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Sr isotopic ratios of hydrothermal fluids from the Okinawa Trough and the implications of variation in fluid-sediment interactions

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Abstract

Sr isotope ratios of hydrothermal fluids were observed at five sediment-associated sites in the Okinawa Trough to investigate the diversity of subseafloor fluid-rock-sediment interactions. The estimated ⁸⁷Sr/⁸⁶Sr ratios of the hydrothermal endmember fluids at the five sites were all higher than those at the sediment-starved sites. The endmember Sr isotopic ratios of hydrothermal fluids were diverse within the Okinawa Trough, ranging from 0.7077 at the Iheya North Knoll site to 0.712 at the Yonaguni Knoll IV site. To our knowledge, 0.712 is the highest value reported to date for seafloor hydrothermal fluids. This variation is likely attributable to the relative contributions of multiple subseafloor Sr reservoirs, which are ⁸⁷Sr-poor volcanic rock and ⁸⁷Sr-rich hemipelagic sediments containing clay minerals of terrestrial origin. These data support a model based on the carbon isotope ratio of CH₄, which indicates whether volcanic rocks or terrestrial sediments are distributed in the high-temperature reaction zone of the hydrothermal system.

Key points

- The Sr isotopic ratios of hydrothermal fluids from the Okinawa Trough are exceptionally high.
- The enrichment of ⁸⁷Sr at Yonaguni Knoll IV cannot be explained without the influence of terrestrial clay minerals in sediments.
- High Sr isotopic ratios are a common feature of sediment-associated hydrothermal systems.

Keywords: Hydrothermal system, Sr isotopic ratio, Okinawa Trough, Solid phase, Clay mineral

1 Introduction

Deep-sea hydrothermal activity in sedimentary basins (Von Damm et al. 1985b; Butterfield et al. 1994; Kawagucci 2015; Baumberger et al. 2016) involves fluid chemistry that differs from sediment-starved site activity (Von Damm et al. 1985a; Bonatti 1975) because of

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hydrothermal fluid-sediment interactions. As deep-sea sediments consist of various materials, such as organic matter, clay minerals, and biogenic carbonate, constituents of these compounds are released and characterize the fluid chemistry at sediment-associated sites. For example, strontium (Sr), boron (B), and lithium (Li) are released into fluids through high-temperature alteration of sedimentary clay minerals (Araoka et al. 2016; Chiba et al. 1993; Yamaoka et al. 2015; You and Gieskes 2001). Furthermore, methane (CH_4) and ammonia (NH_4^+) enrichment of fluids at sediment-associated sites is



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considered to be a result of sedimentary organic matter decomposition (Ishibashi et al. 1995; Gamo et al. 1991).

Isotopic ratios are powerful geochemical tools for tracing the origins and fates of environmental constituents. Recent studies have reported significant variations in CH4 isotopic ratios in sediment-associated fluids (e.g., Kawagucci et al. 2013). This variation strongly suggests two styles of fluid-sediment interaction on the subseafloor. Kawagucci et al. (2011) hypothesized that microbes inhabiting sedimentary environments in low-temperature fluid recharge zones generate ¹³C-depleted CH₄, whereas thermal decomposition of sedimentary organic matter in high-temperature fluid discharge zones generates ¹³C-rich CH₄. However, this model can only be applied when sediments contain sufficient carbon. Some sediments lack carbon; hence, variation in carbon isotopes cannot be applied to assess the style of subsurface sediment-fluid interactions.

⁸⁷Sr/⁸⁶Sr ratios are widely used as tracers to identify the origin of Sr, because terrestrial (continental) and marine (volcanic) Sr reservoirs have distinct signatures (Chiba et al. 1993; Zhang et al. 2022, 2020; Noguchi et al. 2011). The Sr isotopic ratios of hydrothermal endmember fluids occurring at sediment-starved vent sites exhibit values within a specific range on a global scale (0.7029-0.7058; n = 87; Diehl and Bach 2020). In contrast, the Sr isotopic ratios of hydrothermal endmember fluids in the Okinawa Trough (0.7089 for Izena Hole: Chiba et al. 1992; 0.7100 for Minami-Ensei Knoll: Chiba et al. 1993; Kawagucci et al. 2013), a sediment-covered backarc basin containing more than 20 hydrothermal vent sites (e.g., Kawagucci 2015), have been found to be higher than those of hydrothermal endmember fluids occurring at sediment-poor vent sites. The high Sr isotopic ratios are likely related to subseafloor fluid-sediment interactions, because Sr is present in sedimentary organic matter, clay minerals, and biogenic carbonate (e.g., Yoshimura et al. 2020). This study systematically discusses the causes of the diversity of hydrothermal endmember fluids that exhibit high Sr isotopic ratios or Sr isotopic ratios comparable to those of surrounding volcanic rocks and contributes to our understanding of the mechanisms that produce such diversity.

In the present study, we determined the Sr isotopic ratios in addition to the major and trace element concentrations in hydrothermal fluids collected from five vent sites in the Okinawa Trough, particularly in the central and southern regions. The Sr isotope ratios of the vent fluids at the five sites were considerably higher than those reported previously for sediment-poor seafloor hydrothermal fluids. The possible mechanism generating this high Sr isotopic ratio at the Okinawa Trough was explored based on the Sr isotopic ratios of hydrothermal fluids from the Izena Hole and Minami-Ensei Knoll in the middle Okinawa Trough (MOT), as reported previously (Chiba et al. 1992, 1993).

2 Geological setting

The Okinawa Trough is a backarc basin formed by subduction of the Philippine Sea plate beneath the Eurasian Plate (Lee et al. 1980; Fig. 1a). The trench-arc-back-arc system is ~ 1200 km long; the northern end extends to the west of Kyushu, and the southern end extends to northeastern Taiwan (Letouzey and Kimura 1986). Particles transported from Eurasia and Taiwan Island were deposited in the Okinawa Trough (Dou et al. 2010). The Okinawa Trough is divided into northern, middle, and southern regions bordered by the deep-sea canyon of the Tokara and Kerama gaps (Fig. 1b). The sediment layers in the northern and southern regions of the trough are 8 km and ~ 2 km thick, respectively (Sibuet et al. 1987).

The Minami-Ensei Knoll is located at the bottom of the MOT at a water depth of ~1200 m, with a specific height of 600 m and a diameter of $\sim\!10$ km (Chiba et al. 1993; Kawagucci et al. 2013). The top of the knoll has four depressions, among which only the "C depression" exhibits submarine hydrothermal activity, venting hydrothermal fluids at temperatures of up to 278 °C (Chiba et al. 1993; Kawagucci et al. 2013). Studies of multichannel seismic profiles and P-wave velocity models in the surrounding area have reported that the MOT is covered by a 2–3-km-thick Shimajiri Formation (Nishizawa et al. 2019). Ishibashi et al. (2015) speculated that the Minami-Ensei Knoll intrudes through the thick sediments of the Shimajiri Group of the Okinawa Trough. Kawagucci et al. (2013) and Kawagucci (2015) inferred that hydrocarbon decomposition occurs through CH4 formation and interacts with sediments outside the knoll on the recharging side of the reaction zone.

The Iheya North Knoll is a large volcanic complex with a specific height of ~ 130 m and diameter of ~ 10 km and is located at the bottom of the MOT at a water depth

⁽See figure on next page.)

