

**PAST AND PRESENT RECORDS OF GAS HYDRATE GEOCHEMICAL  
SIGNATURES IN A TERRIGENOUS MATERIALS DOMINATED ACTIVE  
MARGIN, SOUTHWEST OF TAIWAN**

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**ABSTRACT**

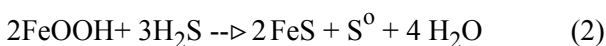
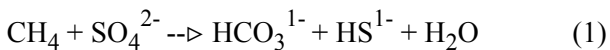
Temporal variations in gas hydrate related geochemical signatures under different deposition conditions are the primary purposes of this study. Accreted wedge located offshore Southwestern Taiwan receives high terrigenous river materials, 100 MT/yr, at present time. It is not clear how seep environment varied during the past glacial. A 25 meters long piston core was taken offshore Southwestern Taiwan on r/v *Marion DuFresne*. Short piston cores and box cores were also taken on r/v OR-1. Samples were analyzed for pore water dissolved sulfide, sulfate, methane, chloride,  $\delta^{18}O$ , calcium, magnesium, alkalinity, pH, and sediment AVS, pyrite, inorganic carbon,  $\delta^{18}O$ ,  $C^{13}$ . Changes in deposition environment play a major role in the study area. Three stages of geochemical processes are identified in the 25 meters long core, interchange between reduce and oxic depositional environments, with reducing condition in the top 10 m, oxic in between 10-20 meter and reducing below the 20 meter. High concentrations of dissolved sulfide, rapid sulfate depletion, increase of methane, decrease of calcium were found in pore water in the top 10 m of sediments together with high concentrations of pyrite, relatively higher proportion of coarse-grained sediment. Concentrations of pyrite were very low in sediments between 15 to 20 meters but increased rapidly from 20 to 25 meters with a maximum concentration at 400  $\mu\text{mol/g}$ . Chloride concentrations also increased to a maximum concentration of 630 mM at 20 m. The rapid increase of chloride indicated gas hydrate formation at this depth. Authigenic carbonate

nodules were found in sediments below 20 m. The carbonate content also increased rapidly beneath this depth. Stable isotopic carbon composition of the carbonate varied rapidly beneath 20 m with a low at -28 per mil. The existence of oxic/reducing alterations indicates that methane seep may vary in the past in the study area.

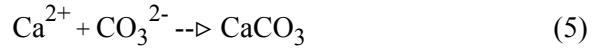
*Keywords:* gas hydrate, active margin, gas seep, South China Sea, Taiwan

## INTRODUCTION

Gas venting as a result of gas hydrate dissociation through sediments could induce a number of geochemical processes. Strong geochemical variations, e.g., abnormal pore water chloride, sulfate depletion, stable oxygen isotope variation, authigenic carbonate formation with associated stable carbon and oxygen isotopic variations, often registered their representative processes in sediments [1, 2] which enable easy identification of various stages of gas migrations and their imprints. Migration of gas to the surface could discontinue when conduit from subsurface is blocked by tectonic activity, sealed by authigenic carbonate or hydrate formation or exhausted reservoir. Subsequent sediment deposition could conceal the geochemical signatures leaving little traces of gas hydrate related activities on the sea floor. While a number of factors could induce gas venting within the sediment, substantial evidence indicated that sea level changes could produce large scale of gas hydrate dissociation and gas/fluid flow [3]. However, opening and sealing of the conduit could also occur irregularly in a tectonic active environment as versus a result of pressure difference during the sea level low/high stand. In this study, we examine a 25 meters long giant piston core collected at the northeastern South China Sea continental margin near Taiwan, where active tectonic activities have been found. Methane migration up to the sea floor becomes a primary energy source for the chemosynthetic communities near the sea floor. In anoxic sediments, rapid anaerobic methane oxidation (AOM) occurred via sulfate reduction. Sulfate is used during methane oxidation with the production of dissolved sulfide and bicarbonate.



Iron oxides are unstable in reducing sediments and react with dissolved sulfide to form meta-stable iron sulfide minerals (FeS and Fe<sub>3</sub>S<sub>4</sub>) with pyrite (FeS<sub>2</sub>) being the predominant form of stable iron sulfide mineral [4]. With oxidation of methane, calcium carbonate may precipitate and forming authigenic carbonate.



Authigenic carbonate and pyrite become two minerals commonly found in the AOM related environments.

## STUDY AREA

Southwestern Taiwan is situated at the boundary between the Philippine and Eurasia Plates with a fast moving rate of about 8 cm per year [5]. The accretionary wedge offshore southwestern Taiwan is characterized by a series of anticline and faults with a trend switching from NNW-SSE, south of 22°N to NNE-SSW, north of 22°N [6]. This deformation zone is located at the frontal edge of the accretionary wedge of the Luzon Arc and the China passive continental margin subduction-collision system [7]. Frequent earthquakes occurred in the region as a result of rapid plate movements. The existence of a series of normal faults intersected by thrust faults in the accretionary prism off southwestern Taiwan may provide good conduits for gas and fluid venting upward to the surface. Mud volcanoes were reported on land [8] as well as on the sea floor [9]. In addition to the accreted wedge, the study area also receives a high flux of terrigenous suspended sediment exported from the adjacent Kaoping, Erjen and Tsengwen rivers with a combined average river particle load of 120 MT/yr. High concentrations of gas hydrate derived methane were found in sediments and overlying water [10]. Shallow SMI (sulfate methane interface) as shallow as 1 meter beneath the sediment/water interface occurred on top of the anticline ridges [11].

