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Geochemical Variation of Miocene Basalts within Shikoku Basin: Magma Source Compositions and Geodynamic Implications

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Abstract: Shikoku Basin is unique as being located within a trench-ridge-trench triple junction. Here, we report mineral compositions, major, trace-element, and Sr-Nd-Pb isotopic compositions of bulk-rocks from Sites C0012 (>18.9 Ma) and 1173 (13–15 Ma) of the Shikoku Basin. Samples from Sites C0012 and 1173 are tholeiitic in composition and display relative depletion in light rare earth elements (REEs) and enrichment in heavy REEs, generally similar to normal mid-ocean ridge basalts (N-MORB). Specifically, Site C0012 samples display more pronounced positive anomalies in Rb, Ba, K, Pb and Sr, and negative anomalies in Th, U, Nb, and Ta, as well as negative Nb relative to La and Th. Site 1173 basalts have relatively uniform Sr-Nd-Pb isotopic compositions, close to the end member of depleted mantle, while Site C0012 samples show slightly enriched Sr-Nd-Pb isotopic signature, indicating a possible involvement of enriched mantle 1 (EM1) and EM2 sources, which could be attributed to the metasomatism of the fluids released from the dehydrated subduction slab, but with the little involvement of subducted slab-derived sedimentary component. Additionally, the Shikoku Basin record the formation of the back-arc basin was a mantle conversion process from an island arc to a typical MORB. The formation of the Shikoku Basin is different from that of the adjacent Japan Sea and Parece Vela Basin, mainly in terms of the metasomatized subduction-related components, the nature of mantle source, and partial melting processes.

Keywords: geochemistry; isotopes; back-arc basin; Shikoku Basin; subduction zone; Philippine Plate

1. Introduction

The Shikoku Basin in the Philippine Plate is one of the most complex plate tectonic systems on Earth. To date, it has undergone rapid and complex temporal and spatial changes [1–4]. The detailed tectonic process can be summarized as follows: (1) Earlier than 30 Ma, the whole Northeast Asia was affected by the subduction of the Pacific Plate (Figure 1A). Until approximately 30–15 Ma, Shikoku Basin was formed behind the Izu-Bonin-Mariana (IBM) arc by the intense extension, creating a typical back-arc basin [2,5–12]. The tensile force in Shikoku Basin led to the Kyushu-Palau Ridge (KPR) gradually separating away from the IBM arc to finally form a new oceanic crust (Figure 1B) [2,10], which is a preliminary formation model of the Philippine Plate. (2) Around 15 Ma, Japan Sea was already a back-arc spreading basin created by the rifting of the Asian continental margin [13,14]. The opening of Japan Sea resulted in the NE Japan arc rotating counterclockwise as it drifted east, while the SW Japan arc occurred at roughly 45° clockwise rotations as it drifted south (Figure 1C) [15]. Moreover, the opening of Japan Sea and the
associated clockwise rotation of the SW Japan arc sliver finally led to the subduction of the young Shikoku oceanic lithosphere. Simultaneously, the Shikoku Basin was undergoing the back-arc spreading processes (Figure 1C). (3) Later than 15 Ma, the shapes of the Japan Sea and Philippine Plate were basically formed, but the Shikoku Basin was still spreading. From 15 to 6 Ma, the triple junction was formed owing to the plate evolution and motions between the Pacific Plate, the Philippine Sea Plate, and SW Japan arc (Figure 1D). Until the period of 6–5 Ma, more rapid and deeper subduction of the Philippine Plate introduced large volumes of fluids into the SW Japan arc (Figure 1E) [3]. (4) Due to the continuous expansion of the Philippine Plate, the Izu-Bonin Island constantly collided with the Honshu Island. However, the collision time between these two island arcs was controversial in that, although most scientists have proven its occurrence at 15 Ma [16–18], other studies believe that the collision time was roughly 6–8 Ma [3,19–21]. (5) The Shikoku Basin continued spreading and finally formed the current plate tectonic shape (Figure 1F).

Shikoku Basin is quite special from a global perspective because it was not only a back-arc basin formed behind the IBM arc during episodes of east-west spreading in the Middle Miocene (Figure 1C) [2,6,8,10,22] but also being subducted beneath the Shikoku island along the central part of the Nankai Trough (Figure 1F). These geological features make Shikoku Basin distinct from those typical back-arc basins located at conventional convergent plate boundaries [23]. Shikoku Basin could provide us a rare opportunity to clarify the special nature of mantle source because it is situated within a special tectonic environment where the subduction of the spreading ridge, called trench-ridge-trench (TRT) triple junction or inter-arc basin, is recognized [2]. A study on the basaltic volcanic rocks that erupted in such basin could have yielded information of the components in the mantle source of the back-arc basin and, potentially, the geodynamic influence of the actively spreading ridge [8–10,12]. Thus, it appears particularly important to study the relationships between the volcanic rock series within the Shikoku Basin and their
TECTONIC SETTINGS (TRT TRIPLE JUNCTION) AND ELUCIDATE THE DIFFERENCES BETWEEN THE FORMATION OF VOLCANIC ROCKS FROM THE SHIKOKU BASIN AND THE TYPICAL BACK-ARC BASIN, I.E., PARECE VELA BASIN.

The Shikoku Basin is merged to the Parece Vela Basin in the south, which is also located in the Philippine Plate and formed simultaneously as a back-arc basin behind the IBM arc [10]. These two basins share similarities in evolutionary processes, the changed direction of spreading axis, and spreading rate [9,10]. However, they are different in terms of bathymetric characteristics of their spreading axes, three-dimensional shear wave velocity structure, asthenospheric thermal conditions, etc. [10,24–26]. All these differences are reflected and clarified by volcanic activities, and the origin of the two basins eventually helped us trace the key factors involved in the basin’s unique geochemical characteristics.

Accordingly, in this study, we conducted a combined study of mineral chemistry, bulk rocks geochemistry, and Sr-Nd-Pb isotope geochemistry on volcanic rocks from Site 1173 and Site C0012 in the Shikoku Basin. Potential source components and the nature of mantle source of the Shikoku Basin are discussed in this paper. Besides, the geodynamic processes accounting for the unique geochemistry were evaluated on the basis of the comparison with those volcanic rocks in Japan Sea Basin [27] and Parece Vela Basin [10,28].

2. GEOLOGICAL SETTING

The Shikoku Basin in the Philippine Plate is bounded by the Izu-Bonin Ridge to the east, the KPR to the west, and the Nankai Trough to the north (Figure 2). It is generally considered to have been formed by typical back-arc basin rifting located along the back-arc side of the Izu-Bonin volcanic arc chain during Late Oligocene to Middle Miocene [6,8,9,12,22] (25 to 15 Ma). Moreover, the basin subducts beneath the Eurasian continent (SW Japan arc; Figure 2) [29,30] at the Nankai Trough and exhibits a rock sequence that is divided into five major stratigraphic units (Units I to V) from the top downward [31,32].

Drilling activities carried out by the Deep Sea Drilling Project (DSDP) and Integrated Ocean Drilling Program (IODP) recovered many oceanic drilling cores within the Shikoku Basin and the Nankai Trough on the subducting Philippine Sea Plate (Figure 2). In these oceanic drilling cores, the back-arc basin basement below the sedimentary complex was only reached in Sites 1173, C0012 in the Nankai Trough, and Sites 442, 443, and 444 in the Shikoku Basin [31,33] (Figure 2). More specifically, IODP Site C0012 was situated near the crest of a prominent bathymetric seafloor high, the Kashinosaki Knoll, which is located 100 km southeast of the Kii Peninsula and 150–200 km west of the Izu-Bonin arc [34,35] (Figure 2). The igneous basement was recovered at 36-m thickness and the sediment and basalt interface intact was recovered at 540 m below the sea floor (mbsf) at Site C0012 (Figure 3). The back-arc basin basement at Site C0012 was determined to be older than 18.9 Ma [32,36] (Figure 3), and was divided into an upper aphyric pillow (Unit 1) and a lower massive flow (Unit 2). IODP Site 1173 was drilled 11 km seaward of the deformation front, which is located in the outer margin of the Nankai Trough (Figure 2). The basement rocks were encountered in IODP Site 1173 at a depth of 737.1 mbsf, and a total of 19.5 m of igneous rocks, Middle Miocene (13–15 Ma) in age, was penetrated [37,38], with two main basalt lava units including the sparsely vesicular plagioclase-phyric basalt with rare olivine phenocrysts (Unit 1) and the same phenocryst assemblage pillow lavas [37,38] (Unit 2). Approximately 680 m of hemipelagic sediments were present directly over the basement of the subducting oceanic plate (Figure 3).

The southward end of Shikoku Basin is connected with Parece Vela Basin without any physical barrier. The spreading model of Parece Vela Basin is similar to that of the adjacent Shikoku Basin formed by seafloor back-arc basin spreading behind the Mariana volcanic arc that occurred between 30 and 18 Ma [39]. The Parece Vela Rift may represent the extinct spreading center within the center of Parece Vela Basin [40,41] (Figure 2) that separates the west Mariana Ridge (WMR) and the KPR [42–45] (Figure 2). As one of a number of marginal basins that lie along the western edge of the Pacific Ocean, Japan Sea is generally understood to have formed by back-arc basin rifting [46,47]; it comprises two sub-basins,
namely the Yamato Basin and the Japan Basin, which are separated by the Yamato Rise (Figure 2).

Figure 2. Simplified geotectonic map (cross-section) of the Shikoku Basin in the Philippine plate with the locations of the oceanic drilling cores within the Shikoku Basin and the Nankai Trough on the subducting Philippine Sea plate. Seismic in-line section showing locations of Sites C0011, Site C0012, Site 1173, Site 1174, and Site 808 (modified after Reference [31]).
Figure 3. Stratigraphic columns for IODP Sites C0012 and 1173 drilled in the Shikoku Basin (modified after Reference [31]).