Fig. 1 a Location of the Okinawa Trough. The box denotes the area shown in Fig. 1b. b Locations of the hydrothermal fields in the Okinawa Trough (stars). Triangles indicate Quaternary volcances. Bathymetric contours are indicated every 200 m (thin lines) and 1000 m (thick lines). Dashed lines represent depth contours (100 and 200 km) in the Wadati-Benioff zone (Letouzey and Kimura 1986; Pezzopane and Wesnousky 1989). Solid circles indicate the volcanic rock sampling sites: red for those in Shinjo et al. (1999), blue for those in Shinjo and Kato (2000), and yellow for those in this study. MOT and SOT represent the middle Okinawa Trough and southern Okinawa Trough, respectively. Boundaries between NOT and MOT and between MOT and SOT are indicated by light blue dashed lines



of ~ 1100 m. Three hydrothermally active zones have been described: the Original, Natsu, and Aki sites (Monma et al. 1996; Kasaya et al. 2015; Nakamura et al. 2015). The Original site was drilled in the Integrated Ocean Drilling Program (IODP) Expedition 331 (Takai et al. 2011; Yeats et al. 2017), whereas the CK14-04 and CK16-01 cruises drilled the Aki site in expeditions 907 (Takai et al. 2015) and 908 (Kumagai et al. 2017), respectively. Based on the results of drilling the Original site, the seafloor in this region is covered by low-permeability hydrothermally altered clay mineral layers with a thickness of tens of meters. Mineral layers confine the horizontal hydrothermal flow (Miyoshi et al. 2015; Takai et al. 2011; Masaki et al. 2011). The surrounding trough floor is covered by the 2-3-km-thick Shimajiri Formation, and the knoll itself has no significant cover (Ishibashi et al. 2015). Kawagucci et al. (2011) reported that the contribution of microbial CH₄ to hydrothermal fluids is large. Microbial CH₄ is assumed to be produced in the sedimentary layers of the recharge zone surrounding the knoll body and incorporated into hydrothermal fluids (Kawagucci et al. 2011; Kawagucci 2015). The Pb isotopic ratios in galena collected from hydrothermal vent chimneys suggest that the sediment influence on hydrothermal fluids at the Iheya North Knoll is lower than that at the Izena Hole (Totsuka et al. 2019).

The Izena Hole is also located in the MOT~300 m above the surrounding seafloor at a depth of 1610 m, and it has a rectangular caldera of approximately $6 \text{ km} \times 4 \text{ km}$ on the western slope of a collapsed knoll body. The Izena Hole hydrothermal field has two hydrothermal sites: the HAKUREI and JADE sites (Ishibashi et al. 2014). Both sites have distinct fluid compositions (Ishibashi et al. 2014) and thus, were treated as individual sites in this study. The JADE site is located on the northeast wall of the caldera, and the HAKUREI site is situated in a depression on the southwest side of the caldera floor (Ishibashi et al. 2014; Kawagucci et al. 2010; Halbach et al. 1989). During the CK16-05 cruise (Exp. 909), the area around the HAKUREI site was drilled, and pumice was found several tens of meters below the seafloor. Additionally, hydrothermally altered clay minerals are distributed up to 180 m below the seafloor (Nozaki et al. 2021). The carbon isotopic ratios of CH_4 in the JADE and HAKUREI hydrothermal fluids suggest that both microbial and thermogenic CH₄ were supplied in the recharge area (Kawagucci et al. 2010; Kawagucci 2015). However, even if hydrogen is produced in the recharge zone during thermogenesis, it is decomposed by magmatic volatiles from oxic silicic magma in the reaction zone (Kawagucci et al. 2013). The reason for the hydrogen enrichment only at the HAKUREI site could be the influence of sediment cover around the discharge zone, and organic matter in the sediment could be decomposed to generate hydrogen (Ishibashi et al. 2014). This theory also explains ethane enrichment only at the HAKUREI site.

The Yonaguni Knoll IV is located at the foot of the western slope of the Yonaguni Knoll in the southern Okinawa Trough (SOT) at a water depth of 1385–1336 m. Hydrothermal fluids emanate from nearly 10 m high chimneys, and the surrounding area is covered by muddy sediments (Suzuki et al. 2008). Studies of seismic structures in the vicinity have reported that the SOT is covered with 2–3-km-thick submarine sediments (Nishizawa et al. 2019). The origin of CH_4 is based on the thermogenic decomposition of organic matter, and the high hydrogen concentration suggests that the knoll body, with little organic matter, acts as a recharge zone, with the thermal breaking of organic matter in the sediments around the vent (Kawagucci 2015).

3 Samples and sample preparation

3.1 Sample collection

Fluid samples were collected from the Iheya North Knoll (during the KY11-02, NT11-16, and NT12-06 cruises), Izena Hole (during the NT10-17 cruise at the JADE site and NT10-17 and NT11-15 cruises at the HAKUREI site), Hatoma Knoll (during the YK07-04, NT07-12, NT08-13, and NT09-11 cruises), and Yonaguni Knoll IV (during the YK03-05 cruise). KY, NT, and YK in the cruise names indicate the vessels KAIYO, NATSUSHIMA, and YOKO-SUKA, respectively, all of which are owned by the Japan Agency for Marine-Earth Science and Technology (JAM-STEC); the two-digit numbers preceding and following the hyphen indicate the post-2000 year and the serial number of the voyage, respectively. The sample IDs provided information on the cruise, dive, sampler type, and sample number (Table 1). The samplers used included the water and hydrothermal fluid Atsuryoku Tight Sampler (WHATS) (Tsunogai et al. 2003; Saegusa et al. 2006; Miyazaki et al. 2017), Ti-syringe sampler (Von Damm et al. 1985a), Cheap-WHATS sampler (Kawagucci et al. 2016), vacuum sampler (Sedwick et al. 1994), bag sampler (a 2-L plastic bag connected to an impeller pump), and Niskin sampler. The samplers were loaded onto the JAM-STEC ROV Hyper Dolphin and DSV Shinkai 6500. The sampling locations (latitude, longitude, and depth) and the maximum temperature of the fluid observed during sampling are shown in Table 1.

After the samples were brought on board, the liquid was immediately distributed to a polyethylene bottle for pH measurement, followed by a polyethylene syringe with a mixed cellulose ester membrane filter (mesh size: 0.45 μ m) as described by Toki et al. (2016). The samples were filtered and divided into two polyethylene bottles for onboard NH₄⁺ concentration analysis and laboratory