## MATERIALS AND ANALYTICAL METHOD

A giant piston core was collected on r/v *Marion Dufresne* at the Yuan-An Ridge in the active continental margin, offshore southwestern Taiwan (Figure 1).

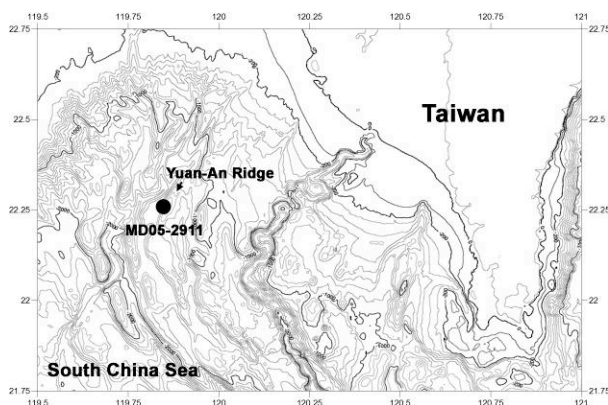


Figure 1. Study area.

Sediment samples were sectioned into 2-cm sections and centrifuged for pore water. Pore water sulfate and chloride concentrations were measured by a Dionex 4500i ion chromatograph equipped with a conductivity detector and an IonPac AS4A anion exchange column. Pore water dissolved sulfide concentrations were analyzed by the methylene blue method [12]. Methane concentrations in pore water were collected on board by the headspace method and measured by gas chromatography. Pore water iron and manganese ion were analyzed using flame atomic absorption spectrometer (Perkin-Elmer 3300). Pore water stable O-18 isotopic values were measured following the Epstein-Mayeda technique [13] and analyzed using a SIRA-10 ratio mass spectrometer and reported as per mill relative to the V-SMOW (Vienna Standard Mean Ocean Water) standard. Grain sizes were measured by a laser grain-size particle size analyzer (Coulter LS230). Pyrite-sulfur and acid volatile sulfide (AVS) concentrations in sediments were determined by the Cr(II)+6N HCl extraction technique and the cold 6N HCl method [14, 15]. Total carbon and organic carbon were analyzed using LECO C/S Analyzer (SC-444) equipped with a high temperature resistance furnace and an IR detector. Calcium carbonate content was calculated from difference between the total carbon and organic carbon content assuming calcite was the only carbonate phase. Carbon and

oxygen isotopic analyses of calcite were performed on a Finnigan MAT-DELTA isotope ratio mass spectrometer equipped a gear system with automatic tube crackers. The  $\delta$  C-13 and O-18 values are expressed as per mill relative to the V-PDB (Vienna Pee Dee Belemnite) standard.

## RESULTS AND DISCUSSIONS

Abundant evidences showed that methane are migrating to the surface sediment in the active margin, southwest of Taiwan in the present time. High concentrations of gas hydrate derived methane were found in the study area sediments [10]. Near surface rapid sulfate depletions were also found in the same region as a result of high flux of methane [11]. In addition, chemosynthetic vent community and large sizes of authigenic carbonate were also found in the study region [16, 17].

The phenomena of gas venting to the surface occurred not only at the present time but also in the past with intermittent stage in the active margin sediments, southwest of Taiwan. Three different depositional stages were found in the vertical sequences in the giant piston core collected at the Yuan-An Ridge, a lower section older vent, the middle oxic sediment, and an upper, new vent type sediments. The lower section is characterized by high concentrations of methane, high in pore water chloride, complete depletion of sulfate, and high in methane, authigenic carbonate and pyrite. The middle section is unique in high iron oxide, very low in pyrite, but also high in methane and pore water chloride. The upper section differs from the other two lower sections in the normal seawater chloride, rapid depletion of sulfate and appearing of high dissolved sulfide, almost no methane, and high in coarse-grained sediments. In addition, high concentrations of authigenic carbonate appeared at the boundary of these three stages. The appearances of high concentrations of iron oxide in the middle section indicate that the middle section is deposited in oxic environment while the upper and lower sections are deposited in anoxic condition with rapid methane oxidation.

## Conclusion

While gas hydrate derived methane venting may be a continuous process that may transport considerable amount of methane to the ocean and may play a significant role in altering the atmospheric green house gas composition, different stages of methane migration were found in the active margin in the South China Sea near Taiwan. Existence of high proportion of iron oxide in the middle section indicated that sediments were deposited during oxic normal marine condition. Upper and lower sections were characterized by anaerobic methane oxidation and gas hydrate formation.

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