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Fabrication of Multi-parameter Chemical Sensor and its Application in the Longqi Hydrothermal Field, Southwest Indian Ocean

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All-solid-state electrodes are potentially suitable as *in situ* sensors for deep-sea environments because of their pressure resistance, rapid response, and ease of integration. Nonetheless, few studies report the application of such electrodes in hydrothermal systems. In this study, we fabricated a multi-parameter chemical sensor (MPCS) incorporating self-made reference, pH, redox (Eh), and H₂S electrodes. During the Chinese Dayang 34I and 49II cruises at the Southwest Indian Ridge (SWIR), the assembled MPCS, equipped with a deep-sea towed camera system, was continuously monitored *in situ* at depths exceeding 2,000 m. The potential anomalies of the Eh, H₂S, and pH electrodes were 49, 98, and 18 mV, respectively, in the Longqi hydrothermal plume area. In the undetected area, the MPCS showed slight anomalies, indicating the presence of an unknown hydrothermal plume at the site. All potential anomalies of the MPCS were consistent with those of commercial sensors (methane, turbidity, and temperature sensors). The test results suggested that the MPCS can sensitively detect changes in chemical quantities caused by hydrothermal fluid, and it provides an effective technique for exploring hydrothermal vents.

Keywords: Chemical sensor, All-solid-state selective ion electrode, Hydrothermal plume, Anomalies, Southwest Indian Ridge

1. INTRODUCTION

Hydrothermal vents are pathways of heat and matter connecting the Earth's interior and surface.

On the one hand, the hydrothermal environment provides energy for bacterial chemosynthesis, and serpentinization coupled with Fischer–Tropsch-type reactions in hydrothermal systems offers a clue to organic matter production [1]. Thus, studying hydrothermal systems is key to understandthe origin of life [2]. On the other hand, various metals from the Earth's interior are carried to its surface with hydrothermal vent fluids. The formed polymetallic sulfides are potential deep-sea mineral resources as they are rich in metals such as Cu, Zn, Pb, Au, Fe, and Ag [3]. Consequently, detecting hydrothermal activity is fundamentally important from both biological and geochemical viewpoints.

A preliminary study indicates that hydrothermal activity was triggered by magmatic activity associated with active seawater circulation. This occurs at seafloor spreading zones and is widespread in ocean spreading ridges and subduction zones [4]. Cold seawater penetrates downward from cracks in the crust or rock fractures. During infiltration, it is heated by the magma chamber and other heat sources. The heated fluid leaches metals (including Cu, Fe, Zn, and Pb) from the surrounding host rocks, which then upwell along the main pathways. Venting fluid contains H_2S , H_2 , Fe^{2+} , Mn^{2+} , and CH₄. It has stronger acidity and reducibility and is less dense than seawater. The hydrothermal fluid rapidly mixes with ambient seawater, and the hydrothermal components are rapidly diluted to an initial concentration of 10^{-5} – 10^{-4} times [5]. The mixed fluid can rise by several hundred meters from the seabed before reaching neutral buoyancy, accompanied by several kilometers of lateral diffusion to form a hydrothermal plume [6]. Hydrothermal plumes are the main signs of hydrothermal discharges [7]. Chemical (acidity and reducibility) and physical (temperature and turbidity) anomalies are important characteristics of hydrothermal plumes [8].

