Calcium isotope fractionation and its controlling factors over authigenic carbonates in the cold seeps of the northern South China Sea

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In this study, we analyzed stable calcium isotope results of authigenic carbonates from two cold seep areas of the Dongsha area and the Baiyun Sag in the northern South China Sea. The stable isotopes of carbon and oxygen as well as the mineral composition of authigenic carbonates were used to investigate control calcium isotope fractionation. The $\delta^{44/40}$Ca ratios of the southwestern Dongsha area samples ranged from 1.21‰ to 1.52‰ and the ratio of the Baiyun Sag sample was 1.55‰ of the SRM915a isotope standard. X-ray diffraction analysis showed that the carbonate samples consisted of dolomite, calcite and aragonite, with small amounts of high-Mg calcite and siderite. The δ^{13}C values of the carbonates of the southwestern Dongsha area varied between −49.21‰ and −16.86‰ of the Vienna PeeDee Belemnite (VPDB) standard and the δ^{18}O values ranged from 2.25‰ to 3.72‰ VPDB. The δ^{13}C value of the Baiyun Sag sample was 2.36‰ VPDB and the δ^{18}O value was 0.44‰ VPDB. The δ^{13}C values of the carbonates of the southwestern Dongsha area revealed there is methane seeping into this area, with a variable contribution of methane-derived carbon. The sampled carbonates covered a range of δ^{13}C values suggesting a dominant methane carbon source for the light samples and mixtures of δ^{13}C values for the heavier samples, with possibly an organic or seawater carbon source. The δ^{18}O values indicated that there is enrichment in ^{18}O, which is related to the larger oxygen isotope fractionation in dolomite compared to calcite. The results of the Baiyun Sag sample exhibited normal seawater carbon and oxygen isotopic values, indicating that this sample is not related to methane seepage but instead to precipitation from seawater. The relatively high $\delta^{44/40}$Ca values indicated either precipitation at comparatively high rates in pore-water regimes with high alkalinity, or precipitation from an evolved heavy fluid with high degrees of Ca consumption (Raleigh type fractionation). The dolomite samples from the Dongsha area revealed a clear correlation between the carbon and calcium isotope composition, indicating a link between the amount and/or rate of carbonate precipitation and methane contribution to the bicarbonate source. The results of the three stable isotope systems, mineralogy and petrography, show that mineral composition, the geochemical environment of authigenic carbonates and carbon source can control the calcium isotope fractionation.

authigenic carbonate, cold seeps, calcium isotope, northern South China Sea, gas hydrates

Cold seeps occur extensively along active and passive continental margins worldwide, and are characterized by the expulsion of hydrocarbon-rich fluids (especially methane) from the sedimentary column to the seafloor at seepage sites [1,2]. The ascending methane is mainly derived from microbial methanogenesis or from thermochemical decomposition of organic matter at depth. The emanation of gas from the deep subsurface into the water column has a profound effect on the marine environment, providing an environment for chemosynthetic biota along the seafloor local to the

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seepage sites, as well as on the chemistry of the sediments [3]. Carbonate precipitation at hydrocarbon seepage sites results from anaerobic oxidation of methane by archaea microbes and sulfate reduction of heavier hydrocarbons by sulfate reducing bacteria [4,5]. Authigenic carbonates are therefore common at cold vent sites [6], and can be used to unravel the evolution of past cold seep activity. In particular, stable isotopes of carbon and oxygen have been proven to be useful proxies in such carbonate minerals [7,8]. In addition, during the last decade, the use of the isotope composition of Ca has shown considerable potential as a geological tracer. In the marine realm, Ca isotopes have been used for the reconstruction of the marine Ca-budget [9–11], paleo-temperature reconstructions [12–14], characterization of relationships in ancient food webs [15,16], the study of biomineralization and related Ca isotope fractionation mechanisms [17–21], and the study of processes during early diagenesis [22–24].

