



# Using stable Mg isotopes to distinguish dolomite formation mechanisms: A case study from the Peru Margin



Vasileios Mavromatis<sup>a,\*</sup>, Patrick Meister<sup>b,\*\*</sup>, Eric H. Oelkers<sup>a,c</sup>

<sup>a</sup> Geosciences Environment Toulouse (GET), CNRS, UMR 5563, Observatoire Midi-Pyrénées, 14 Av. E. Belin, 31400 Toulouse, France

<sup>b</sup> Max-Planck-Institut für Marine Mikrobiologie, Celsiusstr. 1, 28357 Bremen, Germany

<sup>c</sup> Department of Earth Sciences, University College London, Gower Street, WC1E 6BT, UK

## ARTICLE INFO

### Article history:

Received 6 January 2014

Received in revised form 21 July 2014

Accepted 21 July 2014

Available online 27 July 2014

Editor: Michael E. Böttcher

### Keywords:

Early diagenesis

Dolomite formation

Mg isotopes

Pore fluid composition

## ABSTRACT

The magnesium isotope composition of diagenetic dolomites and their adjacent pore fluids were studied in a 250 m thick sedimentary section drilled into the Peru Margin during Ocean Drilling Program (ODP) Leg 201 (Site 1230) and Leg 112 (Site 685). Previous studies revealed the presence of two types of dolomite: type I dolomite forms at ~6 m below seafloor (mbsf) due to an increase in alkalinity associated with anaerobic methane oxidation, and type II dolomite forms at focused sites below ~230 mbsf due to episodic inflow of deep-sourced fluids into an intense methanogenesis zone. The pore fluid  $\delta^{26}\text{Mg}$  composition becomes progressively enriched in  $^{26}\text{Mg}$  with depth from values similar to seawater (i.e.  $-0.8\text{‰}$ , relative to DSM3 Mg reference material) in the top few meters below seafloor (mbsf) to  $0.8 \pm 0.2\text{‰}$  within the sediments located below 100 mbsf. Type I dolomites have a  $\delta^{26}\text{Mg}$  of  $-3.5\text{‰}$ , and exhibit apparent dolomite-pore fluid fractionation factors of about  $-2.6\text{‰}$  consistent with previous studies of dolomite precipitation from seawater. In contrast, type II dolomites have  $\delta^{26}\text{Mg}$  values ranging from  $-2.5$  to  $-3.0\text{‰}$  and are up to  $-3.6\text{‰}$  lighter than the modern pore fluid Mg isotope composition. The enrichment of pore fluids in  $^{26}\text{Mg}$  and depletion in total Mg concentration below ~200 mbsf is likely the result of Mg isotope fractionation during dolomite formation. The  $^{26}\text{Mg}$  enrichment of pore fluids in the upper ~200 mbsf of the sediment sequence can be attributed to desorption of Mg from clay mineral surfaces. The obtained results indicate that Mg isotopes recorded in the diagenetic carbonate record can distinguish near surface versus deep formed dolomite demonstrating their usefulness as a paleo-diagenetic proxy.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

Magnesium (Mg) isotope composition has been suggested to be a useful proxy for deducing mineral formation temperature, mineral growth rate, and identifying weathering regimes (Galy et al., 2002; Tipper et al., 2006; Pogge von Strandmann et al., 2008; Immenhauser et al., 2010; Pokrovsky et al., 2011; Li et al., 2012; Riechelmann et al., 2012; Mavromatis et al., 2012a, 2013; Shirokova et al., 2013). This element is abundant in seawater, silicate rocks, and many carbonate minerals; Mg-isotope fractionation among these phases is sufficiently large to distinguish natural processes (e.g. Young and Galy, 2004). In particular, the high concentration and the homogeneous chemical and isotopic distribution of Mg in modern seawater and its presence in biogenic and abiotic carbonates (Hippler et al., 2009; Wombacher et al., 2011; Yoshimura et al., 2011; Mavromatis et al., 2012a) make

Mg-isotopes an excellent tool to trace oceanographic and biogeochemical conditions in the rock record. Notably, Mg-isotopes provide a promising tool to investigate the formation and diagenetic transformation of carbonate minerals.

With its high Mg concentration, dolomite [ $\text{MgCa}(\text{CO}_3)_2$ ] offers one of the richest Mg archives, ideal for Mg isotopic studies. While much dolomite is formed during burial diagenesis and hydrothermal alteration, numerous examples of penecontemporaneous or early diagenetic dolomite have been reported (cf. examples reviewed in Meister et al., 2013). This latter dolomite is of particular interest as it may preserve paleo-ocean geochemical and isotopic signatures. In addition, Mg isotopes have the potential to reveal carbonate precipitation mechanism (Mavromatis et al., 2013) and, thus, may hold the key to understanding dolomite formation at near-Earth's surface conditions.

