



Magnesium isotope composition of sabkha porewater and related (Sub-) Recent stoichiometric dolomites, Abu Dhabi (UAE)



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ABSTRACT

Earliest marine diagenetic sabkha type dolomites are widespread in Earth's geological record. Potentially, these carbonates may act as archives of past seawater magnesium isotope ($\delta^{26}\text{Mg}$) ratios. At present, however, the fractionation of magnesium isotopes ($\Delta^{26}\text{Mg}$) between seawater – here evaporated marine porewater – and sabkha dolomite is not constrained. In order to explore $\Delta^{26}\text{Mg}_{\text{dol-Mg}(\text{porewater})}$, we make use of actualistic sabkha type dolomite precipitation in the Gulf region (Trucial coast, United Arab Emirates). This paper documents and discusses the first detailed sabkha $\delta^{26}\text{Mg}$ data set of Mg-bearing solids including stoichiometric dolomites (degree of ordering >0.9 ; mean $\delta^{26}\text{Mg}_{\text{dol}} = -0.79\% \pm 0.41\ 2\sigma$, $n = 17$) and related marine pore waters. The presence of dolomite crystals with a broad range of ordering in shallow cores is documented using X-ray diffraction and scanning electron microscopy, but individual crystals are too small ($<10\ \mu\text{m}$) to be mechanically separated from their host sediment. Hence, a method was developed to chemically separate the most stoichiometric dolomite crystals from coexisting less stoichiometric dolomites and other Mg-bearing minerals and fluid phases by using disodium ethylenediaminetetracetic acid. Sabkha shallow ground water collected in trenches displays $\delta^{26}\text{Mg}$ values of about -0.59% , i.e. is only moderately enriched in ^{26}Mg relative to the present-day seawater signature of -0.83% . Conversely, the $\delta^{26}\text{Mg}$ of evaporated porewater is enriched by $+0.43\%$ relative to that of $\delta^{26}\text{Mg}_{\text{seawater}}$. Here we use the term “apparent” fractionation for the variable $\Delta^{26}\text{Mg}_{\text{dol-Mg}(\text{porewater})}$ ($+0.1$ and -0.7%) obtained that cannot be compared with experimentally deduced fractionation factors from controlled laboratory settings. Moreover, evaporated sabkha porewater differs, in terms of its isotope signature, from seawater. With regard to the current level of knowledge, the hypothesis that earliest diagenetic sabkha dolomites represent direct archives of secular changes of seawater $\delta^{26}\text{Mg}$ values with time is not supported by our dataset. Our present understanding is that the magnesium isotope signature of sabkha dolomites is related to complex kinetics of precursor formation, dissolution/precipitation reactions including microbiological effects and involves variable Mg sources and sinks in a temporally and spatially variable microenvironment.

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1. Introduction

Magnesium is a main component of dolomite and a minor element in many carbonates (Warren, 2000). In marine settings, the main source of Mg for dolomite formation is seawater. Consequently, the Mg concentration and the $\delta^{26}\text{Mg}$ isotopic composition of seawater and of marine porewaters are of particular interest. Modern seawater $\delta^{26}\text{Mg}$ values are in the order of -0.83% independent of water depth or geographic location (see references in Hippler et al., 2009) and long $\text{Mg}_{\text{seawater}}$ residence times of $\tau \sim 13$ Myr were suggested by Broecker and Peng (1982).

These considerations form a strong motivation to explore earliest diagenetic (marine porewater/sabkha) dolomites as archives of secular changes in past seawater $\delta^{26}\text{Mg}$ values. Nevertheless, this approach is severely hampered by the, at present, poorly constrained dolomite-aqueous Mg isotope fractionation factor. This factor, and the difference between seawater and evaporated sabkha porewater $\delta^{26}\text{Mg}$, is required to hindcast past seawater magnesium isotope ratios from fossil sabkha dolomites. Sabkha-type, non-stoichiometric dolomites have received considerable attention as bacterial sulfate reduction and methanogens trigger the dolomitization process (Hardie, 1987; Compton, 1988; Wright, 1997; Vasconcelos et al., 1995; Vasconcelos and McKenzie, 1997; Mazzullo, 2000; Warthmann et al., 2000; Van Lith et al., 2002, 2003a, 2003b; Roberts et al., 2004, 2013; Wright and Wacey, 2005; Sánchez-Román et al., 2008, 2009, 2011; Kenward et al., 2009; Deng et al., 2010; Bontognali et al., 2010). Previous research indicates a

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significant depletion of modern microbial dolomite $\delta^{26}\text{Mg}$ by up to 2–3‰ relative to the water from which it is formed (Carder et al., 2005) but the obtained $\Delta^{26}\text{Mg}_{\text{dol-Mg(aq)}}$ values do not discriminate between equilibrium and kinetic effects.

Azmy et al. (2013) reported that the Mg isotopic fractionation between seawater and bulk sabkha sediment is minor ($\Delta^{26}\text{Mg} = +0.22\%$). These authors analyzed dolomite-bearing sabkha bulk sediments containing a variety of Mg-bearing phases (such as 22–32 wt.% calcite and 47–55 wt.% anhydrite) along with dolomite, which is one of the volumetrically least important phases (~10 wt.%). In a comprehensive study, Higgins and Schrag (2010) analyzed porewater and authigenic dolomites in several ODP cores (Upper Miocene to Upper Pleistocene). These authors found that the Mg isotope values of the authigenic dolomites are depleted by 2 to 2.7‰ relative to the porewater. While the work of Higgins and Schrag (2010) is at present the most rigorous and quantitative approach dealing with magnesium isotope fractionation in Neogene early diagenetic dolomites, two important questions remain open: (i) is the present-day porewater in the Neogene cores representative for the original porewater from which these dolomites precipitated and (ii) is the presently measured $\delta^{26}\text{Mg}$ of these fossil dolomites representative of the pristine values at precipitation?

