ISOTOPIC STUDIES OF CARBONATES FROM CIROS-1 DRILLHOLE, WESTERN McMURDO SOUND, ANTARCTICA

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Abstract: Carbonates from core samples from the CIROS-1 drillhole, western McMurdo Sound, Antarctica, were analyzed for isotopic, chemical and mineralogical compositions. Carbonates occur as both cement (Mg-calcite and aragonite) and vein filling (aragonite).

Samples are generally depleted in ^{18}O to a level that is consistent with pore-water chemistry and downhole temperatures as high as 67°C. However, the samples from the upper part of the hole (<300 m sub-bottom depth) contain extremely ^{18}O-depleted aragonite, suggesting precipitation from glacier- or ice-sheet-source meteoric water.

Carbon isotopic ratios of aragonite are enriched in ^{13}C relative to the neighboring Mg-calcite. Low $\delta^{13}C$ values of Mg-calcite may be ascribed to precipitation under the sulfate reduction layer where ^{13}C-depleted carbon dioxide might be released. It is plausible, however, that the high $\delta^{13}C$ values of aragonite are due to precipitation under the methane fermentation layer or CO_2 reduction layer, which underlay the sulfate reduction layer and produced ^{13}C-enriched carbon dioxide.

Semi-micro scale isotopic analyses along two transects of aragonite veins revealed that $\delta^{13}C$ values vary from 3 to 5‰ within a vien. Near the bottom of the drillhole, $\delta^{18}O$ values in pore water remained constant during the aragonite precipitation. At shallow depths about 260 m below the sea floor, $\delta^{18}O$ values in pore water were variable, probably owing to the different contribution of glacier or ice-melt water during the precipitation.

1. Introduction

During diagenetic processes, sediments are commonly cemented by minerals of authigenic phases such as carbonate and/or silica. These authigenic minerals are derived from pore water solutes and their chemical and isotopic compositions should reflect the compositions of pore water. The study of such minerals will provide an understanding of the geochemical and biogeochemical processes in the post-depositional environment. These processes in sedimentary sequences may strongly affect the carbon and oxygen isotopic compositions of carbonates formed. Here we report some results of chemical and isotopic analyses of carbonate cement in the samples collected from the CIROS-1 drill-core retrieved in the Ross Sea, Antarctica.

As shown in Fig. 1, the CIROS-1 drillhole was set up on the sea ice located at Lat. 77°35′54.74″ S and Long. 164°29′55.90″ E. The core sediment samples down to 702.14 m beneath the sea floor were almost completely recovered.

2. Geology

The CIROS-1 drill-site is located about 12 km offshore the south-western edge of the Victoria Basin (BARRETT, 1989). As shown in Fig. 1, the continental region of
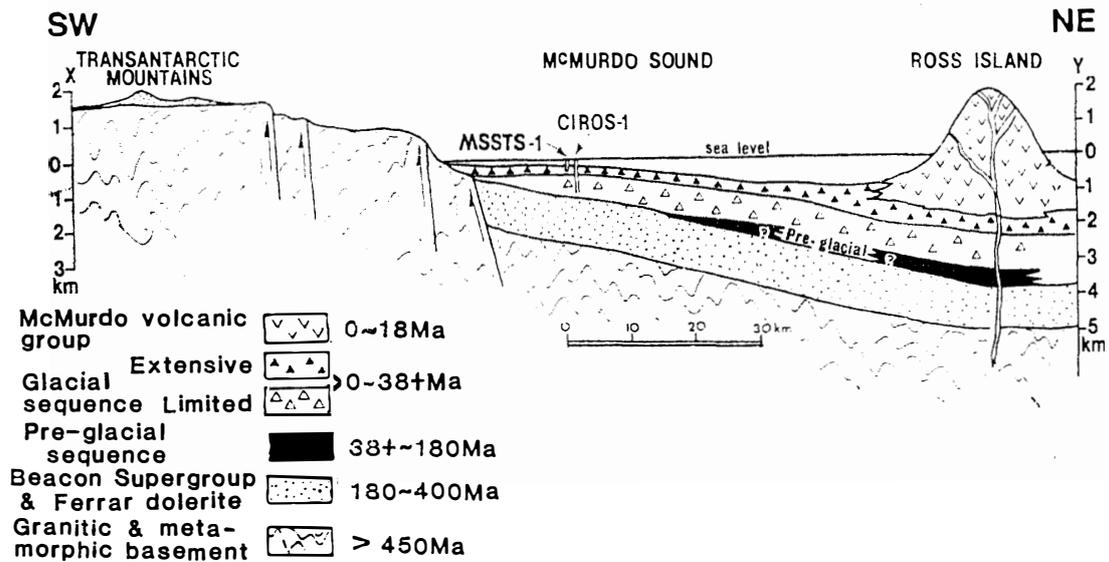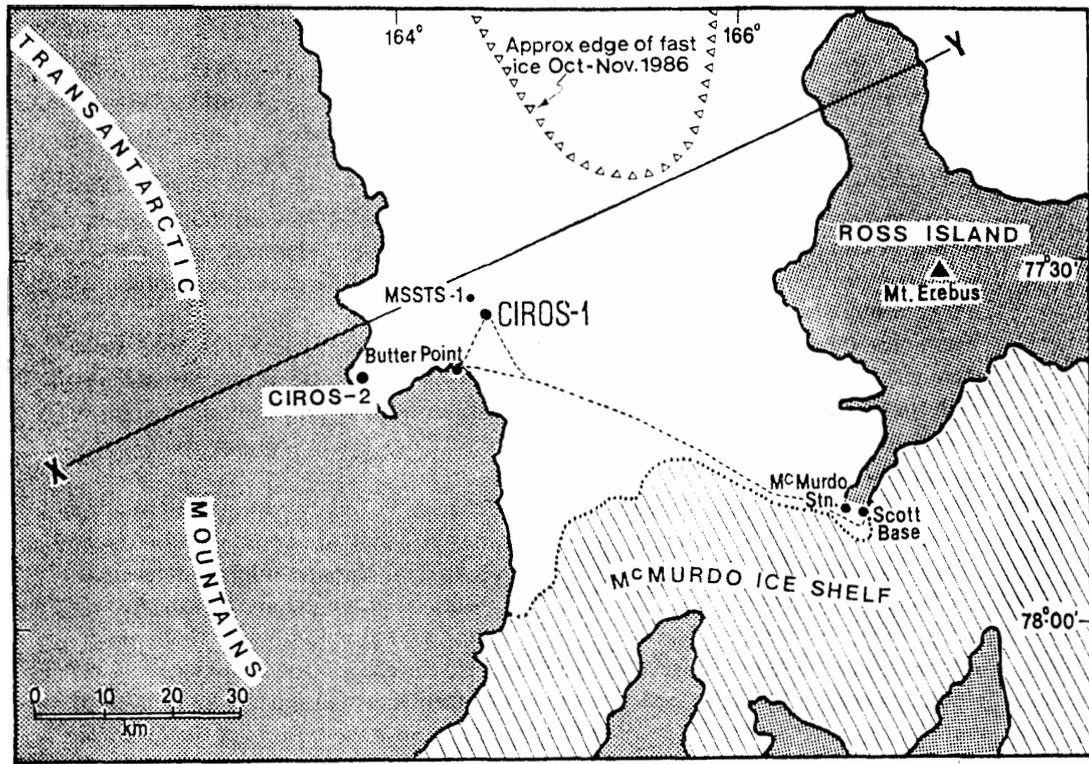
Fig. 1. Map of the McMurdo Sound region, Antarctica, showing the location of the CIROS-1, CIROS-2 and MSSTS-1 drillholes. A geological cross-section along X-Y is shown below (after ROBINSON et al., 1987).

the Victoria Land consists of widespread metamorphic and granitic rocks including Precambrian basement. The Beacon Supergroup composed mainly of sandstones of Devonian to Jurassic age constitutes the top of the Transantarctic Mountains. Huge sills and dikes of the Ferrar dolerite intrude the Precambrian basement and the Beacon Supergroup. It is presumed that the pre-Tertiary strata underlie the CIROS-1 drill-site as shown in Fig. 1.

