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Sr/Ca and Mg/Ca ratios in Niger Delta sediments: Implications for authigenic carbonate genesis in cold seep environments

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Abstract

We report on a reconnaissance analysis of the geochemical composition of authigenic carbonates and sediment samples collected from various seepage sites on the Niger deep-sea fan. Our aim has been to investigate whether evidence for the presence of authigenic carbonates and gas hydrates within sediments is discernible from solid-phase sediment geochemistry. We show that sedimentary Sr/Ca and Mg/Ca ratios can be used to infer the presence of authigenic aragonite (Sr-rich) and Mg-rich carbonate phases (high-Mg calcite, dolomite) in cold seep settings. Using Sr/Ca and Mg/Ca ratios, the proportion (wt.%) of authigenic carbonates in Niger Fan sediments can be calculated from a mixing model between sediment fractions of terrigenous material, biogenic calcite, aragonite and high-Mg calcite. This approach was applied to high-resolution geochemical profiles along sediment cores recovered from various cold seep settings (mud volcano, diapirs, pockmarks, gas-hydrate bearing sediments). Our data reveal that authigenic carbonates occur as discrete phases in sediments from gas-hydrate-bearing areas, suggesting that such carbonate-rich sediment layers may represent paleo-indicators for ancient methane seepage in marine sediments, possibly associated to gas-hydrate reservoirs.

Keywords: authigenic carbonates; Sr/Ca; Mg/Ca; cold seeps; gas hydrates; Niger Delta

1. Introduction

Since their first discovery in 1984, on the Cascadia margin (Suess et al., 1985; Kulm et al., 1986; Ritger et al., 1987), numerous deposits of carbonate crusts and nodules have been documented on continental margins, in areas where gas-rich fluids escape from the seafloor (e.g. Ritger et al., 1987; Matsumoto, 1989, 1990; Hovland et al., 1997; Bohrmann et al., 1998; Aloisi et al., 2000; Pierre et al., 2000; Greinert et al., 2001; Mazzini et al., 2004; Orphan et al., 2004). It is now well established that carbonate precipitation in cold seep environments is closely related to the anaerobic oxidation of methane (AOM). Methane is oxidised when gas-rich fluids migrating upward, toward the seafloor, encounter seawater sulphate. The AOM is driven by a consortium of microbes (e.g. Boetius et al., 2000), which releases bicarbonate (HCO_3^-) and sulphide (HS^-) into surrounding

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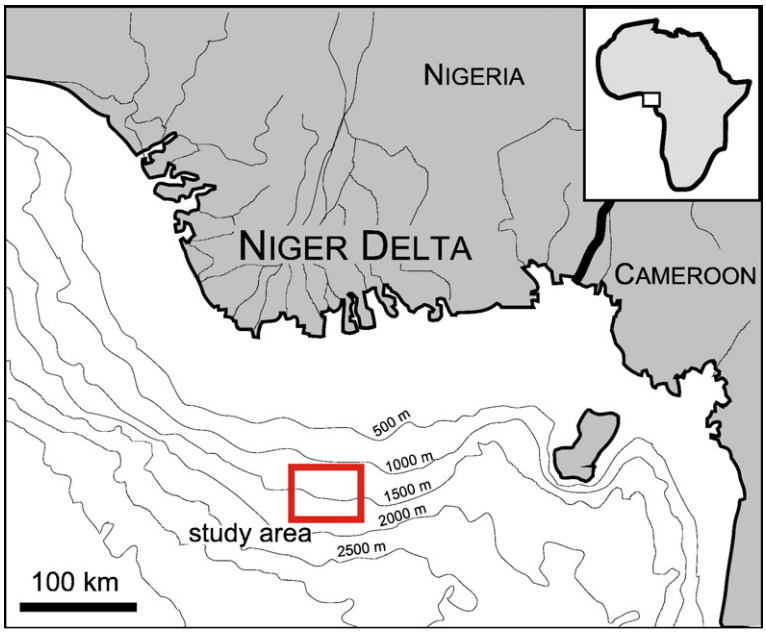

Fig. 1. Location of the study area on the Niger Delta deep province.

pore waters. In such cold seep settings, a significant portion of HCO_3^- produced through AOM precipitates as authigenic carbonates (Luff and Wallmann, 2003).

Two main types of cold seep carbonates have been described previously; *chemoherm carbonates* and *carbonate-cemented mudstones*, which relate to distinct formation processes in cold seep environments (see Greinert et al., 2001). Chemoherm complexes correspond to those massive deposits, composed of various fragments of shells cemented by authigenic carbonates (typically aragonite), which develop on the seafloor above focussed fluid flow pathways (e.g. faults). Carbonate mudstones may precipitate instead at various depths within the sediment column, whenever carbonate supersaturation is induced by diagenetic processes. Mudstones exhibit a wide variety of lithologies (e.g. crusts, nodules, small concretions) and carbonate compositions (e.g. aragonite, high-Mg calcite, dolomite, siderite), depending on their mode of formation.

Authigenic carbonates may also be present as dispersed discrete phases within cold seep sediments (e.g. Rodriguez et al., 2000; Pierre et al., 2000). For example, a mineralogical study of gas-hydrate-bearing sediments from the Blake Ridge (ODP Leg 164; off southeastern North America) showed clearly that such discrete carbonate phases could occur throughout the sedimentary column, in relation with the presence of gas hydrates (Naehr et al., 2000; Pierre et al., 2000; Rodriguez et al., 2000). Identification of such carbonate phases in marine sediment records can hence provide a window into the distribution and magnitude of ancient seep settings. The advent of XRF core scanners (Jansen et al., 1998; Koshikawa et al., 2003), which allow rapid determination of sub-continuous geochemical profiles along sediment cores, could provide in future studies a new tool for identifying methane-derived carbonate-rich layers in marine sediments. But first, the assumption that elemental signatures may represent reliable indicators of methane-derived carbonates in marine sediments needs to be validated.

The main purpose of this study has been to analyse bulk sediments collected from various cold seep environments on the Niger deep-sea fan to investigate whether geochemical signatures of authigenic carbonates can be detected. Sediments, nodules of gas hydrates and authigenic carbonates were collected by sediment coring and dredging during two expeditions on the continental slope off Nigeria (NERIS 1 and 2; PI's: M. Voisset and E. Cauquil), in 2003 and 2004. The work presented here focusses primarily on the inorganic geochemical composition of authigenic carbonates and sediment solid phases. We show that Sr/Ca and Mg/Ca ratios can be used as proxies for the presence of discrete authigenic carbonate phases (aragonite and high-Mg carbonates) in cold seep sediments.

2. Geological setting and samples

The area investigated during the NERIS project is located in the deep province of the Niger Delta (Gulf of