STRONTIUM ISOTOPES IN PALEozoic GEOSYNCLINAL BASALT IN JAPAN*

TSUYOSHI TANAKA**, RYUICHI SUGISAKI***, KEN SHIBATA**
and HAJime KURASAWA**

Abstract Rubidium and strontium contents and initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were determined for 14 Paleozoic geosynclinal basalts in Japan. Samples from the Mikabu zone have low initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.703~), similar to abyssal basalts. Volcanics of the Chichibu belt, which forms both flanks of the Mikabu zone, seem to have slightly higher initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.704~0.705) than rocks of the Mikabu zone, though some samples have low initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios similar to the Mikabu zone. High $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in some rocks may be the result of alteration.

The spatial variation of initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in these Paleozoic rocks differs from the variation in Quaternary volcanic isotopic ratios in both Southwest and Northeast Japan, suggesting that the mantle or crustal isotopic conditions in the Paleozoic differed from those in the Quaternary.

Introduction

Geosynclinal basalts intercalated in the Paleozoic and Mesozoic groups of Japan (Fig. 1) differ in many petrochemical characteristics from Quaternary basaltic rocks in the Japanese Islands. They are in fact remarkably similar to ocean floor basalts (TANAKA, 1970; SUZUKI et al., 1971; SHINDA et al., 1971; SUGISAKI et al., 1972; KAWABE, 1974). Like the Quaternary volcanics the Paleozoic basalts show lateral and temporal variations, but the patterns are different (UCHIDA, 1967; HASHIMOTO et al., 1970; SUGISAKI & TANAKA, 1971; KANISHWA, 1971; HATTORI et al., 1972; TANAKA & SUGISAKI, 1973; SAWADA, 1973; MARUYAMA, 1976).

Although these geosynclinal basalts have many oceanic affinities, SHIBATA & ADACHI (1974) discovered spatially associated Precambrian granitic and gneissic clasts in a conglomerate (Kamiaso in Fig. 1), which suggest an acidic crust beneath a part of the geosyncline. SUGISAKI & TANAKA (1971) and KAWABE et al. (1979) discussed the crustal development and tectonics of pre-Cenozoic Japanese Islands on the basis of major and trace elements in several hundred samples. SUGISAKI et al. (1972) have synthesized much new and existing geologic and geochemical data to propose a rifting model for the Paleozoic geosyncline in Southwest Japan.

Sr isotopic studies are very effective in clarifying crust and mantle processes. Sr isotopes in Japanese Quaternary volcanics were studied by KURASAWA (e.g. 1975). He found that the volcanics of Northeast and Southwest Japan have low $^{87}\text{Sr}/^{86}\text{Sr}$ (<0.705) and high $^{87}\text{Sr}/^{86}\text{Sr}$ (>0.705) ratios, respectively. KURASAWA (e.g. 1975) suggested that crustal contamination affected the volcanics of Southwest Japan. SHUTO et al. (1977) found a similar pattern in Japanese Cenozoic volcanics; however, they proposed two different kinds of mantle to produce the isotopically distinct magma groups. In this paper, we report Rb and Sr contents
and Sr isotopes of 14 Paleozoic geosynclinal basalts. Alteration of the Sr isotope ratios by weathering or metamorphism is also discussed.

**Samples and analytical methods**

Samples currently examined are aliquots of the same powders used previously for studies of major elements, Rb, Sr, transition metal elements and rare earth elements (Tanaka, 1970, 1977; Hattori et al., 1972; Kawabe, 1974; Sugisaki et al. unpublished). Sampling locations of geosynclinal basalt examined here are shown in Fig. 1. Petrological descriptions and detailed localities of the samples examined here have been previously published (Tanaka, 1977).

Rb and Sr were determined using an X-ray fluorescence spectrometer (Hattori et al., 1972). The analytical error is expected to be within 15% (relative) in the case of more than 10 ppm; however, it may be much larger at the 1 ppm level.

The mass spectrometric analyses were done on a JEOL-05RB mass spectrometer with a 90°, 30 cm radius analyser. The standard deviation of one measurement of \({}^{87}\text{Sr}/{}^{86}\text{Sr}\) ratio is about 0.0005. One standard deviation of each measurement is shown in Table 1 as an error value. \({}^{87}\text{Sr}/{}^{86}\text{Sr}\) ratios of standard Sr Eimer and Amend, and GSJ standard basalt JB-1, were analyzed as 0.7081±0.0005 and 0.7043±0.0004, respectively.

