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Geochemical Characterization of Intraplate Magmatism from Quaternary Alkaline Volcanic Rocks on Jeju Island, South Korea

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Abstract: The major and trace elements of Quaternary alkaline volcanic rocks on Jeju Island were analyzed to determine their origin and formation mechanism. The samples included tephrite, trachybasalts, basaltic trachyandesites, tephriphonolites, trachytes, and mantle xenoliths in the host basalt. Although the samples exhibited diversity in SiO₂ contents, the relations of Zr vs. Nb and La vs. Nb indicated that the rocks were formed from the fractional crystallization of a single parent magma with slight continental crustal contamination (r: 0–0.3 by AFC modeling), rather than by the mixing of different magma sources. The volcanic rocks had an enriched-mantle-2-like ocean island basalt signature and the basalt was formed by partial melting of the upper mantle, represented by the xenolith samples of our study. The upper mantle of Jeju was affected by arc magmatism, associated with the subduction of the Pacific Plate beneath the Eurasian Plate. Therefore, we inferred that two separate magmatic events occurred on Jeju Island: one associated with the subduction of the Pacific Plate beneath the Eurasian Plate (represented by xenoliths), and another associated with a divergent setting when intraplate magmatism occurred (represented by the host rocks). With AFC modeling, it can be proposed that the Jeju volcanic rocks were formed by the fractional crystallization of the upper mantle combined with assimilation of the continental crust. The xenoliths in this study had different geochemical patterns from previously reported xenoliths, warranting further investigations.

Keywords: Jeju Island; alkaline volcanic rock; rare-earth element; oceanic island basalt; Quaternary

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1. Introduction

Jeju Island lies approximately 90 km south of the Korean Peninsula and has a maximum elevation of 1950 m above sea level. It is an elliptical island, 73 km in length and 31 km in width, and is characterized by thick voluminous basaltic lava flows, minor pyroclastic rocks, and numerous small monogenetic volcanoes [1]. The volcanic rocks form a continuous series of alkali/sub-alkaline basalt–trachyte associations. The geology of Jeju Island has been studied by many researchers since 1925 [2–10]. Two separate magmatic events occurred on Jeju Island. The first was associated with the subduction of the Pacific Plate beneath the Eurasian Plate during the late Cretaceous and early Tertiary, while the other was associated with an extensional tectonic setting and is represented by Quaternary intraplate magmatism [11–14].

Over the last two decades, the Quaternary volcanic rocks on Jeju Island, comprising alkaline and sub-alkaline rocks formed by intraplate volcanism in a continental margin setting, have been studied [15–18]. Based on stratigraphic relationships, the volcanic activity of Jeju Island can be divided into four stages [16,19–21]: the first stage that formed

the Seoguipo Formation and basal basalts, the second ‘lava plateau’ stage, the third ‘shield’ stage that created Mt. Halla and formed the bulk of the island, and the final ‘scoria cone’ stage that generated the dispersed small-volume vents visible on the surface [9]. In contrast, based on the geochemical development, Brenna et al. (2015) divided the volcanism into three main stages associated with changes in the depth and degree of partial melting of magma, with two sub-stages based on chemical differences observed in drill cores. Stage 1 produced high-Al alkaline basalts (stage 1b) and derivative evolved trachytic lavas (stage 1t), stage 2 produced high-Al and low-Al alkaline basalts, and stage 3 included the contemporaneous extrusion of primitive low-Al alkaline and sub-alkaline magmas (stage 3b) and evolved trachytes (stage 3t) [14].

The volcanic activity on Jeju Island began at <1.9 Ma and persisted until ~1000 C.E. [9,16–18]. Geochemical studies using Sr-Nd-Pb radiogenic isotope ratios can help determine the genesis of these volcanic rocks [17,22]. Based on Sr-Nd-Pb isotopic systematics, the mantle source for Jeju volcanism has been characterized as a mixture of depleted mid-ocean ridge basaltic (MORB) mantle (DMM) and enriched-mantle-type-2 (EM2) components [16,17].

Woo et al. (2014) proposed that the isotopic signatures of the enriched-mantle (EM1–EM2) source beneath East Asia are from recycling of the sub-continental lithosphere, oceanic crust, and/or subducted sediment [13]. Moreover, the recycling of those source materials is related to late Cretaceous to early Tertiary magmatism caused by the subduction of the Pacific Plate beneath the Eurasian Plate prior to the opening of Cenozoic back-arc basins [22–24].

Two chemically distinct magma series (alkaline and sub-alkaline) have accumulated on Jeju Island during the Quaternary period to form voluminous volcanic deposits [9,16,25].