The study of the Ca isotope ratios of authigenic carbonate minerals can contribute to our understanding of geochemical processes. This is because the ratio of Ca isotopes is influenced by several variables including temperature [25,26], precipitation rate [26,27], the crystal structure of the minerals [28,29], the composition of the Ca in the fluid and the fraction of Ca removed during precipitation [22].

The calcium isotope research of cold seeps and gas hydrate is a frontier field [22,24,30,31]. At cold seep sites, methane-derived authigenic carbonates are a significant calcium sink in the sediments. The strong depletion of dissolved Ca in the pore-waters of shallow sedimentary sections (centimeters-tens of meters) because of carbonate formation has been widely observed [31]. Where $CaCO_3$ precipitation is faster than diffusion, the carbonate precipitation causes ^{44}Ca enrichment in the surrounding pore-waters because of the preferred incorporation of ^{40}Ca into the precipitate [25,26,32,33]. It was shown by Teichert et al. [22] that the combined application of the stable isotopes of C, O and Ca on cold seep carbonates provides insight into multiple factors influencing the isotopic composition of the authigenic carbonate. In addition, the application of these isotopes provides a tool to record the evolution of the geochemical environment of gas hydrate systems.

The aim of this study was to understand the mechanisms controlling Ca-isotope fractionation during the biogeochemical processes at cold seeps. This was achieved through characterization of authigenic carbonates by use of petrography, mineralogy and stable carbon and oxygen isotope results. We focused on environmental parameters and processes that govern Ca isotope fractionation in the authigenic carbonates and investigated if they can be used to indicate the formation and destabilization of gas hydrate. The $\delta^{44/40}Ca$ values of the authigenic carbonates represent the first Ca isotope data of cold seep carbonates derived from the northern South China Sea.

1 Geological setting

The South China Sea is one of the largest marginal seas in the western Pacific, with an average water depth of about 1200 m and a maximal depth of about 5380 m. Its bottom topography is complex, showing spatial variability with several plateaus, troughs, valleys and island reefs. The northern margin is composed of fault controlled terraces and basins (Figure 1), where the deposition of sediments with abundant organic matter favors gas (mainly methane) generation with subsequent hydrate formation and conservation within the gas hydrate stability zone. In early 1984, evidence for bottom simulating reflectors (BSR) in the Nansha Trough of the southern South China Sea was discovered based on seismic data. These are mainly located at 300–600 m below the seabed along the southeastern slopes of the Nansha Trough, at water depths between 1500–2800 m [34].

The northern South China Sea is presently a key area for the exploration and research of gas hydrate resources within China. In 1998, evidence of BSRs was reported in the northern South China Sea [37]. Several areas of gas hydrates occurrence, including two of high concentration, the northeastern Dongsha area and Xisha Trough, were discovered based on the presence of BSRs and geochemical anomalies [36,38–42]. In recent years, many gas hydrate cold seeps have been found in the northern South China Sea. Occurrences of gas hydrates by the observation of BSRs and cold seeps have also been reported in southwestern Taiwan [43–45]. Chen et al. [46] reported for the first time the occurrence of carbonates originating from cold seeps in the South China Sea and showed that those carbonates probably formed at presently active gas seepage sites. The presence of active gas seepage sites has direct implications for gas exploration and hydrate accumulation in that area. The Guangzhou Marine Geological Survey has discovered large seafloor areas covered by authigenic carbonates, bacterial mats, tube worms and bivalves in the northeastern Dongsha area, which were interpreted as evidence of gas hydrates occurrence [47–49]. The discovery of large carbonates of massive and irregular forms, carbonate crusts and pavements, carbonate chimneys and tube worms in the southwestern Dongsha area, took place during cruises organized by the South China Sea Institute of Oceanology of the Chinese Academy of Sciences in 2005 [36]. Authigenic carbonates were also found in the gas hydrate prospect area of Qiongdongnan. These discoveries constitute important evidence of the widespread presence of methane seepage in this area [36].

