# Geochemical characteristics of hydrothermal sediments from Iheya North Knoll in the Okinawa Trough\*

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**Abstract** Thirty sediment subsamples were recovered from the Iheya North hydrothermal field (with an average of 38 m away from the hydrothermal vent) in the middle Okinawa Trough. Samples were obtained by the ROV (Remote Operated Vehicle) *Faxian* during the virgin cruise of the R/V *Kexue* in 2014 with the application of push cores. The chemical compositions of the sediments show that the hydrothermal sediments near the hydrothermal vent are mainly composed of SO<sub>3</sub>, ZnO and Fe<sub>2</sub>O<sub>3</sub>. Moreover, the hydrothermal sediments are also highly enriched in Pb, As, Sb, Hg, Se, Ag, Ba, Mo and Cd comparing with previous analysis results. On the other hand, the concentrations of Sr, Hg and Ag in studied sediments are strongly and positively correlated, these elements can be used as an hydrothermal indicator. In addition, a factor analysis of the sediments suggested that the sediments were mainly influenced by hydrothermal origin, and terrestrial and biogenic input are limited in studied area. It is also suggested that different stages of crystallization were involved in the formation of hydrothermal chimney from factor analysis.

Keyword: hydrothermal vent; hydrothermal sediments; Okinawa Trough

## **1 INTRODUCTION**

Studies of the modern seafloor conducted over the past four decades have resulted in the discovery of hydrothermal activity in different tectonic settings, such as in the Mid-Ocean Ridge system, intra-oceanic and intra-continental back-arc rifts, and the craters of submerged arc volcanoes (Yoshikawa et al., 2012; Wang et al., 2014; Resing et al., 2015). In recent years, physical and chemical anomalies have been discovered in the water column in different hydrothermal settings, indicating the wide existence of hydrothermal activities (Charlou et al., 2000).

The Okinawa Trough behind the Ryukyu Trench is an active back-arc basin (Glasby and Notsu, 2003). The chemical compositions of the submarine hydrothermal fluids in the Okinawa Trough are variable in contrast with the relatively homogeneous fluids in the sediment-starved hydrothermal areas of the Mid-Ocean Ridge (Gamo et al., 2006; Deng, 2007). The chemistry of the hydrothermal fluid in the Iheya North field has been investigated since its discovery (Kawagucci et al., 2011). Hydrothermal activities were first discovered during the R/V Kaiyo K95-07-NSS cruise in 1995 from a deep-sea TV camera survey (Kawagucci et al., 2011). Following this discovery, more than 50 dives by ROVs and submersibles and a seismic reflection survey have been conducted (Tsuji et al., 2012). Previous researches have shown geochemical characteristics of sediments with the application of traditional TV guided grab in Mid-Okinawa Trough (Zhao and Yan, 1994; Marumo and Hattori, 1999; Gao et al., 2000; Monecke et al., 2014). In addition, relevant mineralogy studies of the hydrothermal chimneys have also been performed in the IODP Exp. 331 in 2010 (Shinnosuke et al., 2014; IODP Expedition 331 Preliminary Report).

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Fig.1 Location map of the Okinawa Trough (adapted by Kawagucci et al., 2011) (a); event map of the Iheya North field (b) The red star represents the NBC, and the different colored circles represent the sampling sites.

In this study, the geochemical properties of hydrothermal sediments that close to the hydrothermal vent (~38 m) are analyzed to illustrate the unique geochemical characteristics near hydrothermal vent with the application of novelty sediment samplers "push core".

#### 2 GEOLOGICAL BACKGROUND

Iheya North Knoll (27°47′N, 126°53′E) is located approximately 150 km away from Okinawa Island at a depth of approximately 1 100 m. In the middle of Iheya North Knoll, the Central Valley represents the subseafloor structure and has relatively strong subbottom seismic reflectors (up to 300 m below the surface of the seafloor). Based on geophysical investigations and seafloor observations, the Central Valley is buried beneath abundant deposits from volcanic flows and pumiceous rocks interbedded with minor layered sediments. However, the surface of the seafloor around the Iheya North hydrothermal field and the Central Valley are covered with pelagic sediments (Kawagucci et al., 2011).