Previous studies on Jeju volcanic rocks have focused on the history of volcanism, the magma sources, and the tectonic settings [14,16,18,21,26–28]. Our study, additionally, aimed at investigating the underlying mechanism in the generation of the evolved volcanic rocks (trachybasalt to trachyte) on the island.

2. Geologic Setting

Jeju Island is a symmetrical shield-shaped volcanic edifice, the peak of which is located at Mt. Halla (1950 m). Topographically, the volcanic landforms can be divided into the lava plateau, the shield-shaped Halla volcanic edifice, and more than 360 monogenetic volcanoes [1,29]. Quaternary volcanism occurred on 25–35 km-thick continental crust [30], which is located ~650 km behind the Ryukyu Trench/Nankai Trough where the Philippine Sea Plate subducts below the Eurasian Plate. The lithosphere beneath Jeju Island is estimated to be ~60 km thick [21,31].

The geology of the island is characterized by lavas ranging from basaltic to trachytic. The lavas occur extensively on the island together with diverse volcanic landforms, including Mt. Halla at the center of the island and about 360 volcanic cones that are scattered throughout the island. In the subsurface, phreatomagmatic volcanoes (tuff rings and tuff cones) produced by explosive hydrovolcanic activity occur extensively, together with intervening volcanoclastic sedimentary deposits [1,32,33].

Researchers have previously studied the petrography of volcanic rocks from Jeju Island [16,28]. On Jeju Island, lava flows display a compositional spectrum from alkali basalt/basanite to trachyte. Less-evolved rocks (basalt to trachybasalt) generally consist of phenocrysts of clinopyroxene and olivine in modal abundances of <15%; the groundmass comprises plagioclase, olivine, and clinopyroxene microlites, with or without dispersed titanomagnetite. The more evolved rocks (basaltic trachyandesite) contain phenocryst phase of plagioclase and groundmass of alkali-feldspar microlites [28]. On examining the samples from deep cores (400–500 m) of the central Jeju Island, dominant phenocryst assemblages were visible in the hand specimens. These varied systematically from the olivine-and-pyroxene-dominated base to a plagioclase-rich top. Tatsumi et al. (2005)

reported that, in Jeju basalts, spinel crystals were included in olivine phenocrysts. This is indicative of the equilibrium of basalt magmas with the residual spinel in the mantle [16].

The volcanism of Jeju Island comprises the syn-depositional (~1.88–0.5 Ma) and post-depositional (0.5 Ma) Holocene Seoguipo Formation, which is composed of basaltic volcanoclastics and fossiliferous deposits. The syn-depositional volcanism is characterized by hydrovolcanism with minor alkali basaltic lava effusions (~1 Ma), domed extrusions with evolved alkaline lavas, and alkaline lava effusions that erupted locally and sporadically during the deposition of the Seoguipo Formation. The post-depositional volcanism is characterized by extensive terrestrial volcanism after the termination of the deposition of the Seoguipo Formation at ~0.5 Ma [18].

The basement rocks of Jeju Island include granites and silicic volcanic rocks of Jurassic to Cretaceous age, as well as gneisses of unknown age that were observed in drill cores as xenoliths in the basalts and tuffs [9,16,17,20,21]. Mantle xenoliths are observed within volcanic rocks distributed extensively on Jeju Island and include spinel peridotites and pyroxenites [21,27,34], as well as gabbroic and anorthite xenoliths [11–13,20,21,34,35].

3. Analytical Methods

Ten fresh rock samples from trachyte outcrops and two samples of mantle xenoliths from basalts were collected for analysis (Figure 1). Fresh whole-rock samples were cut down into chips, which were then cleaned ultrasonically in distilled water with <5% HNO₃, and then in distilled water only. The chips were then dried and handpicked to avoid visible contamination. The weathered rims were removed, and all of the chips were crushed to a millimeter scale. The crushed chips containing no xenocrysts or amygdules were handpicked under a magnifier. Only fresh rock chips without any xenocrysts or amygdules were selected for further analyses. An agate mill was used to crush and pulverize the samples, and the resulting powders were analyzed to determine their major and trace-elemental compositions. The trachytic specimens were sent to the Center for Research Facilities, Chonnam National University, for major elemental analysis using an X-ray fluorescence spectrometer (PW1480, Philips). The relative error rates reported from the analyses using a standard sample (BHVO-1) were <1% for Si, Ti, Al, Mg, Ca, and Na; 1–2% for Fe, K, and P; and 2–3% (one standard deviation; 1σ) for Mn.

The samples were sent to the National Center for Inter-University Research Facilities, Seoul National University, for trace-elemental analysis using inductively coupled plasma mass spectrometry (ICP-MS; ELAN 6100, Perkin-Elmer SCIEX) with an argon plasma source (6000 K) and a mass resolution of 0.3–3.0 amu. The comparison between the average and recommended values obtained from repeated analyses of BHVO-1 exhibited relative error rates of 12% for Er and Ho; <5% for Ba, Cr, Cu, Nb, Sr, Rb, Y, Zr, La, Ce, Sm, and Lu; and 5–10% for Nd, Eu, Gd, Pr, Tb, Dy, and Yb.