The McMurdo volcanic province is composed of strongly undersaturated alkaline lavas of basanite to phonolite compositions (GOLDICH et al., 1975). Volcanic activity older than 15 Ma near the head of the Ross Ice Shelf may have been linked with the uplift of the Transantarctic Mountains. A number of volcanoes were also formed later than 3 Ma around the McMurdo Sound area. Mount Erebus is the only Antarctic volcano still active today. The sedimentary sequence, which is post-Transantarctic Mountains in age according to ROBINSON et al. (1987) is given based on the previous drillholes in the area, notably MSSTS-1 (BARRETT, 1986) and CIROS-2 (PYNE et al., 1985) (Fig. 1).

3. Samples and Experiments

Many carbonated sediments are found throughout the whole core succession, as shown by ROBINSON et al. (1987). Samples containing carbonate minerals, sampling depths of which were shown in Fig. 2, were made into polished thin sections and are analyzed with Electron Micro-Analyzer, JXMA-733 at Shizuoka University. The beam current for analyses was about 1.2×10^{-8}A with a beam diameter of 20 μm and counting time of 5 s.

Pulverized samples were analyzed with X-ray diffractometer (CuKα) DX-GE3SC at Shizuoka University for carbonate mineralogy. The mole percent $MgCO_3$ was determined by measruing the 2θ shift in the calcite peaks.

Carbon and oxygen isotopic compositions of selected carbonate minerals were analyzed with the MAT-250 mass-spectrometer at Shizuoka University. Pulverized samples were put into a small stainless steel cup and dropped into a reaction vessel which is connected to the mass-spectrometer and contains concentrated phosphoric acid at 60°C (WADA et al., 1982, 1984). For two aragonite veins, semi-micro scale isotopic analyses were made by scratching up with a knife edge under the microscope. All isotopic values of carbonates are reported as δ values with respect to the PDB standard (CRAIG, 1957).

4. Mineralogy and Texture of Carbonate Minerals

Carbonate is common constituent of the CIROS-1 drill-core, as both skeletal debris (HAMBREY et al., 1989) and authigenic minerals (BRIDLE and ROBINSON, 1989). The suite of samples analyzed and discussed here were taken to study the nature of authigenic carbonates.

A brief description of each sample is given in Table 1. Sandstones are composed mostly of carbonate-cemented quartzose arenite and partly of calcareous feldspathic arenite and quartzose wacke, according to OKADA's (1971) classification scheme.
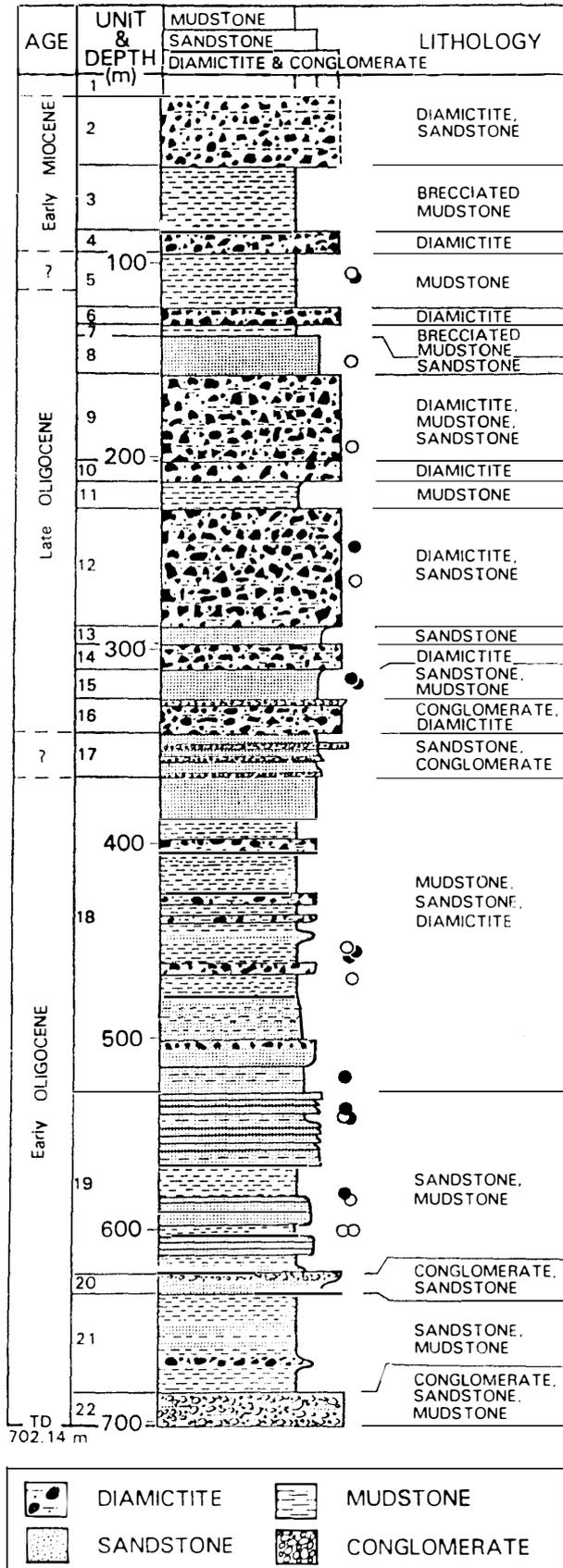
Fig. 2. Sampling locations of carbonate samples in the CIROS-1 drill-core, western McMurdo Sound, Antarctica. Open and solid circles indicate aragonite and calcite, respectively. Lithologic column is after ROBINSON et al. (1987).

Some thin sections of carbonate veins and cements are shown in Plate 1. The results of the modal analysis of some selected sandstone samples are given in Table 2. Sand grains are generally more or less sorted and subrounded to well-rounded in shape.

Table 1. List of carbonates and samples collected from the CIROS-1 drillhole showing the lithologic features.