The study area (Fig.1) is located in the North Big Chimney (NBC) vent field in the center of Iheya North Knoll in the Mid-Okinawa Trough (Ishibashi et al., 2014). Hydrothermal activities occur within a restricted area of 250 m in diameter at the foot of the knoll (Glasby and Notsu, 2003). Previous research has shown that hydrothermal fluids have a maximum



Fig.2 North Big Chimney

temperature of 311°C, which is near the boiling point at seafloor pressure (100 bar), and are being emitted at a faster flow-rate than they have been for the past 10 years. These results indicate that the NBC stands on the main hydrothermal flow or passage. Moreover, the NBC mound has hosted numerous diffusive fluids, and the average ambient seawater temperature is 4°C (Kawagucci et al., 2011, 2013).

The NBC mound (Fig.2) is the most active mound, reaching ca. 32 m in height, and is pyramid-shaped with well-developed, multi-layered flange structures and massive aggregations of vent animals, particularly towards the peak of the structure (Tokeshi, 2011). The top of the mound contains an active orifice where hydrothermal fluid flows out.



Fig.3 The push core is collecting sediment samples

## **3 MATERIAL AND METHOD**

#### 3.1 Sampling sites

Samples were collected using push cores (Fig.3) during the virgin cruise of the R/V Kexue in 2014 by the Institute of Oceanology of Chinese Academy of Sciences. In this study, a total of 30 sediment samples were selected from six push cores for the determination of geochemical compositions. Each push core was about 15 cm, and it was seperated into 5 subsamples of 3 cm interval. The push core mounted on the ROV Faxian (made by SMD, UK) can be used for precise sampling of the hydrothermal sediments near the hydrothermal vent with the help of ultra short baseline (USBL) positioning system. Three push cores (PC24, PC26 and PC8) were obtained at the location of 126°53.826'E, 27°47.449'N, with the distance of 35 m from the NBC, and three push cores (PC27, PC29 and PC4) were obtained at the location of 126°53.827'E, 27°47.445'N, with a distance of approximately 40 m from the NBC (Fig.1). As a result, the average distance to the NBC is about 38 m. The sampling depth was about 1 009 m.

#### 3.2 Sample analysis

After the sediment samples were collected, they were immediately subsampled then stored in a freezer at -20°C for further analysis in the laboratory. The bulk sediment samples were rinsed three times with deionized water, dried at 60°C for 12 h, and ground to less than 63 µm using an agate mortar. Then, these pretreated samples were analyzed to determine their chemical compositions. The samples used for determining the concentrations of Na<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub>, CaO, SiO<sub>2</sub>, CuO, Fe<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, MgO, MnO, SO<sub>3</sub> and ZnO were pretreated using lithium borate fusion before performing X-Ray fluorescence spectroscopy (XRF) measurements at the ALS Minerals Laboratory in Guangzhou. The finely pulverized samples were oven dried before pre-oxidation and decomposition by fusion with lithium borate flux containing sodium nitrate as an oxidizing agent. The resulting melt is manually poured to form a fused disk. Sodium nitrate enables the fusion of material containing sulfides. During fusion with a standard lithium metaborate flux, sulfides only partially oxidize forming gaseous compounds; hence sulphur is lost to the atmosphere. With the use of this strongly oxidizing flux, sulphur is oxidized beyond the gaseous form and retained in the fused disk, allowing it to be quantitatively measured. This disk is then analyzed using a wavelength dispersive X-Ray fluorescence spectrometer. The Cu, Pb, Zn, Fe, As, Ba, Mo, Sb, Ag, Hg, Se and Cd concentrations were measured using induced coupled plasma mass spectrometry (ICP-MS) and the inductively coupled plasma atomic emission spectrometry (ICP-AES). The precision and accuracy were monitored by national geostandards GSR-5, GSR-6, and GSR-9 provided by

Sample No. Al<sub>2</sub>O CaO CuO Fe<sub>2</sub>O<sub>3</sub>  $K_2O$ MgO SiO SO3 ZnO Na<sub>2</sub>O MnO LOI PC4 0.47 0.31 5.55 26.3 0.15 0.46 5.75 86.90 0.36 0.11 36.33 20.86 PC8 0.40 0.05 3.39 29.1 0.13 0.10 4.74 92.00 33.74 0.30 0.09 20.95 PC24 0.40 0.05 3.97 28.5 0.13 0.10 4.64 93.43 33.84 0.27 0.09 18.63 PC26 0.40 0.04 3.28 25.9 0.14 0.08 4.96 90.17 37.05 0.30 0.09 17.51 PC27 0.34 0.05 3.60 25.3 0.13 0.14 4.59 88.23 38.75 0.19 0.10 22.42 PC29 0.38 0.04 4.42 26.9 0.14 0.14 5.55 88.54 34.78 0.26 0.11 20.29 Jade1 0.10 0.12 0.34 13.55 7.56 35.12 0.09 \_ \_ \_ - $OT^2$ 13.96 6.78 3.69 2.35 2.59 49.26 2.81 1.35 14.00