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	[Sr] _{EHF} µmol/ kg	4 79.2	5 76.9	5 79.6	4 75.5	3 76.3	3 76.5	2 81.8	9 81.1	3 120.4	8 121.2	1 129.1	1 98.8	1 99.3	8 52.7
	Error	0.00001	0.00001:	0.00001	0.00001	0.00001	0.00001.	0.00001	0.00000	0.00001	0.00000	0.00001	0.00001	0.00001	0.00001
	⁸⁷ Sr/ ⁸⁶ Sr	0.70765	0.70765	0.70768	0.70769	0.70769	0.70770	0.70764	0.70769	0.70924	0.70923	0.70920	0.70895	0.70891	0.70852
	Mg/Sr mmol/ µmol	1.52×10^{-3}	1.30 × 10 ⁻²	2.00 × 10 ⁻³	2.21×10^{-3}	1.49×10^{-3}	1.48×10^{-3}	3.68 × 10 ⁻³	1.14×10^{-2}	4.11 × 10 ⁻²	4.75×10^{-2}	1.67×10^{-2}	8.77 × 10 ⁻²	4.58×10^{-2}	5.79×10^{-2}
	Sr µmol/ kg	79.3	77.6	79.7	75.6	76.4	76.6	82.0	81.8	121.7	122.6	129.4	103.4	101.7	56.1
	B mmol/ kg	2.0	2.0	2.0	1.8	1.9	1.9	2.0	2.0	3.5	4.E	3.5	2.9	2.8	2.5
	NH₄ ⁺ mmol/ kg	2.0	2.1	1.8	1.9	2.0	1.9	1.9	1.9	3.7	4.3	4.3	3.5	3.4	8.0
	K mmol/ kg	74.6	73.4	74.2	69.5	70.0	70.4	66.6	66.4	64.5	62.9	64.3	56.1	52.9	45.5
s stuay	Ca mmol/ kg	22.0	21.4	22.0	20.9	21.1	21.1	23.1	23.0	22.2	22.1	22.4	19.8	19.5	11.2
Ign In th	Mg mmol/ kg	0.1	1.0	0.2	0.2	0.1	0.1	0.3	0.9	5.0	5.8	2.2	9.1	4.7	3.3
iawa Iror	Na mmol/ kg	454	456	451	423	430	431	444	444	460	457	447	435	388	246
rom Ukin	Cl ⁻ mmol/ kg	571	584	576	574	571	572	596	591	I	600	598	582	I	337
riuias ti	рН 25 °C	I	I	I	5.46	4.95	5.11	4.69	4.62	5.43	4.75	5.10	5.21	4.88	5.51
iermai	°C °C	310	309	311	306	306	306	309	309	248	179	251	316	I	I
ins of hydroth	itude Depth m	°53.861′ 1028	°53.803′ 978	°54.048′ 1048	°54.043′ 1057	°54.043′ 1057	°54.043′ 1057	°53.890′ 1035	°53.890′ 1035	•04.134′ 1593	•03.962′ 1617	•03.995′ 1623	°04.786′ 1340	•04.786′ 1340	。50.471′ 1474
compositic	ude Long E	47.410′ 126	47.454′ 126	47.413' 126	47.420′ 126	47.420' 126	47.420′ 126	47.416' 126	47.416′ 126	14.938′ 127	14.858′ 127	14.841′ 127	16.177' 127	16.177′ 127	51.522′ 123
l isotopic	Latit	nal 27º	JREI 27°	JREI 27º	JREI 27º	25°	25°	ku 24°							
cal anc	Site	Origi	Origii	HAKL	HAKL	HAKL	JADE	JADE	Gusu						
Chemi	Sample ID	KY11-02 D1247 W-2	KY11-02 D1247 W-4	KY11-02 D1249 W-3	NT11-16 D1315 W-1	NT11-16 D1315 W-2	NT11-16 D1315 W-3	NT12-06 D1356 W-2	NT12-06 D1356 W-4	NT10-17 D1191 W-B	NT11-15 D1313 W-3	NT11-15 D1313 W-4	NT10-17 D1184 W-A	NT10-17 D1185 B-1	YK07-04 D999 A
lable	Field ID	lheya North Knoll								lzena Hole					Hatoma Knoll

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Field ID	sample ID	Site	Latitude N	Longitude E	uepth n	°C	рн 25 °C	cr mmol/ kg	Na mmol/ kg	Mg kg	ca mmol/ kg	k mmol/ kg	NH4 ⁺ mmol/ kg	B mmol/ kg	kg kg	Mg/sr mmol/ µmol	15 ⁰⁰ /15 ⁰⁰	Error	l'sr] _{EHF} µmol/ kg
	ΥΚ07-04 D999 W-2	Gusuku	24° 51.522′	123° 50.471	, 1474	321	I	1	307	20.5	9.4	30.5	1	1.6	60.4	3.40 × 10 ⁻¹	0.70886	0.000032	34.9
	ҮК07-04 D999 W-3	Gusuku	24° 51.522′	123° 50.471	1474	323	5.41	361	271	8.4	10.5	43.2	6.8	2.4	54.2	1.54×10^{-1}	0.70866	0.000017	44.7
	ҮК07-04 D999 B-2	Gusuku	24° 51.522′	123° 50.471	1474	I	I	484	382	34.7	9.6	28.4	2.2	1.0	73.6	1.54×10^{-1}	0.70900	0.000017	I
	YK07-04 D999 B-3	Gusuku	24° 51.522′	123° 50.471	1474	I	I	537	437	46.8	8.9	13.7	I	0.4	83.2	5.62×10^{-1}	0.70921	0.000017	I
	YK07-04 D1000 A	Gusuku	24° 51.522′	123° 50.471	1473	I	6.34	493	400	39.8	10.3	18.0	1.1	0.7	81.7	4.87 × 10 ⁻¹	0.70907	0.000013	I
	YK07-04 D1001 A	Gusuku	24° 51.488′	123° 50.468	ار 1469	I	5.61	414	315	10.5	13.2	48.7	5.7	2.5	62.7	1.67 × 10 ⁻¹	0.70868	0.000013	51.7
	ҮК07-04 D1001 W-1	Gusuku	24° 51.488′	123° 50.468	8′ 1469	322	5.38	394	288	2.8	7.0	55.4	7.2	3.0	57.0	4.86 × 10 ⁻²	0.70850	0.000016	54.2
	ҮК07-04 D1001 W-2	Gusuku	24° 51.488′	123° 50.468	8′ 1469	255	I	I	279	00 00	10.8	45.5	I	2.3	51.6	1.70 × 10 ⁻¹	0.70854	0.000022	41.4
	NT07-12 D706 W-1	Gusuku	24° 51.496′	123° 50.467	1474	322	I	I	204	0.2	12.4	42.9	I	I	49.2	4.95 × 10 ⁻³	0.70857	0.000017	49.0
	NT07-12 D707 V-2	BSW	24° 51.564′	123° 50.387	" 1527	4	7.38	542	457	52.8	10.3	10.6	I	I	81.4	6.48 × 10 ⁻¹	0.70917	0.000015	I
	NT07-12 D709 W-2	Gusuku	24° 51.509′	123° 50.466	5' 1477	320	5.44	356	254	1.8	13.5	49.0	6.2	I	53.3	3.33 × 10 ⁻²	0.70854	0.000017	51.4
	NT07-12 D709 W-3	Ē	24° 51.464′	1 23° 50.38C)' 1532	75	I	I	367	26.4	12.2	29.5	I	I	69.1	3.82 × 10 ⁻¹	0.70880	0.000014	37.0
	NT07-12 D709 W-4	Ē	24° 51.464′	123° 50.380)' 1532	70	5.71	479	388	31.0	12.1	28.1	2.7	I	71.2	4.35×10^{-1}	0.70886	0.000014	I
	NT08-13 D866 W-1	Gusuku	24° 51.498′	123° 50.479)' 1474	10	5.67	I	457	52.3	9.8	10.3	0.1	0.4	87.5	5.97×10^{-1}	0.70914	0.000014	I
	NT08-13 D866 W-4	Gusuku	24° 51.498′	123° 50.479	9' 1474	325	I	I	186	0.8	6.6	35.6	0.004	2.0	39.8	1.93 × 10 ⁻²	0.70856	0.000018	38.9

