

Authigenic carbonates from the Cascadia subduction zone and their relation to gas hydrate stability

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ABSTRACT

Authigenic carbonates are intercalated with massive gas hydrates in sediments of the Cascadia margin. The deposits were recovered from the uppermost 50 cm of sediments on the southern summit of the Hydrate Ridge during the RV *Sonne* cruise SO110. Two carbonate lithologies that differ in chemistry, mineralogy, and fabric make up these deposits. Microcrystalline high-magnesium calcite (14 to 19 mol% MgCO_3) and aragonite are present in both semiconsolidated sediments and carbonate-cemented clasts. Aragonite occurs also as a pure phase without sediment impurities. It is formed by precipitation in cavities as botryoidal and isopachous aggregates within pure white, massive gas hydrate. Variations in oxygen isotope values of the carbonates reflect the mineralogical composition and define two end members: a Mg-calcite with $\delta^{18}\text{O} = 4.86\text{‰}$ PDB and an aragonite with $\delta^{18}\text{O} = 3.68\text{‰}$ PDB. On the basis of the ambient bottom-water temperature and accepted equations for oxygen isotope fractionation, we show that the aragonite phase formed in equilibrium with its pore-water environment, and that the Mg-calcite appears to have precipitated from pore fluids enriched in ^{18}O . Oxygen isotope enrichment probably originates from hydrate water released during gas-hydrate destabilization.

INTRODUCTION

Gas hydrates are crystalline compounds consisting of gas and water that form at high pressures and low temperatures when the low molecular weight gas is present in excess of solubility. Natural gas hydrates occur within sea-floor sediments almost everywhere in the world's oceans where water depths exceed 300 to 500 m (Kvenvolden and McMenamin, 1980; Kvenvolden,

1993). Most of the data allowing estimates of the total volume of gas hydrates in continental margin sediments are derived from bottom-simulating reflectors (BSRs) evident in seismic profiles (Shipley et al., 1979; Hyndman and Spence, 1992). Limited deep-sea drilling results document that the BSR is associated with an abrupt velocity reversal at the base of the gas-hydrate layer, resulting in a strong reflection that cuts

across stratigraphic horizons. Several studies (e.g., Shipley et al., 1979; Hyndman et al., 1992; Trehu et al., 1995) have confirmed that this reflection is approximately where the base of hydrate stability would be on the basis of thermodynamic considerations. The reflector is thought to be generated by the seismic velocity contrast at the base of the solid hydrate layer in the sediment as a result of free gas trapped below (MacKay et al., 1994). This lower boundary of solid gas hydrates is present from ~100 to 1100 m below the sea floor (Kvenvolden, 1993).

Gas-hydrate deposits have been reported near the sediment surface only in a few areas associated with gas vents or oil seeps. Such shallow deposits were sampled by gravity and piston cores in the Black Sea (Yefremova and Zhizhchenko, 1974), the Caspian Sea (Ginsberg et al., 1992), the Gulf of Mexico (Brooks et al., 1986; MacDonald et al., 1994), the Eel River basin (Brooks et al., 1991), the Sea of Okhotsk (Zonenshayn et al., 1987; Ginsburg et al., 1993), the Norwegian Sea (Vogt et al., 1997), and in the eastern Mediterranean Sea (Woodside et al., in press). The co-occurrence of authigenic car-

