Hydrothermal mineralization in the Mid-Okinawa Trough

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Abstract—Three active hydrothermal fields have been discovered by the submersible “Shinkai 2000” from the Okinawa Trough; JADE site of Izanagi Cauldron, CLAM site of Iheya Ridge and Minami-Ensei Knoll. Samples of active chimneys and mounds from the CLAM and Minami-Ensei sites were examined by microscopy, X-ray diffractometry and electron microprobe analysis. Mineral compositions of active chimneys from the Minami-Ensei site, consisting of abundant anhydrite, gypsum, sphalerite and pyrite, resemble those from the JADE site, whereas the CLAM site is characterized by abundant Mn carbonate, wurtzite and amorphous silica. These mineral abundances are closely related to high temperature fluids of nearly boiling temperature for the JADE and Minami-Ensei sites, and low temperature and manganiferous fluids for the CLAM site. The mineral assemblage and chemistry have revealed that the Minami-Ensei deposits exhibit the most oxidized conditions in submarine hydrothermal systems, similar to the black ore in the Kuroko deposits, whereas the CLAM deposits show intermediate conditions between the most reduced Guaymas Basin chimneys and the most oxidized Minami-Ensei deposits.

Active chimneys from MAR and EPR are chalcopyrite-rich with high bulk Cu/Zn ratios, whereas those from the Guaymas Basin and CLAM site are poor in chalcopyrite with low bulk Cu/Zn ratios. The pH-\(f_{O_2}\) relations and solubility data indicate that the Cu/Zn ratio in hydrothermal deposits is connected largely with temperature and pH. Galena is common in the hydrothermal deposits from the Okinawa Trough and Izu-Mariana back arc basins, whereas it is very rare in MOR-type deposits. The solubility data of PbS and some geological evidences indicate that the lead of the Okinawa Trough is likely derived from the continental crust or sediments.

INTRODUCTION

The Okinawa Trough, situated in the back-arc basin of the Ryukyu arc, is thought to be an incipient stage of rifting and spreading (Kimura et al., 1986). Since the discovery of hydrothermal venting of 50°C at the “Natsushima 84-1 Knoll” in 1986
(KIMURA et al., 1987, 1988), extensive surveys of more than 100 dives using the submersible "Shinkai 2000" have been carried out in the Okinawa Trough. Three active hydrothermal fields have been discovered (Fig. 1); Izena Cauldron and Iheya Ridge in 1988 (HALBACH et al., 1989; NAKAMURA et al., 1989; KIMURA et al., 1989; TANAKA et al., 1989) and Minami-Ensei Knoll in 1990 (HASHIMOTO et al., 1990). Among them, the hydrothermal deposits in the Izena Cauldron have attracted attention for their high contents of Au and Ag (NAKAMURA et al., 1988; HALBACH et al., 1989; URABE, 1989) and for the first discovery of the Kuroko-type deposits in the present seafloor. The Kuroko-type mineralization was also found in the Mariana Trough and Izu-Bonin back arc spreading axis (KUSAKABE et al., 1990; URABE and KUSAKABE, 1990). In this study, we present the mineral composition and

Fig. 1. Locations of active hydrothermal fields in the Okinawa Trough.
chemistry of the Iheya and Minami-Ensei hydrothermal deposits and characterize the Okinawa Trough hydrothermal mineralization as compared with other submarine hydrothermal deposits.

GEOLOGICAL SETTING OF SULFIDE DEPOSITS

JADE site, Izena Cauldron

Active hydrothermal activity was discovered in the Izena Cauldron, and was called JADE site (26°16’ N, 127°05’ E; water depth of 1350 to 1400 m) to commemorate the joint research of Germany and Japan onboard the research vessel “Sonne” (HALBACH et al., 1989). The cauldron has a rectangular shape of 6 × 3 km and a water depth of 1665 m in the deepest part of the cauldron (Fig. 2). The cauldron is composed of pumice of dacite to rhyolite compositions (KATO et al., 1989; TANAKA et al., 1990). The active hydrothermal field with discharging fluids up to 320°C is located on the northeast slope of the cauldron. Several active chimney swarms are found in a 1000 × 200 m area (TANAKA et al., 1990).

CLAM site, Iheya Ridge

The Iheya Ridge rises to water depths of 1400 to 900 m as compared to the surrounding seafloor which lies in water depth of 1650 to 1700 m (Fig. 2). Highly vesicular basalt breccias and pillow lavas were observed on the ridge (NAKA et al., 1989). An active hydrothermal field, called the CLAM site (27°33’ N, 126°58’ E; water depth of 1392 m) is located on the eastern part of the Iheya Ridge. The CLAM site was named after the Calymptogenia community in the hydrothermal field and was first appeared in SAKAI et al. (1990). Though intensive hydrothermal alteration of the rocks is restricted to an area of 100 × 50 m, white hydrothermal precipitates or bacterial mats exist sporadically in the surrounding area of 1 km across. A hydrothermal vent with the highest temperature of 220°C was observed in 1988 (TANAKA et al., 1989). Three principal vent swarms called Pyramid chimney, Kiko chimneys and Baby chimneys are recognized in the CLAM site (Fig. 3).