The goal of this study is to improve our understanding of Mg isotope fractionation between carbonate minerals and their coexisting fluids. At present, only a limited number of Mg-isotope datasets are available from carbonates that formed in either laboratory or natural systems (e.g. Galy et al., 2002; Young and Galy, 2004; Buhl et al., 2007; Hippler et al., 2009; Immenhauser et al., 2010; Pokrovsky et al., 2011; Mavromatis et al., 2012a, 2013; Azmy et al., 2013; Shirokova et al., 2013). While it is

\* Correspondence to: V. Mavromatis, Institute of Applied Geosciences, Graz University of Technology, Rechbauerstrasse 12, 8010 Graz, Austria.

\*\* Correspondence to: P. Meister, Department of Geodynamics and Sedimentology, University of Vienna, Althanstr. 14, 1090 Vienna, Austria.

E-mail address: [mavromatis@tugraz.at](mailto:mavromatis@tugraz.at) (V. Mavromatis).

generally accepted that carbonates preferentially incorporate light Mg, fractionation factors and their mechanistic controls are still poorly understood. Moreover, the degree to which reaction kinetics affects the fractionation among carbonate minerals and fluids remains unclear (cf. Immenhauser et al., 2010; Pearce et al., 2012; Mavromatis et al., 2013). This study builds upon these past efforts by characterizing the Mg-isotope compositions of dolomites and their adjacent pore fluids recovered from drill cores collected from the Peruvian Trench Ocean Drilling Program (ODP) Site 1230. This Site provides an ideal model case, as two distinct dolomite types are present, one at shallow and one at greater depths, where the Mg isotope composition of the dolomites can be studied together with those of their adjacent pore fluids.

## 2. Study site

This study focuses on the Mg isotope chemistry of two drill cores collected from the Peru Margin. The Peru Margin (Fig. 1) is one of the Earth's largest upwelling zones with deposition of large amounts of biogenic silica and organic matter. Site 1230 (9° 06.78' S, 80° 35.01' W) was drilled during ODP Leg 201 on the lower slope of the Peru Trench below 5086 m water depth, at the same location as Site 685 of Leg 112. Site 1230 is characterized by high sedimentation rates exceeding 100 m/my (Kastner et al., 1990) and organic carbon contents ranging from 2 to 4%. Its stratigraphic sequence consists of Miocene to Holocene diatom ooze, silt, and clay. At ~223 mbsf, the sequence is dissected by a décollement that formed due to tectonic activity within the Peruvian Trench accretionary complex (D'Hondt et al., 2003). A lithostratigraphic description of Sites 685 and 1230 is provided in the Electronic Supplementary Material (ESM) Fig. S1.

### 2.1. Pore fluid geochemistry

The pore fluid chemistry at Site 1230 is influenced by intense microbial activity with sulfate depletion above 10 mbsf, and strong methanogenic activity beneath (Kastner et al., 1990). Within the top 200 mbsf, this high activity resulted in the accumulation of up to 40 mM of NH<sub>4</sub> and ~300 mM of CH<sub>4</sub> (Spivack et al., 2006). At several depths, gas hydrates were observed (Inagaki et al., 2006). Alkalinity reaches ~150 mM at around 150 mbsf. Accordingly, dissolved inorganic carbon (DIC) production is high, but its exact concentration is difficult to

measure, as some DIC may have degassed upon sampling. Since organic matter fermentation produces CO<sub>2</sub>, the methanogenic zone is likely acidified (Meister et al., 2011). In addition, the methanogenic zone at this site also showed enrichment of dissolved organic carbon (DOC) up to 20 mM (Smith, 2005).

Chlorine concentration (Fig. 2) is close to constant with depth and similar to that of seawater with the exception of the depths at which gas hydrates occur. Pore fluid Mg concentrations (Fig. 2) show a similar distribution as the metabolites, while Ca concentrations show an opposite distribution. Pore fluid Ca concentration is depleted to ~4 mM at 13.6 mbsf (see Fig. 2) and remains as low down to 237 mbsf. Below this depth, aqueous Ca concentration increases to 17.8 mM at 450 mbsf (ODP 112, Site 685; Kastner et al., 1990). In contrast, the aqueous Mg concentration increases downward at Site 1230 from 55 mM (seawater composition) to ~70 mM at ~100 mbsf, but below this depth it decreases to 28 mM at 450 mbsf (ODP 112, Site 685; Kastner et al., 1990). The increase in Mg above seawater concentration, observed between 17 and 100 mbsf, has been interpreted to result from an exchange between ammonium and magnesium ions on clay mineral surfaces (Von Breyman et al., 1990; Donohue et al., 2006). Von Breyman et al. (1990) also argued that pore fluid Mg depletion below ~150 mbsf is the result of the formation of dolomite, which is abundant at this Site below ~230 mbsf (see Thornburg and Suess, 1992).

