

# Clathrites: Archives of near-seafloor pore-fluid evolution ( $\delta^{44/40}\text{Ca}$ , $\delta^{13}\text{C}$ , $\delta^{18}\text{O}$ ) in gas hydrate environments

Barbara M.A. Teichert  
Nikolaus Gussone

Forschungszentrum Ozeanränder, Universität Bremen, Postfach 330440, D-28334 Bremen, Germany

Anton Eisenhauer

Leibniz-Institut für Meereswissenschaften (IFM), GEOMAR, Dienstgebäude Ostufer, Wischhofstrasse 1-3, D-24148 Kiel, Germany

Gerhard Bohrmann

Forschungszentrum Ozeanränder, Universität Bremen, Postfach 330440, D-28334 Bremen, Germany

## ABSTRACT

**Aragonitic clathrites are methane-derived precipitates that are found at sites of massive near-seafloor gas hydrate (clathrate) accumulations at the summit of southern Hydrate Ridge, Cascadia margin. These platy carbonate precipitates form inside or in proximity to gas hydrate, which in our study site currently coexists with a fluid that is highly enriched in dissolved ions as salts are excluded during gas hydrate formation. The clathrites record the preferential incorporation of  $^{18}\text{O}$  into the hydrate structure and hence the enrichment of  $^{16}\text{O}$  in the surrounding brine. We measured  $\delta^{18}\text{O}$  values as high as 2.27‰ relative to Peedee belemnite that correspond to a fluid composition of  $-1.18\text{‰}$  relative to standard mean ocean water. The same trend can be observed in Ca isotopes. Ongoing clathrite precipitation causes enrichment of the  $^{44}\text{Ca}$  in the fluid and hence in the carbonates. Carbon isotopes confirm a methane source for the carbonates. Our triple stable isotope approach that uses the three main components of carbonates (Ca, C, O) provides insight into multiple parameters influencing the isotopic composition of the pore water and hence the isotopic composition of the clathrites. This approach provides a tool to monitor the geochemical processes during clathrate and clathrite formation, thus recording the evolution of the geochemical environment of gas hydrate systems.**

**Keywords:** clathrite, clathrate,  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ ,  $\delta^{44/40}\text{Ca}$ , gas hydrate brine, aragonite, Ca isotope fractionation.

## INTRODUCTION

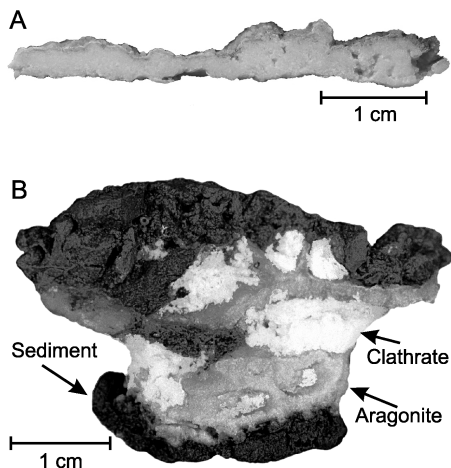
Gas hydrates (clathrates) are crystalline solid compounds that host low-molecular-weight gases such as methane within cages formed by water molecules. The gas hydrates at the summit of southern Hydrate Ridge of the Cascadia margin have been found together with clathrites (Fig. 1), which are a unique form of methane-derived high-Mg calcite and aragonite (Bohrmann et al., 1998; Greinert et al., 2001; Teichert et al., 2003). The term “clathrite” was introduced by Kennett and Fackler-Adams (2000, p. 218) for “sedimentary rocks exhibiting an association of soft-sediment deformation that resulted from gas hydrate formation or dissociation.” Bohrmann et al. (2002) further refined the definition to emphasize the close relationship between these carbonates and gas hydrates. The carbonates are found directly inside massive gas hydrate layers (Fig. 1) and sometimes exhibit surface morphologies that image the morphology of the gas hydrate bubble fabric (Bohrmann et al., 2002). Furthermore, pore-water chemistry indicates that aragonite forms in the interstices of solid gas hydrate (Suess et al., 2001).