(1) Pyramid chimney

The Pyramid chimney is a cone-shaped or pagoda-like spire of about 2 m in height. There are several vents on the foot of the chimney, while the slope is composed of several horizontal “eaves” and spreads gently towards the seafloor. Each eave is about 10 cm in thickness. Such eave-shaped deposits have also been discovered from the Guaymas Basin (LONSDALE and BECKER, 1985; PETER and SCOTT, 1988). Intermittent discharge of hydrothermal fluids was observed from an active vent on the east foot of the Pyramid chimney (GAMO et al., 1991b; NAKASHIMA et al., 1993). However, the discharge of hydrothermal fluids from the crest had ceased before June, 1990.

(2) Kiko chimneys

Kiko chimneys constitute a few chimneys of 20 to 30 cm in height which grow within the fissures on the eaves extending from the Pyramid chimney. The highest fluid temperature of 214°C was obtained in 1990 (GAMO et al., 1991b), but the activity had ceased by June, 1992.
(3) Baby chimneys

A white hydrothermal vent area of $2 \times 3$ m wide, called the Baby chimneys, is exposed on the western side of the CLAM site. There are a few tens of small chimneys, each less than 10 cm high, and calm venting has occurred (GAMO et al.,
Fig. 3. Topographic map of the CLAM site showing major chimney sites, Iheya Ridge (modified after Gamó et al., 1991b).

Fig. 4. Bathymetric map of the Minami-Ensei Knoll. The broken line indicates the inner rim of the cauldron (after Aoki et al., 1993). Arrows indicate depressions.
1991b). White materials in the Baby chimneys are composed of fragments of broken chimneys and bacterial mats. The measured temperatures of discharging fluids were 110°C in June, 1992 and 95°C in May, 1993.

Minami-Ensei Knoll

In 1990 intense hydrothermal activity was discovered in the C-depression (28°23′40″N, 127°38′40″E) on the Minami-Ensei Knoll. The Minami-Ensei Knoll has an elliptical shape with a long radius of 2 km (Fig. 4). Several depressions which are considered to be volcanic in origin exist on the knoll (Aoki et al., 1993). Water depth of the C-depression is as shallow as 700 m, so the observed highest temperature of 278°C is almost equal to the boiling temperature of seawater at this depth (Chiba et al., 1993).

Mineralogy

Hydrothermal precipitates recovered by the submersible “Shinkai 2000” from the CLAM site in 1990 (Dive 487; Observer: T. Gamo) and 1992 (Dive 621; Observer: K. Nakashima) and from the Minami-Ensei Knoll in 1992 (Dive 622; Observer: H. Chiba) were examined by microscopy, X-ray diffractometry and electron microprobe analysis.

CLAM site, Iheya Ridge

Stacked eaves of the Pyramid chimney are composed mainly of carbonates. Mineral paragenesis of the Pyramid samples was already described by GamO et al. (1991b) and Nakashima et al. (1993). Thus only a brief description will be given here. Sample No. 487-A was collected from an active vent side on the foot of the Pyramid chimney (Fig. 3). The mineral composition of 487-A includes a large quantity of calcite, rhodochrosite and minor amounts of anhydrite, gypsum, pyrite, pyrrhotite, wurtzite, chalcopyrite, isocubanite, alabandite, realgar and native sulfur (Table 1). Most of the anhydrite and gypsum have been altered to carbonates and sulfides with relicts of their crystal shape. Sample No. 487-D constitutes a part of the flat eaves away from the vent and shows a lateral layered texture. This sample is composed mainly of carbonates and amorphous silica. The chemistry of the carbonates can be expressed in the CaCO₃-MnCO₃ system and shows a wide range of composition, 16–86 mole % MnCO₃ and manganese increases from the bottom to upper layer. Wurtzite, pyrrhotite, isocubanite, chalcopyrite, galena, realgar and Fe-hydroxide are found in trace amounts. Wurtzite is the sole zinc sulfide in the CLAM site and contains much Fe and Mn (up to 32 wt.%, respectively). The chemical compositions of the wurtzite are consistent with those reported by Izawa et al. (1991). No wurtzite containing such extraordinary amounts of Fe and Mn has ever been reported from seafloor hydrothermal deposits.

