared to younger rocks can be explained by the significant influence of enriched previously metasomatized mantle material rather than fluids or sediment melts from the subducting slab. In contrast, the geochemical nature of the youngest King George Island volcanic rocks suggests a relatively large contribution of a slab-derived fluid component to the magma generation, but a minor role of the enriched component.

Keywords: trace elements, Sr–Nd–Pb isotopes, subduction component, heterogeneous mantle, South Shetland Islands

INTRODUCTION

Subduction zones extending from trenches to beneath volcanic arcs are places of profound chemical change. Subduction is a key process transferring hydrothermally altered oceanic rocks produced at mid-ocean ridges (e.g., basalts, gabbros) and sediments deposited on the oceanic crust into deep mantle. The transfer of material in subduction zones occurs in steps, and the agents are generally considered to be H_2O-rich fluids liberated by dehydration, or hydrous melts produced by partial melting of subducted lithosphere (e.g., Ulmer, 2001; Eiler *et al.*, 1998, 2000; Manning, 2004). There is a current consensus that trace element and radiogenic isotopic compositions of arc basalts represent mixtures among: (1) melts from a compositionally heterogeneous wedge mantle; (2) fluids coming from dehydration of altered oceanic crust and/or overlaying sediments; (3) hydrous silicate melts from subducted sediments and/or oceanic crust (Woodhead *et al.*, 1993; Turner and Foden, 2001).

The South Shetland Islands (SSI) from King George Island to Livingston Island constitute a narrow sialic crustal block bounded to the northwest by the South Shetland Trench and to the southeast by the Bransfield Strait (Fig. 1). They formed during the Meso–Cenozoic subduction of the former Phoenix Plate (Zheng *et al.*, 1998; Machado *et al.*, 2005a). The volcanic activity began during the latest Jurassic or earliest Cretaceous in the southwestern part of the archipelago (Smellie *et al.*, 1984; Machado *et al.*, 2005a). Geochemical characteristics and Sr–Nd–Pb isotopic compositions of these Meso–Cenozoic

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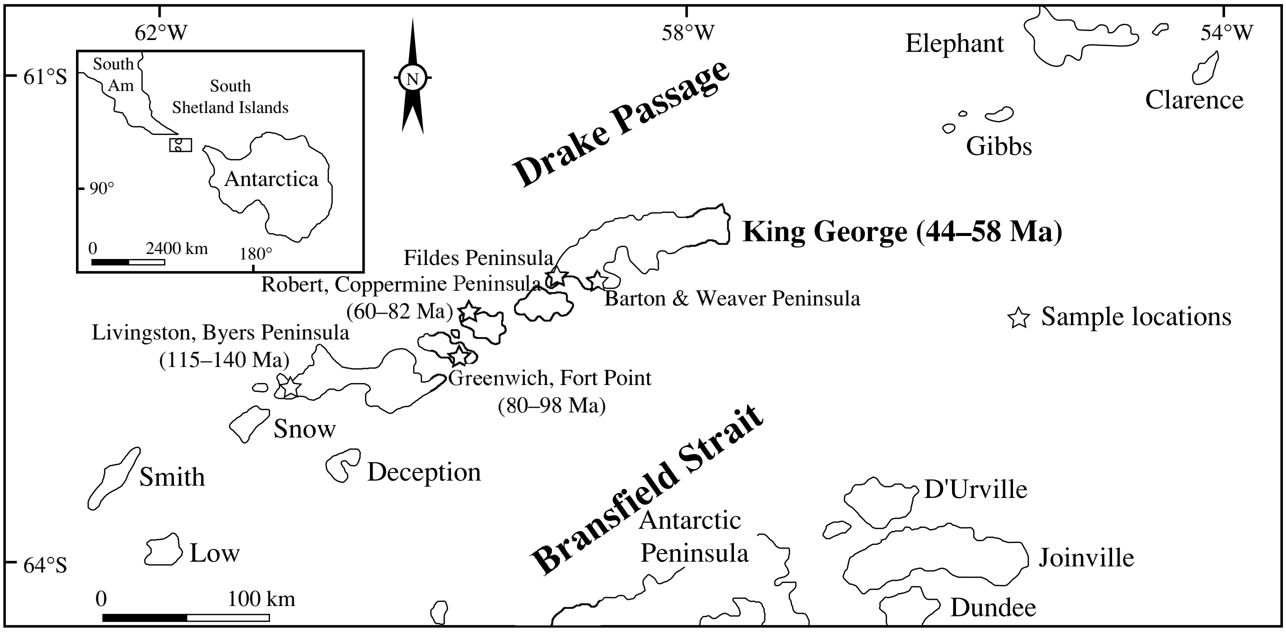

Fig. 1. Location map of the South Shetland Islands (modified from Smellie et al., 1984). The age data were compiled from the previous works (Smellie et al., 1984; Hathway, 1997; Zheng et al., 1998; Machado et al., 2005b). Locations of samples investigated are displayed as open stars.

arc volcanic rocks have been reported by Machado *et al.* (2005a, b). They suggested that the isotopic variation of the Meso–Cenozoic SSI arc magmas can be explained by a mixing model between altered MORB and Pacific sediments. However, they did not examine the geochemical variations possibly derived by the addition of elements through dehydration and melting of subducting sediments to arc magma sources nor address the changes in subduction components and magma compositions with time.

King George Island (KGI) where we sampled volcanic rocks for the present study is the largest island in the SSI and is situated in the northeastern end of the archipelago (Fig. 1). We present new Sr–Nd–Pb isotope data of the volcanic rocks from Barton and Weaver peninsulas, KGI, and integrate not only the previous isotope data but also the trace element data from the other Meso–Cenozoic islands in the SSI. These geochemical data are used to characterize the geochemical nature of the sources and to constrain subduction components involved in the generation of the SSI volcanic rocks. In this study, we focus on tracing the geochemical change of the Meso–Cenozoic SSI volcanic rocks with time. Temporal geochemical variation within an arc could be related to the change of subduction components (fluids or melts) released from the downgoing oceanic plate, or the interaction between slab-derived components and mantle wedge during transit. The same variation could be also ascribed to the background wedge mantle heterogeneity prior to the addition of slab-derived components. In this study, we apply some constraints on these possible causes by examining the geochemical and isotopic variations in order to provide new insights into the petrogenesis of the Meso–Cenozoic SSI arc volcanism.

Geological Background

The Antarctic Peninsula is bordered by a complex system of tectonic plates, including the South America, Scotia, Phoenix (former Drake), South Orkney and Sandwich Plates, which are dominated by extensional and strike-slip tectonic limits (Fig. 2). However, the tectonic evolution of this area over the past 190 Ma has been dominated by the subduction of oceanic plate of the Drake (currently called Phoenix) Plate beneath the Antarctic Plate (Tanner *et al.*, 1982). Subduction-related volcanism formed the Mesozoic volcanic terranes of the Antarctic Peninsula and the Meso–Cenozoic SSI arc (Pankhurst, 1983; Barker *et al.*, 1991; Hole *et al.*, 1991; Grunow *et al.*, 1992; Birkenmajer, 1994). No arc-related magmatism younger than 20 Ma has been reported in the SSI, although reconstructions of plate motions based on geophysical data indicate that subduction must have continued until about 3 Ma (Barker, 1982; Lawver *et al.*, 1995).

