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Metal sources of black smoker chimneys, Endeavour Segment, Juan de Fuca Ridge: Pb isotope constraints

Hui-Qiang Yao [a,b,c], Huai-Yang Zhou [a,b,*], Xiao-Tong Peng [a,b], Shen-Xu Bao [a,b,c], Zi-Jun Wu [a,b], Jiang-Tao Li [a,b], Zhi-Lei Sun [a,b,c], Zhi-Qiang Chen [a,b,c], Ji-Wei Li [a,b,c], Guang-Qian Chen [a]

[a] Guangzhou Institute of Geochemistry Chinese Academy of Science, Guangzhou 510640, China
[b] National Key Lab of Marine Geology, Tongji University, Shanghai 200092, China
[c] Graduate University of Chinese Academy of Sciences, Beijing 100049, China

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ABSTRACT

Hydrothermal chimney sulfides, vent cap chimney samples, Fe-oxide and basalts from sediment-starving Juan de Fuca Ridge, in the Endeavour segment, exhibit a range of Pb isotope ratios ($^{206}Pb/^{204}Pb$ = 18.658–18.769; $^{207}Pb/^{204}Pb$ = 15.457–15.566; $^{208}Pb/^{204}Pb$ = 37.810–38.276). The data array is not parallel to the northern hemisphere mantle reservoirs indicating a possible sediment component within the sulfides. By assuming that the potential end-member sediment component has a $^{207}Pb/^{204}Pb$ (15.70) similar to Middle Valley sediment, it is suggested the potential end-member sediment component may have $^{206}Pb/^{204}Pb$ = 18.90; $^{208}Pb/^{204}Pb$ = 38.82. Basalt-derived Pb for the Endeavour segment hydrothermal system involves about 50/50 leaching of E-MORB and T2-MORB. Detailed observations show the Mothra field derives more Pb from T2-MORB than the Main Endeavour field does. According to the binary mixing model, the results show little Pb (<1.5%) or no Pb derivation from sedimentary sources. However, the high NH_4^+, CH_4 and Br/Cl ratios in hydrothermal fluids are consistent with a sediment component within the segment. Reconciling the Pb isotope data with the chemistry data of hydrothermal fluids, it is suggested that the sediment component may be located in a lower temperature recharge zone where Pb could not be mobilized from the sediment.

1. Introduction

Since the late 1970s, active and inactive seafloor hydrothermal systems that host poly-metallic massive sulfide deposits have been found in various tectonic settings on the modern seafloor, including mid-ocean ridge, intra-oceanic arcs, back-arc rifts and seamounts (Delaney et al., 1992; Hannington et al., 2005; Peter and Shanks, 1992; Styrt et al., 1981; Teagle et al., 1998a,b; Tivey et al., 1999). Mid-ocean ridges can be divided into two categories: sediment-covered ridges, such as the Escanaba Trough in southern Gorda Ridge (Von Damm et al., 2005; Zierenberg et al., 1993), the Guaymas Basin in the Gulf of California (Charlou et al., 2002; LeHuray et al., 1988), and the Middle Valley in the northern Juan de Fuca ridge (Bjerkgård et al., 2000; Cousens et al., 2002; Stuart et al., 1999); and sediment-starved ridges, like the TAG field in the Atlantic ridge (Andrieu et al., 1998), the Southern Juan de Fuca Ridge (SJDF) (Hegner and Tatsumoto, 1987; LeHuray et al., 1988), East Pacific Rise (9–10°, 11°,13°, 21°N, 17°S, 18°S, 21°S) (Bluth and Ohmoto, 1988; Fornari et al., 1998; Rachel and Kastner, 1981; Woodruff and Shanks, 1988) and the Endeavour Segment in the Juan de Fuca Ridge (Glickson et al., 2007; Kelley et al., 2001). Hydrothermal fluids from the Endeavour segment have anomalous highly CH_4 and NH_4^+, similar to that of sediment-covered ridges. Therefore, it is inferred that interaction between hydrothermal fluid and organic material has occurred somewhere below the seafloor. The source of the organic material could be either buried sediments or biomass generated by chemosynthetic bacteria inhabiting the sulfide structures. Since the isotopic characteristics of the CH_4 and NH_4^+ in the fluid do not match those of hydrothermal biota sampled from the Endeavour vent sites, interaction with organic matter in sediment is the preferred explanation for the chemical anomalies (Lilley et al., 1993). The anomalously high concentrations of alkalis and B also support the hypothesis that hydrothermal fluid at the Endeavour segment interacts with buried sediments (Butterfield et al., 1994; You et al., 1994).

Studying Pb isotopes is important for the understanding of seafloor hydrothermal processes and the sources of metals in hydrothermal deposits, for the chemical behavior of Pb is similar to that of the other chalcophile elements concentrated in black smoker chimney sulfides (Fouquet and Marcoux, 1995). Lead isotopes can also provide constraints on whether Pb in hydrothermal

* Corresponding author. Address: National Key Lab of Marine Geology, Tongji University, Shanghai 200092, China. Fax: +86 21 65987615.
E-mail addresses: hqyao11@yahoo.com (H.-Q. Yao), zhouhy@tongji.edu.cn (H.-Y. Zhou).