Since the first *in situ* monitoring of seawater based on conductivity, temperature, and depth (CTD) measurements [9–10], in situ chemical sensors have been widely studied for determining the chemical parameters in various aquatic systems, especially marine environments [11–16]. Among these *in situ* sensors, the all-solid-state ion-selective electrode is an emerging technology because of its high sensitivity, rapid response, small size, and pressure resistance [17-20]. Additionally, it is easily assembled with other electrodes to simultaneously monitor multiple parameters. As hydrothermal plumes normally show redox (Eh), pH, temperature, turbidity, and H₂S anomalies with ambient seawater, various all-solid-state pH, Eh, and H₂S electrodes have been used to monitor hydrothermal plumes [21–23]. Eh and turbidity sensors were combined to investigate hydrothermal plumes at the Eastern Lau Spreading Center, the southern Mariana Trough, and the Valu Fa Ridge [24-25]. Eh and pH sensors were mounted on underwater vehicles to detect hydrothermal plumes in the Myojin Knoll Caldera [26]. Eh and pH sensors were used in 2014 to study the spatial distribution of seafloor hydrothermal vents at the Kueishantao hydrothermal system offshore Taiwan Island [27]. Eh and H_2S electrodes indicated potential anomalies in the Zouyu-1 and Zouyu-2 hydrothermal fields of the southern Mid-Atlantic Ridge [28]. In 2015, Ding et al. applied pH, Eh, and H₂S electrodes to the offshore Kueishan Tao, a shallow sea area of Taiwan (water depth < 200 m), and the three electrodes showed potential anomalies close to the hydrothermal vent [29].

The Southwest Indian Ridge (SWIR) is an ultraslow spreading ridge. The mantle hotspots, including Crozet, Del Cano, and Marion, are close to the SWIR, indicating strong ridge–hotspot interactions [30]. In recent years, the Chinese Dayang Cruises (CDCs) were undertaken by China

Ocean Mineral Resources R&D Association (COMRA) to investigate hydrothermal sulfides on the SWIR, and multiple hydrothermal fields were found [31]. In this study, we assembled a self-made multi-parameter chemical sensor (MPCS) with all-solid-state pH, Eh, and H₂S electrodes incorporating a deep-sea towed camera system (DTCS) to explore hydrothermal vents at the SWIR at water depths exceeding 2,000 m during the CDCs. The MPCS can simultaneously monitor anomalies in the pH, Eh, and S^{2–} concentration in aquatic environments. The large memory capacity and low power consumption of the MPCS ensured its longevity.

2. MATERIALS AND METHODS

2.1. Materials

Silver chloride, potassium chloride, lithium hydroxide, hydrochloric acid, sodium sulfide, silver nitrate, sodium hydroxide, edetate disodium (EDTA-2Na), ascorbic acid, and standard pH buffers were of analytical grade and were purchased from Aladdin (Shanghai, China). A silver wire (99.9%, 0.4 mm in diameter), iridium wires (99.9%, 0.25 mm in diameter), and a platinum wire (99.9%, 0.4 mm in diameter) were obtained from the Precious Materials Company of Changzhou, China. The electrode substrate was cleaned ultrasonically (KQ218, Shumei Company, China). Wires, data loggers, sealing device, pressure cylinder, and batteries were provided by Hangzhou Dianzi University.

2.2. Electrode preparation

2.2.1. Preparation of the reference electrode

The Ag/AgCl reference electrode was prepared using a melting method [32]. A given quantity of AgCl powder was placed in a platinum crucible and heated to melt. A polished Ag wire with a length of 2 cm was immersed in the platinum crucible containing fused AgCl (455° C) for about 3 s. The thickness of the AgCl layer was modified by repeatedly immersing the Ag wire in the AgCl melt. After cooling to room temperature, the prepared Ag/AgCl reference electrode was soaked in saturated KCl solution for 4 h to activate it.

2.2.2. Preparation of the pH electrode

The $Ir/Ir(OH)_x$ pH electrode [33] incorporated an iridium wire as the working electrode, a commercial Ag/AgCl sensor as the reference electrode, and a Pt wire as the auxiliary electrode (Gaoss Union Electronic Technology Company, China). The iridium wire, with a length of about 2 cm, was ultrasonically cleaned in 0.1 mol/L HCl for 5 min and then cleaned in deionized water for 3 min. The $Ir(OH)_x$ film was electroplated on the iridium wire using a cyclic voltammetry (CV) technique with 5% LiOH solution. The scanning voltage ranged from 0 to 0.9 V at a rate of 50 mV/s. The electroplating process was repeated six times using a CHI660D electrochemical workstation (Chenhua Company, China). The prepared $Ir/Ir(OH)_x$ electrode was washed with distilled water and dried in air.