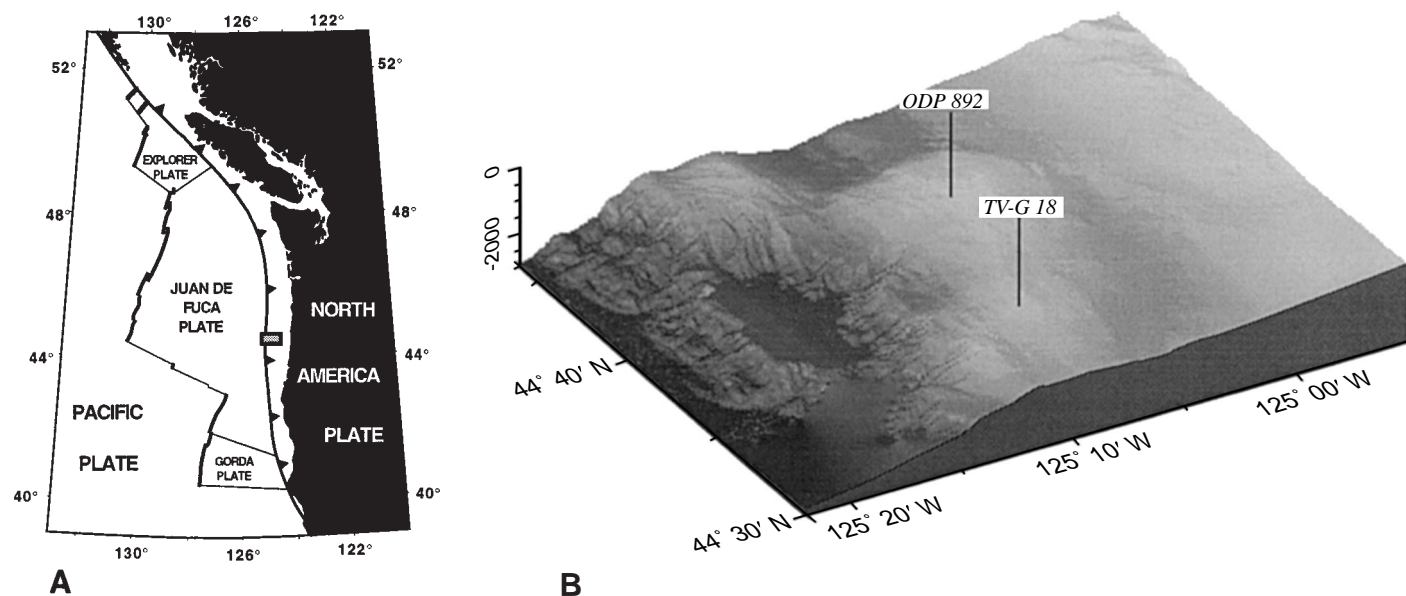


Figure 1. A: Present plate boundaries at northwestern continental margin of North America. Box outlines area shown. B: Regional bathymetry of the first and second accretionary ridges at Cascadia subduction zone showing Ocean Drilling Program Site 892 and the site TV-G 18 (lat $44^{\circ}34.23'N$; long $125^{\circ}08.89'W$) at the Hydrate Ridge where massive gas hydrates intercalated with authigenic carbonates were recovered during RV *Sonne* cruise 110-1a.

bonates has been documented in nearly all gas-hydrate sites, indicating that carbonate formation may be related to the mechanisms controlling the formation and decomposition of gas hydrates. However, until now there has been no proof of a causal relationship of this hydrate-carbonate association. Here we present data from carbonate phases that are intercalated with gas hydrates in sediments of the Cascadia margin. The data document variations in the O isotopic and mineral phase composition of the carbonates, variations that we believe are related to past changes in the stability limits of the gas-hydrate host deposit.

GEOLOGIC SETTINGS

The Cascadia accretionary margin evolved in response to the subduction of the oceanic Juan de Fuca plate beneath the continental North American plate (Fig. 1A). Terrigenous sediments were deposited rapidly in several basins created by folding and faulting on the slope. The currently active accretionary wedge off Oregon is composed of folded thrust slices of Pliocene-Pleistocene age (Westbrook et al., 1994).

A well-developed BSR underlies the crest of the Hydrate Ridge¹ east of the deformation front (MacKay et al., 1992; Westbrook et al., 1994). Downhole logs and vertical seismic profiles conducted by the Ocean Drilling Program (ODP) at Site 892 (670 m water depth; Fig. 1B) established that the BSR is caused by the presence of free gas below 71 m below sea floor (bsf; Westbrook et al., 1994). No massive accumulations of gas hydrate were encountered at this site; rather, most of the hydrate appears to be disseminated within the pore space. Temperature measurements and negative Cl anomalies in the pore waters at these sites suggest that less than 10%–40% of the pore space is filled with hydrates. Solid gas hydrate recovered at Site 892 between 2 and 19 m bsf was not associated with the BSR. This near-surface deposit contains as much as 10% H₂S (Kastner et al., 1995; Whiticar et al., 1995).

During RV *Sonne* cruise SO110, a giant video-guided grab sampler retrieved nearly 50 kg of massive hydrate from the southern summit of the Hydrate Ridge under 785 m of water (TVG-18; Fig. 1B). Video surveys of the area indicate that the sea floor there is paved with gas hydrates, which extend for several hundreds of square meters, on an otherwise flat sea floor covered with soft sediment (Suess and Bohrmann, 1997). The gas-hydrate pavement is lined with bacterial mats, but there is no indication of communities of vent organisms, nor are there large outcrops of carbonate, which indicate that focused fluid flow along thrust faults like at the northern summit may not occur. The presence of gas hydrate

directly on the sediment surface indicates that gas hydrates are stable at present, and that gas seepage at the southern summit of the ridge may occur only as a diffuse transport from below. In contrast, at the northern summit of the ridge (585 m water depth, Fig. 1B), rising bubble trains from the decomposition of the gas hydrate support a huge methane plume that has methane concentrations of as much as 50 000 nL/L. Active vent communities and authigenic carbonate at the sea floor have been documented by video surveys of the northern ridge (Suess and Bohrmann, 1997), and by sampling (Sample and Reid, 1998). The carbonates are associated with faults that act as active fluid conduits, with fluids migrating upward (Westbrook et al., 1994).