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deposits was derived from leaching of oceanic crust during high-temperature alteration, from seawater, or from sediment. Previous studies of Pb isotopic compositions of sulfides sampled from sediment-starved ridges show that the Pb isotope compositions of sulfides are more homogeneous than that of adjacent volcanic rocks, suggesting that Pb isotopes have been homogenized during hydrothermal circulation. However, studies of the Pb isotopic composition of sulfides and basalts from the Endeavour segment are limited. The few published Pb isotopic composition data of sulfides from this segment show that sulfides from the Endeavour segment are more radiogenic than sulfides from the Southern Juan de Fuca Ridge, also a sediment-starved ridge, and are lower than those of sulfides from the Middle Valley (LeHuray et al., 1988). This paper presents the Pb isotope composition of hydrothermal chimney sulfides, vent cap chimney samples, Fe-oxide and basalts from the Endeavour segment to determine the metal sources and evaluate the potential influence of a sediment component within the area.

2. Geological settings

The Juan de Fuca Ridge (JFR) system, located between 44°N and 48°N off the coasts of British Columbia, Canada, and Washington and Oregon, USA is a medium-rate spreading center with a half-spreading rate of about 3–4 cm/a (Fig. 1a). The JFR is divided into the Middle Valley segment, the West Valley segment, the Endeavour segment, the Cobb segment, the CoAxial segment, the Axial segment, the Vance segment and the Cleft segment from north to south. The approximately 90 km long Endeavour segment, bounded both north and south by overlapping spreading centers, contains six main hydrothermal vent fields, Sasquatch, Salty Dawg, High Rise, Clam Bed, Main Endeavour and Mothra, from north to south in sequence. The axis of the Endeavour segment is a 25 km long volcanic high split by a 75–200 m deep, 0.5–1 km wide, steep-sided axial valley, which widens to the south, reaching a width of about 3 km at the south end of the segment (Glickson et al., 2007). SeaMARC I and Alvin observations testify that recent volcanism is restricted to the narrow floor of the valley (Delaney et al., 1992; Kappel and Ryan, 1986; Tivey and Delaney, 1986).

The Main Endeavour vent field, located near 47°57′N and 129°05′W (Fig. 1b and c), is situated on the axial valley floor at a depth of ca. 2200 m. This field has been studied for more than two decades and hydrothermal vents have been mapped in detail. Both the size of the sulfide structure and the quantity of high-temperature fluid discharge at this field are large, compared to most other hydrothermal fields (Butterfield et al., 1994). The Clam Bed vent field, characterized by diffuse flow and a single major vent within pillow basalts, is located ca. 1.4 km north of the Main Endeavour field (Tivey et al., 1999). The Mothra vent field parallels the ridge axis, located ca. 2.7 km south of the Main Endeavour vent field, and covers an area of at least 500 m long (Fig. 1d). The sulfide structures in the Mothra field are characterized by steep-sided pinnacles that reach up to 20 m above the seafloor, which distinguishes it from other Endeavour segment venting fields (Kelley et al., 2001). The Sasquatch, Salty Dawg and High Rise vent fields were not sampled, so they are not discussed in the paper.

3. Samples and analytical techniques

All the samples were collected by DSRV Alvin from the Endeavour segment during the AT11-31 cruise. Vent cap chimney samples are the fragments of new formed chimney on a test collar which includes an array of thermocouples deployed on a vent chimney. The temperature of 1#Cap, 2#Cap and 3#Cap shown by the thermocouples were 332 °C, 310 °C and 290 °C, respectively. The