2.2.3. Preparation of the H₂S electrode

The H₂S electrode used in this study was a modified all-solid-state Ag/Ag₂S electrode [29]. A silver wire with a length of 2 cm was initially polished. Ag nanoparticles were then electroplated on the Ag wire according to the following procedure: the Ag wire was used as the cathode electrode, a 0.1 M AgNO₃ solution was used as the electrolyte, and the electroplating lasted for 30 s at a frequency of 50 Hz and potential of 500 mV. The product was then immersed in a 0.1 mol/L Na₂S solution for 10 min to produce a uniform Ag₂S film. The prepared Ag/Ag₂S electrode was washed with distilled water and dried in air.

2.2.4. Eh electrode

A traditional platinum electrode was used to detect the Eh of the aquatic environment [34]. The sensor comprised an ultrasonically cleaned platinum wire with a length of 2 cm as the working electrode and an Ag/AgCl reference electrode.



2.3. MPCS assembly

Figure 1. Schematic of the MPCS [29]

All prepared electrodes were assembled as an MPCS. The reference electrode was surrounded by pH, Eh, and H₂S electrodes to reduce distance effects [33]. The MPCS comprises six parts (Fig. 1): integrated electrodes, a connector for communication, a datalog to record data, a 3.6 V battery to provide energy, a pressure cylinder to protect the data log, and a sealing device for waterproofing. It is cylindrical with a length of 280 mm and a diameter of 72 mm. A titanium alloy was employed to fabricate the pressure cylinder because of its high strength and resistance to seawater corrosion. The assembled MPCS can be used in oceans at depths exceeding 6,000 m, and its battery can power the system for over a year.

2.4. Applications of MPCS in the SWIR

The ultraslow SWIR with a distance of about 8×10^3 km, extends from the east Rodriguez Triple Junction (RTJ) to the west Bouvet Triple Junction (BTJ), segregating the African and Antarctic plates [35] (Fig. 2). The combined effects of the magma supply and the unique tectonic setting produce an extremely complex hydrothermal system, with sulfide mineralization along the SWIR. Large-scale hydrothermal activities were recently found during submarine explorations at the SWIR [36–39]. The Longqi hydrothermal field (49.650°E/37.783°S) lies at the high pier on the southeast wall of the ridge valley, which is located on a small non-transform offset and ridge valley junction point [35]. The morphology of the surrounding area is significantly relieved by the appearance of basalt and lack of sediment. Where the long-lived detachment fault exposes the intrusive and ultramafic rocks of the seabed, it forms an oceanic core complex, which is ubiquitous on the slow/ultraslow spreading ridges, as well as important structures characteristic of hydrothermal activity [40-41]. Longqi is a typical active hydrothermal field on the SWIR; it has been extensively researched, and a black chimney can be observed by deep-tow video imaging [42]. Sulfide samples collected on site by TV grab consist primarily of sulfide chimneys and massive sulfides. Two types of sulfides were observed, Zn-rich and Fe-rich sulfides, and two mineralization stages were confirmed [43]. On December 13, 2014, the assembled MPCS with methane sensor (Franatech Company, Germany), temperature sensor and depth sensor (Seabird Company, USA) were used to detect hydrothermal anomalies in the Longqi hydrothermal plume during the first leg of the Chinese Dayang 34th cruise (34I). We mounted the MPCS compared with turbidity sensor (RBR Company, Canada), temperature sensor and depth sensor on a DTCS (Fig. 3), which was towed by the research vessel Dayang Yihao at a speed of 1–2 knots, at a height of 3–5 m above the seafloor. On March 3, 2018, the MPCS was mounted on a DTCS towed by the research vessel Xiangyanghong 10 to verify stability in the non-plume area on the SWIR during the second leg of the Chinese Dayang 49th cruise (49II).



Figure 2. The geological setting of the SWIR





3. RESULTS AND DISCUSSION

3.1. Electrode calibration

Here, we used a traditional Eh electrode prepared from platinum wire to determine the redox potential of seawater. This was used without calibration.