3. Analytical Methods

Major element compositions of feldspars and pyroxenes in the Site C0012 and Site 1173 volcanic rocks were measured by a JEOL JXA8100 electron probe microanalyzer (EPMA) at Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS), Beijing, China, with operating conditions of 15 kV accelerating voltage, 10 nA beam current, 5 μm beam spot, and 10~30 s counting time. We conducted multiple analyses of different grains within a sample. The analytical precisions are generally better than 1.5%. Details on the analytical techniques were given in Chen et al. [27]. The data are presented in Supplementary File S1 and Supplementary File S2.

Bulk major elements were performed by a Phillips PW1400 sequential X-ray fluorescence spectrometer (XRF) at the Analytical Laboratory of the Beijing Research Institute of Uranium Geology (BRIUG), China. Samples were cleaned and carved up for whole rock analysis, crushed in a tungsten carbide swing mill, and then powdered in an agate mortar to ~200 mesh. The powders were fused with Li₂B₄O₇ at 1050 °C in a CLAISSEFLUXERVI fusion furnace. Loss on ignition (LOI) was calculated after volatilize at 1000 °C for 10 h. Whole-rock major element data are presented in Table 1.

Bulk trace element analyses were conducted at BRIUG (China) by use of a Finnigan-MAT element I inductively coupled plasma mass spectrometer (ICP-MS). The powders were dissolved in 1 mL HF + 0.5 mL HNO₃ and then ultrasonically stirred for 15 min in Savillex Teflon screw-cap capsules. The solutions were dried at 150 °C, dissolved with 1.5 mL HF + 0.5 mL HNO₃, heated again to 170 °C for 10 days, dried, and re-dissolved in 2 mL HNO₃. The solutions were heated at 150 °C for 5 h to dissolve completely, then evaporated, dried, and re-dissolved in 2 mL HNO₃ + 2 mL 1% HNO₃. The solutions were finally diluted to 50 mL by use of 1% HNO₃. The analytical precisions for trace elements were better than 5% (Table 2).
Table 1. Major-element (wt.%) concentrations of Site C0012 and Site 1173 volcanic rocks from the Shikoku Basin.

|                  | C0012-3X-08 | C0012-1R-01X | C0012-1R-01 | C0012-2R-01X | C0012-2R-01 | C0012-14R-01 | C0012-14R-03 |
|------------------|-------------|--------------|-------------|--------------|-------------|--------------|--------------|
| SiO₂             | 49.29       | 49.09        | 48.63       | 48.75        | 49.28       | 47.98        | 48.06        |
| TiO₂             | 1.21        | 1.28         | 1.16        | 1.21         | 1.21        | 1.21         | 1.49         |
| Al₂O₃            | 14.98       | 14.69        | 14.51       | 14.21        | 14.36       | 14.14        | 12.39        |
| FeO              | 9.83        | 10.22        | 10.89       | 10.26        | 10.24       | 12.79        | 14.39        |
| MnO              | 0.26        | 0.46         | 0.51        | 0.29         | 0.27        | 0.25         | 0.25         |
| MgO              | 7.15        | 7.00         | 6.80        | 7.59         | 7.14        | 6.16         | 6.32         |
| CaO              | 9.48        | 9.17         | 10.08       | 9.22         | 9.28        | 8.70         | 8.17         |
| Na₂O             | 3.34        | 3.27         | 2.68        | 3.19         | 3.32        | 3.68         | 3.02         |
| K₂O              | 0.53        | 0.71         | 1.03        | 0.66         | 0.91        | 1.02         | 1.99         |
| P₂O₅             | 0.15        | 0.15         | 0.12        | 0.15         | 0.14        | 0.16         | 0.16         |
| LOI              | 3.78        | 3.94         | 3.54        | 4.42         | 3.84        | 3.58         | 3.64         |
| **Total**        | 99.99       | 99.98        | 99.95       | 99.95        | 99.95       | 99.95        | 99.95        |

|                  | C0012-13R-01 | C0012-12R-01X | C0012-12R-01 | C0012-12R-02 | C0012-10R-02X | C0012-10R-02 | C0012-9R-01 |
|------------------|-------------|--------------|-------------|--------------|--------------|--------------|-------------|
| SiO₂             | 49.15       | 49.10        | 50.35       | 50.82        | 48.32        | 44.61        | 47.09       |
| TiO₂             | 1.41        | 1.51         | 1.50        | 1.51         | 1.63         | 1.27         | 1.29        |
| Al₂O₃            | 13.07       | 15.26        | 13.96       | 13.54        | 14.05        | 15.99        | 14.16       |
| FeO              | 10.99       | 10.39        | 11.22       | 11.66        | 12.52        | 12.81        | 11.48       |
| MnO              | 0.23        | 0.24         | 0.25        | 0.23         | 0.29         | 0.22         | 0.21        |
| MgO              | 6.94        | 5.61         | 6.22        | 6.17         | 6.45         | 4.98         | 6.38        |
| CaO              | 7.59        | 9.23         | 8.92        | 8.02         | 8.36         | 9.52         | 7.69        |
| Na₂O             | 2.33        | 3.18         | 2.92        | 2.81         | 2.71         | 3.53         | 3.55        |
| K₂O              | 3.56        | 1.97         | 2.19        | 2.88         | 2.32         | 1.12         | 2.05        |
| P₂O₅             | 0.17        | 0.13         | 0.14        | 0.15         | 0.17         | 0.12         | 0.14        |
| LOI              | 4.54        | 3.36         | 2.28        | 2.15         | 3.12         | 6.19         | 5.94        |
| **Total**        | 99.97       | 99.99        | 99.94       | 99.94        | 99.94        | 99.95        | 99.99       |

|                  | C0012-8R-01 | C0012-5R-01 | 1173-3R-01X | 1173-2R-01X |
|------------------|-------------|-------------|-------------|-------------|
| SiO₂             | 50.14       | 50.39       | 49.03       | 48.65       |
| TiO₂             | 1.49        | 1.56        | 1.53        | 1.59        |
| Al₂O₃            | 12.63       | 13.45       | 17.36       | 16.67       |
| FeO              | 10.93       | 11.14       | 8.68        | 9.25        |
| MnO              | 0.18        | 0.20        | 0.21        | 0.18        |
| MgO              | 6.74        | 6.78        | 5.45        | 6.17        |
| CaO              | 7.77        | 6.53        | 12.16       | 11.62       |
| Na₂O             | 5.57        | 3.48        | 3.02        | 3.10        |
| K₂O              | 0.42        | 2.72        | 0.09        | 0.14        |
| P₂O₅             | 0.15        | 0.19        | 0.17        | 0.18        |
| LOI              | 3.92        | 3.53        | 2.30        | 2.41        |
| **Total**        | 99.94       | 99.98       | 100.00      | 99.95       |
Table 2. Trace-element (ppm) concentrations of Site C0012 and Site 1173 volcanic rocks from the Shikoku Basin.

|                | C0012-3X-08 | C0012-1R-01X | C0012-1R-01 | C0012-2R-01X | C0012-2R-01 | C0012-14R-01 | C0012-14R-03 |
|----------------|-------------|--------------|-------------|-------------|-------------|-------------|-------------|
| Porphyritic Basalt | 0.09        | 0.09         | 0.08        | 0.11        | 0.06        | 0.09        | 0.22        |
| Aphyric Basalt   | 0.09        | 0.09         | 0.08        | 0.11        | 0.06        | 0.09        | 0.22        |
| Sb              | 0.09        | 0.09         | 0.08        | 0.11        | 0.06        | 0.09        | 0.22        |
| Ni              | 54.8        | 58.0         | 49.3        | 52.4        | 52.7        | 39.6        | 43.5        |
| Cr              | 112         | 99           | 138         | 124         | 150         | 65.7        | 72.9        |
| V               | 324         | 331          | 356         | 309         | 318         | 370         | 398         |
| Rb              | 6.03        | 12.7         | 26.9        | 8.73        | 14.9        | 11.8        | 27.0        |
| Sr              | 139         | 134          | 140         | 128         | 126         | 290         | 300         |
| Ba              | 77.4        | 43.8         | 45.6        | 164         | 302         | 42.7        | 40.0        |
| Zr              | 76.4        | 79.9         | 76.7        | 76.3        | 74.5        | 99.2        | 101         |
| Sb              | 0.05        | 0.08         | 0.05        | 0.07        | 0.05        | 0.20        | 0.12        |
| Ni              | 47.4        | 62.7         | 111         | 41.6        | 45.6        | 42.3        | 36.9        |
| Cr              | 62.4        | 52.9         | 214         | 70.5        | 41.9        | 57.1        | 68.3        |
| V               | 346         | 394          | 350         | 342         | 362         | 308         | 306         |
| Rb              | 29.0        | 21.1         | 31.8        | 37.4        | 27.4        | 24.9        | 25.5        |
| Sr              | 437         | 501          | 308         | 346         | 434         | 469         | 384         |
| Ba              | 1009        | 33.0         | 50.7        | 414         | 142         | 18.2        | 172         |
| Zr              | 91.0        | 89.7         | 92.6        | 97.6        | 110         | 82.2        | 72.6        |
| Nb              | 1.74        | 1.66         | 1.73        | 1.85        | 2.01        | 1.53        | 1.55        |
| Y               | 33.7        | 30.0         | 29.9        | 31.8        | 36.8        | 29.1        | 33.8        |
| La              | 3.50        | 3.39         | 3.50        | 3.84        | 3.68        | 3.48        | 3.70        |
| Ce              | 9.84        | 9.44         | 10.6        | 11.1        | 11.5        | 9.17        | 9.82        |
| Nd              | 10.2        | 10.0         | 10.8        | 11.2        | 11.6        | 9.31        | 9.95        |
| Pr              | 1.83        | 1.85         | 1.87        | 2.03        | 2.05        | 1.61        | 1.62        |
| Sm              | 3.47        | 3.36         | 3.48        | 3.67        | 3.80        | 2.82        | 3.37        |
| Eu              | 1.29        | 1.19         | 1.31        | 1.28        | 1.44        | 1.18        | 1.12        |
| Gd              | 2.95        | 3.91         | 3.86        | 4.18        | 4.65        | 3.44        | 3.81        |
| Tb              | 0.93        | 0.88         | 0.89        | 0.91        | 3.00        | 0.78        | 0.85        |
| Dy              | 5.39        | 5.10         | 5.28        | 5.60        | 6.16        | 4.70        | 5.18        |
| Ho              | 1.24        | 1.10         | 1.14        | 1.18        | 1.30        | 1.05        | 1.19        |
| Er              | 3.41        | 3.06         | 3.08        | 3.35        | 3.61        | 3.12        | 3.35        |
Sr and Nd isotopic compositions were measured by a Finnigan-MAT 262 mass spectrometer at IGCCAS, Beijing, China. Sample powders were dissolved with a mixed acid (HF:HClO₄ = 3:1) at 120 °C for 7 days. By virtue of AG50W×8 (H⁺) cationic ion-exchange resin columns, Rb, Sr, Sm, and Nd were separated from other rare earth element fractions in solution. Collected Sr and Nd fractions were evaporated and dissolved with 2% HNO₃ for preparing analyses. In order to conduct mass fractionation corrections, we used international standard NBS987 of \(^{87}\text{Sr}/^{86}\text{Sr} = 0.710265 \pm 13\) and international JNd1-1 standard of \(^{143}\text{Nd}/^{144}\text{Nd} = 0.512115 \pm 8\). The BCR-2 standard testing value is \(^{87}\text{Sr}/^{86}\text{Sr} = 0.705037 \pm 13\) and \(^{143}\text{Nd}/^{144}\text{Nd} = 0.512630 \pm 14\). The detailed analytical processes are referred from Chen et al. [27]. Analytical results and errors (2σ) are presented in Table 3.

