Spatial distribution of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of stream sediments in Shikoku Island and the Kii Peninsula, Southwest Japan

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Geochemical mapping of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in Shikoku Island and the Kii Peninsula of Southwest Japan was performed using 233 samples of stream sediments ($<180\ \mu\text{m}$). The spatial distribution of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios successively increases from northern to southern geological units, with a gap at the Median Tectonic Line (MTL). In the Inner Zone divided by the MTL, a zone with Cretaceous granitoid rocks of the Ryoke Belt and sedimentary rocks of the Izumi Group, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are measured at ~ 0.710 . In the Outer Zone, a zone with Cretaceous metamorphic rocks of the Sanbagawa Belt and Jurassic to Miocene accretionary complexes of the Chichibu Belt and Shimanto Belts, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios tend to fall in the range from 0.706 to 0.715, tend to increase from north to south, and are highest in the youngest accretionary complex of the Southern Shimanto Belt.

The $^{87}\text{Rb}/^{86}\text{Sr}$ – $^{87}\text{Sr}/^{86}\text{Sr}$ plots for stream sediments more clearly reveal the differences and similarities of their bed-rocks, such as the different trends among the stream sediments of the Inner and Outer Zones. Samples collected from the Inner Zone show almost the same $^{87}\text{Rb}/^{86}\text{Sr}$ – $^{87}\text{Sr}/^{86}\text{Sr}$ field as their source rocks, while most of the samples derived from accretionary complexes in the Outer Zone are plotted around a mixing line of older continental detritus and igneous-rock-derived materials. In light of the other geochemical characteristics observed, particularly the REE chemical features of the stream sediments and zircon ages in the basemental sedimentary rocks, the accretionary complexes in the Outer Zone may be mainly formed from the same source rocks, namely, igneous-rock-derived materials and continental detrital materials with different mixing ratios and a larger ratio of continental materials in the Southern Shimanto Belt. This study indicates that $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of stream sediments strongly reflect the isotopic composition of the source rocks and are very useful for distinguishing the various geological and geochemical settings of the source rocks.

Keywords: geochemical map, stream sediment, $^{87}\text{Sr}/^{86}\text{Sr}$ ratio

INTRODUCTION

Geochemical maps rendering the spatial distribution of element concentrations in the earth surface are useful for mineral exploration and environmental assessments. Nationwide geochemical maps have been published in Europe and America (e.g., Webb *et al.*, 1978; Weaver *et al.*, 1983; Fauth *et al.*, 1985; Kautsky and Bølviken, 1986; Thalmann *et al.*, 1988; Gustavsson *et al.*, 2001). Investigators have also recently been conducting cross-boundary and sub-continental geochemical mapping projects (e.g., Reimann *et al.*, 1998, 2003; Salminen *et al.*, 2005). In our country, the Geological Survey of Japan used stream sediments to produce a series of nation-

wide geochemical maps (Imai *et al.*, 2004, 2010). The spatial distribution patterns of element concentrations in stream sediments are strongly controlled by geology and mineral occurrences. Stream sediments consist of gravels, sands, and soils supplied from catchment areas upstream from the sampling points. The element concentrations of the samples thus tend to represent the geology of upstream areas, though they may correspond poorly with the distributions of surface geology when hidden basement rocks and/or weathered materials are distributed.

Unlike element concentrations, isotope ratios are little affected by weathering processes and serve well as tracers in mapping geology. Strontium isotope ratio, $^{87}\text{Sr}/^{86}\text{Sr}$, has recently been used to detect food-producing areas and patterns of ancient human migration (e.g., Price *et al.*, 2004; Ariyama *et al.*, 2012). For these studies, we must know the factors controlling the spatial distribution of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. A few studies, however, have been pub-

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Fig. 1. Bedrock geology of Shikoku Island and the Kii Peninsula, Japan. Points A and B are sampling locations of sandstones for CHIME dating. The figure is depicted on a seamless digital geological map of Japan at a scale of 1:200,000 (Geological Survey of Japan, 2010).

lished on distribution maps based on strontium isotopes (e.g., Hodell *et al.*, 2004; Voerkelius *et al.*, 2010; Frei and Frei, 2011). Investigators in Japan have produced geochemical maps of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in limited areas in Aichi Prefecture (Asahara *et al.*, 2006). Our group, meanwhile, has started a nationwide spatial distribution mapping project of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. For sample media we are using stream sediments collected earlier for the nationwide geochemical mapping project by the Geological Survey of Japan (AIST). The Geological Survey of Japan analyzed these samples for 53 elements and explained the geochemical features in relation to the lithology and distribution of mineral deposits (Ohta *et al.*, 2004a, 2004b, 2005a, 2005b; Ujiie-Mikoshiba *et al.*, 2006, 2011).

Stream sediments approximate the composite of weathered rock and soil in the catchment area upstream from the sampling site (Howarth and Thornton, 1983). Stream sediments may thus represent catchment areas better than rocks and make better samples than rocks for geochemical mapping. The samples used in this study were sieved to 80 mesh ($<180\ \mu\text{m}$), as coarse grains sometimes have heterogeneous and specific compositions while highly fine grains are likely to be composed of concentrated heavy minerals. In an investigation of the dependence of chemical composition on grain size, Imai (1987) concluded that an 80 mesh fraction ($<180\ \mu\text{m}$) has a chemical composition similar to that of a no-sieved bulk sediment. Asahara *et al.* (2006) founded that $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of fine stream sediments ($<180\ \mu\text{m}$) corresponded well to those of the bedrocks, even though stream sediments they sampled were weathering products from source rocks distributed in their drainage basins.