Table 1	(continu	(par																	
Field ID	Sample ID	Site	Latitude N	Longitude E	Depth m	°C °C	рН 25 °C	CI ⁻ mmol/ kg	Na mmol/ kg	Mg mmol/ kg	Ca mmol/ kg	K mmol/ kg	NH ₄ + mmol/ kg	B mmol/ kg	Sr µmol/ kg	Mg/Sr mmol/ µmol	⁸⁷ Sr/ ⁸⁶ Sr	Error	[Sr] _{EHF} µmol/ kg
	NT08-13 D867 W-2	Gusuku	24° 51.501′	123° 50.476	/ 1470	~		1	419	47.4	9.6	9.5	D.N	0.4	83.6	5.68 × 10 ⁻¹	0.70914	0.000014	1
	NT08-13 D869 V-1	Agari	24° 51.480′	1 23° 50.503	1478	301	I	I	281	0.8	16.8	53.3	I	2.9	68.1	1.23×10^{-2}	0.70854	0.000016	67.4
	NT08-13 D869V-2	Agari	24° 51.480′	1 23° 50.503	1478	I	I	425	321	11.4	15.3	46.9	4.8	2.5	70.0	1.63 × 10 ⁻¹	0.70870	0.000015	59.0
	NT08-13 D869 W-2	Gusuku	24° 51.514′	1 23° 50.468	/ 1475	Ø	5.71	538	454	52.3	10.1	10.1	0.1	0.4	89.0	5.87×10^{-1}	0.70922	0.000015	I
	NT08-13 D869 W-4	Gusuku	24° 51.514′	123° 50.468	/ 1475	œ	5.47	522	451	51.9	10.4	10.1	0.1	0.4	92.0	5.64 × 10 ⁻¹	0.70917	0.000015	I
	NT08-13 D870 W-1	Gusuku	24° 51.505′	123° 50.483	1475	I	6.29	535	454	52.5	10.1	6.6	0.01	0.4	89.2	5.88×10^{-1}	0.70914	0.000019	I
	NT08-13 D870 W-4	Agari	24° 51.468′	123° 50.515	1479	6	I	I	424	48.6	9.7	9.3	I	0.4	83.8	5.80×10^{-1}	0.70921	0.000022	ļ
	NT08-13 D871 V-1	BSW	24° 51.609′	1 23° 50.350	/ 1452	I	7.49	539	454	52.8	10.2	10.0	0.005	0.4	89.6	5.89 × 10 ⁻¹	0.70917	0.000013	I
	NT08-13 D871 W-1	Chura	24° 51.594′	123° 50.392	, 1504	206	I	435	345	18.4	13.4	39.7	4.3	2.0	71.6	2.56 × 10 ⁻¹	0.70878	0.000017	52.5
	NT08-13 D871 W-3	Chura	24° 51.594′	123° 50.392	1504	178	I	I	369	32.3	11.3	24.2	I	1.2	76.2	4.24×10^{-1}	0.70899	0.000015	I
	NT08-13 D872 V-1	Gusuku	24° 51.512′	123° 50.477	' 1474	89	I	I	421	46.8	9.8	10.0	I	0.4	85.2	5.50×10^{-1}	0.70916	0.000015	I
	NT08-13 D872 W-1	Gusuku	24° 51.522′	123° 50.467	1476	I	I	I	210	1.6	11.7	39.4	I	2.2	48.3	3.26 × 10 ⁻²	0.70859	0.000021	46.5
	NT08-13 D872 W-4	Agari	24° 51.489′	1 23° 50.504	1479	I	I	I	425	47.8	9.5	9.5	I	0.4	83.7	5.71×10^{-1}	0.70916	0.000016	I
	NT08-13 D873 V-1	Gusuku	24° 51.493′	1 23° 50.450	/ 1483	180	I	I	409	44.2	16.7	12.4	I	0.5	110.1	4.02 × 10 ⁻¹	0.70902	0.000018	I
	NT08-13 D873 V-2	Gusuku	24° 51.493′	123° 50.450	/ 1483	180	I	526	453	50.9	10.1	10.2	N.D	0.4	89.1	5.72×10^{-1}	0.70915	0.000018	I
	NT08-13 D873 V-3	Gusuku	24° 51.501′	123° 50.466	/ 1472	I	I	549	426	45.1	13.8	16.2	6.0	0.7	97.8	4.61×10^{-1}	0.70902	0.000019	I

Table 1	(continu	(pər																	
Field ID	Sample ID	Site	Latitude N	Longitude E	Depth m	° C ^{max}	рН 25 °C	Cl ⁻ mmol/ kg	Na mmol/ kg	Mg mmol/ kg	Ca mmol/ kg	K mmol/ kg	NH ₄ + mmol/ kg	B mmol/ kg	Sr µmol/ kg	Mg/Sr mmol/ µmol	⁸⁷ Sr/ ⁸⁶ Sr	Error	[Sr] _{EHF} µmol/ kg
	NT08-13 D873 V-4	Gusuku	24° 51.521′	123° 50.467′	1477	I		366	279	14.9	13.5	33.3	5.7	1.7	70.0	2.13 × 10 ⁻¹	0.70878	0.000014	54.9
	NT08-13 D873 W-1	Gusuku	24° 51.510′	123° 50.467'	1477	I	6.35	536	449	51.5	10.0	6.6	0.004	0.4	88.2	5.83×10^{-1}	0.70916	0.000016	I
	NT09-11 D1035 W-1	Gusuku	24° 51.511′	123° 50.473′	1473	320	5.49	312	239	2.0	12.2	41.8	6.6	2.6	49.3	4.00 × 10 ⁻²	0.70852	0.000016	47.1
	NT09-11 D1037 W-3	Gusuku	24° 51.487′	123° 50.463′	1472	320	5.16	391	287	1.0	16.0	47.4	6.2	3.0	62.4	1.60 × 10 ⁻²	0.70855	0.000016	61.5
Yonaguni Knoll IV	YK03-05 D759-W1	Tiger	24° 50.891′	122° 42.035′	1362	323	5.29	550	450	49.2	9.4	6.6	0.1	0.4	81.6	6.02 × 10 ⁻¹	0.70922	0.000007	I
	YK03-05 D760-B	Tiger	24° 50.897′	122° 42.025′	1362	I	5.05	525	I	40.7	10.0	17.3	I	0.8	58.7	6.94 × 10 ⁻¹	0.70961	0.000011	I
	YK03-05 D762-N1	Plume	24° 50.905′	122° 42.033′	1358	I	6.55	563	437	48.0	8.9	9.4	0.04	0.3	79.0	6.08×10^{-1}	0.70920	0.000010	I
	YK03-05 D762-N2	Plume	24° 50.905′	122° 42.033′	1358	I	6.95	553	437	49.0	8.9	9.3	N.D	0.3	79.2	6.18×10^{-1}	0.70917	0.000010	I
	YK03-05 D762-W1	Tiger	24° 50.897′	122° 42.020′	1365	I	I	606	I	18.4	20.5	64.4	5.9	2.8	105.3	1.74×10^{-1}	0.71126	0.000012	95.3
	YK03-05 D762-B	Abyss	24° 50.787′	122° 42.038′	1379	I	5.30	547	456	45.9	9.6	14.4	1.0	0.7	84.1	5.45×10^{-1}	0.70935	0.000013	I
	YK03-05 D763-W2	Tiger	24° 50.885′	122° 42.014′	1361	210	4.91	600	454	22.0	17.8	58.0	5.0	2.5	98.8	2.23 × 10 ⁻¹	0.71104	0.000014	83.8
	YK03-05 D763-W3	Tiger	24° 50.885′	122° 42.014′	1361	210	4.74	589	I	32.1	10.3	41.5	3.3	1.8	63.8	5.03×10^{-1}	0.71054	0.000016	I
	YK03-05 D763-W4	Tiger	24° 50.885′	122° 42.014′	1361	210	4.84	583	465	30.7	15.6	43.7	3.7	1.9	0.76	3.17 × 10 ⁻¹	0.71053	0.000011	I
	YK03-05 D763-B	Tiger	24° 50.885′	122° 42.014′	1361	I	I	583	I	49.4	10.6	10.1	I	0.4	87.3	5.66×10^{-1}	0.70929	0.000010	I

–: No data

Cl⁻ concentration analysis and for on-land cation (Na, Mg, Ca, K, B, and Sr) concentrations and Sr isotopic ratio analyses. The samples in polyethylene bottles for cation concentration and Sr isotopic ratio analyses were further acidified (pH < 2) with 3 M HNO₃ and transported to the laboratory.

