

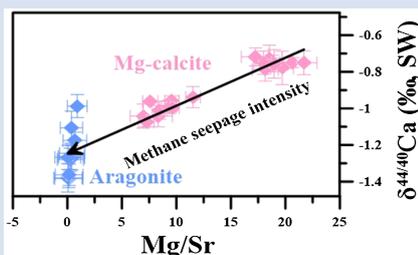
# A dual role of methane seepage intensity on calcium isotopic fractionation

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## Abstract



Calcium isotopes are an important indicator to study the global calcium cycle, however the controls on calcium isotopic fractionation in marine carbonates are still under debate. Seep carbonates are widely precipitated on the continental margins. Constraining the calcium isotopic fractionation mechanism operating during the precipitation of seep carbonates is important for understanding the global calcium cycle. In this paper, we report the calcium isotopic composition of authigenic carbonates recovered from seep sites in the South China Sea, and discuss how the methane seepage intensity controls the calcium isotopic fractionation. The result shows that the calcium isotopic composition of the aragonite ( $-1.17$  ‰ SW) is lower than that of the calcite ( $-0.79$  ‰ SW). Compared to calcite, aragonite is usually formed in the

near-seafloor environment (or close to the sediment-seawater interface) with a higher precipitation rate, both of which indicate high methane seepage intensity. Therefore, we propose that methane seepage intensity is the fundamental factor in controlling the calcium isotopic fractionation of the seep carbonates. The calcium isotopic composition of the seep carbonates could be used as an important proxy to reconstruct the palaeo cold seep activities and to better constrain the calcium cycling.