Increasing efforts are being allocated to studies of gas hydrates and their host lithologies because methane hydrates are regarded not only as a potential energy source but also as a significant geohazard risk because of their common occurrence along continental margins. The most original pore-water samples in the immediate vicinity of clathrates have been obtained by recovery and sampling of sediment cores and grabs (Haackel et al., 2004; Torres et al., 2004). These pore waters that surround the gas hydrates are called brines, because they are highly enriched in dissolved ions as opposed to unaltered, pristine pore water. During gas hydrate formation, the ions are excluded from the salt-free cages of water molecules of the hydrates. These brines can only form because of the highly dynamic nature of the gas hydrate system and the rapid growth of the gas hydrates, which is much faster than the fluids can be modified by diffusion (Torres et al., 2004). The previously sampled gas hydrate brines can only provide a snapshot of the current in situ conditions and thus bear a significant risk of sampling artifacts.

Here we present new data that reveal the isotopic composition and evolution from pristine pore fluid to a gas hydrate brine due to gas hydrate and clathrite formation. The  $\delta^{18}\text{O}$  values of the clathrites allow the reconstruction of the fluid composition and show the enrichment of  $^{16}\text{O}$  in the fluid due to the preferred incorporation of  $^{18}\text{O}$  in the clathrate structure. The  $\delta^{13}\text{C}$  values of the clathrites seem to reflect depletion of  $^{12}\text{C}$  in the fluid. The  $\delta^{44/40}\text{Ca}$  values of the clathrites are the first Ca isotope data of seep carbonates. The data show an enrichment of  $^{44}\text{Ca}$  in the clathrite and indicate the presence of a fluid that is highly enriched in  $^{44}\text{Ca}$  compared to seawater.

## MATERIALS AND METHODS

Eight samples of clathrites from four different locations of Hydrate Ridge were selected for stable isotope ( $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}$ ,  $\delta^{44/40}\text{Ca}$ ) analyses (Table 1). The carbonate samples were retrieved from near-surface sediments down to a depth of  $\sim 0.5$  m below seafloor (mbsf) with a video-guided grab sampler during R/V *Sonne* cruises SO143 (Bohrmann et al., 2000) and SO148 (Linke and Suess,



**Figure 1. Photographs of clathrite samples.** A: Platy, aragonitic clathrite (yellow color) with more or less flat bottom (proximal to gas hydrate) and irregular top (distal to gas hydrate). B: Aragonitic clathrite (yellow) with gas hydrate attached (sample stored in liquid nitrogen).

2001). Each sample was subsampled with a hand-held microdrill at the lower and the upper parts of the carbonate crust. The subsamples were analyzed for their oxygen, carbon, and calcium isotope composition. The oxygen and carbon isotopes were measured at the University of Bremen following standard procedures. All values are reported in per mil (‰) relative to the Peedee belemnite (PDB) standard by assigning a  $\delta^{18}\text{O}$  value of  $-2.20\text{‰}$  to NBS 19. Analytical standard deviation is  $\sim\pm 0.05$  for  $\delta^{13}\text{C}$  and  $\pm 0.07$  for  $\delta^{18}\text{O}$ .