This paper describes the spatial distribution of $^{87}\text{Sr}/^{86}\text{Sr}$ for Shikoku Island and the Kii Peninsula in Southwest Japan. This study area has large and continuous tectonic zones of various ages, which makes it suitable for investigating the relationships of original large-scale Sr isotope distributions with geology. The paper will discuss the $^{87}\text{Sr}/^{86}\text{Sr}$ values of stream sediments in Shikoku Island and the Kii Peninsula in association with the geology of the source rocks and geological ages.

GEOLOGY OF SHIKOKU AND KII PENINSULA

The geological map in Fig. 1 shows the geology of the study area of Shikoku and the Kii Peninsula. The Shikoku Mountains and the Kii Mountains are arranged in a NE–SW trend parallel to the Median Tectonic Line (MTL). The two mountain ranges form the outer arc of the SW Japan tectonic division. The main rivers are the Shimanto and Yoshino Rivers in Shikoku Island. The Yoshino River flows eastward along the Shikoku Mountains and the Shimanto River flows southward to the Pacific Ocean from the Shikoku Mountains. The main riv-

ers in the Kii Peninsula are the Kinokawa River flowing westward along the MTL and the Kumano River flowing on the east peninsular coast.

As the map in Fig. 1 shows, some of the tectonic belts exposure in the E–W direction across Shikoku and the Kii Peninsula. The Ryoke Belt, Sanbagawa Belt, Chichibu Belt, and Shimanto Belt are distributed from north to south, and the MTL separates the Ryoke and Sanbagawa Belts.

The Ryoke Belt consists mainly of Late Cretaceous metamorphic and granitic rocks. Ryoke metamorphic rocks derived from the Jurassic accretionary complex are distributed in western Shikoku and central parts of the Kii Peninsula. These rocks are partly covered by the Izumi Group extending in a narrow zone along the northern border of the MTL. The Izumi Group is composed of a thick sequence of conglomerate, sandstone, and mudstone deposited in the marine environment during the Late Cretaceous period.

The Sanbagawa Belt is a high P/T regional metamorphic belt predominately consisting of metamorphic rocks of greenschists, pelitic/psammitic schists, and minor siliceous, conglomeratic, and calcareous schists. The constituent rocks are products of tectonic accretion during subduction of the oceanic plates in the Jurassic to Cretaceous periods which later metamorphosed during the Early Cretaceous period (e.g., Isozaki and Itaya, 1990). Greenschists are distributed to the west in Shikoku and the western part in Kii Peninsula. As minor components, the Eocene coarse clastic rocks (Kuma Group) and Miocene andesitic volcanoclastic rocks (Ishizuchi Group) are found in the greenschists (Nagai, 1957; Yoshida, 1984). Pelitic/psammitic schists are common throughout the Sanbagawa Belt, but relatively abundant in the eastern area. Koboake and Kawaguchi Formations in the northern central part, which are composed mainly of pelitic/psammitic schists, are reported to correspond to the Late Cretaceous accretionary complex, and they are equivalent to the Northern Shimanto Belt (Aoki *et al.*, 2007). In the edge of the southern area of the Sanbagawa Belt, the Mikabu greenstone complex consisting of mafic rocks is distributed.

The Chichibu Belt is a Late Jurassic accretionary complex consisting of weakly-metamorphosed sedimentary rocks, mainly clastic assemblages of mudstone and sandstone associated with basaltic lavas and pyroclastic rocks. The Kurosegawa Belt is a narrow zone located in the southern area of the Chichibu Belt, and consists of Paleozoic accretionary complexes, schist serpentinite melange, exotic blocks of Paleozoic shallow marine sediments, granitic rocks, and metamorphic rocks.

The Shimanto Belt is mainly composed of sandstone and mudstone with subordinate greenstone, chert, acidic tuff and conglomerate. The Northern Belt consists of Cre-

taceous accretionary complexes. The Southern Belt consists of Eocene to Miocene accretionary complexes. Miocene conglomerate, sandstone, and mudstone are distributed in the southern Kii Peninsula (Tanabe and Kumano Groups) and in the western part of southern Shikoku (Misaki Group). Felsic volcanic rocks (Kumano and Ohmine acidic rocks) are distributed in the southeastern Kii Peninsula.

METHODS

Samples

Stream sediment samples collected and stored by the Geological Survey of Japan were used for this $^{87}\text{Sr}/^{86}\text{Sr}$ geochemical mapping project. The sampling density was about one point per 100 km² area (Imai *et al.*, 2004). Collected stream sediment samples were dried in air and sieved through a 180 μm stainless steel screen. Magnetic minerals (mainly magnetite) in the samples (<180 μm) were removed by magnet to minimize the effect of magnetic mineral accumulations. It is reported that removal of magnetite does not affect Sr concentration, unlike Fe, Co and V concentrations, in stream sediments (Furukawa *et al.*, 2005). The result suggests the magnetic separation could not affect Sr isotope ratios.

One hundred and fifty-eight samples out of 173 samples collected in Shikoku and 75 samples out of 96 samples collected in the Kii Peninsula were selected for the Sr isotope analysis. The sample numbers and locations were reported earlier by Imai *et al.* (2010).

Analytical procedures

An aliquot of 50–70 mg was heated in a furnace at 950°C for 5 h to remove organic matter and then digested with an HF/HClO₄ mixture. The degraded product was evaporated to dryness and the residue was dissolved in 2.4 M HCl. Sr in sample solutions was separated from the other elements using a quartz column filled with cation exchange resin (BioRad AG 50WX8, 200–400 mesh). The resin-separated Sr fraction was loaded on a tantalum filament and Sr isotope ratios were measured with a thermal ionization mass spectrometer (TIMS; VG Sector 54). $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were normalized to $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$. The value of repeated analyses of standard NIST-SRM987 during this study was 0.710247 ± 0.000016 (2σ , $n = 54$). Supplementary Table S1 lists the $^{87}\text{Sr}/^{86}\text{Sr}$ values of stream sediments thus determined. For comparison, Table S1 also tabulates Rb and Sr concentrations reported by Imai *et al.* (2010) and representative geologies. The representative geologies will be explained in the following section.

