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# Intensity of methane seepage reflected by relative enrichment of heavy magnesium isotopes in authigenic carbonates: A case study from the South China Sea

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## ABSTRACT

Changing conditions including steep redox gradients result in different Ca-Mg-carbonates forming at methane seeps as a consequence of sulfate-driven anaerobic oxidation of methane (SD-AOM). Since  $Mg^{2+}$  is one of the main cations in Ca-Mg-carbonates, Mg isotope composition may reflect the mode of mineral authigenesis at seeps. Seep carbonates were collected from the Shenhu area and the Southwest (SW) Taiwan basin in the South China Sea. The carbonate phases in Shenhu samples are dolomite accompanied by accessory Mg-calcite, while SW Taiwan samples consist of Mg-calcite and dolomite. Correspondingly, Shenhu carbonates show systematically higher Mg/Ca ratios. Low  $\delta^{13}C$  values of seep carbonates confirm their derivation from the oxidation of methane,  $\delta^{18}O$  values reflect formation in equilibrium with coeval seawater. The  $\delta^{26}Mg$  value of a reference sample of biotrital carbonate ( $-4.28\text{‰}$ ) is lower than those of seep carbonates ( $-3.25$  to  $-2.95\text{‰}$ ). Since only little variability of  $\delta^{26}Mg$  values of pore waters is expected based on previous work, differences in the  $\delta^{26}Mg$  values of seep carbonates were apparently caused by changing degrees of isotopic fractionation during precipitation. Trends between  $\delta^{26}Mg$  values and Mg/Ca ratios and between  $\delta^{26}Mg$  and  $\delta^{13}C$  values suggest that Mg isotope fractionation was controlled by a kinetic mechanism affecting the incorporation of  $Mg^{2+}$  ions into the carbonate lattice in the course of SD-AOM. By consuming sulfate and by producing sulfide, SD-AOM reduces the energy differences for the dehydration of ions of light and heavy Mg isotopes, lowering isotope fractionation. Additionally, the two trends have been found to be steeper for Shenhu samples, suggesting more pronounced SD-AOM in the Shenhu area. Our study indicates that Mg isotope composition of methane-derived carbonates is affected by the process that drives carbonate precipitation – SD-AOM. Future work is required to confirm the utility of Mg isotopes as a new proxy for this major biogeochemical process.

## 1. Introduction

Cold seeps are globally distributed on the seafloor of continental margins, transporting hydrocarbons, mainly methane, from sediments into the ocean (Hovland and Judd, 1988; Campbell, 2006; Suess, 2014). Methane expelled at cold seeps accounts for a large portion of the

methane in the ocean (Boetius and Wenzhöfer, 2013). In addition, under suitable temperature and pressure conditions, methane is captured within gas hydrate, which has potential as a future energy resource but also poses an environmental hazard (Milkov, 2004). It is consequently warranted to develop approaches that allow to assess the degree of methane emission at marine cold seeps and to look into the

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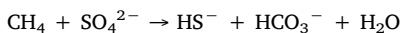
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factors that influence methane release.

Much of the methane at cold seeps is converted into bicarbonate through sulfate-driven anaerobic oxidation of methane (SD-AOM) mediated by the consortium of methane-oxidizing archaea and sulfate-reducing bacteria (Boetius et al., 2000).



The released sulfide and bicarbonate promote the precipitation of pyrite (Lin et al., 2016a, 2016b) and carbonate minerals (Greinert et al., 2001; Roberts et al., 2010). Authigenic carbonates forming under these conditions of increased alkalinity represent a geological archive of cold-seep environments. Seep carbonates are commonly typified by extremely negative  $\delta^{13}\text{C}$  values inherited from methane (e.g., Roberts et al., 2010). The oxygen isotope compositions of seep carbonate, on the other hand, reflect fluid sources and formation temperatures (Malone et al., 2002; Han et al., 2013; Tong et al., 2013). Recent work on seep carbonates has demonstrated that the great variability of seepage activity over time is recorded by trace metal and lipid biomarker patterns, stable isotope signatures of carbonate-associated sulfate, as well as carbonate fabrics and mineralogical composition (Feng et al., 2009, 2016; Peckmann et al., 2009; Haas et al., 2010; Nöthen and Kasten, 2011). Trace elements have been shown to be useful since some of them are very sensitive to changing redox conditions and are not easily affected by diagenetic alteration. Particularly, Ce anomalies (Birgel et al., 2011; Feng et al., 2013) and the relative contents of U, V, and Mo (Ge et al., 2010; Hu et al., 2014) of seep carbonates have been found to be good recorders of past redox conditions. Periods of high seepage activity have been shown to result in positive Ce anomalies. Variable trace element characteristics may occur in different parts of one hand sample (Feng et al., 2009), in a paragenetic mineral sequence, or even within different growth zones of individual mineral phases (Himmler et al., 2010; Crémière et al., 2016). Methanotrophic archaea of the ANME-1 and ANME-2 clusters are better adapted to low and high seepage rates, respectively (Peckmann et al., 2009; Haas et al., 2010). Carbonate-associated sulfate can be used to trace past seepage, as a small slope of its  $\delta^{18}\text{O}$  vs  $\delta^{34}\text{S}$  values has been found to typify methane-rich environments (Feng et al., 2016). Aragonite and various Ca-Mg-carbonates (low-Mg calcite = LMC, high-Mg calcite = HMC, and dolomite) are commonly identified in carbonate rock forming at seeps (Greinert et al., 2001; Roberts et al., 2010). Aragonite preferentially forms under conditions of high, advective seepage flux at shallow depth close to the seafloor, whereas calcite and dolomite tend to form during diffusive seepage deeper in the sediment (Peckmann et al., 2009; Haas et al., 2010; Nöthen and Kasten, 2011; Magalhães et al., 2012) or in fluids with special compositions (Crémière et al., 2012; Feng et al., 2014). Alternatively, a rising  $\text{MgCO}_3$  content has been suggested to reflect an increase of seepage activity from LMC over HMC to dolomite (Lu et al., 2015).