About 100–120 mg rock powder was completely decomposed with a mixture of HF-HNO₃ in Savillex Teflon screw-cap beaker at 160 °C for seven days. Pb fraction with high purity was separated from rock matrix by use of HBr-HCl elution procedure on Teflon® columns containing ~0.15 mL anion resin (AG1-X8, 100–200 mesh). Whole chemical procedural blank of Pb was approximately 200 pg. Pb fraction with high purity was re-dissolved by use of a mixture solution of silica gel and H₃PO₄ and loaded onto a single-Re
filament. Pb isotopic ratio determinations were performed on a Thermofisher Triton Plus multi-collector thermal ionization mass spectrometer at the IGGCAS, Beijing, China. The detailed analytical methods were given in Li et al. [48]. Repeat analysis of BCR-2 yielded $^{206}\text{Pb}/^{204}\text{Pb} = 18.743 \pm 0.010$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.617 \pm 0.010$, and $^{208}\text{Pb}/^{204}\text{Pb} = 38.716 \pm 0.011$. The average $2\sigma$ uncertainties for measured ratios of $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ are, respectively, 1.0%, 1.0%, and 1.1%. The Pb isotope data are presented in Table 3.

### Table 3. Whole-rock Sr, Nd, Pb isotope data of Site C0012 and Site 1173 volcanic rocks from the Shikoku Basin.

|                | C0012-1R | C0012-2R | C0012-3X | C0012-5R | C0012-8R | C0012-9R | C0012-10R | C0012-12R |
|----------------|----------|----------|----------|----------|----------|----------|-----------|-----------|
| **Aphyric Basalt** |          |          |          |          |          |          |           |           |
| $^{87}\text{Sr}/^{86}\text{Sr}$ | 0.703235 | 0.703369 | 0.703221 | 0.703615 | 0.704432 | 0.703679 | 0.703735 | 0.703342 |
| $2\sigma$ (10$^{-6}$) | 15       | 12       | 12       | 13       | 12       | 12       | 13        | 13        |
| $^{143}\text{Nd}/^{144}\text{Nd}$ | 0.513113 | 0.513102 | 0.513102 | 0.513111 | 0.513112 | 0.513109 | 0.513113 | 0.513127 |
| $2\sigma$ (10$^{-6}$) | 9        | 9        | 10       | 11       | 9        | 11       | 9         | 7         |
| $^{206}\text{Pb}/^{204}\text{Pb}$ | 18.081   | 17.963   | 17.962   | 17.931   | 18.099   | 18.110   | 17.949    | 17.941    |
| $2\sigma$ (%) | 0.013    | 0.008    | 0.012    | 0.010    | 0.011    | 0.012    | 0.009     | 0.008     |
| $^{207}\text{Pb}/^{204}\text{Pb}$ | 15.496   | 15.464   | 15.471   | 15.469   | 15.530   | 15.511   | 15.458    | 15.455    |
| $2\sigma$ (%) | 0.013    | 0.008    | 0.012    | 0.010    | 0.012    | 0.012    | 0.010     | 0.008     |
| $^{208}\text{Pb}/^{204}\text{Pb}$ | 37.937   | 37.780   | 37.823   | 37.783   | 38.031   | 37.976   | 37.748    | 37.704    |
| $2\sigma$ (%) | 0.013    | 0.008    | 0.013    | 0.009    | 0.016    | 0.013    | 0.009     | 0.008     |

|                | C0012-13R | C0012-14R | 1173-2R | 1173-3R | BCR-2 | NBS987 | JNd1-1 |
|----------------|------------|------------|---------|---------|-------|--------|--------|
| **Porphyritic Basalt** |          |          |         |         |       |        |        |
| $^{87}\text{Sr}/^{86}\text{Sr}$ | 0.703646 | 0.703463 | 0.702840 | 0.702860 | 0.705037 | 0.710265 |
| $2\sigma$ (10$^{-6}$) | 14       | 14       | 14       | 14       | 13     | 13     |
| $^{143}\text{Nd}/^{144}\text{Nd}$ | 0.513124 | 0.513131 | 0.513103 | 0.513095 | 0.512630 | 0.512115 |
| $2\sigma$ (10$^{-6}$) | 9        | 12       | 11       | 11       | 14     | 8      |
| $^{206}\text{Pb}/^{204}\text{Pb}$ | 17.992   | 17.829   | 17.884   | 17.823   | 17.823 | 18.743 |
| $2\sigma$ (%) | 0.016    | 0.008    | 0.013    | 0.010    | 0.010  | 0.010  |
| $^{207}\text{Pb}/^{204}\text{Pb}$ | 15.496   | 15.430   | 15.438   | 15.427   | 15.427 | 15.617 |
| $2\sigma$ (%) | 0.017    | 0.006    | 0.012    | 0.011    | 0.011  | 0.011  |
| $^{208}\text{Pb}/^{204}\text{Pb}$ | 37.937   | 37.588   | 37.682   | 37.580   | 38.716 | 38.716 |
| $2\sigma$ (%) | 0.016    | 0.007    | 0.013    | 0.010    | 0.011  | 0.011  |

### 4. Petrographic and Mineralogical Characteristics

Fresh rocks with porphyritic and aphyric textures have been evenly selected from a 36-m-thick basement in Site C0012 and a 19.5-m-thick basement in Site 1173. Samples C0012-1R-1 and C0012-14R-1 are aphyric to slight phytic basalts with phenocrysts of clinopyroxene (20 vol.%; 0.4–1.0 mm) and needle-like plagioclase (20 vol.%; 0.1–0.4 mm), as well as considerable dark minerals or cryptocrystalline phases in the matrix (Figure 4A,B). Samples C0012-8R-1 and C0012-10R-2 are porphyritic basalts (Figure 4C,D) with phenocrysts of interlocking anhedral clinopyroxene (50 vol.%; 0.3–0.6 mm) and euhedral tabular plagioclase (20 vol.%; 0.4–0.6 mm). All samples from Site 1173 drill cores (1173-1R-2, 1173-3R-1) are relatively fresh tholeiitic basalts and have porphyritic texture (Figure 4E,F) with phenocrysts of euhedral high anorthite plagioclases (60 vol.%) with different size (0.05–1.2 mm). Detailed sampling depth, phenocryst, and matrix characteristics are presented in Table 4.
Table 4. Petrological description of Site C0012 and Site 1173 volcanic rocks from the Shikoku Basin.

| Sample        | Depth of Locality | Rock Type          | Phenocrysts | Matrix Characters | K-Ar Age (Ma) | Reference |
|---------------|-------------------|--------------------|-------------|-------------------|----------------|-----------|
| C0012-1R-01   | 542mbsf in SiteC0012 | Aphyric basalt    | 20% Cpx + 30% Pl | 50% cryptocrystalline matrix with dark minerals | >18.9 Ma [32,36]  |
| C0012-1R-01X  | 544mbsf in SiteC0012 | Aphyric basalt    | 20% Cpx + 30% Pl | 50% cryptocrystalline matrix with dark minerals | >18.9 Ma [32,36]  |
| C0012-2R-01   | 546mbsf in SiteC0012 | Aphyric basalt    | 20% Cpx + 15% Pl | 65% cryptocrystalline matrix | >18.9 Ma [32,36]  |
| C0012-2R-01X  | 546mbsf in SiteC0012 | Porphyritic basalt| 70% Cpx + 15% Pl | 60% cryptocrystalline matrix | >18.9 Ma [32,36]  |
| C0012-3X-08   | 550mbsf in SiteC0012 | Porphyritic basalt| 40Cpx + 15% Pl  | 45% cryptocrystalline matrix | >18.9 Ma [32,36]  |
| C0012-5R-01   | 552mbsf in SiteC0012 | Aphyric basalt    | 10% Cpx + 10% Pl | >18.9 Ma [32,36]  |
| C0012-8R-01   | 554mbsf in SiteC0012 | Porphyritic basalt| 50% Cpx + 20% Pl | 30% cryptocrystalline matrix with minor plagioclase | >18.9 Ma [32,36]  |
| C0012-9R-01   | 556mbsf in SiteC0012 | Porphyritic basalt| 30% Cpx + 10%Kfs + 10% Pl | 50% cryptocrystalline matrix | >18.9 Ma [32,36]  |
| C0012-10R-02  | 559mbsf in SiteC0012 | Porphyritic basalt| 40% Cpx + 10% Kfs + 10% Pl | 40% cryptocrystalline matrix | >18.9 Ma [32,36]  |
| C0012-10R-02X | 559mbsf in SiteC0012 | Porphyritic basalt| 40% Cpx + 10% Kfs + 10% Pl | 40% cryptocrystalline matrix | >18.9 Ma [32,36]  |
| C0012-12R-01  | 563mbsf in SiteC0012 | Porphyritic basalt| 30% Cpx + 20% Pl  | 50% cryptocrystalline matrix with minor plagioclase | >18.9 Ma [32,36]  |
| C0012-12R-01X | 563mbsf in SiteC0012 | Porphyritic basalt| 35% Cpx + 15% Pl  | 50% cryptocrystalline matrix with minor plagioclase | >18.9 Ma [32,36]  |
| C0012-12R-02  | 566mbsf in SiteC0012 | Porphyritic basalt| 30% Cpx + 20% Pl  | 50% cryptocrystalline matrix with minor plagioclase | >18.9 Ma [32,36]  |
| C0012-13R-01  | 568mbsf in SiteC0012 | Porphyritic basalt| 20% Cpx + 15% Pl  | 65% cryptocrystalline matrix | >18.9 Ma [32,36]  |
| C0012-14R-01  | 570mbsf in SiteC0012 | Basalt             | 20% Cpx + 10% Kfs + 10% Pl | 60% cryptocrystalline matrix with dark minerals | >18.9 Ma [32,36]  |
| C0012-14R-03  | 573mbsf in SiteC0012 | Basalt             | 20% Cpx + 10% Kfs + 10% Pl | 60% cryptocrystalline matrix with dark minerals | >18.9 Ma [32,36]  |
| 1173-3R-01X   | 740mbsf in Site1173 | tholeiitic basalt  | 65% Pl + 5% Cpx | 30% cryptocrystalline matrix | 13–15 Ma [37,38]  |
| 1173-2R-01X   | 751mbsf in Site1173 | tholeiitic basalt  | 60% Pl + 5% Cpx | 35% cryptocrystalline matrix | 13–15 Ma [37,38]  |
| 1173-1R-02    | 755mbsf in Site1173 | tholeiitic basalt  | 60% Pl + 5% Cpx | 35% cryptocrystalline matrix | 13–15 Ma [37,38]  |