**Results and discussion**

The results are listed in Table 1. The

---

**Fig. 1. Sketch map showing the location of rock samples and the distribution of the Paleozoic and Mesozoic formations in Japan.**

---

NII-Electronic Library Service
Table 1. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and Rb and Sr contents (ppm)* in the Japanese Paleozioc geosynclinal basalt.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rb</th>
<th>Sr</th>
<th>$^{87}\text{Sr}/^{86}\text{Sr}$</th>
<th>Initial $^{87}\text{Sr}/^{86}\text{Sr}$</th>
<th>Fossil $^{87}\text{Sr}/^{86}\text{Sr}$</th>
<th>Age</th>
</tr>
</thead>
<tbody>
<tr>
<td>A4</td>
<td>100</td>
<td>841</td>
<td>0.7068±100.0007</td>
<td>0.7048</td>
<td></td>
<td>Permian</td>
</tr>
<tr>
<td>C86</td>
<td>23.4</td>
<td>468</td>
<td>0.7057±100.0003</td>
<td>0.7032</td>
<td></td>
<td>Permian</td>
</tr>
<tr>
<td>C92</td>
<td>1.6</td>
<td>267</td>
<td>0.7067±100.0006</td>
<td>0.7055</td>
<td></td>
<td>Devonian</td>
</tr>
<tr>
<td>C104</td>
<td>5.4</td>
<td>401</td>
<td>0.7060±100.0007</td>
<td>0.7066</td>
<td></td>
<td>Devonian</td>
</tr>
<tr>
<td>E4</td>
<td>6.5</td>
<td>257</td>
<td>0.7087±100.0005</td>
<td>0.7084</td>
<td></td>
<td>Permian</td>
</tr>
<tr>
<td>F59</td>
<td>&lt;1.0</td>
<td>2.5</td>
<td>0.7096±100.0006</td>
<td>0.7091</td>
<td></td>
<td>Permian</td>
</tr>
<tr>
<td>F75</td>
<td>2.8</td>
<td>191</td>
<td>0.7052±100.0004</td>
<td>0.7050</td>
<td></td>
<td>Permian</td>
</tr>
<tr>
<td>G10</td>
<td>10.5</td>
<td>412</td>
<td>0.7041±100.0005</td>
<td>0.7039</td>
<td></td>
<td>Permian</td>
</tr>
<tr>
<td>G29</td>
<td>3.2</td>
<td>180</td>
<td>0.7058±100.0006</td>
<td>0.7055</td>
<td></td>
<td>Permian</td>
</tr>
<tr>
<td>H2</td>
<td>7.9</td>
<td>71</td>
<td>0.7070±100.0004</td>
<td>0.7074</td>
<td></td>
<td>(Mikabu)</td>
</tr>
<tr>
<td>H15</td>
<td>9.0</td>
<td>315</td>
<td>0.7047±100.0004</td>
<td>0.7044</td>
<td></td>
<td>Permian</td>
</tr>
<tr>
<td>H22</td>
<td>19</td>
<td>362</td>
<td>0.7052±100.0005</td>
<td>0.7046</td>
<td></td>
<td>Permian</td>
</tr>
<tr>
<td>T19</td>
<td>1.3</td>
<td>74.6</td>
<td>0.7036±100.0004</td>
<td>0.7034</td>
<td></td>
<td>(Mikabu)</td>
</tr>
<tr>
<td>T21</td>
<td>&lt;1.0</td>
<td>45.6</td>
<td>0.7041±100.0008</td>
<td>0.7039</td>
<td></td>
<td>(Mikabu)</td>
</tr>
<tr>
<td>JB-1</td>
<td></td>
<td></td>
<td>0.7043±100.0004</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E4A</td>
<td></td>
<td></td>
<td>0.7081±100.0005</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* No correction for absolute water and carbonate contents was made.
** The error value is one standard deviation for one measurement.
† $^{87}\text{Sr}$ content less than 1 ppm was considered as 0.5 ppm for decay correction.
†† 280 m.y., 280 m.y. and 380 m.y. were used for the ages of the Permian system, Mikabu zone and Devonian system, respectively.

initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio was calculated for each sample from the Rb/Sr ratio and the fossil age of sedimentary rocks adjacent to geosynclinal basalt. Mesozoic ages for some localities, previously considered as Paleozoic, were determined by conodont fossil. However, as shown in Table 1, age correction of initial $^{87}\text{Sr}/^{86}\text{Sr}$ is quite small except A4. If the Permian age assignments (in Table 1) are changed to Triassic, no significant change for initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is produced.