The SSI represent a Jurassic–Tertiary island arc founded on a sialic basement of schist and deformed sedimentary rocks. Lava flows with subordinate pyroclastic deposits, small intrusive bodies and mafic to felsic plutons

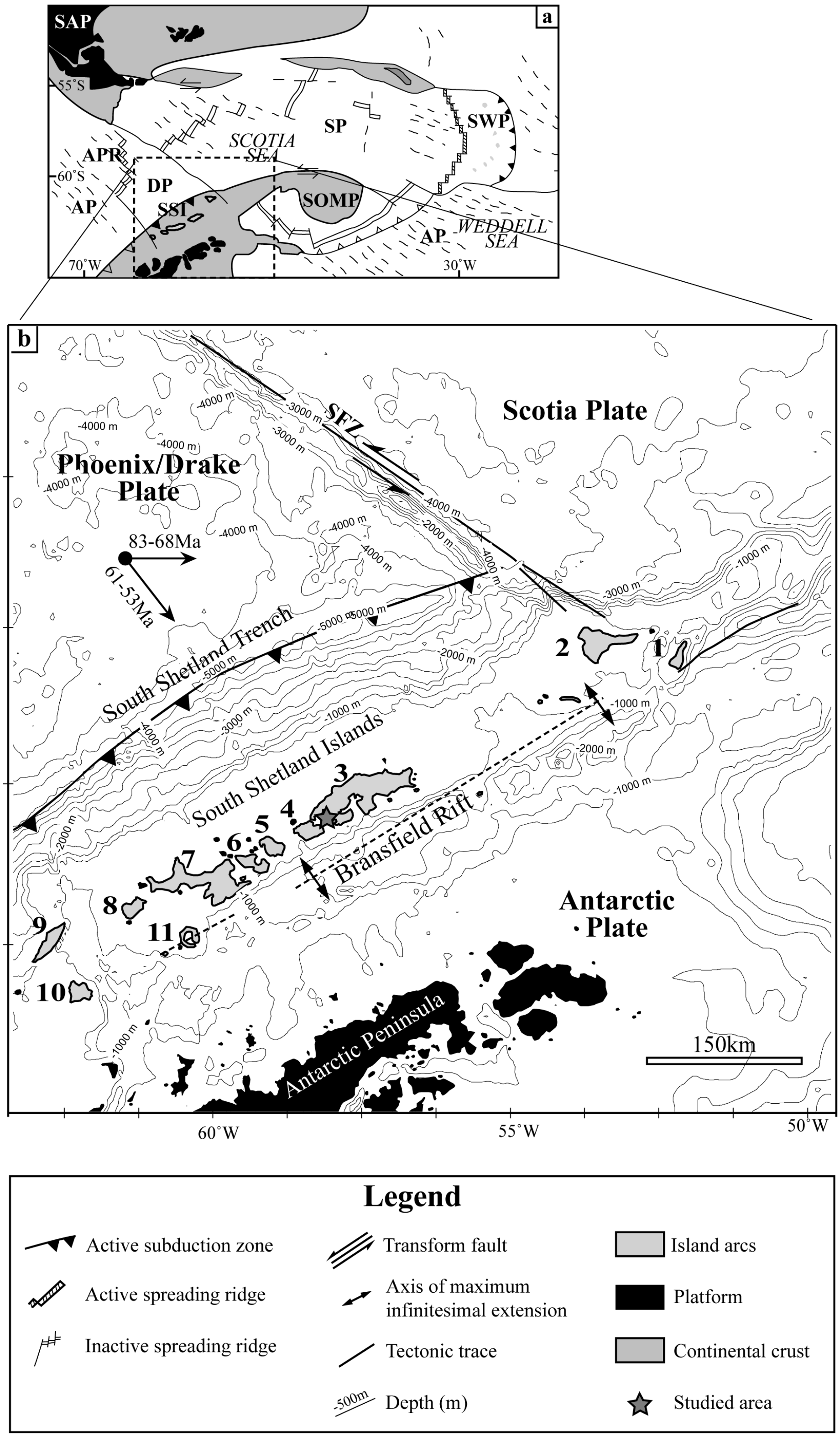

Fig. 2. (a) Geotectonic map of the southern South Atlantic region showing the distribution of main tectonic plates. SAP, South America Plate; SP, Scotia Plate; AP, Antarctic Plate; APR, Antarctic Phoenix Ridge; SOMP, South Orkney Microplate; SWP, Sandwich Plate; DP, Drake Plate and features; SSI, South Shetland Islands and SFZ, Shackleton Fracture Zone (modified from Trouw et al., 2000). (b) Tectonic setting of the South Shetland Islands consisting of the following islands: Clarence (1); Elephant (2); King George (3); Nelson (4); Robert (5); Greenwich (6); Livingston (7); Snow (8); Smith (9) and Low (10) (modified from Lawver et al., 1996). Arrows indicate direction of plate motion in the Cretaceous and Tertiary (McCarron and Larter, 1998).

Table 1. Rb–Sr and Sm–Nd isotope data, calculated ε-values and model ages for the volcanic rocks from King George Island

Sample No.	Rock type	Rb (ppm)	Sr (ppm)	$^{87}Sr/^{86}Sr$	$(^{87}Sr/^{86}Sr)_i$	$\varepsilon_{Sr(t)}$	Sm (ppm)	Nd (ppm)	$^{143}Nd/^{144}Nd$	$(^{143}Nd/^{144}Nd)_i$	$\varepsilon_{Nd(t)}$
0107	BA	5.6	683.6	0.703626 ± 28	0.703609	−11.8	4.9	20.3	0.512921 ± 5	0.512873	5.8
0601	A	19.1	662.8	0.703936 ± 11	0.703877	−8.0	5.9	25.9	0.512936 ± 6	0.512891	6.2
1105-1	BA	31.5	503.3	0.703579 ± 15	0.703451	−14.1	6.8	28.9	0.512918 ± 4	0.512872	5.8
1213	BA	6.9	581.1	0.703571 ± 23	0.703547	−12.7	3.3	13.4	0.512838 ± 5	0.512790	4.2
1215	BA	8.0	650.5	0.703469 ± 13	0.703444	−14.2	3.2	13.3	0.512933 ± 6	0.512885	6.1
0705-1	BA	31.0	511.7	0.703528 ± 15	0.703403	−14.7	4.6	19.1	0.512950 ± 6	0.512903	6.4
1507-2	B	8.7	680.0	0.703485 ± 22	0.703459	−13.9	2.5	9.8	0.512952 ± 6	0.512902	6.4
1507-3	B	10.6	900.2	0.703366 ± 10	0.703342	−15.6	2.6	10.3	0.512954 ± 4	0.512905	6.5
0926	BA	7.1	642.4	0.703419 ± 12	0.703396	−14.8	5.2	23.1	0.512945 ± 6	0.512901	6.4
0929	BA	12.0	568.4	0.703409 ± 8	0.703366	−15.3	5.4	24.5	0.512902 ± 5	0.512858	5.5