Quantitative analyses of pyrrhotite by electron microprobe including newly suplemental analyses indicate that the Fe contents range from 45.9 to 47.2 atom. %, which are close to those of monoclinic pyrrhotite (46.4 to 47.3 atom. %; Kisshin and Scott, 1982). Crystallographic identification by X-ray diffraction has not been
Table 1. Comparative mineralogy of the Okinawa Trough hydrothermal deposits

<table>
<thead>
<tr>
<th>Mineral</th>
<th>CLAM Site (IHEYA)</th>
<th>MINAMI-ENSEI</th>
<th>JADE Site (IZENA)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Baby C.</td>
<td>Pyramid C.</td>
<td>Chimney*</td>
</tr>
<tr>
<td>Calcite (CaCO₃)</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Rhodochrosite(MnCO₃)</td>
<td>-</td>
<td>++</td>
<td>-</td>
</tr>
<tr>
<td>Dolomite (Ca,Mg)CO₃</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>Cerussite (PbCO₃)</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>Anhydrite (CaSO₄)</td>
<td>-</td>
<td>+</td>
<td>+++</td>
</tr>
<tr>
<td>Gypsum (CaSO₄·2H₂O)</td>
<td>-</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>Barite (BaSO₄)</td>
<td>-</td>
<td>+</td>
<td>+++</td>
</tr>
<tr>
<td>Anglesite (PbSO₄)</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>Sphalerite (ZnS)</td>
<td>-</td>
<td>-</td>
<td>+++</td>
</tr>
<tr>
<td>Wurtzite (ZnS)</td>
<td>-</td>
<td>++</td>
<td>-</td>
</tr>
<tr>
<td>Pyrrhotite (Fe₇S₈)</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Pyrite (FeS₂)</td>
<td>++</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>Marcasite (FeS₂)</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>Galena(PbS)</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Chalcopyrite (CuFeS₂)</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Iss-cubanite (CuFe₂S₄)</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Stibnite (Sb₂S₃)</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>Tennantite [(Cu,Fe)₁₂As₄S₄]</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>Tetrahedrite [(Cu,Fe)₁₂Sb₄S₄]</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ablandite (MnS)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Amorphous silica (SiO₂)</td>
<td>-</td>
<td>+++</td>
<td>+</td>
</tr>
<tr>
<td>Talc (Mg₃Si₂O₅(OH)₄)</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>Chrysotile (Mg₃Si₂O₅(OH)₄)</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>Sulfur (S)</td>
<td>+++</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Realgar (AsS)</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Cinnabar(HgS)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mn-hydroxide(MnO₂)</td>
<td>-</td>
<td>++</td>
<td>-</td>
</tr>
<tr>
<td>Fe-Pb oxyhydroxide</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
</tbody>
</table>

Water Depth (m)  1,400 m  700m  1,350 - 1,400m
Fluid Temperature (°C)  110°C  220 °C  280°C  320°C

+++: Abundant, ++: common, +: rate, -: not observed.

*Combined with chimney and mound samples.

**Compiled from Urabe (1989) and Tanaka et al. (1990).

***Compiled from Halbach et al. (1993).

made because of the very fine-grained nature. Taking into account the temperatures of discharging fluids obtained in the Pyramid chimney, most of pyrrhotite is considered to be monoclinic.

Minami-Ensei Knoll

Samples from mounds (A and B in Fig. 5), chimneys (C in Fig. 5) and sheeted sulfides (D in Fig. 5) were collected from the C-depression in the Minami-Ensei Knoll. The sulfide minerals from the mound samples are pyrite, sphalerite, galena and chalcopyrite. Non-sulfide phases are anhydrite, gypsum, calcite, dolomite and talc. The chimney samples are fragile and composed mainly of anhydrite and gypsum with minor chalcopyrite, sphalerite, pyrite, galena, anglesite, cerussite, calcite, talc and amorphous silica (Table 1). Chimney walls typically consist of massive Cu-Zn-Fe sulfides in inner zones enclosed by outer zones of disseminated sulfides in an anhydrite and gypsum matrix. These textures in mineral zoning resemble closely the black smoker chimneys in EPR (e.g., Styrt et al., 1981; Haymon, 1983; Graham
et al., 1988) and in MAR (e.g., THOMPSON et al., 1988).

The upper and lower surfaces of the sheeted sulfide are composed of thin clastic layers of volcanic and hydrothermal particles. In the interior of the sheeted sulfide, angular clastics are filled with hydrothermal minerals. The clastic fragments of silicates are pumice, plagioclase (An 25–43) and K-feldspar, and those of sulfides are sphalerite, pyrite, chalcopyrite and galena. Tetrahedrite, barite, realgar, stibnite, amorphous silica and native sulfur fill up the above fragments. The fragmented silicate particles are considered to be brought from the subsurface to the seafloor by explosive volcanism and then they are compacted with hydrothermal precipitates. The maximum measured temperature of 278°C in the Minami-Ensei Knoll is close to the boiling point of seawater at this depth. Therefore, the hydrothermal activity in the Minami-Ensei Knoll appears to have been violent with repeated explosions.