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## Introduction

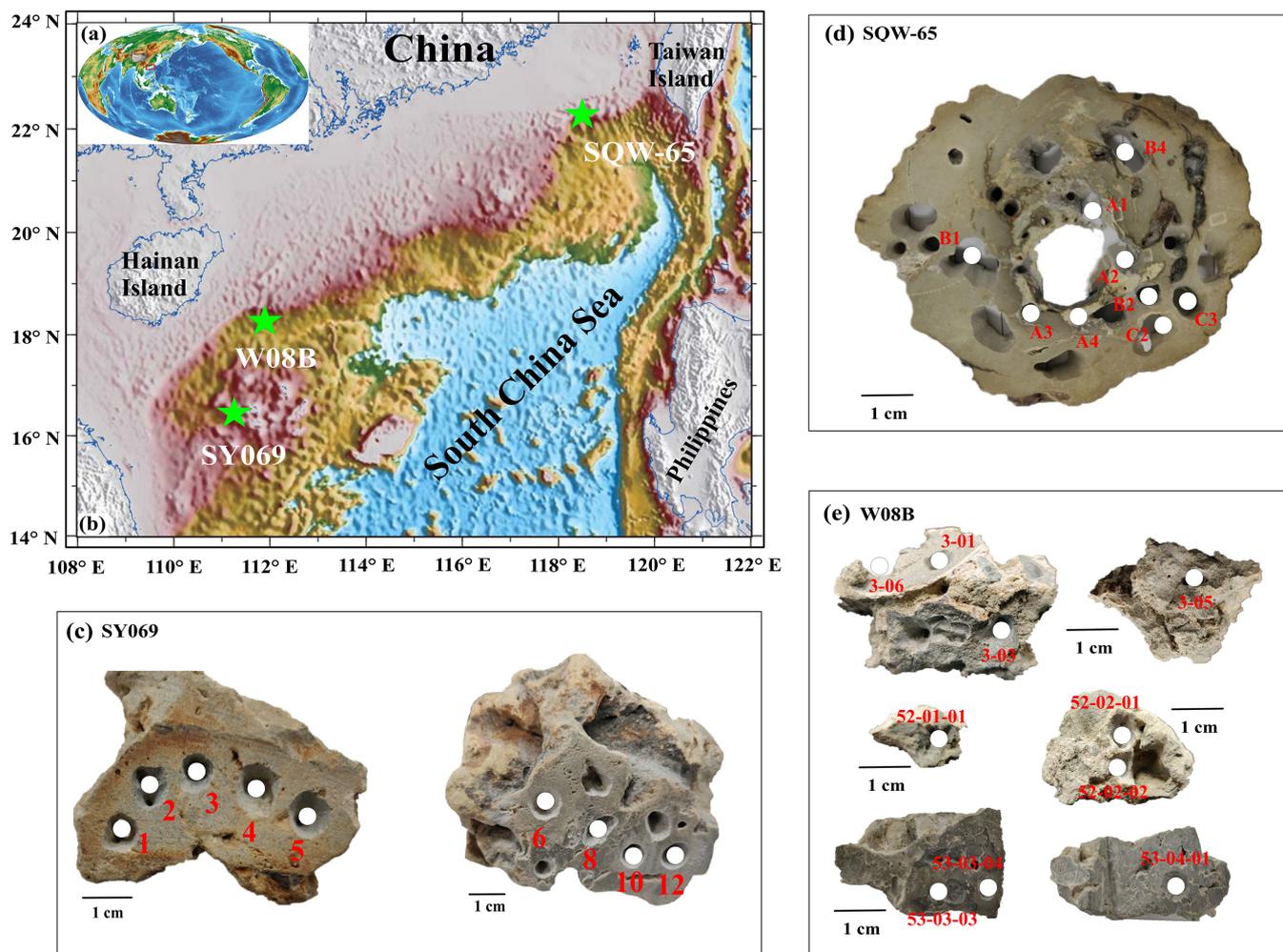
Calcium (Ca) is the fifth most abundant element in the Earth's lithosphere and plays an important role in geological and biological processes (Fantle and Tipper, 2014; Griffith and Fantle, 2021). Ca isotopes have been used as a geochemical proxy in the Ca cycle, carbonate (organic and inorganic) mineralisation, and early diagenesis on both global and regional scales (De La Rocha and DePaolo, 2000; Farkaš *et al.*, 2007; Kasemann *et al.*, 2008; Blättler *et al.*, 2021). To ensure the reliability and applicability of this proxy, it is necessary to fully understand the factors affecting Ca isotopic fractionation in the seep carbonates (Gussone *et al.*, 2005; Teichert *et al.*, 2009; Griffith and Fantle, 2021). Experimental and theoretical evidence shows that the precipitated mineral is typically enriched in the lighter isotopes of Ca relative to source fluids, and this relationship is strongly dependent on the precipitation rate (Marriott *et al.*, 2004; Gussone *et al.*, 2005; Blättler *et al.*, 2012, 2021; Alkhatib and Eisenhauer, 2017; Mills *et al.*, 2021).

Cold seep is a widely observed phenomenon on the continental margins (Michaelis *et al.*, 2002; Teichert *et al.*, 2009; Miao *et al.*, 2022), which typically develops extensive authigenic carbonates due to a local increase of alkalinity resulted from sulfate driven anaerobic oxidation of methane (SD-AOM) (Michaelis *et al.*, 2002; Teichert *et al.*, 2009; Blättler *et al.*, 2021).

In recent years multiple studies have reported Ca isotope ratios in pore waters and carbonates recovered from methane seeps and discussed the factors controlling the Ca isotopic fractionation in these environments (Teichert *et al.*, 2005; Henderson *et al.*, 2006; Bradbury and Turchyn, 2018; Thiagarajan *et al.*, 2020; Blättler *et al.*, 2021). The impact of the carbonate precipitation rate on the Ca isotopic fractionation has also been demonstrated (Teichert *et al.*, 2005; Henderson *et al.*, 2006; Bradbury and Turchyn, 2018; Thiagarajan *et al.*, 2020; Blättler *et al.*, 2021). However, since the seep carbonate mineral facies and precipitation rate are mainly determined by the methane seepage intensity (Tang *et al.*, 2008; Thiagarajan *et al.*, 2020; Blättler *et al.*, 2021; Smrzka *et al.*, 2021), it is reasonable to anticipate methane seepage intensity is one of the key controls on Ca isotopic fractionation. In addition, the depth of the sulfate-methane transition zone (SMTZ) changes when the methane seepage intensity changes (Blättler *et al.*, 2021). This may affect the extent to which Ca isotope fractionation occurs under shallow open system conditions where dissolved Ca is replenished as carbonate precipitation proceeds, *versus* deeper closed system conditions where there is no replenishment of dissolved Ca during carbonate formation, allowing for the preferential accumulation of  $^{44}\text{Ca}$ , which in turn affects the Ca isotopic composition of the carbonates. Therefore, it is believed that methane seepage intensity plays a dual role on the composition of Ca isotopes in the seep carbonates. In this study, we