$(^{87}Sr/^{86}Sr)_i$, $\varepsilon_{Sr(t)}$, $(^{143}Nd/^{144}Nd)_i$ and $\varepsilon_{Nd(t)}$ at 50 Ma were calculated using the following parameters: $^{87}Sr/^{86}Sr_{CHUR(0)} = 0.7045$, $^{87}Rb/^{86}Sr_{CHUR(0)} = 0.0827$, $\lambda^{87}Rb = 1.42 \times 10^{-11}$ y^{-1}, $^{143}Nd/^{144}Nd_{CHUR(0)} = 0.512638$, $^{147}Sm/^{143}Nd_{CHUR(0)} = 0.1966$, $\lambda^{147}Sm = 6.54 \times 10^{-12}$ y^{-1}.
Abbreviations: B, basalt; BA, basaltic andesite; A, andesite.

Table 2. Pb isotopes for the volcanic rocks from King George Island

Sample No.	Rock type	Concentration			Measured ratio			μ	κ	Initial ratio (at 50 Ma)		
		U (ppm)	Th (ppm)	Pb (ppm)	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{238}U/^{204}Pb$	$^{232}Th/^{204}Pb$	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$
0107	BA	0.58	2.38	5.1	18.589	15.530	38.160	7.133	30.445	18.534	15.527	38.084
0601	A	0.75	3.05	4.2	18.561	15.542	38.163	11.214	47.279	18.475	15.538	38.046
1105-1	BA	0.86	4.13	5.2	18.717	15.645	38.537	10.595	52.514	18.636	15.641	38.407
1213	BA	0.29	0.72	4.8	18.625	15.587	38.279	3.791	9.799	18.596	15.586	38.254
1215	BA	0.29	0.76	2.6	18.638	15.573	38.267	7.042	18.762	18.584	15.571	38.220
0705-1	BA	0.44	1.75	4.4	18.586	15.549	38.196	6.467	26.384	18.536	15.547	38.130
1507-2	B	0.26	1.07	2.5	18.579	15.540	38.157	6.590	27.893	18.528	15.537	38.088
1507-3	B	0.31	1.25	2.5	18.534	15.499	38.067	7.638	32.005	18.475	15.496	37.988
0926	BA	0.84	2.77	7.3	18.666	15.589	38.326	7.363	24.996	18.610	15.586	38.264
0929	BA	1.03	3.20	6.9	18.653	15.563	38.290	9.565	30.590	18.579	15.560	38.215

Abbreviations: B, basalt; BA, basaltic andesite; A, andesite.

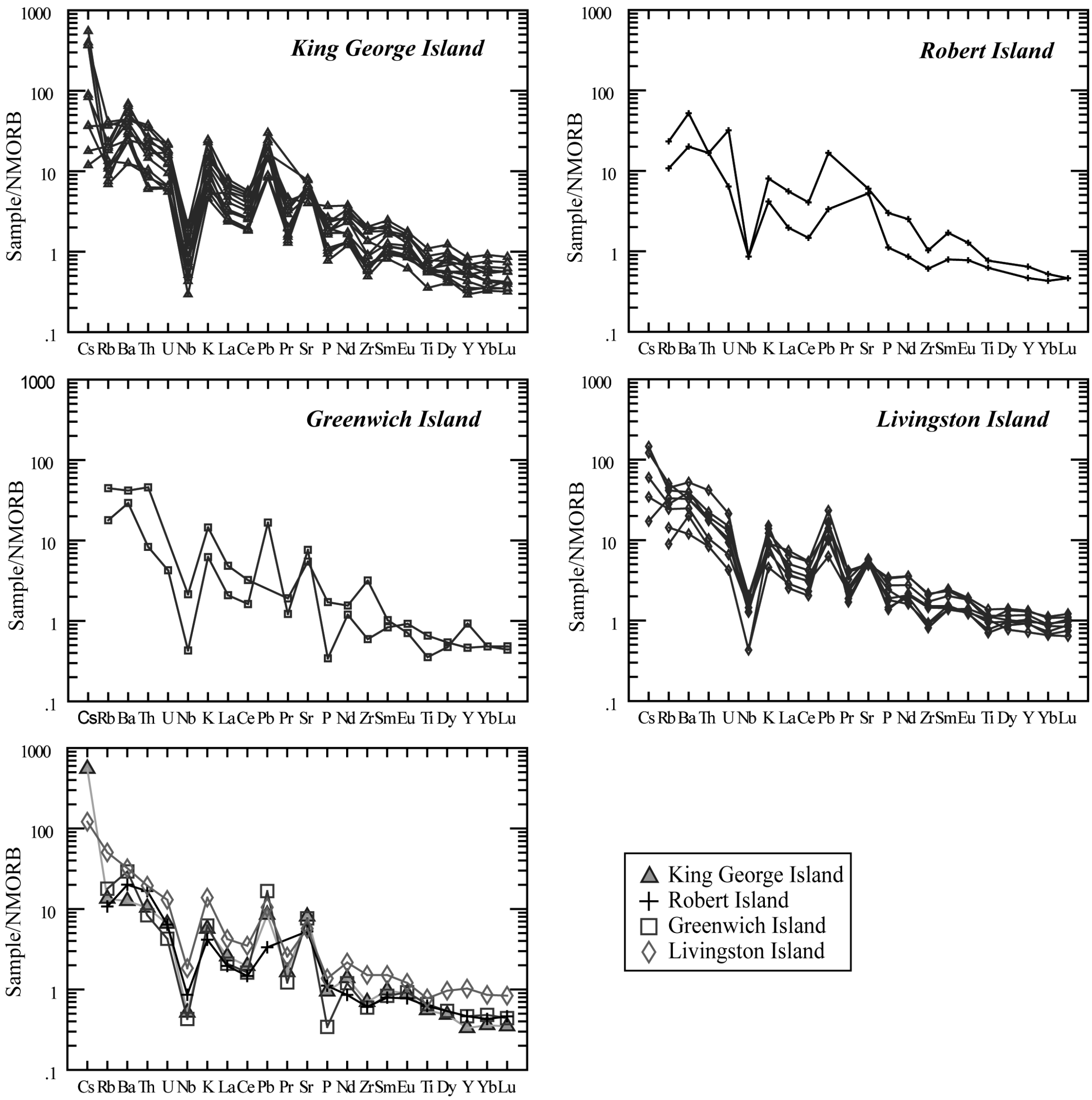

Fig. 3. NMORB normalized multi-element plots for volcanic rocks from the South Shetland Islands. We compared incompatible element abundances for the representative samples with similar silica contents. Data Sources: Zheng et al. (1998); Yeo et al. (2004); Machado et al. (2005a). The Normalized NMORB composition is from Sun and McDonough (1989).

make up a typical subduction-related association with calc-alkaline to tholeiitic compositions. The magmatic centers migrated northeastward along the arc's length by shifting of the subduction focus. Birkenmajer (1994) interpreted that this was attributed to the rotation of the Antarctic continental plate margin with respect to the South Pacific Plate and the presence of a fixed hotspot-like structure within the mantle.

