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Trace element behaviour at cold seeps and the potential export of dissolved iron to the ocean

Nolwenn Lemaitre[a,b,c], Germain Bayon[a,*], Hélène Ondréas[a], Jean-Claude Caprais[d], Nicolas Freslon[a,b], Claire Bollinger[b,c], Marie-Laure Rouget[b,c], Alexis de Prunelé[a,b], Livio Ruffine[a], Karine Olu-Le Roy[d], Géraldine Sarthou[b,e]

[a] *IFREMER, Unité de Recherche Géosciences Marines, F-29280 Plouzané, France*
[b] *UEB, Université Européenne de Bretagne, F-35000 Rennes, France*
[c] *IUEM, Institut Universitaire Européen de la Mer, Université de Bretagne Occidentale, CNRS UMS 3113, IUEM, F-29280 Plouzané, France*
[d] *IFREMER, Unité de Recherche Etudes des Ecosystèmes Profonds, F-29280 Plouzané, France*
[e] *LEMAR, UMR 6539, CNRS, Université de Brest, IRD, Ifremer, IUEM, F-29280 Plouzané, France*

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ABSTRACT

Seawater samples were collected by submersible above methane seeps in the Gulf of Guinea (Regab and Baboon pockmarks) in order to investigate the behaviour of iron (Fe), manganese (Mn) and rare earth elements (REE) during fluid seepage. Our aim was to determine whether cold seeps may represent potential sources of dissolved chemical species to the ocean. Dissolved (<0.45 µm filtered samples) and total dissolvable (unfiltered samples) concentrations were determined over ∼50 m long vertical transects above the seafloor and at various discrete locations within the pockmarks.

We show that substantial amounts of Fe and Mn are released into seawater during seepage of methane-rich fluids. Mn is exported almost quantitatively in the dissolved form (more than 90% of total Mn; mean $\mathrm{Mn_{DISS}}$ $\sim 12 \pm 11$ nmol/kg). Although a significant fraction of Fe is bound to particulate phases, the dissolved iron pool still accounts on average for approximately 20 percent of total iron flux at vent sites (mean $\mathrm{Fe_{DISS}}$ $\sim 22 \pm 11$ nmol/kg). This dissolved Fe fraction also appears to remain stable in the water column. In contrast, there was no evidence for any significant benthic fluxes of pore water REE associated with fluid seepage at the studied sites.

Overall, our results point towards distinct trace element behaviour during fluid seepage, with potential implications for the marine geochemical budget. The absence of any dissolved REE enrichments in bottom waters clearly indicates effective removal in sub-surface sediments. Most likely, precipitation of authigenic mineral phases at cold seeps (i.e. carbonates) represents a net sink for these elements. While Mn appears to behave near-conservatively during fluid seepage, the observed relative stability of dissolved Fe in the water column above seepage sites could be explained by complexation with strong organic ligands and/or the presence of Fe-bearing sulfide nanoparticles, as reported previously for submarine hydrothermal systems. Considering the ubiquitous occurrence of methane vents at ocean margins, cold seeps could represent a previously unsuspected source of dissolved Fe to the deep ocean.

1. Introduction

At ocean margins, the progressive accumulation of organic-rich sediments on the seafloor leads, with time and microbial degradation, to diagenetic remineralization of organic compounds and to methanogenesis (e.g. Martens and Berner, 1974). The migration of methane-rich fluids in sediment and subsequent release into bottom waters typically result in the formation of venting structures, such as pockmarks or mud volcanoes (e.g. Suess, 2010). These so-called 'cold' seeps are particularly common at margins, and hence could play an important role in the exchange processes between seawater and sediment, and in the distribution of trace elements in the water column.

Fluid venting at cold seeps sustains the development of abundant seafloor ecosystems, which rely on the chemosynthetic use of reduced chemical compounds (e.g. Sibuet et al., 1998). The main biogeochemical process in fluid venting areas is the anaerobic oxidation of methane (AOM). The AOM is generally coupled with sulfate reduction in anoxic sediments, which are both driven by

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[*] Corresponding author. Tel.: +33 2 98 22 46 30.
E-mail address: gbayon@ifremer.fr (G. Bayon).

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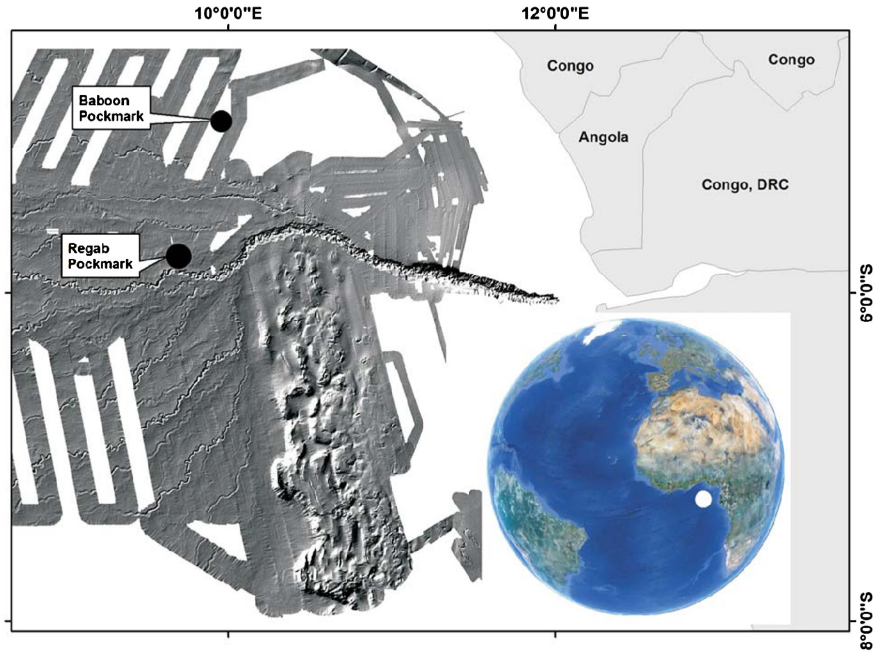

