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Notes

Dolomite formation within the methanogenic zone induced by tectonically driven fluids in the Peru accretionary prism

Patrick Meister^{1*}, Marcus Gutjahr², Martin Frank³, Stefano M. Bernasconi⁴, Crisógono Vasconcelos⁴, and Judith A. McKenzie⁴

¹Max-Planck-Institute for Marine Microbiology, Celsiusstrasse 1, 28359 Bremen, Germany

²Bristol Isotope Group, Department of Earth Sciences, University of Bristol, Queens Road, Bristol BS8 1RJ, UK

³Leibniz Institute of Marine Sciences, IFM-GEOMAR, Wischhofstrasse 1-3, 24148 Kiel, Germany

⁴Geological Institute, ETH Zürich, 8092 Zürich, Switzerland

ABSTRACT

Early diagenetic dolomite formation in methanogenic marine sediments is enigmatic because acidification by CO₂, a by-product of methanogenesis, should lead to carbonate dissolution and not precipitation. However, petrographic relationships indicate that dolomite breccia layers with δ¹³C values of ~+15‰, recovered from the lower slope of the Peru continental margin (Ocean Drilling Program Site 1230), formed deep in the methanogenic zone during tectonic activity of a décollement. Based on radiogenic Sr isotope ratios (⁸⁷Sr/⁸⁶Sr > 0.711) and positive δ¹⁸O values (+6‰), we present evidence that the dolomite breccias mainly formed from fluids originating from deep sedimentary units within the accretionary prism, where they interacted with continental crust and/or siliciclastic rocks of continental affinity. Due to silicate alteration and dehydration, such fluids are likely alkaline and thus have the potential to neutralize the acidification imposed by the high dissolved CO₂ concentrations. This scenario provides a potential mechanism by which dolomite formation can be induced deep in a highly active methanogenic zone.

INTRODUCTION

Early diagenetic dolomite layers, commonly observed in organic carbon-rich marine sediments (e.g., Murata et al., 1969; Burns and Baker, 1987; Pisciotto and Mahoney, 1981; Kelts and McKenzie, 1984), are a unique archive that may provide a window into past subsurface environments and allow, based on the elemental and isotopic composition preserved in the mineral phase, reconstruction of past biogeochemical conditions. Studies (e.g., Moore et al., 2004; Meister et al., 2007; Ussler and Paull, 2008) have shown how dolomite layers commonly form at relatively shallow depths in the zone of anaerobic methane oxidation (AMO) due to an elevation of pH (cf. Soetaert et al., 2007). Although dolomites often contain isotopically heavier carbon, which is indicative of fractionation during methanogenesis, only a few studies have reported evidence for the formation of dolomite at greater depths within a methanogenic zone (e.g., Bernoulli et al., 2004). Dolomite formation in the methanogenic zone is enigmatic because corrosive conditions at high dissolved CO₂ partial pressure should lead to partial dissolution of the early diagenetic carbonates (Rodriguez et al., 2000).

We report the finding of dolomite breccia layers, as thick as 20 cm, from beneath a 200-m-thick Pleistocene sediment deposit containing high concentrations of methane and gas hydrates in the Peru Trench (Ocean Drilling Program [ODP] Leg 201, Site 1230; Fig. 1; Meister et al., 2006). Virtually no carbonate is found within the overlying 200-m-thick CH₄-rich zone. This study evaluates the petrographic relationships and distribution of dolomite and its Sr, C, and O isotope compositions at Site 1230 in relation to porewater chemistry in order to explain the formation of dolomite in this otherwise unfavorable environment for dolomite formation. The understanding of the processes that control the enigmatic dolomite precipitation in the Peru Trench will also contribute to an improved understanding of the presence or absence of