The determination of the Ca isotope ratios was performed on a Finnigan TRITON T1 thermal-ionization mass spectrometer at the Leibniz-Institute for Marine Sciences at Kiel University (IFM-GEOMAR), following procedures of Heuser et al. (2002). The isotope variations are expressed as  $\delta^{44/40}\text{Ca}$  values ( $\delta^{44/40}\text{Ca} = [({}^{44}\text{Ca}/{}^{40}\text{Ca})_{\text{sample}}/({}^{44}\text{Ca}/{}^{40}\text{Ca})_{\text{standard}} - 1] \times 1000$ ), relative to SRM915a from the National Institute of Standards and Technology, as suggested by the International Union of Pure and Applied Chemistry (Coplen et al., 2002; Eisenhauer et al., 2004). The  $\delta^{44/40}\text{Ca}$  value of the in-house  $\text{CaF}_2$  standard, previously used for normalization, is  $1.450\text{‰} \pm 0.025\text{‰}$  SRM915a ( $2\sigma_m$ ) (Heuser et al., 2002; Gussone et al., 2003). The reproducibility ( $2\sigma_m$ ) of our samples is  $\sim 0.12\text{‰}$ , as determined by repeated measurements of various sample materials. All samples were measured at least twice.

## CLATHRITES

Clathrites occur in two different lithologies (Bohrmann et al., 1998). One kind is composed of sediments cemented with high-Mg calcite and often brecciated. The other kind is a pure aragonitic precipitate of yellow to or-

TABLE 1. STABLE ISOTOPE DATA OF CLATHRITE AND WATER

Sample*	Label	$\delta^{13}\text{C}$ (‰, PDB)	$\delta^{18}\text{O}$ (‰, PDB)	$\delta^{18}\text{O}^\dagger$ (‰, SMOW)	$\delta^{44/40}\text{Ca}_{\text{carb}}$ (‰, SRM915a)	$\delta^{44/40}\text{Ca}_{\text{fluid}}^\S$ (‰, SRM915a)
<b>44°34.21'N, 125°08.81'W</b>						
21-2-B-d	C1	-46.25	2.74	-0.71	1.18	3.05
21-2-B-p	C1	-48.16	3.04	-0.42	0.83	2.71
21-2-H-d	C2	-46.45	3.26	-0.19	0.68	2.55
21-2-H-p	C2	-48.10	3.49	0.04	0.65	2.53
<b>44°34.19'N, 125°08.84'W</b>						
36-A-d#	C3	-46.54	3.32	-0.14	0.72	2.59
36-A-p#	C3	-53.10	3.34	-0.11	0.44	2.31
<b>44°34.23'N, 125°08.84'W</b>						
222-C-d	C4	-41.95	2.27	-1.18	1.05	2.92
222-C-p	C4	-49.60	3.56	0.11	0.49	2.37
<b>44°34.22'N, 125°08.84'W</b>						
56-1-F-d	C5	-42.18	3.14	-0.31	0.78	2.65
56-1-F-p	C5	-40.70	3.28	-0.18	0.84	2.71
56-1-H-d	C6	-39.75	2.83	-0.63	0.73	2.60
56-1-H-p	C6	-39.25	2.97	-0.49	0.63	2.51
56-1-M-d	C7	-40.33	3.34	-0.11	0.79	2.67
56-1-M-p	C7	-43.06	3.19	-0.27	0.55	2.42
56-1-N-d	C8	-43.88	3.35	-0.11	0.63	2.51
56-1-N-p	C8	-44.88	3.50	0.04	0.69	2.56
Pristine pore water (Haeckel et al., 2004)				-0.04		
				-0.01		
Clathrate brine (Suess et al., 1999)				-2.88		
				-1.24		

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

\*d = distal; p = proximal.

$\delta^{18}\text{O}$  calculated for the fluid from clathrite measurements after Hudson and Anderson (1989).

$\delta^{44/40}\text{Ca}_{\text{fluid}}$  calculated for the fluid from clathrite measurements after Gussone et al. (2003).

#Cruise SO148; other samples are from cruise SO143.

