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Continuous monitoring of dissolved CO_2 and H_2S: Technical application in the submarine hydrothermal system of Panarea, Italy

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Abstract

Additionally to flow rate measurements of fluid discharges in submarine hydrothermal systems, in-situ-measurements of concentrations of dissolved gases like CO_2 and H_2S can provide important information about the state of a hydrothermal system. Sampling and following laboratory methods are costly and not sufficient with respect to sampling intervals. Commercial sensors to monitor dissolved CO_2 and H_2S in seawater are so far unavailable. Therefore a sensor device based on commercially available sensors for gas monitoring was designed, constructed, and tested. The sensor array was tested in the submarine hydrothermal system of Panarea, Aeolian Islands, Italy. The first application provided important insight into variations of CO_2 and H_2S concentrations. Besides influences by earth tides, also additional fluctuations can be monitored by long term records.

Keywords: CO_2, H_2S, continuous monitoring, hydrothermal system, gas monitoring, submarine

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1. Introduction

Global ocean water currently absorbs over 25 million tons of CO_2 every day [1]. Long-term ocean acidification has been published by different authors (e.g. [2] [3]). Besides long-term changes in pH, there is also scientific interest in monitoring variations of flow rates in submarine gas emissions and their

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influence on surrounding waters. Results of long-term monitoring of flow rate measurements have been described by some authors [4], [5]. Periodic sampling is one option to show changes in fluid geochemistry and in the flow rate of venting hydrothermal fluids. Usually, there is a need for water sampling to get information about dissolved gases like CO_2 and H_2S. After sampling determination of e.g. CO_2 in submarine hydrothermal systems can be done according to ISO standards (DIN 38409). Commercially available CO_2 meters [e.g. Model 503 pH / CO_2 Analyzer, Royce Instrument Cooperation, New Orleans, LA 70 129, USA] provide a direct reading of pH and temperature, while alkalinity of the water must be determined independently and provided as additional information. Sampling has to be at short intervals to evaluate short time-scale temporal modifications. But this may be tedious and costly if the sampling intervals are getting in the range of hours and minutes.

Potentiometric electrochemical sensors are based on two membranes separating liquids (1 - sample solution, 2 - HCO_3^- containing solution). Due to diffusion of CO_2 pH-changes in the electrolyte solution occur. The corresponding voltage of the sensor is proportional to the CO_2 concentration in the measured sample. Advantages of electrochemical sensors over other analytical methods are the easy use, low interferences with other ions, and in-situ determination in liquids. A disadvantage of electrochemical sensors is the need of regular calibration in order to avoid a drift of the sensor's signal.

Direct determination of TDIC (total dissolved inorganic carbon) can be done by the conversion of dissolved carbonate species in CO_2 by acidification. CO_2 can be separated by stripping or gas diffusion in an acceptor solution. CO_2 in the aqueous or gaseous phase can be determined by gas chromatography (GC), spectrometry, non-dispersive (IR) spectrometry, coulometric, potentiometric or conductometric methods. As mentioned before there's a need for periodic sampling to recognize temporal modifications. Degassing while transport or sample preparation has to be mentioned as main disadvantages.

Spectrometric measurements using fiber optic sensors have the advantage to be suitable for in-situ measurement, high sensitivity, accuracy, and low energy consumption. The principle is based on the detection of changes in an indicator solution within a membrane cell by fiber optic fibers. Major disadvantages are large sample amounts to reach equilibrium state, and the non-applicability for long-term readings.

2. Methods

Because the above mentioned sensors appeared to be not feasible for long term monitoring of geothermal impacted seawater a novel sensor system for online measurement of CO_2 and H_2S based on commercially available gas sensors was designed.

The sensor setup used is shown in Fig. 1: separation of the aqueous solution (1) from the dissolved gas (3) using a gas-permeable membrane (silicon hose, outer diameter 4.0 mm, thickness 0.5 mm, Lindemann, Germany; (2). Thus water (and solids) cannot enter the sensor system itself. CO_2 and H_2S molecules present in the water migrate by diffusion through the membrane reaching equilibrium between the surrounding water and the gas phase within the hose. The gas phase in this tube is continuously pumped (pump: type SP 135 FZ Fa., Schwarzer Precision, Germany; (4) through the sensor array in order to accelerate the sensor's reaction and response time.