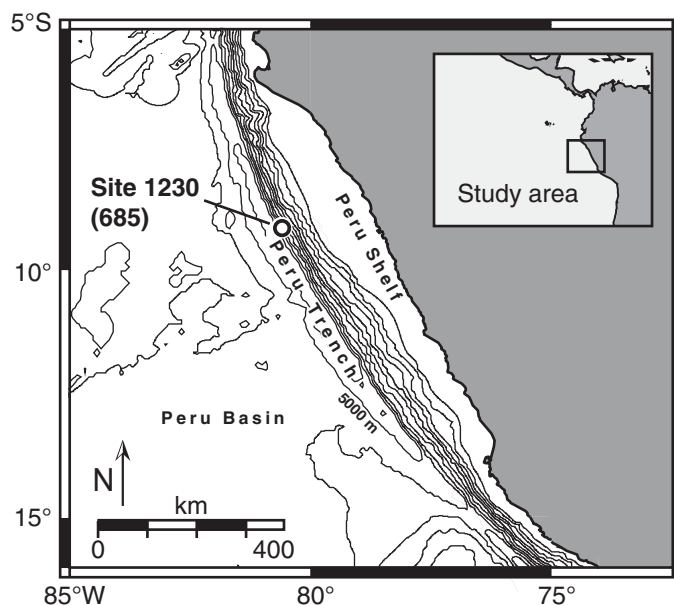


Figure 1. Map of Peru margin showing location of Ocean Drilling Program (ODP) Leg 201 Site 1230, which is reoccupied ODP Leg 112 Site 685.

dolomite in other ocean margin settings, as well as in ancient organic carbon-rich sedimentary rocks.

GEOLOGICAL SETTING

The Peru margin is an active continental margin with an accretionary prism that has developed since the Miocene (Suess et al., 1990). A 278-m-thick sedimentary sequence was drilled at ODP Site 1230 (9°6.7525'S, 80°35.010'W) at a water depth of 5086 m (Fig. 1). At the same location, a 468-m-thick sequence had been drilled during ODP Leg 112 (Site 685). The top 220 m of the sequence consists of Pleistocene organic carbon-rich diatom ooze with variable amounts of siliciclastic material. These sediments were deposited near the upwelling area offshore Peru and have a total organic carbon content of ~3%. The total inorganic carbon content is <1% throughout the sequence. High concentrations of methane are present and stable gas hydrate was recovered from a zone between 80 and 156 m below seafloor (mbsf) (D'Hondt et al., 2003). The Pleistocene part of the sequence is underthrust by more compacted and schistose Miocene diatomaceous muds. Below this tectonic contact, a décollement belonging to the accretionary prism (~223 mbsf), a horizontal shaly cleavage is present (D'Hondt et al., 2003). Crust of continental affinity underlies the lower slope of the Peru margin in the deep subsurface (von Huene et al., 1996).

DEPTH OF DOLOMITE PRECIPITATION

During ODP Legs 112 and 201, ~8 dolomite layers were recovered from the underthrust part of the sequence between 226 mbsf and

*E-mail: patrick.meister@alumni.ethz.ch.

468 mbsf that showed partially brecciated structure (Fig. 2A; Thornburg and Suess, 1992; Meister et al., 2006). The microtexture of the dolomite layers clearly contrasts with the shallow AMO dolomites found at several Peru margin sites, as well as with those recovered near the surface at 6.5 mbsf (Site 1230). Polygonal grain boundaries are indicative of simultaneous crystal growth within cavities (compromise boundaries; Fig. 2B), as opposed to the euhedral rhombic texture of the shallow dolomites (Meister et al., 2006). Petrographic relationships revealed by cathodoluminescence (Fig. 2C) show several generations of cement related to brittle deformation structures, indicating a syntectonic formation (Meister et al., 2006). Dolomite breccias are thus formed at depth during tectonic activity at the décollement within the accretionary prism. Brittle deformation probably occurred under semilithified conditions of the relatively well compacted sediment.

Dolomites show ordered stoichiometry, while the zoned crystals visible under cathodoluminescence (Fig. 2C) indicate a variable Fe or Mn content. Also, applying alizarine red resulted in a blue staining of the dolomites, indicative of Fe in the crystal lattice. The partitioning of Fe in the dolomite phase is indicative of a formation in the sulfide-free zone as Fe is insoluble under sulfidic conditions.

In addition to the petrographic observations, Ca^{2+} and Mg^{2+} profiles are indicative of the site of mineral precipitation. Changes in slope of Ca^{2+} and Mg^{2+} profiles (Fig. 3A; Suess et al., 1990; Donohue et al., 2006) occur at 6.5 mbsf (the modern AMO zone) and ~230 mbsf, indicating a

net consumption of both ions and possibly dolomite precipitation in the recent past.