 Table 1 Chemical compositions of hydrothermal surface sediments from Iheya North Knoll (wt.%)

Jade1: massive sulfide samples from the Jade hydrothermal field (Halbach et al., 1989); OT2: surface sediments in the Okinawa Trough (Jiang and Li, 2002).

the National Research Center for Geoanalysis, based on the repetitive measurements of GSR-9, the analytic precisions for most major and trace elements are 5%-10%. Here are the analysis processes. Two pulp subsamples were prepared. One subsample is digested with perchloric, nitric and hydrofluoric acids. The residue is leached with dilute hydrochloric acid and diluted to volume. The solution is then analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) for ultra-trace level elements. And, the same digestion solution is also analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) for trace level elements. Results are corrected for spectral inter-element interferences. The other subsamples is added to lithium metaborate/lithium tetraborate flux, mixed well and fused in a furnace at 1025°C. The resulting melt is then cooled and dissolved in an acid mixture containing nitric, hydrochloric and hydrofluoric acids. This solution is then analyzed by inductively coupled plasma- mass spectrometry. As a result, according to the actual situation of the sample and the digestion effect, the comprehensive value is the final test results. There are thirty subsamples were involved in the analysis of minor components and principal component analysis (PCA) analysis in hydrothermal sediments in order to have а comprehensive understanding of their sources.

A statistical multivariant correlation analysis performed by SPSS.19 of element concentration in suites of related samples is done to seek communality of variation near the hydrothermal vent. Factor analysis is a well described mathematical method to reduce the dimensionality of the variable space on the basis of the reduced factor solution. Factor analysis usually proceeds in four steps: first, the correlation matrix for all variables (features) is computed. Then, measured features that do not appear to be related to other features can be identified from the matrix and associated statistics; second, factor extraction: the number of factors have to represent the data and the method of their calculation must be determined. Third, rotation focuses on transforming the factors to make them more interpretable; finally, scores for each factor can be computed for each case. In our study, an orthogonal rotation by the varimax method was added to minimize the medium loaded elements in the extracted factors and to maximize low and high loadings of the elements.

## **4 RESULT AND DISCUSSION**

### 4.1 Components characteristics

The geochemical analysis of all subsamples shows that the five subsamples in each push core share a similar abundance of chemical components. Therefore, the surficial subsample (0-3 cm) of each push core was chosen to reflect the major components of sediments in Table 1.

The results indicate that the hydrothermal sediments are mainly composed of SO<sub>3</sub>, ZnO and Fe<sub>2</sub>O<sub>3</sub>. For comparison, results from previous studies of the surface sediments and massive sulfide samples from the Jade hydrothermal field in the Okinawa Trough are shown in Table 1. Through comparison, there are significant distinction between hydrothermal sediments in this study and previous studies, which are mainly composed of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and CaO (Jiang and Li, 2002; Zhai et al., 2007). Particularly, the  $SiO_2$  concentration in previous studied sediments was approximately 49.26%, and the SiO<sub>2</sub> concentration in the sediments analyzed in this study was approximately 5%, which shows similar concentration with massive sulfide samples. Compared with the other components (e.g.,  $Al_2O_3$ , CaO and  $Fe_2O_3$ ) in the sediments of different samples, similar component concentrations were also observed between the studied samples and massive sulfide samples. On the other hand, the sediment samples collected in this

 
 Table 2 Correlation coefficient matrix of the major elements in the studied hydrothermal sediment

