

## Formation of authigenic carbonates within the seepage structures of Lake Baikal (Eastern Siberia)

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Lake Baikal (Eastern Siberia) is the largest and deepest in the world rift lake and the only one freshwater basin with gas hydrates. The presence of gas hydrates in the Baikal sediments was first inferred from the observation of a BSR on multichannel seismic reflection profiles, which corresponds to the base of the gas hydrate stability zone (Hutchinson et al., 1992; Golmshtok et al., 1997). In 1997, hydrate samples were retrieved in a 225-m-long well from the Southern Baikal Subbasin (Kuzmin et al., 1998). Later, gas hydrates accumulation was discovered in subsurface sediments at shallow depth within the South and Central Subbasins of Lake Baikal (De Batist et al., 2002; Van Rensbergen et al., 2002; Matveeva et al., 2003; Khlystov, 2005). In the marine environment, gas hydrates below the seafloor is usually marked by authigenic carbonate precipitation. In case of Lake Baikal, a number of papers reported the absence of carbonates in sediments (Knyazeva, 1954; Fagel et al., 2005 etc). I.B. Mizandrontsev (1975) had calculated that formation of calcium carbonate in the bottom sediments of the Lake Baikal is impossible, because the pore waters are on 1-2 order under saturated in calcium concerning the concentrations required for calcite formation. He had predicted that carbonates here can be mainly represented by rhodochrosite. It is well-known, that Mn and Fe often form layers in the upper 15-25 cm of Baikal sediments (Deike et al., 1997; Granina et al., 2004). Mn and Fe are very soluble with respect to most inorganic ions, but siderite or rhodochrosite can be formed (Davison, 1993). First carbonates within the Baikal seeps were discovered in the surface layer (0-15 cm) of sediments at the Malenky structure in the 2003. During Russian-Japanese expedition onboard of RV G.Yu.Vereshchagin in autumn 2005, one hard carbonate within Malenky seep (level 102-105 cm below lake floor) and several soft carbonates at the Koukuy canyon (K-2 mud volcano, levels: 34, 60-64 cm; 184-193 cm blf) were sampled. It was first observation of carbonates in the sediments from Koukuy canyon. Results of XRD-analyses of the carbonates had confirmed that main mineralogical phase of these constitutions are siderite and rhodochrosite. Quartz, feldspars and clay minerals were determined as admixture. The carbonates in Lake Baikal are confined to gas-hydrate bearing seepage structures that allow us consider the latter as source for hydrocarbonate ions. The  $\delta^{13}\text{C}$  values of carbonates are varied between +2.7 and +21.2 per mille, PDB. In case of oxidization of methane or organic matter (e.g. sulfate reduction), the carbon of forming carbonates must be depleted in  $^{13}\text{C}$ . Thus, this mechanism is unlikely for explanation of Baikal carbonates formation. Due to large carbon isotope fractionation between  $\text{CO}_2$  and  $\text{CH}_4$ , important  $^{13}\text{C}$  enrichments characterize the  $\text{CO}_2$  remaining in the pore fluids after methanogenesis. Aceticlastic methanogenesis is considered to be the predominant methanogenic pathway in anoxic, freshwater environments (Whiticar, 1999; Hornibrook et al., 2000). Accordingly, process of microbial fermentation of acetate (methanogenesis) is most reliable mechanism of supply  $\text{CO}_2$ , which are strongly enriched in  $^{13}\text{C}$ . Thus, hydrocarbonate ions enriched by  $^{13}\text{C}$  and consumed during carbonates formation were produced by bacterial fermentation both in situ, and in the deeper deposits (e.g. BSR zone). In latter case, hydrocarbonates can be delivered in subbottom sediment by ascending fluid within the seepage structures.