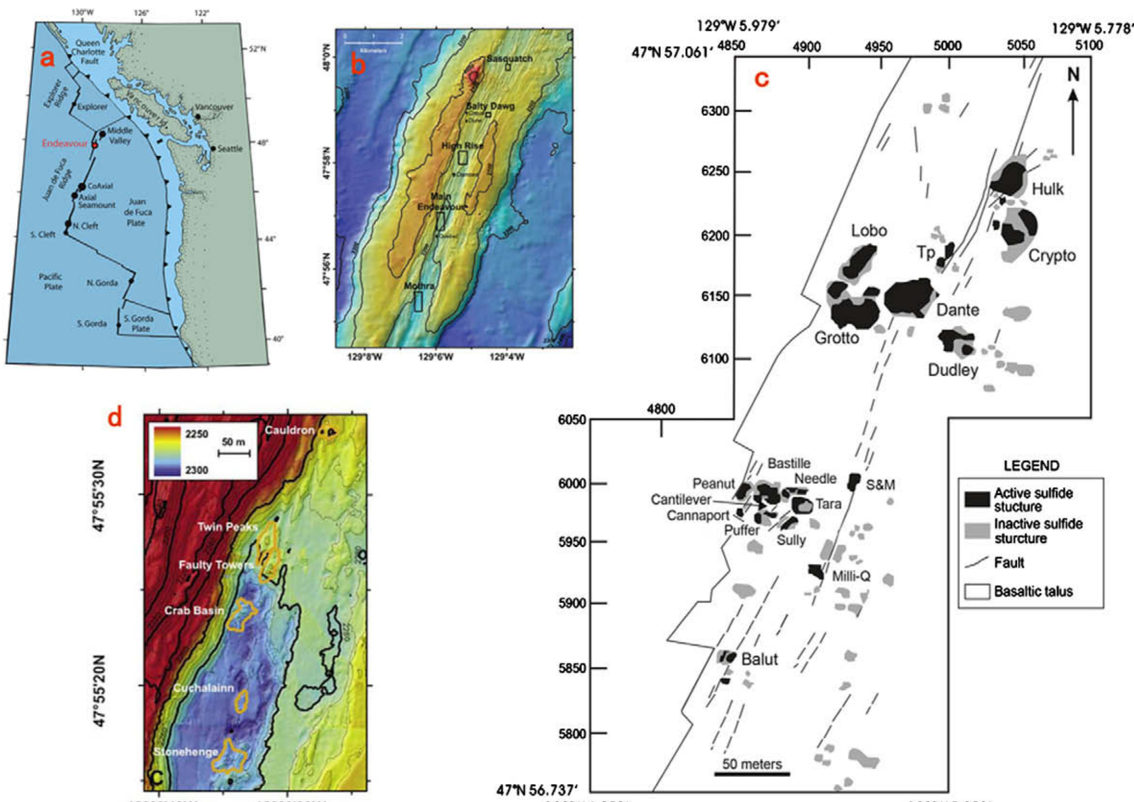

Fig. 1. (a) General geologic map showing the location of the Endeavour Segment, Juan de Fuca Ridge; (b) the main hydrothermal fields on the Endeavour Segment; (c) detailed geologic map of Main Endeavour hydrothermal field; (d) detailed geologic map of the Mothra hydrothermal field. Modified from Delaney et al. (1992) and Kelley et al. (2001).

Fe-oxide sample was collected carefully from the outer wall of a black smoker chimney. Table 1 gives information about sampling location, mineralogy of the related vent field. All the samples used for Pb isotopic determination were ultrasonically cleaned in ultra-pure water three times in order to remove the influence of seawater. About 30 mg of hydrothermal chimney sulfide samples and one Fe-oxide were dissolved in an HCl–HNO_3 mixture. About 1 g of basaltic rock powder was dissolved by an HF–HNO_3–$HClO_4$ mixture at 100 °C. Insoluble matter was removed from the final HNO_3 solution by centrifugation, and the final solution was dried, and redissolved in HBr for Pb separation and isotopic analysis. Lead was separated twice using the HBr–HCl anion exchange method. The separated Pb was loaded on single Re filaments with H_3PO_4 and silica gel. Isotope ratios were measured on a Finnigan MAT 262 mass spectrometer and corrected for mass fractionation of +0.09% a.m.u-1 on the basis of multiple analysis of NIST 981 with an external reproducibility of 0.05%. One duplicate run of sample 4143-3 showed good agreement between the two results (Table 2). Total procedural blanks for sulfides and Fe-oxide were <1 ng and total procedural blanks for basalt samples were about 50 pg.

Lead abundances were measured on separate 40 mg splits of bulk sulfide by ICP-AES using the dissolution procedure outlined above for isotope determinations. Duplicate runs of internal standards gave a reproducibility of ±5%.

4. Results

A total of 26 samples, including 20 hydrothermal black smoker chimney sulfides, three vent cap chimney samples, two basaltic rocks and one Fe-oxide, were analyzed and the results are listed in Table 2. The Pb isotopic compositions of hydrothermal sulfides display a substantial range of values ($^{206}Pb/^{204}Pb$ = 18.658–18.769; $^{207}Pb/^{204}Pb$ = 15.457–15.566; $^{208}Pb/^{204}Pb$ = 37.810–38.276). The $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ values show a similar span compared with published data ($^{206}Pb/^{204}Pb$ = 18.58–18.75; $^{207}Pb/^{204}Pb$ = 15.45–15–53; $^{208}Pb/^{204}Pb$ = 37.84–38.10), while $^{208}Pb/^{204}Pb$ values are higher (Labonte et al., 2006; LeHuray et al., 1988). The three vent cap chimney samples show a narrower range ($^{206}Pb/^{204}Pb$ = 18.692–18.697; $^{207}Pb/^{204}Pb$ = 15.491–15.495; $^{208}Pb/^{204}Pb$ = 38.018–38.020), indicating that the Pb isotopic compositions of modern discharging hydrothermal fluids are homogenized by the circulation of high-temperature fluids. The two basaltic rocks from the Clam Bed hydrothermal field display a relatively wide range of Pb isotopic composition ($^{206}Pb/^{204}Pb$ = 18.656–18.715; $^{207}Pb/^{204}Pb$ = 15.485–15.525; $^{208}Pb/^{204}Pb$ = 37.036–38.121) with the average value identical to that of the three vent cap samples. The one Fe-oxide sample has a Pb isotope composition similar to hydrothermal chimneys ($^{206}Pb/^{204}Pb$ = 18.749; $^{207}Pb/^{204}Pb$ = 15.524; $^{208}Pb/^{204}Pb$ = 38.153).