Since the modern seawater is in the so-called “Aragonite Sea” mode, aragonite will preferentially precipitate when sufficient degrees of supersaturation are reached (cf. Hardie, 1996). It has been argued that the very reducing conditions required for calcite and dolomite formation are created at cold seeps, which allows for  $\text{Mg}^{2+}$  ions to enter the carbonate lattice (Greinert et al., 2001; Peckmann et al., 2001; Haas et al., 2010; Zhang et al., 2012). Consequently, not only the content but also the stable isotope composition of Mg in seep carbonates should be controlled by seepage intensity, because precipitation rate, pH, and mineralogy are known to influence the fractionation of Mg stable isotopes (Saenger and Wang, 2014; Schott et al., 2016).

Magnesium stable isotopes have been increasingly used in different disciplines including the application as paleoenvironmental proxy (Saenger and Wang, 2014). For example, Mg isotope fractionation between fluids and some biogenic carbonates have a weak functional relationship with temperature (Wombacher et al., 2011). Magnesium stable isotopes have also been applied to trace the fluid sources of

carbonates (Azmy et al., 2013; Walter et al., 2015) and the provenance of river load (Brenot et al., 2008; Mavromatis et al., 2014a, 2014b, 2016). The weathering of rocks of the upper continental crust and its influence on the lower crust are reflected by variations of Mg isotopes (Teng et al., 2010, 2013). Some marine biogenic carbonates have been suggested to qualify as a potential recorder of the Mg isotope composition of coeval seawater (Wombacher et al., 2011). Importantly, the Mg isotope composition of seawater shows very little fluctuation consistent with the long residence time of Mg in the ocean (Broecker and Peng, 1982). Magnesium isotopes have been used to constrain the Mg cycle in marine pore water and sediments, also looking into effects of carbonate diagenesis (Higgins and Schrag, 2010), distinguishing neoformed dolomites from different layers (Mavromatis et al., 2014a, 2014b), and identifying signatures of authigenic carbonates (Blättler et al., 2015). However, despite these wide applications, to the best of our knowledge, seep carbonates have surprisingly not been studied for their Mg isotope patterns to date.

Since it has been established that the conditions during carbonate mineral precipitation affect fractionation of Mg stable isotopes (Immenhauser et al., 2010; Li et al., 2012; Mavromatis et al., 2013; Saenger and Wang, 2014), and because it is known that the highly variable environmental conditions at seeps pose a strong control on the partitioning of Mg, Mg isotope compositions of seep carbonates are likely to mirror changes in seepage activity. In this paper, we assess the potential of Mg isotope compositions as a recorder of environmental conditions at seeps, comparing Mg isotope compositions with carbonate mineralogy, carbonate chemistry, and carbon isotope compositions of authigenic carbonates precipitated at seeps on the northern slope of the South China Sea.

## 2. Geological setting

The South China Sea is situated in the intersection of the Pacific and the Eurasian plates. Its northern slope is located between the Xisha trough and southeastern Taiwan. From west to east the South China Sea encompasses the Shenhu reef rise, Panyu low rise, Dongsha rise and Qiongdongnan basin, Zhujiangkou basin, and the SW Taiwan basin. The geological settings of the Shenhu area and the SW Taiwan basin are prone to the seepage of hydrocarbons and numerous seeps have been documented (Huang et al., 2006; Lin et al., 2006; Hou et al., 2008; Yu et al., 2014).

The Shenhu area is typified by pronounced sediment accumulation along a passive margin (McDonnell et al., 2000). Two types of tectonic systems have been recognized, which are a deep system of large normal faults reflected in the distribution of gas chimneys, mud diapirs, and mud volcanos, as well as a shallow system of minor normal faults reflected in migrating canyons, mass transport deposits, contourites, and the distribution of pockmarks (Sun et al., 2012). Pronounced methane anomalies have been detected within the sediments and in the bottom water of the Shenhu area. The depth of the sulfate-methane interface was found to be locally at very shallow depth as little as 7.7 m below the seabed (Wu et al., 2013).

The SW Taiwan basin was originally situated on a passive margin with thick sedimentary cover, but it is now placed along an active margin (McDonnell et al., 2000). Multiple oil and hydrocarbon source layers were explored including Mesozoic deltaic facies and littoral mudstones containing coal seams, Paleocene to Eocene lacustrine and palustrine mudstones, as well as a thick sequence of Miocene and Pliocene marine mudstones (Huang et al., 2008). Similar to the situation in the Shenhu area, multiple structural elements are developed in this area, such as faults, diapirs, mud volcanos, and imbricate thrust faults that connect deep, hydrocarbon prone strata with shallow sediments and the seafloor (Huang et al., 2008). High contents of methane have been detected in the bottom water, and the sulfate-methane interface was found to be locally placed at shallow depth (Huang et al., 2006). In the year 2013, gas hydrates were drilled in the eastern area of

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