Sample No.	Depth from sea bottom (m)	Description
Ant-1	102.22	Aragonite cemented foraminifera-bearing, sandy vitric siltstone
Ant-2	105	Calcite cemented, well-sorted quartzose arenite
Ant-3	147.5-6	Aragonite cemented, sorted quartzose arenite
Ant-4	192.69	Aragonite vein-filled poorly-sorted, rounded quartzose wacke
Ant-6	248.24	Calcite cement
Ant-7	264.01	Aragonite vein-filled silica cemented, quartzose fine-grained arenite
Ant-8	314.58	Calcite cemented siltstone with sand laminae
Ant-9	319.0	Calcite cement
Ant-18	453.39-45	Aragonite-calcite cemented poorly-sorted, calcareous silty very fine wacke
Ant-19	455.60-65	Calcite-cemented, quartzose fine-grained wacke with fragmental organic remains
Ant-20	459.23-25	Calcite cemented, biotite-foraminifera-bearing, fine-grained, quartzose wacke
Ant-21	468.05-07	Aragonite-calcite cement
Ant-22	523.32-33	Calcite cemented sandy siltstone
Ant-17A	533.01-08	Calcite cemented, well-rounded, quartzose arenite
Ant-17B	533.01-08	Calcite cemented, calcareous quartzose arenite
Ant-15	537.07-15	Sparry aragonite-cemented quartz arenite
Ant-16	539.69-72	Calcite cemented, sandy siltstone with shell fragments
Ant-14	547.35	Sparry aragonite-cemented, well-sorted, well-rounded quartzose arenite
Ant-11	580.76	Calcite-cemented, sandy siltstone
Ant-10	584.50-57	Sparry aragonite-cemented, well-sorted quartz arenite
Ant-12	599.46-53	Aragonite-vein-filled and cemented, well-sorted quartzose arenite
Ant-13	599.82-86	Aragonite vein-filled, clast-common and biotite-rich, siltstone rarely with foraminifera.

Table 2. Modal analysis of sandstone composition in carbonate-cemented samples collected from the CIROS-1 drillhole.

Sample	Qm	Qp	Fk	Fp	Lv	Ls	HM	Cement	Clay matrix
Ant-3A	25.4	2.2	10.0	9.0	7.4	1.4	0.8	43.8	
Ant-3B	41.8	1.4	6.6	5.6	3.2	0.2	0.4	40.8	
Ant-4	30.6	1.4	4.0	2.2	6.6		0.2	55.0	
Ant-7	48.6	10.6	2.0	6.1	6.5		1.1	24.1	1.1
Ant-17A	46.6	1.6	3.0	0.8	1.2	1.6	0.8	44.4	
Ant-17B	40.4	0.6	1.6	1.2	5.6	2.6	0.6	47.4	
Ant-15	67.8	1.6	4.8	0.2	4.4		21.2		
Ant-14	62.2	4.4	5.2	2.2	3.0		0.2	22.8	
Ant-10	60.8	1.4	4.8	0.6	2.4		0.2	29.8	

Qm: Monocrystalline quartz, Qp: Polycrystalline quartz, Fk: K-feldspar, Fp: Plagioclase, Lv: Igneous rock clast, Ls: Sedimentrary rock clast, HM: Heavy mineral.

Particularly, Nos. Ant-10, 14 and 17 sandstone samples contain many well-rounded quartz grains (Plate 1b), presumably derived from the Beacon Supergroup (GEORGE, 1989).

The cementing substance is mostly sparry carbonate and micrite, and rarely silica (Ant-7). Fibrous and sparry aragonite crystals make a vein up to about 7 mm in thickness and grow perpendicular to vein-wall, filling the full width of the vein (Plate 2a). An interesting feature is that sparry aragonite fills the pore spaces (Ant-4) which are developed on both sides of quartz grain, perpendicular to aragonite veins (shown in Plates 1c and 1d). The micrographs show aragonite crystals in the vein grew parallel to the direction of the vein itself.

The sandstone grains include lithic fragments of dolerite, granitoids, serpentinite(?) and carbonate. Siltstones are characterized by angular quartz grains and biotite flakes. One sample (Ant-1) contains considerable amounts of glass shards, and foraminifers are occasionally seen (Plate 1a). Petrographic features of sandstones suggest that they were deposited in continental shelf to littoral environments sometimes under high energy conditions.

5. Results

Carbonate mineralogy was determined by X-ray diffraction analysis and the results are given in Tables 1 and 3. Calcite occurs only as cemented micrite, and aragonite as sparry crystals. Four vein-filling carbonates (Ant-4, 7, 12 and 13) consist only of sparry aragonite.

As shown in Table 3, the spacing of d(104) of calcite gives small values from 3.012 to 3.030 Å relative to the pure calcite (3.035 Å), suggesting that the substitution of calcium by magnesium took place. As the crystal size was too small to confirm by electron microprobe analysis, we calculated the magnesium content in calcite assuming such substitution had occurred (Table 3). The chemical analyses of aragonite samples show that they are relatively pure calcium carbonate. One aragonite contains strontium about 0.3 % by weight, and the proportions of other significant elements (Mg, Fe, Mn) are close to or below the detection limits of EPMA analyses (Table 4).

The results of isotopic analysis are listed in Table 3 and plotted against downhole depth in Figs. 3 and 4. Four aragonites from the upper depth interval (102–264 m) indicated by open circles in Figs. 3 and 4, are scattered in oxygen isotopes from -9.66 to $-24.11‰$ and have high $\delta^{13}C$ values from $+4.65$ to $+7.04‰$. Aragonites from the lower depth interval (314–600 m) give nearly constant $\delta^{18}O$ values from -10.19 to $-10.72‰$ and $\delta^{13}C$ values from -4.63 to $-8.75‰$. $\delta^{18}O$ values of calcite give a range from -3.02 to $-12.26‰$, whereas $\delta^{13}C$ values vary from -2.31 to $-26.32‰$. As shown in Fig. 4, $\delta^{13}C$ values of aragonite are larger than those of calcite, though they overlaps partly. Two samples collected from depths of 453 and 468 m in the core, containing equivalent amounts of aragonite and calcite, have $\delta^{13}C$ values intermidiate between those of calcite and aragonite. Isotopic variations in two transects of an aragonite vain detected by semi-micro scale isotopic analyses are shown in Fig. 5. Values of $\delta^{13}C$ are significantly variable from 3 to 5‰ in both transects (Figs. 5A and 5B). On the other hand, values of $\delta^{18}O$ of the upper interval (Ant-7, 264 m) of the

core are also highly variable up to 4‰, whereas those of the lower interval (Ant-12, 599 m) sequence, are nealy constant.

6. Discussion

6. 1. Carbonate chemistry

Calcite from CIROS-1 drill-core has low to high magnesium contents (0–8.0% in Table 3) comparable with inorganically precipitated marine calcite (1.6 to 7.5%;

Table 3. Carbon and oxygen isotopic ratios and mineralogical properties of carbonates from the CIROS-1 drillhole.