	$Al_2O_3$	CaO	$\mathrm{Fe}_2\mathrm{O}_3$	$K_2O$	MgO	$SiO_2$	$SO_3$	${\rm TiO}_2$	$P_2O_5$
Al <sub>2</sub> O <sub>3</sub>	1								
CaO	0.063	1							
$\mathrm{Fe}_2\mathrm{O}_3$	-0.208	0.052	1						
$K_2O$	0.772	0.030	-0.097	1					
MgO	0.316	0.226	-0.348	-0.244	1				
${\rm SiO}_2$	0.245	0.220	-0.415	0.390	-0.133	1			
$SO_3$	-0.194	-0.157	0.616	-0.208	-0.135	-0.721	1		
${\rm TiO}_2$	0.471	-0.006	0.097	0.478	-0.232	0.036	0.042	1	
$P_2O_5$	-0.006	0.761	-0.036	-0.228	0.522	-0.094	0.053	-0.149	1

study are very close (with an average distance of 38 m) to the hydrothermal vent (NBC), indicating unique hydrothermal influences characteristics.

Ueno et al. (2003) have put forward to the formation of hydrothermal chimneys in Iheya North Knoll. The chimneys are mainly composed of sulfide minerals, including sphalerite, wurtzite, galena, pyrite, marcasite, chalcopyrite and tetrahedrite, which are enriched in Zn, Fe, Cu and Pb. In addition, from the morphology and chemical compositions analysis of sediments using SEM and EDS by Shao et al. (2015) in the same research area, the results clearly suggest the ubiquity of the hydrothermal deposits and various metal sulfides in the Iheya North Knoll. Combined with the components of the studied sediments, it is suggested that the samples are probably composed of corroded chimney fragments due to fallout and the mass wasting of the hydrothermal chimney walls.

To further illustrate the unique characteristics of hydrothermal sediments, the correlation coefficient matrix of the major components of 30 subsamples is provided in Table 2. In a related analysis, we found that 1) Al<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>O are strongly and positively related. It is well known that Al<sub>2</sub>O<sub>3</sub> represents terrigenous input, the positive relationship between them indicates the terrigenous origin of K<sub>2</sub>O. However, Gamo et al. (2006) have provided that plate subduction is the main source of K<sub>2</sub>O in Mid-Okinawa Trough. As a result, it is inferred that near-hydrothermal vent sediments are mainly influenced by distance rather than plate subduction; 2) sulphur trioxide (SO<sub>3</sub>) and  $Fe_2O_3$  are positively correlated, with a correlation coefficient of 0.616. However, both SO<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> were negatively correlated with SiO<sub>2</sub>. SO<sub>3</sub> and SiO<sub>2</sub> have the strongest negative relationship with a correlation coefficient of -0.721, while Fe<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> have weaker negative relationship. It is well known that SiO<sub>2</sub> is a typical



Fig.4 K<sub>2</sub>O/Na<sub>2</sub>O-SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios in the sediments in the study area and other geologic settings (adapted by Gao et al., 2000, Xu et al., 2012)

terrigenous component, and SO<sub>3</sub> is enriched in the studied hydrothermal field. Therefore,  $Fe_2O_3$  is a unique component in the studied hydrothermal area; 3) CaO and  $P_2O_5$  show strong positive correlation, with a correlation coefficient of 0.761. Therefore, we suggest that  $P_2O_5$  may reflect the biogenic orign like CaO rather than hydrothermal origin. The further explanation is discussed in Section 4.2.

The characteristics of sediments can be largely depended on their typical chemical components. From the K<sub>2</sub>O/Na<sub>2</sub>O-SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios of the sediments sampled in different geological settings (Fig.4), it clearly shows that the ratios of normal pelagic seafloor sediments, oceanic crust, continental crust, oceanic basalt and volcanic rocks are within the same range. In this range, the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio is relatively stable at approximately four. However, the K2O/Na2O ratios vary between 0.1 and 1.8. Therefore, it is suggested that no distinctive changes occur in the SiO<sub>2</sub>-dominated detrital material and Al<sub>2</sub>O<sub>3</sub>-dominated clay minerals in these sediments or rocks. However, the K<sub>2</sub>O/Na<sub>2</sub>O concentrations of these sediments vary greatly, reflecting different kinds of terrigenous components. On the other hand, the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios of the hydrothermal sediments in this study and sulfide are not as stable as those in the normal seafloor sediments, changing from 6 to 16. On the contrary, the  $K_2O/Na_2O$ ratios remain stable at approximately 0.4, which reflects hydrothermal sediments are not dominated by terrigenous materials. Interestingly, the values from volcanic rocks in OT are located between hydrothermal