Figure 1. Geologic map of Jeju Island (modified from Park et al., 2000) [36] with the sampling locations of trachytic rocks (1~10) and mantle xenoliths (X1~2).

4. Results

4.1. Major Elements

The major and trace-elemental compositions of the samples are presented in Table 1. Based on the SiO_2 vs. $\text{K}_2\text{O} + \text{Na}_2\text{O}$ classification diagram of Bas et al. (1986) [37], the volcanic rock samples were classified as basaltic trachyandesites, trachyandesites, tephrites, tephriphonolites, and trachytes (Figure 2). Half of the samples were basaltic trachyandesites. All of the analyzed samples were in the alkaline region of the diagram, even though two chemically distinct (alkaline and sub-alkaline) magma series are present on Jeju Island (Figure 2) [14,16,18].

The basaltic trachyandesites (Samples 1, 2, 6, 8, and 9) contained SiO_2 (49.73–51.95 wt.%), Na_2O (6.23–5.89 wt.%), and K_2O (2.19–1.38 wt.%). The tephrite (samples 3 and 7) exhibited the lowest SiO_2 contents (47.82–48.21 wt.%), Na_2O contents (5.99–6.49 wt.%), and K_2O contents (1.39–2.19 wt.%). The trachybasalt (sample no. 5) had an SiO_2 content of 50.126 wt.%, a Na_2O content of 5.32 wt.%, and a K_2O content of 0.89 wt.%. The tephriphonolite (sample no. 10) contained SiO_2 (55.21 wt.%), Na_2O (7.87 wt.%), and K_2O (3.45 wt.%). Trachyte, which was the most felsic sample (Sample No. 4), had an SiO_2 content of 61.94 wt.%, a Na_2O content of 8.79 wt.%, and a K_2O content of 5.01 wt.%. All of the samples fell along the Na-series, since the $\text{Na}_2\text{O}/\text{K}_2\text{O}$ values were ~1.76–6.01. In an AFM diagram, the samples plotted near the boundary between the calc-alkaline and tholeiitic fields (Figure 3). The AFM diagram displays the fractional crystallization trend, which will be explained in detail later.

Table 1. Major and trace-elemental compositions of Jeju Island alkaline volcanic rocks.