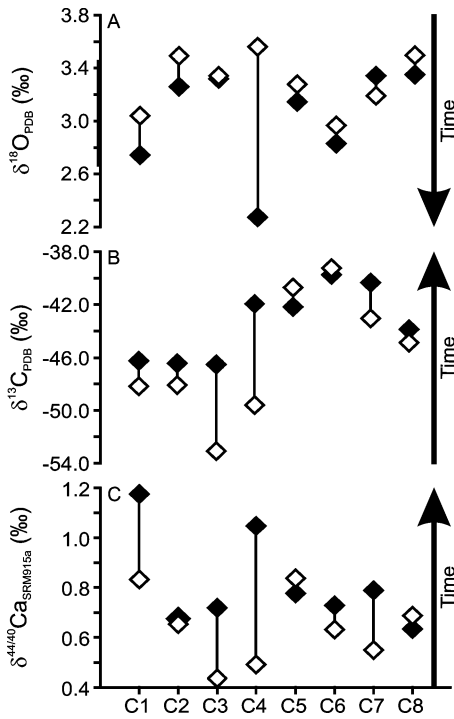
ange color. In the following we only refer to the latter, which can be described as crusts because of their platy appearance (Fig. 1; see Teichert et al., 2003). Individual samples vary in thickness but are usually as much as 1 cm thick and  $\sim 15$  cm across. Microscopic investigations reveal that the clathrites are composed of botryoids with a radius of as much as 500  $\mu\text{m}$ . Most samples exhibit one more or less flat surface, suggesting precipitation parallel to sediment stratification, whereas the other side is irregular. Petrographic investigations reveal that the flat surfaces form at the beginning of clathrite precipitation. The injection of methane-rich gases causes sediment disruption and the opening of pore spaces (Bohrmann et al., 1998) in which the clathrites can precipitate, as indicated by the pure, botryoidal aragonite. Because the flat surfaces of the clathrites sometimes exhibit shapes that partially image the inner surface of gas hydrate bubbles, it is most likely that the clathrites started to precipitate next to or within gas hydrates.

A characteristic feature of all methane-derived carbonates is the enrichment in  $^{12}\text{C}$ . The resulting low  $\delta^{13}\text{C}$  values clearly identify methane as the carbon source. During the microbially mediated anaerobic oxidation of methane,  $^{12}\text{C}$ -enriched bicarbonate ( $\text{HCO}_3^-$ ) is produced. The increase in alkalinity then induces the precipitation of calcium carbonate.

## STABLE ISOTOPES

The measured  $\delta^{18}\text{O}_{\text{PDB}}$  values of all clathrites range from 2.27‰ to 3.56‰ (Table 1; Fig. 2A). The  $\delta^{18}\text{O}_{\text{PDB}}$  equilibrium value for an aragonite precipitated from seawater (0‰ relative to standard mean ocean water [SMOW]) at the measured bottom-water temperature of 4.7 °C is 3.46‰ (calculated after Hudson and Anderson, 1989). Most of the measured values are lower than the calculated equilibrium value. A prominent feature of most samples is the  $\delta^{18}\text{O}$  variation between the distal and proximal sides of the sample (Table 1). Here we define a “proximal” subsample as an early carbonate layer precipitated close to gas hydrate and a “distal” subsample as a late carbonate layer precipitated farther away from gas hydrate toward the gas hydrate brine. The samples that are most enriched in  $^{18}\text{O}$ , except 56-1-M, occur proximal to the gas hydrate, whereas the samples that are most depleted in  $^{18}\text{O}$  are usually found distal to the gas hydrate. The largest  $\delta^{18}\text{O}_{\text{PDB}}$  difference between the proximal and distal subsamples is 1.29‰, which was measured in sample 222-C (Table 1).

The most important parameters influencing the oxygen isotope fractionation are probably the precipitating fluids, which might be seawater, pristine pore water, gas hydrate brine, or gas hydrate water (freshwater enriched in  $^{18}\text{O}$  that is released during decomposition of



**Figure 2. Oxygen, carbon, and calcium isotopes of all clathrite samples. Open symbols are samples precipitated proximally to gas hydrate; closed symbols are samples precipitated distally to gas hydrate. See Table 1 for labels. A:  $\delta^{18}\text{O}_{\text{PDB}}$ . B:  $\delta^{13}\text{C}_{\text{PDB}}$ , (PDB—Pee Dee belemnite standard). C:  $\delta^{44}\text{Ca}_{\text{SRM915a}}$**

hydrate). An important process in this environment is the preferential uptake of  $^{18}\text{O}$  in gas hydrates and a brine enriched in  $^{16}\text{O}$  as a result of solid-fluid isotope fractionation (e.g., Hesse, 2003). In this specific setting, other parameters that might influence the oxygen isotope fractionation play either a minor role (temperature, global ice volume) or have not been measured precisely enough (pH).