Geosynclinal basalts are considered as products of submarine volcanism in the late Paleozoic, and they still have clear igneous texture with primary pyroxene, plagioclase and hornblende. However, mafic minerals of them are often altered to chlorite, actinolite, epidote and calcite. Muscovite, leucoxene, prehnite, pumpellyite and stilpnomelane are identified rarely as metamorphic minerals.

Concentrations of rubidium and strontium are considered to alter significantly during long-term chemical weathering. Wasserburg et al. (1964) studied hornblende diorite dikes from the Panamint Mountains of California. They reported an apparent enrichment in radiogenic $^{87}\text{Sr}$ of whole rock samples during metamorphism. Hart & Nalwalk (1970) analyzed basalt dredged from the Puerto Rico trench and reported high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios accompanied by high Sr concentration, which probably was due to sea water alteration. Very recently, Satake & Matsuda (in press) studied the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of dredged basalt and metabasalt from Mid-Atlantic Ridge. They found a sharp correlation between $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and water contents and hydrogen isotope ratios in H2O (+). Satake & Matsuda (in press) concluded that variation of strontium isotope ratios in the Mid-Atlantic Ridge basalt is due to the complete isotope exchange of strontium in chlorite of the basalt with strontium in sea water. The nature of hydration in Japanese Paleozoic geosynclinal basalts was studied carefully by Hattori et al. (1972). They found only a slight and systematic variation of elements along with increasing contents of H2O (+), and concluded that the effect of reaction with sea water was not significant.
The occurrence of secondary minerals in the Paleozoic geosynclinal basalts of this study suggests the possibility of alteration of $^{87}\text{Sr}^{86}\text{Sr}$ initial ratios. All of the presumed alteration processes that may be responsible for $^{87}\text{Sr}^{86}\text{Sr}$ ratio variations are shown in Table 2. Almost all of the processes drive present $^{87}\text{Sr}^{86}\text{Sr}$ ratios to higher than original values (unaltered). Such secondary increases of $^{87}\text{Sr}^{86}\text{Sr}$ by interaction with country rock, sediments and weathering have been observed (e.g. Hart & Nakai, 1970; O'Nions & Pankhurst, 1976; Satake & Matsuda, in press).

Relations between $^{87}\text{Sr}^{86}\text{Sr}$ and $\text{H}_2\text{O}(\pm)$, and $^{87}\text{Sr}^{86}\text{Sr}$ and $\text{CaCO}_3+\text{MgCO}_3$ in the Paleozoic geosynclinal basalts of Japan are shown in Figs. 2 and 3. No clear correlation exists between them. However, geosynclinal basalts with high carbonate contents (E4, F39) have high $^{87}\text{Sr}^{86}\text{Sr}$ ratios. Paleozoic limestones in Japan contain significant amounts of Sr (473 ppm (av.) for Akasaka, 180 ppm (av.) for Akiyoshi and 160~806 ppm. for Kitakami), though the abundance is different from place to place (Fujiwara, 1968, 1971). Sr in limestone is considered to have the same $^{87}\text{Sr}^{86}\text{Sr}$ ratio as sea water (0.7075~0.7090 during the late Paleozoic) (Peterman et al., 1970). The $^{87}\text{Sr}^{86}\text{Sr}$ ratios of these two rocks, E4 and F39, are considered to be altered by the contamination with limestone. Minor alteration of $^{87}\text{Sr}^{86}\text{Sr}$ ratio in other samples cannot be ruled out, but the effects would slightly raise the initial $^{87}\text{Sr}^{86}\text{Sr}$ ratios as discussed above.

