Marine and Petroleum Geology 66 (2015) 542–554

Contents lists available at ScienceDirect

Marine and Petroleum Geology

journal homepage: www.elsevier.com/locate/marpetgeo

Research paper

The "chimney forest" of the deep Montenegrin margin, south-eastern Adriatic Sea

L. Angeletti [a], S. Canese [b], F. Franchi [a, c], P. Montagna [a, d], J. Reitner [e], E.O. Walliser [a, e, f], M. Taviani [a, g, *]

[a] ISMAR-CNR, U.O.S. Bologna, via Gobetti 101, I-40129 Bologna, Italy
[b] ISPRA, Via Brancati 48, 00144 Rome, Italy
[c] Department of Earth and Environmental Sciences, Botswana International University of Science and Technology, Private Bag 16, Plot 10017 Palapye, Botswana
[d] Laboratoire des Sciences du Climat et de l'Environnement, UMR 8212 UVSQ-CNRS-CEA, Avenue de la Terrasse, F-91198 Gif-sur-Yvette, France
[e] Department of Geobiology, Geowissenschaftliches Zentrum der Universität Göttingen, Goldschmidtstraße 3, D-37077 Göttingen, Germany
[f] Institute of Geosciences, University of Mainz, Johann-Joachim-Becher-Weg 21, 55128 6 Mainz, Germany
[g] Biology Department, Woods Hole Oceanographic Institution, 266 Woods Hole Road, Woods Hole, MA 02543, USA

ARTICLE INFO

Article history:
Received 4 November 2014
Received in revised form
27 March 2015
Accepted 1 April 2015
Available online 10 April 2015

Keywords:
Carbonate chimneys
Hydrocarbon
Adriatic Sea
ROV
Sessile fauna
Corals

ABSTRACT

A spectacular field of columnar carbonates has been discovered on the Montenegrin margin in the southern Adriatic Sea at a depth of about 450 m. The site exposes many columnar carbonates protruding from the substrate or abated on the bottom. Such carbonates attain maximum visible lengths of ca. 60 cm with diameters up to 20 cm; display an annular growth, and are either hollow or plugged by indurated sediment. Petrographic and geochemical analyses document the pervasive presence of dolomite, and $\delta^{13}C$ values as low as −30‰ VPDB. These 'chimneys' are therefore interpreted as former conduits related to hydrocarbon expulsion in this sector of the Adriatic basin. However, available data suggest that hydrocarbon flows at this site have ceased. Our results show that chimneys formed inside the local depositional units, glacial Pleistocene shelf shelly-rich muddy sediment and were successively exhumed from the host sediment. Today, the chimneys offer substrate to benthic life, including cold water corals and sponges. The U-series dating of these carbonate concretions is complicated by the presence of a significant fraction of detrital sediment, which represents a major source of initial ^{230}Th. AMS-^{14}C and $^{87}Sr/^{86}Sr$ dating of shells embedded in one of the chimney provided ages beyond the range of radiocarbon dating and <600 kyrs, indicating a Pleistocene age of the host sediment. Uncorrected U-series dating of the carbonate chimneys yielded and age of ca. 250–270 kyrs, providing a temporal upper limit for conduit formation driven by lithification caused by the degradation of seeping hydrocarbons. In addition, U/Th dating of cold water coral bases settled on chimneys indicates a Holocene age for their first exposure after exhumation and subsequent function as hard substrate for benthic organisms. The Montenegrin 'chimney forest' is a rare case where many such carbonate columnar concretions are still in their original vertical position.

1. Introduction

A vast and growing literature addresses the topic of authigenic carbonates formed in connection with hydrocarbon seepage in the submarine domain. Some of contributions also take into consideration descriptive and formative aspects of tubular carbonate concretions at times found associated with hydrocarbon seeps. The geological context, petrographic evidence, and geochemical signatures, corroborate a link between the genesis of such carbonate concretions and hydrocarbon-enriched fluid seepage, supporting their final interpretation as former conduits (e.g., Stakes et al., 1999; Díaz-del-Río et al., 2001; Aiello, 2005; Campbell, 2006; Nyman et al., 2006; Logvina et al., 2007; Takeuchi et al., 2007; Campbell