Two sandstone rocks were collected from the Northern and Southern Shimanto Belt in Tokushima and Kochi Prefectures (see points A and B in Fig. 1). Zircon grains

separated from the sandstone samples by panning were dated by the Chemical Th–U-total Pb Isochron Method (CHIME) using JEOL JXA-733 microprobe analyzer equipped with four wavelength-dispersive type spectrometers. The instrument operating conditions were as follows: accelerating voltage of 15 kV, beam diameter of 5 μm , beam current of 0.02–0.1 μA , and counting time of 40–300 s. The details of the analytical procedures and CHIME age calculations have been described by Suzuki *et al.* (1991).

Preparation of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios geochemical map and selection of the representative geologies in the catchment area

Geographic Information System software (Arc View GIS; ESRI) was used to prepare the Sr isotopic geochemical maps and to select the representative geologies in the catchment area. The $^{87}\text{Sr}/^{86}\text{Sr}$ data obtained are plotted as differently sized symbols over the geological map (Fig. 2). The sizes of the symbols increase as the $^{87}\text{Sr}/^{86}\text{Sr}$ values increase.

The chemical composition of the stream sediment is thought to closely approximate the composite sample of the catchment area upstream from the sampling site (Howarth and Thornton, 1983): geochemical data of stream sediments are strongly influenced by the geologies of the catchment areas. The same notion can be applied to Sr isotopic data. Yet the mean sampling density (about 100 km²) makes it difficult to determine the unique lithology of each watershed (Imai *et al.*, 2004). For convenience we assumed that when a specific rock type underlies more than 50% of the area of a river basin, that rock type represents the geology of the catchment area and mainly controls the elemental concentrations and Sr isotope ratios. While this assumption is admittedly rough, the model has been successful in explaining the geochemical features of stream sediments (Ohta *et al.*, 2004a, 2004b, 2005a, 2005b). Six tectonic zones (Ryoke Belt, Izumi Group, Sanbagawa Belt, Chichibu Belt, Northern Shimanto Belt, and Southern Shimanto Belt), two Miocene covers (Kumano Group and Kumano acidic rocks), and two types of Neogene–Quaternary sediment rocks are selected for the intended geology. The Sanbagawa metamorphic rocks are mainly composed of greenschists and pelitic/psammitic schists, but the greenschists differ from the pelitic/psammitic schists in both origin and chemical composition, especially in Ca content. Most of the pelitic and psammitic schists in the Sanbagawa Belt contain less than 3.7 wt.% CaO, while most of the greenschists contain abundant CaO (Kiminami and Ishihama, 2003; Kiminami and Toda, 2007). The Sanbagawa Belt is therefore divided into two geological zones, one consisting of greenschists and pelitic/psammitic schists with more than 3.7 wt.% CaO (2.6 wt.%

Fig. 2. $^{87}\text{Sr}/^{86}\text{Sr}$ geochemical map of Shikoku Island and the Kii Peninsula. The plots of the stream sediments with high $^{87}\text{Rb}/^{86}\text{Sr}$ values are enclosed by solid lines, as shown later in Fig. 6d.

Fig. 3. $^{87}\text{Sr}/^{86}\text{Sr}$ values of stream sediments classified by geologic units. Open squares show median values.

of Ca) and one consisting of greenschists and pelitic/psammitic schists with less than 3.7 wt.% CaO. The pelitic/psammitic schists in the Koboke and Kawaguchi Formations are also divided into separate geological zones. Table S1 lists the representative geology for each sample along with the $^{87}\text{Sr}/^{86}\text{Sr}$ values. The first to third representative lithologies of the catchment area are shown in parentheses for reference.

RESULTS

Influence of geology on $^{87}\text{Sr}/^{86}\text{Sr}$ variations in stream sediments supplied from the geological zones

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the stream sediments classified from the geological zones have several distinguishing features (Fig. 2). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios on the $^{87}\text{Sr}/^{86}\text{Sr}$ geochemical map show a zonal variation in the SW–NE direction. Specifically, they change in succession from the northern to southern geological units, with a gap at the MTL. This variation is clearly recognizable in Fig. 3, which summarizes the statistics of the $^{87}\text{Sr}/^{86}\text{Sr}$ values of stream sediments classified into 7 geological zones. The $^{87}\text{Sr}/^{86}\text{Sr}$ values of stream sediments in each geological zone have a certain width because sediments consist of various rocks and minerals, but the trend of successively increase in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from northern to southern geological zones can be recognized. In the Inner Zone, the northern side of the MTL, the median $^{87}\text{Sr}/^{86}\text{Sr}$ values are 0.709 and 0.711 for stream sediments originated from granitic rocks (Ryoke Belt) and sedimentary rocks (Izumi Group), respectively. The median values systematically increase southward. In the Outer Zone, the southern side of the MTL, the median values are 0.706 in samples de-

rived from greenschists (Sanbagawa Belt), 0.710 in samples from pelitic/psammitic schists (Sanbagawa Belt), 0.711 in samples from the Chichibu Belt, 0.713 in samples from the Northern Shimanto Belt, and 0.716 in samples from the Southern Shimanto Belt. Some samples collected from the Southern Shimanto Belt, consisting of younger accretionary complexes from the Eocene to Miocene, have higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than the other samples derived from the Shimanto Belt. These features, however, appear to be specific to Shikoku and are not clearly observable in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the Kii Peninsula.