An Ag/Ag₂S electrode can detect the S²⁻ concentration. The higher the S²⁻ concentration, the lower the potential of the Ag/Ag₂S electrode. Ag/Ag₂S electrode calibration was performed in the laboratory, and a sulfur antioxidant buffer (SAOB) was used as a solvent to prevent S²⁻ oxidation. The SAOB contains 80 g of NaOH, 35 g of ascorbic acid, 67 g of EDTA-2Na, and 35 g of NaCl per liter [44–45]. The Na₂S solution (0.1 mol/L) was prepared by dissolving 24.0 g Na₂S•9H₂O in SAOB (100 mL). The Na₂S stock solution was then diluted with SAOB solution to produce a series of Na₂S

standard solutions with concentrations of 10^{-2} – 10^{-7} mol/L. The Ag/Ag₂S electrode was immersed in the Na₂S standard solutions for calibration. The calibration curve is represented by E = -32.75log*c* -872.21 ($R^2 = 0.984$) (*c* is the S²⁻ concentration), and its line range was 10^{-1} – 10^{-7} mol/L for S²⁻.

An Ir/Ir(OH)_x pH electrode was calibrated with standard solutions (pH = 4.01, 6.86, and 9.18) prepared with 3.5% NaCl as a solvent. The calibration curve was E = -64.90pH + 715.87 ($R^2 = 0.999$).

The calibration results indicated that the MPCS can quantitively determine the pH, Eh, and H_2S of seawater. However, these calibration curves cannot be used to directly calculate the ion concentrations at depth, especially in seafloor hydrothermal systems, because the temperature–pressure conditions of the deep-sea environment were difficult to simulate in the laboratory. Thus, the raw data obtained here were not converted to concentrations in this study. The MPCS data were recorded at a rate of 5 s per reading, and a high counting frequency can improve the detection accuracy of the sensor.

3.2. The Dayang 34I cruise

The DTCS was dragged at 15:49 and recovered at 23:14 on December 13, 2014. It was towed by the research vessel Dayang Yihao at a depth of 2,400–3,500 m. The raw data recorded by the MPCS mounted on the DTCS during the 34I are shown in Fig. 4. All parameters varied significantly during dragging, indicating that the chemical sensors used can record variations in ambient seawater. The signals from 15:49-17:30 and 21:00-23:14 were not used in this study because the DTCS was descending/ascending during these time intervals. Thus, only the near bottom data between 17:30 and 21:00 are presented. All three electrodes showed smooth potentiometric responses from 17:30 to 18:55 (Fig. 5). At 18:56, all potentials dropped significantly with a depth of 2,700 m, e.g., the potential of the Eh electrode decreased from -170 to -219 mV, accompanied by a decrease in the H₂S electrode potential from -166 to -264 mV. It is suggested that the MPCS was passing through a reducing water body with an increased H₂S concentration. The pH electrode exhibited decreasing potentials (from -256 to -274 mV) in the same region, indicating that the pH of the water body was lower than that of the background seawater. The potential anomalies of Eh, H₂S, and pH electrodes were 49, 98, and 18 mV, respectively. This water body was probably a hydrothermal plume as indicated by the low Eh and pH values and elevated H₂S concentrations [46]. Additionally, the methane sensor showed a significant anomaly (from 3.6 to 2.6 V) and the anomaly of the temperature was about 0.13 °C (from 2.21 to 2.34 °C), which were also detected in this region, further testifying that the detected water body was a hydrothermally affected area because the hydration of ultramafic rock (serpentinization) could produce hydrogen, which fueled abiogenic methane production via Fischer–Tropsch-type reactions [47–50]. After 20 min, all signals slowly returned to the background values for seawater, indicating that the DTCS had passed through the hydrothermal plume.



Figure 4. The raw MPCS data from a survey line obtained during the Dayang 34I cruise



Figure 5. The pH, Eh, H₂S, depth, temperature, and methane data obtained from a DTCS during a survey on the Dayang 34I cruise



Figure 6. Correlation coefficients among pH, Eh, H₂S, methane, and temperature during a survey on the Dayang 34I cruise



Figure 7. Spatial distributions of pH, Eh, H₂S, and methane obtained from a DTCS during a survey on the Dayang 34I cruise. The existing Longqi vent is marked as a red dot.