CO_2 is detected by a non-dispersive infrared two channel detector (NDIR CO_2-Sensor Model 400, Digital Control Systems, (5). This sensor emits two pulsed infrared signals which are absorbed by CO_2 molecules. The intensity of the two beams reaching the detector is processed and ex-pressed as CO_2 concentrations. H_2S is detected with an electrochemical H_2S gas sensor (3001 SI, Analox Sensor Technology, 0 – 100 ppm), (6)). The data from both sensors are visible on a digital display. Due to the

existence of pH-dependent species (CO_2 or H_2CO_3 / HCO_3^- / CO_3^{2-}; H_2S / HS^- / S_2^-), a pH probe (7) is integrated in the sensor arrangement. All values are processed (9) and stored in a low cost data logger (Tinytag Plus Re-Ed Voltage Input Logger (TGPR-0704), (10).

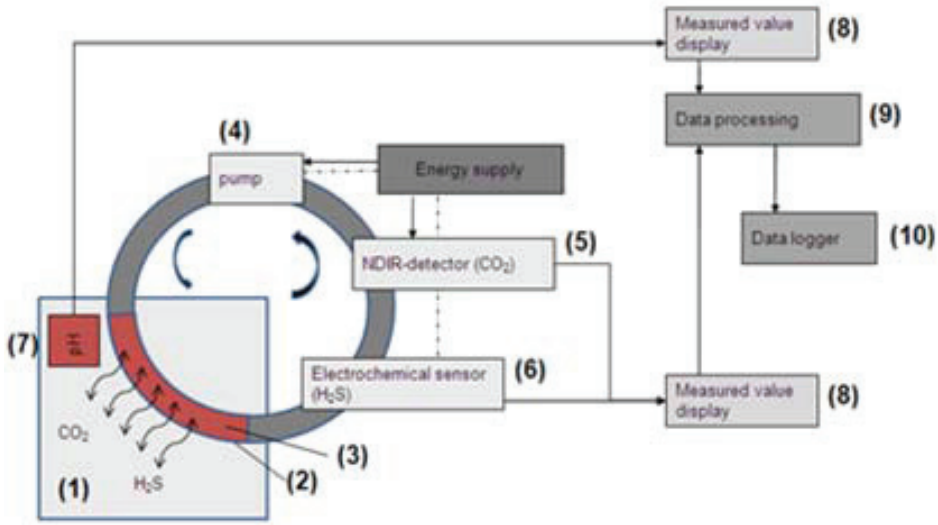

Fig. 1. Schematic sketch of the sensor set-up. 1: water containing the gas to be monitored. 2: membrane separating gas and water 3: gas in the hose circulated by the pump

Power supply is provided by a rechargeable battery (12 V/ 20 Ah). The whole device was capsulated water tight as can be seen in Fig. 2. Compression springs (VKM-13604, company Gutekunst &Co, Germany) were used to stabilize the semi-permeable membrane in the submarine environment and protected by an acryl-glass perforated pipe. Installation of the sensor can be easily maintained by one diver. At the sea bottom, the sensor system has to be fixed e.g. by some weights (Fig. 2a).Compared to prior setups, the combination of 2 or more commercial available gas sensors in combination with a gas-sensitive membrane and a pump in the array is an essential improvement because pumping the gas in the array improves the response time of the sensor by far. Compared to an application without pump, a 50 – 60 times higher response time was reached. Furthermore, by choosing a suitable membrane an enrichment of gas is reached in the membrane. Thus an overall faster transport of the gas from the liquid to the gas phase takes place. Other advantages are the relatively simple construction, the possibility to combine different sensors, and the suitability for short- and long-term monitoring of fluids. In regard to the field of application, the sensor was calibrated in different chemical/environmental conditions. The calibration showed no significant differences and interactions in pure 5 mM $NaHCO_3$ solutions, in solutions with higher ionic strength (5 mmol/L compared to 44 mmol/L), and with particular reference to other IR-sensitive gases (e.g. H_2S). During calibration pH was adjusted with 1 M HCl. The depending aquatic species of C and S were modeled by the hydrochemical code PhreeqC [6] (database: wateq4f.dat).In situ tests The in-situ measuring device was successfully used to record variations of dissolved CO_2 and H_2S concentrations in the submarine hydrothermal system of Panarea (2009 – 2010).