The sheeted sulfide comprises about 20 vol.% of sphalerite which contains 0.9 to 3.8 mole % FeS, and Cu and Cd in trace amounts. Chemical compositions of sphalerite agree well with those reported by NEDACHI et al. (1992).

FLUID INCLUSIONS

Sample description and analytical method

Microthermometry of fluid inclusions have been carried out for samples of hydrothermal deposits from the Iheya Ridge and Minami-Ensei Knoll. Samples from the Iheya Ridge are coarse-grained calcite which constitute the Pyramid chimney, and those from the Minami-Ensei Knoll are anhydrite from the chimney, calcite from the mound and clastic sphalerite in the sheeted sulfide (Fig. 5). The fluid inclusions observed are two-phase (aqueous fluid and a vapor bubble at room conditions) and less than 70 μm in diameter. Vapor-rich inclusion and inclusions with various liquid/vapor ratios are frequently observed in the CLAM calcite (Fig. 6a) and rarely observed in the Minami-Ensei samples. Secondary inclusions are also frequently
Fig. 6. Microphotograph of fluid inclusions in calcite from the CLAM site, Iheya Ridge. 
a: Fluid inclusions with various liquid (L)/vapor (V) ratios according to the process of necking down (?).  
b: Large primary inclusions and typical group of planes of small secondary inclusions. Scale bars represent $50 \, \mu m$.

observed, but these inclusions are less than $5 \, \mu m$ in diameter (Fig. 6b) and inadequate for microthermometric measurement. Thus, microthermometry measurements were only carried out on the large primary inclusions.

A FLUID INC. adapted U.S.G.S. Gas-Flow Heating/Freezing System was used for microthermometric measurements. Repeated calibration, utilizing the known melting points of various substances within the temperature range of interest, indicates that the errors are $\pm 1^\circ C$ for heating experiments and $\pm 0.1^\circ C$ for cooling experiments. No evidence of clathrate melting in fluid inclusion was observed.

Microthermometry

(1) CLAM site, Iheya Ridge

Filling temperatures of Iheya calcite ranged from 204 to 338°C and salinities ranged from 3.37 to 5.70 equiv.wt.% NaCl (Table 2; Fig. 7a). It should be noted that the filling temperatures of calcite are higher than the maximum measured temperature of hydrothermal vent fluids (220°C), and the salinities are significantly higher
Table 2. Summary of fluid inclusion microthermometry data

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>FILLING TEMP. (°C)</th>
<th>SALINITY (EQUIV.WT.% NaCl)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N</td>
<td>RANGE</td>
</tr>
<tr>
<td>CLAM SITE (IHEYA)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>calcite</td>
<td>25</td>
<td>204 - 338</td>
</tr>
<tr>
<td>MINAMI-ENSEI</td>
<td></td>
<td></td>
</tr>
<tr>
<td>calcite</td>
<td>17</td>
<td>268 - 305</td>
</tr>
<tr>
<td>anhydrite</td>
<td>21</td>
<td>236 - 300</td>
</tr>
<tr>
<td>sphalerite</td>
<td>2</td>
<td>239 - 241</td>
</tr>
</tbody>
</table>

Fig. 7. Homogenization temperature-salinity relations of fluid inclusions in some hydrothermal minerals from the Okinawa Trough. The data plotted in this figure uses only those homogenization temperature and salinities which could be obtained from the same inclusion. $T_{\text{max}}$: maximum temperature of discharging fluids, b.p.: boiling point of seawater.
than the ambient seawater (3.5 equiv. wt.% NaCl). Salinities are also higher than fluid inclusions from 21°N EPR (STYRT et al., 1981; LE BEL and OUDIN, 1982) and are similar to the Guaymas Basin calcite (KOSKI et al., 1985). Since measured data showed very wide ranges of temperature and salinity, we should pay attention to the necking down (ROEDDER, 1984) after fluids were trapped in the calcite crystal (Fig. 6a).

(2) Minami-Ensei Knoll

Conspicuous features of fluid inclusions in anhydrite are that salinities are almost constant or slightly increase with decreasing temperature, though filling temperatures have a very wide range (Fig. 7b). The higher measured temperatures are close to the present vent fluids (280°C) except for the highest point of 300°C. In general, anhydrite is one of the first precipitates when the hydrothermal fluids reach the seafloor and constitutes the outer surface of chimneys. Therefore, the wide range of filling temperatures indicates that the fluids were trapped while they were being cooled by ambient seawater.