Spatial distribution patterns of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the geological zones

Ryoke Belt The $^{87}\text{Sr}/^{86}\text{Sr}$ values of stream sediments collected in the Ryoke Belt range from 0.708 to 0.713 (Fig. 3). These are congruent with the whole rock values of the Late Cretaceous granites in northern Shikoku (0.708–0.717) (Kagami *et al.*, 1988, 1992). The $^{87}\text{Sr}/^{86}\text{Sr}$ values of the stream sediments originated from the Izumi Group tend to be higher than those from the Ryoke Belt. Ujiie-Mikoshiha *et al.* (2011) reported that stream sediments collected from the Ryoke Belt have the highest Na, Ba, and Rb concentrations and lowest Fe, V, and Cr concentrations in Shikoku Island. The chemical compositions may be reflected by the main rock units of the Cretaceous granitoids at the active continental margin and sedimentary rocks derived from felsic sources. The negative and positive correlations between $^{87}\text{Sr}/^{86}\text{Sr}$ values versus Fe and Rb concentrations respectively shown in Fig. 4 indicate that stream sediments in the Ryoke Belt and the Izumi Group are controlled by the mixing of the granitoids and sedimentary rocks.

Fig. 4. $^{87}\text{Sr}/^{86}\text{Sr}$ versus (a) Fe and (b) Rb concentrations of stream sediments derived from the Ryoke Belt and Izumi Group. The Fe and Rb data are from Imai *et al.* (2010). The arrows show the mixing trend of granitoids and sedimentary rocks.

The $^{87}\text{Sr}/^{86}\text{Sr}$ values of stream sediments in the Ryoke Belt decrease in the eastward direction to the Kii Peninsula, suggesting a difference of the granitoid's geochemical feature between Shikoku and the Kii Peninsula. Overall, however, no systematic difference in the $^{87}\text{Sr}/^{86}\text{Sr}$ values of the stream sediments is observed between the Izumi Group in Shikoku and that in the Kii Peninsula.

Sanbagawa Belt The Sanbagawa metamorphic rocks are mainly composed of greenschist and pelitic/psammitic schist with variations in chemical features, especially in Ca contents, as described above. We find a good negative correlation between the $^{87}\text{Sr}/^{86}\text{Sr}$ values and Ca contents of the stream sediments supplied from the Sanbagawa Belt (Fig. 5). The $^{87}\text{Sr}/^{86}\text{Sr}$ values of the stream sediments originated from greenschist areas range from 0.705 to 0.707; those from pelitic/psammitic schist areas range from 0.707 to 0.714. The variation of the $^{87}\text{Sr}/^{86}\text{Sr}$ values found in the stream sediments can be explained by the simple mixing of the source rocks. There is no evidence that the $^{87}\text{Sr}/^{86}\text{Sr}$ values of stream sediments originated from the Sanbagawa Belt differ between Shikoku and the Kii Peninsula.

Chichibu Belt The $^{87}\text{Sr}/^{86}\text{Sr}$ values of the stream sediments collected from the Chichibu Belt range from 0.707 to 0.714, with one plot of 0.719 on sample 15002 in western part of the Chichibu Belt (Fig. 3). This variation can be explained by the various lithologies in the Chichibu Belt, where the accretionary complexes encompass granitic rocks, old sedimentary rocks, serpentinite, greenstone, and other rocks (Kurosegawa Belt). The samples with higher $^{87}\text{Sr}/^{86}\text{Sr}$ values tend to be distributed in the southern area of the Chichibu Belt (Fig. 2). The stream sediments collected from the northern Chichibu Belt are poor in mafic rock elements such as Fe and Cr, while the

Fig. 5. $^{87}\text{Sr}/^{86}\text{Sr}$ versus Ca contents of stream sediments derived from the Sanbagawa Belt. The Ca data are from Imai *et al.* (2010).

sediments in the southern part are rich in Rb and Ba (Ujiie-Mikoshiba *et al.*, 2011). The higher $^{87}\text{Sr}/^{86}\text{Sr}$ values in the southern part can thus be attributed to the contribution of the older complex of the Paleozoic Kurosegawa Belt distributed in the southern part of the Chichibu Belt (Fig. 1).

Shimanto Belt The $^{87}\text{Sr}/^{86}\text{Sr}$ values of stream sediments from rivers in the Shimanto Belt range from 0.710 to 0.719 (Fig. 3). The values are highest along the eastern coastal areas of the Southern Shimanto Belt and are higher overall in the Southern Shimanto Belt than in the Northern Shimanto Belt. This tendency is somewhat less clear in the Kii Peninsula than in Shikoku, however, presumably because of the younger sedimentary rocks and felsic volcanic rocks of the Miocene Tanabe Group, Kumano Group, and Kumano acidic rocks. The extremely low $^{87}\text{Sr}/^{86}\text{Sr}$ values measured in the two samples collected from

Fig. 6. Plots of $^{87}\text{Sr}/^{86}\text{Sr}$ versus $^{87}\text{Rb}/^{86}\text{Sr}$ for stream sediments derived from (a) the Ryoke Belt and Izumi Group, (b) the Sanbagawa Belt, (c) the Chichibu Belt, and (d) the Shimanto Belt. The plots of the stream sediments supplied from the pelitic/psammitic schist area in the Sanbagawa Belt in (b), are enclosed by short-dashed lines, while those from the green greenschist area are enclosed by long-dashed lines. (c) shows the enclosed lines for comparison with the plots of the stream sediments in the Chichibu Belt. The plots of the stream sediments with high $^{87}\text{Rb}/^{86}\text{Sr}$ values in (d) are enclosed by solid lines. The solid arrows in (d) show the mixing trend of continental detrital materials (abbreviated to CD) and igneous-rock-derived materials (abbreviated to IR) observed in the stream sediments in Shikoku. The dotted arrows in (d) show a linear array of the stream sediments in the Kii Peninsula.