Sample	1	2	3	4	5	6	7	8	9	10	X1	X2
Rock Type ¹	BTA	BTA	Te	Tr	TB	BTA	Te	BTA	BTA	TP	Xe	Xe
wt. %												
SiO ₂	51.95	49.90	47.82	61.94	50.13	51.85	48.21	49.73	50.43	55.21	40.08	42.70
Al ₂ O ₃	16.77	17.74	16.76	16.84	15.85	17.35	15.89	15.91	17.50	18.20	1.97	2.35
Na ₂ O	6.17	5.95	6.49	8.80	5.32	6.23	5.99	5.89	6.23	7.87	0.13	0.23
Fe ₂ O ₃ ²	11.37	10.50	11.47	3.49	11.50	8.89	12.26	12.49	10.47	6.57	10.74	9.96
CaO	6.05	9.06	8.67	2.58	9.53	8.15	8.73	8.03	8.54	5.62	1.46	1.83
K ₂ O	2.13	1.40	1.28	5.01	0.89	2.20	1.51	1.43	1.39	3.45	0.05	0.08
TiO ₂	2.15	2.40	2.64	0.47	2.11	1.88	2.58	2.22	2.27	1.23	0.08	0.12
MgO	2.10	2.20	3.86	0.23	4.08	2.72	3.90	3.46	2.20	0.88	45.06	42.36
P ₂ O ₅	0.93	0.50	0.66	0.12	0.25	0.43	0.61	0.47	0.63	0.43	nd	nd
MnO	0.17	0.13	0.16	0.23	0.15	0.11	0.17	0.17	0.14	0.24	0.13	0.12
Total	99.78	99.79	99.80	99.70	99.80	99.79	99.83	99.80	99.79	99.71	99.70	99.75
Mg # ³	34.32	37.28	48.79	15.74	50.12	46.44	47.37	44.00	37.29	27.56	92.24	92.33
Concentrations in ppm												
Sc	10.67	12.68	14.57	nd	14.37	7.21	12.94	14.80	10.64	3.18	0.69	1.02
La	39.54	22.71	26.69	113.39	17.38	25.44	20.33	24.12	20.96	79.74	0.69	1.02
Ce	81.16	45.82	53.19	206.62	35.22	47.52	41.82	49.80	42.20	147.15	1.40	1.67
Pr	9.74	5.70	6.58	20.84	4.44	5.69	5.25	6.06	5.26	16.01	0.16	0.25
Nd	40.14	24.13	27.50	67.80	19.34	22.12	22.21	25.25	22.51	55.41	0.65	0.99
Sm	9.05	5.76	6.36	11.99	5.09	5.05	5.17	6.23	5.53	10.52	0.16	0.25
Eu	2.99	2.08	2.22	3.20	1.75	2.33	1.79	2.16	2.00	3.31	0.06	0.08
Gd	9.76	6.49	7.08	13.02	5.89	5.40	5.75	7.07	6.30	11.31	0.21	0.32
Tb	1.29	0.86	0.92	1.55	0.81	0.69	0.75	0.94	0.84	1.36	0.03	0.05
Dy	6.53	4.44	4.70	7.96	4.29	3.46	3.87	4.90	4.31	6.92	0.21	0.32
Ho	1.17	0.78	0.83	1.53	0.77	0.60	0.69	0.87	0.77	1.30	0.05	0.07
Er	3.06	2.05	2.17	4.56	2.02	1.62	1.83	2.29	2.00	3.69	0.14	0.20
Tm	0.37	0.25	0.26	0.85	0.25	0.20	0.22	0.28	0.24	0.49	0.02	0.03
Yb	2.25	1.48	1.57	3.97	1.51	1.19	1.33	1.67	1.45	3.11	0.14	0.20
Lu	0.31	0.21	0.22	0.60	0.21	0.17	0.19	0.24	0.20	0.46	0.02	0.03
Zr	259.11	111.05	118.45	562.64	103.64	118.45	81.43	185.08	103.64	384.96	3.94	6.22
Nb	41.94	20.97	27.96	83.88	13.98	27.96	20.97	27.96	20.97	69.90	0.97	1.34
Rb	36.58	27.43	27.43	118.87	27.43	45.72	18.29	27.43	18.29	91.44		
Ba	483.48	277.56	268.60	787.90	223.84	510.34	349.18	304.42	295.46	671.51	9.12	9.78
Th	6.10	3.28	3.72	16.19	2.86	4.51	2.26	3.31	3.06	11.05	0.12	0.19
U											0.05	0.10
Ta											0.12	0.14
K											412.97	644.25
Pb											0.27	0.40
Sr	338.24	422.80	388.97	481.99	295.96	549.63	388.97	304.41	380.52	668.02	8.95	11.51
Ti											484.22	702.62
Y	27.21	19.70	20.14	40.39	18.93	16.35	14.07	20.58	17.61	32.66	1.35	2.05
(La/Sm) _N	2.73	2.46	2.62	5.91	2.13	3.15	2.46	2.42	2.37	4.73	2.64	2.57
(La/Lu) _N	13.05	11.32	12.60	19.58	8.57	15.71	11.28	10.53	10.67	17.99	3.09	3.41
(Eu/Eu*)	0.97	1.04	1.01	0.78	0.97	1.36	1.00	0.99	1.03	0.93	0.90	0.86
(Ce/Ce*)	1.00	0.97	0.97	1.03	0.97	0.96	0.98	1.00	0.97	1.00	1.02	0.81
CIPW normative mineralogy(wt.%) ⁴												
plag	54.61	49.51	39.21	47.38	49.75	44.67	38.71	45.81	50.46	41.52	5.86	7.09
or	12.59	8.27	7.56	29.61	5.26	13.00	8.92	8.45	8.21	20.39	0.30	0.47
ne	5.08	9.96	15.45	6.15	6.50	11.33	12.99	9.09	9.72	15.83	-	-
cpx	10.17	19.99	21.13	8.14	23.65	20.29	22.38	19.82	18.73	12.98	2.15	3.09
opx	-	-	-	-	-	-	-	-	-	-	1.00	13.35
wo	-	-	-	1.12	-	-	-	-	-	2.34	-	-
ol	5.36	1.01	4.11	-	4.25	1.45	4.34	5.01	1.61	-	84.84	70.48
ac	-	-	-	3.04	-	-	-	-	-	-	-	-
ns	-	-	-	2.86	-	-	-	-	-	-	-	-

Table 1. Cont.