The  $\delta^{13}\text{C}_{\text{PDB}}$  values of the clathrites vary from  $-38.35\text{‰}$  to  $-53.10\text{‰}$  (Table 1; Fig. 2B). The  $\delta^{13}\text{C}$  values vary within each sample. The samples proximal to gas hydrate are more enriched in  $^{12}\text{C}$  than the distal samples, except for samples 56-1-F and 56-1-H. The largest difference between the proximal and distal samples is  $7.65\text{‰}$ , measured in sample 222-C.

The  $\delta^{44/40}\text{Ca}$  ratios of the clathrites show a range between  $0.44\text{‰}$  and  $1.18\text{‰}$  relative to the SRM915a isotope standard (Table 1). The  $\delta^{44/40}\text{Ca}_{\text{SRM915a}}$  equilibrium value for an inorganically precipitated aragonite from seawater with a  $\delta^{44/40}\text{Ca}_{\text{SRM915a}}$  value of  $1.88\text{‰}$  (cf. Eisenhauer et al., 2004) at  $4.7\text{ °C}$  is  $0.09\text{‰}$ , calculated after Gussone et al. (2003) as follows:  $\delta^{44/40}\text{Ca} = (0.015T - 2.23) + \Delta_{\text{N}} + \Delta_{\text{F}}$  ( $T$  is temperature in degrees Celsius;  $\Delta_{\text{N}} = 1.45$ , for renormalization from  $\text{CaF}_2$  to SRM915a standard;  $\Delta_{\text{F}} = 0.8$ , for the differ-

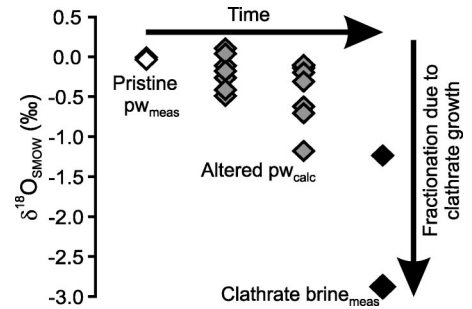
ence between the artificial solution used in Gussone et al. [2003] and seawater). The measured  $\delta^{44/40}\text{Ca}$  of all samples is higher than the calculated equilibrium value. The Ca isotope composition for four of the samples shows variations between samples proximal and distal to gas hydrate larger than the precision of the measurement; the largest variations ( $0.56\text{‰}$ ) are in sample 222-C (Fig. 2C). Proximal layers of the samples are less enriched in  $^{44}\text{Ca}$  ( $\delta^{44/40}\text{Ca}_{\text{SRM915a}} \leq 0.69\text{‰}$ ), whereas distal layers are highly enriched in  $^{44}\text{Ca}$  ( $\delta^{44/40}\text{Ca}_{\text{SRM915a}} \leq 1.18\text{‰}$ ) except for samples 56-1-F and 56-1-N (Table 1; Fig. 2C). In this particular setting, the  $\delta^{44/40}\text{Ca}$  of the clathrite samples is mainly affected by changes in the isotopic signature of the fluid, because both temperature changes of the fluid and the temperature dependence of Ca isotope fractionation in inorganic aragonite are small ( $0.015\text{‰}$  per  $1\text{ °C}$ ; Gussone et al., 2003).