GAS HYDRATES

Large amounts of pure white gas hydrates in layers ranging from a few millimeters to 10 cm in thickness were recovered with a video-guided grab (station TV-G 18). The trapped gas phase in the hydrate contained 97.4% methane, 2.6% hydrogen sulfide, and small amounts of CO₂, C₂H₆, and C₃H₈. The hydrates are densely intercalated with soft, muddy, sulfide-rich sediments. Large amounts of the hydrate samples were stored in liquid nitrogen for later fabric analyses of the frozen material in a shore-based cold laboratory (at -23 °C). By cutting the specimens with a saw and a planing device, we

were able to obtain cross sections perpendicular to stratification as well as thin sections of the pure gas-hydrate layers.

The fabric of the frozen samples shows a dense interfingering of gas hydrate in all sediment samples. In the muddy host sediment there were several small hydrate linings; in most cases, we found layers of as much as 10 cm of pure white hydrate parallel to bedding. Sediment remnants are present as small clasts within a pure matrix of gas hydrate (Fig. 2A). Cross sections through the gas hydrates show a spongy structure (Fig. 2A). Thin sections reveal small bubbles of different sizes (1 mm to 2 cm), which are elongated along the bedding plane (Fig. 2B). All samples have this globular fabric, in which the gas hydrate occurs only on the surface of the cavities. This fabric is similar to that of a gas-hydrate mass formed by recent, remotely operated vehicle experiments in 900 m water depth (Brewer et al., 1997). The globular form is consistent with the presence of gas bubbles, from which hydrate precipitates at the gas-water interface. Hence, we believe that at the sampling site on the Cascadia margin, supersaturation of gas occurs very close to the sediment surface. The gas bubbles create cavities by being trapped under an impermeable layer in which subsequent addition of free gas leads to the formation of globular gas hydrate. Details of the time and conditions of such a process are not known.

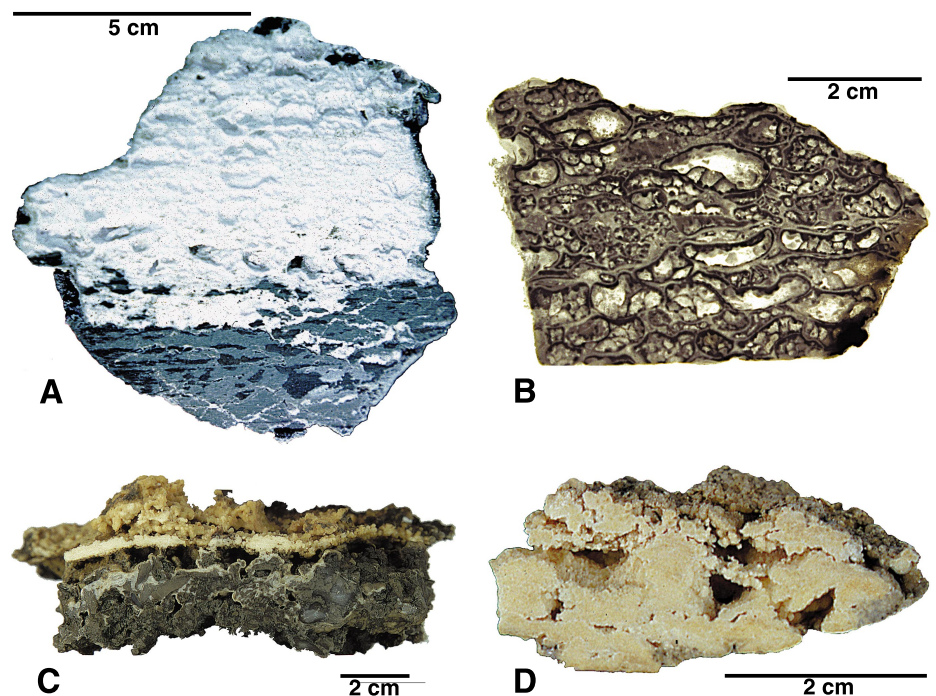


Figure 2. A: Massive whitish gas-hydrate layer parallel to stratification in contact with host sediment. **B:** Thin section of pure gas-hydrate layer showing globular structure of gas hydrate outlining former gas bubbles. **C:** Vertical section through authigenic carbonate layer showing more or less continuous aragonite layer underlain by breccia composed of Mg-calcite-cemented clasts. **D:** Pure aragonite precipitates recovered within massive white gas-hydrate layer; surface morphology of carbonate partially outlines shape of bubble structure shown in B.