The reliability of our MPCS was further assessed using correlation coefficients among the detected parameters (Fig. 6). The pH, Eh, CH₄, and H₂S, but not temperature, showed significant

positive correlation at the 0.05 level. It is suggested that the self-made pH, Eh, and H₂S sensors showed potentiometric responses simultaneously with the commercial methane sensor. The temperature showed no significant correlation with any other parameters, which is partly ascribed to the temperature difference being below 0.13° C and the seawater temperature being sensitive to the water depth [51]. The spatial distributions of the detected parameters are shown in Fig. 7. All the evaluated parameters (pH, Eh, H₂S, and CH₄) exhibited significant anomalies at longitude 49.6493° and latitude -37.768° (site A). It is suggested that the seawater here (site A) may have been affected by hydrothermal plumes from adjacent vents (e.g., the Longqi vent 1.5 km away from site A). Significant pH and slight Eh anomalies were also observed at longitude 49.6490° and latitude -37.742°. This site, however, may be affected by the current rather than the hydrothermal plume, since H₂S and CH₄ anomalies were detected in this region. According to the *in situ* MPCS observation, we conducted a TV grab at site A and retrieved sulfide samples. Thus, site A may belong to the plume area of the Longqi hydrothermal vent.

3.3. Dayang 49II cruise

On Mar 4, 2018, we further tested the applicability of the MPCS during the Dayang 49II cruise. The MPCS mounted on the DTCS recorded pH, Eh, H₂S, temperature, and turbidity data from 8:00 am to 9:30 am at a depth of 2,500–2,800 m (Fig. 8). All the detected parameters showed relatively stable responses during the observation, indicating that the observed region was dominated by ambient seawater and was not significantly affected by hydrothermal activity.



Figure 8. The pH, Eh, H₂S, temperature, depth, and turbidity data obtained from a DTCS during a survey on the Dayang 49II cruise



Figure 9. Correlation coefficients among pH, Eh, H₂S, turbidity, and temperature during a survey on the Dayang 49II cruise



Figure 10. Spatial distributions of pH, Eh, H₂S, and temperature obtained from a DTCS during a survey on the Dayang 49II cruise

Nonetheless, the correlation matrix among these parameters (Fig. 9) indicated that pH, Eh, and H_2S were positively correlated at a 0.01 significance level. It suggested that the prepared electrodes respond simultaneously even for low variation ranges, further testifying the high precision of these

sensors. Turbidity and temperature did not present significant correlations with these electrodes, which was ascribed to the small variations in both parameters.

Although all of the detected parameters exhibited narrow data ranges, two anomalies were identified from their spatial distributions (Fig. 10). The first site is located at longitude $48.80-48.84^{\circ}$ and latitude ~ -37.969° and showed slight anomalies in pH, Eh, H₂S, and temperature. Therefore, this site may have been affected by hydrothermal activity. Hydrothermal vents may be adjacent to this area. The second site is situated at longitude ~ 48.785° and latitude -37.966 to -37.967° and exhibited pH, Eh, and H₂S anomalies. No temperature anomaly was observed at this site, which may have been influenced by cold seeps [52]. Nonetheless, the results indicated that our prepared electrodes are highly applicable to searching for hydrothermal activity in deep-ocean environments.

