First Sighting of Active Fluid Venting in the Gulf of Cadiz

The Mercator mud volcano, located in the Gulf of Cadiz off the coasts of Spain, Portugal, and Morocco (Figure 1), may provide an accessible field laboratory for studying local active venting and its possible internal and external controls. The recent discovery of the first active deep ocean 'brown smoker' chimney in this area can possibly be linked with the disintegration of a gas hydrate layer between the seafloor and a subsurface level that is dependent on pressure and temperature.

For more than a decade, the international marine scientific community has deployed considerable efforts in exploring the Gulf of Cadiz. Since the discovery of the Gulf's first mud volcano in 1999, research cruises have steadily unveiled one mud volcano after another [Gardner, 2001; Pinheiro et al., 2003; Somoza et al., 2003]. These mud volcanoes are clustered in several fields on the Portuguese, Spanish, and Moroccan margins (Figure 1). Extensive geophysical evidence of shallow gas and subsurface fluid flow has been reported in the Gulf of Cadiz [Baraza and Ercilla, 1996; Pinheiro et al., 2003].

Rodrigues and Cunha [2005] described cold seep communities (specific deep-sea fauna around fluid hydrocarbon escape ways) in the area. The highest number of specimens in these communities has been collected in the Moroccan sector, especially on mud volcanoes that show evidence of relatively recent (between now and Upper Quaternary outflows) activity. Despite numerous observations of carbonate crusts, fossil vent pipes, and chemosynthetic pogonophoran worms—which are signs of active venting (the process of cold seepage: when fluid actively escapes from the sea floor)—no such venting had yet been reported.

The 2002 discovery of giant mud volcanoes and cold-water coral communities at depths between 200 and 800 meters off Larache, Morocco [Van Rensbergen et al., 2005a] has moved this part of the Moroccan margin to the forefront of European and international projects. These include the UNESCO Intergovernmental Oceanographic Commission's Training-Through-Research and Geosphere-Biosphere Coupling Processes projects, the European Science Foundation's (ESF) Euromargins program, and the European Union's (EU) Sixth Framework Programme (FP6) integrated project HERMES (Hotspot Ecosystem Research on the Margins of European Seas).

Furthermore, in May 2005 the CADIPOR 2 cruise of the research vessel Belgica surveyed this exceptional area, in particular using a video frame (a steel frame in which deep-sea cameras are mounted).

During a survey of a proposed Integrated Ocean Drilling Program site on the southern flank of the Mercator mud volcano (Figures 1 and 2), an active chimney was for the first time sighted in this region in a water depth of about 400 meters. The Mercator...
mud volcano, with a diameter of about 2.5 kilometers, towers about 200 meters above the seafloor [Van Rensbergen et al., 2005a, 2005b], and it features an intriguing internal reflector that resembles a bottom simulating reflector (BSR) [Depreiter et al., 2005].

On video sequences collected during the cruise, the mud volcano flank generally showed a muddy, bioturbated seafloor with rocks that were conspicuous by their presence and resemblance to chimneys. One of the cone-shaped rocks appearing below the camera featured a steady flux of white-brown suspended matter (Figure 3). The horizontality of the plume indicates that a benthic current may sweep the flank of this mud volcano. The observation of this new brown smoker-type chimney could indicate that many of the surrounding conical rock outcrops actually are the exposed heads of extinct chimneys, the product and proof of previous fluid venting.

### Regional Context of Mud Volcanism and Fluid Venting

The geological setting of the Gulf of Cadiz is complex. The high tectonic deformation area is characterized by the presence of an accretionary wedge formed during the middle of the Miocene Epoch by the westward motion of the front of the Gibraltar Arc. Mud volcanism in the Gulf of Cadiz is closely associated with this accretionary wedge-type setting, which is related to the Cenozoic Era convergence of the African and Eurasian plate boundaries.

The El Arraiche mud volcanoes are located at the southeastern extremity of the Spanish-Moroccan field (Figure 1). Van Rensbergen et al. [2005a] described eight mud volcanoes of various sizes. Morphologically, these mud volcanoes feature a typical conical shape, with varying slope profiles. Acoustically, they are characterized by a generally reflection-free seismic facies (Figure 2), showing stacked outflow lenses (stacked products (mud outflows) of mud volcano ‘eruptions’) intruding within the stratified sedimentary series [Van Rensbergen et al., 2005b]. These features argue for the episodic expulsion of fluidized sediment.

