GSA DATA REPOSITORY 2010236

EXPLANATORY NOTES

Sampling Site, Sampling and Analyses

Samples were taken during IODP Expedition 316 on the DV Chikyu. Site C0007 is located at the Nankai Trough, off Japan. Holes A, B and C are all at the same location and therefore discussed as one hole. Hole C0007A-C (33°01.2326'N, 136°47.9485'E) at 4081.0 m water depth was cored to a depth of 163.5 mbsf.

Pore water samples were obtained from 20 to 30 cm long whole-round sections. The whole rounds were cut and capped immediately after the core arrived on deck. Prior to squeezing, the exterior of the whole-round sample was removed in a N₂ flushed glove bag and discarded to avoid any potential contamination from drilling and core recovery. The sediments were transferred into titanium squeezers in the glove bag and squeezed in a hydraulic press at ambient temperatures through 0.45 µm filters into sample vials. Pore water samples for shore-based analyses were stored at a temperature of 4°C. After the pore fluid extraction was complete, the sub-sampled sediment squeeze cakes were immediately stored in vacuum-sealed plastic bags for shore-based analyses. The storage temperature for all sediments was -20°C to avoid oxidation of reduced species. For methane analyses 3 cm³ sediment samples were collected and extruded into a He flushed 20 mL glass serum vial, containing 10 mL of 4% NaOH.

Alkalinity was determined by Gran titration with a pH electrode and a Metrohm autotitrator immediately after pore fluid extraction. Sulfate concentrations were analyzed by ion chromatography (IC) with an ICS-1500 Dionex ion chromatograph using subsamples that were diluted by 1:100. The samples for minor element shipboard analysis were acidified with sub-boiled 6 M HCl for at least 24 h and diluted by a factor of 20 prior to shipboard analysis. Pore water iron was measured with inductively coupled plasma atomic emission spectrometry (ICP-OES). No free sulfide was detected, olfactoryly. Methane analyses were performed using an Agilent 6890N gas chromatograph (GC) instrument equipped with a flame ionization detector (FID). The concentrations were subsequently corrected for sediment porosity. All pore water measurements were conducted on board the RV Chikyu (Expedition 316 Scientists, 2009).

Total organic carbon (TOC) content was calculated by subtraction of inorganic carbon (IC) from total carbon (TC). IC concentrations were measured using a Coulometrics 5012 CO2 coulometer. TC concentrations were determined using a Thermo Finnigan Flash EA 1112 CHNS analyzer. All carbon measurements were carried out on board the RV Chikyu (Expedition 316 Scientist, 2009).

Elemental sulfur (S⁰) was extracted for 24 h on a rotary shaker from approximately 5-30 g wet sediment with pure methanol (sample-to-extractant ratio was ~1/10) (Zopfi et al., 2004). A Sykam pump (S1100), a UV–Vis Detector (Sykam S3200), a Zorbax ODS-column (125 × 4 mm, 5 μ m; Knauer, Germany), and 100% methanol (HPLC grade) at a flow rate of 1 mL per minute were employed. S0 eluted after 3.5 min and was detected at 265 nm. The detection limit was about 1 μ M, and the analytical precision of the method was ±0.5% (1 $_{-}$). For determination of AVS and CRS samples of about 0.5 g were treated with a two-step acid Cr(II) method (Fossing and Jørgensen, 1989) and the trapped sulfide (5% Zn-Acetate solution) from each step (AVS and CRS) was analyzed upon dilution by the methylene blue method (Cline, 1969).

Iron phases were extracted sequentially by using an ascorbate solution in followed by a Na-dithionite solution (März et al., 2008). All subsampling and the additions of extraction and washing solutions were carried out in an argon flooded glove bag. Samples were centrifuged and filtered (pore size $0.2 \ \mu m$) after each step and were stored at 4°C immediately after filtration until analysis. Extraction and washing solutions were diluted (1:10) and measured with inductively coupled plasma atomic emission spectrometry (ICP-OES, Thermo Nicolet Iris Intrepid) at the Alfred Wegener Institute for Polar and Marine Research. The amount of iron that was extracted by dithionite and ascorbate solutions was defined as reactive ferric iron (Fe(III)_{reac}). All solid phase values were calculated on dry sediment mass.

Sulfate was precipitated with an acidified barium chloride (BaCl₂) solution as barium sulfate (BaSO₄), filtered and dried. For sulfur isotope analysis of AVS and CRS, zinc sulfide was converted to silver sulfide (Ag₂S) with a 5% silver nitrate (AgNO₃) solution. The precipitate was rinsed with deionized water and washed with 1 M NH₄OH. For sulfur isotope analysis of S⁰, methanol extracted sulfur was treated with hot acid Cr(II) solution. The evolving sulfide was trapped with a 5% AgNO₃ solution, collected as Ag₂S, and rinsed. In a final step, all Ag₂S precipitates were rinsed with MilliQ and dried in an oven at approximately 50°C over night.

Sulfur and oxygen isotope measurements were performed by continuous flow gas source stable isotope ratio mass spectrometry (GS-IRMS) model Delta V (Finnigan; Thermo Fisher Scientific, Waltham, MA, USA). The sulfur isotope measurements were calibrated with reference materials NBS 127 (δ^{34} S = 20.3‰) and IAEA-SO-6 (δ^{34} S = -34.1‰) relative to the Vienna Cañon Diablo Troilite (VCDT) standard. The standard errors (σ 1) of the measurements were less than 0.2‰ for δ^{34} S values. The oxygen isotope measurements were calibrated with NBS 127 (δ^{18} O = 8.6‰) and IAEA SO-5 (δ^{18} O = 12.0‰; Boschetti & Iacumin, 2005) and IAEA-SO-6 (δ^{18} O = -11.3‰; Halas et al., 2007) relative to the standard Vienna Standard Mean Ocean Water (VSMOW). The standard errors (σ 1) of the measurements were less than 0.3‰ for δ^{18} O.

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