Sampling was carried out during fieldworks in 1997 and 1998 for the purpose of whole rock geochemical and Sr–Nd–Pb isotope studies on Barton and Weaver peninsulas, KGI. The volcanic rocks in Barton and Weaver peninsulas are mafic to intermediate (basaltic andesite to andesite, ~48–60 wt% SiO_2) and usually contain euhedral to subhedral phenocrysts of either plagioclase only or plagioclase and clinopyroxene. Modal proportions of phenocrysts are mostly about 10–20% and less than 40%. All samples are quite fresh, and secondary minerals are rare. Major and trace element compositions for the samples can be found in Yeo *et al*. (2004). They belong to subalkaline series, and the majority of the samples have a tholeiitic composition.

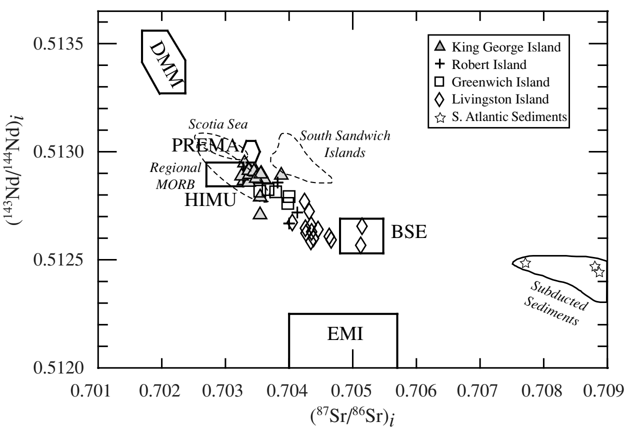

Fig. 4. Conventional Sr–Nd isotope plot for volcanic rocks of the South Shetland Islands (data from Zheng et al., 1998; Machado et al., 2005a and Table 1). Compositional fields of the regional MORB (Castillo et al., 1998), bulk South Atlantic sediments (Ben Othman et al., 1989; Plank and Langmuir, 1998), Scotia Sea Ridge lavas (Fretzdorff et al., 2002) and South Sandwich Island arc (Pearce et al., 1995) have been plotted together. The compared regional mantle products are younger than 5 Ma.

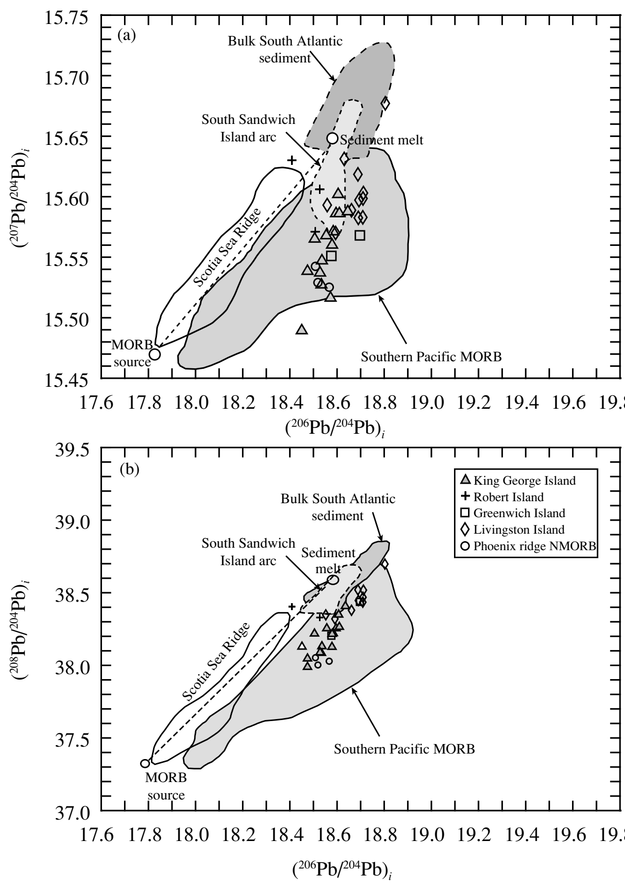

Fig. 5. Plots of (a) $^{207}Pb/^{204}Pb$ and (b) $^{208}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ for volcanic rocks of the South Shetland Islands. The data sources are the same in Fig. 4.

The samples selected from the literature (Zheng *et al.*, 1998; Machado *et al.*, 2005a) are basalts to basaltic andesites, ranging in age from 143 to 44 Ma and geochemically show tholeiitic to calc-alkaline affinities.

ANALYTICAL METHODS

Sr, Nd and Pb isotope analyses were performed at the Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing, China, in an ultraclean laboratory conditions. Unleached whole rock powders were dissolved with a mixture of HF–$HClO_4$ in a Teflon vessel. Isotopic ratios were measured using a VG354 thermal ionization mass spectrometer. Rb, Sr, Sm and Nd concentrations were determined by isotope dilution method. Chemical separation of Rb, Sr, Sm and Nd was carried out by cation exchange technique. Total blank levels for the whole procedure were about 200 pg for Sr and about 50 pg for Nd. Measured $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ ratios were normalized to $^{86}Sr/^{88}Sr = 0.1194$ and $^{146}Nd/^{144}Nd = 0.7219$, respectively. Replicate analysis of NIST SRM-987 and La Jolla standards gave $^{87}Sr/^{86}Sr = 0.710208 \pm 0.000009$ (N = 10) and $^{143}Nd/^{144}Nd = 0.511826 \pm 0.000008$ (N = 12), respectively. Pb was eluted and purified in HBr media using the standard anion exchange technique. Total procedure blanks were less than 50 pg. From replicate analyses of NIST SRM-981, the maximum errors (2σ) for $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ were estimated as 0.031, 0.038 and 0.055, respectively. The initial Sr, Nd and Pb isotopic ratios at 50 Ma were calculated using the decay constants of 1.42×10^{-11} y^{-1} for ^{87}Rb, 6.54×10^{-12} y^{-1} for ^{147}Sm, 1.55×10^{-11} y^{-1} for ^{238}U, 9.85×10^{-10} y^{-1} for ^{235}U and 4.95×10^{-11} y^{-1} for ^{232}Th (Steiger and Jäger, 1977). The measured Sr, Nd and Pb isotopic ratios with age (50 Ma) corrected values are given in Tables 1 and 2.