Filling temperatures of calcite are close to temperatures of the present vent fluids except for two points around 300°C (Fig. 7b). Salinities of the calcite inclusion fluids are slightly lower than those of anhydrite and are almost the same as the seawater value.

Filling temperatures of sphalerite are lower with salinities higher than those of anhydrite and calcite (Fig. 7b). Since the measured sphalerite is from clastics in the sheeted sulfide, it may have been blown off from the subsurface to the floor surface. Therefore, filling temperatures and salinities of sphalerite may reflect the conditions of deposition under the seafloor.

MINERALOGICAL CHARACTERS OF EACH HYDROTHERMAL DEPOSITS IN THE OKINAWA TROUGH

Mineral compositions observed in the Okinawa Trough are summarized in Table 1 along with maximum fluid temperatures measured during submersible surveys. HALBACH et al. (1993) examined the massive sulfide ores from the JADE site, and reported many sulfides, sulfoalts and others in addition to minerals listed in Table 1; such as anglesite, bornite, covellite, energite, jalpaite, kermasite, melnicovite, native gold, native silver, orpiment and tetrahedrite. The mineral assemblage of the Minami-Ensei Knoll resembles that of the JADE site, although the CLAM site shows quite different mineralogy. Anhydrite, gypsum, and sphalerite are abundant in the JADE and Minami-Ensei sites, while calcite, rhodochrosite and amorphous silica are rich in the CLAM site. Anhydrite can be precipitated by mixing of Ca-rich hot hydrothermal fluid and SO₄-rich seawater at temperatures above 140°C for EPR (HAYMON and KASTNER, 1981; MARCHIG et al., 1988) and Mariana Trough (KUSAKABE et al., 1990) and above 120°C for Okinawa Trough (GAMO et al., 1991b), although they dissolve below these temperatures. In a sample of the Pyramid chimney (487-A), most of anhydrite has changed to sulfides and carbonates. Thus, during the progress of hydrothermal activity in the CLAM site, anhydrite dissolved and sulfides and carbonates precipitated. Amorphous silica becomes less soluble
with decreasing temperature. Silica contents in discharging fluids of the Okinawa Trough range from 10 to 13 mM/Kg (GAMO et al., 1990; CHIBA et al., 1993). These silica contents indicate that amorphous silica begin to precipitate near 150°C (e.g., TIVEY and DELANEY, 1986). Therefore, amorphous silica-containing deposits of the CLAM site are modified by dissolution of anhydrite and precipitation of amorphous silica around 150°C or below.

Solubility of calcite in hydrothermal fluids can be affected by temperature and CO₂ concentration. Discharging fluids from the Okinawa Trough contain CO₂ concentrations of 209 mM/Kg for the JADE site (GAMO et al., 1990), ca. 100 mM/Kg for the CLAM site (ISHIBASHI et al., 1990), and 64–96 mM/Kg for the Minami-Ensei site (CHIBA et al., 1993). These values are much higher than that of the MOR-type fluids (SAKAI et al., 1990). In these CO₂ concentrations, calcite solubility increases with increasing CO₂ concentration under a constant temperature, and also increases with decreasing temperature under a constant CO₂ pressure (e.g., HOLLAND and MALININ, 1979). Temperatures of 320°C for the JADE site and of 278°C for the Minami-Ensei fluids are very close to boiling points of seawater at each corresponding depth. On the other hand, measured temperatures for the CLAM site vent have progressively lowered from 220°C in 1988 through 216°C in 1989 to 130°C in 1992. Solubility of carbonate in hydrothermal solution at 150°C is one or two orders of magnitude greater than at 300°C under a constant CO₂ pressure. Vent fluids of such chemical characteristics as well as their low temperatures at the CLAM site allow carbonates to precipitate when they are mixed with low CO₂-containing seawater.

Wurtzite is the sole zinc sulfide at the CLAM site. It contains a large amount of Fe and Mn. Sphalerite is a principal zinc sulfide in the Minami-Ensei (NEDACHI et al., 1992; NAKASHIMA et al., 1993). Wurtzite is stable under sulfur-deficient or zinc-rich conditions relative to sphalerite (SCOTT and BARNES, 1972; VAUGHAN and CRAIG, 1978). Sulfur fugacity of the CLAM site fluids is lower than that of the Minami-Ensei fluids as discussed later. Manganese activity of the hydrothermal fluids at the CLAM site is high (ISHIBASHI et al., 1990) and this is supported by the presence of alabandite, rhodochrosite and encrustation of manganese hydroxide. Sulfur deficient and cation-predominant fluid is suitable for wurtzite deposition in the CLAM site. A difference in the rate of nucleation may also be an important factor controlling the ZnS mineralogy as discussed by GRAHAM et al. (1988); rapid nucleation caused by quenching on the seafloor leads to the formation of wurtzite at the CLAM site, whereas slower nucleation in warmer environments under the seafloor leads to the precipitation of sphalerite at the Minami-Ensei site.

