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Possibility of organic matter formations in irradiated CO2 and CH4 hydrates on Mars

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To look for evidence of life on Mas, explorations of organic matter is important. There are some possibilities of the formations of organic matter on Mars; for example, by biological activity and by radiolysis and photolysis of mixtures of icy materials. If organic matter exist on Mars, to identify the detected organics as the matter by biological activity, it is necessary to investigate reaction products and their amount by radiolysis and photolysis of the ice mixtures, and to distinguish organics by biological activity from ones by radiolysis and photolysis. As the icy materials on Mars, it is suggested that gas hydrates would exist on Mars, based on the discussion of temperature and pressure conditions. Gas hydrates are crystalline inclusion-compounds, which are composed of hydrogen bonded water molecules encaging gas molecules (e.g. CO_2, CH_4). Most of them are stable at high pressures and/or low temperatures. Average temperature of Martian surface is about 210 K, the Martian atmosphere consists of about 95% CO_2 and the average atmospheric pressure is about 0.56 kPa (Kieffer et al., 1993). From the observations of the Mars Express spacecraft, methane with 10-40 ppmv concentrations has been detected in the Martian atmosphere and on surface of the ground (Formisano et al., 2004; Mumma et al., 2009). In Martian conditions, it is suggested that CO_2 and CH_4 hydrates are formed in about 10 m below the ground and on the polar caps in winter (e.g. Max and Clifford 2001; Prieto-Ballesteros et al., 2006). Since water ice exists on Martian surface, the environment on the Martian surface should be enough to form CO_2 and CH_4 hydrates. In this case, Martian gas hydrates should be irradiated by natural radiation from radioisotopes in sediments as well as cosmic rays, which may cause radical formation in CO_2 and CH_4 hydrates.

Radiation-induced radicals in CH_4 and CO_2 hydrates have been investigated by electron spine resonance (ESR) measurements. Methyl radical is mainly formed by gamma-ray irradiation at 77 K in CH_4 hydrate (Takeya et al., 2004), and not stable above 180 K at 0.1 MPa (Tani et al., 2006). Carboxyl radical, hydrogen atom and hydroxyl radical are formed by gamma-ray irradiation at 77 K in CO_2 hydrate, hydrogen atom and the hydroxyl radical are not stable above 120 K at 0.1 MPa and the carboxyl radical quickly disappears at 180 K (Oshima et al., submitted). In thermal conditions on Mars, these radicals in the hydrates are unstable, and some products may form through the radical reactions. In this study, to investigate the organic products from radicals induced in CO_2 and CH_4 hydrates on Martian conditions, we analyzed the aqueous solution after dissociation of the hydrates irradiated at 195 K by ion chromatography and gas chromatography-mass spectrometry (GC-MS).

Formic acid and oxalic acid are observed in aqueous solution after dissociation of irradiated CO_2 hydrate. Methanol and formaldehyde are observed in irradiated CH_4 hydrate. If CO_2 and CH_4 hydrates exist on Mars, these organics will be formed in the hydrates and accumulated on the polar caps and below subsurface.

Keywords: Gas hydrates, Organic matter, Radicals, Ion chromatography, Gas chromatography-mass spectrometry (GC-MS), Mars