TRACE ELEMENT AND ISOTOPIC GEOCHEMISTRY

The volcanic rocks investigated here are mostly basalts and basaltic andesites, and contain phenocrysts of olivine, plagioclase, clinopyroxene and titanomagnetite. Major element variations are considered to be mainly controlled by the fractionation of these phases. Since the focus of this study is to understand the processes responsible for the inter-island geochemical variations, we characterize the compositions of lavas from the SSI volcanic suites using incompatible element ratios that are largely unaffected by crystal fractionation or accumulation.

The NMORB-normalized trace element patterns exhibited by all samples are typical of subduction-related magmas: strong enrichment in large-ion lithophile elements (Cs, Rb, Ba, K, Sr) over high field strength elements (Nb, Zr, Ti), and also enrichment in LREE (La, Ce, Pr) over HREE (Fig. 3). They show strong positive spikes at Pb and Sr, and negative anomaly for Nb. A negative Ti anomaly, which is commonly observed in arc samples, is not well developed in the SSI samples. Chondrite-normalized $(La/Yb)_N$ ratios of the SSI samples vary from 1.61 to 6.81, and show a gradual increase towards younger volcanic rocks. The HREE concentration of the oldest Livingston volcanic rocks is significantly higher than those of the other rocks.

Compositional variations of Sr, Nd and Pb isotopes are presented in Figs. 4 and 5. The previously published SSI regional data and reference fields have been plotted together for comparison with rocks derived from similar tectonic settings and locales.

The initial $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ ratios of the KGI volcanic rocks display a very limited variation ranging from 0.703342 to 0.703877 and 0.512790 to 0.512905 and a slightly enriched signature compared to those of NMORB (Fig. 4). The SSI volcanic rocks define a linear trend on a $^{143}Nd/^{144}Nd$ vs. $^{87}Sr/^{86}Sr$ diagram, which lies along the mantle array. The KGI samples have the lowest $^{87}Sr/^{86}Sr$ and the highest $^{143}Nd/^{144}Nd$ ratios. There is a clear tendency for Sr isotopic ratio to decrease and Nd isotopic ratio to increase towards younger samples. It is apparent from Fig. 4 that most SSI arc samples are displaced to significantly lower initial $^{143}Nd/^{144}Nd$ ratios in comparison with the younger regional mantle products. The initial $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios of the KGI volcanic rocks range from 18.48 to 18.64, 15.50 to 15.64 and 37.99 to 38.41, respectively. The SSI volcanic rocks also show increasing tendency for radiogenic Pb towards older samples. The increase of enrichment towards older samples may be caused by the contribution of subduction components which have lower $^{143}Nd/^{144}Nd$ ratios and higher radiogenic Pb isotopes to arc magmas, or the melting from heterogeneous mantle sources including enriched material resulted from previous mantle metasomatism. Now, the question is whether the isotopic enrichment is inherited from the background mantle sources or resulted from the contribution of subduction components. In the following section, we examine possible processes and different components that created the geochemical variations of the SSI volcanic rocks.

Discussion

We now know that nearly all of the major elements in arc magmas come from partial melting of convecting asthenosphere above the downgoing oceanic plate, and that components from the subducting slab provide LIL

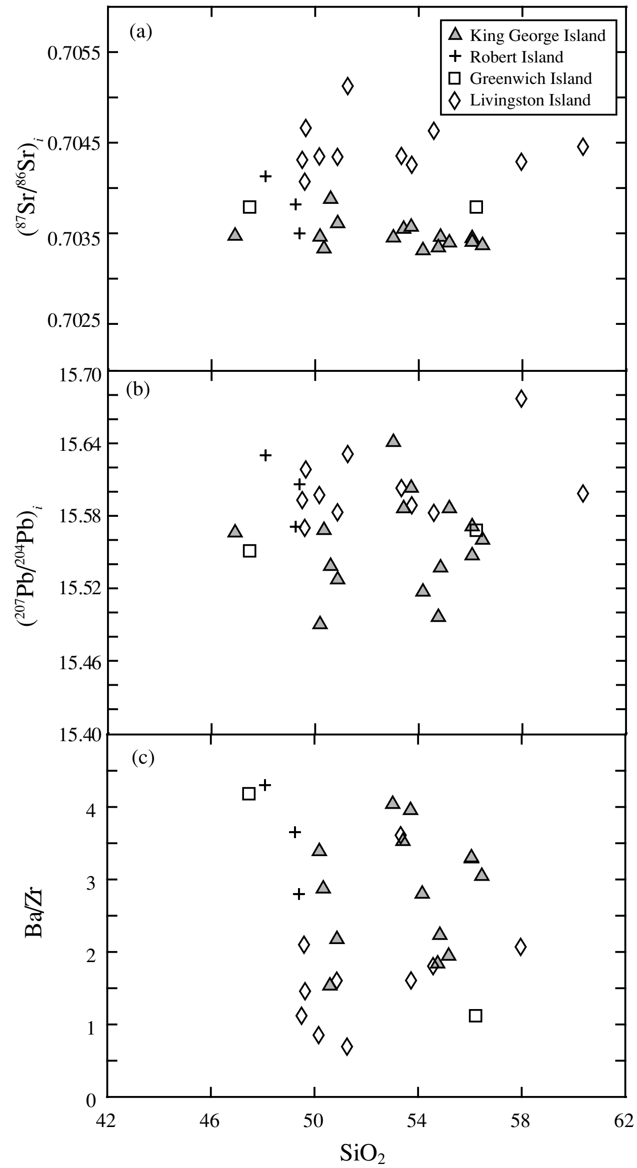

Fig. 6. Plots of (a) $^{87}Sr/^{86}Sr$, (b) $^{207}Pb/^{204}Pb$ and (c) Ba/Zr vs. SiO_2 for volcanic rocks of the South Shetland Islands. Data sources: Tables 1 and 2; Zheng et al., 1998; Yeo et al., 2004; Machado et al., 2005a.

and other incompatible element abundances (Hochstaedter *et al.*, 2001; Robert *et al.*, 2006). Subducting components possibly contributing to the subarc mantle include hydrous fluids and silicate melts from altered oceanic crust and overlaying sediment. The geochemical and isotopic signatures of the altered basalt are clearly distinguished from those of the sediment. Moreover, incompatible elements released from the partial melting of subducting slab behave differently in aqueous fluids. It is thus possible to constrain the distinct subduction components derived from

