



Evidence for a large methane release during the last deglaciation based on diploptene and diplopterol records from Marmara Sea sediments

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The Sea of Marmara, enclosed between the Mediterranean and Black Seas, is a tectonically active basin with intense gas hydrate formation. Because depths in the basin are shallower than 1100 m, temperature is expected to have a great influence in destabilizing methane clathrates (Buffett and Archer, 2004, EPSL 227, 185). Both arguments make it an interesting location to study the potential impact of climate on methane releases. Among a suite of biomarkers, we focus here on the diplopterol and diploptene profiles in core MD012430 retrieved in the central basin of Marmara Sea at 580 m water depth. These profiles are compared with the alkenone profile, which gives an useful insight on the sea surface temperature variations. Identification and quantification of biomarkers were performed by single ion monitoring GC-MS. Individual compound carbon isotopic compositions were analyzed on diploptene when permitted by the compound concentration. During the last 15,000 years, both markers show important concentration variations, by an order of magnitude, with a pronounced peak starting around 11,500 cal. years B.P. The $\delta^{13}\text{C}$ signature of diploptene is around -46 per mil versus PDB at its concentration maximum, significantly lighter than the other compounds of the chromatograms. Diplopterol and diploptene have been found to be synthesized *de novo* by various aerobic bacteria, notably in methanotrophic bacteria. They are produced in large amounts in presence of methane (Hinrichs et al., 2003, Science 299, 1214; Uchida et al., 2004, G3 5(8), 1). Both the concentration profiles of the two hopanoids and the carbon isotopic values suggest that an important methane release took place at the start of the Holocene in the Marmara Sea. This

corresponds to the maximum of sea surface temperature change as reconstructed with C37 alkenones. The sensibility of the hydrate stability zone to changes in temperature and pressure under this range of water depths, as well as the relative timing of the diploptene maximum and the sea surface temperature rise provide arguments to decipher between the potential triggers of methane release in the water column.