* Corresponding author. ISMAR-CNR, U.O.S. Bologna, via Gobetti 101, I-40129 Bologna, Italy. Tel.: +39 0516398874.
E-mail address: marco.taviani@bo.ismar.cnr.it (M. Taviani).

http://dx.doi.org/10.1016/j.marpetgeo.2015.04.001
0264-8172/

et al., 2008; Mazzini et al., 2008; Haas et al., 2010; Magalhães et al., 2012; Sun et al., 2015). We adopt here the descriptive term 'chimney' for these concretions in agreement with the current literature, (e.g., Díaz-del-Río et al., 2001; Magalhães et al., 2012; Han et al., 2013).

So far, only a few examples of extensive fields of such tubular concretions have been reported in modern oceans, for example in the Gulf of Cadiz (Díaz-del-Río et al., 2001, 2003; Somoza et al., 2003; Magalhães et al., 2012), in the Monterey Bay in California (Stakes et al., 1999), off the Otago peninsula in New Zealand (Orpin, 1997), on the Kuroshima Knoll off the Ryukyu islands (Takeuchi et al., 2007), in the Dongsha area in the South China Sea (Han et al., 2013), in the Campos basin off Brazil (Wirsig et al., 2012), within the Kouilou pockmarks in the Congo deep sea fan (Haas et al., 2010), and in the Kattegat (Jørgensen, 1992). Chimneys have been seldom recorded from outcrops as testified by the lower Eocene Pobiti Kamani in Bulgaria (De Boever et al., 2006a, b), the Miocene Santa Cruz Mudstone and the Paleocene Panoche Hills sandstones in California (Aiello et al., 2001; Schwartz et al., 2003; respectively), and the Pleistocene Enza River in Northern Italy (Capozzi et al., 2013; Gunderson et al., 2014; Oppo et al., in this issue; Viola et al., in this issue).

The recent investigation of the Montenegrin continental slope in the south-eastern Adriatic Sea (Fig. 1) using a Remotely Operated Vehicle (ROV) led to the unexpected discovery between 430 and 490 m water depth of a field of columnar carbonates protruding from the seafloor with many other abated on the ground (Fig. 2). While scattered carbonate chimneys have been located in the Mediterranean Sea (Trincardi et al., 2007; Bayon et al., 2013), this is the very first time that the occurrence of an almost intact submerged field is reported so far from this basin.

Here we provide a preliminary description of the most relevant aspects of the Montenegrin field discussing the genetic processes responsible for the formation of chimneys.

2. Material and methods

The study area is part of the Montenegrin continental margin at 41°40′ Latitude N – 18°36′ Longitude E, roughly 30 nautical miles (ca. 60 km) offshore of the city of Bar (Fig. 1). Data were collected during cruises ALTRO (December 2012–January 2013) and CROMA (February 2014) of R/V *Urania* in the frame of the EU Hermione and CoCoNET projects. Morpho-bathymetric data were acquired using a Kongsberg Simrad EM710 multibeam echo-sounder with a nominal frequency of 70–100 kHz. High-resolution Chirp profiles were acquired using a hull-mounted 16 transducer Benthos Chirp II sub-bottom profiler with a modulated frequency of 3.5 kHz. Water column attributes were measured with a Seabird SBE 11 PLUS CTD. Sea bottom sampling was performed using a large-volume (60l) Van Veen Grab, with the ROV robotic arm and with a small epibenthic dredge (Table 1). Visual inspection, for a total track length of 3500 m, was conducted using ROV 'Pollux III' equipped with two video cameras, a low-definition CCD camera for navigation and a high-definition digital video camera Sony HDR-JC7.

Thin sections of carbonate chimneys were produced at the Geobiology Department (Geowissenschaftliches Zentrum der Universität Göttingen) and at ISMAR-CNR. The petrographic- and microfacies-based analyses were performed through uncovered thin sections (ca. 30 μm foil thickness) at ISMAR-CNR.

Cathodoluminescence petrography was conducted using a Cold Cathode Luminescence system at the operating conditions of ca. 20 kV beam voltage and ca. 200 μA beam current, at the University of Padua.