This paper presents a comprehensive $\delta^{26}\text{Mg}$ data set of modern seawater, sabkha shallow ground water, sabkha porewater and related stoichiometric dolomites from short cores taken in the modern Abu Dhabi (Lokier and Steuber, 2008) sabkha environment. The data set also includes $\delta^{26}\text{Mg}$ ratios of all other volumetrically significant Mg bearing mineral phases (calcite and gypsum) as well as data from organic material in microbial mats. We here aim to (i) establish a protocol for the extraction and analysis of volumetrically subordinate, 5–10 μm -sized stoichiometric dolomite crystals from a Mg-phase-rich host sediment; (ii) to assess the apparent Mg isotope fractionation between stoichiometric dolomites, their corresponding porewater, and local sea water and, finally, (iii) to decipher potential trends of $\delta^{26}\text{Mg}$ values as a function of profile depth.

2. Geological setting

2.1. Sampling sites

The sampling sites are located on the Persian Gulf shoreline of the United Arab Emirates (UAE) about 50 km south-west of Abu Dhabi Island. The four representative locations are referred to Site 1a (rSD1a) (24 07.016 N; 54 03.229 E), Site 1b (rSD1b) (24 07.025 N; 54 03.171 E), Site 3 (rSD3) (24 07.051 N; 54 02.994 E) and Site 5 (rSD5) (24 07.087 N; 54 02.759 E; Fig. 1; Lokier and Steuber, 2008). The upper intertidal zone is characterized by living microbial mats (Butler, 1969). Tidal flat mud core from Sites 1b (rSD1b) and 3 (rSD3), investigated in this study, are located in the upper intertidal zone of the sabkha (Fig. 1). Absolute altitudes of sabkha cores are approximately 2.8 m (rSD1b) and 2.7 m (rSD3) above sea level. Samples were taken from seawater, lagoon water (24 30.820 N; 54 23.483 E); (24 09.306 N; 54 04.642 E) and shallow groundwater draining the sabkha (24 08.045 N; 54 05.565 E).

The southern coast of the Persian Gulf is a low-angle ramp (0.4 m/km) composed of Holocene carbonate and evaporite sediments that unconformably overlie Pleistocene carbonate-rich sandstones and Paleogene/Neogene bedrock (Evans et al., 1969). Flandrian sea-level rise peaked between 4000 and 6000 years BP at a height 1–2 m above today's sea level (Evans et al., 1969; Kinsman, 1969; Patterson and Kinsman, 1977). The resulting interbedded carbonate and clastic transgressive sediments exhibit an upwards-finishing trend and reach up to 3 m in thickness (Evans et al., 1969). This flooding event removed the source of sand to the southern Gulf shoreline, thus promoting deflation of the coastal land surface to the level of the water table. Sabkhas began to form along the present coastline at ~4000 years BP (Evans et al., 1969; Kinsman, 1969). Sampling sites are located in the upper intertidal zone of the sabkha and the oldest radiocarbon ages of the investigated tidal flat cores vary between 1441 and 786 years cal BP (Lokier and Steuber, 2008).

The earliest diagenetic sabkha (non-stoichiometric) dolomites precipitated from evaporated porewater in microbial mats within the

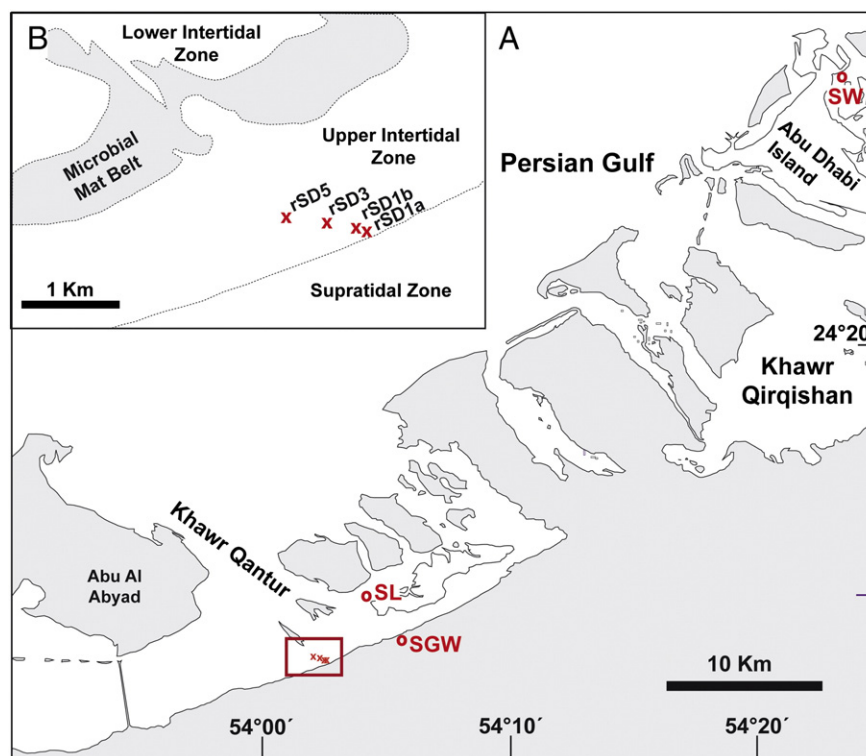


Fig. 1. A) Map of the United Arab Emirates coastline between Abu Dhabi and Abu Al Abyad islands showing the location of the study area and localities where water samples were taken (SL = lagoon water; SGW = groundwater; SW = seawater). B) Map of the study area showing the location of the sampling sites. The two maps are modified after Lokier and Steuber (2008).

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