Pyroxenes and feldspars were the phenocrysts in Sites C0012 and 1173 volcanic rock samples from Shikoku Basin. Feldspar minerals in the Site 1173 volcanic rocks mainly belonged to the plagioclase series with compositions of Ab$_{16.2-49.9}$An$_{49.6-83.6}$Or$_{0-0.5}$ (bytownite and labradorite), while those in the Site C0012 volcanic rocks were composed of massive plagioclase series with compositions of Ab$_{35.6-59.5}$An$_{39.2-64.0}$Or$_{0-2.3}$ (andesine and labradorite) and small amounts of alkali feldspar series with a composition of
Ab_{1.2-6.5}An_{0.2-8.1}Or_{85.4-98.2} (sanidine; Figure 4G; Supplementary File S1) [49]. The few sanidine may not be phenocryst but would belong to the matrix of fine particles. Pyroxene minerals in the Site 1173 volcanic rocks mainly occurred as salite with a composition of WO_{48}En_{34}Fs_{18} (Supplementary File S2) [50], whereas those in the Site C0012 volcanic rocks mainly occurred as clinopyroxene with a composition of WO_{35-45}En_{36-52}Fs_{10-24} (augite) (Supplementary File S2) [50]. Overall, Site C0012 volcanic samples have a higher Na_2O content in plagioclase and a lower CaO content in clinopyxene in comparison with those of the Site 1173 volcanic rocks (Figure 4H). The 100*Mg/(Mg + Fe) number (Mg#) of clinopyroxene in the Shikoku Basin varies from 62 to 82, significantly lower than the clinopyroxene in Parece Vela Basin (Mg# = 72-93) but similar to the clinopyroxene in Japan Sea (Mg# = 56-81). The Mg# value shows a negative correlation with TiO_2 (Figure 5A), a unconspicuous correlation with Cr_2O_3 (Figure 5B), and a positive correlation with CaO in clinopyroxene (Figure 5C).

Figure 4. Microphotos of the Site C0012 and Site 1173 volcanic rocks from the Shikoku Basin. (A,B) Phenocrysts of clinopyroxene and plagioclase in C0012-1R-1 and C0012-14R-1 basalts; (C,D) porphyritic texture with phenocrysts of clinopyroxene, plagioclase, and K-feldspar in C0012-8R-1 and C0012-10R-2 basalts; (E,F) porphyritic texture with phenocrysts of plagioclases in tholeiitic basalts (1173-1R-2, 1173-3R-1); Ol, olivine; Cpx, clinopyroxene; Pl, plagioclase. Plots of the Feldspar classification (G) and Pyroxene classification (H) for the Site C0012 and 1173 volcanic rocks from Shikoku Basin. The data from Parece Vela Basin are cited from Reference [51]; the data from Japan Sea are cited from Reference [27]. Figure 4G is modified from Reference [49]; Figure 4H is modified from Reference [50].
Figure 5. Clinopyroxene compositional plots of Mg# versus TiO$_2$ wt.% (A); Mg# versus Cr$_2$O$_3$ wt.% (B); Mg# versus CaO wt.% (C) for the Site C0012 and 1173 volcanic rocks from Shikoku Basin, the Site 449 and 450 peridotites from Parece Vela Basin, and the Site 794 and Site 797 volcanic rocks from Japan Sea. Data sources as for Figure 4.

5. Major and Trace Element Bulk Rock Geochemistry

There are only a few geochemical studies available on the Cenozoic volcanic rocks of the Shikoku Basin [52–55]. We introduced new major and trace element data from Site C0012 and Site 1173 volcanic samples in the Shikoku Basin, as listed in Tables 1 and 2. All the data illustrated in Figures 6 and 7 were recalculated to 100 wt.% on a volatile-free basis. For the purpose of preventing the influence of seawater alteration on the error of lithology discrimination of volcanic rocks, we use a variety of major and trace elements (Figure 6) to make lithology discrimination. Sites C0012 and 1173 volcanic samples were characterized by relatively low Nb/Y, Zr/TiO$_2$, La/Yb ratios and relatively high FeOT/MgO ratio, suggesting these samples mainly belong to tholeiitic basalts (Figure 6). In comparison, Site C0012 volcanic rocks have relatively lower Nb/Y (0.05–0.06), Zr/TiO$_2$×0.0001 (0.006–0.007),
and La/Yb (0.93–1.42) ratios and relatively higher total alkali contents (Na₂O + K₂O = 3.7–6.2 wt%), K₂O/Na₂O ratios (0.08–1.53), and K₂O contents (0.4–3.6 wt%), relative to those of Site 1173 volcanic samples (Na₂O + K₂O = 3.1–3.2 wt%; K₂O/Na₂O = 0.03–0.04; K₂O = 0.09–0.14 wt%; Nb/Y = 0.12; Zr/TiO₂ × 0.0001 = 0.008–0.009; La/Yb = 1.54–1.72) (Figure 6).

Sites C0012 and 1173 volcanic rocks possessed low-to-medium values of Mg# (molar 100 (Mg/(Mg + Fe²⁺)), ranging from 28 to 43, and MgO (5.0–7.6 wt.%), over a range of SiO₂ content from 44.6 to 50.8 wt.% (Table 1). A positive correlation between MgO and Al₂O₃, negative correlations between MgO and Na₂O, K₂O, inconspicuous correlations between SiO₂ and MgO versus trace element plots, most volcanic rocks showed distinct positive trends for Sc, Cr, and Ni, as well as inconspicuous trends for La, Th, Ta, and Zr, and nearly constant Zr, Th, and La concentrations (Figure 8).

Cr and Ni concentrations in the samples mostly ranged from 42 to 226 ppm and from 37 to 111 ppm, respectively, and MgO content ranged from 5.0 to 7.6 wt%, suggesting relatively unevolved magmas (Table 2). In comparison, samples from Sites C0012 and 1173 had relatively low TiO₂ (1.2–1.6 wt%) and CaO (6.5–12.2 wt%) contents, as well as slightly high K₂O contents (0.4–3.6 wt%) (Figure 7), as compared to the volcanic rocks from Japan Sea (Site 797; Site 794). Sites 449 and 450 samples demonstrated the highest FeO⁺, Na₂O, TiO₂, and P₂O₅ values relative to other samples.

Figure 6. Classification diagrams for Cenozoic volcanic rocks from the Shikoku Basin: (A) Nb/Y versus Zr/TiO₂ × 0.0001; (B) Zr/TiO₂ × 0.0001 versus SiO₂ (wt.%); (C) SiO₂ (wt.%) versus FeO⁺/MgO; (D) Ti (ppm) versus La/Yb. Filled symbols represent new original data. Cross symbols represent referenced data. The Site 797, 794 data in the Japan Sea are from Reference [27], the Site 449, 450 data in the Parece Vela Basin are from Reference [28], and the seamount chains in Shikoku Basin are from Reference [2].
Figure 7. MgO versus major elements of Cenozoic volcanic rocks from the Shikoku Basin. The Site 442, 443, 444 data in the Shikoku Basin are from Reference [52–55]. Other data sources as for Figure 6.
Chondrite-normalized rare earth elements (REE) plots for Site C0012 samples (>18.9 Ma) from Shikoku Basin were characterized by relative depletion in light REEs (LREEs; \((\text{La}/\text{Yb})_N = 0.67–1.02\)) and relatively low total REE contents (\(\sum\)REE = 41–58 ppm), and showed no Eu anomalies \((\delta\text{Eu} = 2\text{Eu}/(\text{Sm} + \text{Gd}) = 0.95–1.16\); Figure 9A). Their REE spectra were similar to those of normal mid-ocean ridge basalts (N-MORB) [56], but their REE contents were slightly higher than those of N-MORB (Figure 9A). In comparison, the Site 1173 volcanic rocks (15–13 Ma) had relatively flat REE differentiation \((\text{La}/\text{Yb})_N = 1.11–1.23\) and showed slightly higher LREE contents relative to the older Site C0012 samples (>18.9 Ma; Figure 9A). The younger Japan Sea samples (<15 Ma) displayed depletion of LREE and total REE contents, as in the case of the N-MORB, whereas the older samples (>19 Ma) showed higher REE contents and resembled those of enriched-type (E-MORB) (Figure 9B). The seamount chains in the Shikoku Basin exhibited relatively flat REE differentiation, resembling the MORB-type REE distribution pattern (Figure 9C).
The seamount chains in the Shikoku Basin exhibited relatively flat REE differentiation, resembling the MORB-type REE distribution pattern (Figure 9C). Accordingly, the primitive mantle-normalized multi-element spectra for Site 1173 samples (13–15 Ma) from Shikoku Basin exhibited normal large-ion lithophile element (LILE) contents, similar to a typical N-MORB pattern but higher than those of N-MORB (Figure 9A). Site C0012 volcanic rocks displayed significantly positive Rb, Ba, K, Pb, and Sr anomalies and negative Nb, Ta, Th, U, and Ti anomalies, which is consistent with the geochemical features of the IBM arc lava [57]. However, we noticed a significant difference between the Site C0012 volcanic samples and the arc lava, such as Zr-Hf negative anomalies and relatively high Th content [57]. Additionally, although the REE patterns of Japan Sea samples and seamount chains in the Shikoku Basin resembled those of MORB, their trace element characteristics were closely similar to those of arc lava, such as Rb and Ba positive anomalies, as well as Nb, Ta, and Ti negative anomalies (Figure 9B,C). The older Japan Sea samples (>19 Ma) had more enriched incompatible element compositions relative to those of the younger rocks (<15 Ma) (Figure 9B). Although only a few incompatible elements for Sites 449 and 450 volcanic rocks were collected, the multi-element spectra of samples from Parece Vela Basin resembled the patterns for E-MORB (Figure 9D).