Sample No.	Depth from sea bottom (m)	Carbonate mineralogy	d(104) of calcite (A)	Magnesium content in calcite*	Carbonates $\delta^{13}C$ v. PDB	$\delta^{18}O$ v. PDB	Equilibrated pore water calculated $\delta^{18}O$ (SMOW)**
Ant-1	102. 22	A	—	—	+ 5. 83	−15. 64	−20. 4~−21. 2
Ant-2	105	Cc	3. 013	7. 5	−23. 97	− 7. 97	−11. 3~−12. 6
					−26. 32	− 7. 89	
Ant-3	147. 5–6	A≫Cc	—	—	+ 5. 77	−24. 11	−27. 9~−29. 7
Ant-4	192. 69	A≫Cc	—	—	+ 7. 04	−21. 57	−24. 9~−27. 2
Ant-6	248. 24	Cc	3. 023–3. 012	4. 1–8. 0	− 3. 73	−12. 26	−14. 1~−17. 0
Ant-7	264. 01	A	—	—	+ 4. 65	− 9. 66	−12. 6~−15. 3
Ant-8	314. 58	Cc	3. 030–3. 014	1. 7–7. 2	− 4. 86	−10. 83	−12. 0~−15. 5
Ant-9	319. 0	Cc	3. 030b	1. 7	− 2. 31	−10. 50	−11. 6~−15. 2
Ant-18	453. 39–45	A=Cc	3. 021	4. 8	− 7. 93	−11. 14	−11. 0~−15. 8
Ant-19	455. 60–65	Cc	3. 016b	6. 5	−15. 74	− 6. 66	− 6. 5~−11. 4
Ant-20	459. 23–25	Cc	3. 023–3. 015	4. 1–6. 9	−16. 55	− 3. 02	− 2. 8~− 7. 7
Ant-21	468. 05–07	A=Cc	3. 022b	4. 5	−11. 30	−11. 79	−11. 5~−16. 4
Ant-22	523. 32–33	Cc	3. 021–3. 015	4. 8–6. 9	−15. 72	− 6. 76	− 6. 0~−11. 5
Ant-17A	533. 01–08	Cc	3. 023b	4. 1	−13. 34	− 9. 24	− 8. 3~−13. 9
Ant-17B	533. 01–08	Cc	3. 024b	3. 8	−10. 63	−11. 88	−11. 0~−13. 9
Ant-15	537. 07–15	A>Cc	3. 025b	3. 5	− 8. 75	−10. 19	− 9. 7~−16. 8
Ant-16	539. 69–72	Cc	3. 017b	6. 2	− 9. 29	− 8. 11	− 7. 2~−12. 8
Ant-14	547. 35	A≫Cc	3. 025	3. 5	− 4. 63	−10. 50	− 9. 8~−16. 2
Ant-11	580. 76	Cc	3. 029–3. 017	2. 1–6. 2	—	—	—
Ant-10	584. 50–57	A	—	—	− 5. 57	−10. 58	− 9. 5~−16. 2
					− 4. 34	−10. 72	
Ant-12	599. 46–53	A≫Cc	3. 024b	3. 8	− 6. 88	−10. 35	− 9. 1~−16. 0
Ant-13	599. 82–86	A≫Cc	3. 038–3. 021	0–4. 8	− 6. 61	−10. 42	− 9. 2~−16. 2

Abbreviation: A; aragonite, Cc; calcite, b; broad peak, *· **; see the text.

Table 4. Chemical composition (wt %) of aragonite from the CIROS-1 drillhole.

Sample No.	Occurrence	CaO	MgO	FeO	SrO
Ant-7	Vein-filling	56. 90	<0. 01	0. 02	0. 26
Ant-14	Cementing	56. 23	<0. 01	0. 01	—
Ant-10	Cementing	55. 52	<0. 01	0. 02	—
Ant-12	Vein-filling	58. 07	<0. 00	0. 03	—
Ant-15	Cementing	57. 68	<0. 01	0. 03	—

VEIZER, 1983). However, as listed in Table 4, the strontium content of CIROS-1 aragonite is much lower than Veizer's values for marine aragonite (0.7 to 0.93%) suggesting that the pore water from which carbonate has precipitated was not solely of marine origin.

6. 2. Oxygen isotopes

The $\delta^{18}O$ values in carbonates from the CIROS-1 core have been determined from some combination of temperature at the time of precipitation and isotopic composition of the pore water. If precipitation took place soon after deposition and the very low temperatures implied by the glacial character of the sequence were taken into account (HAMBREY et al., 1989), then one might expect values similar to carbonates precipitated in deep-sea sediments (-4 to $+5‰$, HEIN et al., 1979; WADA, et al., 1981; WADA and OKADA, 1982). CIROS-1 $\delta^{18}O$ values are quite different from those of deep-sea sediments, as they are highly negative, ranging down to $-24.11‰$. HEIN et al. (1979), who studied samples from the Bering Sea ($\delta^{18}O$ from -12.8 to $+1.7‰$), concluded that they might have been precipitated from sea water at temperature as high as 82°C. The temperature measured at the bottom of CIROS-1 drillhole was about 27°C (WHITE, 1989), but could have reached 41–64°C during subsequent burial, judging from vitrinite reflectance studies (LOWERY, 1989). Precipitation at this temperature could probably account for the moderate negative values of the lower part of the core.

Highly negative $\delta^{18}O$ values observed in the core samples from the depth between 100 and 300 m (Fig. 3) seem to require more than an increase in temperature, which should have also influenced lower samples in the core if it were the cause. A more likely explanation comes from a consideration of possible pore water composition.
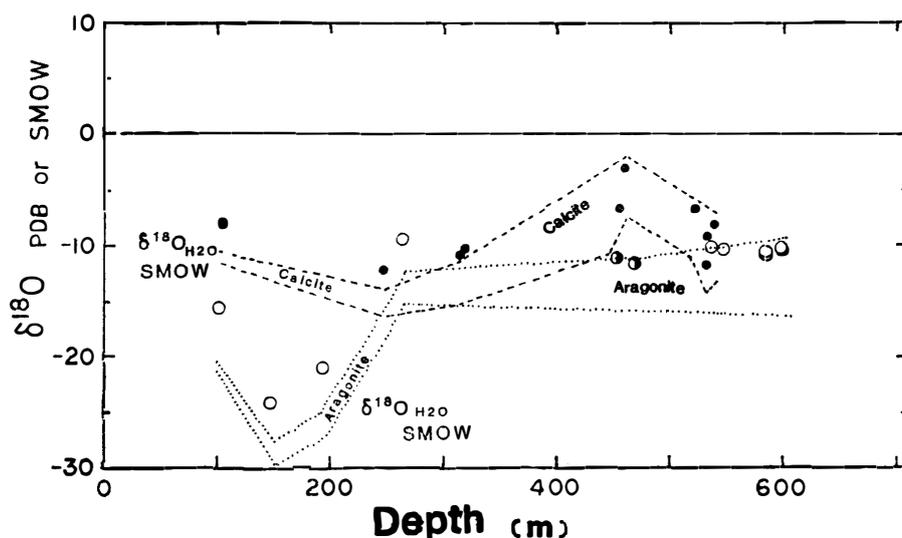
Fig. 3.   Relationship between oxygen isotopic ratio ($\delta^{18}O$: ‰ in PDB) and the sampling depth. Open and solid symbols indicate aragonite and calcite, respectively. Half-solids represent samples with equivalent amounts of calcite and aragonite. Dotted and dashed lines indicate the oxygen isotopic composition (‰ in SMOW) of pore water calculated (see the text).