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**Figure 1** (a) World map with the red rectangle showing the study area. (b) Topographic map of the study area and the locations of the seep carbonates (green stars). (c) SY069 seep carbonate. (d) SQW-65 seep carbonate. (e) W08B seep carbonate. The sampling locations of the seep carbonates are illustrated by the red dots.

report the mineralogical composition, Ca isotopic composition, major and trace elements of the seep carbonates recovered from different seep sites on the northern continental slope of the South China Sea (Fig. 1), and further discuss the influence of methane seepage intensity on the Ca isotopic fractionation.

## Materials and Methods

All the seep carbonates are reported for the first time except W08B (Wei *et al.*, 2020, 2022). The sample location, experimental methods, and data processing are described in the [Supporting Information](#).

## Results

The XRD results show that the W08B carbonates are mainly composed of aragonite with a small amount of calcite, while the SY069 and SQW-065 carbonates are dominated by calcite with no aragonite detected. The calcite is primary (Fig. S-2).

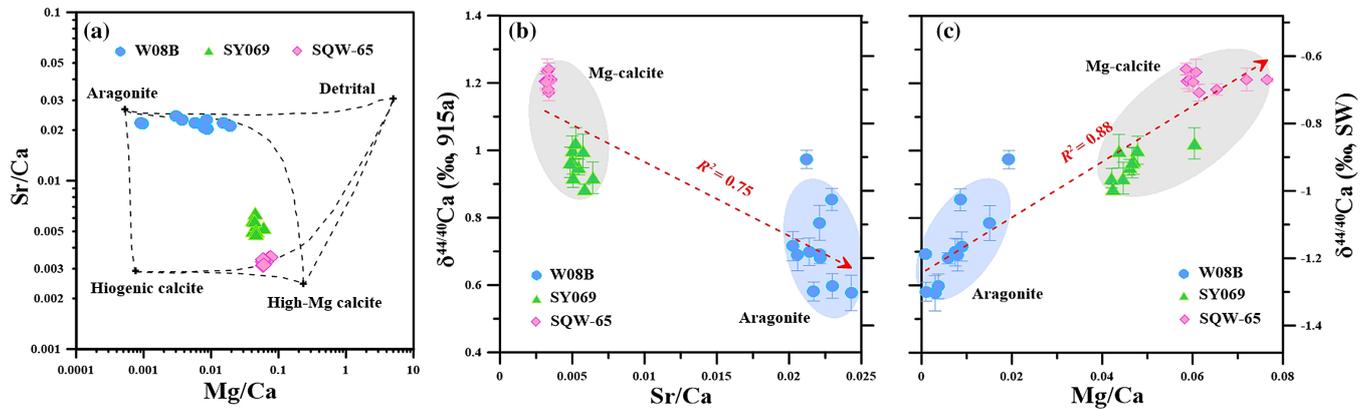
The average Sr/Ca and Mg/Ca ratios of W08B are 0.022 and 0.007 ( $n = 11$ ), respectively. The average Sr/Ca and Mg/Ca ratios of SY069 are 0.005 and 0.047 ( $n = 9$ ), respectively. The average Sr/Ca and Mg/Ca ratios of SQW-065 are 0.003 and 0.063 ( $n = 10$ ), respectively (Fig. 2a, Tables S-1, S-2).