There are no obvious differences in Pb isotopic compositions of hydrothermal chimneys among the different hydrothermal fields. Four samples from the Clam Bed hydrothermal field with average values of $^{206}Pb/^{204}Pb$ = 18.734; $^{207}Pb/^{204}Pb$ = 15.536; $^{208}Pb/^{204}Pb$ = 38.167, and nine samples and one repeated analysis result from the Main Endeavour hydrothermal field have average values of $^{206}Pb/^{204}Pb$ = 18.711; $^{207}Pb/^{204}Pb$ = 15.508; $^{208}Pb/^{204}Pb$ = 38.066, and seven samples from the Mothra hydrothermal field show average values of $^{206}Pb/^{204}Pb$ = 18.727; $^{207}Pb/^{204}Pb$ = 15.499; $^{208}Pb/^{204}Pb$ = 38.073. Samples from the Clam Bed hydrothermal field and the Main Endeavour hydrothermal field have higher $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios at given $^{206}Pb/^{204}Pb$ than those from the Mothra hydrothermal field.

Table 1
The description of samples from the Endeavour Segment of Juan de Fuca Ridge.

Sample	HF	Vent site	Description	Mineralogy
Hydrothermal chimney sulfides				
4136-A	Clam Bed	Clam Bed	Fragment of chimney 4136	Cpy, Py, Sph
4136-B		Clam Bed	Fragment of chimney 4136	Cpy, Sph
4136-1-1		Clam Bed	Fragment of chimney 4136-1	Sph, Py, Ba
4136-1-8		Clam Bed	Fragment of chimney 4136-1	Sph, Py, Cpy, Ba
4132	NMEHF	Dudley	Fragment of chimney 4132	Cpy
4137-3		Dante	Fragment of chimney 4137	Py, Sph
4137-5		Dante	Fragment of chimney 4137	Py, Cpy, Sph
4133-A	SMEHF	S&M	The inner wall of chimney 4133	Cpy, Py, Sph
4133-C		S&M	The outer wall of chimney 4133	Py, Sph, Cpy
4148-A		Sully	The inner wall of chimney 4148	Cpy
4148-C		Sully	The outer wall of chimney 4148	Py, Sph
4135-1		Peanut	The top part of chimney 4135-1	Py, Sph
4135-2		Peanut	Fragment of chimney 4135-1	Py, Sph, An
4140	Mothra	FT	Fragment of chimney 4140	Py, Sph, An,
4143-A		FT	The inner part of chimney 4143	Py, Cpy, Sph
4143-C		FT	The outer wall of chimney 4143	Py, Sph
4143-2-C		FT	Fragment of chimney 4143-2	Cpy, Py, Sph
4143-2-E		FT	Fragment of chimney 4143-2	Py, Sph
4143-3-B		FT	The outer wall of chimney 4143-3	An, Sph, Py, Cpy
4143-3-F		FT	The outer wall of chimney 4143-3	Sph, Py, Cpy
Vent cap chimney samples				
1#Cap	MEHF	Dudley	Vent cap chimney, with about 15 days history	An, AmSi, Py, Cpy, Sph
2#Cap		S&M		An, AmSi, Py, Sph
3#Cap		Gremlin		An, AmSi, Py, Sph
Fe-oxide				
4143-2-D	Mothra	FT	Red, on the outer wall of chimney 4143-2	Fe-oxide
Basalt				
4136-1-8B	Clam Bed	Clam Bed	At the bottom of chimney 4136-1	Whole rock
4136-2-3B		Clam Bed	At the nearby of chimney 4136-2	Whole rock

HF indicates hydrothermal field; NMEHF indicates the North of Main Endeavour Hydrothermal Field (at the north of the coordinate 6050 shown in the Fig. 1c); SMEHF indicates the South of Main Endeavour Hydrothermal Field (at the South of the coordinate 6050 shown in the Fig. 1c); FTs indicates Fawlty Towers; Minerals are Py, pyrite; Cpy, chalcopyrite; Sph, sphalerite, An, anhydrite; Ba, barite; AmSi, amorphous silica.

Table 2
Pb isotope compositions of black smoker chimney sulfides, vent cap chimney samples and Fe-oxide and basalts from the Endeavour Segment of Juan de Fuca Ridge.

