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# Controls on the $^{129}$I/I ratio of deep-seated marine interstitial fluids: 'Old' organic versus fissiogenic 129-iodine

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ABSTRACT

Iodine and its radioisotope $^{129}$I have been successfully used to trace the origin of pore waters in submarine fluid escape structures because of their close association with organic material in deeply buried sediments. We report here halogen concentrations and $^{129}$I/I ratios for fluids of five mud volcanoes sampled along an E–W transect across the Gulf of Cadiz in the NE Atlantic Ocean. Concentrations of iodide and bromide increase consistently seaward accompanied by a decrease in $^{129}$I/I ratios from $6490 \times 10^{-15}$ to $663 \times 10^{-15}$. The exceptionally high $^{129}$I/I ratios at the near-shore locations reflect the presence of fissiogenic $^{129}$I, produced in situ by spontaneous fission of $^{238}$U within terrigenous sediments and released into pore water during clay mineral diagenetic processes. The observed $^{129}$I/I and halogen trends, together with similar changes in $^{87}$Sr/$^{86}$Sr ratios, indicate a progressive seaward transition from inorganic-terrigenous to organic-marine fluid sources.

Comparison of our results with literature data for varying geological settings reveals a general relationship between fissiogenic $^{129}$I, radiogenic $^{87}$Sr and the lithology or provenance of rocks and sediments, respectively. While $^{129}$I/I ratios in continental rock-hosted aquifers and terrigenous sedimentary systems are dominated by in situ production of fissiogenic $^{129}$I, iodine isotopes in oceanic settings or volcanogenic marine sediments reflect the release of 'old' iodine from deeply buried organic matter. The Gulf of Cadiz represents the full transition between these continental and oceanic $^{129}$I/I and $^{87}$Sr/$^{86}$Sr end members. This is the first systematic investigation of fissiogenic $^{129}$I production in marine sedimentary environments.

## 1. Introduction

### 1.1. Scientific objective

Submarine mud volcanoes (MVs) and cold seeps represent shortcuts in geochemical cycles connecting deeply buried sediments or basement rocks with the global ocean reservoir. Numerous articles have been published about the origin and diagenetic evolution of deep-sourced interstitial waters seeping through continental margin sediments (e.g. Elderfield et al., 1990; Dia et al., 1995; Martin et al., 1996; Aloisi et al., 2004; Hensen et al., 2004). Nonetheless, the overall relationship between tectonic setting, sediment thickness, provenance and/or composition of ambient sediments or rocks and the geochemical signals in the rising fluids is still poorly constrained.

The Gulf of Cadiz is a prime location to study varying controls on fluid chemistry. Mud volcanism and other phenomena related to fluid expulsion are widespread in this area, occurring from the Iberian and Moroccan shelf to almost 4000 m water depth. In a recent study, Scholz et al. (2009) investigated the lateral variability of geochemical signals in deep-sourced MV fluids in the Gulf of Cadiz. Based on strontium and lithium isotope systematics, the authors demonstrated a systematic pattern of fluid sources and deep-seated diagenetic processes across the continental margin. At the near-shore locations fluids are primarily influenced by interactions with fine-grained, terrigenous sediments. By contrast, at the deep-sea sites this sediment-diagenetic signature is less pronounced due to admixing of a basement-derived fluid component (Scholz et al., 2009). Because of the well-defined controls on fluid chemistry, deep-sourced pore fluids in the Gulf of Cadiz may provide insights into how other diagenetic tracers respond to lateral changes in sediment thickness, lithology and diagenetic conditions.

Iodine is commonly associated with organic matter in marine sedimentary environments. As a consequence, dissolved concentrations of iodine and its radioisotope $^{129}$I are commonly applied as tracers for the origin of hydrocarbon gases and the age of organic matter in deep subsurface sediments (e.g. Fehn et al., 2000, 2003; Lu et al., 2007, 2008a,b; Tomaru et al., 2007). In the Gulf of Cadiz, however, pore fluids are additionally affected by in situ production of $^{129}$I within terrigenous sediments. Common trends in $^{129}$I concentrations and other geochemical tracers across the margin provide insights into the factors controlling in situ production of $^{129}$I in marine sedimentary environments. Finally, the presented results and

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literature data are used to derive a general relationship between tectonic or geological setting and iodine isotope systematics in interstitial water.

### 1.2. Geochemistry of iodine in marine sediments

Due to its strong biophilic character, iodine is assimilated by phytoplankton in surface waters (Elderfield and Truesdale, 1980; Harvey, 1980) and reaches the sediment surface associated with sinking organic matter (Price and Calvert, 1973, 1977). A considerable amount of the delivered iodine is released into the pore water during early diagenesis and undergoes shallow recycling in the surficial sediments (Kennedy and Elderfield, 1987a, 1987b). Another portion, however, is buried to greater depth (Martin et al., 1993), especially on continental margins where high organic matter fluxes lead to long-term storage of organic carbon and associated compounds in deeply buried sediments. In such environments, on-going microbial or thermal decomposition of organic matter produces high iodine concentrations in deep intersitital fluids, often exceeding 1000 µM (e.g. Fehn et al., 2000, 2007; Lu et al., 2007; Gieskes and Mahn, 2007). Under the strongly reducing conditions that prevail in deeply buried sediments, iodide ($I^-$) is the stable species of iodine in pore water. Because of its negligible affinity for interactions with ambient sediments, $I^-$ travels over large distances in overpressured sedimentary environments (Martin et al., 1993; Fehn et al., 2000; Lu et al., 2008a).