Calcium isotopic composition (reported as  $\delta^{44/40}\text{Ca}$ ) was determined by a Neptune Plus MC-ICP-MS. The average value of W08B  $\delta^{44/40}\text{Ca}$  is  $-1.17\text{‰ SW}$  ( $n = 11$ ; Fig. 2b,c). The SY069 and SQW-065  $\delta^{44/40}\text{Ca}$  are relatively high, with average values of  $-0.92\text{‰ SW}$  ( $n = 9$ ) and  $-0.68\text{‰ SW}$  ( $n = 10$ ) (Fig. 2b,c), respectively. The  $\delta^{44/40}\text{Ca}$  of all the samples are negatively correlated with the Sr/Ca ratio ( $R^2 = 0.76$ ) and positively correlated with the Mg/Ca ratio ( $R^2 = 0.88$ ).

## Discussion

**Precipitation environment of seep carbonates.** It is difficult to reconstruct the palaeo carbonate precipitation environment by analysing the pore water because the pore water during carbonate growth cannot be obtained. However, the carbonate mineralogy and geochemistry at methane seeps are mainly influenced by pore water chemistry. Therefore, the seep carbonate precipitation environment can be reconstructed using specific elemental composition and mineral phases (Burton, 1993; Blättler *et al.*, 2021; Smrzka *et al.*, 2021).

Strong methane seepage results in a shallow SMTZ (near the seafloor), the presence of dissolved sulfate is thought to inhibit precipitation of high-Mg carbonates and hence favours aragonite formation (Burton, 1993; Thiagarajan *et al.*, 2020). When the SMTZ is located at deeper sediment horizons (weak



**Figure 2** Geochemical properties of the seep carbonates (adapted from Bayon *et al.*, 2007). (a) Sr/Ca vs. Mg/Ca. (b) Sr/Ca vs.  $\delta^{44/40}\text{Ca}$  (‰, relative to SRM 915a). (c) Mg/Ca ratios vs.  $\delta^{44/40}\text{Ca}$  (‰ SW).

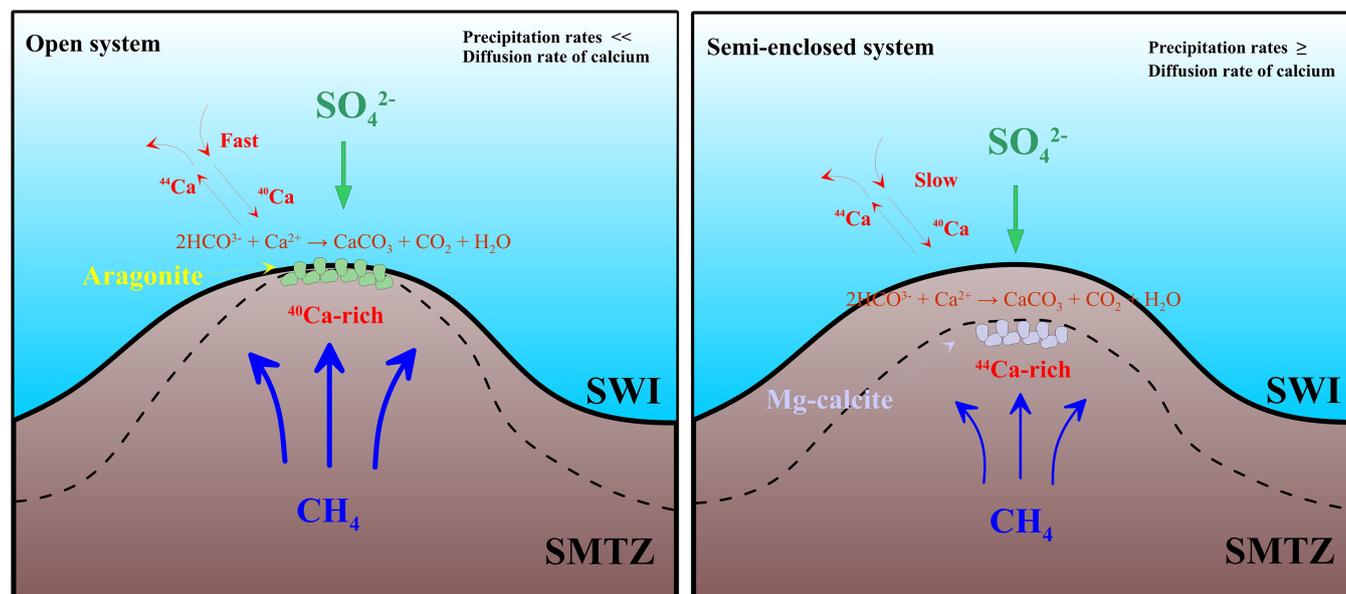
methane seepage), high-Mg carbonates generally precipitate (Thiagarajan *et al.*, 2020; Smrzka *et al.*, 2021). In this study, W08B is dominated by aragonite, indicating a shallow SMTZ; while SY069 and SQW-065 are mainly calcite, indicating a deeper SMTZ (Fig. 2a, Table S-1). In addition, studies have shown that the carbonate precipitation rate affects the composition of specific trace element ratios (Sr/Ca, Mg/Ca), and this is the basis for us to potentially use the specific trace element ratios to reconstruct the palaeo carbonate precipitation rate (Luff and Wallmann, 2003; Tang *et al.*, 2008; Thiagarajan *et al.*, 2020; Smrzka *et al.*, 2021). Lab experiments and carbonate diagenesis studies have shown that the partitioning of Mg and Sr, and the fractionation of Ca isotopes in inorganic carbonates are related to the carbonate precipitation rates. For the same fluid composition, high Sr/Ca and low Mg/Ca in the carbonates are associated with high carbonate precipitation rates, while low carbonate precipitation rates result in low Sr/Ca and high Mg/Ca (Luff and Wallmann, 2003; Tang *et al.*, 2008; Thiagarajan *et al.*, 2020; Blättler *et al.*, 2021). In Figure 2a, W08B is dominated by aragonite with high Sr/Ca and low Mg/Ca, indicating a high precipitation rate, while SY069 and SQW-065 are mainly calcite with low Sr/Ca and high Mg/Ca, indicating a low precipitation rate. This is consistent with previous studies, in which the precipitation rate of aragonite is higher than calcite (Luff and Wallmann, 2003; Gussone *et al.*, 2005; Bayon *et al.*, 2007; Thiagarajan *et al.*, 2020; Blättler *et al.*, 2021).

