Detection of new hydrothermal sources thanks to in situ manganese analysis

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Hydrothermal anomalies found in the deep sea are a place where unique ecosystems exist[i]. They are also a possible new resource for metallic ore mining[ii]. Indeed, while present in tiny quantities in the ocean, elements such as iron and manganese are found in high concentration in hydrothermal vents. Therefore such metal ions can be used as a tracer to detect and evaluate new hydrothermal sources[iii].

During the cruise NT10-16, aboard the Natsushima vessel, we used a miniaturized and integrated microfluidic system for the detection of manganese in deep-sea environment, called IISA-Mn (In Situ Integrated Analyzer for Mn^{2+}). The miniaturization has several advantages such as a low volume, low power and low reagent consumption. This system is composed of a microdevice for mixing and reaction (Fig.1), a pumping unit, several valving units, and a PMT (photomultiplier) detector (Fig.2). The detection system is based on the chemiluminescence reaction of manganese with luminol: a reagent mix composed of luminol (light emission), potassium periodate (oxidant), triethanolamine (signal enhancer and manganese specificity), sodium hydroxide (pH adjustment), and sodium citrate (precipitation preventer) is mixed with the seawater sample to analyze. The presence of manganese catalyzes the chemiluminescence reaction and light is emitted. The emitted photons are counted by the PMT and are depending linearly on the Mn^{2+} concentration. Concerning the fluids handling (Fig. 3), the reagent mix and the samples are sucked in the device. A second layer (pneumatic layer) is bonded on top of this fluidic layer to add a system for flow regulation (controlled variation of the device height combined with a flow sensor) to ensure that the liquids are coming at the desired rate, and a system of valves (normally closed valve) that can be selectively actuated by electro-osmotic pumps to choose between the sample and the calibration solutions.

A calibration curve obtained with the lab setup is displayed in Figure 4. The system is able to detect concentration above 100 nM, and gives a linear response until 1 µM. It is also able to work continuously during the 8 hours of each dive. In Figure 5, the results obtained during the dive #1180, #1181 and #1182 near Okinawa are shown. The results prove clearly that a strong signal occurs when the system is in the vicinity of a hydrothermal anomaly. This has lead to the discovery of three previously unknown hydrothermal sources. The analysis of the data is on his way.

While already promising, future work on the IISA-Mn system will concern the enhancement of the detection limit.

References:

[i] Lutz R.A., Kennish M.J (1993). Ecology of deep-sea hydrothermal vent communities: A review. *Reviews of Geophysics*, 31(3), 211-242.

[ii] Francheteau J. et al. (1979). Massive deep-sea sulphide ore deposits discovered on the East Pacific Rise. *Nature*, 277(5697), 523-528.

[iii] Okamura K. et al. (2001). Development of a deep-sea in situ Mn analyzer and its application for hydrothermal plume observation. *Marine Chemistry*, 76(1-2), 17-26.