3.2 Analytical procedure

Analyses of various chemical components of the fluid were performed as previously described (Toki et al. 2016). The pH of the fluid was analyzed using a glass electrode at room temperature, ~20 to 25 °C. Fluid Clconcentrations were analyzed by Mohr titration, and values were determined using standard seawater (IAPSO) to within 1% precision. Fluid NH_4^+ concentrations were analyzed using the colorimetric method, and a calibration curve was constructed using an ammonium chloride solution to determine the concentration. One sample was measured three times for each analysis to determine the analytical precision. Analytical precision was within 1%. Cations in the fluid were analyzed using inductively coupled plasma optical emission spectroscopy (ICP-OES; Model 5100, Agilent Technology, Santa Clara, CA, USA) at Kyushu University. Concentrations were determined using standard solutions prepared by mixing standard reagents for atomic absorption with an analytical precision within 3%.

Sr was separated from fluid samples with a Sr-Spec resin (mesh size: 50-100 µm; Eichrom Industries), as described by Pin et al. (1994). A 0.15-mL aliquot was placed into a precleaned vial made of perfluoroalkoxy alkane, dried at ~100 $^\circ$ C and then, dissolved in 0.15 mL 2 M HNO₃ (EL grade). A mini-column with a 0.1 mL Sr-Spec resin bed was first washed with 1 mL ultrapure water (Resistivity at 25 °C:18.2 MΩ·cm) and then, conditioned with 0.5 mL 2 M HNO₃. Next, 0.15 mL of the sample solution was loaded onto the column, and the major ions were washed out with 0.15 mL 2 M HNO₃. Barium was eluted with 1.2 mL of 8 M HNO₃. Next, we washed the column with 0.4 mL 2 M HNO₃ and eluted the Sr fraction on the column by adding 1 mL of 0.05 M HNO₃. The Sr fraction was collected in a precleaned vial made of perfluoroalkoxy alkane and dried at ~ 100 °C on a hot plate.

The Sr isotopic ratio (${}^{87}\text{Sr}/{}^{86}\text{Sr}$) of the samples from the Hatoma Knoll in the SOT was measured using thermal ionization mass spectrometry (MAT262; Finnigan). The dried eluent was dissolved in 2 µL of 1 M H₃PO₄, and the solution was loaded onto a Ta filament. The drop was heated and transferred to a thermal ionization mass spectrometer. The measured ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ ratio was normalized to an ${}^{86}\text{Sr}/{}^{88}\text{Sr}$ value of 0.1194. We obtained an average value of 0.710235 ± 0.000028 (1 σ , n = 9) for the National

Institute of Standards and Technology (NIST) SRM-987 standard.

The ⁸⁷Sr/⁸⁶Sr ratios of the other samples were measured via multiple collector-inductively coupled plasma-mass spectrometry (Neptune Plus) with a solution sample of 200 ppb Sr prepared with 0.3 M HNO₃. The values were standardized to NIST SRM-987 (⁸⁷Sr/⁸⁶Sr = 0.71025). The precision is the standard deviation of the measured SRM-987 sample: 0.710252 ± 0.000025 (2σ ; n = 16).

3.3 Endmember calculation

The sample may inevitably be mixed with seawater from the sampling inlet, or the hydrothermal fluids may be combined with seawater below the seafloor before venting. Therefore, it is customary to determine the chemical composition of pure hydrothermal fluids by assuming that they do not contain Mg (Von Damm 1995). This is because laboratory experiments have shown that when basalt, andesite, and rhyolite react with seawater, most of the Mg is removed from the seawater (Bischoff and Dickson 1975; Mottl and Holland 1978; Seyfried Jr and Bischoff 1981; Hajash and Chandler 1982; Shiraki et al. 1987). The endmember Sr concentration for each sample was estimated using the following equations:

 $[Mg]_{sample} = (1-f) \times [Mg]_{EHF} + f \times [Mg]_{SW}$ (1)

$$[Sr]_{sample} = (1-f) \times [Sr]_{EHF} + f \times [Sr]_{SW}$$
(2)

where subscripts indicate the sample, endmember hydrothermal fluid (EHF), and seawater (SW). [Mg]_{EHF}, [Mg]_{SW}, and [Sr]_{SW} were 0, 53 mmol/kg, and 87 µmol/ kg, respectively (Von Damm et al. 1985a); therefore, [Sr]_{FHF} can be calculated from the analytical results of the [Mg]_{sample} and [Sr] _{sample}. Because Mg-poor hydrothermal fluids are obtained from most hydrothermal systems (Table 1; Fig. 2), pure hydrothermal fluids are assumed to be Mg-free to obtain the endmembers. However, this study did not receive Mg-free hydrothermal fluids from the Yonaguni Knoll IV hydrothermal system. Suzuki et al. (2008) also collected samples from the Yonaguni Knoll IV hydrothermal system and obtained almost Mgfree hydrothermal fluids. Therefore, even in the Yonaguni Knoll IV hydrothermal system, pure hydrothermal water was assumed to be Mg-free, and endmembers were obtained. Only by standardization will it be possible to compare hydrothermal waters and chemical compositions worldwide (Von Damm 1995).

To estimate the ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ ratio of the pure hydrothermal fluid at each sampling site, the ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ ratio in the fluid sample was plotted against the $[Mg]_{\text{sample}}/[Sr]_{\text{sample}}$ ratio (Fig. 3). In this plot, mixing between pure fluid and seawater is represented by a straight line. The Mg-free



regression lines through all data and seawater for each site. No such line was drawn for the Yonaguni Knoll IV because of poor fit



y-intercept of the regression line for a hydrothermal site represents the ⁸⁷Sr/⁸⁶Sr ratio of the pure hydrothermal fluid for the hydrothermal site (Albarède et al. 1981).

4 Results

Table 1 lists the analytical results, including the Mg and Sr concentrations and the 87 Sr/ 86 Sr ratios. The endmember Sr concentrations of each sample were calculated using Eq. (1) and (2), which yielded concentrations of 75.5–81.8 µmol/kg (Iheya North Knoll), 120.3–129.1 µmol/kg (HAKUREI), 98.7–99.3 µmol/kg (JADE), 34.7–67.4 µmol/kg (Hatoma Knoll), and 83.6–95.1 µmol/kg (Yonaguni Knoll IV) (Table 1). As the error for endmember extrapolation increases with seawater

entrainment, we limited the discussion to samples with Mg < 30 mmol/kg (Table 1).

The Sr isotopic ratios of the fluid samples collected at Iheya North Knoll, HAKUREI, JADE, Hatoma Knoll, and Yonaguni Knoll IV were 0.70764-0.70770, 0.70920-0.70850-0.70922, 0.70924, 0.70891-0.70895, 0.70917-0.71126, respectively (Table 1). The ⁸⁷Sr/⁸⁶Sr ratios of the pure hydrothermal fluid at each hydrothermal site were estimated based on the 87Sr/86Sr-[Sr]/ [Mg] plot (see Sect. 3.3, Endmember calculation) and are listed in Table 2. The estimated Sr isotopic ratios of the endmembers ranged from 0.7077 (Iheya North Knoll) to 0.7120 (Yonaguni Knoll IV). The endmember Sr isotopic ratio of the hydrothermal fluid at Yonaguni Knoll IV was the highest among all Sr isotopic ratios reported to date from hydrothermal sites worldwide (Table 2 and Fig. 4). The endmember Sr isotopic ratios differed between the HAKUREI (0.7092) and JADE (0.7089) sites. However, both sites are located at the Izena Hole (Ishibashi et al. 2014). The Sr isotopic ratios of the endmembers did not correlate with the Sr concentrations of the endmembers. The Okinawa Trough exhibited no geographic trends in Sr isotopic ratio (Fig. 1 and Table 2).