the western part of the Southern Shimanto Belt in Shikoku may also be influenced by the Miocene felsic plutonic rocks partly distributed near the sampling locations. The contribution of the stream sediments supplied from the younger sedimentary rocks and felsic volcanic rocks covering the Shimanto Belt unconformably may conceal the

systematic change of $^{87}\text{Sr}/^{86}\text{Sr}$. If we were to plot the graphs in Fig. 3 without the stream sediments collected from the covered areas, the predominance of higher $^{87}\text{Sr}/^{86}\text{Sr}$ values in the Southern Shimanto Belt would become all the clearer.

Fig. 7. Chondrite-normalized REE patterns of stream sediments from the Ryoke Belt in northwestern and northeastern Shikoku. The averaged REE concentrations for samples 15022, 15027, 16039, and 22003 in northeastern Shikoku and samples 23008, 24018, 24019, and 24020 from northwestern Shikoku are used to construct the respective REE patterns.

DISCUSSION

Rb–Sr isotopic composition of stream sediments and bed-rocks

Figures 2 and 3 demonstrate the strong influence of the parent lithologies over the $^{87}\text{Sr}/^{86}\text{Sr}$ isotope in stream sediments. We still find large variations in $^{87}\text{Sr}/^{86}\text{Sr}$ values in the stream sediment samples originated from even the same geological units. The variation may be caused by the heterogeneity of the Sr isotope in the various source materials forming the bedrocks in the catchment areas of the samples. For clarification, we investigate the source materials by plotting the $^{87}\text{Sr}/^{86}\text{Sr}$ against $^{87}\text{Rb}/^{86}\text{Sr}$ for the stream sediments grouped according to the geologic zones (see Figs. 6a–d). The relation between the $^{87}\text{Rb}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios among the stream sediments on the north and south sides of the MTL follows different trends.

Factors controlling the $^{87}\text{Sr}/^{86}\text{Sr}$ variation in the stream sediments of the Inner Zone

Figure 6a plots $^{87}\text{Sr}/^{86}\text{Sr}$ versus $^{87}\text{Rb}/^{86}\text{Sr}$ for the stream sediments in the Ryoke Belt and Izumi Group. The Rb–Sr isotopic compositions of stream sediments in the Ryoke Belt form roughly two linear trends: samples 15022, 15027, 16039, and 22003 in western Shikoku are plotted in a line. The linear array is congruent with the Rb–Sr whole rock isochron age of 93 Ma and the initial ratio of 0.7077 for Late Cretaceous granites distributed in northwestern Shikoku (Kagami *et al.*, 1988). Meanwhile, samples 23008, 24018, 24019, and 24020 collected from the eastern part of Shikoku show another linear re-

lation congruent with the Rb–Sr whole rock isochron age of 74 Ma to 69 Ma for granitic rocks in northeastern Shikoku (Yuhara *et al.*, 2000). Yuhara *et al.* (2000) reported that igneous activities in the Ryoke Belt were initiated at *ca.* 120 Ma, continued up to *ca.* 70 Ma with migration eastwards, and were followed by cooling immediately after the youngest granitic bodies were emplaced.

The averaged REE patterns for samples 15022, 15027, 16039, and 22003 from northeastern Shikoku and samples 23008, 24018, 24019, and 24020 from northwestern Shikoku also differ (Fig. 7). The REE concentration data were cited from Imai *et al.* (2010). We note here that the northeastern samples in the Ryoke Belt have a negative Ce anomaly and lower REE concentrations than the northwestern samples. The different REE chemical features could indicate different source bedrock of granites according to igneous activities with migration eastwards. The result shows that the REE chemical features and Rb–Sr isotopic compositions of stream sediments in the Ryoke Belt agree with those of source bedrock of granites, even though stream sediments are weathering products from original rocks. Further study will be needed to analyze REE chemical features of source bedrock of granites for clarifying geochemical difference between northeastern and northwestern Ryoke Belt.

This can be applied to stream sediments in the Izumi Group. One of the source rocks of Cretaceous sedimentary rocks in the Izumi Group is reported to be granitic rocks in the Ryoke Belt (Nishimura, 1976). The sediments originated from the Cretaceous sedimentary rock area of the Izumi Group are plotted in the field between the above two linear arrays (Fig. 6a), suggesting that most of the

source rocks of stream sediments in the Izumi Group originated from granitic rocks of the Ryoke Belt. The results indicate that stream sediments can reflect the Rb–Sr isotopic composition of source rocks upstream from sampling sites and serve well as source data for mapping the Sr isotope distributions of bedrock geology.