## DISCUSSION

The described data set of oxygen, carbon, and calcium isotopes shows isotopic variations between the samples precipitated proximally to gas hydrate and distally, where precipitation stopped. Earlier studies from Teichert et al. (2003) suggest that the carbonate samples used in this study had all ceased growing. The variations in the isotopic composition indicate that at least one parameter (e.g., fluid signature, temperature, fractionation due to gas hydrate formation) changed continuously during the precipitation of the clathrites and caused successive isotope fractionation within the carbonates.

First, we consider the oxygen isotope composition of all subsamples precipitated proximally to gas hydrate as representing the conditions at the beginning of carbonate precipitation. The  $\delta^{18}\text{O}_{\text{PDB}}$  values scatter from  $2.97\text{‰}$  to  $3.56\text{‰}$  around the calculated equilibrium value ( $3.46\text{‰}$ ), indicating precipitation from a fluid with near-seawater oxygen isotope composition (Fig. 2A). During ongoing precipitation (distal samples), the  $\delta^{18}\text{O}$  values become enriched in  $^{16}\text{O}$  (Fig. 2A) because of gas hydrate formation that successively enriches the ambient pore fluid in  $^{16}\text{O}$ . Because gas hydrate decomposition would release  $^{18}\text{O}$ -enriched water, our measured data of the carbonates are consistent with carbonate precipitation during ongoing gas hydrate formation.

With our measured  $\delta^{18}\text{O}$  values of the clathrites, we can now reconstruct the evolution of the  $\delta^{18}\text{O}$  value of the gas hydrate brine (Table 1; Fig. 3). By assuming a temperature of  $4.7\text{ °C}$ , we can calculate the oxygen isotope composition of the water from which the carbonates precipitated (after Hudson and Anderson,



**Figure 3. Graph of measured (meas)  $\delta^{18}\text{O}_{\text{SMOW}}$  values of pristine pore water (pw) and clathrate brine taken from Suess et al. (1999) and Haeckel et al. (2004) and calculated (calc) composition of altered pore water derived from our measured  $\delta^{18}\text{O}_{\text{PDB}}$  values of clathrite samples (see Table 1). PDB—Pee Dee belemnite; SMOW—standard mean ocean water.**

1989). The calculated  $\delta^{18}\text{O}_{\text{SMOW}}$  values from the subsamples distal to gas hydrate range from  $-1.18\text{‰}$  to  $-0.05\text{‰}$ . Figure 3 shows how these reconstructed ratios are related to  $\delta^{18}\text{O}$  measurements of clathrate brine and pristine pore water from similar depth. The calculated  $\delta^{18}\text{O}_{\text{SMOW}}$  values range from measured pore-water signatures to measured  $\delta^{18}\text{O}_{\text{SMOW}}$  values of a clathrate brine of  $-1.24\text{‰}$ . The variability in the measured  $\delta^{18}\text{O}$  of the clathrate brine might be caused by differing primary pore-water compositions and by the gas hydrate growth rate (Tomaru et al., 2004).

The low  $\delta^{13}\text{C}$  of the clathrites clearly indicates that they are methane derived. Because the fractionation of carbon isotopes between fluid and carbonate is negligible, the  $\delta^{13}\text{C}_{\text{PDB}}$  values of the subsamples precipitated proximally to gas hydrate ( $-53.10\text{‰}$  to  $-39.25\text{‰}$ ; Table 1) can be regarded as the isotopic composition of the fluid from which the carbonates precipitated. During ongoing carbonate precipitation, the fluid seems to have been enriched in  $^{13}\text{C}$  (Fig. 2B). A possible explanation for the enrichment in  $^{13}\text{C}$ , observed in six of eight samples, might be that microbes preferably consume the  $^{12}\text{C}$ . Another explanation might be that the methane carbon is exhausted through gas hydrate formation, so that the influence of biogenic carbon enriched in  $^{13}\text{C}$  in the fluid would increase. Because only six of eight samples show the enrichment in  $^{13}\text{C}$ , other mechanisms may control changes in the dynamic fluid regime that are driven by microbial response.