Fig. 1. Location of the Regab and Baboon pockmarks in the Gulf of Guinea. Regab is situated in close proximity to the Congo submarine canyon.

microbial assemblages of archaea and bacteria, respectively (e.g. Boetius et al., 2000). This results in the release of bicarbonate ions and hydrogen sulfide into pore waters, which, in turn, often leads to precipitation of authigenic minerals, such as carbonates and sulfides (e.g. Aloisi et al., 2002).

Both microbial activity and carbonate precipitation represent a net sink for methane at cold seeps (e.g. Luff and Wallmann, 2003; Boetius and Wenzhöfer, 2013). However, in highly active environments, excess methane can be expelled into bottom waters. Methane plumes can rise up to several kilometers through the water column, as inferred from direct CH_4 measurements and acoustic investigations of gas flares at margins worldwide (Charlou et al., 2003, 2004; Sauter et al., 2006; Greinert et al., 2006; Mastalerz et al., 2007; Solomon et al., 2009; Westbrook et al., 2009; Brothers et al., 2013; Kannberg et al., 2013). The emission of methane-rich fluids at the seafloor is also typically associated with high particulate contents, which can be detected using nephelometers and/or measurements of high concentrations of Fe and Mn in seawater (e.g. Charlou et al., 2004; Sauter et al., 2006; Bayon et al., 2011a). By analogy with submarine hydrothermal systems, it is generally assumed that the mixing of anoxic fluids with oxygen-rich bottom waters leads to the precipitation of Fe and Mn oxyhydroxides in methane plumes (Charlou et al., 2004; Bayon et al., 2011a). However, with the exception of barium (Kasten and Jorgensen, 2000; Dickens, 2001; Torres et al., 2002; Aloisi et al., 2004; Riedinger et al., 2006; McQuay et al., 2008; Kasten et al., 2012; Griffith and Paytan, 2012), the behaviour of iron, manganese and other trace elements during fluid seepage remains largely unexplored. In particular, it is unknown whether cold seeps may represent, or not, a source of dissolved iron to seawater.

Most dissolved iron in seawater is complexed with natural organic ligands (e.g. Rue and Bruland, 1995; Laglera and van den Berg, 2009; Gledhill and Buck, 2012; Misumi et al., 2013). Iron-organic complexes are characterized by high stability constants in the marine environment, which prevents (or delays) precipitation and enhances dissolved Fe concentrations in seawater (e.g. Sander and Koschinsky, 2011; Gledhill and Buck, 2012). Over recent years, several studies have demonstrated the presence of Fe-binding organic complexes in hydrothermal fluids and plumes, with global implications for the global Fe budget (Sander et al., 2007; Sander and Koschinsky, 2011; Bennett et al., 2008; Toner et al., 2009; Tagliabue et al., 2010; Wang et al., 2012; Hawkes et al., 2013; Saito et al., 2013). The hypothesis that reduced iron species could leak from hydrothermal vents was also suggested by speciation studies of plume particles, revealing the presence of non-sulfide iron(II) phases associated with carbon-rich material (Statham et al., 2005; Toner et al., 2009, 2012). In addition, Fe-bearing sulfide nanoparticles are also typically present within hydrothermal plumes (Yücel et al., 2011; Gartman et al., 2014). Because nanoparticulate sulfides are not retained onto filters with a 0.45 μm or 0.22 μm pore size filters, they have been shown to account for a significant fraction (as high as 25 wt%) of the so-called ‘dissolved’ iron at hydrothermal vents (Yücel et al., 2011; Gartman et al., 2014). At present, the fate of these very fine sulfide particles within methane plumes is unknown, but they could possibly be transported over long distances in the deep ocean (Carazzo et al., 2013).

The main objective of this study was to investigate the behaviour of iron and manganese at cold seeps, and to assess the potential significance of fluid seepage to the global oceanic budget. The work presented here focused on methane seeps from the Gulf of Guinea, including the Regab pockmark, a well-studied highly active seepage site on the Congo margin (Ondréas et al., 2005). In addition to Fe and Mn, we also used the rare earth elements (REE), because their behaviour at cold seeps is presumably related to Fe and Mn cycling (Bayon et al., 2011a). The REE also represent potentially interesting tracers of fluid seepage at margins, because they are generally highly enriched in pore waters relative to overlying bottom waters (Haley et al., 2004). A study conducted above methane seeps at the Niger delta margin suggested however that REE could be quantitatively scavenged during fluid emission, presumably due to scavenging onto Fe–Mn oxyhydroxide phases in sub-surface sediments (Bayon et al., 2011a).

2. Study area

In the Gulf of Guinea, the Congo margin is the location of several active sites of venting fluid (Ondréas et al., 2005; Sahling et al., 2008; Pierre et al., 2012). The most studied site in this area is Regab, a giant pockmark of about 800 m wide, located at 3160 m depth near the Congo submarine canyon (Fig. 1). This