**Figure 9.** Chondrite normalized rare earth elements (REE) patterns and primitive mantle normalized multi-element patterns for the Site C0012 and 1173 volcanic rocks from the Shikoku Basin (A), the Site 797 and 794 volcanic rocks from the Japan Sea (B), the seamount chains from the Shikoku Basin (C), and the Site 449 and 450 volcanic rocks from the Parece Vela Basin (D). The data of general Izu-Bonin-Mariana (IBM) arc lava are from Reference [57]. Data sources as for Figure 6.

Accordingly, the primitive mantle-normalized multi-element spectra for Site 1173 samples (13–15 Ma) from Shikoku Basin exhibited normal large-ion lithophile element (LILE) contents, similar to a typical N-MORB pattern but higher than those of N-MORB (Figure 9A). Site C0012 volcanic rocks displayed significantly positive Rb, Ba, K, Pb, and Sr anomalies and negative Nb, Ta, Th, U, and Ti anomalies, which is consistent with the geochemical features of the IBM arc lava [57]. However, we noticed a significant difference between the Site C0012 volcanic samples and the arc lava, such as Zr-Hf negative anomalies and relatively high Th content [57]. Additionally, although the REE patterns of Japan Sea samples and seamount chains in the Shikoku Basin resembled those of MORB, their trace element characteristics were closely similar to those of arc lava, such as Rb and Ba positive anomalies, as well as Nb, Ta, and Ti negative anomalies (Figure 9B,C). The older Japan Sea samples (>19 Ma) had more enriched incompatible element compositions relative to those of the younger rocks (<15 Ma) (Figure 9B). Although only a few incompatible elements for Sites 449 and 450 volcanic rocks were collected, the multi-element spectra of samples from Parece Vela Basin resembled the patterns for E-MORB (Figure 9D).
6. Nd, Sr, and Pb Isotope Variations

Figures 10 and 11 present the Sr, Nd, and Pb isotopic ratios for Sites C0012 and 1173 volcanic rock samples from the Shikoku Basin. Apparently, Site 1173 volcanic rocks showed relatively high $^{143}\text{Nd}/^{144}\text{Nd}$ ratios ranging from 0.513095 to 0.513103, and low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios ranging from 0.702840 to 0.702860 (Table 3), plotting close to the depleted mantle (DMM) end members [58,59] (Figure 10). The older Site C0012 (> 18.9) displayed relatively higher Sr and Nd isotopic compositions ($^{87}\text{Sr}/^{86}\text{Sr} = 0.703221–0.704432; ^{143}\text{Nd}/^{144}\text{Nd} = 0.513102–0.513131$) compared to those of the younger Site 1173 samples (13–15 Ma), plotting close to the field of Izu and Mariana volcanic front (Figure 10). Comparatively speaking, Sites 449 and 450 volcanic rocks from Parece Vela Basin and the seamount chains from the Shikoku Basin showed low Sr and Nd isotopic compositions, plotting close to DMM end members (Figure 10). By contrast, the Japan Sea volcanic rocks had relatively low $^{143}\text{Nd}/^{144}\text{Nd}$ ratios and high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, plotting close to enriched mantle 1 (EM1) and enriched mantle 2 (EM2) end members and within the field of ocean island basalts (OIB). Furthermore, the older Japan Sea basalts had significantly higher Sr and Nd isotopic compositions relative to the younger samples (Figure 10).

In the Pb isotopic plots, Sites C0012 and 1173 volcanic rocks were plotted above the North Hemisphere Reference Line (NHRL; Figure 11). Here, Site 1173 samples were characterized by relatively low Pb isotopic ratios: $^{206}\text{Pb}/^{204}\text{Pb} = 17.823–17.884$; $^{207}\text{Pb}/^{204}\text{Pb} = 15.427–15.438$ and; $^{208}\text{Pb}/^{204}\text{Pb} = 37.580–37.682$ (Table 3), plotting close to the depleted mantle end member (Figure 11). The older Site C0012 samples (> 18.9 Ma) had higher Pb isotopic ratios ($^{206}\text{Pb}/^{204}\text{Pb} = 17.829–18.110$; $^{207}\text{Pb}/^{204}\text{Pb} = 15.430–15.530$; $^{208}\text{Pb}/^{204}\text{Pb} = 37.588–38.031$) relative to those of the younger Site 1173 samples (13–15 Ma), plotting between the depleted mantle, EM1, and EM2 end members [60]. Additionally, the Parece Vela Basin samples and the seamount chains in the Shikoku Basin showed low Pb isotopic compositions, plotting close to primitive mantle (PREMA) end members (Figure 11). The Japan Sea volcanic rocks had significantly high ratios of $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ (Figure 11; Table 3), with the involvement of EM1 and EM2 compositions. The older Japan Sea samples (> 19 Ma) had more enriched Pb isotopic compositions relative to those of the younger samples (<15 Ma) (Figure 11). The lead isotopes of the Site C0012 and the Japan Sea samples were roughly consistent with those of Izu rear-arc volcanic samples (Figure 11).

![Figure 10. Nd and Sr isotopic compositions of Cenozoic volcanic rocks of the Site C0012 and Site 1173 in the Shikoku Basin. Data sources as for Figure 6. The Site 449, 450 data in the Parece Vela Basin are from Reference [61]; the fields of Izu-Bonin arc lava and Mariana arc lava are cited from Reference [57]; the fields of PSP-MORB (Philippine Sea Plate-MORB), PSP-OIB (Philippines Sea Plate-OIB), Shikoku and Parece Vela back-arc basins, Izu rear-arc, Izu volcanic front (Izu VF) are cited from Reference [62]; the fields of EM1, EM2, depleted mantle (DMM) are cited from Reference [56].](image-url)
7. Discussion

7.1. Effect of Post-Magmatic Alteration

The relatively high loss-on-ignition (LOI) values (2.15–6.19 wt.%; Table 1) in the Shikoku Basin samples indicate they likely experienced a variable degree of alteration because LOI is an effective indicator for the degree of alteration. However, our studied samples have extremely low Sb contents (0.05–0.22 ppm) and Sr/Ba ratios (0.42–25.8) in spite of relatively high LOI contents, likely suggesting the inconspicuous post-magmatic alteration. MacKenzie et al. [64] have authenticated that post-magmatic alteration will result in the relatively high LOI and Sb contents, elevated strontium, depleted Ba contents, and relatively high Sr/Ba ratios. Additionally, to discuss the effect of hydrothermal alteration [65], isocon diagrams were plotted in Figure 12 [66], comparing the compositions of samples with minimal alteration (C\textsuperscript{O}) to the chemical compositions of the six progressing states of alteration (C\textsuperscript{A}). The isocons are all characterized by a slope very close to one [66,67].
The tight scattering of most elements around the defined reference lines [67] reveals relatively immobile elements participated in the hydrothermal alteration process. Elements plotting above these lines indicate enrichment, while elements plotting below it indicate depletion during the alteration [67]. In these samples with high LOI, the scattering of most elements is minor, but the slight depletion of Rb, Ba, Cr, Zr, and the relative enrichment of Sr are observed. With the increase of LOI contents, the degree of the enrichment of Sr and the depletion of Ba and Zr are more obvious (Figure 12).

Figure 12. Isocon diagrams of six volcanic rocks with increasing loss on ignition (LOI) contents (C^A) from Shikoku Basin showing gains and losses of single-element concentrations compared to samples with minimal alteration (C^O). C0012-12R sample with minimal alteration (2.15 wt.% LOI) versus (A) C0012-5R sample with 3.53 wt.% LOI, (B) C0012-14R sample with 3.58 wt.% LOI, (C) C0012-14R-03 sample with 3.64 wt.% LOI, (D) C0012-13R sample with 4.54 wt.% LOI, (E) C0012-9R sample with 5.94 wt.% LOI, and (F) C0012-10R sample with 6.19 wt.% LOI.