In contrast to the general convergent setting of the Gulf of Cadiz, the El Arraiche area is characterized by superficial, detached extensional tectonics, expressed as large rotated blocks of sedimentary cover bound by large normal faults, controlling the Pliopleistocene sedimentary accommodation space (the available space for sediment deposition (i.e., a basin)). The El Arraiche mud volcanoes are positioned above these faults, which may serve as fluid migration pathways. Gas generation in the Mesozoic source rocks and focused fluid flow along the basal detachment of the accretionary wedge are both possible sources for sustained and repeated fluid injection into the upper sediment [Van Rensbergen et al., 2005a].

Depreiter et al. [2005] inferred the presence of a gas hydrate stability zone (GHSZ) inside the Mercator mud volcano from the occurrence of a BSR-like feature on seismic profiles. Gas hydrates occur within a restricted zone, the GHSZ, that is bound by well-described temperature and pressure...
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Method Allows for Continuous Monitoring of Volcanic Gases

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Many ongoing geophysical and geochemical studies are attempting to understand how volcanoes work and to forecast volcanic eruptions. While many geophysical methodologies for studying volcanoes have been completely standardized, continuous geochemical monitoring in active volcanic areas is still in its infancy.

One reason geochemical approaches lag behind geochemical ones is because current technologies are not able to cope with prohibitive environmental conditions. The development of techniques that allow monitoring of geochemical parameters in the harsh environments of active volcanoes should be a goal to achieve within a decade.

One method that may allow continuous monitoring of volcanic gases is the use of a diode laser spectrometer (DLS), which can provide an accurate determination of the ratio of carbon isotopes in carbon dioxide (13CO2/12CO2) that is present in these gases.

The study of the chemistry and isotopic composition of volcanic gases offers the possibility to follow over time the ‘life’ of volcanoes, which can involve variations in gas composition that occur on both long and short timescales, often inexplicable oscillations, and, more important, changes in source-region feeding systems.

Recent tests of continuous measurements of chemical species in harsh volcanic environments [Zimmer and Erzinger, 2003; Gianfrani et al., 2000, 2003; Rocco et al., 2004] respond to the above challenge. These new studies also help to meet the need for the development of new surveillance strategies that can be applied in active volcanic areas. The continuous measurements of chemical species, and quick and reliable field analysis of carbon isotopes seem to be among the most critical needs for the continuous monitoring of volcano geochemistry.

This article demonstrates the field operation of a DLS. During the period from July to October 2004, the authors performed three field tests at the Solfatara crater in the Campi Flegrei caldera (north of Naples, Italy). Fluids from Bocca Grande, the hottest vent (150°C), were collected for laboratory tests and field isotopic measurements.

Chemical analysis showed that water (H2O) and CO2 are the main components (~80 and ~20%, respectively) of the gas, and that species such as hydrogen sulfide (H2S), methane (CH4), hydrogen gas (H2), argon (Ar), helium (He), and neon (Ne) are present in small amounts.

During the last 30 years, carbon isotope data from CO2 emissions at Bocca Grande have shown remarkable stability with an average δ13C value of approximately -1.6‰ [Tedesco and Scarsi, 1999; Tedesco, 1994]. This indicates that a mixing between magmatic and sedimentary fluids is occurring probably at mantle level [Tedesco, 1994].

The near-infrared DLS is a simplified and more compact version that reports elsewhere [Gagliardi et al., 2003]. Designed to work in a volcanic environment, it is housed in a 60 by 60 centimeter square broadband, thermally-insulated, and is fully-controlled by a laptop computer (Figure 1). CO2 is conveyed to the DLS after the fluid is cooled in a Pyrex trap and the H2O is separated from the whole gas phase.

Two methods of analysis were done: (1) collecting the dry volcanic gas phase into flasks (off-line) and (2) allowing gas to flow directly from the fumarolic vent to the optical cell (online). Optical cells are transparent containers (for the two-micron wavelength)