CONDITIONS OF MINERAL DEPOSITION

Temperature and sulfur fugacity

Filling temperatures of calcite from the CLAM site range from 204 to 338°C and are typically between 250 to 300°C. Monoclinic pyrrhotite in the Pyramid chimney indicates that the formation temperature is lower than about 255°C (KISSHIN and SCOTT, 1982). These evidences indicate that the carbonate-dominated
Pyramid chimney was formed around 250°C.

Sulfur fugacity and T relations for the CLAM and Minami-Ensei Knoll hydrothermal deposits have been examined. In Fig. 8, the conditions of the discharging fluid were estimated from dissolved gas compositions and calculated using the activity coefficient of KISHIMA and SAKAI (1984) and KISHIMA (1989). At the CLAM site, the vent fluids from the Pyramid and Baby chimneys are expressed as points B and C in Fig. 8, respectively. On the other hand, the formation conditions of the Pyramid chimney itself are displayed as point A. This was estimated by the chemical composition of pyrrhotite and the filling temperatures of fluid inclusion as mentioned above, and indicates similar sulfur fugacity as, and higher temperature than, the present fluids.

At the Minami-Ensei Knoll, FeS contents in sphalerite indicate that its depositional condition is estimated as point D (log$_{f_0}$ = -10.5~11.0 at 230°C corresponding about -10.2~10.7 at 250°C), whereas the present vent fluids are ex-

![Graph](image)

Fig. 8. Estimated log$_{f_0}$ — temperature conditions for hydrothermal activity in the Okinawa Trough. A: Deposition of the Pyramid chimney, B: dissolved gas composition in the Pyramid chimney vent fluids, C: dissolved gas composition in the Baby chimneys vent fluids, D: deposition of sphalerite under the seafloor of the Minami-Ensei, E: dissolved gas composition in the Minami-Ensei vent fluids, po: pyrrhotite, py: pyrite.
pressed as point E. Since the sphalerite is composed of sheeted sulfide, it is likely to have been formed under the seafloor near the vent and deposited on the seafloor by gas explosion. Therefore, the conditions indicated by points D and E in Fig. 8 may reflect a difference in the place of formation.

*Oxygen fugacity and pH*

Oxygen fugacity and pH of hydrothermal fluids can be estimated from the stability relations among Fe, Mn, Ca and Pb minerals, using thermochemical data from Holland (1965) and Crerar and Barnes (1976). The probable $f_{O_2}$-pH fields for the CLAM and Minami-Ensei deposits were determined for 250°C, total dissolved sulfur of $10^{-2}$ M/Kg, total dissolved carbon of $10^{-0.7}$ M/Kg and total dissolved calcium of $10^{-1.7}$ M/Kg and ionic strength of 0.7. The concentration of dissolved species and the ionic strength were selected from the chemical analyses of hydrothermal vent fluids from each site (Gamo et al., 1991a; Chiba et al., 1993).

At the CLAM site, pyrrhotite coexisting with pyrite indicates that the log $f_{S_2}$ at 250°C is −10.6 to −11.6 (Fig. 8). The pyrrhotite and pyrite equilibration curve in the H$_2$S-predominant field (Fig. 9) can be written as follows:

$$2\text{FeS} + 2\text{H}_2\text{S} + \text{O}_2 = 2\text{FeS}_2 + 2\text{H}_2\text{O}.$$ 

Maximum $f_{\text{H}_2\text{O}}$ at the CLAM site (140 bars) can be given as 37 bars (Burnham et al., 1969). This reaction with maximum $f_{\text{H}_2\text{O}}$ sets the maximum $f_{\text{O}_2}$ as $10^{-35.9}$. Taking account of the dissolved gaseous concentration in the Okinawa Trough venting fluids and of non-stoichiometry of pyrrhotite compositions, $f_{\text{O}_2}$ can be estimated as $10^{-36}$ to $10^{-38}$ atm (point I in Fig. 9). Acidity of the CLAM deposits can be estimated from anhydrite and calcite dissolution relations such as:

$$\text{CaSO}_4 + 2\text{H}^+ = \text{Ca}^{2+} + \text{H}_2\text{S} + 2\text{O}_2,$$

$$\text{CaCO}_3 + 2\text{H}^+ = \text{Ca}^{2+} + \text{H}_2\text{CO}_3.$$  

Calcite is abundant and anhydrite is absent in the main stage of the Pyramid chimney formation. Therefore, pH can be estimated as $\text{pH} \geq 5$ for the CLAM hydrothermal fluids (Fig. 9).