It is commonly believed that major elements (e.g., Si, Na, K, Ca) and LILEs (e.g., Rb, K, Ba, and Sr) are easily mobilized by post-magmatic fluids or under metamorphism [68]. However, REEs, most high-field-strength elements (HFSEs: Zr, Nb, Hf, and Ta), and Th, Ni, and Cr contents are generally not influenced by a wide range of metamorphic conditions [69]. Additionally, Allan and Gorton [70] have proposed the correlation between elemental composition and LOI could be used to identify whether these elements are immobile. In our samples, the FeO_T and MgO values display positive correlations, and the K_2O, Al_2O_3, and CaO values show negative correlations with the LOI, as well as some LILEs (e.g., Rb, Ba, and Sr) increase along with the increasing LOI content (Supplementary File S3), suggesting these major-elements and LILEs compositions are easily modified during alteration. However, REEs and most high-field-strength elements (HFSEs: Zr, Nb, Hf, and
Ta), and Th, Ni, and Cr values vary little and do not show correlations with the LOI, likely revealing these elements are relatively immobile during the low-temperature alteration (Supplementary File S3). Furthermore, the poor correlations between the incompatible element ratios (e.g., Ta/U, Nb/Th, Th/Yb, Nb/Yb, Sm/Th, U/Th, Cs/Th, Ba/La) and LOI indicate these ratios are not easily modified by the post-magmatic alteration (Supplementary File S3). Additionally, it is noteworthy that seawater alteration will inevitably cause changes in Sr and Pb isotopes of volcanic samples. Thus, the following discussion does not exclude the possibility of the influence of post-magmatic alteration. We still seriously consider the possibility of the existence of post-magmatic alteration, especially in the discussion of the origin of the enriched components.

Because Shikoku Basin was formed by the spreading of an oceanic plate [2,12], it is necessary to discuss whether Shikoku Basin volcanism may be affected by the assimilation of oceanic crust before discussing the nature of mantle source. However, multifarious geochemical features suggested that such assimilation could be minor. (1) The ratios of incompatible elements are not easily affected by the processes of magmatic evolution and used to reveal the nature of mantle source. The Th/Ce (0.02–0.03) and Th/La (0.04–0.07) ratios of our studied samples are totally different from those ratios of oceanic crust [71] (Th/Ce = 0.11–0.13; Th/La = 0.21–0.26) but similar to those of primitive mantle [56] (Th/Ce = 0.02–0.05; Th/La = 0.12). (2) Oceanic crustal contamination generally leads to the extremely high $^{87}\text{Sr}/^{86}\text{Sr}$ (0.709288–0.723619) and low $^{143}\text{Nd}/^{144}\text{Nd}$ ratios (0.511664–0.512157), as well as large variations of $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ isotope ratios [71], whereas limited range of $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ isotope ratios (17.823–18.110; 15.427–15.530; 37.580–38.031, respectively), relatively low Sr, and high Nd isotopic ratios of Shikoku Basin volcanic samples were observed in Figures 10 and 11. (3) The contamination of oceanic crust likely causes the positive anomalies of U-Th [71,72]; thus, relative U-Th negative anomalies in our samples (Figure 9) basically do not conform to the features of oceanic crustal contamination. Therefore, we believe that the assimilation of oceanic crust en route to surface is negligible.

7.2. Fractional Crystallization and Clinopyroxene Crystallization Temperature and Pressure

The Sites C0012 and 1173 samples are mafic in composition, have relatively high and wide variation of MgO, Cr, and Ni contents (Figures 7 and 8), and show inconspicuous correlations between MgO and SiO$_2$, CaO, TiO$_2$, P$_2$O$_5$, La, Th, Ta, and Zr (Figures 7 and 8), indicating relatively unevolved magmas and an insignificant process of fractional crystallization. However, the minor degree of fractionation of olivine + clinopyroxene ± plagioclase assemblage was evidenced by the presence of these phenocrysts (Table 4), positive correlations between MgO and Al$_2$O$_3$, Sc, Cr, and Ni (Figures 7 and 8), and negative correlations between MgO and Na$_2$O, K$_2$O (Figure 7).

Irving and Frey [73] first proposed the equilibrium constant $K_{dpx}$ to identify the chemical equilibrium between clinopyroxene and melts. The formula is given by $K_{dpx} = (\text{FeO/MgO})_{pax}/(\text{FeO/MgO})_{basalt}$. When $K_{dpx}$ values are between 0.2 and 0.4, the clinopyroxene minerals are considered to be in the chemical equilibrium. Herein, the $K_{dpx}$ values of the Shikoku Basin and Parece Vela Basin volcanic rocks mostly ranged from 0.24 to 0.43, indicating that the clinopyroxene minerals and magmatic melts were in chemical equilibrium; thus, the phenocryst assemblage may be used to calculate the equilibrium temperature and pressure.

Clinopyroxenes are the major phenocrysts in the Shikoku Basin and Parece Vela Basin volcanic rocks, as well as are excellent minerals for estimating the equilibrium temperature and pressure of magmatic crystallization [74–76]. Many clinopyroxene geothermobarometers have been proposed on the basis of their different formation conditions [74–78]. However, the clinopyroxene Al-thermometer suggested by Thompson [77] had relatively large errors because the aluminum content is usually influenced by the composition, formation conditions (e.g., temperature and pressure), and cooling rate. The pyroxene geothermobarometer of Nimis and Ulmer [78] was only suitable for pyroxene that crystal-
lizes at less than 15.4 kbar. The pyroxene geothermobarometers of Putirka et al. [74,75] and Putirka [76] are a good fit for our samples; their crystallization temperature and pressure yields are summarized in Supplementary File S2, and the detailed calculations are presented in Supplementary File S4. The average crystallization temperature and pressure of clinopyroxene phenocrysts in the Shikoku Basin volcanic rocks were: \( T = 1161 \, ^\circ\text{C}–1233 \, ^\circ\text{C}, P = 2.0–8.7 \, \text{kbar} \) [74]; \( T = 1162 \, ^\circ\text{C}–1219 \, ^\circ\text{C}, P = 4.2–9.2 \, \text{kbar} \) [75]; and \( T = 1082 \, ^\circ\text{C}–1192 \, ^\circ\text{C}, P = 3.3–9.1 \, \text{kbar} \), respectively [76]. The average crystallization temperature and pressure of Parece Vela Basin volcanic rocks were: \( T = 1238 \, ^\circ\text{C}–1307 \, ^\circ\text{C}, P = 8.0–15.4 \, \text{kbar} \) [74]; \( T = 1259 \, ^\circ\text{C}–1302 \, ^\circ\text{C}, P = 6.6–12.3 \, \text{kbar} \) [75]; and \( T = 1219 \, ^\circ\text{C}–1300 \, ^\circ\text{C}, P = 5.9–12.3 \, \text{kbar} \) [76]. The average crystallization temperature and pressure of clinopyroxene phenocrysts in the Japan Sea volcanic rocks ranged from 1133 \(^\circ\text{C}\) to 1252 \(^\circ\text{C}\), from 0.5 to 9.6 kbar [74]; from 1131 \(^\circ\text{C}\) to 1221 \(^\circ\text{C}\), from 0 to 11.1 kbar [75]; and from 1111 \(^\circ\text{C}\) to 1207 \(^\circ\text{C}\), from 1.8 to 9.8 kbar [76]. These results show that the crystallization temperature and pressure of clinopyroxene in the Shikoku Basin volcanic rocks were significantly lower than those of clinopyroxene in the Parece Vela Basin samples but similar to those of clinopyroxene in the Japan Sea basalts, indicating that the Parece Vela Basin region has the higher thermal anomalies relative to Shikoku Basin and Japan Sea. Additionally, the clinopyroxene crystallization temperature of the Site C0012 samples (1082 \(^\circ\text{C}\)–1192 \(^\circ\text{C}\)) is slightly lower than that of the Site 1173 samples (1204 \(^\circ\text{C}\)).

7.3. Constraints on the Partial Melting Processes

As we have discussed above, our studied samples are characterized by relatively high MgO, Cr, Ni contents and belong to primitive samples without the significant process of fractional crystallization. Thus, we could use the non-modal batch melting formula which are generally used for primitive samples to constraint the degree of partial melting and the depth of mantle source. On the basis of partition coefficients, batch partial melting equation \( C_L/C_o = 1/(F + D - FP) \), and presumed components of mantle source, we performed geochemistry-based melting modeling using the Sm-Yb systematics. The detailed calculation process is presented in Supplementary File S5. In the calculated plot of Sm versus Sm/Yb (Figure 13), the Sites C0012 and 1173 volcanic rocks were plotted along the melting lines of spinel lherzolite without garnet, which suggests their derivation at 5% to 10% degree of partial melting. The Site 1173 samples were from relatively deeper mantle source with slightly lower degree of partial melting relative to the Site C0012 volcanic rocks (Figure 13), which was also proved by the slightly higher degree of HREE differentiation (Gd/YbN = 1.05–1.08) compared to the Site C0012 volcanic rocks (Gd/YbN = 0.86–1.07) (Figure 9; Table 2), although only few Site 1173 data were presented. However, the case of the Japan Sea volcanic rocks was opposite; the younger Site 797 volcanic rocks samples (<15 Ma) were derived from relatively shallower mantle source, which underwent higher degree of partial melting with respect to the older Japan Sea samples (>19 Ma).
7.4. Nature of the Mantle Source

The REE and incompatible element patterns of the Sites C0012 and 1173 volcanic rocks from Shikoku Basin are similar to but slightly more enriched than those of N-MORB (Table 2; Figure 9): the REE spectra are depleted in the LREE (La/Yb<sub>N</sub> = 0.67–1.02) and have no differentiated HREE (Gd/Yb<sub>N</sub> = 0.86–1.08). These volcanic samples have lower ratios of (Nb/La)<sub>pm</sub> and (Nb/Th)<sub>pm</sub> ((Nb/La)<sub>pm</sub> = 0.40–0.53; (Nb/Th)<sub>pm</sub> = 1.00–1.30; Table 2), suggesting that they present the MORB-type geochemical characteristics [56]. In the plots of Th/Yb versus Nb/Yb and Th/Y versus Sm/Th (Figure 14A,B), the Sites C0012 and 1173 volcanic samples from Shikoku Basin are plotted within the mantle array and are characterized by relatively low Th/Yb (0.05–0.08) and Nb/Yb ratios (0.47–1.14), close to the N-MORB end member. Comparatively, the Japan Sea samples and seamount chains in the Shikoku Basin are distributed between the N-MORB and E-MORB end member. Furthermore, the older Japan Sea samples (>19 Ma) exhibit the E-MORB-type multi-element patterns and E-MORB trace element ratios with respect to the N-MORB patterns and ratios of the younger samples (<15 Ma) (Figures 9 and 14). Although only small amounts of Parece Vela Basin data have been reported, we could see from these data that the Sites 449 and 450 volcanic rocks from Parece Vela Basin display depletion in K<sub>2</sub>O and relatively depleted incompatible element, which have probably originated from a shallow MORB-type mantle source, as seen in the REE patterns (Figure 9), bearing similarities with that of the Site 1173 volcanic samples.