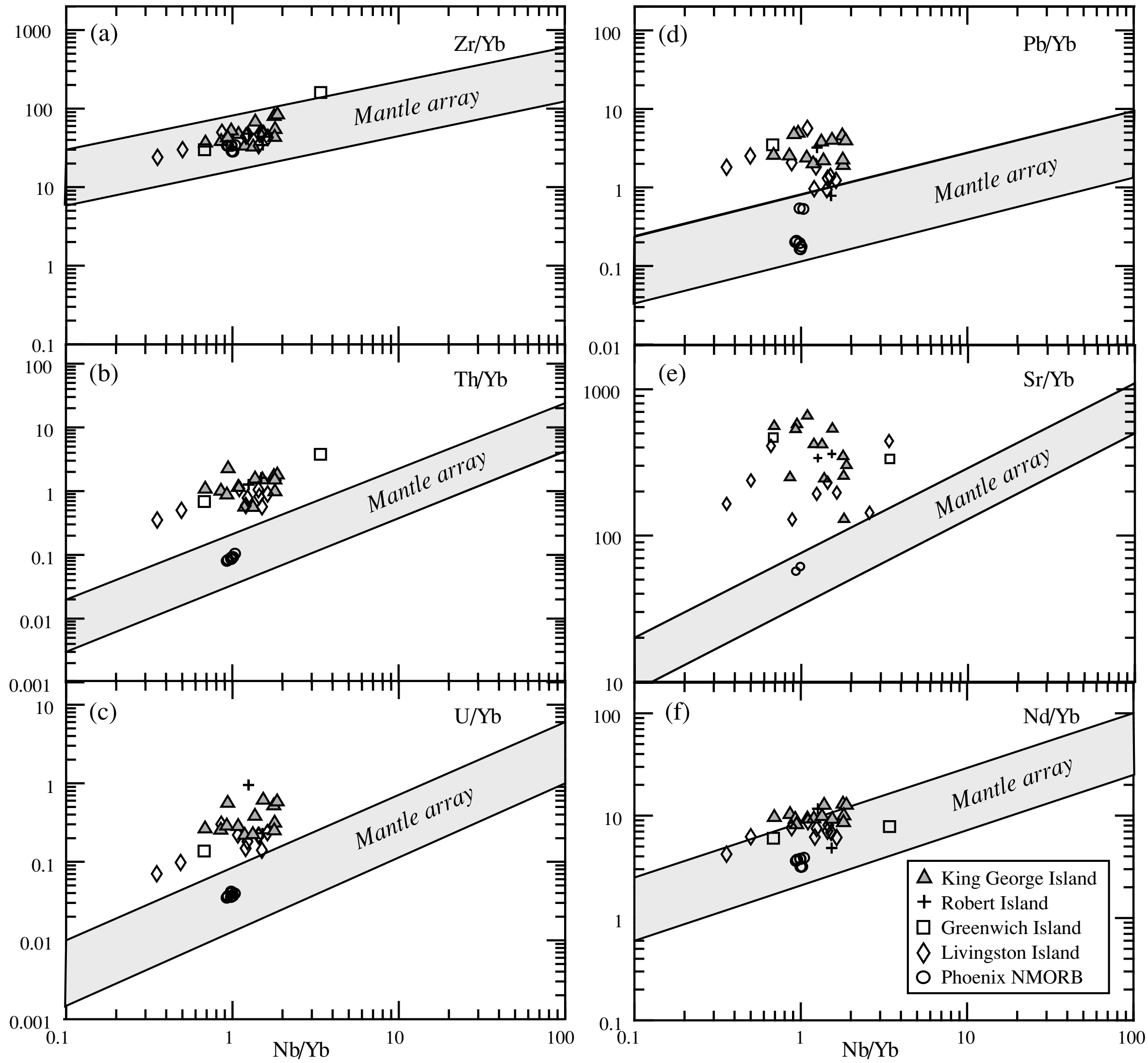

Fig. 7. Plots of X/Yb vs. Nb/Yb for volcanic rocks of the South Shetland Islands (data from Zheng et al., 1998; Yeo et al., 2004; Lee et al., 2005; Machado et al., 2005a). Shaded regions indicate the range of incompatible element ratios in average MORB and OIB (Green, 2006).

dehydration and melting processes of the altered oceanic basalt and sediment.

Another factor we have to consider for understanding the geochemical variations of the SSI volcanic rocks is the influence of high-level contamination, before assessing the processes operating in the subarc mantle. Crustal contamination generally results in the simultaneous increase of SiO_2 and incompatible elements. Although the more silicic samples have more radiogenic Pb isotopes, Sr and Nd isotopic ratios actually show no correlation with their SiO_2 contents (Figs. 6a and b), arguing against a major role for crustal contamination. Moreover, there is no significant difference in incompatible element ratios (e.g., Ba/Zr; Fig. 6c) between less fractionated basalts and more fractionated samples in the SSI. These observations suggest that the variations in chemical and isotopic compositions recorded in the SSI arc samples reflect mantle source characteristics and processes.

Mantle source

High field strength elements (HFSE) are generally not considered to be transferred to the mantle wedge during subduction because of the low mobility of HFSE in fluids (McCulloch and Gamble, 1991; Brenan *et al*., 1995) and the low concentrations of HFSE in sediments (e.g., Plank and Langmuir, 1998). Based on this long-held assumption, HFSE have often been used as indices that can see through the slab signature and investigate the