Factors controlling the $^{87}\text{Sr}/^{86}\text{Sr}$ variation in the stream sediments of the Outer Zone

The arrays of the Rb–Sr isotopic compositions of the stream sediments collected in the Outer Zone differ from those of the samples collected in the Inner Zone. As Fig. 6b shows, most of the samples in the greenschist areas supplied from the Sanbagawa Belt have lower values (0.705–0.706) than the samples supplied from the pelitic/psammitic schist areas. The different bedrocks provide different $^{87}\text{Rb}/^{86}\text{Sr}$ values for stream sediments due to the differential between the low Rb and high Sr concentrations for the mafic protoliths of the greenschist and the higher Rb and lower Sr concentrations for the protoliths of the pelitic/psammitic schists. Figure 6b also plots the Rb–Sr isotopic compositions for the metamorphosed pillow basalts in the Sanbagawa Belt in Shikoku Island (Watanabe *et al.*, 1998). The Rb–Sr whole rock isochron age is 107 Ma and the initial Rb–Sr ratio is 0.704. This age is assumed to be metamorphic, consistent with the previously reported Rb–Sr whole rock age for the Sanbagawa pelitic schists (e.g., Yamaguchi and Yanagi, 1970; Minamishin *et al.*, 1979). The stream sediments originated from the greenschists areas (open square symbol) also have a similar regression line to the metamorphosed pillow basalts (cross symbol). Assuming that this linear array is a pseudo-isochron line, the initial ratio is around 0.705 (Fig. 6b). The stream sediments supplied from the pelitic/psammitic schist areas, on the other hand, are scattered in a higher $^{87}\text{Rb}/^{86}\text{Sr}$ – $^{87}\text{Sr}/^{86}\text{Sr}$ field than the stream sediments from the greenschists. Figure 6b plots them as an extension of the pseudo-isochron line drawn for the samples from the greenschists, though in fact they are rather dispersive. This dispersive distribution implies that the stream sediments originated from the pelitic/psammitic schists are probably explainable by the mixture of two kinds of source rocks, that is, igneous-rock-derived materials with low $^{87}\text{Rb}/^{86}\text{Sr}$ – $^{87}\text{Sr}/^{86}\text{Sr}$ values and older continental materials with high values. The stream sediments originated from the Chichibu Belt were found to have various Rb–Sr isotopic compositions with widely variable $^{87}\text{Rb}/^{86}\text{Sr}$ values ranging from 0.8 to 5.4 and $^{87}\text{Sr}/^{86}\text{Sr}$ values ranging from 0.707 to 0.719 (Fig. 6c). The samples in the northern part in the Chichibu Belt (closed circle plots in Fig. 6c) appear near the plots of the pelitic/psammitic schists in the Sanbagawa Belt, while the samples in the southern part of the Chichibu Belt (open circle plots in Fig. 6c) are plotted in the higher $^{87}\text{Sr}/^{86}\text{Sr}$

field. The source rocks of the southern Chichibu Belt may differ from those of the northern Belt.

Stream sediments in the Shimanto Belt show higher $^{87}\text{Sr}/^{86}\text{Sr}$ values ranging from 0.710 to 0.719 (Fig. 6d). The $^{87}\text{Rb}/^{86}\text{Sr}$ values change significantly from 1.2 to 7.5 (Fig. 6d). The sediments derived from the Shimanto Belt in Shikoku appear in almost the same region as those from the southern part of Chichibu Belt in the Rb–Sr isotopic plots. This implies that both of the southern Chichibu Belt and Shimanto Belt share common origins. Most of the samples derived from the Shimanto Belt can be explained by the mixing of older detrital materials with extremely high $^{87}\text{Rb}/^{86}\text{Sr}$ – $^{87}\text{Sr}/^{86}\text{Sr}$ values and igneous-rock-derived materials with low $^{87}\text{Rb}/^{86}\text{Sr}$ – $^{87}\text{Sr}/^{86}\text{Sr}$ values like the sediments from the greenschist area in the Sanbagawa Belt. Given the age of the baserocks, it seems very unlikely that the Shimanto Belt could be younger than the Chichibu and Sanbagawa Belts. We assumed that a greater amount of continental detrital materials from the eastern Asia areas elevate the $^{87}\text{Rb}/^{86}\text{Sr}$ – $^{87}\text{Sr}/^{86}\text{Sr}$ of the Shimanto Belt. We will discuss this assumption in the following section.

The above results clearly suggest that the Rb–Sr isotopic compositions of stream sediments are insusceptible to the weathering process of source rocks. Furthermore, fine stream sediments sieved with 80 mesh ($<180\ \mu\text{m}$) indeed reflect the Rb–Sr isotopic composition of source rocks upstream from the sampling sites. This allows us to discuss the pseudo-isochrones of samples and source detrital materials of sedimentary rocks as the points of origin of stream sediments on the Rb–Sr fields. Put more simply, we can make Sr isotope distribution maps using stream sediments as a reliable data source in place of the more compositionally variable bedrocks.

Comparison with $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of stream sediments collected from the Shimanto Belt in Shikoku and the Kii Peninsula

Many of the stream sediment samples collected in the Kii Peninsula are plotted in a $^{87}\text{Rb}/^{86}\text{Sr}$ – $^{87}\text{Sr}/^{86}\text{Sr}$ field similar to that of the samples collected from geographically separate sites in Shikoku. The stream sediments derived from the Shimanto Belt in the Kii Peninsula, on the other hand, tend to be plotted in a different $^{87}\text{Rb}/^{86}\text{Sr}$ – $^{87}\text{Sr}/^{86}\text{Sr}$ field with a higher $^{87}\text{Rb}/^{86}\text{Sr}$ and lower $^{87}\text{Sr}/^{86}\text{Sr}$ than the samples collected in Shikoku (Fig. 6d). The stream sediments nearby the boundary between the Northern and Southern Shimanto Belts in the Kii Peninsula (enclosed by solid lines in Figs. 2 and 6d) have rather high $^{87}\text{Rb}/^{86}\text{Sr}$ values. This could be a consequence of detrital materials with high $^{87}\text{Rb}/^{86}\text{Sr}$ values.

Comparing the mean concentrations of the major and trace elements of the sediment samples in the Shimanto Belt between Shikoku and the Kii Peninsula, the Ca and

Fig. 8. (a) K/Ti ratios and (b) Ca/Ti ratios of stream sediments derived from the pelitic/psammitic schist area in the Sanbagawa Belt, the Chichibu Belt, and the Northern and Southern Shimanto Belts. Open squares show median values.