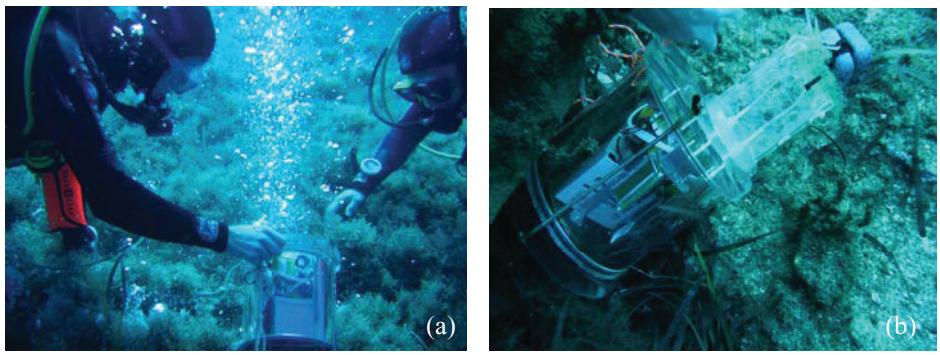

Fig. 2. (a) Installation of the CO_2/H_2S sensor by scientific divers (b) CO_2/H_2S sensor at Black Point, Panarea.

Fig. 3 shows monitored data (09/07/2009 – 09/11/2009) for CO_2 in comparison to tidal data. Sampling point was a small fumarole at the location Black Point, Panarea (water depth 21 m). Tidal data were calculated by means of WXTide24. No data for H_2S are available for this period, because the H_2S-sensor used has a detection range from 0.1 to 100 ppm and was thus much too low for monitoring water in the direct contact with fumaroles (up to 4000 ppm H_2S).

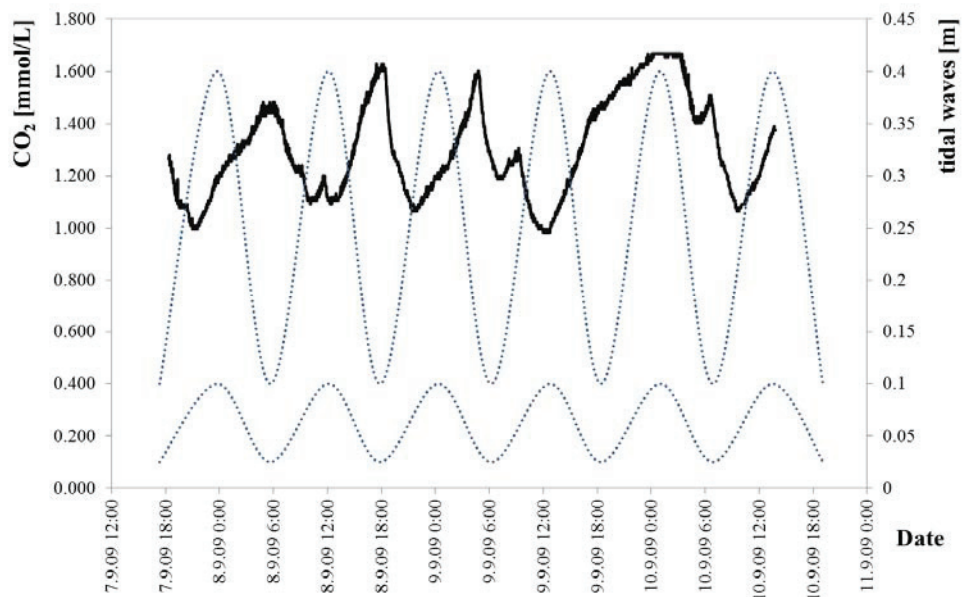

Fig. 3. Dissolved CO_2 concentration recorded from 09/07/2009 – 09/11/2009 (black). Dotted, blue curve represents calculated tidal waves (WXTide24).

Tidal influences are obviously. Besides this main behavior, smaller variations in CO_2 concentrations (c_{CO2} 0.9 – 1.6 mmol/L) are visible in Fig. 3. Additionally, it must be considered that other complex

factors such as weather influence and currents affect the quantity and quality of fluid discharges and thus influence the CO_2 concentration in water surrounding the fumaroles.