In situ, non-destructive Raman analyses were performed to identify the distribution of different mineral phases. Analyses were conducted at the Geowissenschaftliches Zentrum der Universität Göttingen using a Horiba Jobin Yvan HR800-UV spectrometer coupled to an Olympus BX41 microscope (operating conditions: 488 nm Ar + laser set at 0.3–0.5 mW and spectral grating at 600 l/mm). The spectral values were calibrated against the Si-waver line 520.4 cm^{-1}. Raman spectra of studied samples were compared with reference spectra from the RRUFF Data-Base, using the Crystal Sleuth software (Downs, 2006), and from literature (Cavalazzi et al., 2012 and reference therein).

X-ray diffraction (XRD) data were acquired with a PANalytical diffractometer equipped with a Cu X-ray tube (operating conditions: 40 kV and 40 mA), at the University of Padua. The analyzed powders refer to three bulk samples extracted from chimney walls and two bulk samples from chimney infills. Identification of minerals, quantification and cell parameter determination were performed using High Score Plus and the ICSD database (PANalytical). The $MgCO_3$ contents of dolomites were calculated using the equation given by Goldsmith and Graf (1958). Lattice constants were determined by Rietveld refinements (Rietveld, 1969).

Carbonate powder samples were collected for carbon ($\delta^{13}C$) and oxygen ($\delta^{18}O$) isotopes analysis from the inner surface of the slabs and the position of the drilling spots was chosen based on two main criteria: i) the spatial characterization of the isotope signature of structurally homogeneous samples portions. In this case, drilling spots were placed along vertical and horizontal transects; ii) the characterization of isotopic heterogeneity of the different microfacies within one sample. In this case, drilling spots were chosen based on macroscopical textural features of the different rock portions. Thus, 32 individual carbonate powder samples (between 50 and 80 μg) were drilled from the chimney slabs using a hand dental drill equipped with a diamond-coated bit of 0.8 mm in diameter. The isotope measurements were performed at the Geowissenschaftliches Zentrum der Universität Göttingen at 70 °C using a Thermo Scientific Kiel IV carbonate device coupled to a Finnigan DeltaPlus gas mass spectrometer. Both $\delta^{13}C$ and $\delta^{18}O$ values were normalized to the international standard NBS19. Reproducibility, based on replicate analysis of standard NBS19, was better than 0.1‰ for $\delta^{13}C$ and $\delta^{18}O$ values. The $\delta^{13}C$ values are relative to VPDB, whereas $\delta^{18}O$ values were measured against the SMOW scale. In order to better compare the two isotopic systems, $\delta^{18}O$ values were subsequently converted to VPDB (Table 2) using the equation of Coplen et al. (1983): $\delta^{18}O_{VPDB} = 0.97002*\delta^{18}O_{VSMOW} - 29.98$.

Samples of an encrusting serpulid and an embedded bivalve were analysed for AMS-^{14}C dating at the Poznán Radiometric Laboratory in Poland. Calibrated ages were calculated with the Calib7.0.2 (Stuiver and Reimer, 1993) using the Marine09.14c curve of Reimer et al. (2013) with a ΔR of 46 years and a σR of 104 years calculated from the Marine Reservoir Correction Database of Reimer and McCormac (2002) (Table 3).

Uranium and thorium isotopes were analyzed at the Laboratoire des Sciences du Climat et de l'Environnement (LSCE) in Gif-sur-Yvette. Small coral fragments were carefully cleaned using a handheld fine diamond saw in order to remove sediment-filled cavities. The fragments were examined under a binocular microscope to ensure against the presence of bioeroded zones and finally crushed into a coarse-grained powder with an agate mortar and pestle. In addition, two small chunks were extracted from the wall of one carbonate chimney, cleaned from visible contaminants and crushed. The coral and chimney material was transferred to acid cleaned Teflon beakers, ultrasonicated in MilliQ water, rinsed twice and then leached with 0.1 N HCl. The clean samples were dissolved in 3–4 ml dilute HCl (ca. 10%), equilibrated with a mixed $^{236}U/^{233}U/^{229}Th$ spike, and the U and Th fractions separated using UTEVA resin (Eichrom Technologies, USA). The U and Th separation