DISCOVERY OF MATURE THERMOGENIC HYDROCARBONS IN FERROMANGANESE NODULES FROM THE GULF OF CADIZ: A NEW TOOL FOR OIL AND GAS EXPLORATION

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Ferromanganese nodules were firstly collected during the Tasyo Project cruises from mud-carbonate mounds and mud volcanoes at the Guadalquivir Diapiric Ridge (Central Eastern Atlantic). The mineralogical and geochemical studies have revealed their genesis, linked to the anaerobic oxidation of hydrocarbons and organic matter via bio-mineralization processes. The primary deposit can be defined as seep Fe-Mn carbonate concretions formed below the redox boundary, within the Sulphate-Methane Transition Zone. The $\delta^{13}C$ values for siderite and rhodochrosite from the internal parts of the nodules vary from -5.9 to -8.3 per mil (vs. PDB) and the $\delta^{18}O$ values range from +2.8 to +3.8 per mil (vs. PDB). These isotopic values are coherent with an origin in relation with a mixing of carbon sources: derived from methanogenesis, methane oxidation, fermentation of organic matter, dissolved of organic tests and marine seawater. Gas hydrates dissociation could be the responsible for the higher oxygen isotopic values.

N-alkanes have been discovered in all the nodules, which were analyzed by Gas Chromatography, comprising a unimodal distribution maximizing at the n–C_{18} isomer with an important presence of n-C_{16} and n-C_{20}. Pristane and phytane and/or crocetane (2, 6, 11, 15-tetrametilhexadecane) were detected in all the samples studied. Isotopic values of $\delta^{13}C$ for these compounds, measured by Gas Chromatography-Combustion-Isotope Ratio Mass Spectrometry, ranged between -20 and -37 per mil (vs. PDB). These values are sustaining the idea of deep thermal maturation. Moreover, the carbon preference index (CPI) ranged from 0.66 to 1.15, which is also distinctive of mature samples. In the same way, polycyclic aromatic hydrocarbons as phenanthrene and anthracene, present in mature substances such as petroleum, have also been detected in the nodules.

We propose the use of these ferromanganese nodules as tools for reconstructing the fluid venting history in modern or ancient hydrocarbon-seeps from the Gulf of Cadiz. The nodules acted as "traps" for fluids during their growth, remaining for long time when the fluids responsible of the mineralization have disappeared in the area. Therefore, they can be valuable for seep detection. In addition, these nodules and their thermogenic hydrocarbons may be used as indicators to explore and define deep-seated reservoirs for oil and gas, giving important information on sub-seafloor fluids composition and migration patterns, geology and tectonic conditions.

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