Then, it is considered that these initial $^{87}\text{Sr}^{86}\text{Sr}$ ratios in Table 1 show a maximum value of each sample. Initial $^{87}\text{Sr}^{86}\text{Sr}$ ratios of C86, I19, G10 and I121 are at the level of 0.703, a very low ratio among terrestrial rocks. These ratios indicate that the samples were

---

**Table 2. Hypothetical alteration processes which can affect $^{87}\text{Sr}^{86}\text{Sr}$ ratio.**

<table>
<thead>
<tr>
<th>Case</th>
<th>Migration of Rb</th>
<th>Migration of Sr</th>
<th>Alteration Trends of $^{87}\text{Sr}^{86}\text{Sr}$ Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>+</td>
<td>+</td>
<td>increase*</td>
</tr>
<tr>
<td>b</td>
<td>+</td>
<td>+</td>
<td>decrease**</td>
</tr>
<tr>
<td>c</td>
<td>-</td>
<td>+</td>
<td>increase*</td>
</tr>
<tr>
<td>d</td>
<td>-</td>
<td>-</td>
<td>no change</td>
</tr>
</tbody>
</table>

* $^{87}\text{Sr}^{86}\text{Sr}$ ratios of all rocks other than the geosynclinal basalts (e.g. country rocks, sediments, sea water) are considered to be higher than the $^{87}\text{Sr}^{86}\text{Sr}$ ratios of the geosynclinal basalts. Peterman et al. (1970) estimated the $^{87}\text{Sr}^{86}\text{Sr}$ ratio of Phanerzoic sea water to be 0.7077~0.709.

** If a large amount of Rb was added, the estimated initial $^{87}\text{Sr}^{86}\text{Sr}$ will be too low, because of excess age correction (by decay of $^{87}\text{Rb}$). However, as shown in Table 1, the Rb content in geosynclinal basalt is not high, and even if we assume that all of the Rb is added from an external source, excess decay corrections of $^{87}\text{Sr}^{86}\text{Sr}$ for most samples are less than 0.0005. Therefore, case b should be very rare in geosynclinal basalt.

If isotopic exchange occurred between geosynclinal basalt and surrounding materials without migration of elements, $^{87}\text{Sr}^{86}\text{Sr}$ ratio would increase in any case.
altered very little in terms of their Sr isotopic compositions. Hofmann & Hart (1975) summarized the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of rocks in oceanic regions, and they showed abyssal basalt (ridge basalt) to have ratios between 0.7025–0.7035. Japanese Paleozoic geosynclinal basalt samples, C86, I19, G10 and I121, have similar $^{87}\text{Sr}/^{86}\text{Sr}$ ratios to those of abyssal basalts. H15 and H22 were sampled from different parts of a series of lava flows (TANAKA & SUGIKAWA, 1973). Both samples have almost the same $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.7044 and 0.7046). This fact suggests that these $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were not altered very much, and the ratios are essentially slightly higher than those of C86 and I19.

Sr isotopes of Quaternary volcanic rocks in the Japanese Islands were studied by Kurasawa (e.g. 1975). He found spatial variations, with high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in Southwest Japan and low ratios in Northeast Japan and Hokkaido. Kurasawa (e.g. 1975) considered that the high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in lavas from Southwest Japan were caused either by contamination with crustal material, or the primary magmas of these volcanics derived from the lower crust. Shibata & Adachi (1974) discovered Precambrian conglomerate in Paleozoic system in Central Japan, and they suggested acidic Precambrian crust beneath a part of the Paleozoic geosyncline. Geosynclinal basalts, C10, I19 and I121 are from Southwest Japan and have significantly lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than those of Quaternary volcanics. These results suggest either that Paleozoic mantle material differed from that of the Quaternary or the Paleozoic crust had not developed as thick as the Quaternary crust.

No Quaternary volcanics having $^{87}\text{Sr}/^{86}\text{Sr}$ ratios as low as Paleozoic geosynclinal basalt (I19) has been reported from Southwest Japan. However, many dredged basalts from the Pacific Ocean (Shikoku Basin and northern part of the West Philippine Basin), which opens south of Southwest Japan, do have low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.7028–0.7037) like I19 and I121 (Matsuda, in press). This fact suggests to us that the Paleozone geosynclinal basalts in Southwest Japan must have erupted in a basin like the Philippine basin as suggested by Kawabe (1974).