	Hydrothermal sediment	Sulfide ores <sup>1</sup>	Chimney component <sup>2</sup>	Massive sulfide <sup>3</sup>	Surface sediment <sup>4</sup>
Cu (%)	4.7	3.1	4.6	0.3	26.0
Fe (%)	16.5	1.98	15.6	13.5	-
Pb (%)	0.8	-	9.1	15.8	27.0
Zn (%)	30.3	18.8	31.4	35.12	82,0
Ba (%)	1.0	1.0	28	0.6	0.039
As	769.0	800	1 730	1 380	9,0
Sb	163.8	1 200	1 140	-	1.2
Hg	67.5	80	19.9	-	0.1
Se	14.7	-	-	-	0.4
Te	7.1	-	-	-	0.1
Ag	110.5	1 100	465	120	0.1
Sr	848.9	-	-	1 100	590.0
Mo	98.4	-	-	-	1.7
Cd	936.21	N.D.	-	600	0.6
Mn	713.9	1 100	-	900	400.0
Ce	2.5	-	-	-	62.0
Zr	8.4	-	-	-	120.0
Hf	0.1	-	-	-	3.2
Co	0.4	-	-	-	12.5
Cr	7.3	-	-	-	58.0
Ni	11.9	-	-	-	36.0
V	36.8	-	-	-	78.0
Li	2.4	-	-	-	32.0
Rb	4.3	-	-	-	87.0

Table 3 Concentrations of trace elements in the studied hydrothermal sediments and other hydrothermal fields

Cu, Fe, Pb, Zn and Ba in the hydrothermal sediments, sulfide ores<sup>1</sup>, chimney components<sup>2</sup> and massive sulfide<sup>3</sup> in units of wt.(%). Other values are presented using the unit mg/kg. Sulfide ores <sup>1</sup>: hydrothermal ore deposits from the Mid-Okinawa Trough (Noguchi et al., 2007). Chimney component <sup>2</sup>: fragments of the hydrothermal chimney from Iheya North Knoll (Ueno et al., 2003). Massive sulfide<sup>3</sup>: massive sulfide samples from the Jade hydrothermal field (Halbach et al., 1989). Surface sediments <sup>4</sup>: surface sediments from the Okinawa Trough (Zhai et al., 2007). N.D.: not detected.

sediments and normal seafloor sediments, indicating a transient stage in terms of major components ratios. Therefore, the distinction between hydrothermal sediments and normal seafloor sediments are obvious in terms of major components ratios.

Al and Ti behave relatively conservative during earth surface processes and are resistant to chemical weathering and diagenetic alteration and thus, primarily reside in the detrital fraction in marine sediments (Shao et al., 2015).

In addition, Al and Ti have been used to estimate

the terrigenous inputs in ocean sediments. The Al/Ti ratio is an effective indicator of the presence of excess aluminum. Al/Ti for upper continental crust is 24.8, and for lower crust is 16.4 (Wedepohl, 1995). The ratio of Al/Ti in the continental crust origin is approximately 17, which potentially indicates that the crust is enriched in authigenic aluminum (Jiang et al., 2006). Interestingly, the maximum Al/Ti ratio in hydrothermal sediments is much higher than continental crust, with an average ratio of Al/Ti ~34. Consequently, the samples collected in the studied hydrothermal area were highly influenced by hydrothermal activity.

The concentrations of trace elements in the hydrothermal sediments in the studied area and other hydrothermal fields are shown in Table 3. The hydrothermal sediments in the NBC are enriched in Cu, Pb, Zn, Fe, As, Sb, Ag, Hg, Se, Ba, Mo and Cd, while depleted in Co, Cr, Ni and V. Vanadium as an abundant trace element in earth's crust, usually substitutes for Fe and is concentrated in mafic rocks and in Shale. Shao et al. (2015) have found the terrigenous clays inevitably have high V contents, while the leaching of the pelagic detrital sediments and pumices by hydrothermal fluid leads to low V contents in the OT hydrothermal clays. Therefore, it is reasonable to explain the relative depletion of vanadium and other insensitive elements such as Co, Cr and Ni. The concentrations of trace elements are similar to hydrothermal sulfide in the Mid-Okinawa Trough, but different from the sediments that were not influenced by hydrothermal activity (Zhao and Yan, 1994; Gao et al., 2000; Jiang and Li, 2002; Zhai et al., 2007).