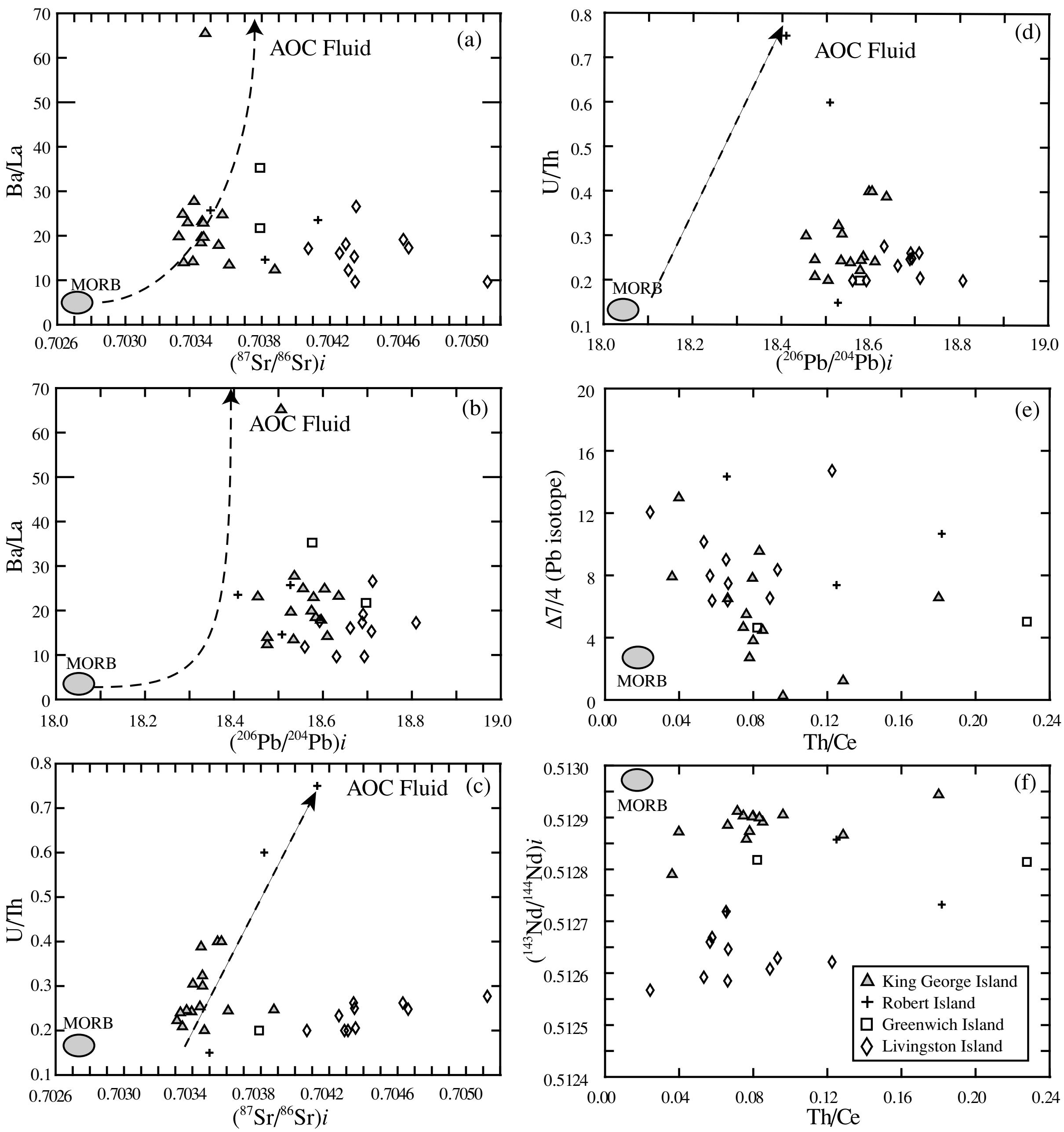

Fig. 8. Correlation diagrams between incompatible trace element ratios and isotopes. (a) Ba/La vs. ^{87}Sr/^{86}Sr, (b) Ba/La vs. ^{206}Pb/^{204}Pb, (c) U/Th vs. ^{87}Sr/^{86}Sr, (d) U/Th vs. ^{206}Pb/^{204}Pb, (e) Δ7/4 of Pb isotopes vs. Th/Ce, and (f) ^{143}Nd/^{144}Nd vs. Th/Ce. The trends towards higher Ba/La and U/Th ratios represent the addition of a fluid contribution to the mantle wedge. Data sources: Tables 1 and 2; Zheng et al., 1998; Yeo et al., 2004; Machado et al., 2005a. AOC Fluid composition is from Class et al. (2000).

geochemical nature of pre-subduction mantle wedge.

The geochemical compositions of the SSI volcanic rocks show a temporal variation, towards older ones having higher radiogenic Pb and Sr isotopes, and lower ^{143}Nd/^{144}Nd ratios (Figs. 4 and 5). These geochemical distinctions may be explained by the compositional change of mantle source or the transferred material from slab to mantle wedge, or even a combination of both. In attempt to estimate the relative contributions of background mantle and subduction input to the SSI volcanism, we follow the approach of Pearce *et al*. (1995) in plotting diagrams of the form *X*/Yb versus Nb/Yb, where *X* is the element under consideration. As neither Nb nor Yb are considered to be mobile by subduction-related fluids or melts, variable addition of an X-enriched slab component to a source could result in different X/Yb from those defined by mantle-derived oceanic basalt compositions (the "mantle" array). The amount of X/Yb displacement from the mantle array should be dependent on the magnitude of subduction-related contributions and the degree of enrichment or depletion of the mantle source (Pearce, 1983; Pearce and Peate, 1995). In these diagrams, we have plotted together the composition of NMORB samples (3.5–6.5 Ma, Choe *et al.*, 2007) from the fossilized spreading center of the Antarctic-Phoenix Ridge, Drake Passage. The compositional field of these samples is assumed to represent products derived by partial melting of unmodified original background mantle.

The samples in the first plot, Zr/Yb vs. Nb/Yb (Fig. 7a), form a linear trend and pass through the values of the Antarctic-Phoenix NMORB and do not show any considerable displacement from the mantle array. This indicates that Zr and Nb (HFSE) are not present in significant amounts in the subduction component. The subsequent plots show elemental variations considered to be more readily mobilized from the subducting slab. Contrast to the Zr trend which is sub-parallel linear to the mantle array, the other elemental ratios are displaced from the mantle array towards higher X/Yb ratios with slightly negative or flat slopes (Fig. 7). The largest degree of displacement is observed in the Sr variation, which suggests a significant Sr contribution from the subduction component to the mantle source.

The overall flat trends of the SSI volcanic rocks are highly important for constraining the nature of subduction components and mantle sources. If a subduction component with constant composition is added to a common mantle source and then followed by variable melting, the variation trends should run parallel to but displaced from the MORB array. If we then consider the case of a variable subduction component added to a constant mantle source, the resulting trend should then run vertically increasing displacement with increase of subduction components.

On the other hand, the addition of a constant subduction component to a chemically variable mantle source may result in negative, flat or small positive slopes because depleted mantle representing in lower left field of the diagrams is affected more than enriched mantle. Therefore, the observed flat trends crossing the mantle array in Fig. 7 imply that the SSI volcanic rocks have been derived from variable mantle sources rather than from the same background wedge mantle source. It is noted that the degree of displacement of X/Yb from the mantle array increases towards younger samples. It indicates that the relative contribution of the subduction component to the mantle sources of the SSI arc magmas have increased with time.

Constraints on fluid and sediment-derived melt components

Sr and Pb are strongly partitioned into fluids relative to crystalline phases (Brenan *et al.*, 1995). Therefore, constraints on the fluid contribution from altered oceanic crust or sediment can be obtained from the correlation between Sr or Pb isotopes and the enrichment of fluid mobile elements. As Sr and Pb isotopic compositions of altered oceanic crust are estimated to be slightly higher or comparable to those of MORB mantle (Staudigel *et al.*, 1996; Class *et al.*, 2000), the addition of fluid from altered oceanic crust could not significantly modify the isotopic signatures of MORB source mantle. In contrast, subducting sediment fluid could affect the Sr and Pb isotopic compositions (Class *et al.*, 2000; Ishizuka *et al.*, 2003).