¹The name Hydrate Ridge was approved by the United States Board on Geographic Names (Advisory Committee on Undersea Features) for the second accretionary ridge at 44°40'N of Cascadia Margin.

However, the globular fabric of the gas hydrate constitutes definite evidence for the existence of free gas prior to hydrate precipitation.

CARBONATES AND ISOTOPES

Carbonate formation occurs in close association with methane hydrates. The minor carbonate phase is a Mg-calcite (14–19 mol% Mg) that occurs as submicrometer anhedral crystals within the intergranular pore space of the terrigenous sediment, which also contains small amounts of aragonite. Cemented sediment clasts that show various degrees of brecciation are often present within a matrix of pure hydrate (Fig. 2A). Brecciation appears to be caused by the growth of the gas hydrates and subsequent fracturing.

The main carbonate mineral present is aragonite, which appears disseminated as well as in yellow layers of remarkable purity. The aggregates consist of needles (2–10 μm thick) that form either botryoids with radii of 0.15–3.0 mm, or thin isopachous layers (40 to 600 μm) that clearly precipitated within open cavities. Continuous large aragonite layers (0.5 to 2 cm thick) parallel to stratification seem to have grown directly within gas-hydrate layers (Fig. 2C). In one instance we recovered a single distinct aragonite precipitate directly from within a pure gas-hydrate layer. The precipitate exhibits a surface morphology having an outline that at least partially images the shape of the bubble fabric from the gas hydrate (Fig. 2D). The cavities in the spongy gas hydrates are thus thought to be the sites where aragonite precipitation occurs.

Samples of these carbonates were used for X-ray diffraction, and carbon and oxygen isotope analyses. By using standard calibration curves we determined the magnesium content of the Mg-calcite phase, as well as the weight fraction of aragonite, in the bulk sample. Carbon isotope values range from -40.6‰ to -54.2‰ PDB (Peedee belemnite), consistent with a methane source for the carbon in both aragonite and Mg-calcite (Ritger et al., 1987). The carbon isotopic composition of the methane in the gas hydrate ranged from -63.3‰ to -65.8‰ PDB, thus clearly identifying the C reservoir.

The oxygen isotopic composition ranged from $+3.27\text{‰}$ to $+4.84\text{‰}$ PDB, and the variations are clearly related to the mineralogy of the samples (Fig. 3). This relationship can be used to define two end members: an aragonite phase with a $\delta^{18}\text{O}$ of $+3.68\text{‰} \pm 0.12\text{‰}$ and a Mg-calcite phase with a $\delta^{18}\text{O}$ of $+4.86\text{‰} \pm 0.07\text{‰}$ PDB.

DISCUSSION AND CONCLUSIONS

Petrographic and mineralogical evidence supports the formation of two distinct carbonate phases associated with the gas hydrates recovered from the southern summit of the Hydrate Ridge of the Cascadia margin. The chemical control on whether aragonite or Mg-calcite forms is difficult to evaluate (Burton, 1993); however, our

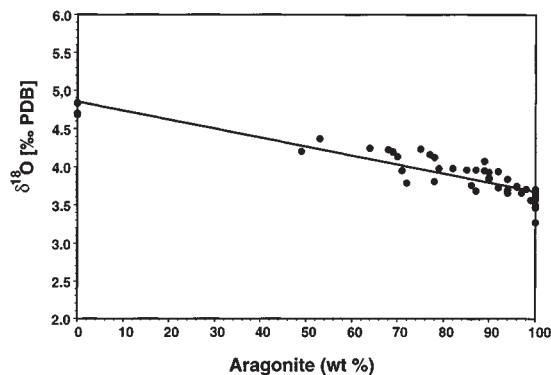


Figure 3. Weight percent of aragonite content vs. $\delta^{18}\text{O}$ composition of authigenic carbonate samples recovered from station SO110-TV-G 18. PDB is Peedee belemnite.

data clearly distinguish two generations of carbonate precipitation with highly distinct oxygen isotope compositions. The oxygen isotope composition of waters, from which the carbonates may have precipitated at any given temperature, can be evaluated from the equations of Hudson and Anderson (1989) for aragonite, and Friedman and O'Neil (1977) for Mg-calcite, the latter modified for the Mg-content after Tarutani et al. (1969). Assuming that the minerals formed at the present bottom-water temperature of $4.06\text{ }^\circ\text{C}$ (Suess and Bohrmann, 1997), the $\delta^{18}\text{O}$ composition of the formation waters would differ from standard mean ocean water (SMOW) values by only 0.08‰ for the aragonite phase, but by 0.95‰ for the Mg-calcite phase. This difference supports our conclusion, based on the petrographic relations, that with this hydrate association, there are two distinct generations of carbonates that precipitated from two highly distinct pore-water environments.