On the other hand, $f_{\text{O}_2}$ of the Minami-Ensei chimneys can be estimated from the anglesite-galena coexistence:

$$\text{PbS} + 2\text{O}_2 = \text{PbSO}_4.$$  

Anhydrite predominates and calcite is lacking in the Minami-Ensei chimneys. Taking account of FeS contents in sphalerite and existence of pyrite and anglesite, the depositional conditions of the Minami-Ensei chimneys at 250°C are estimated as log $f_{\text{O}_2} = -31$ to $-33$ and $\text{pH} \leq 5$ (point M in Fig. 9).

These results indicate that hydrothermal fluids at the CLAM site are less
oxidized than the Minami-Ensei site. The Minami-Ensei deposits exhibit the most oxidized conditions similar to the black ore in the Kuroko deposits, whereas the CLAM deposits show an intermediate oxidation condition between the most reduced Guaymas Basin and the most oxidized Minami-Ensei deposits (Fig. 9).

**COMPARISON WITH OTHER SUBMARINE HYDROTHERMAL SYSTEMS**

Representative mineral compositions of active chimneys from seafloor massive sulfide deposits are summarized in Table 3. Chalcopyrite is abundant at the MAR and EPR sites, and is not a principal sulfide of the Juan de Fuca, Guaymas Basin, Mariana Trough and Okinawa Trough sites. The MAR and EPR hydrothermal sites are deeper and their fluid temperatures are higher than the latter. Solubility of sphalerite and chalcopyrite in hydrothermal solution increases with increasing temperature and decreasing pH. Solubility of sphalerite in hydrothermal solutions is 2 to 5 orders of
Table 3. Mineral abundance of active chimneys from representative hydrothermal systems

<table>
<thead>
<tr>
<th></th>
<th>MAR</th>
<th>JUAN DE FUCA</th>
<th>GUAYMAS BASIN</th>
<th>EPR</th>
<th>MARIANA</th>
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<tbody>
<tr>
<td></td>
<td>26°N</td>
<td>13°N</td>
<td>44°-38°N</td>
<td>27°N</td>
<td>21°N</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>C</td>
<td>M</td>
<td>C</td>
<td>C</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>++</td>
<td>+</td>
<td>++</td>
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<td>+</td>
</tr>
<tr>
<td>Isocubanite</td>
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<td>+</td>
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<tr>
<td>Bornite</td>
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<tr>
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<td>++</td>
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<tr>
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<td>++</td>
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<td>Sulfur</td>
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<tr>
<td>Anhydrite</td>
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</tr>
<tr>
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<tr>
<td>Talc</td>
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<td></td>
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<tr>
<td>Mg-hydroxy-sulfate</td>
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<td></td>
<td></td>
<td></td>
<td>+</td>
</tr>
</tbody>
</table>

Water Depth (m): 3,700, 3,500, 2,200, 2,000, 2,600, 2,630, 2,520, 3,600-3,700

++: Abundant; +: common or less; C: chimney; M: mound.


X: XRD; E: EPMA; S: SEM; M: MICROSCOPE.
magnitude greater than that of chalcopyrite at a constant temperature (e.g., HELGESON, 1969; CRERAR and BARNES, 1976). Amongst the submarine hydrothermal systems the 21°N EPR is chalcopyrite-rich (e.g., HAYMON and KASTNER, 1981; TIVEY and DELANEY, 1986) and its formational conditions show low pH (Fig. 9). On the other hand, the Guaymas Basin and CLAM sites are high in pH and poor in chalcopyrite, resulting in low bulk Cu/Zn ratios (Fig. 10a). Solubility of sulfides increases with increasing acidity; the difference of pH 2 corresponds to the solubility of about 5 orders of magnitude. Thus, pH of the hydrothermal fluids can affect the abundance of Cu and Zn minerals. As shown in Fig. 10a, Cu/Zn ratios of bulk deposits show a slight positive correlation with temperature. That is, chimney or hydrothermal systems of higher temperature (>300°C) are rich in Cu and those of lower temperature (<300°C) are rich in Zn (e.g., STYRT et al., 1981). Therefore, the Cu/Zn ratio in hydrothermal deposits is connected with temperature and pH. Bornite occurs at sites where chalcopyrite predominates (Table 3), indicating high activity of copper in hydrothermal fluids.