Sample	1	2	3	4	5	6	7	8	9	10	X1	X2
Rock Type ¹	BTA	BTA	Te	Tr	TB	BTA	Te	BTA	BTA	TP	Xe	Xe
il	4.08	4.56	5.01	0.89	4.01	3.57	4.90	4.22	4.31	2.34	0.15	0.23
mt	4.96	4.57	5.00	-	5.02	3.87	5.34	5.44	4.57	2.86	4.68	4.34
ap	2.15	1.16	1.53	0.28	0.58	1.00	1.41	1.09	1.46	1.00	-	-
Total	99.00	99.03	99.00	99.47	99.02	99.18	98.99	98.93	99.07	99.26	98.98	99.05

¹ BTA: Basaltic andesite; Te: Tephrite; Tr: Trachyte; TB: Trachybasalt; TP: Tephriphonolite; Xe: Xenolith. ² Total iron as Fe₂O₃. ³ Mg # [=100 × Mg/(Mg + Fe²⁺)], assuming Fe²⁺/Fe_{total} = 0.9. ⁴ plag: Plagioclase; or: Orthoclase; ne: Nepheline; cpx: Clinopyroxene; opx: Orthopyroxene; wo: Wollastonite; ol: Olivine; ac: acmite; ns: Sodium metasilicate; il: Ilmenite; mt: Magnetite; ap: Apatite.

Figure 2. SiO₂ vs. K₂O + Na₂O classification (TAS) diagram of late Cenozoic volcanic rocks on Jeju Island [37]. Published data of other researchers are from Kim et al. (2019) and Brenna et al. (2012b) [21,28].

As depicted in Harker diagrams of the variations in major oxide and SiO₂ contents (Figure 4), the basaltic trachyandesite samples had low MnO, Na₂O, and K₂O contents, but it had high Al₂O₃, Fe₂O₃, TiO₂, CaO, P₂O₅, and MgO contents. The P₂O₅ content decreased as the SiO₂ content increased and started to decrease at 53% of SiO₂ (Figure 4), suggesting the crystallization of apatite. The tephrite and trachybasalt samples had major oxide contents similar to those of the basaltic trachyandesites, except that trachybasalts had lower P₂O₅ and Al₂O₃ contents. However, the tephriphonolite and trachyte contained high Na₂O and K₂O contents and pronounced high MnO contents. The Na₂O, K₂O, MnO, and SiO₂ contents of the more felsic rocks, such as tephriphonolites and trachytes, were positively correlated. These two rock types also exhibited negative correlations of Al₂O₃, Fe₂O₃, P₂O₅, MgO, CaO, and TiO₂ contents with SiO₂ contents. The fractional crystallization of clinopyroxene and plagioclase is indicated by the negative correlation

between CaO and SiO₂ contents, and the positive correlation followed by the negative correlation between Al₂O₃ and SiO₂ contents (Figure 4). The fractional crystallization of plagioclase was evident in the trachyte sample (sample no. 4), in which a negative Eu/Eu* anomaly was observed (Table 1 and Figure 5).

Figure 3. AFM diagram of late Cenozoic volcanic rocks on Jeju Island, including the boundary between the calc-alkaline and the tholeiitic fields (after Irvine and Baragar, 1971) [38]. Symbols are the same as in Figure 2. FeO* is total iron as FeO assuming $\text{Fe}^{2+}/\text{Fe}_{\text{total}} = 0.9$.

4.2. Trace and Rare-Earth Elements

The chondrite-normalized rare-earth-element (REE) plots for the volcanic rock samples from Jeju Island showed a notable enrichment in light REEs (LREEs) and a depletion of heavy REEs (HREEs) (Figure 5). The HREEs displayed a flat trend. The pattern resembles that of oceanic island basalts (OIBs) [39], and the $(\text{La}/\text{Lu})_{\text{N}}$ and $(\text{La}/\text{Sm})_{\text{N}}$ ratios were 8.85–20.22 and 2.20–6.10, respectively. The trachyte sample (sample no. 4) exhibited a pronounced negative Eu anomaly ($\text{Eu}/\text{Eu}^* = 0.78$), whereas the other samples exhibited slightly negative and positive Eu anomalies ($\text{Eu}/\text{Eu}^* = 0.93$ – 1.37 ; Table 1). The (Ce/Ce^*) anomalies were steady and negative, with values of 0.92–0.97, indicating that the volcanic rocks were not affected by oxidation.

The two most-evolved rocks (tephriphonolite and trachyte) contained higher concentrations of incompatible elements, in the form of the large-ion lithophile elements (LILEs) Rb and Ba and the high-field-strength elements (HFSEs) Nb and Zr, than the other rock types analyzed in this study (Table 1 and Figure 6). The two xenolith samples displayed depletion of the trace elements and REEs compared to the alkaline volcanic rocks, but the patterns look similar to those of the volcanic rocks (Figures 5 and 6), which indicates their origins are linked.