ORIGIN OF FLUIDS

In the top 150 mbsf of Site 1230, the measured porewater $^{87}\text{Sr}/^{86}\text{Sr}$ is identical to seawater Sr isotope compositions of the sediments of corresponding burial age (Veizer et al., 1999) (Fig. 3B; see the GSA Data Repository¹). At ~150 mbsf, porewater and dolomite Sr isotope values diverge from paleoseawater compositions toward more radiogenic compositions. Such radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ signatures indicate contributions of fluids originating from greater depth, where they interacted with terrigenous sediments or the underlying continental crust (cf. Von Huene et al., 1996). The most radiogenic Sr isotope compositions (>0.711) were measured for a dolomite breccia at 229 mbsf. Furthermore, $\delta^{18}\text{O}$ values measured in this dolomite breccia are ~2‰ more positive than dolomite formed in equilibrium with modern seawater (Fig. 3C; see the Data Repository). Isotopically heavier water could have been released during syndeformational decomposition of gas hydrates, but such an effect is not observed in modern porewater $\delta^{18}\text{O}$ or in the porewater Cl^- profile (Fig. 3C). The positive $\delta^{18}\text{O}$ values are therefore explained by the composition of the fluid, which contributed more positive $\delta^{18}\text{O}$ values originating from clay-mineral dehydration during the illite-smectite transition in the deeper subsurface at higher temperatures (Hensen et al., 2004); this is why we refer to these fluids as hydrothermal in the following.

Taken together, radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$, positive $\delta^{18}\text{O}$ values, and syntectonic precipitation of dolomite are consistent with the expulsion of fluids from greater depth as commonly observed within accretionary prisms (e.g., Hensen et al., 2004). The high taper angle and convergence rate at the Peru accretionary prism result in rapid burial of low-permeability sediments; this, in turn, forces the fluids upward (Matmon and Bekins, 2006). The fluid was able to rise advectively along décollements that provided conduits of low permeability (Matmon and Bekins, 2006) and to influence the chemistry of the marine porewater in higher stratigraphic levels.

CARBONATE SUPERSATURATION AND DOLOMITE FORMATION

The origin of the porewater dissolved inorganic carbon (DIC) can be reconstructed from its carbon isotope composition. In particular, the extremely high concentration of DIC between 9 and 220 mbsf (as much as 155 mM at 130 mbsf; Fig. 3E; D'Hondt et al., 2003), showing $\delta^{13}\text{C}$ compositions of ~5‰ (Fig. 3F; Meister et al., 2007), was essentially produced by methanogenesis. Methanogenic DIC produced in the form of CO_2 ($\text{C}_{\text{org}} \rightarrow \text{CH}_4 + \text{CO}_2$) can drastically lower the in situ pH under the prevailing pressure. Such conditions are not favorable for dolomite precipitation and are expected to be corrosive for dolomite previously formed at shallower depth (cf. Rodriguez et al., 2000). Given CH_4 concentrations of >150 mM (Fig. 3G; Spivack et al., 2006) and in situ DIC concentrations of 150 mM, dolomite should not form at Site 1230 due to CO_2 acidification. The in situ pH was likely lower than the measured pH (Fig. 3H; Suess et al., 1990), because some CO_2 may have degassed during core recovery (Wallmann et al., 2008).

Nevertheless, alkalinity as high as 150 mM, practically identical with the DIC concentration (Fig. 3E), was measured in the midst of the methanogenic zone at Site 1230. High alkalinity leading to carbonate precipitation under such strongly methanogenic conditions can only be explained by a strong pH buffering effect, and there are essentially three