MATSUBAYA et al. (1979) reported $\delta^{18}O$ values of meteoric water around Ross Island (less than 100 km east of CIROS-1 drill-site) from -14 to $-23\%_o$ (SMOW) and values from the Taylor Glacier (only 50 km west but fed from cold inland ice) of less than $-40\%_o$ (SMOW). $\delta^{18}O$ values of sea water in the McMurdo Sound range from $+0.4$ to $+1.3\%_o$ with an average of $+0.85\%_o$ (SMOW) (NAKAI et al., 1977). The right-hand column in Table 3 and Fig. 3 show the isotopic composition of the pore water, in which the CIROS-1 samples were precipitated, not only assuming the present temperature regime of the strata but also using the paleotemperature scale for calcite-water (CRAIG, 1965; EPSTEIN et al., 1953) and aragonite-water (GROSSMAN and KU, 1981). The effect of isotopic exchanges between pore water and silicates in the sediment (MATSUHISA and MATSUMOTO, 1985) was ignored in the calculation. The minimum $\delta^{18}O$ values of pore water calculated on the assumption that the precipitation took place at the top of the sediment at $0°C$. The calculated values suggest a pore water composition due to mixing of marine water and glacial meltwater.

The extremely negative values for samples from the upper part of the hole are best explained by the pore water mostly derived from glacial meltwarer likely from a more extensive and temperate Ferrar Glacier. Calculations for samples from 147.50 and 192.69 m suggest that around 70% of the pore water came from inland polar ice. The sample from 102.22 m indicates a slightly lower proportion. As shown in a later section, semi-micro scale analyses of $\delta^{18}O$ values of ANT-7 (264.01 m) revealed that there may be a considerable change of $\delta^{18}O$ in pore water resulting from a change in the mixing ratio of sea water and glacier meltwater. HAMBREY et al. (1989) show that grounded ice covered the drill-site during the deposition of at least 2 younger units (2 and 6) after the deposition of these strata. Values of $\delta^{18}O$ for other samples from the upper part of the core and all values from the lower part (below 366 m) may be better explained in terms of elevated temperatures.

6. 3. Carbon isotopes

Values of $\delta^{13}C$ for marine carbonates are normally around $0\%_o$, whereas those for planktonic and detrital organic material from the Ross Sea are around $-27\%_o$ (SACKETT, 1986). It has been well established (MURATA et al., 1969; DEUSER, 1970; CURTIS et al., 1972; SCHIDLOWSKI et al., 1976; WADA et al., 1981) that ^{13}C-enriched carbonate is precipitated in a closed system under anaerobic conditions. In contrast, ^{13}C-depleted carbonate is precipitated at relatively shallow depths where other influences such as the reduction of sulfate by microbial activity can control pore fluid chemistry. $\delta^{13}C$ values in carbonate from CIROS-1 span this range and presumably imply a range in depositional environment.

All four aragonite samples above 300 m have positive $\delta^{13}C$ values. This may have come about by either a) reduction of CO_2 with light carbon preferentially removed by methane-forming bacteria using molecules of organically available hydrogen, or b) CO_2 released by methanogenesis of organic matter (may be acetete fermentation). In either cast is likely that the aragonite precipitated in the methane fermentation layer that generally underlies the sulfate reduction layer in sediments. The large crystal size and the mode of occurrence as filling veins (Plate 2b) and secondary cavities (Plates 1c, 1d, 2a) suggest it is secondary in origin.
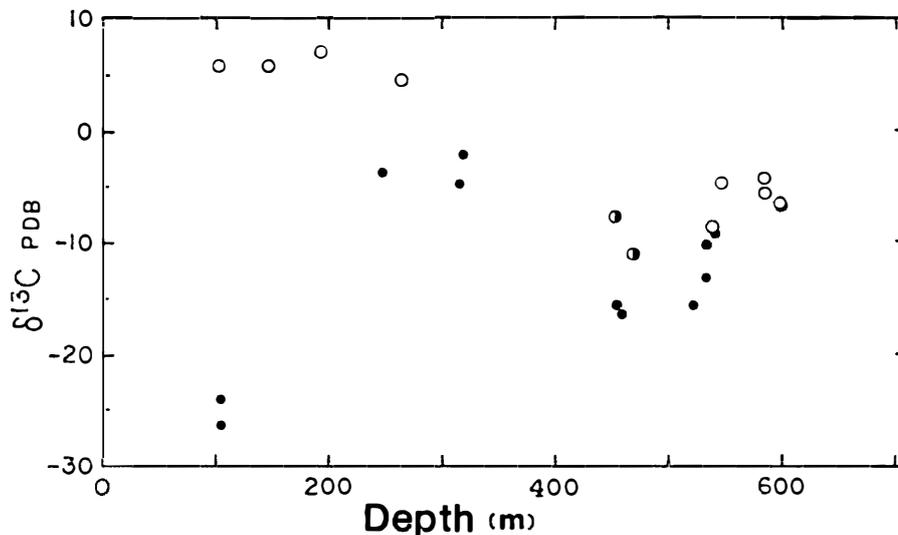
Fig. 4. Relationship between carbon isotopic ratios ($\delta^{13}C$: ‰ in PDB) and sampling
depth.   Symbols are the same as in Fig. 3.

$\delta^{13}C$ values for aragonite from deeper parts of the core are intermediate between normal marine and reduced Ross Sea values, and are not much different from those of calcite in the same strata.   The carbon may have come from a mixture of CO_2 from sulfate reduction and from methanogenesis (Fig. 4).

6. 4.   Carbon and oxygen isotopes in aragonite veins

In order to know the change of depositional environments, we have made the semi-micro scale isotopic determination for the two aragonite veins (ANT-7 and ANT-12).   Figure 5A and 5B show the isotopic results of ANT-7 and -12 collected from 264.01 and 599.46–53 m of the core depth, respectively.   As shown in Plate 2a, fibrous sparry aragonite crystals about 7 mm in length grew perpendicular to the vein of ANT-7. Values of $\delta^{13}C$ change from +3.3 to +5.9‰ and those of $\delta^{18}O$ are a highly variable from −12.3 to −8.0‰.   Both isotopic patterns throughout the vein transect show roughly symmetrical isotopic distribution.   This may indicate that the aragonite precipitation proceeded on both sides of the vein.

As shown in Plate 2b, sparry aragonite crystals filling a vein and large sparry crystals are found in the central part of the vein.   As shown in Fig. 5B, $\delta^{13}C$ values up to 5‰ of variation show a U-shaped isotopic distribution.   On the other hand, a constant $\delta^{18}O$ values of about −10‰ was observed throughout the vein.   Because the texture and the distribution of $\delta^{13}C$ values of aragonite show a symmetrical feature, it is supposed that aragonite precipitation was also set on both sides of the vein.   A constant $\delta^{18}O$ value may have resulted from the constant temperature and oxygen isotopic composition in pore water during the precipitation of aragonite.   The carbon isotopic pattern may be caused by the change of $\delta^{13}C$ value of carbon solute species in pore water.