4. CONCLUSION

We assembled a multi-parameter electrochemical sensor (MPCS) mounted with self-made reference, pH, Eh, and H₂S electrodes. The assembled MPCS was used to continuously *in situ* monitor pH, Eh, and H₂S anomalies during two Chinese Dayang Cruises on the Southwest Indian Ridge. All of the integrated electrodes showed significant signal anomalies when passing through hydrothermal plumes, indicating that our prepared sensors can be used to detect hydrothermal activity. Additionally, the spatial distributions of the detected parameters suggested the presence of an unknown hydrothermal plume, which was later confirmed by the occurrence of sulfide. It is indicated that our MPCS was extremely reliable during practical application in the deep ocean. With their *in situ* monitoring, long life, resistance to high temperatures and pressures, and high sensitivity, our prepared electrodes and MPCS are potentially suitable tools for *in situ* monitoring of chemical parameters in various seawater environments. Nonetheless, it is difficult to convert potentials into ion concentrations because of the challenge of calibration at high temperatures and pressures. Future work will focus on developing a more accurate regression curve for different temperatures and pressures.

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References

- 1. M. D. Brasier, R. Matthewman, S. Mcmahon and D. Wacey, Astrobiology, 11 (2011) 725.
- 2. W. Martin, J. Baross, D. Kelley and M. J. Russell, Nat. Rev. Microbiol., 6 (2008) 805.
- 3. K. L. Von Damm, J. M. Edmond, B. Grant and C. I. Measures, *Geochim. Cosmochim. Ac.*, 49 (1985) 197.
- 4. C. R. German, J. Lin and L. M. Parson, Atmos. Environ., 148 (2004) 256.
- 5. J. E. Lupton, D. G. Pyle, W. J. Jenkins and R. Greene, Geochem. Geophy. Geosy., 5 (2004) 241.