### 2.2. Authigenic dolomite formation

The carbonate content is generally low (0–5 wt.%; Suess et al., 1990) throughout the sediment sequence at Sites 1230 and 685 (Suess et al., 1990). Authigenic dolomites occur at ~6 mbsf and at several depths below ~230 mbsf; the dolomites from these two locations also differ in texture and formation process. They are here referred to as Type I and Type II dolomite, respectively. While the authigenic dolomite at ~6 mbsf is induced by the anaerobic oxidation of methane (AOM) based on its δ<sup>13</sup>C composition (Meister et al., 2007), dolomite formation in the deeper strata is most likely induced by upward migrating fluids that buffered pH in the methanogenic zone (Meister et al., 2011). Upward fluid transport along the décollement has been observed (Matmon and Bekins, 2006) and further evidenced by the strongly radiogenic pore fluid <sup>87</sup>Sr/<sup>86</sup>Sr ratios, suggesting interaction of the fluid with the continental basement at greater depth (Kastner et al., 1990; Meister et al., 2011). In fact, a wedge of continental basement is present beneath the sedimentary sequence at this site (Von Huene et al., 1996). This fluid was also enriched in <sup>18</sup>O due to clay mineral dehydration during smectite–illite transformation (cf. Hensen et al., 2004; Mavromatis et al., 2012b). Fluid migration is also consistent with the heavy oxygen isotope composition of pore fluids and precipitated dolomites (Meister et al., 2011).

## 3. Material and methods

### 3.1. Mineralogical and carbon/oxygen isotope analyses

The mineralogy of solid samples was characterized using a Philips XPERT pro X-ray diffractometer at University of Bremen. CuKα radiation was used and the samples were scanned from 3 to 85° (2θ) at a scan rate of 1.63°/min and a step size of 0.0167°. The proportions of different minerals were estimated from integrated peak areas. Total inorganic carbon (TIC) was measured using a CM 5012 CO<sub>2</sub> Coulometer (UIC) by acidification with 3 M phosphoric acid. Analytical precisions (2σ) were 0.2 wt.% for total carbon and 0.1 wt.% for TIC.

Carbon and oxygen isotopes in powdered bulk sediments were analyzed using a Finnigan MAT 251 mass spectrometer coupled to an automated acidification device (type “Kiel”) at the Geological Institute, University of Bremen. The analytical precision of the mass spectrometer, based on repeated standard analyses, is ±0.05‰ for δ<sup>13</sup>C, and ±0.07‰ for δ<sup>18</sup>O. Powdered Solnhofener Plattenkalk, calibrated against the NBS standard, was used as a working standard and the δ<sup>13</sup>C and δ<sup>18</sup>O values

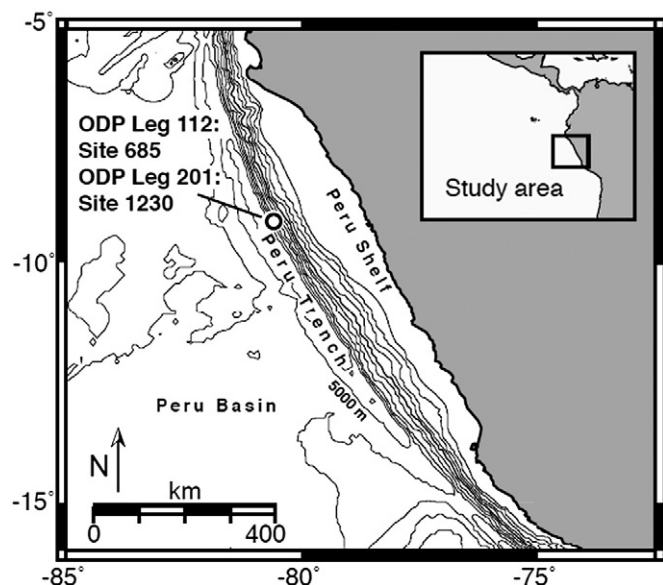


Fig. 1. Map of the Peru Margin showing the location of the drill Sites 685 and 1230 near the Trench axis, modified after Meister et al. (2011).

Download English Version:

<https://daneshyari.com/en/article/4698714>

Download Persian Version:

<https://daneshyari.com/article/4698714>

[Daneshyari.com](https://daneshyari.com)