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Silver-based electrochemical sensors for sulfide monitoring in deep-sea environments: New approaches based on autonomous measurement

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A large variety of sulfidic environments have been described in the deep-sea since the late seventies, such as hydrothermal vents, cold seeps, organic falls or sub-seafloor microbial habitats. The reactivity of sulfide toward living organisms is a key concern in the exploration and study of these ecosystems, especially at hydrothermal vents where sulfide is a predominant energy source for chemosynthesis. However, the dynamics of sulfide gradients in these marine environments are still poorly documented, constraining the knowledge of their biogeochemical and ecological consequences. In this context, the development of sulfide autonomous sensors became a primary challenge. Measurement tools capable to capture the temporal variability of sulfide concentrations and related parameters are particularly needed, owing to the variability of environments at hydrothermal vents. Silver sulfide potentiometry, which was already applied in situ for punctual measurements, and a new voltammetric method based on bare silver, an electrode material which avoids the need for complex and repeated conditioning of the electrodes, are particularly suitable for unattended use. The advantages and limits of the potentiometric and voltammetric sensing techniques using solid-state electrodes were compared, with respect to the major requirements: concentration ranges; sensitivity to change of pH and temperature; minimum measurement rate; spatial resolution; autonomy; stability and reliability over time. Laboratory tests, combined with unprecedented series of in situ deployments in deep sea and other shallow water sulfidic environments, depict the potential of these tools for monitoring sulfide fluctuations in deep-sea habitats over weeks to months, and their use for investigation of the biogeochemical transformation of sulfur over time. Such sensors, improves the knowledge from these hardly accessible environments and could also reveal usefull to study shallow coastal waters, where sulfidic environments have been known for long. Mangroves, salt-marshes and submarine groundwater discharge zones had proven their importance in local, regional and even global scale processes. The need to monitor sulfide in this context is increasing, due to the probable increase of sulfide exposure episodes as a result of global changes, particularly with the increase of coastal anoxia.