Based on the comprehensive analysis of the mineralogy and geochemistry of carbonates, we conclude that W08B carbonate was formed in a shallow SMTZ with high precipitation rate. However, SY069 and SQW-065 are formed in a deep SMTZ with low precipitation rate. Moreover, it is believed that the main controlling factor of this difference is the methane seepage intensity.

**The methane seepage intensity affects the Ca isotopic fractionation.** In general, carbonate precipitation results in preferential incorporation of light Ca isotopes, which results in pore waters becoming enriched in heavier Ca isotopes (*i.e.* higher  $\delta^{44/40}\text{Ca}$  values) (Blättler *et al.*, 2012, 2021; Alkhatib and Eisenhauer, 2017; Mills *et al.*, 2021). Lab experiments and theoretical models have shown that the Ca isotopic fractionation of the carbonates increases with higher precipitation rates (Tang *et al.*, 2008; DePaolo, 2011; Nielsen *et al.*, 2012). The  $\delta^{44/40}\text{Ca}$  of these samples showed a negative linear correlation with Sr/Ca ( $R^2 = 0.76$ ; Fig. 2b) and positive linear correlation with Mg/Ca ( $R^2 = 0.88$ ; Fig. 2c). The results indicate that high carbonate precipitation rates (aragonite dominated) lead to the accumulation of light Ca isotopes, while low carbonate precipitation rates (calcite dominated) result in heavy Ca isotopes, which is consistent