Our calculated  $\delta^{44/40}\text{Ca}_{\text{SRM915a}}$  equilibrium value is  $0.09\text{‰}$ . However, the measured  $\delta^{44/40}\text{Ca}_{\text{SRM915a}}$  values of the subsamples precipitated proximally to gas hydrate ( $0.44\text{‰}$ – $0.83\text{‰}$ ; Table 1; Fig. 2C) are significantly enriched in  $^{44}\text{Ca}$  relative to the calculated equilibrium value. We can then reconstruct the

$\delta^{44/40}\text{Ca}_{\text{SRM915a}}$  of the fluid from which the proximal samples precipitated (after Gussone et al., 2003) because the precipitation rates of our samples were slow enough to exclude major disequilibrium effects [at a maximum,  $\sim 8 \mu\text{mol}/(\text{m}^2\cdot\text{h})$ ]. The calculated  $\delta^{44/40}\text{Ca}_{\text{SRM915a}}$  values for the fluid range from 2.31‰ to 2.71‰ (Table 1). These values are 0.43‰–0.83‰ more enriched in  $^{44}\text{Ca}$  than seawater, which has a uniform calcium isotope composition of  $\sim 1.88\%$  (cf. Eisenhauer et al., 2004). To date there are no published  $\delta^{44/40}\text{Ca}$  values in pore-fluid samples to compare with our calculated values. Nevertheless it is conceivable that pore fluids are becoming enriched in  $^{44}\text{Ca}$  during their ascent owing to diagenetic processes or deep carbonate precipitation.

Because calcium is not incorporated into the hydrate structure, the most probable process responsible for a fractionation of Ca isotopes in the gas hydrate brine is the formation of the carbonate. If the clathrites precipitate faster than diffusion,  $^{44}\text{Ca}$  will be successively enriched in the fluids surrounding the carbonates because the  $^{40}\text{Ca}$  is preferentially incorporated into the carbonate (cf. Skulan and DePaolo, 1999). This effect will have an even greater impact if the advection of fluids from deeper is partially restricted through layers of gas hydrate or authigenic carbonate. A simple Raleigh fractionation can be used to calculate that  $\sim 30\%$  of the Ca ions in the brine are incorporated into the clathrites; this calculation employs a fractionation factor of  $\alpha = (^{44}\text{Ca}/^{40}\text{Ca})_{\text{arag}}/(^{44}\text{Ca}/^{40}\text{Ca})_{\text{fluid}} = 0.99813$  at  $4.7^\circ\text{C}$  between aragonite and fluid and assumes a pore-fluid  $\delta^{44/40}\text{Ca}_{\text{SRM915a}}$  value of 2.31‰, obtained from the subsample proximal to gas hydrate of sample 36-A (which is the least enriched sample) as the best approximation because pore-water data are not available.

## SUMMARY AND CONCLUSION

While clathrites precipitate, they function as unique in situ recorders of the geochemical environment during clathrate formation. This study indicates that the fluid is modified by the precipitation of two solid phases, the clathrites and clathrates. Thus, the clathrites are the first seep carbonates that can clearly be associated with gas hydrate growth. Dating of these carbonates, as done in Teichert et al. (2003), provides ages that correspond to times of probably enhanced methane flux and fast gas hydrate growth.

The combination of calcium, carbon, and oxygen isotope analyses of clathrites opens a valuable archive of geochemical changes in environments of rapid gas hydrate formation that are still difficult to sample and often biased by sampling artifacts. The three proxies

provide information about the composition of the gas hydrate brine that has only been sampled twice (Haeckel et al., 2004; Torres et al., 2004). But even these two measurements are only snapshots and cannot tell us anything about the temporal evolution of the brines. The carbonates, in contrast, have the potential to record the temporal evolution and thus enhance reconstructions of the geochemical environment of fossil hydrate deposits.

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