2 Materials and methods

2.1 Samples

The authigenic carbonates analyzed in this study were collected with a grab sampler. Six samples were collected from the seafloor in the southwestern Dongsha area in 2005 and
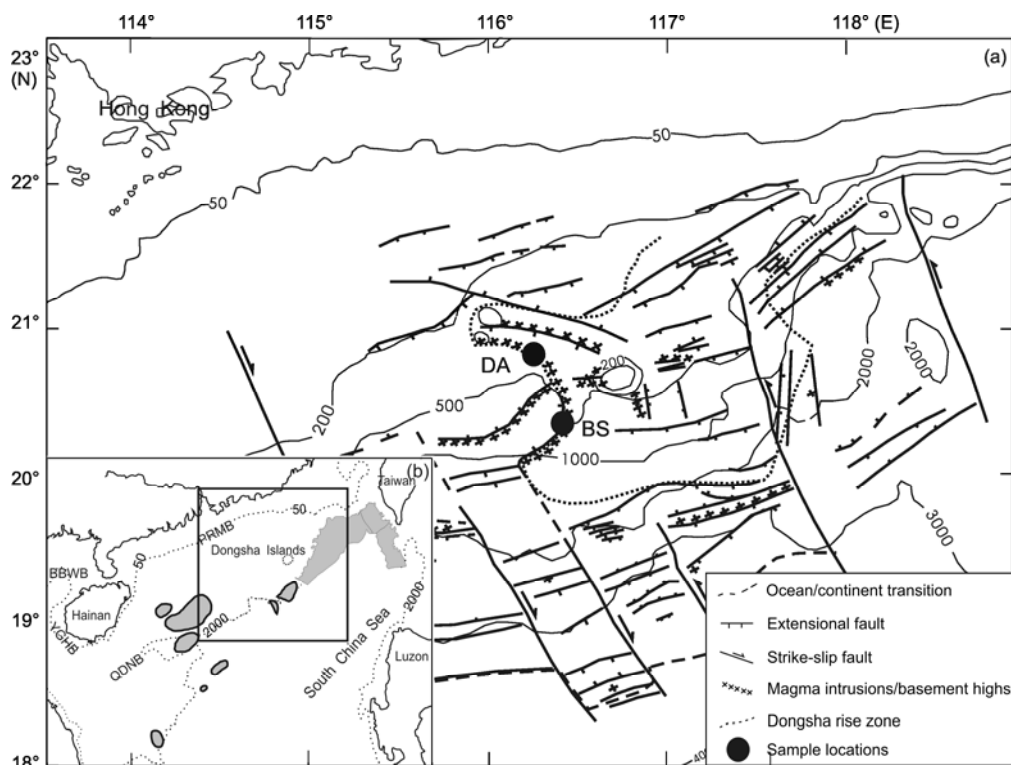
Figure 1 Distribution of the main fault systems within the Dongsha Islands area of the northern South China Sea margin [35,36]. DA, Southwestern Dongsha area; BS, Baiyun Sag; PRMB, Pearl River Mouth Basin; QDNB, Qiongdongnan Basin; YGHB, Yinggehai Basin; BBWB, Beibuwan Basin.

one sample was collected from Baiyun Sag in 2008 during the integrated research cruises organized by the South China Sea Institute of Oceanology, Chinese Academy of Sciences. The authigenic carbonates were washed with freshwater immediately after collection, cleaned using ultrasound for 15 min, and dried in the air. Samples were then cut into sub-sampling sections for X-ray diffraction (XRD) and stable carbon, oxygen and calcium isotope analyses.