At the meantime, Shao et al. (2015) have also focused on the clay minerals of the same studied area. Their research results also indicate the bulk clays of NBC are characterized by higher concentrations of Pb and Mn and lower Na, K, Ca, Ba and P relative to the detrital clays. In addition, the sulfide mainly contained Fe, Zn, Cu and Ba as major components, with minor amounts of Mn, Ag, As, Sb, Cd and Hg (Noguchi et al., 2007). The trace elemenet concentrations in this study were only slightly lower than those in the sulfide ores, and were much greater than those in the sulfide ores, sediments from the Okinawa Trough (Zhai et al., 2007). Thus, these results further suggest that the samples collected in this study are mainly composed of sulfide.

However, the concentration of Pb in the studied sediments was much lower than that in the massive sulfide, and the concentrations of the other elements remained relatively consistent. Previous studies have

· · · ·		<b>J</b>		
	F1	F2	F3	F4
$Al_2O_3$	0.099	-0.030	0.933	0.084
Na <sub>2</sub> O	-0.035	-0.134	0.796	0.334
CaO	0.145	0.027	0.037	0.907
K <sub>2</sub> O	0.303	0.057	0.792	-0.099
$P_2O_5$	-0.157	-0.143	-0.081	0.911
$SiO_2$	-0.947	0.028	0.131	0.085
$SO_3$	0.794	0.423	-0.127	-0.013
Ag	0.890	-0.180	0.281	-0.058
As	0.109	0.776	0.170	0.104
Ni	-0.081	0.850	0.199	0.022
Cd	0.858	-0.150	0.223	-0.036
Со	-0.064	0.512	0.655	-0.151
Cr	0.126	0.667	0.538	0.191
Cs	0.933	-0.051	0.182	-0.087
Mn	0.566	-0.351	0.489	0.112
Pb	0.508	-0.434	0.195	0.208
V	-0.120	0.234	0.326	0.843
Hg	0.894	-0.027	0.077	-0.124
Fe	0.907	0.143	-0.038	0.119
Cu	0.180	-0.872	0.192	-0.187
Zn	0.730	-0.529	-0.035	-0.010
Sb	0.628	0.061	0.286	-0.257
Sr	0.920	0.101	-0.135	-0.019
Communality (%)	35	20	18	12

 Table 4 Results of R-mode factor analysis of the chemical compositions of the hydrothermal sediments

Bold represents the characteristic elements value in each common factor.

shown that the sediment-covered hydrothermal fields are enriched in galena, with none of the sedimentcovered areas depleted in galena (Gamo et al., 2006). Considering the relatively thin sediment cover in the studied area and the 10-20 m thick sediment in the Jade hydrothermal field (Halbach et al., 1989), the depletion of Pb in the studied samples may reflect the relative depletion of galena. Ueno et al. (2003) described the following sequence for the crystallization of the minerals in hydrothermal chimney in Iheya North Knoll. Sphalerite grows and galena and fine pyrite crystalize. Since higher concentration of Fe occur in the hydrothermal sediment than in the massive sulfide from Jade, it gives an insight into that pyrite formation was prioritized over galena in the crystallization sequence. As a result, another probable explanation of depleted Pb may be the priorities of the crystallization of the different minerals.

#### 4.2 Element assemblage and control factors

The element concentrations in sediment can not only reveal the geochemistry behavior of sediments but also illustrate their origins. Therefore, the R-mode factor analysis was performed to have a fully awareness of the origins of these sediments.

Twenty-two major and trace element components were analyzed using PCA based on the R-mode factor analysis of the chemical compositions shown in Table 4. The results show that most of the common factor variances are greater than 0.85. The accumulated variance contribution rate reaches up to 85%. The results are satisfactory and can be used to explain most of the sediment samples. Altogether, four common factors indicate the sediment source types, respectively.

