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Authigenic carbonates from the eastern Black Sea as an archive for shallow gas hydrate dynamics – Results from the combination of CT imaging with mineralogical and stable isotope analyses

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ABSTRACT

Authigenic carbonates associated with cold seeps provide valuable archives of changes in the long-term seepage activity. To investigate the role of shallow-buried hydrates on the seepage strength and fluid composition we analysed methane-derived carbonate precipitates from a high-flux hydrocarbon seepage area ("Batumi seep area") located on the south-eastern Black Sea slope in ca. 850 m. In a novel approach, we combined computerized X-ray tomography (CT) with mineralogical and isotope geochemical methods to get additional insights into the three-dimensional internal structure of the carbonate build-ups.

X-ray diffractometry revealed the presence of two different authigenic carbonate phases, i.e. pure aragonitic rims associated with vital microbial mats and high-Mg calcite cementing the hemipelagic sediment. As indicated by the CT images, the initial sediment has been strongly deformed, first plastic then brittle, leading to brecciation of the progressively cemented sediment. The aragonitic rims on the other hand, represent a presumably recent carbonate growth phase since they cover the already deformed sediment.

The stable oxygen isotope signature indicates that the high-Mg calcite cement incorporated pore water mixed with substantial hydrate water amounts. This points at a dominant role of high gas/fluid flux from decomposing gas hydrates leading to the deformation and cementation of the overlying sediment. In contrast, the aragonitic rims do not show an influence of ^{18}O-enriched hydrate water. The differences in δ^{18}O between the presumably recent aragonite precipitates and the older high-Mg cements suggest that periods of hydrate dissociation and vigorous fluid discharge alternated with times of hydrate stability and moderate fluid flow. These results indicate that shallow-buried gas hydrates are prone to episodic decomposition with associated vigorous fluid flow. This might have a profound impact on the seafloor morphology resulting e.g. in the formation of carbonate pavements and pockmark-like structures but might also affect the local carbon cycle.

1. Introduction

Vast amounts of methane are stored in gas hydrates in the submarine seafloor. The Black Sea is an important marine gas hydrate reservoir as it is estimated to contain ca. 10–50 × 10^3 km^3 of hydrate-bound methane (Vassilev and Dimitrov, 2002). Especially shallow-buried methane hydrates are sensitive to changes in the environmental conditions controlling hydrate stability (i.e. temperature, salinity, hydrocarbon availability, hydrostatic pressure) compared to their deeply buried counterparts. In case one or more of these factors change, submarine hydrates might dissociate quickly and release significant methane amounts to the hydrosphere with consequences for the seafloor topography (e.g. by creating pockmarks; Limonov et al., 1997; MacDonald et al., 1994), biogeochemical carbon cycling, and global climate (Dickens, 2003; Kennett et al., 2000). Despite the relevance of shallow-buried marine gas hydrates for these processes, relatively few is known about their dynamic behaviour. An aspect of particular interest is e.g., whether hydrate-derived methane is released constantly over

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time or mostly in form of huge bursts rapidly exhausting the hydrate reservoir. An improved understanding of processes affecting hydrate formation and dissociation in the past will contribute to a refined prediction of similar processes in the future if global warming leads to an increase of deep water temperatures.

Since optical and/or hydro-acoustic monitoring is cost-intensive and provides only snapshots of current geological processes taking place (cf. photographic time-series observations at Hydrate Ridge, MacDonald et al., 2005), the study of natural archives of gas hydrates and related fluid seepage is the primary source of information on former processes we have to rely on. Authigenic methane-derived carbonates, formed as by-products of the microbially mediated anaerobic oxidation of methane (AOM, Barnes and Goldberg, 1976; Reeburgh, 1976; Ritger et al., 1987), are promising archives since they preserve the geochemical signature of the interstitial water and therefore reflect varying methane seepage activity and gas hydrate decomposition (e.g. Bohrmann et al., 1998; Botz et al., 1988; Campbell et al., 2010; Naehr et al., 2007; Peckmann et al., 2001; Reitner et al., 2005; Stadnitskaia et al., 2005). Particularly in the Black Sea, numerous hydrocarbon seepage sites accompanied by the occurrence of shallow gas hydrates and authigenic carbonates were discovered and analysed using various techniques in recent years (see Pape et al. (2008) for refs.).

Here we present analyses obtained on seep-carbonates from the Black Sea integrating computerized X-ray tomography (CT), stable isotope analyses, and X-ray diffractometry that shed light on the variability of past seepage activity and the stability of shallow-buried gas hydrates.