5 Discussion

5.1 Sr isotopic ratios of venting fluids and subseafloor reservoirs

To understand the diverse fluid–sediment interactions through interpretation of the Sr isotopic ratios, we compared the Sr isotopic ratios of hydrothermal fluids observed to date with those of representative subseafloor Sr reservoirs worldwide (Fig. 4), classified based on tectonic setting and sediment occurrence at the sites. The Sr isotopic ratios of hydrothermal fluids in sediment-starved mid-ocean ridge systems fell within a specific range of 0.7030–0.7042 at EPR21° N and EPR13° N (Albarède et al. 1981; Michard et al. 1984), Kairei (Gamo et al. 2001), and the Kane Fracture Zone and the Endeavor Segment of the Juan de Fuca Ridge (Campbell et al. 1988; Jamieson et al. 2016). The Sr isotopic ratios of sediment-starved

Table 2End-members of Sr isotope ratios in hydrothermal fluidsfrom hydrothermal fields in Okinawa Trough

Field ID	Site	⁸⁷ Sr/ ⁸⁶ Sr
lheya North Knoll		0.7077
Izena Hole	HAKUREI	0.7092
	JADE	0.7089
Hatoma Knoll		0.7085
Yanaguni Knoll IV		0.7120
Minami-Ensei Knoll		0.7100



backarc systems were somewhat higher and within a certain range (0.7036-0.7056) in the Lau Basin (Mottl et al. 2011), Manus Basin (Reeves et al. 2011), North Fiji Basin (Grimaud et al. 1991), and Mariana Trough (Kusakabe et al. 1990). The Sr isotopic ratios of sediment-associated MOR (Mid-ocean ridge) systems are 0.7043 in the Middle Valley (Butterfield et al. 1994), 0.7056 in the Guaymas Basin in the Gulf of California (Piepgras and Wasserburg 1985), 0.7081 at Loki's Castle on the Arctic MOR (Baumberger et al. 2016), and 0.7099 at the Escanaba Trough of the Juan de Fuca Ridge (Campbell et al. 1994), which are relatively high compared with those of sediment-starved hydrothermal systems. Sr isotopic ratios of volcanic rocks were 0.704–0.706 in the Okinawa Trough (Appendix) and 0.7023-0.7030 at the MOR (MOR basalt, MORB; White et al. 1987). The Sr isotopic ratios of bulk sediment on the continental shelf of the East China Sea were virtually identical to those of bulk sediment in the Okinawa Trough (0.713–0.719; Asahara et al. 1995).

5.2 Relationships of Sr isotopic ratios with representative chemical and isotopic compositions of hydrothermal fluids

To assess the co-variation between Sr isotopic ratios and other chemical and isotopic components from the global vent dataset, we plotted several representative parameters of the endmember hydrothermal fluids against the Sr isotopic ratios (Fig. 5a-g). No clear correlation between Sr/Cl and Sr isotopic ratios was detected among global sediment-associated sites, including the Okinawa Trough sites (Fig. 5a), whereas Sr/Cl ratios varied even within the sediment-starved sites. This finding indicates that the Sr isotopic ratios of sediment-associated sites are determined not by a single Sr reservoir or the degree of Sr leaching from a reservoir but by multiple Sr reservoirs. Moreover, no clear correlation was observed between the Ca/Cl and Sr isotopic ratios in the global hydrothermal fluids (Fig. 5b). Reeves et al. (2010) conducted a series of observations in the Manus backarc basin. They found



that the Ca/Cl ratio variation among hydrothermal fluids in this basin is related to the host rock type. For example, the Vienna Wood site is basalt-hosted with a Ca/Cl ratio of approximately 0.12. In contrast, the felsic rock-hosted sites have Ca/Cl ratios lower than 0.06 (Fig. 5b). The relatively low Ca/Cl ratios and variable Sr isotopic ratios in the Okinawa Trough fluids may be attributable to a lower contribution from the Ca-rich mafic rock and comparable contributions from multiple Sr reservoirs (Table 3). Similarly, the large variation in the Ca/Cl ratio but constant Sr isotopic ratios similar to the mid-ocean ridge basalt (MORB) value in sediment-starved hydrothermal fluids may be explained by Ca leaching from plagioclase in basalt (partly substituted by Sr) via albitization (Rosenbauer et al. 1988; Von Damm and Bischoff 1987). No correlation was observed between the K/Cl and Sr isotopic ratios in the hydrothermal fluids analyzed (Fig. 5b and c). Because felsic rocks are more enriched in K than mafic rocks (Sakai et al. 1990), felsic rock-hosted hydrothermal systems, such as the Okinawa Trough and Manus Basin (Reeves et al. 2011), have higher K/Cl ratios than basalthosted hydrothermal systems (Fig. 5c). The K/Cl ratios at the sediment-associated sites were not always high, and we found no clear correlation between the K/Cl and Sr isotopic ratios. This finding suggests that the Sr isotopic ratios in hydrothermal fluids are regulated by factors other than the host rock type (Fig. 5a-c).

The B, NH₄⁺, CH₄, and H₂ concentrations were higher in fluids at sediment-associated hydrothermal sites and were relatively strongly correlated with Sr isotopic ratios (Fig. 5d–g), suggesting that ⁸⁷Sr-rich Sr reservoirs in the fluids were mainly derived from the same B, NH₄⁺, CH₄, and H₂ reservoir sources at sediment-associated hydrothermal sites. NH₄⁺, CH₄, and H₂ in fluids are thought to be generated by the decomposition of sedimentary organic matter, represented by (CH₂O)₁₀₆ (NH₃)₁₆ H₃PO₄ (Redfield 1934), as follows (Piepgras and Wasserburg 1985): suspended particles, including organic particles (Spivack et al. 1987). Sedimentary B is bound to the lattice of clay minerals during burial (Williams et al. 2001) and is released after exposure to high temperatures (> 300 °C; You and Gieskes 2001). Although B enrichment in fluids at sediment-associated sites is not directly related to the decomposition of organic matter (unlike CH₄ and NH₃), sedimentary B and its release at high temperatures are responsible for the abundance of B in fluids.

5.3 Virtually complete removal of seawater-derived Sr

suggested from sediment-starved system observations The Sr isotopic ratios of hydrothermal endmember vent fluids were comparable to those of major subseafloor Sr reservoirs, such as volcanic rocks, recharged seawater, and bulk sediment (Fig. 4). Thus, the Sr isotopic ratios of the hydrothermal endmember fluids can be explained by the Sr influx/efflux of these reservoirs during subseafloor hydrothermal-fluid circulation. The Sr isotopic ratios of hydrothermal fluids in the sediment-starved MOR and backarc systems were within a certain range (0.7034-0.7056), and the Sr isotopic ratios of hydrothermal endmember fluids in the sediment-starved setting were much lower than the seawater value (0.7092) and close to the value for volcanic rocks (0.7023-0.7056). The low Sr isotopic ratios and consistency between fluids and volcanic rocks demonstrate that virtually all seawaterderived ⁸⁷Sr recharged into the subseafloor was removed, and ⁸⁷Sr-depleted Sr was leached from volcanic rocks into the fluid. This observation-based model is consistent with experimental simulation studies on hydrothermal fluid-mineral interactions, in which Sr in the liquid phase (i.e., recharged seawater) is removed through co-precipitation with anhydrite when heated to 200 °C (Albarède et al. 1981; Wilckens et al. 2019), whereas Sr in some minerals (e.g., from volcanic rock and sediment) is released into fluids at temperatures above 200 °C (Wei