2.2   Ca isotope analysis

Powders of authigenic carbonates were weighed into Teflon screw top vials and dissolved in 2.5 N HCl at 70°C on a hotplate. Aliquots (approximately 400 ng Ca) of the samples were mixed with a ^{42}Ca-^{43}Ca-doublespike [29,50] to correct for isotope fractionation during data acquisition in the mass spectrometer. The spike sample mixture was dried, recovered in 6 N HCl and loaded on outgassed Re-single filaments using the sandwich technique (TaF$_5$-sample-TaF$_5$). Calcium isotope ratios were determined by thermal ioniza-tion mass spectrometry on a Thermo-Fisher Triton T1 ther-mal ionization mass spectrometer (Institut für Mineralogie, University of Münster). Measurements were performed in static mode, simultaneously measuring the masses of ^{40}Ca, ^{42}Ca, ^{43}Ca, and ^{44}Ca isotopes. Potential interference of ^{40}K on ^{40}Ca was determined by monitoring the mass of ^{41}K, but this was always found to be negligible. Instrumental mass fractionation was corrected using the iterative approach of

Heuser et al. [51], based on the approach of Compston and Oversby [52]. Calcium isotope ratios are expressed as $\delta^{44/40}$Ca values relative to the NIST SRM 915a standard ($\delta^{44/40}$Ca [‰]=((^{44}Ca/^{40}Ca)$_{sample}$/(^{44}Ca/^{40}Ca)$_{SRM\ 915a}$−1)×1000). The dolomite standard J-Do revealed a $\delta^{44/40}$Ca value of 0.70‰ ± 0.04‰ (*n*=7). The twofold standard deviation of our J-Do measurements is ±0.07‰ and agrees with the av-erage 2 S.D. of 0.08‰ obtained from replicate analysis of different samples.

2.3   XRD analysis

XRD patterns were obtained using a Scintag X-ray diffrac-tometer with Cu Kα radiation (λ=1.5405 Å) in the range of 5°–60° 2θ at 0.02°/s, using 40 kV accelerating voltage and a 30 mA current. Peak identification and relative abundance of minerals estimation were performed using the PANalyti-cal and MacDiff® interpretation software packages. As the intensity of the diffraction pattern of a mineral in a mixture is proportional to its concentration, estimates of the relative proportions of the minerals in each sample were made by measuring their relative peak areas.

2.4   C and O isotope analysis

Samples for carbon and oxygen stable isotopic analyses were prepared by reaction at 90°C with 100% phosphoric acid on an automated carbonate device connected to a

VGPRISM mass spectrometer calibrated with NBS 19, NBS 18 and NBS 20. For the temperature calculations of the dolomite samples (>20% of dolomite), $\delta^{18}O$ values were corrected for the analytical offset of +1.63‰, which are a consequence of the unequal oxygen isotope fractionation factor during reaction with 100% H_3PO_4 to form CO_2 [53]. The results are reported in the conventional δ‰-notation with reference to the Vienna PeeDee Belemnite (VPDB) standard. Analytical reproducibility of the method, based on repeated standards, is better than ±0.1‰ for both carbon and oxygen.

3　Results and discussion

3.1　Carbonate mineralogy and petrography

Petrographic and XRD analyses on bulk carbonate concretions revealed that most of the samples from the southwestern Dongsha area were predominantly composed of dolomite (more than 78% (weight percent)), with small amounts of other minerals (quartz, albite, siderite and clay minerals; Table 1). One sample was primarily composed of aragonite (41%) and high-Mg calcite (20%) with other non-carbonate minerals, mainly quartz (27%). The detrital fraction was mainly composed of silty terrigenous grains of quartz, biogenic calcite, feldspars and clays, which corresponds to a fossiliferous matrix with scarce bioclasts of planktonic foraminifera (globigerinoides), and scarce pellets. Almost all the samples contained iron and manganese oxy-hydroxides, which resulted in the samples having a variable brownish color, depending on the degree of oxidation. The XRD results showed that the Baiyun Sag sample was composed of pure calcite (Table 1).

In cold seep environments, it is commonly accepted that aragonite forms preferentially when the anaerobic oxidation of methane-rich fluids occurs at a close proximity to sea-water, that is, in the near-seafloor environment [54,55]. The crystallization of Mg-calcite preferentially occurs under slightly more anoxic conditions with lower SO_4^{2-} and higher total alkalinity concentrations [6]. Dolomite formation is favored in relation to calcite or aragonite when sulfates are removed from the pore waters by an intense reducing bacterial activity (sulfate reduction) [56].

