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12. DATA REPORT: AUTHIGENIC CARBONATES AT SITES 1150 AND 1151[1]

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ABSTRACT

Several carbonaceous layers or fragments were recovered from sediments of Sites 1150 and 1151 on the deep-sea terrace of the Japan Trench during Leg 186. The X-ray diffraction analysis (XRD) data indicate that these are predominantly dolomitic. In this study, carbon and oxygen isotopes of these carbonates recovered at Sites 1150 and 1151 are presented. The oxygen isotope ratios of the dolomites analyzed range from +0.4‰ to +4.1‰ vs. Peedee formation belemnite (PDB) and those of calcites from +0.6‰ to +2.8‰ PDB. The isotopic composition of carbon varies from –7.0‰ to +12.3‰ PDB in dolomite and from –13.4‰ to –24.1‰ PDB in calcite. The wide range of carbon isotopic compositions indicates that the carbonate samples were formed by the decomposition of organic matter through reactions such as oxidation, sulfate reduction, and methane formation during diagenesis.

INTRODUCTION

Organic materials in marine sediments are decomposed by several processes operating at different depths during burial diagenesis such as oxidation, sulfate reduction, methane production, thermally induced decarboxylation, and so on (Claypool and Kaplan, 1974). Through these processes, the concentration of carbonate ions increases in the pore water, and subsequently, authigenic carbonates precipitate (Irwin et al., 1977). The carbon isotope ratios ($\delta^{13}C$) of the authigenic carbonates in sediment reflect mainly those of the carbonate ions dissolved in the pore water (Irwin et al., 1977; Matsumoto and Matsuhisa, 1985;

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Matsumoto, 1992; Malone et al., 2002). On the other hand, the oxygen isotope ratios ($\delta^{18}O$) of authigenic carbonates may indicate the temperature and $\delta^{18}O$ of the pore water (Irwin et al., 1977; Matsumoto and Matsuhisa, 1985; Matsumoto, 1992; Sample, 1996; Malone et al., 2002). Also, mineral and chemical compositions of the authigenic carbonates mirror the pore fluid they precipitated from (Matsumoto and Matsuhisa, 1985; Matsumoto, 1992). Therefore, the geochemistry helps to evaluate the diagenetic environment and paleofluid in the time when the authigenic carbonates precipitated. In other words, authigenic carbonates can be used as paleoproxies for fluid processes in subduction zones (Kopf et al., 1995; Sample, 1996; Deyhle et al., 2001). In this study, authigenic carbonates of Sites 1150 and 1151 were analyzed to assess their origin.

SAMPLE PREPARATION

Six carbonate samples from Site 1150 and ten carbonate samples from Site 1151 were collected on board the *JOIDES Resolution* and analyzed (Hokkaido University, Japan) for oxygen and carbon isotopic compositions and mineral and major chemical compositions. The samples are solid carbonate concretions with a light gray color. The samples were cut into two slabs. One-half of the slab was kept as archived sample; the other half of the slab was cut into ~1-cm^3 subsamples. These subsamples were washed with distilled water in an ultrasonic cleaner and dried at 50°C. Dried samples were crushed with a tungsten mill and subsequently powdered with an agate mortar for analysis: X-ray diffraction (XRD) analysis, X-ray fluorescence (XRF) analysis, and oxygen and carbon isotopic analysis. The XRD analysis on board was conducted on the samples from Site 1151 (Sacks, Suyehiro, Acton, et al., 2000). Then, our XRD analysis was conducted on the samples from Site 1150.

METHODS

Mineral compositions of carbonates were determined by XRD analysis, with CuK_α radiation of 40 kV/20 mA (MXP3HF). Major elements of carbonates were determined by XRF analysis at 30 kV and 0.30 mA (JSX-3200 Element Analyzer).

The oxygen and carbon isotopic ratios in carbonate were determined after the method of McCrea (1950). Powdered carbonate samples were reacted with 100% phosphoric acid at 25.0°C under a vacuum. The time needed for the reaction was 6 hr and 72 hr for calcite and dolomite, respectively. The evolved CO_2 gas was injected into the mass spectrometer (Finigan MAT 252) to measure oxygen and carbon isotopic ratios. The results were presented by the δ notation. The analytical precision of the standard sample (calcite) was within ±0.03‰ (1 σ) for $\delta^{18}O$ and within ±0.02‰ (1 σ) for $\delta^{13}C$. The $\delta^{18}O$ of CO_2 extracted from the reaction of phosphoric acid with the carbonate differs from the $\delta^{18}O$ of the initial carbonate. The fractionation factors of 1.01090 and 1.01025 between CO_2 and dolomite and calcite, respectively, reported by Sharma and Clayton (1965), were applied for the correction.