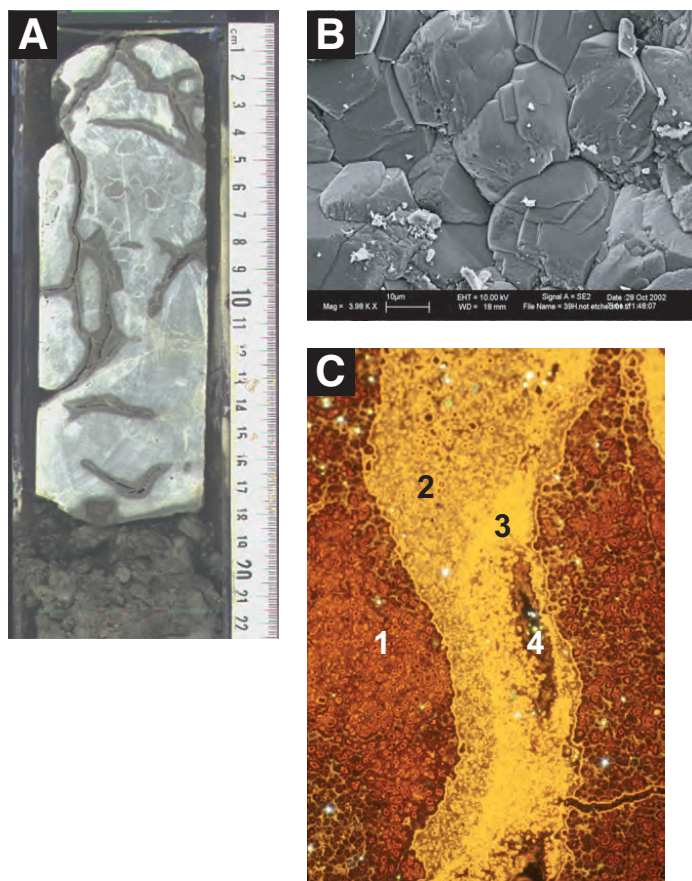
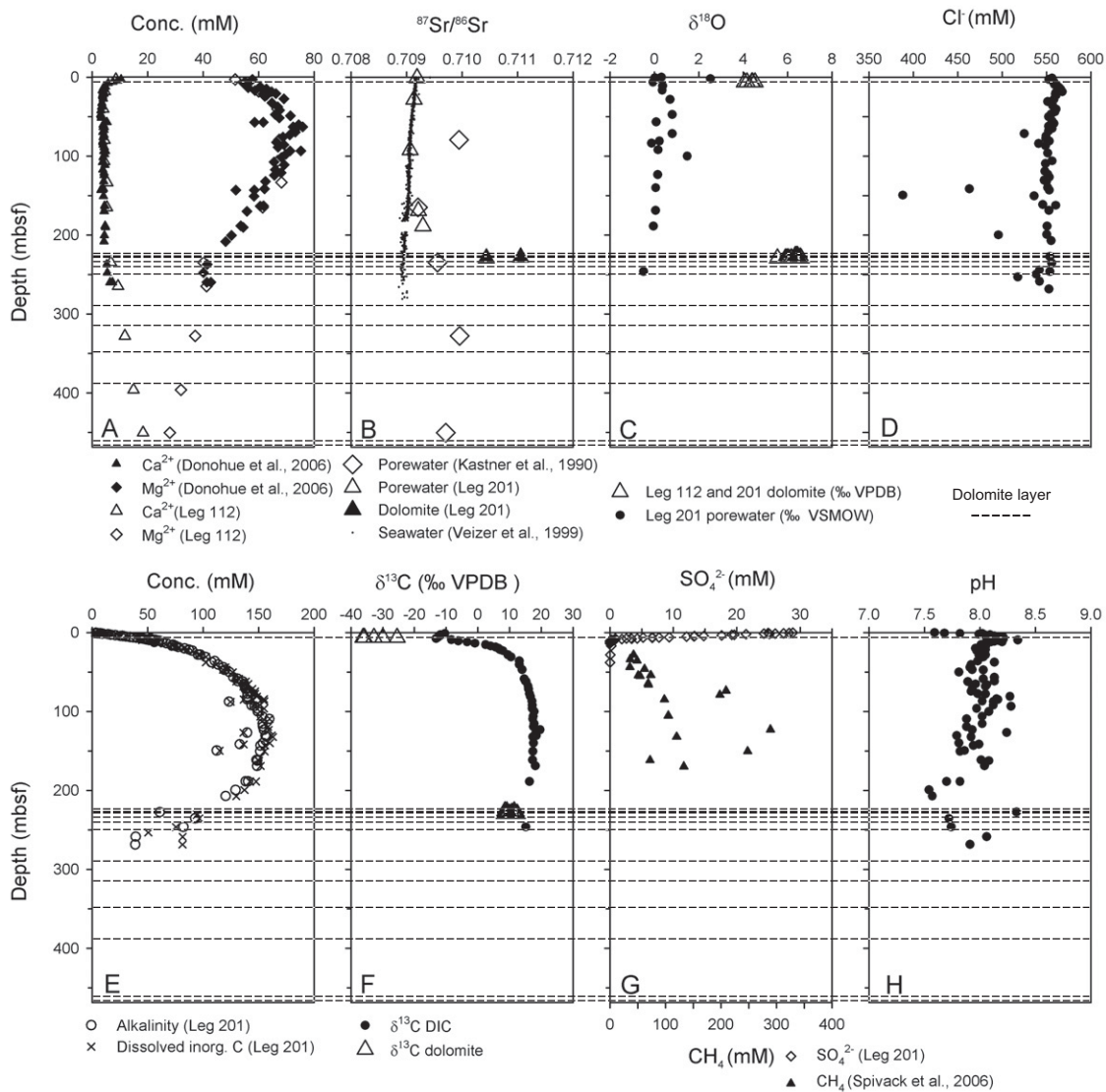