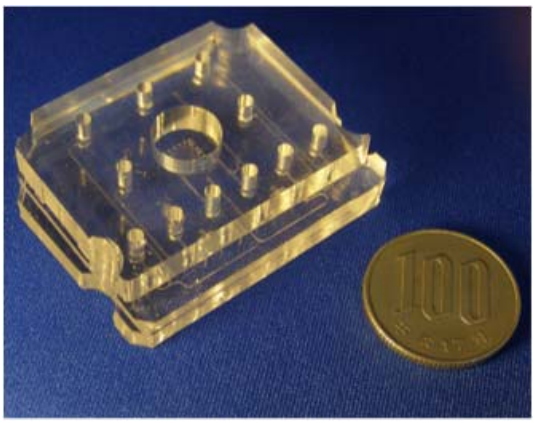

Figure 1. PDMS microdevice

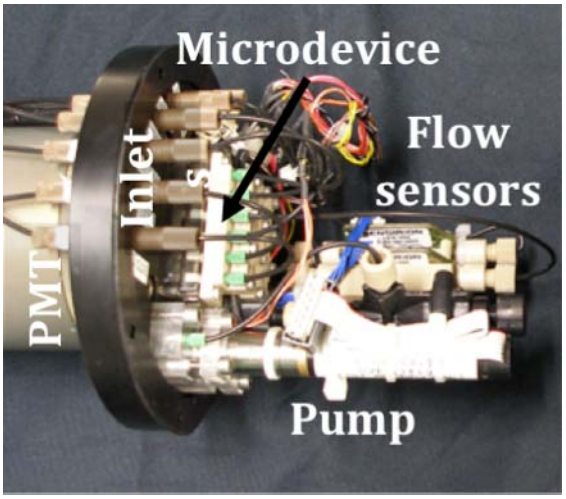

Figure 2. Actual system

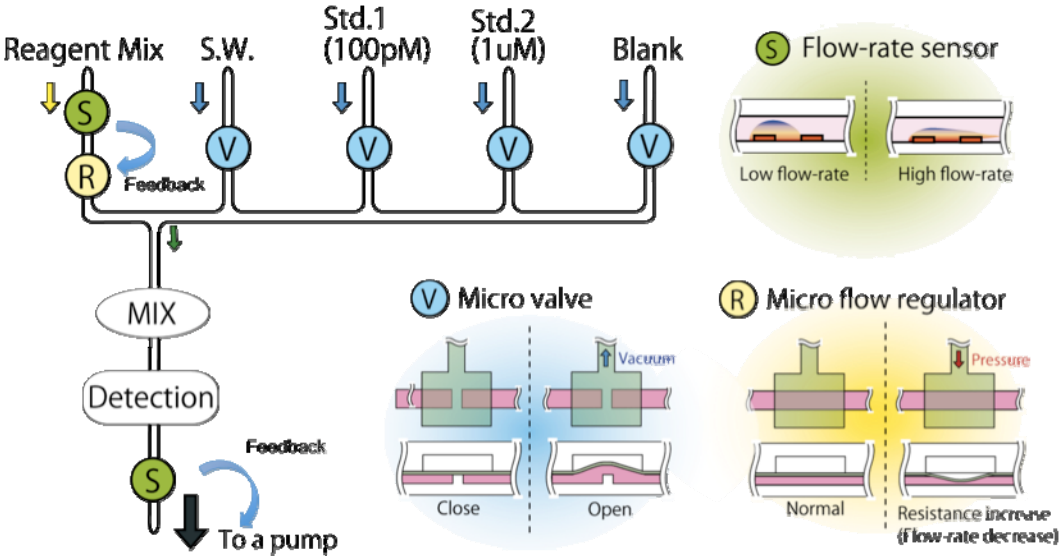

Figure 3. Flow diagram (*S.W. for seawater, Std. for standard*)

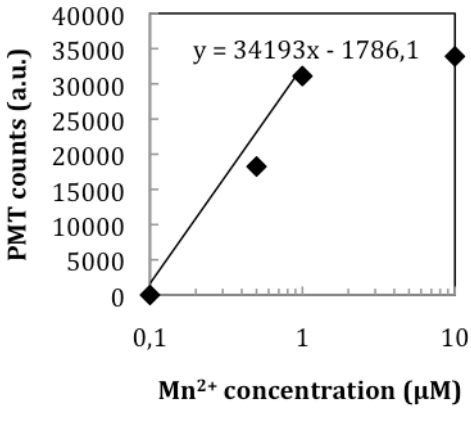

Figure 4. Calibration curve (lab setup)

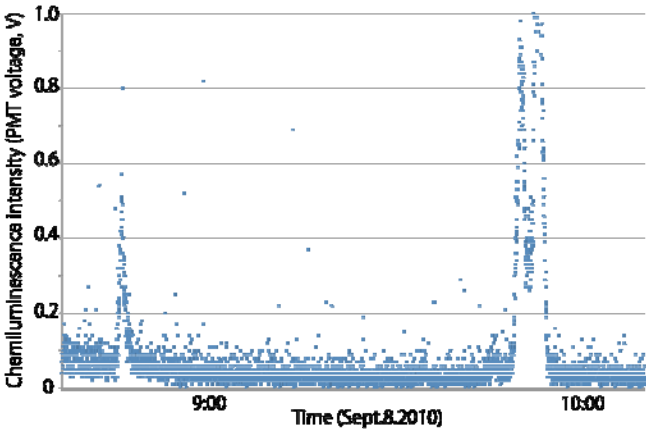

Figure 5. Actual data (peak=anomaly detected)