Figure 4. Variations in major oxide contents vs. SiO_2 content of the volcanic rock samples from Jeju Island, Al_2O_3 vs. SiO_2 (a), Na_2O vs. SiO_2 (b), $\text{Fe}_2\text{O}_{3\text{total}}$ vs. SiO_2 (c), CaO vs. SiO_2 (d), K_2O vs. SiO_2 (e), TiO_2 vs. SiO_2 (f), MgO vs. SiO_2 (g), P_2O_5 vs. SiO_2 (h) and MnO vs. SiO_2 (i). Published data of other researchers are from Kim et al. (2019) and Brenna et al. (2012b) [21,28].

Figure 5. C1-chondrite-normalized [39] rare-earth-element patterns of alkaline volcanic rock and mantle xenolith samples from Jeju Island. The E-MORB, N-MORB, and OIB data are from Sun and McDonough (1989) [39]. The compiled xenolith data are from Yang et al., 2012a; Yang et al., 2012b; Woo et al., 2014 and Choi et al., 2005 [11–13,34].

Figure 6. Primitive-mantle-normalized [39] multi-elemental spidergram. The E-MORB, N-MORB, and OIB data are from Sun and McDonough (1989) [39]. The compiled xenolith data are from Yang et al., 2012a; Yang et al., 2012b; Woo et al., 2014 and Choi et al., 2005 [11–13,34].

The Zr/Nb ratios of the Jeju alkaline volcanic rocks were within the range of OIB mantle sources and were far lower than those of continental crust (16.2), primitive mantle (14.8), and normalized-MORB (N-MORB) (30) [40,41] (Table 2). However, contamination from the continental crust cannot be ruled out, as the plots of Ba/Nb vs. Th/Nb indicate that the samples are within or close to the EM2 range but are slightly scattered in the direction of the continental crustal field (Figure 7).

Table 2. Representative incompatible trace-elemental ratios of Jeju Island alkaline volcanic rocks, with primitive mantle, N-MORB, E-MORB, continental crust, HIMU-OIB, EM1-OIB, and EM2-OIB values for comparison.

	Zr/Nb	La/Nb	Ba/Nb	Ba/Th	Rb/Nb	K/Nb	Th/Nb	Th/La	Ba/La
Primitive mantle *	14.8	0.94	9	77	0.91	323	0.117	0.125	9.6
N-MORB *	30	1.07	1.7–8.0	60	0.36	210–350	0.025–0.071	0.067	4
E-MORB *			4.9–8.5			205–230	0.06–0.08		
Continental crust *	16.2	2.2	54	124	4.7	1341	0.44	0.204	25
HIMU-OIB *	3.2–5.0	0.66–0.77	4.9–6.9	49–77	0.35–0.38	77–179	0.078–0.101	0.107–0.133	6.8–8.7
EM1-OIB *	1.2–11.5	0.86–1.19	11.4–17.8	103–154	0.88–1.17	213–432	0.105–0.122	0.107–0.128	13.2–16.9
EM2-OIB *	4.5–7.3	0.89–1.09	7.3–13.3	67–84	0.59–0.85	248–378	0.111–0.157	0.122–0.163	8.3–11.3
Jeju Island alk. volcanics	3.9–7.4	0.86–1.35	9.4–18.3	49–154	0.87–1.96	394–652	0.108–0.204	0.111–0.177	6.9–20.1
Average of Jeju	5.5	1.05	12.9	88	1.22	501	0.152	0.146	12.7

* Data are from Saunders et al. (1988) and Weaver (1991a) [40,41].

Figure 7. Ba/Nb vs. Th/Nb ratios. The data for the primitive mantle (PM), E-MORB, N-MORB, HIMU, EM1, EM2, and continental crust (CC) are from compilations by Saunders et al. (1988), Weaver (1991a), Plank and Langmuir (1998), and White et al. (2014) [40–43]. Symbols are the same as in Figure 2.

5. Discussion

5.1. Fractional Crystallization and Crustal Contamination

TiO₂ was low in the tephriphonolite and trachyte, indicating that Fe-Ti minerals (titanomagnetite) were removed by fractional crystallization (Table 1; Figure 4f). Basaltic trachyandesite, tephrite, and trachybasalt are believed to have formed from basaltic magma. The Fe₂O₃ and MgO contents were low in tephriphonolite and trachyte, as they are not directly related to basaltic magma and can be related to the fractional crystallization of basaltic magma (Table 1; Figure 4c,g). In addition, the tephriphonolite and trachyte had higher LREE and HREE concentrations than the basaltic trachyandesite, tephrite, and trachybasalt (Figure 5). The (La/Sm)_N and (La/Lu)_N ratios were also higher in the tephriphonolite and trachyte, which suggests that they were produced by a later stage of fractional crystallization from the parent magma (Table 1). The REE and multi-elemental diagrams (Figures 5 and 6) indicate that the volcanic rock samples were derived from OIB.