$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 106H_2O \rightarrow 106CO_2 + 212H_2 + 16NH_3 + H_3PO_4,$$
(3)

$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 106H_2O \rightarrow 53CO_2 + 53CH_4 + 16NH_3 + H_3PO_4$$
(4)

These ideal equations assume a reaction that generates CO_2 and an intermediate product, H_2 (Eq. 1), followed by methanogenesis with 4:1 H_2 : CO_2 stoichiometry (Eq. 4). In these equations, the NH_3 generated was equilibrated with water as follows:

 $NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-(5).$

B in the fluid is considered to originate from B in the sediment. Sedimentary B is generally abundant because of its accumulation by adsorption onto the surfaces of 2007; Berndt et al. 1988; James et al. 2003). The removal of seawater-derived Sr through co-precipitation with anhydrite is also expected in sediment-associated high-temperature hydrothermal fluids because of its sulfate-depleted nature at temperatures higher than 200 °C (Albarède et al. 1981; Wilckens et al. 2019). This suggests that Sr derived from recharged seawater accounts for a negligible proportion of Sr in the hydrothermal vent fluids in the Okinawa Trough.

5.4 Possible contribution of ⁸⁷Sr-rich terrestrial minerals in sediment to Sr isotopic ratios of hydrothermal fluid in the Okinawa Trough

Because the Sr isotopic ratios of volcanic rocks in the Okinawa Trough are low and fall within a specific range (Appendix), the high Sr isotopic ratios of fluids at the Okinawa Trough sites (Fig. 4) are attributable to reactions with ⁸⁷Sr-rich sediments. To understand how sedimentary Sr reservoirs contribute to the venting fluid at sediment-associated sites, we considered the compositional characteristics of the Okinawa Trough sediments and the possible Sr isotopic ratios of each Sr-bearing component.

The sediments of the Okinawa Trough contain several Sr-bearing components, such as organic matter originating from primary production in the ocean surface layer, biological skeletons, and clastic debris weathered from the continental crust. Organic matter occupies < 10% of the bulk sediment, and the Sr content of sedimentary organic matter is approximately 10 ppm (Gao et al. 2008). The Sr content in the organic matter can be as low as ppb in bulk sediments and is negligible as a Sr source for hydrothermal fluids (Gao et al. 2008). The ⁸⁸Sr/⁸⁶Sr ratios of hydrothermal fluids suggest a significant contribution of Sr derived from biogenic carbonates to hydrothermal fluid Sr (Yoshimura et al. 2020). The Sr isotopic ratio of sedimentary biogenic carbonate produced by foraminifera or coccoliths in seawater columns is identical to that of seawater at the time of formation (Stevenson et al. 2009). Throughout the history of the Okinawa Trough, the variation in seawater ⁸⁷Sr/⁸⁶Sr isotopic ratios has remained virtually constant at 0.7092 (Glasby and Notsu 2003; Elderfield and Schultz 1996; McArthur et al. 2001; Mokadem et al. 2015). Some data in the hydrothermal fluid at Yonaguni Knoll IV fall into the seawater value, not on the simple mixing line between the ⁸⁷Srpoor endmember and seawater (Figs. 2 and 3), which may be because of the contribution of sedimentary biogenic carbonate.

Because of their terrestrial origin, sedimentary clay minerals and quartz in the Okinawa Trough have high ⁸⁷Sr/⁸⁶Sr ratios. Clay minerals and quartz deposited in the Okinawa Trough are transported in large quantities from Eurasia via the Yangtze and Yellow Rivers (Yuan et al. 2008). The Sr isotopic ratios of bulk terrestrial sands on the Loess Plateau, one of the largest mineral sources for rivers, ranged from 0.71418 to 0.72045 (Yokoo et al. 2004). Specifically, the Sr isotopic ratios, estimated by processing bulk sand with HCl, were 0.71379–0.71563 and 0.71867–0.72157, respectively (Yokoo et al. 2004). The Sr contents of clay minerals and quartz in the Okinawa Trough have been found to be 100–300 ppm and

100–150 ppm, respectively (Yokoo et al. 2004). Because high ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ isotopic ratios (0.71418–0.72045) of sedimentary clay minerals and quartz were expected in the Okinawa Trough, the ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ isotopic ratio of 0.7120 at the Yonaguni Knoll IV site cannot be explained without the Sr contribution from these terrestrial components. The ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ isotopic ratios observed in this study suggest that in addition to volcanic rocks, sedimentary biogenic carbonate, terrestrial clay minerals, and quartz are likely to be Sr sources for the fluid.

5.5 Involvement of sediment in the high-temperature reaction zone

The higher concentrations of B, NH_4^+ , CH_4 , and H_2 in hydrothermal fluids among sediment-associated systems, including the Okinawa Trough sites, suggest the involvement of sediments in the high-temperature reaction zone. To explain the variation in Sr isotopes among the hydrothermal fluids, we developed a simple hypothesis (Fig. 6). The subseafloor hydrothermal fluid loses seawater-derived Sr during heating by anhydrite precipitation. It monotonously accumulates Sr through Sr leaching from the solid phase. Sr removal, excluding anhydrite precipitation, did not occur until venting. In this hypothesis, the critical parameter is the temperature of the fluid-sediment interaction. For example, at the Yonaguni IV site, which is characterized by high Sr isotopic ratios, high-temperature (>150 °C; Wei 2007) fluid-sediment interactions should be substantial because of the intense leaching of ⁸⁷Sr-rich components in sedimentary clay minerals and quartz. In the Iheya North Knoll and Hatoma Knoll, characterized by relatively low Sr isotopic ratios in hydrothermal systems in the Okinawa Trough, high-temperature fluid-sediment interactions are absent, and both sedimentary and volcanic rock Sr reservoirs play comparable roles in controlling the vent Sr isotopic ratios.

Our hypothesis can be incorporated into a previously developed model that describes how sedimentary organic matter interacts with subseafloor hydrothermal fluid from the perspective of carbon isotopic ratios in CH₄ (Fig. 6; Kawagucci et al. 2011, 2013; Kawagucci 2015; Toki et al. 2016). According to the model, the ¹³C-rich thermogenic CH₄ and ⁸⁷Sr-rich terrestrial Sr in the Yonaguni IV and Minami-Ensei sites indicate a substantial contribution to the thermal decomposition of sedimentary organic matter (>100 °C) in addition to high-temperature leaching of Sr from clay minerals and quartz, representing a high-temperature fluid-sediment interaction in the subseafloor reaction zone (Fig. 6a). In contrast, the model also indicated that the ¹³C-depleted biogenic CH₄ signature and ⁸⁷Sr-poor volcanic Sr signature found at the Iheya North Knoll and Hatoma Knoll



sites suggest metabolic degradation of sedimentary organic matter in the cool fluid recharge zone (< 122 °C), with a supply of volcanic rock-derived Sr following the removal of Sr associated with anhydrite precipitation below 150 °C (Fig. 6b). In this case, ⁸⁷Sr-poor Sr generated through high-temperature fluid–rock interactions in the reaction and discharge zones is likely the Sr source for the venting fluid. Thus, the model provides a reasonable explanation for the observed isotopic compositions of carbon and Sr in the hydrothermal fluids of sediment-associated systems.