The estimated $\delta^{18}\text{O}$ (i.e., $+0.08\text{‰}$ SMOW) and the bottom-water temperature (i.e., $4.06\text{ }^\circ\text{C}$) imply aragonite precipitation from pore water under recent conditions. In contrast, the $\delta^{18}\text{O}$ composition of the pore water from which the Mg-calcite precipitated is significantly enriched (i.e., $+0.95\text{‰}$ SMOW). The enrichment in the heavy oxygen isotope is very likely the result of gas-hydrate dissociation, which yields a cage water with an oxygen isotopic composition of up to $+3.0\text{‰}$ (Davidson et al., 1983). Such an isotope enrichment is otherwise difficult to explain, because these carbonates occur very close to the sea floor, and SMOW should clearly dominate. Furthermore, deep pore fluids obtained by drilling at Site 892 have $\delta^{18}\text{O}$ values actually lower than SMOW. This signature is thought to result from fluid-rock interaction at depths of 1 to 4 km. It is only the near-surface $\delta^{18}\text{O}$ values of pore fluids that show localized positive excursions reflecting the in situ dissociation of the $\text{CH}_4\text{-H}_2\text{S}$ mixed hydrate found off Cascadia (Kastner et al., 1995).

On the basis of these results, it appears that the Mg-calcite phase precipitated in response to destabilization of the gas hydrates. Hydrate decomposition in the marine environment may be

caused by lowering of sea level and/or increase in temperature. Site TV-G 18, currently under 785 m of water, and having a bottom-water temperature of $4.06\text{ }^\circ\text{C}$, is clearly within the stability field of gas hydrate (Fig. 4). For the hydrate to become unstable, the temperature would need to increase by about $6.3\text{ }^\circ\text{C}$ (Fig. 4). During a drop of sea level of 100 m, the bottom water would still need to be raised by about $4.8\text{ }^\circ\text{C}$ to destabilize the gas hydrate (Fig. 4). Such an increase would require an enrichment of the pore-water isotopic composition of $+2.2\text{‰}$ SMOW to precipitate a Mg-calcite with $\delta^{18}\text{O}$ of $+4.86\text{‰}$ PDB. Pore waters so enriched in $\delta^{18}\text{O}$ may exist only during times of hydrate dissociation.

Destabilization of gas hydrate beneath the sea floor could have broad implications for regional sediment stability, as well as for global climate change (MacDonald, 1990; Gornitz and Fung, 1994). It is suggested that dissociation of methane hydrates at the close of the Pleistocene increased postglacial warming (Kvenvolden,

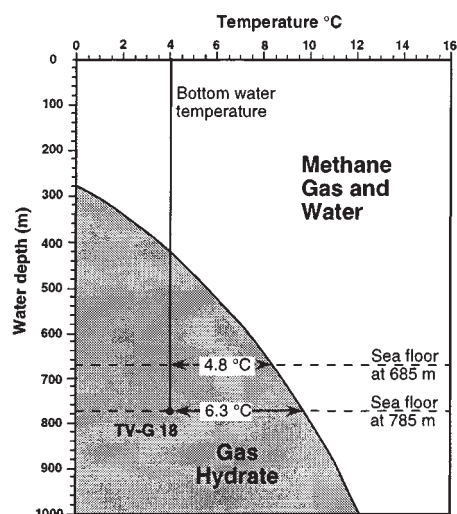


Figure 4. Stability diagram for gas hydrates recovered from station SO110-TV-G 18, which is under 785 m of water; bottom-water temperature is $4.06\text{ }^\circ\text{C}$. Stability curve represents relationship of Sloan (1990) for presence of 97.4% CH_4 and 2.6% H_2S in gas phase, corrected for seawater salinity ($\text{Cl} = 555\text{ mM}$).

1988; Nisbet, 1990). Paull et al. (1991, 1996) argued that lowered sea level during the Pleistocene triggered hydrate dissociation, causing destabilization of slopes and massive methane release, thus acting as a limiting factor in glacial growth and further global cooling. Our results show that the massive gas-hydrate deposit on the southern summit of the Hydrate Ridge has indeed undergone a period of destabilization, and that the carbonate phases now associated with these deposits have recorded such destabilization.

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