RESULTS

XRD data indicated that the carbonates from Site 1150 were predominantly dolomites (Table T1) and one sample was calcite. The XRD analysis on board showed that there were three carbonate samples composed of calcite and dolomite in samples from Site 1151 (Sacks, Suyehiro, Acton, et al., 2000). It is difficult to divide the mixed carbonate minerals for isotopic analysis. Therefore, we did not analyze carbon-oxygen isotope compositions on these samples.

T1. Carbon and oxygen isotope ratios, p. 5.

Isotopic signatures of $\delta^{13}C$ varied from –7.0‰ to +12.3‰ vs. Peedee formation belemnite (PDB) for dolomite samples and –13.4‰ to –24.1‰ vs. PDB in calcite. $\delta^{18}O$ ranged from +0.4‰ to +4.3‰ and +0.6‰ to +2.8‰ vs. PDB in dolomite and calcite, respectively (Table T1). The wide range of carbon isotopic compositions indicates the possibility that the carbonate samples were precipitated in some diagenetic zones as a result of sulfate reduction and methanogenesis (Irwin et al., 1997; Matsumoto and Matsuhisa, 1985).

The results of XRF analysis for three dolomite samples were as follows:

Ca = 26.6–42.7 mol%.
Mg = 15.6–29.2 mol%.
Fe = 1.9–3.3 mol%.
Si = 27.6–49.5 mol% (see Table T2).

T2. Composition of authigenic carbonates, p. 6.

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Table T1. Carbon and oxygen isotope ratios of authigenic carbonates.

Core, section, interval (cm)	Depth (mbsf)	Mineral composition	δ^{13}C (‰ PDB)	δ^{18}O	
				(‰ PDB)	(‰ SMOW)
186-1150A-					
47X-21, 42.0–59.0	436.02	Dolomite	8.97	4.12	35.16
52X-CC, 2.0–6.0	482.32	Dolomite	12.29	4.27	35.31
63X-CC, 22.0–26.0	589.85	Dolomite	11.40	2.40	33.38
186-1150B-					
12R-3, 100–102	810.15	Dolomite	–2.233	2.78	33.77
26R-3, 59–61	944.05	Dolomite	–2.137	3.53	34.55
38R-1, 12.0–40.0	1056.42	Calcite			
186- 1151A-					
19R-CC	244.91	Calcite, dolomite			
20R-1, 0–5	247.30	Calcite, dolomite			
62R-1, 0.0–3.0	651.60	Dolomite	6.32	3.54	34.55
67R-1, 0.0–0.50	699.40	Dolomite	4.14	3.08	34.08
79R-2, 26.0–45.0	826.39	Dolomite	1.79	3.06	34.06
79R-2, 42–44	816.76	Dolomite	3.88	0.41	31.34
90R-1, 25.0–90.0	921.05	Dolomite	–7.021	4.05	35.08
92R-CC, 0.0–31.0	948.02	Calcite, dolomite			
101R-2, 24.0–55.0	1027.91	Calcite	–13.345	0.60	31.53
109R-3, 124–130	1108.04	Calcite	–24.047	2.75	33.74

Note: PDB = Peedee belemnite, SMOW = standard mean ocean water.

Table T2. Minerals and major elements of authigenic carbonates.

Core, section, interval (cm)	Depth (mbsf)	Minerals	Major element oxides (mol%)										
			MgO	Al_2O_3	SiO_2	P_2O_5	S	K_2O	CaO	TiO_2	MnO	Fe_2O_3	BaO
186-1150B-													
12R-3, 100–102	810.15	Dolomite	26.6	2.0	27.6	0.2	0.7	0.7	38	0.2	0.3	3.3	0.3
186-1150A-													
26R-3, 59–61	944.05	Dolomite	15.6	3.0	49.5		0.7	0.8	26.6	0.2	0.3	3.2	
79R-2, 42–44	816.76	Dolomite	29.2	0.9	23.9	0.2	0.7	0.4	42.7		0.3	1.9	0.2