As Ba/La ratio is not significantly modified by melting and crystallization processes, the addition of a fluid-derived component with high Ba/La ratio produces a high ratio in the resulting magmas. In these plots (Figs. 8a and b), the younger volcanic rocks from the KGI have the lowest Sr and Pb isotopic ratios, but higher than MORB, and show relatively high Ba/La ratios. This indicates that the fluid from altered oceanic crust contributed largely to the generation of the KGI magma. The lowest Sr and Pb isotopic ratios of the KGI samples exclude a significant role of subducting sediment fluid. In contrast, the older volcanic rocks from the Greenwich and Livingston islands have significantly higher radiogenic Sr and Pb isotopic ratios, but comparable or slightly lower Ba/La ratios than those of the younger KGI volcanic rocks. As high radiogenic Sr and Pb isotopic ratios for the older volcanic rocks are not associated with high Ba/La ratios, we assume that a fluid component is not significant in the sources of older volcanic rocks. The correlation between U/Th ratios and Sr and Pb isotopes also support the above hypothesis (Figs. 8c and d). U/Th ratio is one of the representative factors which can constrain the fluid contribution in the arc magmas. The U/Th ratios of the youngest KGI volcanic rocks are much higher than those of the other older rocks, implying a greater role for fluids in the KGI rocks. However, the higher Ba/La and U/Th ratios of the older volcanic rocks compared to MORB values clearly suggest smaller, but probable contribution of fluid from the subducting slab.

Besides fluid, bulk sediment or siliceous melt from sediment is another possible contributing material from subducting slab to wedge mantle in arc systems. Generally, subducting sediment has higher Th concentration (>2 ppm) and Th/Ce ratio (>0.005) than the mantle (e.g., Plank and Langumuir, 1998). Since Th shows relatively low solubility in hydrous fluids (e.g., Hawkesworth *et al.*, 1997), enrichment of Th relative to the incompatible elements like LREE can be regarded as an indicator of a sediment contribution as a bulk or melt rather than a fluid.

If the more enriched isotopic ratios in the oldest Livingston Island volcanic rocks have mainly resulted from the contribution of subducted sediments, they also should have higher Th/Ce ratios and Th contents, but lower U/Th ratios. However, there is no significant difference in the Th/Ce ratios and Th contents between the oldest and the youngest volcanic rocks. Moreover, the Th/Ce ratios of the SSI samples do not show any correlation with Nd and Pb isotopes, nor do they have particularly high Δ7/4 Pb isotopes (Figs. 8e and f). This implies that the enriched isotopic signature of the Livingston Island volcanic rocks was inherited from the wedge mantle composition rather than from subducted sediments. This re-emphasizes the indication from Fig. 4 that the geochemical variations of the Meso–Cenozoic SSI arc magmas can be attributed to the background mantle heterogeneity. It is thus considered that the subduction zone component derived from subducted sediment melt did not significantly affect the SSI arc magma compositions.

Temporal evolution of Sr, Nd and Pb isotopes

It is clear from the significant isotopic variations that changes of subduction fluxes cannot fully account for the geochemical variations of the SSI volcanic rocks, and instead these are considered to reflect temporal source heterogeneities beneath the SSI arc. The plots of incompatible element ratios show that subduction inputs in the SSI arc include high Sr, but very low Nd contributions, and increase towards younger samples. These indicate that the large variation in $^{143}Nd/^{144}Nd$ ratios relative to limited variation in $^{87}Sr/^{86}Sr$ ratios is explained by mixing between mantle wedge components of variable isotopic compositions with a relatively constant subduction component. The high Sr contribution from the subducting slab could cause the $^{87}Sr/^{86}Sr$ ratios to be buffered near the ratio of subduction component and mostly mask original background mantle compositions. The little variation of $^{87}Sr/^{86}Sr$ ratios in the SSI volcanic rocks thus appears to reflect the contribution of a relatively constant subduction component through time. On the other hand, the low Nd input from the subduction process means that the $^{143}Nd/^{144}Nd$ isotopic ratios in the SSI volcanic rocks reflect the mantle wedge variation. The distinctly low $^{143}Nd/^{144}Nd$ ratios of the Livingston Island volcanic rocks are more likely to be inherited from a geochemically enriched component that may have been previously metasomatized by earlier subduction-related fluid prior to melt generation.

It is also notable that the youngest KGI volcanic rocks dominated by more fluid mobile components has relatively unradiogenic Sr isotope compositions, implying that the added fluid had low $^{87}Sr/^{86}Sr$ ratios and thus dominantly derived by dehydration of the altered oceanic crust rather than subducted sediment. The Pb isotopic compositions which show moderate enrichments of ^{207}Pb and ^{208}Pb even in the younger samples are considered to reflect source mantle characteristics.

It is difficult to clarify the origin of wedge mantle heterogeneities. If we consider that temporal modifications in subduction input were not significant, tectonic organization of the Cretaceous–Tertiary SSI arc may provide some clues for the apparent temporal change of wedge mantle component. The present configuration of Antarctic Peninsula and SSI was formed only in the last 38 Ma with the opening of Drake Passage and Scotia Sea (Barker and Burrell, 1977; Barker *et al.*, 1991). Before 38 Ma this region had experienced a complex tectonic evolution, forming Meso–Cenozoic accretionary wedges, island arcs and back arc basins (Lawver *et al.*, 1996). It is considered that a northeastward shift of magmatic centers with time, along the arc's length (Pankhurst and Smeillie, 1983), was related to the shift of the focus of subduction, possibly as a result of counterclockwise rotation of Antarctica (Birkenmajer, 1994; McCarron and Larter, 1998). During these complex tectonic episodes, we presume that there was a gradual change of subduction regime (e.g., subduction angles, direction of plate motion), which in turn allowed the incorporation of different mantle sources in the generation of the SSI magmas.

Conclusions

The geochemical signature of the Meso–Cenozoic volcanic rocks from the SSI arc changes with time. The geochemical variation is thought to have resulted from the change of subduction fluxes from subducting slab and mantle source heterogeneity. Ratios of incompatible trace elements such as U/Th, Ba/La, Pb/Y and Sr/Yb indicate that the more fluid mobile elements (U, Ba, Pb and Sr) were transported from the subducted oceanic crust into the mantle wedge through fluid phases. The isotope data from the KGI samples show a slightly more radiogenic Sr and Nd characteristics compared to MORB, but moderately high $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios. These trends can be interpreted as reflecting petrogenesis from a regional MORB source modified by addition of the fluid from subducting altered crust. The contribution of the fluid components from subducting slab is likely to increase with time. The sediment melt contribution was minor in the SSI arc magma generation. The enriched isotopic signature of the older volcanic rocks from the Greenwich and Livingston islands is thought to be inherited from wedge mantle rather than from subducted sediment. We therefore conclude that the geochemical variations of the Meso–Cenozoic SSI arc magmas are mainly attributed to the background mantle heterogeneity.

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