The negative anomalies of Sr and Ti observed in the samples of the most-evolved rocks (tephriphonolite and trachyte) were caused by the fractional crystallization of plagioclase and titanomagnetite, respectively, rather than by a particular magmatic environment.

Except for Sr and Ti depletions in those two samples, all of the samples display similar trends on the spidergram (Figure 6), which indicates that they were derived from the same magma source. The Th/Nb vs. Ba/Nb ratios also indicate that the volcanic rocks originated mainly from an enriched-mantle (EM1, EM2) source and were slightly affected by the continental crust (Figure 7).

No depletion of HFSEs (as shown in Figure 6) and no negative Eu anomaly except in the trachyte sample (as shown in Figure 5) were observed. Therefore, the magma of Jeju volcanism is thought to originate from the spinel peridotite in the upper mantle.

The two mantle xenolith samples displayed relatively depleted REE and trace-elemental patterns but similar trends to the volcanic rocks, which indicates that the xenoliths and the volcanic rocks are related in their origins. The basaltic melt most likely originated from partial melting of the upper mantle, represented by the xenoliths. However, the patterns of the xenoliths obtained in this study on the spidergram (Figure 6) and REE diagram (Figure 5) were different from those of xenoliths described in previous studies of Yang et al., 2012a; Yang et al., 2012b; Woo et al., 2014 and Choi et al., 2005 [11–13,34]. Woo et al. (2014) divided xenoliths from Jeju Island into three groups [13]: the first group comprises Cr-diopside and spinel-bearing ultramafic xenoliths that correspond to fragments of peridotitic mantle, corresponding to Group I of Frey and Prinz (1978) [44]; the second group, which contain Al-Ti-rich black clinopyroxenes, are magmatic cumulates reported to have directly crystallized near the Moho [12] and correspond to Group II of Frey and Prinz (1978) [44]; and the third group comprises gabbroic xenoliths reported to have crystallized in the reservoir-roof environment within the crust [11].

The xenolith samples of this study fall into the first group of Woo et al. (2014) [13], and the rock types are dunite and harzburgite of spinel peridotite. However, they exhibited larger depletions in MREE, HREE, and some HFSEs (Figures 5 and 6) compared to the Group I xenoliths of Yang et al. (2012a) [11] and the two other xenolith groups of Jeju Island (shaded gray areas in Figures 5 and 6), which needs to be further investigated.

The positive anomalies in U and Pb, which are fluid-mobile elements (FMEs), in the whole-rock phases of xenoliths indicate that those elements have been added by a subduction component related to mantle contamination by subduction fluids [45,46]. A slight negative Nb anomaly, which is typical of arc magmatism, is also observed. This subduction signature was probably acquired during arc magmatism in the upper mantle during the late Cretaceous and early Tertiary [22–24].

Yang et al. (2012b) estimated the depth of the Jeju magma chamber to equal the depth of the lower continental crust [12]. Therefore, assimilation of the lower continental crust cannot be ruled out during the fractional crystallization of Jeju magma.

By using the FC–AFC–FCA and mixing modeler [47], we estimated the relative ratio of assimilated material (lower continental crust) to crystallized material (“ r ”) in the AFC process of magmatic evolution.

AFC modeling was carried out with the average trace element concentration of the two xenolith samples as the source of magma and with the lower continental crust as the contaminant in the equation from DePaolo (1981) [48]:

$$C_L = C_0 \cdot f + \frac{r}{(r - 1 + D)} \cdot C_A (1 - f)$$

where C_L is the concentration of the trace element in the resulting magma; C_0 is the concentration of the trace element in the remaining melt and the original magma, respectively; C_A is concentration of trace element in the contaminant, r is the ratio of rate of assimilation to rate of fractional crystallization; f is $F[-(r - 1 + D)/(r - 1)]$; F is the fraction of magma remaining; and D is the bulk distribution coefficient for the fractionating assemblage [48].

In Figure 8, Zr, Nb, and La values are plotted for $r = 0.2$ (Zr vs. Nb) and $r = 0.3$ (La vs. Nb). The partition coefficients of Zr, Nb, and La are referred from Zanetti et al. (2004), McKenzie and O’Nions (1991), Villemant (1988), Foley et al. (1996), Rollinson (1993), and Zack and Brumm (1998) [49–54]. The C_A values of Zr, Nb, and La of the lower continental crust are referred from Taylor and McLennan (1995) [55].

Figure 8. Plots of Zr vs. Nb contents (a) and La vs. Nb contents (b) for the volcanic rocks from Jeju Island by the FC–AFC–FCA and mixing modeler [47]. A 10% increment is marked in the trajectory of AFC ($r > 0$) and FC ($r = 0$).

The figure indicates that the ratio of the assimilation rate of continental crust to the fractional crystallization rate in Jeju magma is 0–0.3.