Figure 2. Petrography of dolomite breccia at Ocean Drilling Program Site 1230, core-section 1230A-31X-1, 0–19 cm (229 m below seafloor). **A:** Core photograph of dolomite breccia. **B:** Electron microscope image showing dolomite texture with polygonal (compromise) boundaries. **C:** Cathodoluminescence image showing different generations of dolomite cement (1–4) that are truncated by brittle deformation.

¹GSA Data Repository item 2011179, Table DR1 ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and $^{87}\text{Sr}/^{86}\text{Sr}$ data of diagenetic dolomites) and Table DR2 ($\delta^{18}\text{O}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ data of porewater), is available online at www.geosociety.org/pubs/ft2011.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.



possible processes that may have caused such a buffering: (1) a rise in pH due to a deep AMO zone; (2) an alkalinity increase due to calcite dissolution; and (3) pH buffering due to alteration of silicates. Although substantial amounts of organic carbon-poor pelagic sediments containing SO_4^{2-} -rich porewater are underthrust at this active continental margin site (cf. ODP Site 1231; D'Hondt et al., 2003), and could potentially supply enough SO_4^{2-} to maintain a deep AMO zone, no clear evidence was found in support of this hypothesis. While abundant pyrite is associated with the dolomite breccias, it is not distinguishable from early-forming pyrite on the basis of a sulfur isotope study. Furthermore, no petrographic evidence was found that supports a syntectonic formation of the pyrite, such that the past presence of a deep AMO zone remains unsupported. The influence of carbonate dissolution on alkalinity is probably small, based on the low Ca^{2+} concentration (not more than a few millimolar). Alternatively, sedimentary silicate alteration can significantly affect the pH and is likely occurring throughout the sequence (see preceding). The high concentrations of Mg^{2+} and the high alkalinity are likely the results of partial dissolution of reactive silicates in methanogenic sediments (Wallmann et al., 2008). This silicate dissolution process helps to neutralize the acidification imposed by high production of CO_2 ; however, it is apparently not sufficient to deplete the dissolved Ca^{2+}

concentration by inducing pervasive dolomite precipitation throughout the methanogenic zone.

In contrast, focused and rapid precipitation of anhedral dolomite cement occurred at the décollement, where high-pH hydrothermal fluids intruded the methane zone. Such fluids can be expected within an accretionary prism, given that they can form by alteration of continental crust in the deep subsurface, and a continental wedge is available beneath the Peru margin. The radiogenic Sr isotope compositions and $\delta^{18}\text{O}$ values indicating higher temperature clay mineral alteration are consistent with a dolomitizing fluid that reacted with crustal rocks.

The dolomitizing fluid is no longer present at 223 mbsf and the décollement most likely became inactivated as a result of the downward propagation of the active fault zone during ongoing accretion. This scenario may explain the formation of deeper dolomite breccias, while the lower dolomitization front progresses further offshore within the prism. Such deep décollement-related dolomite formation may be a general feature at active continental margins with high taper angle and subduction rates, but may also occur at other sites where alkaline fluid is transported into organic carbon-rich sediments. The influence of silicate alteration at greater depth is probably the key process buffering the acidification imposed by CO_2 production in methanogenic zones from below, therefore

leading to a deep dolomitization front. In general, a pH increase due to silicate alteration needs to be evaluated in future studies as a mechanism to induce low-temperature dolomite formation at depth in modern environments and in the geological record.

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