Sr concentrations of the Kii Peninsula samples are 19% and 34% lower, respectively, on average. The Rb–Sr isotopic composition of the stream sediments in Shikoku can be explained by the mixing of continental detrital materials and igneous-rock-derived materials (Fig. 6d). In contrast, the samples collected from the Shimanto Belt in the Kii Peninsula are influenced by more various materials (Fig. 6d). The younger covers of the Miocene Tanabe Group, Kumano Group, and Kumano acidic rocks can influence the elemental concentrations and $^{87}\text{Rb}/^{86}\text{Sr}$ of the stream sediments derived mainly from the Shimanto Belt.

Factors controlling the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the stream sediments derived from the Shimanto Belt

Origin of the high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the Shimanto Belt
As previously stated, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the Southern Shimanto Belt are higher overall than those of the Northern Belt and highest in the areas studied. In this section, therefore, we compare the chemical compositions of the stream sediments in the Northern and Southern Shimanto Belts.

The Cretaceous–Paleogene accretionary complexes in the Shimanto Belt are composed mainly of terrigenous sediments with clasts of felsic-intermediate rocks derived from SW Japan and from the eastern part of the Asian continent (Teraoka *et al.*, 1999). The higher $^{87}\text{Sr}/^{86}\text{Sr}$ values of stream sediments in the Southern Shimanto Belt suggest that the sedimentary rocks (accretionary complexes) in the Southern Shimanto Belt contain material with high Sr isotopes (Fig. 3). This material is unlikely to originate from the Northern Belt, as the stream sediments in the Northern Shimanto Belt have lower $^{87}\text{Sr}/^{86}\text{Sr}$ values. While the material could conceivably originate from the Chichibu Belt adjacent to the Shimanto Belt, the $^{87}\text{Sr}/^{86}\text{Sr}$ values of those stream sediments (0.707–0.714) are also too low to account for the $^{87}\text{Sr}/^{86}\text{Sr}$ values

of the stream sediments in the Southern Belt (0.719). Another possible source of the high $^{87}\text{Sr}/^{86}\text{Sr}$ is ancient granitic rocks. Given the $^{87}\text{Rb}/^{86}\text{Sr}$ values of the stream sediments from the granitic Ryoke Belt and the mean $^{87}\text{Sr}/^{86}\text{Sr}$ of the detrital materials (0.710), a 20% share of the detrital materials would have to come from 1-billion-year-old granitic rocks. Because detrital materials of this type are not likely to be found in present-day in Japan, we suspect that the $^{87}\text{Sr}/^{86}\text{Sr}$ values of the sedimentary rocks in the southern Shimanto Belt may be elevated by ancient detrital materials supplied from the eastern part of the Asian continent to the subduction zone in the Paleogene (not in the Cretaceous).

The Kishu Shimanto Research Group (1968) surveyed the Shimanto Belt of the Kii Peninsula. Their findings of orthoquartzites and surrounding flute cast indicate that the materials were supplied from the southern part. They proposed a hypothesis that a lost continent had existed at the southern side of sedimentary basin of the Shimanto Belt. They named it “Kuroshio paleoland”. The later fashion of the plate-tectonics has made their idea neglectful, but our present data may supply information of paleotectonics.

Contribution of detrital materials from the continent
In the next phase of our research we investigated whether detrital materials from the Asian continent are to be found in the Shimanto Belt, particularly the southern part of it, by examining K/Ti and Ca/Ti ratios and REE chemical features of stream sediment samples from the Shimanto Belt and by dating the zircon in the bedrocks (sandrocks) from the Shimanto Belt by the CHIME method.

K/Ti ratios can be used as a measure of detrital materials supplied from the continent because illite is abundant in detrital materials derived from the eastern part of the Asian continent and K is a major component of illite (Kimura *et al.*, 2003). Figure 8a shows the K/Ti values of stream sediments originated from the Sanbagawa Belt and

Fig. 9. Chondrite-normalized REE patterns of stream sediments derived from the Sanbagawa, Chichibu, and Shimanto Belts. Averaged REE concentrations for 20, 34, 62, and 26 stream sediment samples in the Sanbagawa, Chichibu, Northern Shimanto, and Southern Shimanto Belts were used to construct the respective REE patterns.

Chichibu Belt, and from the Shimanto Belt in Shikoku. The K/Ti values of stream sediments increase moving southward from the Sanbagawa Belt to the Chichibu Belt and Shimanto Belts, and are highest in the Southern Shimanto Belt. The opposite trend is observed for Ca/Ti values (Fig. 8b). The results suggest that continental detrital materials were supplied in greater abundance to the stream sediments of the Shimanto Belt than to the stream sediments of the Sanbagawa and Chichibu Belts, and in greater abundance to the Southern Shimanto Belt than to the Northern Shimanto Belt.

Figure 9 shows the chondrite-normalized REE patterns (Masuda *et al.*, 1973; Masuda, 1975) of stream sediments in the four geological zones, that is, in the pelitic/psammitic schists of the Sanbagawa Belt, Chichibu Belt, Northern, and Southern Shimanto Belts. The REE patterns were produced by averaging the REE concentrations of stream sediments in each zone. The REE values of the stream sediment samples are taken from Imai *et al.* (2010). The four REE patterns are generally similar, each showing an enrichment of light REE (LREE), with negative Eu anomaly, though $(La/Yb)_N$ varies from 8 to 17 and $(Y/Ho)_N$ varies from 31 to 28: the stream sediments in the Southern Shimanto Belt show a more LREE-enriched continental-like feature, while those of the Northern Shimanto, Chichibu, and Sanbagawa (pelitic/psammitic schist areas) Belts are progressively less depleted of HREE. Roughly speaking, the REE patterns for ocean-derived mafic materials exhibit an LREE-depleted and HREE-enriched mantle-like pattern; the pattern for the

continental materials exhibits an LREE-enriched and HREE-depleted continental-like pattern; and the REE patterns of the stream sediments from these accretionary complex areas might have been formed through a mixing with both patterns. Therefore, the most HREE-depleted pattern of the Southern Shimanto Belt could indicate a greater influence from other areas. Further, the flatter REE patterns in the Sanbagawa Belt could indicate more influence by mafic rocks. These data agree with the conclusion obtained from the $^{87}Sr/^{86}Sr$ values and elemental concentration results mentioned above.