2. Sampling area

The Batumi seep area is located in about 850 m below sea level (bsl) on the continental slope offshore Georgia in the south-eastern Black Sea. It is part of an extended region of gas seepage locations (Klaucke et al., 2006), which are confined to east-west trending ridges of diapiric origin (Fig. 1) (Tugolesov et al., 1985). Visual and hydroacoustic examinations identified numerous sites of intense gas seepage (Nikolovska et al., 2008) often covered by carbonate pavements and chimney-like structures (Bohrmann et al., 2007). From the stable carbon and hydrogen isotopic and molecular composition, a mixture of light hydrocarbons of thermogenic origin, most probably derived from the Late Oligocene – Early Miocene Maikopian formation, and from biogenic sources was inferred (Pape et al., 2010). At the carbonate sampling site, the sedimentary blanket of late Holocene coccolith ooze (Unit 1 after Ross and Degens, 1974), is punctuated by numerous cm-sized holes and irregularly-shaped carbonate build-ups (Akhmetzanov et al., 2007) giving rise to a highly irregular seafloor topography. The presence of shallow gas hydrates at the Batumi seep area was inferred from seismic and side scan profiles (Klaucke et al., 2006; Wagner-Friedrichs, 2007), and was evidenced by recovery of hydrate pieces (Klaucke et al., 2006; Mazzini et al., 2007; Pape et al., 2010) and by quantification of gas in sediments (Bohrmann et al., 2007). If hydrates were present in gravity cores, they were found below Unit 1 sediments, in some cases co-occurring with a partial cementation of the overlying Unit 1 sediments (Klaucke et al., 2006; Mazzini et al., 2007; Pape et al., 2010).

3. Materials and methods

3.1. Sampling

Carbonate build-ups from the Batumi seep area were retrieved during TTR 15 cruise with R/V Prof. Logachev in July 2005 with a TV-guided grab from station GeoB 9929-1 (Akhmetzanov et al., 2007; specifics of the sample sites including the respective TTR-

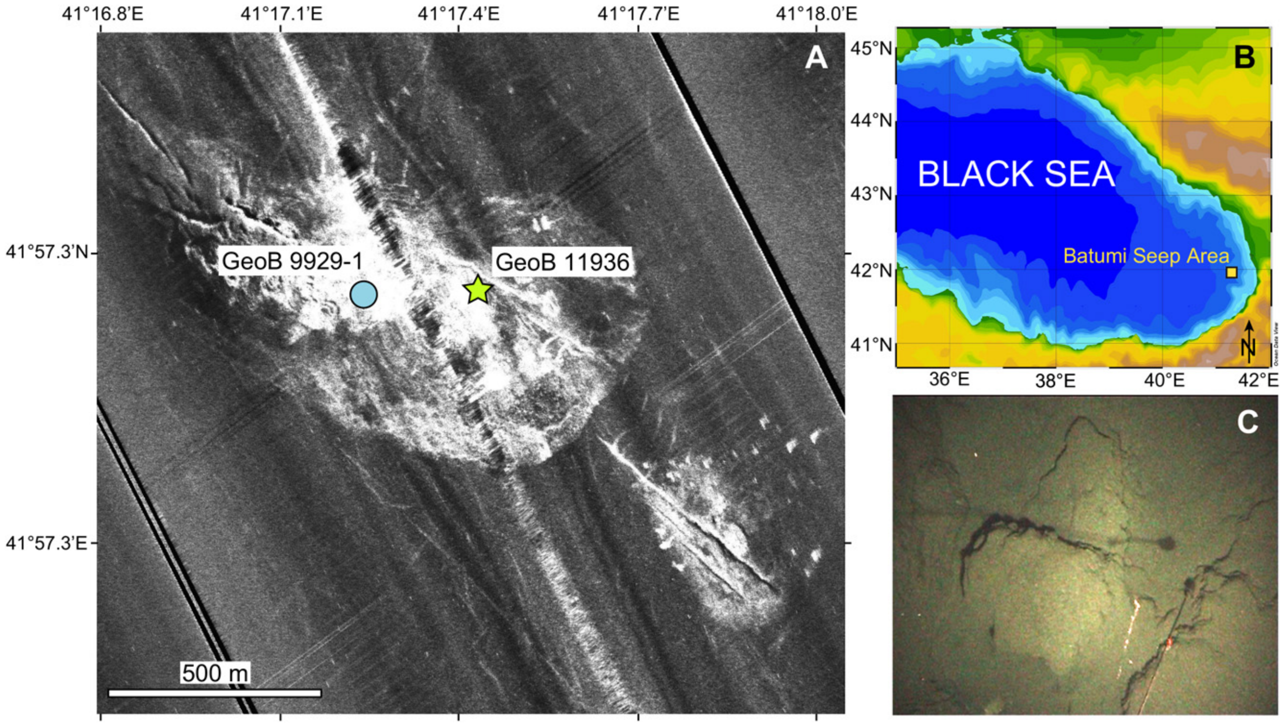

Fig. 1. (A) Location of TV-grab GeoB 9929-1 (TTR-15, 2004, circle), gravity core GeoB 11936 (M72/3, 2007, star) on a sidescan image of the Batumi seep area (Klaucke et al., 2006) illustrating strong backscatter anomalies (in bright colour) attributed to dense occurrences of near-surface carbonates and/or gas hydrates. Note that core GeoB 9922-1 is located about 1 km west of the area shown in (A). (B) Map indicating the position of the Batumi seep area in the eastern Black Sea. (C) TV-grab photo of the seafloor close to the sample location with carbonate build-ups; the width of the image is approx. 1.2 m. The sidescan image was reprinted from Klaucke et al. (2006), with permission from Elsevier.