with current understanding (Gussone *et al.*, 2005; Thiagarajan *et al.*, 2020; Blättler *et al.*, 2021). In normal marine environments, temperature is considered to be a factor controlling the carbonate precipitation rate (Burton and Walter, 1987; Gussone *et al.*, 2005; Thiagarajan *et al.*, 2020). However, based on the *in situ* measurements, the seafloor temperature of W08B (3.5 °C) is similar to that of SY069 (3.1 °C), and slightly lower than that of SQW-065 (8.3 °C) (Supplementary Information). Therefore, temperature difference as the main factor affecting the carbonate precipitation rate can be excluded. In addition, temperature changes in other cold seeps are also not considered as the potential factor in controlling the carbonate precipitation rate (Bradbury and Turchyn, 2018; Thiagarajan *et al.*, 2020; Blättler *et al.*, 2021). However, the  $\text{HCO}_3^-$  concentration varies significantly because the SD-AOM can generate large amounts of  $\text{HCO}_3^-$  (Michaelis *et al.*, 2002). Compared with the weak methane seepage, SD-AOM is stronger in the strong methane seepage, and more  $\text{HCO}_3^-$  will be produced, which increases the alkalinity and the carbonate saturation of the environment (Luff and Wallmann, 2003). In this case, the precipitation rate of the carbonates will be higher in the strong methane seepage than that in the weak methane seepage. Therefore, it is believed that the carbonate precipitation rate caused by the methane seepage intensity is an important factor affecting the Ca isotopic composition.

The seepage intensity not only controls the carbonate precipitation rate, but also controls the depth of the SMTZ (Smrzka *et al.*, 2021), which in turn controls the magnitude of Ca isotopic fractionation. Strong methane seepage results in a shallow SMTZ, and the pore water has a strong mixing effect with the overlying seawater, resulting in a relatively open system (Smrzka *et al.*, 2021). In this scenario, the  $\text{Ca}^{2+}$  diffusion rate is high, and the  $^{40}\text{Ca}$  consumed by the carbonate formation can be replenished from seawater in time, leading to no enrichment in  $^{44}\text{Ca}$ . Therefore, light Ca isotopes are more enriched in the aragonite (Fig. 3a). In addition, sufficient  $\text{SO}_4^{2-}$  supply will also inhibit the formation of calcite by inhibiting Mg entry into the crystal lattice (Burton, 1993; Goetsch *et al.*, 2019), resulting in the precipitation of aragonite, which is consistent with the light Ca isotopic values observed in the W08B aragonite (Fig. 2). Conversely, weak methane seepage results in a deep SMTZ. The thick overlying sediment prevents the exchange of pore water and seawater, resulting in a relatively closed environment (Blättler *et al.*, 2021). The low  $\text{Ca}^{2+}$  diffusion rate is unable to effectively replenish the consumed  $^{40}\text{Ca}$ , therefore, the pore fluid will become enriched in  $^{44}\text{Ca}$ , which means later carbonate minerals will also be enriched in  $^{44}\text{Ca}$  (Fig. 3b). In addition,



**Figure 3** Schematic diagram illustrating the calcium isotopic fractionation in open system vs. semi-enclosed system.

carbonate formation in this environment is dominated by calcite (Goetschl *et al.*, 2019; Smrzka *et al.*, 2021), therefore calcite records heavy Ca isotopic values (Fig. 3b). Therefore, it is suggested that methane seepage intensity also controls the openness of the cold seep environment and further affects the Ca isotopic composition.

## Conclusions

In the study, a dual role of methane seepage intensity on the Ca isotopic fractionation of the seep carbonates is demonstrated for the first time. It is found that authigenic carbonates collected from different seep sites in the northern continental slope of the South China Sea show obvious differences in Ca isotopes. In the high methane seepage intensity environment, the SMTZ is located in the shallow sediment or even near the seafloor. In a closed system (*i.e.* when the SMTZ is located in the deep sediment), seep carbonate precipitation prefers to incorporate light  $^{40}\text{Ca}$ , hence resulting in the enrichment of heavy  $^{44}\text{Ca}$  in the pore water. In this case, with time, the ongoing carbonate precipitation (mostly high-Mg calcite) should indeed be accompanied by a heavy Ca isotope composition. In contrast, in an open system (*i.e.* when the SMTZ is located near the seafloor), aragonite is precipitated from a relatively light  $^{40}\text{Ca}$  pool in the pore water, hence explaining why the aragonite displays light Ca isotopic composition. These results suggest that the Ca isotope of the seep carbonates is potentially a good proxy for understanding and constraining the palaeo SD-AOM activities in the cold seeps, which is of great significance to study the global calcium cycle.

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## Additional Information

Supplementary Information accompanies this letter at <https://www.geochemicalperspectivesletters.org/article2303>.



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