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Vertical distributions and chemical properties of shallow-buried gas hydrates at the *Batumi seep area*, Eastern Black Sea

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Submarine gas hydrates (GH) are an important reservoir of methane and further low-molecular-weight hydrocarbons (LMWHC). For an accurate quantification of gas and GH in sediments, pressure sampling tools, which inhibit gas loss due to decompression, are essential. During R/V METEOR cruise M72/3 in 2007 we continued our earlier investigations on *in situ* inventories and chemical compositions of LMWHC incorporated in shallow-buried GH, dissolved in pore waters and discharged from the sea floor at the *Batumi seep area*, offshore Georgia. This site is located in about 835 m water depth close to the upper boundary of the nominal hydrate stability field. Visual observations using the ROV "QUEST 4000 m" documented sea floor features typical for intense hydrocarbon seepage (e.g., rough morphologies, pockmarks, authigenic carbonates forming pavements, and tower-like structures). For recovering pressurized near-surface sediment cores and gas bubbles in near-bottom waters, autoclave technology was used. During deployments of our Dynamic Autoclave Piston Corer (DAPC) nine pressurized cores were retrieved from that area. Quantitative degassing of DAPC cores yielded gas concentrations strongly exceeding solubilities, which proved the presence of substantial amounts of shallow-buried GH. Gas bubbles collected with the newly developed ROV-based Gas Bubble Sampler as well as gases taken during core degassing and hydrate-bound gases were strongly dominated by methane (up to 99.97 mol % of LMWHC). The presence of GH structure I, as inferred from the

LMWHC composition, was proven by X-Ray diffraction techniques. Molecular ratios of LMWHC ($C_1/[C_2+C_3] > 1,000$) and stable isotopic compositions of methane ($\delta^{13}C$ = –53.5‰ VPDB; D/H = –175‰ SMOW) suggest a gas mixture of biogenic and thermogenic origin. However, the molecular ratios clustered in two groups (I+II). Cores releasing group I gas comprised the Black Sea stratigraphic Units 1 and 2. Group II gas was derived from cores additionally containing Unit 3 material and from dissociated GH, which points to preferential GH accumulations below Unit 2. Pore water chlorinity profiles support these GH distributions. Relative enrichments in ^{13}C of methane in group I gas, as would be typical for sediments characterized by the anaerobic oxidation of methane, were not observed. These findings may suggest that vertical GH distributions at the Batumi Seep Area are primarily controlled by sediment lithologies.