The high dolomite content of the authigenic cement of the southwestern Dongsha area samples indicated that these carbonates were probably formed below the seafloor within the sediment column, if the conditions at the seafloor were mostly oxic with high SO_4^{2-} concentrations and an almost absence of reducing bacterial activity. However, conditions for the growing of dolomite sourced from the anaerobic oxidation of hydrocarbons may have changed, depending on the rate of fluid flow. Thus, anaerobic conditions may have persisted closely below the surface if the rates of hydrocarbon flow were high, allowing the growing of dolomites [57]. The relatively high abundance of aragonite in sample DS-3 suggests that it was formed when and where the oxidation of methane-rich fluids occurred at a close proximity to sea-water, in the near-seafloor and more oxic environment. Samples DS-4 and DS-6 were interpreted as being formed under a slightly depleted SO_4^{2-} environment with higher total alkalinity concentrations.

3.2　Stable carbon and oxygen isotopes

The carbon isotopic composition of the authigenic carbonates indicates the origin of carbon incorporated during carbonate precipitation [36,48,58]. Generally, methane in the marine environment can be generated through two main metabolic pathways: microbial methane formed by CO_2 reduction, and thermogenic methane generated during organic matter maturation [59]. Biogenic methane is strongly depleted in ^{13}C and exhibits $\delta^{13}C$ values ranging from −40‰ to −110‰

Table 1　Mineral composition of the studied samples based on X-ray diffraction and stable carbon and oxygen isotope

Sample	Relative percentages (%)									Stable isotope			Sample characteristics
	Dolomite	High-Mg Calcite	Calcite	Aragonite	Quartz	Apatite	Albite	Siderite	Clays	$\delta^{18}O$	$\delta^{13}C$	$\delta^{44/40}Ca$	
Southwestern Dongsha area													
DS-1	87	—	—	—	4	6	—	—	3	3.13	−29.12	1.21	
DS-2	88	—	—	—	6	5	—	—	1	3.35	−21.32	1.43	Brecciated, spherical and elliptical nodules, which are coarse in their surface and have one or two protuberances, the diameters are ~3–8 cm
DS-3	—	20	—	41	27	—	3		9	2.97	−49.21	1.52	
DS-4	78	3	—	—	3	—	2	8	6	3.72	−16.86	1.47	
DS-5	85	—	—	—	7	—	1	—	6	2.76*	−24.04*	1.28	
DS-6	83	2	—	—	4	6		—	5	2.25*	−23.26*	1.27	
Baiyun Sag													
BY-1	—	—	100	—	—	—	—	—	—	0.44	2.36	1.55	Biogenic carbonate, the external surface is biological crust and the interior has many pores

* The results come from Chen et al. [36].

VPDB, while thermogenic methane typically has values ranging from −20‰ to −60‰ VPDB. Petroleum usually exhibits $\delta^{13}C$ values ranging from −25‰ to −35‰ VPDB, sedimentary organic carbon has a $\delta^{13}C$ value of −20‰ VPDB, and the $\delta^{13}C$ value of marine carbonate equals 0 VPDB [36]. The $\delta^{13}C$ values of the southwestern Dongsha area authigenic carbonates varied from −49.21‰ to −16.86‰ VPDB and most $\delta^{13}C$ values were lighter than −20‰ VPDB (Table 1). This demonstrated that at least part of the samples was strongly influenced by methane seeping. The samples between −25‰ and −16‰ might represent either mixtures of methane and marine inorganic carbon or carbon from marine organic matter. Part of the $\delta^{13}C$ values were also in the range reported for petroleum seeps. However, because we do not have independent evidence for petroleum being involved in this seep system, this hypothesis seems rather unlikely. In addition, the $\delta^{13}C$ values of carbonate as low as −49.21‰ VPDB indicate that the carbon source was not petroleum [36]. A clear distinction between thermogenic and biogenic methane is not a straightforward task, because of evidence for mixing of different carbon sources at the seep site, indicating a mixture of methane (thermogenic or biogenic) with marine inorganic or organic carbon. The $\delta^{13}C$ value of the Baiyun Sag sample was 2.36‰ VPDB (Table 1). The value was very similar to marine carbon and there is no evidence of a methane-derived origin for this sample.