Iodine has one stable isotope, $^{127}$I, and one long-lived radioisotope, $^{129}$I, which decays to $^{129}$Xe with a half-life of 15.7 Ma. The major, natural production mechanisms of $^{129}$I are spallation of Xe isotopes in the atmosphere by cosmic rays and spontaneous fission of $^{238}$U in the earth crust. Both of these mechanisms contribute equal amounts of $^{129}$I to surface reservoirs (Fabryka-Martin et al., 1985). Because of its long residence time (300 ka), the ocean is well-mixed with respect to iodine and has an iodine concentration of 0.44 µM and a $^{129}$I/I ratio of $1500 \times 10^{-15}$ (Broecker and Peng, 1982; Fehn et al., 2007a). Once iodine is removed from the well-mixed surface reservoir, e.g. through sedimentation and burial of organic matter, the initial $^{129}$I/I ratio will decrease due to continuous decay of $^{129}$I. Therefore, iodine released into deep interstitial waters carries an age signal which may be deciphered by determining $^{129}$I/I ratios by Accelerator Mass Spectrometry (AMS) (Elmore et al., 1980). Since $I^-$ has a similar diffusion coefficient and thus migration behavior as methane, $^{129}$I/I ratios in rising pore waters have been used to constrain sources and age of, respectively, hydrocarbons and organic matter in subduction zones, gas hydrate fields and related settings (Fehn et al., 2000, 2003; Lu et al., 2007, 2008a,b; Tomaru et al., 2007).

The iodine age signal in pore water may be altered by addition of $^{129}$I from sources other than the decomposition of deeply buried organic matter. Especially the $^{129}$I/I ratio of near-surface reservoirs has been increased up to several orders of magnitude through addition of anthropogenic $^{129}$I from nuclear weapon tests and reprocessing facilities (e.g. Schink et al., 1995; Wagner et al., 1996). In marine sediments, however, this anthropogenic iodine has not penetrated beyond the depth of bioturbation (Moran et al., 1998). Potentially of greater relevance for deep-seated fluids is $^{129}$I produced in ambient sediments or rocks through spontaneous fission of $^{238}$U. Although this fissiogenic $^{129}$I has been found to be of minor importance in marine settings hitherto investigated (Fehn et al., 2000, 2003; Lu et al., 2007, 2008a,b; Tomaru et al., 2007), it may govern the $^{129}$I/I ratio of groundwaters or crustal fluids in uranium-rich rock formations (Fabryka-Martin et al., 1989; Bottomley et al., 2002; Fehn and Snyder, 2005).

### 1.3. Geological setting

The Gulf of Cadiz is located at the eastern end of the Azores-Gibraltar transform, the transpressional plate boundary between Africa and Eurasia (inlet in Fig. 1). The area has a complex geological

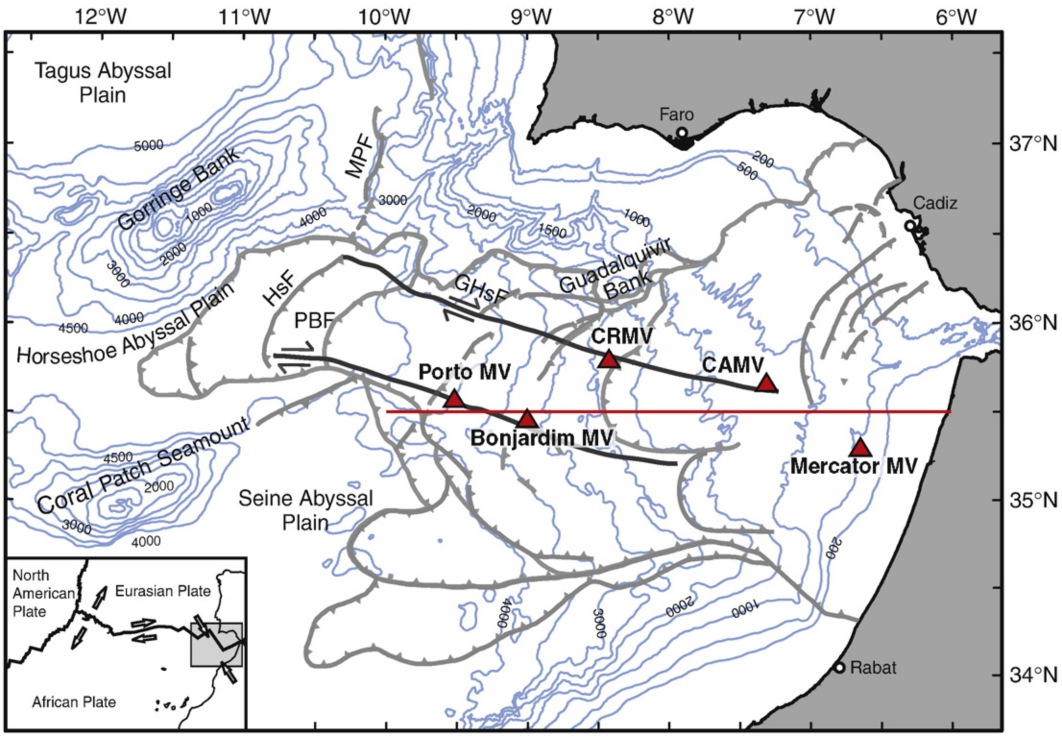

**Fig. 1.** Structural and bathymetrical map of the Gulf of Cadiz within the NE Atlantic Ocean (inlet at lower left side). The major tectonic features (after Medialdea et al., 2004; bathymetry from Diez et al., 2005) are the Marquês de Pombal (MPF) and Horseshoe (HsF) thrust faults, the Porto-Bonjardim (PBF) and Gorringe-Horseshoe (GHsF) strike-slip faults as well as the basement highs Gorringe Bank, Guadalquivir Bank and Coral Patch Seamount. Large triangles represent the five MVs investigated within this study (Table 1). The horizontal line stretching parallel to 35.5°N depicts the transect across the continental margin shown in Fig. 3.