Sample	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	Pb/ppm
Hydrothermal chimney sulfides				
4136-A	18.769 (±3)	15.566 (±3)	38.276 (±8)	309
4136-B	18.720 (±3)	15.503 (±3)	38.075 (±8)	64
4136-1-1	18.741 (±3)	15.559 (±3)	38.228 (±10)	283
4136-1-8	18.707 (±3)	15.517 (±4)	38.090 (±11)	2379
4132	18.678 (±2)	15.472 (±2)	37.957 (±5)	<50
4137-3	18.730 (±3)	15.527 (±2)	38.147 (±7)	935
4137-3[a]	18.728 (±3)	15.522 (±2)	38.138 (±7)	
4137-5	18.699 (±16)	15.496 (±14)	38.030 (±89)	388
4133-A	18.709(±1)	15.506 (±2)	38.070 (±4)	60
4133-C	18.718 (±1)	15.524 (±1)	38.129 (±4)	158
4148-A	18.707 (±2)	15.505 (±3)	38.061 (±7)	<50
4148-C	18.739 (±5)	15.531 (±5)	38.139 (±14)	929
4135-1	18.739n (±7)	15.543 (±6)	38.179 (±18)	1497
4135-2	18.658 (±3)	15.457 (±2)	37.810 (±6)	<50
4140	18.700 (±4)	15.469 (±4)	37.980 (±13)	n.m.
4143-A	18.738 (±2)	15.509 (±2)	38.099 (±7)	210
4143-C	18.720 (±1)	15.495 (±1)	38.049 (±3)	395
4143-2-C	18.738 (±5)	15.508 (±5)	38.106 (±13)	741
4143-2-E	18.765 (±5)	15.546 (±4)	38.229 (±10)	2904
4143-3-B	18.718 (±4)	15.498 (±4)	38.067 (±10)	1230
4143-3-F	18.708 (±4)	15.467 (±4)	37.981 (±13)	2060
Vent cap chimney samples				
1#Cap	18.696 (±1)	15.494 (±1)	38.020 (±2)	<50
2#Cap	18.692 (±1)	15.495 (±1)	38.018 (±2)	<50
3#Cap	18.697 (±2)	15.491 (±2)	38.018 (±4)	<50
Fe-oxide				
4143-2-D	18.749 (±5)	15.524 (±5)	38.153 (±13)	2364
Basalt				
4136-1-8B	18.656 (±3)	15.485 (±2)	38.036 (±5)	n.m.
4136-2-3B	18.715 (±4)	15.525 (±4)	38.121 (±11)	n.m.

All Pb data were corrected for mass fractionation (0.09% per atomic mass unit), and analytical error (2) is reported for each ratio.
[a] Indicates the repeated analysis sample; n.m. indicates not determined.

There are comparable ranges in Pb isotopic composition for different sulfides of individual chimneys in the same hydrothermal field, for example chimneys 4136 and 4136-1 from the Clam Bed hydrothermal field; chimneys 4133, 4137 and 4148 from the Main Endeavour hydrothermal field; chimneys 4143-2 and 4143-3 from the Mothra hydrothermal field. For a single chimney, the difference in $^{208}Pb/^{204}Pb$ decreases from the Clam Bed hydrothermal field in the north (the differences for chimney 4136 is 0.201 and for chimney 4136-1 is 0.138, obviously wider than the variation of sediment-starved ridges samples) to the Main Endeavour hydrothermal field (the differences for chimney 4133 is 0.059 and for 4148 is 0.079, comparable to the analysis error) to the Mothra hydrothermal field in the south (the differences for chimneys 4143 and 4143-2 are within the analysis error). Even though many studies show that there are no differences in Pb isotopic ratios among different minerals in a single hydrothermal deposit (Fouquet and Marcoux, 1995; Hegner and Tatsumoto, 1987; Hinkley and Tatsumoto, 1987), the outer wall sulfides of the Endeavour hydrothermal black smoker chimney are more radiogenic than the inner wall sulfides (chimneys 4133 and 4148). Verati et al. (1999) also observed that euhedral pyrite is more radiogenic than sphalerite and other minerals in the same hydrothermal samples, although no more detailed information about this sample can be obtained from the reference (Verati et al., 1999).

Lead concentrations vary by approximately two orders of magnitude (<50–2904 ppm) and are independent of the Pb isotope composition. These concentrations are comparable to previously measured Pb contents of the clastic massive sulfides from Bent Hill, Middle Valley (33–2600 ppm) (Goodfellow and Franklin, 1993) but lower than seafloor sulfides from sediment-covered ridges at Guaymas Basin (2858–7080 ppm) (Fouquet and Marcoux, 1995) and Gorda Ridge (0.23–7.4%) (Zierenberg et al., 1993). When compared with other sediment-starved ridges, these Pb concentrations are higher than sulfides from the East Pacific Rise 13°N (2–2391 ppm), 17–18°S and 21°S (169–829 ppm) (Fouquet and Marcoux, 1995).