Oxygen isotope ratios may provide additional information related to the temperature and origin of the diagenetic fluids from which the authigenic carbonates have precipitated [59]. The samples from the southwestern Dongsha area had $\delta^{18}O$ values ranging from 2.25‰ to 3.72‰ VPDB (mostly dolomite) and the value of the Baiyun Sag sample (calcite) was 0.44‰ VPDB. The Baiyun Sag sample represented precipitation from a normal seawater ^{18}O isotopic composition and therefore, supported the ^{13}C isotopic signal of non-seepage related formation with a normal seawater origin. Most of the carbonates from the southwestern Dongsha region displayed oxygen isotopic composition that was close to or heavier than 3‰ VPDB. This approximately 2.5‰ offset was mainly related to the different oxygen isotope fraction for calcite and dolomite of approximately 2.6‰.

However, the sample DS-3 contained significant amounts of aragonite and calcite. Because of the smaller isotope fractionation, it indicated precipitation from a roughly 1‰–2‰ heavier fluid or precipitation at lower temperatures. The differences in $\delta^{18}O$ may be related to formation at different depth or during different phases of seeping, or to changes in the fluid composition (Gas hydrate formation, decay or secular variation $\delta^{18}O$ of seawater) or be related to precipitation at a different temperature possibly related to different bottom water temperatures or the episodical expulsion of warm fluids [60].

3.3 Stable calcium isotope fractionation and its controlling factors

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 carbonate precipitation process is faster than diffusion, ^{44}Ca will be successively enriched in the fluids surrounding the carbonates because the ^{40}Ca isotope is preferentially incorporated into the carbonate [20,25, 26,29]. The carbonate precipitation causes ^{44}Ca enrichment in the surrounding pore-waters and the values of carbonate's calcium isotope increase with ongoing precipitation [22,30]. The $\delta^{44/40}Ca$ ratios of the southwestern Dongsha area samples ranged from 1.21‰ to 1.52‰ and the Baiyun Sag sample was 1.55‰ relative to the SRM915a isotope standard. These values were 0.67‰–0.36‰ and 0.33‰ smaller in ^{44}Ca than in seawater, which has a uniform calcium isotope composition of approximately 1.88‰ [61]. The depletion of heavy Ca isotopes in the carbonates relative to seawater was smaller than experimentally determined for precipitation from fluids at similar temperatures [28,33]. This might indicate either precipitation at high rates [32] or precipitation from a fluid with high $\delta^{44/40}Ca$, most probably related to the above discussed Rayleigh-type fractionation effect in semi-enclosed reservoirs.

The mineralogy and petrography results showed that all samples except BY-1 and DS-3 are composed of dolomite, and therefore, probably formed in the sediment under the seafloor. Their $\delta^{44/40}Ca$ ratios ranged from 1.21‰ to 1.47‰. The sample DS-3 consisted of aragonite and high-Mg calcite and probably formed near the seafloor. The sample BY-1 was composed of calcite. The $\delta^{44/40}Ca$ ratios of samples BY-1 and DS-3 were 1.55‰ and 1.52‰ respectively, which was higher than the dolomite samples. These results indicated that the mineral composition of authigenic carbonates might be related to their calcium isotope composition. The calcium isotope fractionation of the dolomite was the smallest, the calcite and aragonite were similar. This result indicated that aragonite is about 0.5‰ more fractionated than calcite. Therefore, at the investigated seep sites, other factors like $\delta^{44/40}Ca$ of the fluid, precipitation rate or Ca consumption in the pore space may play important roles. The calcium isotope values of authigenic carbonates that form under the seafloor were relatively smaller than the authigenic carbonates formed near the seafloor in this study. This may indicate that the location of the formation of authigenic carbonates is an important factor that may affect calcium isotope fractionation. Hence, the geochemical environment of authigenic carbonates formation is an important factor that may dominantly affect calcium isotope composition.