Figure 13. Plots of Sm/Yb versus Sm for Cenozoic volcanic rocks of the Site C0012 and Site 1173 in the Shikoku Basin. Data sources as for Figure 6. The data for the primitive mantle are from Reference [56]. The compositions of spinel lherzolite (Sp Lhz), 1, 5, 10, and 20% garnet lherzolite (Ga Lhz) are Ol<sub>0.59</sub> + Opx<sub>0.05</sub> + Cpx<sub>0.16</sub> + Sp<sub>0.20</sub>, Ol<sub>0.69</sub> + Opx<sub>0.20</sub> + Cpx<sub>0.10</sub> + Gt<sub>0.01</sub>, Ol<sub>0.65</sub> + Opx<sub>0.20</sub> + Cpx<sub>0.10</sub> + Gt<sub>0.05</sub>, Ol<sub>0.60</sub> + Opx<sub>0.20</sub> + Cpx<sub>0.10</sub> + Gt<sub>0.10</sub>, and Ol<sub>0.50</sub> + Opx<sub>0.20</sub> + Cpx<sub>0.10</sub> + Gt<sub>0.20</sub>, respectively. Numbers along melting curves represent the degree of partial melting.
$^{87}\text{Sr}/^{86}\text{Sr}$, $^{143}\text{Nd}/^{144}\text{Nd}$, and $^{206}\text{Pb}/^{204}\text{Pb}$ isotopic ratios of the Site 1173 samples in Shikoku Basin were relatively depleted and plotted close to the field of depleted mantle end member (Figures 10, 11 and 15). In contrast, the Site C0012 samples in Shikoku Basin had relatively higher $^{87}\text{Sr}/^{86}\text{Sr}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios, similar to those of the seamount chains in the Shikoku Basin, Izu rear-arc, and Izu volcanic front (Figures 10 and 11). These isotopic compositions plot close to the EM1 end member, and have the involvement of EM2 composition (Figures 11 and 15). Furthermore, the older Site C0012 (>18.9 Ma) samples exhibited significantly enriched isotopic compositions relative to the younger Site 1173 (13–15 Ma) volcanic rocks. Sites 449 and 450 samples in Parece Vela Basin displayed relatively depleted Sr, Nd, and Pb isotopic components, plotting close to the depleted mantle end member, as in the compositions of the Site 1173 volcanic rocks from Shikoku Basin (Figures 10 and 11). In contrast, the Japan Sea volcanic rocks were characterized by relatively enriched Sr, Nd, and Pb isotopic compositions, plotting close to the EM1 and EM2 end-members with much more involvement of EM2 components relative to the Sites C0012 and 1173 samples (Figures 10, 11 and 15). Moreover, the older Japan Sea samples (> 19 Ma) showed much more enriched isotope with respect to the younger samples (<15 Ma).
Figure 15. The plots of 87Sr/86Sr vs. 206Pb/204Pb (A) and 143Nd/144Nd vs 206Pb/204Pb (B) for Cenozoic volcanic rocks of the Site C0012 and Site 1173 in the Shikoku Basin. Data sources as for Figure 10. The data for MORB, EM1, EM2, and HIMU are cited from Reference [58]. Mixing model between the mantle wedge (MW), fluids from subducted altered oceanic crust (AOC), and subducted slab sediments (SSS) (C, D). The red lines correspond to the mixing of AOC-derived fluids and SSS. The black lines correspond to the mixing trajectory between the mixed AOC-derived fluids, SSS, and MW. Figure 15C,D are modified from Reference [81].

A typical MORB- or OIB-source asthenospheric mantle generally exhibits positive Nb-Ta-Ti anomalies and negative Pb anomalies in the incompatible element diagram, which have high Ce/Pb (~25) and Nb/U (~47) ratios [59]. However, Site C0012 volcanic samples display strongly negative Nb-Ta-Ti anomalies and positive Pb anomalies (Figure 9), relatively low Ce/Pb (2.62–14.29) and Nb/U (4.83–36.44) ratios (Table 2), and relatively high Sr and Pb isotopic ratios (Figures 10 and 11), which are significantly distinct from the essential geochemical features of OIB and MORB [59], suggesting they were not derived from a normal MORB- or OIB-source asthenospheric mantle. Although the Nb-Ta depletion and Ba-Sr enrichment are likely attributed to fractional crystallization, the significant enrichment of Rb, Ba, K, Pb, and Sr, as well as the depletion of Th, U, Nb, and Ta in the Site C0012 samples, could not be easily explained by such a phenomenon. Furthermore, we refute the significant process of fractional crystallization in the above discussion. This indicates that the primary magma of Site C0012 may have been metasomatized by some enriched components. The comparison of enriched Sr-Nd-Pb isotopic compositions of Site C0012 samples with those of MORBs (Figures 10 and 11) further supports that they originate from an enriched mantle source rather than a normal MORB asthenospheric mantle.
7.5. Origin of the Enriched Components

The Site C0012 volcanic samples exhibit significant enrichment in LILE (Rb, Ba, and Sr) and Pb relative to the HFSE (Nb, Ta, Zr, and Hf), with strongly negative Nb-Ta-Ti anomalies and positive Pb anomalies in the spider diagram (Figure 9), consistent with the geochemical features of subduction related magmas [2,82–85]. The subduction-related origin of the back-arc basins was generally attributed to the mantle metasomatism of hydrous fluids/melts and sediments released from the dehydrated subduction slab [2,84,85].

Hydrous fluids released from the dehydrated subduction slab generally carry large amounts of fluid-mobile trace elements, such as LILE (e.g., K, Rb, Ba, Sr, Cs), U, and Pb. Subducted slab sediments commonly exhibit relatively high Th, Nb, and LREE contents [86]. Thus, those volcanic rocks metasomatized by subduction-related fluid are likely characterized by higher Ba/La, Ba/Nb, U/Th, and Cs/Th ratios, while those magmatic rocks interacted with the subducted slab sediments should have higher Th/Nb, Ce/Yb, and Th/Nd ratios (Figure 16). Shikoku Basin volcanic samples, characterized by large variation of the incompatible element ratios (e.g., Ba/Nb, U/Th, Ba/La, and Cs/Th ratios; Figure 16), were likely to have sources that were strongly affected by subduction-related fluid-induced enrichments as manifested by the higher fluid mobility of the numerator with respect to the less fluid-mobile denominator. Large variation of LILE/REE (e.g., Ba/La ratio; Figure 16) suggests the participation of fluids in magma generation, as the LILE were more mobile in hydrous fluids relative to HFSE and REE [87]. The large U/Th variation in the Shikoku Basin lavas further testified the contribution of hydrous fluid metasomatism (Figure 16). These geochemical features of subduction-related fluid metasomatism were best observed in arc volcanics, such as in the Izu-Bonin and other Mariana arc lavas [2,57]. However, volcanic lava from Japan Sea displayed relatively restricted ranges of Ba/Nb, Cs/Th, and Ba/La ratios with a large range of Th/Nb and Ce/Yb ratios (Figure 16), which likely indicates the obvious involvement of subducted slab-derived sedimentary component, but the limit influence of the fluid-induced metasomatism of the mantle source [88].

Figure 16. The plots of Cs/Th versus Th/Nb (A), U/Th versus Th/Nb (B), Ba/La versus Ce/Yb (C), U/Th versus Ce/Yb (D) for Site C0012, 1173 volcanic rocks from the Shikoku Basin. Data sources as for Figure 6.
Subducted slab sediments generally have relatively high Th, Nb, and LREE contents, Th is more incompatible than Nd, and La is more incompatible than Sm during partial melting [89]; thus, partial melts derived from subducted sediments commonly fractionate relatively high Th/Nd and La/Sm ratios, owing to the fluid-immobile nature of Th, Nd, La, and Sm. (Figure 17). Thus, the incompatible element ratios (e.g., La/Sm, Th/Nd) and Sr-Nd-Pb isotopic compositions exhibit a two-end-member mixing array between the subducted sediments and the normal asthenospheric mantle (Figure 17), which could be used to identify the origin of subduction-related magmas [85,86]. One end-member is MORB-type $^{143}$Nd/$^{144}$Nd, Th/Nd, and (La/Sm)$_N$; the other end-member is the composition of the Pacific subducted sediment. The Sites C0012 and 1173 samples are characterized by a relatively high $^{143}$Nd/$^{144}$Nd ratio and low (La/Sm)$_N$ and Th/Nd ratios, and plot close to the N-MORB asthenosphere mantle and far away from the subduction-related sediments (Figure 17), suggesting these volcanic rocks may not have been affected by the apparent subduction-related sediment. On the contrary, the Japan Sea samples and the seamount chains of the Shikoku Basin have likely suffered from the significant influence of subducted Pacific sediments (Figure 17).

On the basis of the combined constraints of trace element ratios and Sr-Nd-Pb isotopic compositions of the mantle wedge (MW), fluids from subducted altered oceanic crust (AOC), and subducted slab sediments (SSS) [90], we conclude the mixing model between MW, AOC, and SSS (Figures 15 and 18) to examine the influence of subducted fluids and sediments on the mantle source of Japan Sea, Shikoku Basin, and Parece Vela Basin [81]. The wide range of $^{87}$Sr/$^{86}$Sr, $^{206}$Pb/$^{204}$Pb, and $^{207}$Pb/$^{204}$Pb ratios were likely affected by the slab-derived fluids (Figure 15). The Sites C0012 and 1173 samples and the seamount chains from the Shikoku Basin, the Sites 449 and 450 samples from the Parece Vela Basin exhibit relatively low $^{87}$Sr/$^{86}$Sr and $^{206}$Pb/$^{204}$Pb ratios, and large variations of Ba/Nb and U/Th ratios (Figures 15 and 18), indicating these volcanic samples were likely metasomatized by hydrous fluids released from the subduction-related altered oceanic crust. However, the Japan Sea samples have relatively high $^{87}$Sr/$^{86}$Sr, $^{206}$Pb/$^{204}$Pb, and $^{207}$Pb/$^{204}$Pb ratios, and low $^{143}$Nd/$^{144}$Nd ratio (Figures 15 and 18), revealing the primary involvement of the subducted slab sediments into a MORB-type source mantle wedge.