5. Discussion

5.1. Constraints on the metal sources

Lead isotopic compositions are a sensitive indicator of the sources of Pb and other chalcophile metals in ancient massive sulfide deposits and modern seafloor sulfide deposits. Sulfides from sediment-starved mid-ocean ridge sites, and the hydrothermal fluids they precipitate from, display Pb isotope compositions indistinguishable from that of the local basalt, indicating the Pb sources of sulfides and hydrothermal fluids in such ridges is basalt rather than seawater (Charlou et al., 2002; Chen, 1987; Hegner and Tatsumoto, 1987; Hinkley and Tatsumoto, 1987; Vidal and Clauer, 1981). Hydrothermal sediments and sulfides from sediment-covered sites, such as the Escanaba Trough (Gorda Ridge), the Guaymas Basin (Gulf of California) and the Middle Valley (Juan de Fuca Ridge) display greater ranges and more radiogenic compositions due to a contribution of Pb from the pelagic and terrigenous sediments, in addition to basalt lavas, through which the hydrothermal fluids have passed (Bjerkgård et al., 2000; Cousens et al., 1995, 2002; German et al., 1995; LeHuray et al., 1988; Stuart et al., 1999; Zierenberg et al., 1993). Woodcock et al. (2006) give the geochemistry of basalt from the Endeavour segment and recognized 6 chemically distinct types of basalt on the basis of microprobe analysis of basaltic glass. They are classified as N, T, or E-MORB based on the K_2O/TiO_2 value. The N and T-MORB groups are divided further into N1, T1 and T2 which have lower SiO_2 and higher FeO^* and TiO_2 than N2 and T3, respectively. According to the spatial distribution of different type of basalt within the Endeavour segment, the E-MORBs and the T2-MORBs were suggested as two main end-member basalts influencing the circulation of hydrothermal fluid within the Clam Bed, Main Endeavour and Mothra hydrothermal fields (Woodcock et al., 2006). The E-MORBs ($^{206}Pb/^{204}Pb = 18.569$; $^{207}Pb/^{204}Pb = 15.493$; $^{208}Pb/^{204}Pb = 37.896$) are less radiogenic than the T2-MORBs ($^{206}Pb/^{204}Pb = 18.852$; $^{207}Pb/^{204}Pb = 15.497$; $^{208}Pb/^{204}Pb = 38.150$). Due to the absence of published Pb isotopic compositions of basalt from the Endeavour segment, the basalts from West Valley were chosen for comparison and shown in the Fig. 2 (Cousens et al., 1995). The line "BF", a best-fit line through the dense cluster of massive sulfides samples, crosses the cyan line between E-MORB and T2-MORB at $^{206}Pb/^{204}Pb = 18.697$; $^{207}Pb/^{204}Pb = 15.495$; $^{208}Pb/^{204}Pb = 38.016$. The cross point has almost the same Pb isotope composition as the average value of the three vent cap samples from the Main Endeavour field. Hence, it is suggested that the average Pb isotope ratio of the three vent cap samples is the result of leaching of the E-MORB and the T2-MORB by hydrothermal fluid at the proportion of about 50/50 (Fig. 2).

Fig. 2 shows that the Pb isotope compositions of hydrothermal chimney sulfides, vent cap chimney samples, and Fe-oxide are all within the range of basalt from West Valley. When compared with other sediment-starved ridges, Pb isotopic compositions in sulfides from the Endeavour segment show a wider variation range. The best-fit line "BF" is not parallel to the reference line for the northern hemisphere mantle reservoirs (NHRL) (Hart, 1984), indicating that in addition to basalt, buried sediments may be another Pb source for the Endeavour segment hydrothermal sulfide deposits (Butterfield et al., 1994; Lilley et al., 1993; You et al., 1994).

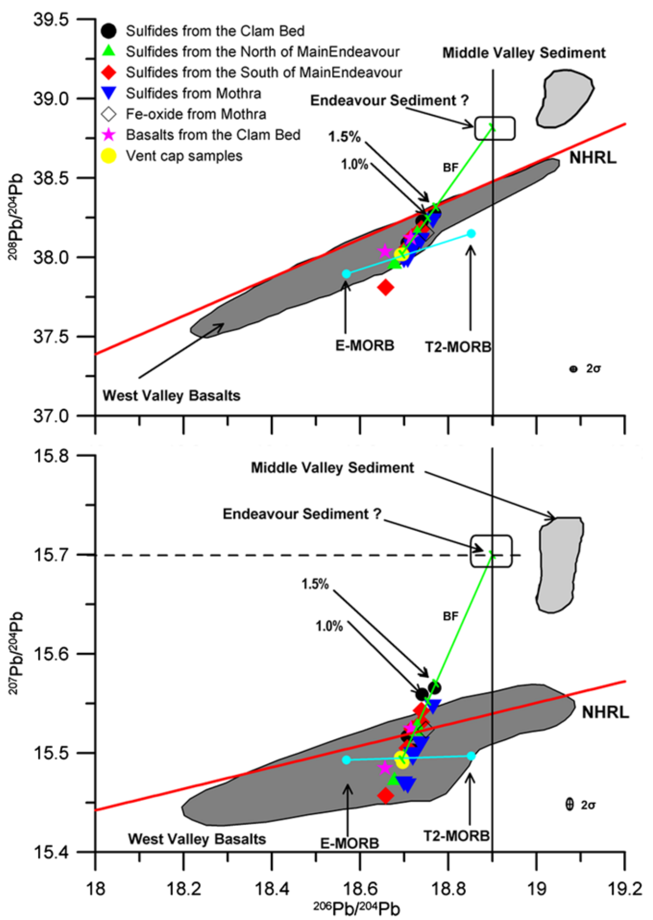

Fig. 2. Pb–Pb isotope plots of black smoker chimney sulfides, vent cap chimney samples, Fe-oxide and basalts from the Endeavour Segment of Juan de Fuca Ridge. The line "BF", through the dense cluster of hydrothermal samples, is a mixing line between the average value of the three vent cap samples and the potential end-member sediment (see text for explanation). The weight percent of the sediment Pb component in the mixing line is indicated by tick marks, assuming Pb concentrations of 0.5 and 20 ppm in basalt and sediment components, respectively. The end-members of E-MORB and T2-MORB are cited from Woodcock et al. (2006); Pb isotopic compositions of sulfide in the South Juan de Fuca Ridge are cited from Hegner and Tatsumoto (1987), West Valley basalt rock from Cousens et al. (1995), and Middle Valley sediment from Cousens et al. (2002) and sulfides of Middle Valley are cited from Stuart et al. (1999) and Bjerkgård et al. (2000). NHRL indicates Northern Hemisphere Reference Line (Hart, 1984). The max 2σ error for all samples (except for sample 4137-5) is also plotted on the figure.