Geosynclinal basalts H2 and G29 have higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than abyssal basalt. However, the chondrite-normalized rare-earth pattern of H2 is a solid-type one which implies low $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (TANAKA, 1977). Therefore, the strontium concentration in H2 may have been altered.

In the Kitakami belt, C92 and C104 have slightly high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.7065 and 0.7066, respectively), while C86 has a low $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (0.7032) similar to abyssal basalt. Both C92 and C104 were sampled from the Motai Group (Devonian) and have almost the same $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. This fact suggests that the high initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are not the results of alteration but are primary features of these samples. A high initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (0.7079) was also reported on the Hikami granite (Devonian) in the Southern Kitakami area (Shibata, 1974). Such high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for both volcanic and intrusive rocks suggest the presence of some amount of pre–Devonian continental crust underneath the Southern Kitakami area. However, C86 (Permian) within 100 km of the Motai Group have low (0.7032) $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, suggesting that the pre–Devonian continental crust was localized. Shibata (1974) also reported Mesozoic granites with low (0.7043) initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in the Northern Kitakami area.

The volcanics of the Motai Group have geochemical similarities with abyssal basalt (Kawabe et al., 1979). If geochemical features of volcanic rocks reflect the tectonic conditions under which the magmas were formed, the tensional tectonic environment in which volcanics of the Motai Group (high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios) were formed differed from the tensional condition under which the Mikabu volcanics (low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios) were formed. More extreme rifting in Southwest Japan may have resulted in less crustal (hence isotopic) contamination of the Mikabu volcanics relative to the volcanics of the Motai Group, which formed in a region of less rifting. Kawabe et al. (1979) suggested tensional tectonics followed rapidly by compressional tectonics in the Southern Kitakami
Acknowledgements

This study was done as one of the Basic Researches in Geochemistry of Geological Survey of Japan. The Authors are grateful to Jun-ichi Matsuda and Glenn MacPherson for their valuable information and comments. Rb and Sr were analyzed by Hitoshi Hattori. The manuscript was typed by Marilyn Bowie. The work was partly financially supported by the Science Research Foundation of the Ministry of Education. This paper was written at the University of Chicago, while one of authors (T. T.) was a Research Associate of the Department of Geophysical Sciences, University of Chicago (June 1978–May 1980).

References


Matsuda, J., (in press): Sr isotopic studies of DSDP samples from the Philippine Basin and some implication for the mantle material under the basin. Tectonophys.


本邦古生界地向斜玄武岩のストロンチウム同位体比について

田中 剛・杉崎 隆一・柴田 賢・倉沢 一

（要 旨）

本邦古生界地向斜玄武岩 14 個についてそのルビジュムおよびストロンチウム含有量、およびストロンチウム同位体比を測定した。その結果、御荷鉱構造帯に属する火山岩の ⁸⁷Sr/⁸⁶Sr 初生値は 0.703～と低く、海底玄武岩のそれに近いことがわかった。御荷鉱構造帯の両翼に分布する古生層中の玄武岩は御荷鉱構造帯の岩石と同程度に低い ⁸⁷Sr/⁸⁶Sr 初生値を持つものと、やや高い初生値（0.704～0.705）を持つものがある。西南日本におけるいくつかの地向斜玄武岩は、同地域の第四紀火山岩について従来報告されたいかなる ⁸⁷Sr/⁸⁶Sr 比よりも低い初生値を持つ。これは SUGISAKI & TANAKA (1971) により地向斜玄武岩にみられる主要化学成分の時代変化から結論されたように、古生代にはこの地域の地殻が第四紀のそれよりも薄く、より海洋性の性格を持っていたことによるか、または上部マントルの状態が第四紀のそれと異なっていたことによると考えられる。

試料のうちあるものは変質作用を受け、⁸⁷Sr/⁸⁶Sr 比が本来の値から変動している可能性がある。ほとんどの変質作用は玄武岩本来の同位体比をより高くする傾向を持っている。したがって、変質した岩石から得られた ⁸⁷Sr/⁸⁶Sr 初生値は本来の値の上限を示すものであろう。しかし、風化・変質による同位体比の変化は同一岩体において複数の分析を行なうこと、および岩相類元素存在度パターンや CaCO₃ 含有量など他の地球化学的データーからチェックされ得ることがわかった。