The calcium carbonate will be enriched in ^{13}C about 2‰, with respect to bicarbonate ions in solution at low temperature (<50°C).   When we assume that the precipi-
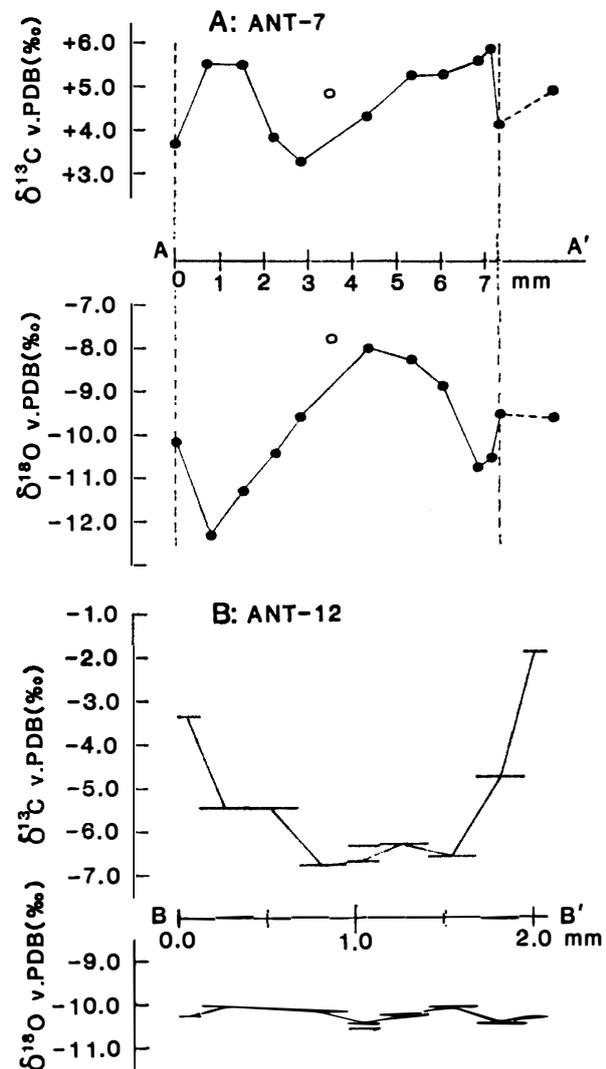
Fig. 5. Semi-micro carbon and oxygen isotopic compositions of vein-filled aragonites collected from 264.01 m (ANT-7, Fig. 5A) and 599.46–53 m (ANT-12, Fig. 5B). Open circles in Fig. 5A indicate isotopic values of the central part of aragonite crystal located about 20 mm apart from the traverse shown in Plate 2a.

tation took place in a closed system, the Rayleigh process may control the carbon isotopic distribution in vein system. The Rayleigh process requires that the carbon isotopic ratio of carbonates in a later stage carbonate should be depeted in ^{13}C. As shown in Fig. 5B, however, δ^{13}C values in aragonite precipitation are drastically lowered in the early stage and give a constant value of about $-6.5‰$ in the central part of the vein (i.e. later stage precipitation). This may indicate that the lowering of δ^{13}C value in aragonite precpitation is ascribed to the influx of carbon solute species enriched in ^{12}C during the early stage.

When we assume that the variation of δ^{18}O values in Fig. 5A is caused by the temperatue change under the existence of pore water with a constant δ^{18}O value, the temperature change equivalent to the δ^{18}O change up to about 8‰ could be calculated to be about 15°C. Although the mineral form of $CaCO_3$ precipitated from pore water is due to many factors in solution, generally speaking, calcium carbonate of the aragonite form is preferentially precipitated from solution when the precipitation rate is high (KITANO, 1990). Therefore, it will be unlikely that aragonite precipitation took place

during the burial interval when the temperature decreased by 15°C. The variation of $\delta^{18}O$ in ANT-7 may be better explained by the $\delta^{18}O$ change in pore water. As shown in Fig. 3, values of $\delta^{18}O$ of aragonites (ANT-3 and 4) are highly negative in the upper sequence and more negative than that in the ANT-7 sequence. As previously mentioned, highly negative $\delta^{18}O$ values of aragonite may be due to the strong influences of glacial meltwater. Highly variable $\delta^{18}O$ values in ANT-7 may be ascribed to the change of the contribution of such meltwater. On the other hand, the constant $\delta^{18}O$ values of ANT-12 collected from the deeper sequence of the core indicates the constant $\delta^{18}O$ value of pore water. Thus, the average $\delta^{18}O$ values of both aragonite veins are similar to each other, though the depositional environments were distinctly different from each other.

Carbonate mineralogy depends to a large extent on pore fluid chemistry. Aragonite is preferentially precipitated from marine water in natural and experimental conditions (KITANO, 1990). Aragonite is also a commonly cemented mineral in shallow sedimentary sequences (ALLEN et al., 1969). BERNER (1975) has shown that the growth of calcite is inhibited by magnesium but that of aragonite is not affected, and furthermore that the rate of calcite precipitation depends on the Mg/Ca ratio in the pore water. WALTER (1986) has shown that aragonite precipitation is favored over calcite by high sulfate and low phosphate solutions. None of these data, however, explains why aragonite precipitation should be favored in the shallowest and deepest parts of the CIROS-1 drill-core. The mineral form of calcium carbonate in the natural enviornment is still an enigma, although we suppose that the aragonite precipitation in the upper interval of this core may have been closely related to the removal of a considerable thickness of sediments due to Late Cenozoic glacial advances (HAMBREY et al., 1989). During this period, the vein system of the core may have been formed.

Acknowledgments

References

ALLEN, R. C., GAVISH, E., FRIEDMAN, G. M. nad SANDERS, J. E. (1969)· Aragonite-cemented sandstone from outer continental shelf off Delaware Bay: Submarine lithification mechanism yields product resembling beachrock. J. Sediment. Petrol., 39, 136–149.

BARRETT, P. J. (1986): Antarctic Cenozoic History from the MSSTS-1 Drillhole, Western McMurdo Sound, ed. by P. J. BARRETT. Wellington, DSIR Publ., 174 p. (DSIR Bull. 237).

BARRETT, P. J. (1989): Introduction. Antarctic Cenozoic History from the CIROS-1 Drillhole, Mc-

Murdo Sound, ed. by P. J. BARRETT. Wellington, DSIR Publ., 5–6 (DSIR Bull. 245).

BERNER, R. A. (1975): The role of magnesium in the crystal growth of calcite and aragonite from seawater. Geochim. Cosmochim. Acta, 39, 489–504.

BRIDLE, I. M. and ROBINSON, P.H. (1989): Diagenesis. Antarctic Cenozoic History from the CIROS-1 Drillhole, McMurdo Sound, ed. by P. J. BARRETT. Wellington, DSIR Publ., 201–207 (DSIR Bull. 245).

CRAIG, H. (1957): Isotope standards for carbon and oxygen and correction factors for mass-spectrometric analysis of carbon dioxide. Geochim. Cosmochim. Acta, 12, 133–149.

CRAIG, H. (1965): The measurement of oxygen isotope paleotemperatures. Stable Isotopes in Oceanographic Studies and Paleotemperatures, ed. by E. TONGIORGI. Pisa, Consiglio Nazionale Richerche, Lab. Geo. Nuclear, 160–182.

CURTIS, C. D., PETROWSKI, C. and OERTEL, G. (1972): Stable carbon isotope ratios within carbonate concretions; A clue to place and time of formation. Nature, 235, 98–100.

DEUSER, W. G. (1970): Extreme $^{13}C/^{12}C$ variations in Quaternary dolomites from the continental shelf. Earth Planet. Sci. Lett., 8, 118–124.