In order to evaluate the sediment contribution, following the method used by Cousens et al. (2002) and Verati et al. (1999), the average value of the three vent cap samples was chosen as the average basalt end-member. Although there is no Pb isotope analyses of a sediment within the Endeavour segment, a possible Pb isotope composition of sediment end-member was attained through the following method. If the sediment within this segment has a similar $^{207}Pb/^{204}Pb$ value to the Middle Valley sediment (dashed line in Fig. 2, the value of $^{207}Pb/^{204}Pb = 15.70$ was chosen), then the dashed line intersects the best-fit line "BF" at about $^{206}Pb/^{204}Pb = 18.90$; $^{208}Pb/^{204}Pb = 38.82$. The crossing point is suggested as the potential end-member sediment. This potential sediment value is consistent with Middle Valley average end-member sediment which has an inferred lower $^{206}Pb/^{204}Pb$ than that of surface sediments (Cousens et al., 2002). Chosen Pb concentrations of basalt and sediment are 0.5 and 20 ppm, respectively (Chen et al., 1986; Verati et al., 1999). The binary mixing results show that the sediment contribution is relatively small and no larger than 1.5%, which is obviously less than that of the Middle Valley where the maximum contribution is about 57% (Stuart et al., 1999). This result is consistent with other reports that there is little or no sedimentary derived Pb contribution to the Endeavour segment hydrothermal system (Harris et al., 2008; Labonte et al., 2006).

It is interesting to note that the Pb isotopic data of the Main Endeavour field and the Clam Bed field overlap significantly, and the Mothra field plots below the Main Endeavour/the Clam Bed field (Fig. 3). This result could be due to the variable leaching of the E-MORB and the T2-MORB rock types. From Fig. 3, it appears that the Mothra field leaches more Pb from T2-MORB than the Main Endeavour field does. This may indicate that each field has its own hydrothermal circulation pathway. The different circulation pathways can be evidenced by two almost parallel lines defined by each cluster of the Main Endeavour field and the Mothra field, respectively. Also note that the two Clam Bed basalts plot close to the Clam Bed sulfide array, and cover at least 50% of the range in the array. This is also consistent with basalt being the major control on sulfide Pb isotopic compositions.

5.2. Reconciling the sulfide Pb isotope data and the hydrothermal fluid chemistry data

The anomalously high concentrations of NH_4^+ and CH_4 and high Br/Cl ratios in hydrothermal fluid from the Endeavour segment vents show that an organic material-rich source exists along this segment (Lilley et al., 1993). The high concentration of B and trace

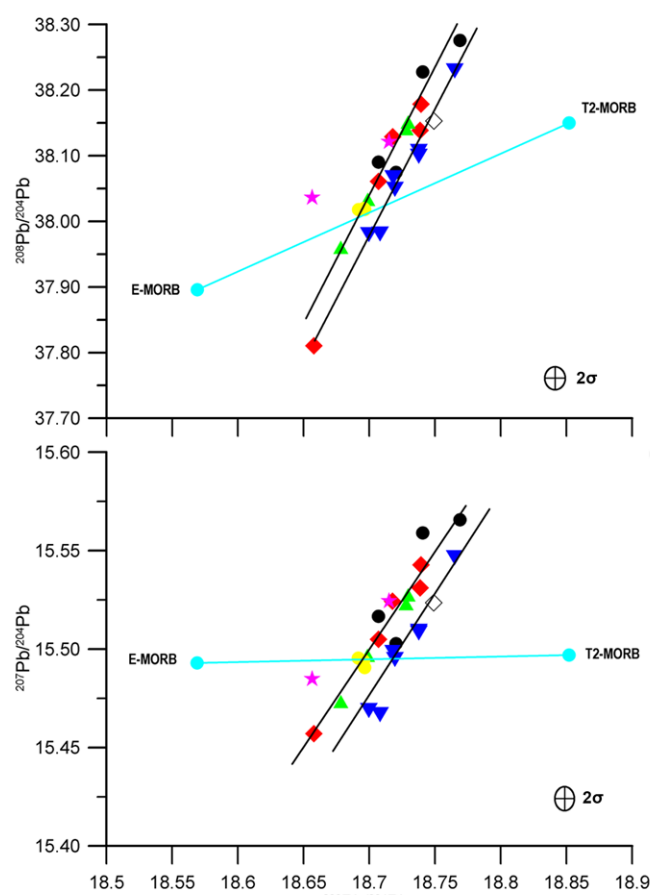

Fig. 3. Enlarged portion of Fig. 2 showing Pb–Pb isotope plots of black smoker chimney sulfides, vent cap chimney samples, Fe-oxide and basalts from the Endeavour Segment of Juan de Fuca Ridge. Line a is the line through the dense part of samples from Main Endeavour field and line b is the line through the dense part of samples from Mothra field (except the bottom data from the Main Endeavour field). Legend as in Fig. 2. The max 2σ error for all samples (except for sample 4137-5) is also plotted on the figure.