The dolomite samples from the Dongsha seep site revealed a correlation between Ca and C isotope ratios (Figure 2). The mechanisms that are responsible for the correlation,
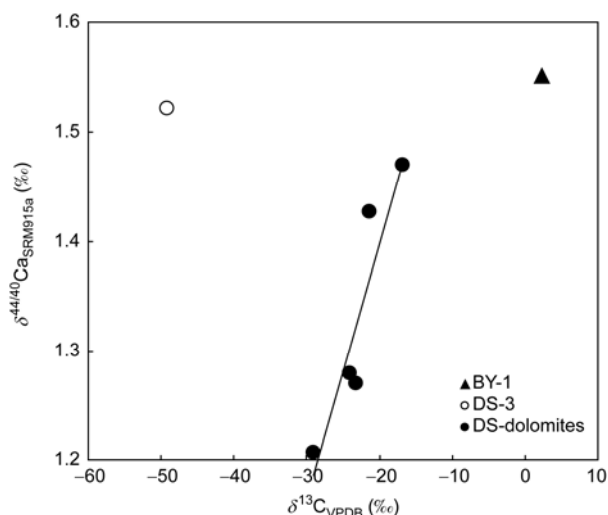
Figure 2   The function of $\delta^{44/40}$Ca and δ^{13}C.

might be related either to the contribution of different carbon sources to bicarbonate production, and related differences in precipitation rates in the respective environment, or alternatively, to the successive depletion of light C and Ca isotopes during ongoing bacterial activity and mineral precipitation [22]. The aragonite and calcite samples (BY-1 and DS-3) did not follow this trend, being influenced by different processes. The results of stable carbon and oxygen isotopes showed that the formation of sample BY-1 was not related to gas hydrates or methane seeping. The mineralogy and carbon isotopic composition of sample DS-3 indicated precipitation near the seafloor during a phase of methane seepage, suggesting a different geochemical environment compared to that in which the dolomites formed, and leading to a different Ca isotope fractionation characteristic. The effect of oxygen isotope on calcium isotope fractionation is very small. Therefore, Ca isotope ratios might be used as tool to better constrain the influences of the carbon source on the formation of authigenic carbonates at cold seep sites.

4   Conclusions

Two areas with carbonate concretions were found in the northern South China Sea. The authigenic carbonates of the southwestern Dongsha area are composed dominantly of authigenic dolomite that cements no-carbonate minerals, mainly of quartz, feldspars, and clay minerals. Only one sample was primarily composed of aragonite, high-Mg calcite, and non-carbonate minerals. The sample of the Baiyun Sag was composed of pure calcite.

Isotopic compositions of the carbonates from southwestern Dongsha area are characterized by medium depleted ^{13}C and relatively enriched ^{18}O, mainly caused by the dolomite specific O isotope fractionation, rather than by a heavy fluid. The carbon isotopic composition indicates that the carbon

source of these carbonates is methane and a mixture of methane with marine organic or inorganic carbon. The petrography, mineralogy, carbon and oxygen isotope values of the Baiyun Sag sample indicate that this sample is not related to methane seepage.

The $\delta^{44/40}$Ca ratios of the southwestern Dongsha area samples ranged from 1.21‰ to 1.52‰ and the ratio of the Baiyun Sag sample was 1.55‰ of the SRM915a isotope standard. The factors that affect the calcium isotope fractionation include mineral composition, super-saturation, precipitation rate and degree of Ca consumption, which are related to the geochemical environment, the formation depth of the authigenic carbonates and the carbon source. The apparent calcium isotope fractionation characteristics of the authigenic carbonates in the seep sites differ from experimental results, indicating that, besides mineralogy, the geochemical environment plays an important role for the incorporation of Ca isotopes into seep carbonates, by affecting precipitation rate, Ca consumption and $\delta^{44/40}$Ca of the pore fluid.

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