EPSTEIN, S., BUCHSBAUM, R., LOWENSTAM, H. A. and URAY, H. C. (1953): Revised carbonate water isotopic temperature scale. Geol. Soc. Am. Bull., 64, 1315–1326.

GEORGE, A. (1989): Sand provenance. Antarctic Cenozoic History from the CIROS-1 Drillhole, McMurdo Sound, ed by P. J. BARRETT. Wellington, DSIR Publ., 159–167 (DSIR Bull. 245).

GOLDICH, S. S., TREVES, S. B., SUHR, N. H. and STUCKLESS, J. S. (1975): Geochemistry of the Cenozoic volcanic rocks of Ross Island and vicinity, Antarctica. J. Geol., 83, 415–435.

GROSSMAN, E. L. and KU, T. L. (1981): Aragonite-water isotopic pareotemperature scale based on the benthic foraminifera Hoeglundia elegans. Geol. Soc. Am. Abstr. Program, 13, 464.

HAMBREY, M. J., BARRETT, P. J. and ROBINSON, P. H. (1989): Stratigraphy. Antarctic Cenozoic History from the CIROS-1 Drillhole, McMurdo Sound, ed. by P. J. BARRETT. Wellington, DSIR Publ., 23–48 (DSIR Bull. 245).

HEIN, J. R., O'NEIL, J. R. and JONES, M. G. (1979): Origin of authigenic carbonates in sediment from the deep Bering Sea. Sedimentology, 27, 577–591.

KITANO, Y. (1990): Tansan-en Taisekibutsu no Chikyû Kagaku (Geochemistry of Carbonate Sediments). Tokyo, Tokai Univ. Press, 391 p.

LOWERY, J. H. (1989): Coal particles and laminae. Antarctic Cenozoic history from the CIROS-1 drillhole, McMurdo Sound, ed. by P. J. BARRETT. Wellington, DSIR Publ., 219–222 (DSIR Bull. 245).

MATSUBAYA, O., SAKAI, H., TORII, T., BURTON, H. and KERRY, K. (1979): Antarctic saline lakes-stable isotope ratios, chemical compositions and evolution. Geochim. Cosmochim. Acta, 43, 7–25.

MATSUHISA, Y. and MATSUMOTO, T. (1985): Oxygen isotopic ratios of interstitial waters from the Nankai Trough and the Japan Trench, Leg 87. Init. Rep. Deep Sea Drill. Proj., 87, 853–856.

MURATA, K. J., FRIEDMAN, I. and MADSEN, B. M. (1979): Isotopic composition of diagenetic carbonates in marine Miocene formations of California and Oregon. U. S. Geol. Surv. Prof. Pap., 614B, B1–B24.

NAKAI, N., MIZUTANI, Y. and WADA, H. (1977): Kussaku shiryô no antei dôitai sosei kara mita Rosu Tô no kazan katsudô (Volcanic events of Ross Island, Antarctica, based on the stable isotope studies of drilled volcanic rocks). Nankyoku Shiryô (Antarct. Rec.), 58, 277–288.

OKADA, H. (1971): Classification of sandstones; Analysis and proposal. J. Geol., 79, 509–535.

PYNE, A. R., ROBINSON, P. H. and BARRETT, P. J. (1985): Core log, description and photographs, CIROS-2, Ferrar Fjord, Antarctica. Antarctic Research Centre, Victoria University of Wellington, 80 p. (Antarct. Data Ser., 11).

ROBINSON, P. H., PYNE, A. R., HAMBREY, M. J., HALL, K. J. and BARRETT, P. J. (1987): Core log, photographs and grain size analyses from the CIROS-1 drillhole Western McMurdo Sound, Antarctica. Antarctic Research Centre, Victoria University of Wellington, 241 p. (Antarct. Data Ser., 14).

SACKETT, W. (1986): Organic carbon in sediments underlying the Ross Ice Shelf. Org. Geochem., 9, 135–137.

Schidlowski, M., Eichmann, R. and Junge, C. E. (1976): Carbon isotope geochemistry of the Pre-cambrian Lomagundi carbonate province, Rhodesia. Geochim. Cosmochim. Acta, **40**, 449–455.

Veizer, J. (1983): Chemical diagenesis of carbonates; Theory and application of trace element technique. Stable Isotopes in Sedimentary Geology, ed. by M. A. Arthur et al. Tulsa, SEPM, 3-1-3-100 (SEPM Short Course Notes **10**).

Wada, H. and Okada, H. (1982): Nature and origin of deep-sea carbonate nodules collected from the Japan Trench. Am. Assoc. Pet. Geol. Mem., **34**, 661–672.

Wada, H., Niitsuma, N., Nagasawa, K. and Okada, H. (1981): Deep sea carbonate nodules from the middle America Trench area off Mixico, Deep Sea Drilling Project Leg 66. Init. Rep. Deep Sea Drill. Proj., **66**, 453–474.

Wada H., Niitsuma, N. and Saito, T. (1982): Carbon and oxygen isotopic measurements of ultra-small samples. Geosci. Rep. Shizuoka Univ., 7, 35–50.

Wada, H., Fujii, N. and Niitsuma, N. (1984): Analytical methods of stable isotope for ultra-small amounts of carbon dioxide with MAT-250 mass-spectrometer. Geosci. Rep. Shizuoka Univ., **10**, 99–108.

Walter, L. M. (1986): Relative efficiency of carbonate dissolution and precipitation during diagenesis; A progress report on the role of solution chemistry. Soc. Econ. Paleontol. Mineral., Spec. Publ., **38**, 1–11.