A further sampling campaign took place for nearly 24 hours (09/12/2009 – 09/13/2009) at the location "fumarolic field" (water depth 16 m). The sensor was positioned on the sea bottom on a very weak fumarole in the north eastern part of the location. H_2S and CO_2 concentration in this case are inverse correlated with tidal data (Fig. 4). CO_2 concentrations were detected in a range of 0.6 to 0.85 mmol/L, whereas H_2S concentrations varied between 0.02 to 0.1 mmol/L. Fig. 4 shows that the membrane migration behavior of H_2S seems to be faster than that of CO_2 because more peaks and dips are visible for H_2S than for CO_2.

Additionally investigations are under way to proof the statistical correlation. The inverse correlation of CO_2 and H_2S concentration with tidal waves can be mainly reasoned by earth tides. Surprisingly the small tidal pressure differences trigger significant changes in the gas concentration and in particular for H_2S with a factor of 5 while the concentration changes for CO_2 are less prominent. Besides this well-known parameter, waves (water level variations = pressure variations, ca. 0.1 bar) and local weather conditions (barometric pressure variations, estimated 0.01 bar) may influence the gas discharge and CO_2 and H_2S concentration. Such effects on flow rates were already recorded additionally to the typical tide-dependent variations in submarine environments (i.e. [7], [8], [9], [10]).

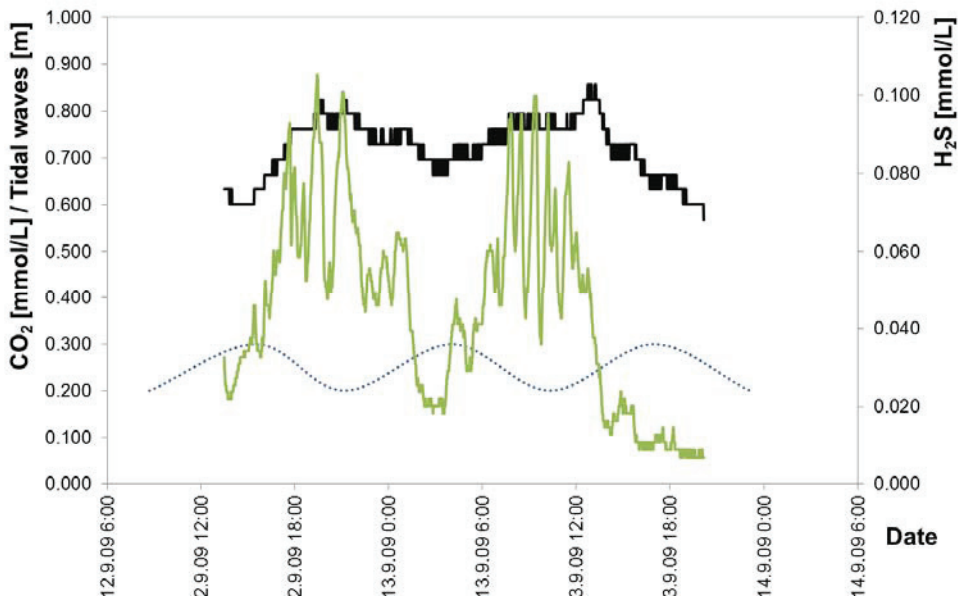

Fig. 4. Dissolved CO_2/H_2S concentration recorded from 09/07/2009 – 09/11/2009 (black). Black line – CO_2, green line – H_2S; dotted blued curve represents calculated tidal waves (WXTide24).

3. Conclusions

Long-term records of variations in the chemical composition of submarine fluid discharges are rarely presented in literature. A first application at Panarea provides an important insight into short term variations of gas composition. The combination of 2 or more commercial available gas sensors and a pump provides an essential improvement of the sensor-setup. 50 – 60 times faster equilibrium times can

be reached. This process can be enhanced by choosing a suitable membrane which leads to an enrichment of the gas and, thus, a faster equilibrium. Inverse correlation of CO_2 and H_2S with tidal waves had been proofed. Besides influences by earth tides, also unpredicted fluctuations like waves and local weather conditions influence the gas discharge and thus CO_2 and H_2S concentrations.

In future, CO_2 and H_2S measurements will be combined with flow rate measurements by a flow meter for submarine volcanic gas emissions ([4], [5]). Further improvements (efficient power supply, online data transmission to a buoy) will be considered.

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