alkali metals (such as Li, Rb and Cs) and elevated $\delta^{11}B$ in Endeavour segment fluids all suggest interaction between a high-temperature fluid and organic material-rich sediment somewhere below the seafloor (Butterfield et al., 1994; You et al., 1994). However, the Pb isotopic data show that the sedimentary derived Pb is very small (<1.5%) or non existent. One possible explanation for the discrepancy between Pb isotopic data and the chemistry of vent fluids is that Pb, CH_4, NH_4^+, alkali metals and B come from different sources. Experimental data show that the extraction of Pb from basalt and sediment requires temperature between 250 and 400 °C and a pH less than 5, whereas the extraction of B and alkali metal from sediment generally requires temperature no more than 200 °C. This is also true for basalt except for B, which is almost constant within the temperature range of 51–350 °C (Bischoff et al., 1981; Seewald et al., 1990; Seewald and Seyfried, 1990; James et al., 2003). Thus it is believed that the lower temperature (<200 °C) is enough to leach organic material including NH_4^+, CH_4, alkalis and B from sediment. From the linear correlation of alkalis with Cl^-, and the positive correlation of alkali/B ratios with Cl^-, Berndt and Seyfried (1990) inferred that the enrichment of alkalis in the fluids occurred before phase separation took place and Butterfield et al. (1994) further suggested that the enriched alkali and B signatures would be derived in the recharge zone or in the high-temperature reaction zone but not in the upflow zone. Combining the Pb isotopic data, it is suggested that the sediment source is in the recharge zone but not in the high-temperature reaction zone. If the sediment component is in the high-temperature reaction zone, only a few % of sediment component will lead to hydrothermal fluid (shown by vent cap chimney samples) and related sulfides that have more radiogenic Pb than the found in the present study.

It is known that the circulation of hydrothermal fluid through basaltic crust should result in uniform Pb isotopic ratios in the hydrothermal fluid, and there is no variation in Pb isotopic compositions of sulfides related to the formation temperature, except for low-temperature silicic chimneys (Fouquet and Marcoux, 1995). Yet the outer wall sulfides have more radiogenic Pb isotopic ratios than the inner wall sulfides in chimneys 4133 and 4148. Because the presence of chalcopyrite indicates that these chimneys were formed from high-temperature fluids, the possible explanation is changing Pb isotope compositions in the hydrothermal fluids. In general, the changes of fluid paths caused by a magmatic/diking event may lead to changes in the chemistry of hydrothermal fluid (Fornari et al., 1998; Rubin et al., 1994; Seyfried et al., 2003; Von Damm et al., 1995). Unfortunately, time-series Pb isotopic ratios of hydrothermal fluids were not determined. Radiometric dating of active chimneys from the Endeavour vent field yields ages greater than 200 a in some cases (Kim and Mcmurtry, 1991), thus implying that the activity of hydrothermal fluids began at least 200 a ago, and it is possible that the initial hydrothermal fluid had different Pb isotopic ratios compared with the recent venting hydrothermal fluid. Thus the analysis of age on Endeavour samples would test the possible explanation. If a variation in vent fluid Pb isotopic composition does occur, the Pb isotopic ratios of sulfides from different chimneys in the same hydrothermal field have comparable variation range that indicates these chimneys all have a similar evolution history of hydrothermal fluids. However, for single chimneys in different fields, the variation range of Pb isotopes decreases from the north Clam Bed field to the middle Endeavour field to the south Mothra field suggesting that vent fluid evolution is different between vent fields.

6. Summary/conclusions

Hydrothermal chimney sulfides, vent cap chimney samples, an Fe-oxide layer and basalts from the sediment-starved Endeavour Segment, Juan de Fuca Ridge, exhibit a relatively large range of Pb isotopic ratios, and the data array is not parallel to the northern hemisphere mantle reservoirs (NHRL) suggesting a sediment component within the hydrothermal system. Assuming that the potential sediment component has similar $^{207}Pb/^{204}Pb$ (15.70) to Middle Valley sediment, it is suggested that a potential sediment component may have $^{206}Pb/^{204}Pb = 18.90$; $^{208}Pb/^{204}Pb = 38.82$. The end-member basalt-derived Pb for the Endeavour segment hydrothermal system involves about 50/50 leaching of E-MORB and T2-MORB. Detailed observations show the Mothra field leaches more Pb from T2-MORB than the Main Endeavour field does. According to the binary mixing model, the results show little (<1.5%) or no Pb derivation from sedimentary sources. However, the chemistries of hydrothermal fluid do show a sediment component within the segment. Reconciling the Pb isotopic data with the chemistry of the hydrothermal fluids, it is suggested that the sediment component may be located in the recharge zone, where lower temperatures mobilize NH_4^+, CH_4 and other light molecule components, but do not mobilize Pb.

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