White, P. (1989): Downhole logging. Antarctic Cenozoic History from the CIROS-1 Drillhole, McMurdo Sound, ed by P. J. Barrett. Wellington, DSIR Publ., 7–14 (DSIR Bull. **245**).
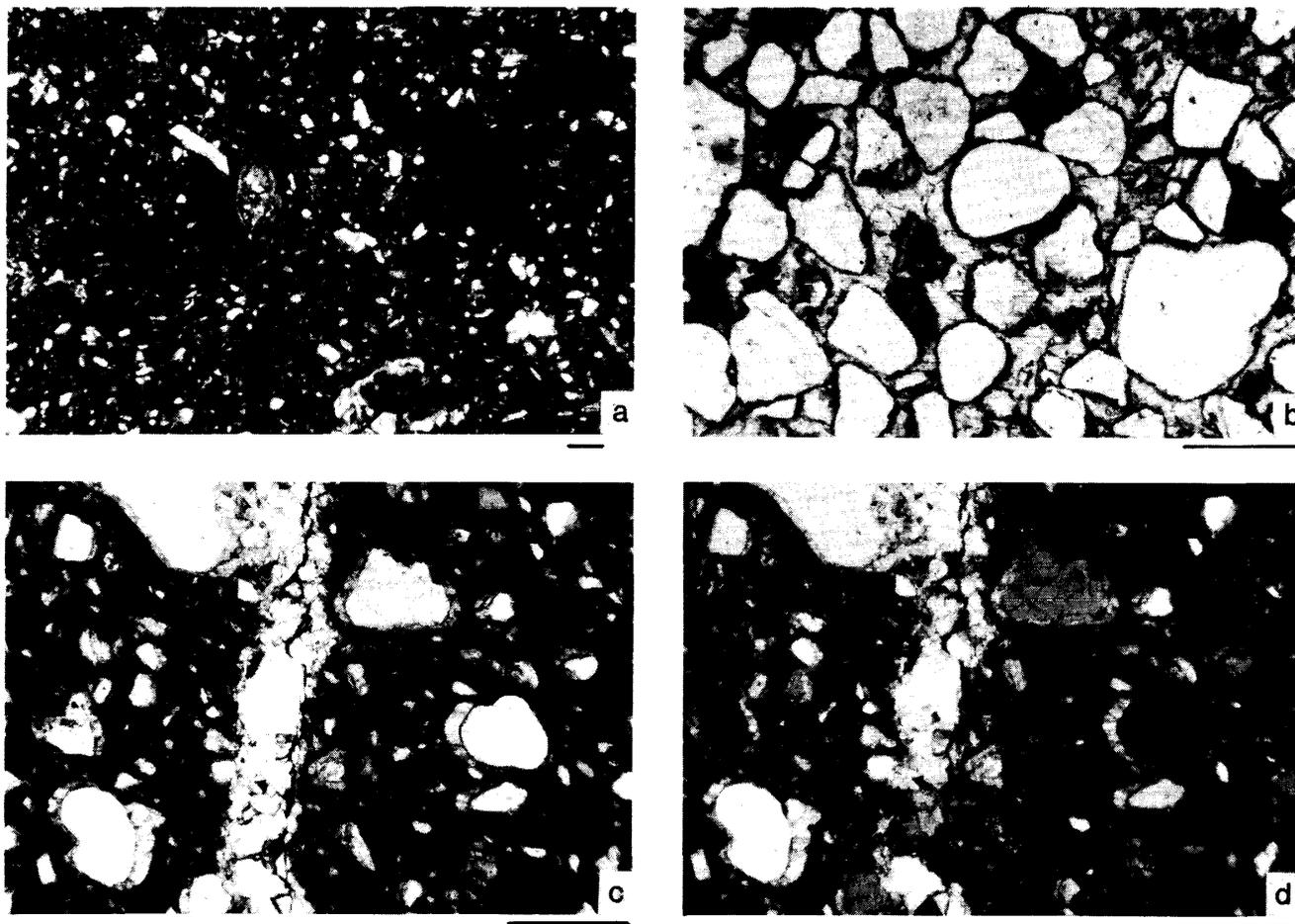
Plate 1. *a:* *Ant-1, 102.22 m subbottom. Foraminifera-bearing, aragonite-cemented sandy vitric siltstone.*
b: *Ant-14, 547.35 m subbottom. Well-sorted, well-rounded, sparry aragonite-cemented quartz arenite.*
c and d: *Ant-4, 192.69 m subbottom. Aragonite vein-filled and developed on both sides of quartz grain.*
Poorly-sorted, rounded quartzose wacke (left-plain polarized light; right-crossed nicols).

(Scale bar =0.1 mm)
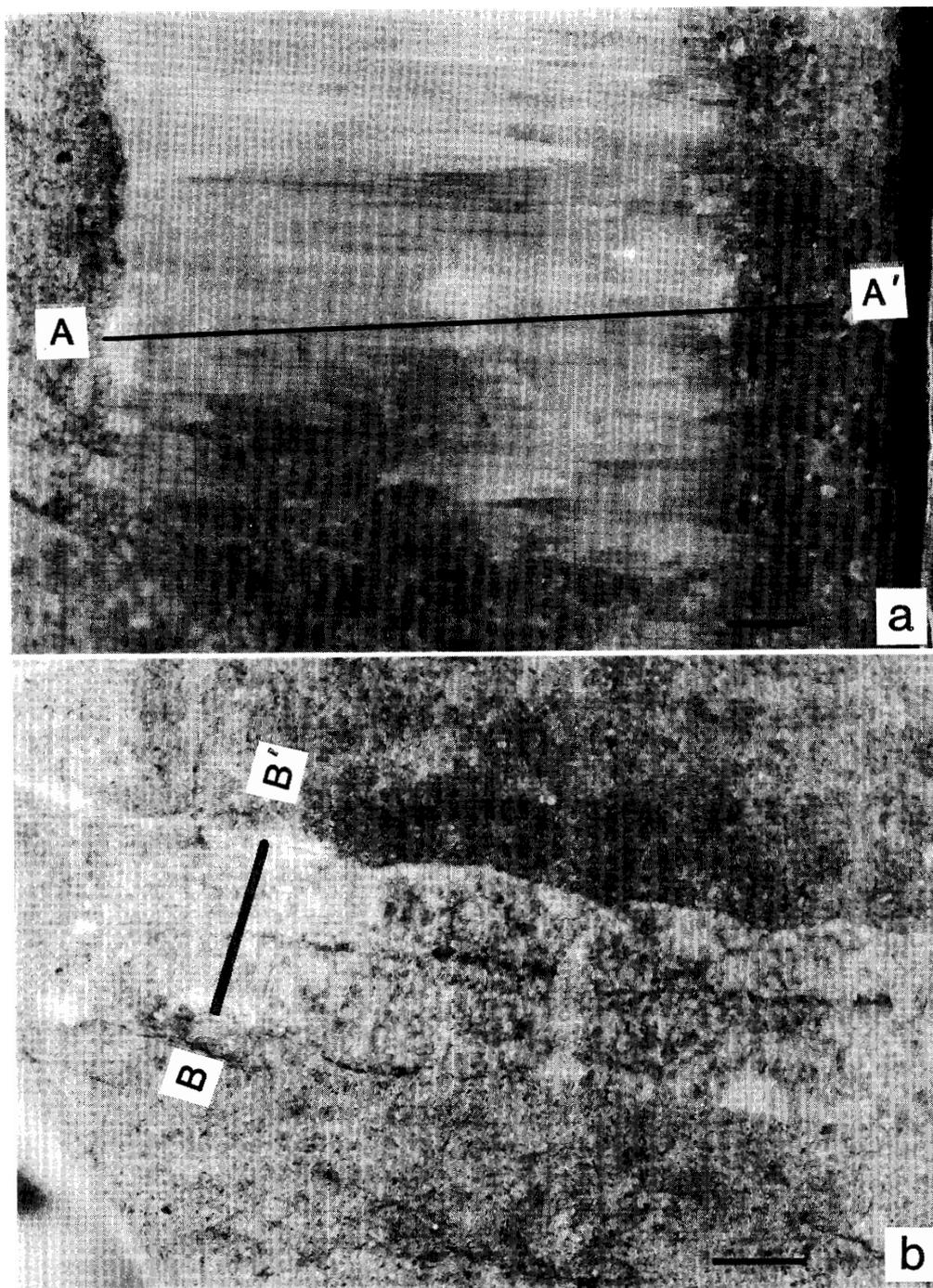
Plate 2.   a: Ant-7, 264.01 m subbottom.   Fibrous sparry aragonite crystal growing per-
pendicualr to the vein.   Semi-micro scale isotopic analyses (Fig. 5A) were
carried out along a transect A-A'.

  b: Ant-12, 599.46–53 m subbottom.   Aragonite vein-filled and cemented, well-
storted quartzose arenite.   Semi-micro scale isotopic analyses (Fig. 5B)
were made along a transect B-B'.   (Scale bar = 1 mm)