For CHIME dating we extracted and analyzed zircon grains in sandstone samples from the Northern and Southern Shimanto Belt on points A and B in Fig. 1. We selected 55 round zircons out of all the zircon grains on point A and 23 round zircons on point B. The round zircons are likely have older ages than those of euhedral zircons. Some zircons in the Shimanto Belt were found to have igneous ages of 600–1000, 1800–2200 Ma (Fig. 10a), ages not found in the present-day bedrock of Southwest Japan. There were more zircons dated at 2200–2800 Ma in the Southern Shimanto Belt than in the Northern Shimanto Belt (Fig. 10b). The amounts of zircons are imprecise, as the CHIME dating method is poor at accurately determining younger ages. It can be estimated that young zircons dated at less than 100–250 Ma make up 80–90% of all the zircons according to microscopic observations, and the old zircons dated at 2200–2800 Ma constitute only 0.5–1.1% of all zircons in the Northern Belt and only 2.2–4.3% of those in the Southern Belt.

Fig. 10. (a) Frequency and (b) proportion of CHIME ages of zircons collected from the Northern Shimanto Belt (point A in Fig. 1) and the Southern Shimanto Belt (point B in Fig. 1).

Assuming that the zircons are present in proportion to the amounts of detrital materials, we can simulate the change of the $^{87}\text{Sr}/^{86}\text{Sr}$ value of the sedimentary rocks in the Shimanto Belt. If, for example, we assume that a 2.5% proportion of hypothetical materials aged 2.8 billion years old, the oldest age in this study, is mixed with the original materials, the $^{87}\text{Sr}/^{86}\text{Sr}$ value is calculated to be 0.713. If, on the other hand, we assume that hypothetical materials make a 4.5% proportion of the original materials, the $^{87}\text{Sr}/^{86}\text{Sr}$ value is 0.715. These values are comparable to the median $^{87}\text{Sr}/^{86}\text{Sr}$ values of the stream sediments collected from the northern and southern Shimanto Belts (see Fig. 3). Even a small difference in the amount of older detrital materials gives a different $^{87}\text{Sr}/^{86}\text{Sr}$ value in the source rocks.

SUMMARY

Our $^{87}\text{Sr}/^{86}\text{Sr}$ geochemical map of Shikoku Island and the Kii Peninsula of SW Japan exhibited a zonal variation almost parallel to the arrangement of major rock units. The $^{87}\text{Sr}/^{86}\text{Sr}$ values of the geological units rose successively from north to south in Shikoku and the Kii Peninsula, with a gap at the MTL. The highest $^{87}\text{Sr}/^{86}\text{Sr}$ values were observed in the Southern Shimanto Belt, which is consisting of younger accretionary complexes.

The stream sediments in different geological units were plotted in different $^{87}\text{Rb}/^{86}\text{Sr}$ – $^{87}\text{Sr}/^{86}\text{Sr}$ fields. The stream sediments of the Ryoke Belt and Izumi Group in the Inner Zone were plotted in the field between two isochron arrays of source bedrock of granites. Meanwhile, stream sediments in the Sanbagawa, Chichibu, and Shimanto Belts in the Outer Zone were plotted in a mix-

ing field with end members of igneous-rock-derived materials and continental detrital components. This result agrees with the conclusion obtained from the REE chemical features of the stream sediments. Importantly, the stream sediments supplied from the Southern Shimanto Belt were plotted in the highest $^{87}\text{Rb}/^{86}\text{Sr}$ – $^{87}\text{Sr}/^{86}\text{Sr}$ field and had more LREE-enriched characteristics than the others. This suggests that the stream sediments of the Southern Shimanto Belt may be more influenced by continental detrital components. According to CHIME dating, zircons dated at 2200–2800 Ma are actually more prevalent in the sandstones of the Southern Belt than in the sandstones of the Northern Belt. This difference in the amount of ancient detrital components derived from the continent accounts for the different $^{87}\text{Sr}/^{86}\text{Sr}$ values of the Southern and Northern Shimanto Belts. We can thus conclude that the geochemical mapping of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in Southwest Japan was very useful for distinguishing the changes of the geological settings of the study area from a continental margin to an island arc.

Our results demonstrate that the $^{87}\text{Sr}/^{86}\text{Sr}$ values of stream sediments accurately reflect the geochemical features of the representative geologic units upstream of the sampling points, and that the $^{87}\text{Rb}/^{86}\text{Sr}$ – $^{87}\text{Sr}/^{86}\text{Sr}$ plot for stream sediments, a description of geochronological features, reveals more about the bedrocks underlying the superficial overburden. An $^{87}\text{Sr}/^{86}\text{Sr}$ spatial distribution map using stream sediments can be extremely useful not only for investigating the geochemical and geological features of bedrocks, but also for detecting regions of agricultural production and human migration in archaeology.

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SUPPLEMENTARY MATERIALS

URL (<http://www.terrapub.co.jp/journals/GJ/archives/data/47/MS248.pdf>)

Table S1