- 6. E. T. Baker and G. J. Massoth, Earth Planet Sci. Lett., 85 (1987) 59.
- 7. S. Chen, C. H. Tao, E. T. Baker and H. M. Li, Mar. Geophys. Res., 38 (2017) 3.
- 8. C. Y. Tan, C. D. Cino, K. Ding and W. E. Seyfried, J. Volcanol. Geoth. Res., 343 (2017) 263.
- 9. P. J. Wangersky, Sci. Mar., 69 (2005) 75.
- 10. G. Mills and G. Fones, Sensor Rev., 32 (2012) 17.
- 11. K. Ding, W. E. Seyfried, M. K. Tivey and A. M. Bradley, Earth Planet Sci. Lett., 186 (2001) 417.
- 12. X. T. Zhang, R. H. Zhang, S. M. Hu and Y. Wang, Sci. China Technol. Sc., 52 (2009) 2466.
- 13. X. P. Yang, K. G. Ong, W. R. Dreschel and K. F. Zeng, Sensors, 2 (2002) 455.
- 14. A. M. Nightingale, A. D. Beaton and M. C. Mowlem, Sensor Actuat. B-Chem., 221 (2015) 1398.
- 15. J. Daoudi, S. Betelu, T. Tzedakis and J. Bertrand, Sensors, 17 (2017) 1372.
- 16. E. Bagshaw, A. Beaton, J. Wadham and M. Mowlem, Trends Anal. Chem., 82 (2016) 348.
- 17. K. N. Mikhelson, Ion-selective electrode, Springer-Verlag, (2013) New York, USA.
- 18. J. Gallardogonzalez, A. Baraket, A. Bonhomme and N. Zine, Anal. Lett., 3 (2018) 348.
- 19. Y. F. Huang, J. Li, T. Y. Yin and J. J. Jia, J. Electroanal. Chem., 741 (2015) 87.
- 20. H. Xu, Y. Wang, Z. Y. Luo and Y. W. Pan, Meas. Sci. Technol., 24 (2013) 1.
- Y. W. Pan, Y. Ye, G. H. Wu and H. W. Qin, Acta Oceanol. Sin., (in Chinese with English abstract), 34 (2012) 179.
- 22. C. H. Tao, G. H. Wu, X. M. Deng and Z. Y. Qiu, Acta Oceanol. Sin., 32 (2013) 85.
- E. T. Baker, J. A. Resing, R. M. Haymon and V. Tunnicliffe, *Earth Planet. Sci. Lett.*, 449 (2016) 185.
- 24. E. T. Baker, J. A. Resing, S. L. Walker and F. Martinez, Geophys. Res. Lett., 33 (2006) L07308.
- 25. E. T. Baker, G. J. Massoth, K. Nakamura and R. W. Embley, *Geochem. Geophy. Geosy.*, 6 (2015) 60.
- 26. K. Komaki, M. Hatta, K. Okamura and T. Noguchi, Underwater Technol. (2015) 1.
- 27. C. H. Han, Y. Ye, Y. W. Pan and H. W. Qin, Acta Oceanol. Sin., 33 (2014) 37.
- 28. S. Chen, C. H. Tao, E. T. Baker and H. M. Li, Mar. Geophys. Res., 38 (2017) 3.
- 29. Q. Ding, Y. Ye, Y. W. Pan and Y. F. Huang, Cont. Shelf Res., 111 (2015) 262.
- 30. D. Sauter, M. Cannat, C. Meyzen and A. Bezos, Geophys. J. Int., 179 (2009) 687.
- 31. X. Han, G. Wu, R. Cui and Z. Qiu. Discovery of a hydrothermal sulfide deposit on the Southwest Indian Ridge at 49.2°E (Abstract). AGU, Fall Meeting, San Francisco, 2010.
- 32. Z. Xie and Y. X. Liu, Chin. J. Nonferrous Met. (in Chinese with English abstract), 8 (1998) 668.
- 33. X. Zhang, Y. Ye, Y. T. Kan and Y. F. Huang, Acta Oceanol. Sin., 36 (2017) 99.
- 34. M. Whitfield, Limnol. Oceanorg., 19 (1974) 857.
- 35. C. H. Tao, H. M. Li, X. B.Jin and J. P. Zhou, Sci. Bull., 59 (2014) 2266.
- 36. Z. G. Li, F. Y. Chu, L Jin and X. H. Li, Acta Oceanol. Sin., 35 (2016) 101.
- 37. W. F. Yang, C. H. Tao, H. M. Li and J Liang, Mar. Geophys. Res., 38 (2017) 71.
- 38. C. H. Tao, T. Wu, C. Liu and H. M. Li, Mar. Geophys. Res., 38 (2017) 17.
- 39. C. H. Tao, G. H. Wu, J. Ni and X. Su. New hydrothermal fields found along the SWIR during the Legs 5-7 of the Chinese DY115-20 expedition (Abstract). AGU, Fall Meeting, San Francisco, 2009.
- 40. Y. Fouquet, P. Cambon. J., Etoubleau and J. L. Charlou, American Geophysical Union, (2010) 321.
- 41. A. M. Mccaig, R. A. Cliff, J. E. Escartin and A. E. Fallick, Geology, 35 (2007) 935.
- 42. C. H. Tao, J. Lin, S. Q. Guo and Y. S. Chen, Geology, 40 (2012) 47.
- 43. J. Ye, X. F. Shi, Y. M. Yang and J. H. Liu, *Acta Miner. Sin.* (In Chinese with English abstract), 31 (2011) 17.
- 44. F. J. Millero, Mar. Chem., 18 (1986) 121.
- 45. F. J. Millero, T. Plese and M. Fernandez, Limnol. Oceanorg., 33 (1988) 269.
- 46. Y. Chen, Y. Ye and C. J. Yang, *China Ocean Eng.*, 19 (2005) 129.
- 47. M. D. Lilley, D. A. Butterfield, E. J. Olson and J. E. Lupton, Nature, 364 (1991) 45.
- 48. J. L. Charlou, J. P. Donval, Y. Fouquet and P. Jean-Buptiste, Chem. Geol., 191 (2002) 345.
- 49. M. J. Cao, K. Z. Qin, G. M. Li and N. J. Evans, Geochim. Cosmochim. Ac., 141 (2014) 179.

- 50. C. Oze, L. C. Jones, J. I. Goldsmith and R. J. Rosenbauer, P. Natl. Acad. Sci. UAS., 109 (2012) 9750.
- 51. N. M. Ridgway, New Zeal. J. Mar. Fresh. Res., 3 (1969) 57.
- 52. D. S. Stakes, D. Orange, J. B. Paduan and K. A. Salamy, Mar. Geol., 159 (1999) 93.

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