Galena is common in the Okinawa Trough and Mariana Trough, whereas it is very rare in MOR-type deposits (Tables 1 and 3). Lead contents in hydrothermal chimneys also show that Pb is high in the Okinawa Trough and negatively correlate with temperature (Fig. 10b). PbS solubility increases with ΣS, P_{H_2S}, and especially temperature (BARNES, 1979). Total sulfur and H_2S concentrations in the Okinawa

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**Fig. 10.** Temperature vs. mean values of Cu/Zn ratio (a) and Pb contents (b) in representative active hydrothermal deposits. Data are compiled from the following: EPR 13, 13°N EPR: HEKINIAN and FOQUET (1985); EPR 21, 21°N EPR: ZIERNBERG et al. (1984); GAL, GALAPAGOS RIDGE: EMBLEY et al. (1988); GB, Guaymas Basin: PETER and SCOTT (1988); IH, Iheya: KIMURA et al. (1989, 1990), Gamo et al. (1991b) and IZAWA et al. (1991); IZ, Izena: KIMURA et al. (1989, 1990) and AOKI and NAKAMURA (1989); JDFa, Juan de Fuca: HANNINGTON and SCOTT (1988); JDFb, Juan de Fuca: FEELY et al. (1987); MAR, Mid Atlantic Ridge: THOMPSON et al. (1988); ME, Minami-Ensei: NEDACHI et al. (1992).
Trough vent fluids are not so high as compared with other ridge type fluids (SAKAI et al., 1990; CHIBA et al., 1993). Therefore these factors cannot explain the high content of Pb in the Okinawa Trough. Lead isotopic compositions of the metalliferous sediments from the EPR are similar to those of oceanic ridge tholeiites but significantly differ from those of pelagic sediments. On the other hand, Kuroko-type lead appears to be derived largely from pelagic sediments or continental materials and not from the oceanic asthenosphere (DOE and ZARTMAN, 1979). Lead abundance in granitic rocks or in pelitic rocks is about 5 times or 10 times as much as basaltic rocks (WEDEPOHL, 1974). In the Okinawa Trough, the oceanic basement is covered by thick continental crust and sediments (e.g., JDRGBB, 1991; KIMURA et al., 1991). This geologic settings is similar to the sediment-filled Guaymas Basin (e.g., PETER and SCOTT, 1988). Thus there is a high possibility that the lead from the Okinawa Trough is derived mainly from continental crust or sediments. This is similar to the results obtained from chemical and isotopic compositions in fluids and dissolved gases, in which some components are strongly influenced by organic matter and continental crust (GAMO et al., 1990; ISHIBASHI et al., 1990; SAKAI et al., 1990).

SUMMARY AND CONCLUSIONS

Mineralogical characteristics of two active hydrothermal fields, CLAM site and Minami-Ensei Knoll site, from the Okinawa Trough have been described and compared with those of other hydrothermal fields. The important results and implications made in this study are:

1. Hydrothermal deposits of the CLAM site are characterized by abundant Mn carbonate, wurtzite and amorphous silica, whereas active chimneys of the Minami-Ensei site are composed mainly of anhydrite, gypsum, sphalerite and pyrite, which resemble those of JADE site.

2. Filling temperatures of Iheya calcite are higher than the maximum measured fluid temperature. The salinity is higher than the ambient seawater, comparable to the sediment-hosted Guaymas Basin calcite. Salinity of the Minami-Ensei anhydrite slightly increases with decreasing temperature, indicating that the fluids were trapped when they were being cooled by ambient seawater.

3. In the main part of the CLAM deposits, absence of anhydrite and abundance of amorphous silica imply that this deposit was modified at temperatures around 150°C or below. A large amount of carbonate at the CLAM site is due to the discharging fluids which are CO2-rich and relatively low in temperature.

4. Mineralogical and chemical compositions of the deposits indicate that depositional conditions at 250°C are as follows: CLAM site, log fO2 = −36~−38, pH ≥ 5, log fS2 = −10.6~−11.6; Minami-Ensei, log fO2 = −31~−33, pH ≤ 5, log fS2 = −10.2~−10.7. The Minami-Ensei deposits exhibit the most oxidized conditions similar to those for the black ore in the Kuroko deposits, whereas the CLAM site shows intermediate oxidation conditions between the Guaymas Basin and Minami-Ensei deposits.

5. Chalcopyrite is poor in the Okinawa Trough and the bulk Cu/Zn ratio is low, whereas it is a principal sulfide in MAR and EPR deposits, resulting in high
Cu/Zn ratios. The pH–$f_{O_2}$ and Cu/Zn-T relations and solubility data indicate that the Cu/Zn ratio in hydrothermal deposits are closely connected with temperature and pH.

(6) Galena is common in the Okinawa Trough and Mariana Trough, both back-arc settings, whereas it is very rare in MOR-type deposits. Solubility of PbS and some geologic characters imply that lead was derived mainly from the continental crust including sediments. This is consistent with the results obtained from chemical and isotopic analyses of discharging fluids and dissolved gases.

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