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Autonomous potentiometric sensor for in situ sulfide monitoring in marine sulfidic media

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Ag-Ag2S electrodes have been implemented in a variety of marine environments. They have been particularly useful for microscale in situ hydrogen sulfide determination in deep-sea sediments, avoiding large pressure and temperature changes and physical disturbance of bacterial mats while cores are brought back to the surface. Potentiometric sulfide electrode yet suffer from several drawbacks, including logarithmic response, potential drift, sensitivity to disturbance. For this reason they have been progressively replaced by amperometric microsensors with a linear response. Silver-silver sulfide electrodes still represent an interesting alternative for sulfide measurements in a number of environmental conditions where neither microsensors not colorimetric analyzers can be effectively deployed: e.g. chemosynthetic habitats on hard substrates such as hydrothermal smokers, carbonate encrustment at cold seeps, or even sunken woods and whale bones. To investigate organismes-environment interactions in these habitats, we have developed small scale potentiometric autonomous sensors equipped with custom-made sulfide electrodes, as done previously with a pH 2mm-electrode. The main advantage of these rugged, cost-effective and readily deployed sensors is to allow the characterization of microhabitat conditions in highly heterogeneous media. The combined sulfide and pH electrode allowed to quantify sulfide with sub-centimetric resolution (e.g. on cracks within carbonate pavements at methane seep, inside the tube of a hydrothermal annelid worm, or a ciliate colony on sunken wood). The selectivity of the electrode to sulfide ions also gave a better indication of bioavail-

able sulfide, when complexing metals are enriched in the environment. For the first time, the autonomous sensors allowed to document the variability of sulfide concentration in sulfidic environment at scale of days to weeks. If the logarithmic response may still limit measurement accuracy, especially as drift can occur over time, the detection range spans over less than 1 μM to at least 10 mM which is undoubtedly an advantage when large variations are experienced. We will present the performances and limitation of the sensor for use in deep-sea hydrothermal and methane seeps environments as well as in shallow water sunken wood habitats in mangrove swamp.