Figure 17. Plots of $^{143}$Nd/$^{144}$Nd versus (La/Sm)$_N$ (A), $^{143}$Nd/$^{144}$Nd versus Th/Nd (B) of Site C0012, 1173 volcanic rocks from the Shikoku Basin. Data sources as for Figure 10. Figure 17A is modified from Reference [91]; Figure 17B is modified from Reference [92]; the data of Pacific MORB, Pacific Sediment are from Reference [58].
It should be noted that the possibility of the influence of seawater alteration for the Shikoku Basin volcanic samples are not completely excluded in the above discussion, which likely changes their LILE contents and Sr and Pb isotopic ratios (Supplementary File S3). Thus, we cannot determine whether the specific geochemical characteristics of Shikoku Basin volcanic samples (Figures 16–18) are fully caused by the involvement of subduction-related fluid/melts. However, the above discussion can at least confirm that the Japan Sea volcanic rocks have suffered more involvement of enriched subduction-related sediment components relative to samples from Shikoku Basin (Figures 16–18). In addition, it is notable that Japan Sea is a back-arc basin formed due to the expansion of the continental margin, while Shikoku Basin and Parece Vela Basin are formed by the extension of oceanic plates, which likely leads to the different enriched components of their volcanic rocks. However, Chen et al. [27] has studied that our cited Sites 797 and 794 volcanic rocks are not subject to the contamination of continent crust. Oceanic crustal contamination plays a negligible role in the petrogenesis of our studied Sites C0012, 1173 volcanic rocks. Thus, we still speculate that the significant differences between Japan Sea and Shikoku Basin are
mainly due to the different involvement of subduction-related enriched components, or, at least, this point cannot be ruled out.

7.6. Formation Process of Shikoku Basin, Parece Vela Basin, and Japan Sea

The above analyses have pointed out that, although Shikoku Basin, Parece Vela Basin, and Japan Sea all belong to the back-arc basin, their volcanic rocks have significantly different geochemical characteristics (Table 5). Specifically, the Shikoku Basin and Japan Sea volcanic samples were mainly metasomatized by enriched components of EM1 and EM2 [60], but the Parece Vela Basin volcanic rocks were not affected by the enriched subduction-related compositions, showing the MORB geochemical features. The Shikoku Basin volcanism was mainly affected by the metasomatism of the subduction-related fluids (the effects of seawater alteration cannot be eliminated), whereas the Japan Sea volcanic activities were influenced by more involvement of the subducted slab sediments compared to those Shikoku Basin volcanism.

The formation process of the back-arc basin was demonstrated herein to be actually caused by the strong extension of the island arc. The back-arc basin was a kind of an island arc before stretching, and has been subjected to the metasomatism of the hydrous fluids/melts released from the dehydrated subduction slab and/or the involvement of subducted slab sediments. However, the back-arc basin exhibits the characteristics of a typical MORB after stretching, large amounts of depleted tholeiites that came from the shallow mantle source, and experienced a higher degree of partial melting erupted violently. Therefore, we propose that the difference between the back-arc basin and the typical island arc lies on the fact that the former has been stretched in a later stage and has the involvement of the geochemical features of typical MORBs. Meanwhile, a back-arc basin can be distinguished from a typical MORB as the former has been affected by the apparent metasomatism of subduction-related fluids and/or sediments from the dehydrated subducted slab. Furthermore, the types and quantities of subduction-related materials in the mantle source are different from those in the typical island arcs, leading to the distinctive geochemical characteristics of the back-arc basin volcanic samples.

The studied volcanic rocks from Sites C0012 and 1173 of the Shikoku Basin and Sites 794 and 797 of the Japan Sea recorded different stages of the back-arc basin. When Shikoku Basin was initially formed, it was affected by a great deal of subduction-related hydrous fluid released from the dehydrated Pacific slab, and relatively older enriched Site C0012 samples with obvious enriched mantle EM1 and EM2 features were formed [60]. Later, in younger formation stage, Shikoku Basin experienced basin stretching and formed the relatively younger depleted Site 1173 volcanic rocks with typical MORB features. Japan Sea recorded the same process. When Japan Sea was initially formed, it was affected by massive subduction-related fluid and sediments, resulting in the formation of relatively enriched Site 794 volcanic rocks with the enriched mantle characteristics of EM1 and EM2. Subsequently, the tensile effect of Japan Sea in the later stage resulted in the formation of depleted Site 797 tholeiite, which has the typical MORB features. Thus, we proposed that Shikoku Basin and Japan Sea just record a mantle conversion process from an island arc to a typical MORB. The geochemical difference of volcanic rocks in each back-arc basin may be due to the fact that they were affected by different types and quantities of subduction-related materials from the dehydrated subduction slab, which were probably caused by the different subduction process. Combining the REE patterns (Figure 9), ratios of incompatible elements (Figure 14), and isotopic compositions (Figures 10 and 11) from our Sites C0012 and 1173 volcanic rocks from Shikoku Basin, we revealed that the depleted Site 1173 tholeiites (13–15 Ma) were mainly formed during back-arc spreading process, whereas the formation and eruption of enriched Sites C0012 samples (>18.9 Ma) occurred before the spreading stage of Shikoku Basin. Therefore, the early enriched basalts and the later depleted tholeiites likely attributed to the extensional thinning of Shikoku Basin, which promoted the shallower depleted MORB magma eruption.
Parece Vela Basin volcanic activities mainly existed as rifting, a completely different phenomenon compared to the expansion process of Shikoku Basin, although both basins were formed as back-arc basins behind the IBM arc during almost the same age [10] (Table 5). A rift valley system with a row of the deep diamond-shaped depressions developed at the spreading center of Parece Vela Basin, separating the arc into the present KPR and the WMR [60] (Figure 2). The back-arc oceanic crust beneath the rift was thinned under an E-W extensional stress field, and faults were developed in the rift zone, causing the rising of magma along these structures. Moreover, the rifting volcanic activities were mainly the results of the extensional tensioning process of the back-arc basin, and Parece Vela Basin volcanism was in a magmatically starved condition at the terminal phase of the basin [10,41,60]. Furthermore, Okino et al. [9] even proposed that the spreading process of Parece Vela Basin was more complex, with the inclusion of segmentation and failing of the spreading axis.

Table 5. The comparative features of the Shikoku Basin, Parece Vela Basin, and Japan Sea.

| Location           | Tectonic Setting                  | Age       | Composition Features                  | Spreading Axes                             | Three-Dimensional Shear Wave Velocity Structure                  | Volcanic Activities                               | Subduction Angle                      |
|--------------------|-----------------------------------|-----------|--------------------------------------|--------------------------------------------|---------------------------------------------------------------|------------------------------------------------|---------------------------------------|
| Shikoku Basin      | Back-arc basin behind the IBM arc | 30–12 Ma  | EM1, EM2; With the involvement of subduction-related fluid | The axial seamount chain                    | A low-velocity layer indicating high-temperature or partially molten asthenosphere widely developed beneath Shikoku Basin | Eruption continued until 12 Ma after the cessation of the back-arc spreading | The low angle of the subducting slab beneath the Izu-Bonin Trench |
| Parece Vela Basin  | Back-arc basin behind the IBM arc | 30–18 Ma  | MORB; Almost not affected by the subducted fluid | A rift valley                               | A 30–40-km thick high-velocity layer indicating cold lithosphere was found beneath the Parece Vela Basin | In the magmatically starved condition at the terminal phase of the evolution | The steep angle of the subducting slab beneath the Marianas Trench |
| Japan Sea          | Back-arc basin behind the Japan arc | 23–15 Ma  | EM1, EM2; With the involvement of subduction-related fluid and sediments | Rift valley and seamount                    | Early to mid-Miocene; 23–15 Ma                               |                                                                                              | The medium angle of the subducting slab beneath the Japan Trench |

8. Conclusions

Shikoku Basin is situated within a special tectonic environment where the subduction of the spreading ridge, providing us the rare opportunity to clarify the nature of different sources during the formation of a back-arc basin. Our paper presented new mineral compositions, major, trace-element, and Sr-Nd-Pb isotopic compositions of bulk-rocks from Sites C0012 (>18.9 Ma) and 1173 (13–15 Ma) of Shikoku Basin. These new data were discussed in correlation with the available literature geochemical data from the back-arc volcanic fields in the adjacent Parece Vela Basin (Sites 449 and 450) and Japan Sea (Sites 797 and 794) and the seamount chains in the Shikoku Basin. Volcanic samples from Sites C0012 and 1173 were tholeiitic in composition. Geochemically, the Site 1173 samples were depleted in typical MORB-type incompatible elements and isotopic compositions.
Specifically, samples from Site C0012 displayed more pronounced positive anomalies in Rb, Ba, K, Pb, and Sr, and negative anomalies in Th, U, Nb, and Ta; here, the enriched Sr-Nd-Pb isotopic signature indicates the possible involvement of EMI and EM2 sources, which could be attributed to the metasomatism of the hydrous fluids released from the dehydrated subduction slab, but with the little contribution of subducted slab-derived sedimentary component. Geochemical modeling indicated that the primary magmas of Sites C0012 and 1173 volcanic rocks were formed by 5% to 10% degree of partial melting of a spinel lherzolite without a garnet source. Shikoku Basin and Japan Sea just record that the formation of the back-arc basin was a mantle conversion process from an island arc to a typical MORB. The formation of the Shikoku Basin was different from the adjacent Japan Sea and Parece Vela Basin, mainly in terms of the metasomatized subduction-related components, the nature of mantle source, and partial melting processes.

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