5.2. Potential Magma Source

All of the samples formed within Stages 2 and 3 of Tatsumi et al. (2005) [16], during which basaltic lavas (Pyosunri basalt) formed the bulk of the exposed volcanic rocks as a lava plateau, and volcanic rocks (basalts, trachyandesites, and trachytes) formed the Halla shield volcano. Geochemical studies regarding continental alkaline suites have shown that alkaline rocks evolve along a lineage of strong silica-undersaturated basanite to phonolite, or along a lineage of a more silica-saturated alkali basalt to trachyte [56,57]. The major and trace-elemental compositions of the evolved rocks can be attributed to the fractional crystallization of mafic rocks dominated by olivine, clinopyroxene, apatite, and Fe–Ti oxides, as well as to plagioclase fractionation in intermediate rocks, while the fractionation of plagioclase, alkali feldspar, zircon, and sphene may have been controlled in the highly evolved rocks [58].

By studying seismic-wave velocities, Song et al. (2018) suggested that edge-driven convective flow at sub-lithospheric depths at the lithospheric thickness transition below the island led to decompression melting [31]. The complex and dispersed intraplate volcanism

on Jeju Island can be attributed to the intense interaction between the ascending magma and the lithosphere.

This study obtained geochemical signatures of volcanism due to FC, with crustal contamination from the lower crust, based on the REE and trace-elemental patterns of volcanic rocks and mantle xenoliths. The chondrite-normalized REE diagrams (Figure 5) indicate an OIB source.

The volcanic rocks had an enriched-mantle-2-like ocean island basalt signature and the basalt was formed by partial melting of the upper mantle, which is represented by the xenolith samples of our study. The upper mantle of Jeju was affected by arc magmatism, which is associated with the subduction of the Pacific Plate beneath the Eurasian Plate.

Comparisons of incompatible and trace-elemental ratios in the basalts and different mantle and crustal sources, including primitive mantle, N-MORB, E-MORB, continental crust, HIMU-OIB, EM1-OIB, and EM2-OIB on Jeju Island are shown in Table 2. The EM1-OIB endmember component was assumed to be related to an ancient SCLM [59–61] and/or to a metasomatized lower portion of an old SCLM [61,62]. Alternatively, it may be attributable to the metasomatic enrichment of ancient oceanic lithospheric mantle from long-term storage in the deep mantle [21,63]. The EM-2 OIB endmember component was generally regarded as originating from an enriched-mantle source that was metasomatized by subduction-related melt and/or fluids [61,64], or from terrigenous sediment-bearing subducted oceanic lithosphere [64–66].

The trace-elemental ratios of the Jeju Island volcanic rocks were similar to those of an EM2-OIB source. Their Th/Nb and Th/La ratios were also within the range of values for the EM2-OIB source (Table 2). Nearly all of the samples plotted within or near the EM-2 OIB field in the Ba/Nb-Th/Nb diagram and were scattered toward the continental crust field (Figure 7). This indicates that the Jeju Island volcanic rocks are mainly the result of AFC of an EM2-OIB source.

The isotopic ratios of Jeju volcanic rocks can be explained as a mixture of DMM and EM2, but the analyses of source mantle reservoirs vary [17]. The volcanic rocks of this study show that the Jeju alkali rocks formed from a partially melted upper-mantle source.

6. Conclusions

Although the alkaline volcanic rocks of Jeju Island exhibited a wide range of SiO₂ contents (47.82–61.94 wt.%), they formed from the FC of a single parent magma with continental crustal contamination. AFC modeling shows the relative ratio of assimilated material (lower continental crust) to crystallized material is 0–0.3. The Jeju volcanic rocks have EM2-like OIB signatures, which was likely related to the extension of the Japan back-arc basin. The mantle xenoliths from the upper mantle beneath Jeju Island show depleted concentration of trace elements and REE but similar patterns to the volcanic rocks. Hence, the origin of Jeju magma is linked to the upper mantle, represented by the basaltic xenoliths. The upper mantle below Jeju Island was affected by arc magmatism which is associated with the subduction of the Pacific Plate. Therefore, we can infer two separate magmatic events occurred on Jeju Island: one associated with the subduction of the Pacific Plate beneath the Eurasian Plate (represented by xenoliths) in late Cretaceous and early Tertiary and another associated with a divergent setting during which intraplate magmatism occurred by partial melting of the upper mantle (represented by the host rocks) in Quaternary (Figure 9). Further study of the mantle xenoliths on Jeju Island is required, as the REE and trace-elemental signatures of the xenoliths reported in this study differ from those reported by previous studies.

Figure 9. Schematic diagram illustrating the origin of the alkaline volcanic rocks and mantle xenoliths on Jeju Island based on the results of this study (not to scale).

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