1) F1: the accumulated variance contribution rate of the first common factor is 35%. The characteristic element group includes SO<sub>3</sub>, SiO<sub>2</sub>, Ag, Cd, Cs, Sr, Hg, Zn, Mn, Fe, Pb and Sb. SiO<sub>2</sub> shows negative factor loading, while the other elements show positive loadings. SiO<sub>2</sub> is a characteristic component of terrigenous sediments, and is negatively correlated with SO<sub>3.</sub> Other elements with positive loadings are characteristic elements in hydrothermal fields. Therefore, we suggest that this group of element mainly reflects hydrothermal origin. On the other hand, in a related analysis, Sr, Hg and Ag are strongly and positively correlated with one another. The correlation coefficients of Sr with Hg and Ag were 0.924 and 0.804, respectively. In addition, the concentrations of Hg and Ag were positively related (R=0.895). Thus, the Sr, Hg and Ag concentrations can be used as indicator elements of the hydrothermal field in the Mid-Okinawa Trough. What is more, the crystallization of the minerals that contained in hydrothermal chimney in Iheya North Knoll was shown as follows. Sphalerite grows first, followed by galena, fine pyrite, and chalcopyrite (Ueno et al., 2003). Sphalerite and galena are highly enriched in Zn, Fe, Mn, Pb, Sb, Ag and Hg. When considering the typical elements in this group, it is not difficult to see that F1 may indicate the early stage of the formation of hydrothermal chimney. Thus the hydrothermal contribution plays an important role in the first group.

2) F2: the accumulated variance contribution rate of the second common factor was 20%. The characteristic element assemblage includes As, Ni, Co, Cr, Cu and Zn. In addition, Cu and Zn are negatively correlated with As, Ni, Cr and Co. Enrichment of Cu and Zn may indicate the presence of chalcopyrite as discussed above. Previous studies have indicated that As is present in more than 200 minerals containing one or more other elements. Many arsenic-containing sulfide minerals originated from geothermal and hydrothermal activity (Lewis et al., 2007). Consequently, it is suggested that As is not predominant in the studied sediments. In a word, the second element assemblage may indicate a late stage of the hydrothermal chimneys near the studied area. In conclusion, both of the first two element groups are associated with hydrothermal activity, and it accounts to 55% of hydrothermal contribution in the studied sediments.

3) F3: the accumulated variance contribution rate of the third common factor is 18%, with an elemental assemblage of  $K_2O$ ,  $Al_2O_3$ ,  $Na_2O$ , Co and Cr. Previous studies of the sediment sources of the Okinawa Trough have indicated that the Na<sub>2</sub>O came from volcanic sources (Xu et al., 2012). In addition,  $Al_2O_3$ and Na<sub>2</sub>O are typical components in clay minerals and terrigenous clasts. Combining the strong positive relationships of  $K_2O$ ,  $Al_2O_3$  and Na<sub>2</sub>O, we inferred that Na<sub>2</sub>O in the studied samples signify terrestrial origin rather than of volcanic origin (Shinjo et al., 2000). Therefore, these components all reflect the terrigenous supply in the Okinawa Trough.

4) F4: the accumulated variance contribution rate of the forth common factor was 12%, with characteristic elements of CaO,  $P_2O_5$  and V, since CaO is the symbol of biogenic characteristic. At the meantime, vanadium is usually concentrated on reducing environment, all organisms require P for nucleic acid, energy reactions and fatty acids.  $P_2O_5$ usually presents as phosphate in sediments, and is highly controlled by biologic activity (Liu et al., 2006). Therefore, CaO,  $P_2O_5$  and V are the representative of biogenic input. However, the overall concentrations of these elements are low, which indicates that the biological contributions are restricted in the hydrothermal field.

## **5** CONCLUSION

In this paper, we present bulk chemical compositions of hydrothermal sediments from the Iheya North field in the Okinawa Trough. The following conclusions were drawn from this study: 1) the major components in hydrothermal sediments are SO<sub>3</sub>, ZnO and Fe<sub>2</sub>O<sub>3</sub>, in contrast with Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and CaO in normal pelagic seafloor sediments. Sr, Hg and Ag can be used as characteristic hydrothermal elements because they are strongly and positively correlated. Moreover, trace elements such as Cu, Pb, Zn, As, Sb, Hg, Se, Ag, Ba, Mo and Cd are highly enriched in hydrothermal sediments; 2) the compositions of the hydrothermal sediments are divided into four groups. The first two element groups represent the crystallization sequence of the hydrothermal chimney, and are hydrothermal contributions. The third group represents the terrigenous inputs, and the fourth group represents the biogenous inputs. Hydrothermal contributions were important in the studied sediments. However, volcanism is limited in the studied area because no Na anomaly was found.

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