6 Conclusions

Hydrothermal fluids were collected from the Okinawa Trough, and their Sr isotopic ratios were measured. The Sr isotopic ratios of hydrothermal fluids from Yonaguni Knoll IV were extremely high, in agreement with previously published results from the Minami-Ensei Knoll. Such ⁸⁷Sr-rich isotopic ratios of hydrothermal fluids might be a common feature of sediment-associated hydrothermal systems. These results are consistent with a recent model describing how sedimentary organic matter interacts with fluid within a subseafloor hydrothermal fluid circulation developed from the perspective of the carbon isotopic ratios of CH₄. In this model, sediments are distributed around the reaction zone at the Yonaguni Knoll IV and Minami-Ensei sites, where the hydrothermal fluids bear ¹³C-rich thermogenic CH₄ and ⁸⁷Sr-rich terrestrial Sr. However, in the Iheya North Knoll and Hatoma Knoll sites, where the hydrothermal fluids bear ^{13}C -depleted biogenic CH₄ and ^{87}Sr -poor volcanic Sr, sediments are distributed around the recharge zone. Thus, both tracers are an advantageous way to determine whether fluids interact with sediments in the hydrothermal reaction zone. To further justify the model's ability to clarify how subseafloor fluid–sediment interactions affect fluid chemistry, exploring the isotope systematics of multiple elements such as B and Li will be helpful.

Appendix

Data from volcanic rocks.

For our analyses, we used previously reported data (Shinjo et al. 1999; Shinjo and Kato 2000) and rock samples collected from dredges and dives (using remotely operated vehicles and submersibles) of the SOT during several cruises. Table 3 lists the locations and identities of the sampling points, which are plotted as solid yellow circles in Fig. 1b. Analytical procedures were based on previously described methods (Pin et al. 1994). Before collecting measurements, we rinsed the rocks in an ultrasonic bath and repeatedly washed them in hot ultrapure water for 1-3 weeks to eliminate the influence of seawater. The rock samples were crushed to powder using an agate mill before leaching in hot 6 M HCl (EL grade). After separation, the measurements were collected using thermal ionization mass spectrometry (MAT262; Finnigan). The dried eluent was dissolved in 1 M H₃PO₄ (2 μ L), loaded onto a tantalum filament, and next, the solution was dried with a current. The ⁸⁷Sr/⁸⁶Sr values were

Cruise	Sample	Latitude	Longitude	Depth	⁸⁷ Sr/ ⁸⁶ Sr	Error	Туре
		Ν	E	m			
YK00-06	562–3	25° 14.26′	124° 52.89′	1913	0.704565	18	Basaltic andesite
	562-8	25° 14.17′	124° 52.84′	1924	0.704133	16	Basalt
	562-10	25° 13.85′	124° 52.41′	1898	0.704706	10	Basaltic andesite
	569-2	25° 14.42′	124° 52.52′	2085	0.704780	28	Basalt
	569-3	25° 14.34′	124° 52.82′	1996	0.704741	18	Andesite
	563-2	25° 15.82′	124° 24.62′	2117	0.704026	16	Basalt
	564-2	24° 59.41′	124° 45.84′	1703	0.704429	18	Basaltic andesite
NT00-06 Leg 1	460-1	24° 57.83′	124° 12.15′	1613	0.704542	16	Dacite
	460-6	24° 58.34′	124° 13.49′	1514	0.704116	16	Dacite
N95-06	956,232	24° 51.00′	124° 05.00′	1633	0.704572	16	Rhyolite
N96-07	9,651,411	24° 46.00′	123° 59.00′	1861	0.705506	16	Andesite
NT00-06 Leg 1	1178-1	24° 42.61′	123° 06.05′	1493	0.704518	16	Basalt
	1178-2	24° 42.58′	123° 06.00′	1439	0.704528	18	Basaltic andesite
	1177-4	24° 56.98′	123° 11.86′	1757	0.704545	18	Basalt
	1177-5	24° 57.00′	123° 12.03′	1749	0.704616	18	Basaltic andesite
YK00-06	559-1	24° 56.24′	123° 06.37′	1902	0.704616	18	Rhyolite
	559-6	24° 55.36′	123° 05.91′	1640	0.704334	34	Rhyolite
KH-02-1 Leg 3	D6-4	24° 51.97′	122° 06.70′	1620	0.704125	18	Basalt
NT00-06 Leg 1	459-1	24° 48.85′	122° 56.93′	1542	0.706055	14	Dacite
	459-3	24° 48.01′	122° 57.00′	1514	0.706077	16	Andesite
	1176-5	24° 51.73′	122° 43.58′	1367	0.705512	18	Rhyolite
	1176-7	24° 51.89′	122° 43.18′	1156	0.705552	16	Rhyolite
YK00-06	560-4	24° 51.28′	122° 41.96′	1284	0.705606	18	Rhyolite
	560-7	24° 51.54′	122° 42.08′	1186	0.705587	14	Rhyolite
KH-02-1 Leg 3	D5-5	24° 54.29′	122° 44.94′	1265	0.705596	18	Rhyolite
	D5-5X	24° 54.29 ′	122° 44.94 ′	1265	0.704502	18	Basaltic andesite

Table 3 Rock sample identities and Sr isotope ratios in this study

normalized using the average value (0.71023 ± 0.00060) of the NBS987 standard material (National Bureau of Standards).

Table 3 lists the analytical results for the rock samples. The values ranged from 0.704026 to 0.706077, indicating that they were more enriched in ⁸⁷Sr than MORB (0.7023–0.7030; White et al. 1987). These rock samples were more radiogenic than basalts collected from the middle to southern regions of the Okinawa Trough (0.703686–0.704620; n = 15; Shinjo et al. 1999). Volcanic rocks collected west of 123°E had a higher ⁸⁷Sr/⁸⁶Sr ratio than those collected from the MOT (0.704018–0.704884; n = 14; Shinjo and Kato 2000). However, volcanic rocks east of 123°E had values comparable to those of volcanic rocks from the MOT (Table 3). Based on these integrated data, the ⁸⁷Sr/⁸⁶Sr ratio of the volcanic rocks in the Okinawa Trough was found to be 0.7030–0.7049 (bold red bar in Fig. 3).

Abbreviations

CK: Drilling vessel *Chikyu*; DSV: Deep-submergence vehicle; EPR: East Pacific Rise; IAPSO: International Association for the Physical Sciences of the Oceans; ICP-OES: Inductively coupled plasma optical emission spectroscopy; IODP: Integrated Ocean Drilling Program; JAMSTEC: Japan Agency for Marine-Earth Science and Technology; KY: Research vessel *Kaiyo*; MOR: Mid-ocean ridge; MORB: Mid-ocean ridge basalt; MOT: Middle Okinawa Trough; NBS: National Bureau of Standards; NIST: National Institute of Standards and Technology; NOT: Northern Okinawa Trough; NT: Research vessel *Natsushima*; ROV: Remotely operated vehicle; SOT: Southern Okinawa Trough; SRM: Standard reference material; SUGAR: Super-cutting-edge Grand and Advanced Research Program; WHATS: Water and Hydrothermal Fluid *Atsuryoku* Tight Sampler; X-star: Institute for Extra-cutting-edge Science and Technology Avant-Garde Research; YK: Research vessel *Yokosuka*.

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Author contributions

TT conceived the study, obtained funding, and conducted the sampling, analysis, data processing, and manuscript writing and revision. TN conducted

the analysis and data processing and wrote the first draft of the manuscript. YU conducted the analysis and data processing and wrote the first draft of the manuscript. RS obtained funding, conducted the analysis and data processing, and wrote and revised the manuscript. SH-W analyzed and processed the data and wrote the first draft of the manuscript. JI conceived the study, obtained funding, conducted the sampling and analysis, and revised the manuscript. SI SK conceived the study, conducted sampling, and revised the manuscript. All authors read and approved the final manuscript.

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Availability of data and materials

All newly obtained data from this study are presented in the manuscript, and data sharing is not applicable.

Declarations

Competing interests

The authors declare that they have no competing interests.

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