GAS PRODUCTION BY IONIZING RADIATION IN SEDIMENTARY ROCKS

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The effects of ionizing radiation on organic matter in sedimentary rocks – either by naturally occurring radioactive material in e.g. uranium-rich black shales or by high-level radioactive waste in underground nuclear repositories – has been investigated mainly by comparing samples with nowadays different uranium contents from within a formation and inferring that apparent differences are caused by the different reconstructed radiation doses (e.g. Dahl et al. 1988; Lewan & Buchardt, 1989). These investigations could not address the processes of gas production during irradiation, as the volatile components are lost from the natural samples. Lewan et al. (1991) investigated the gas production of dried Phosphoria Retort Shale and its extracted kerogen by irradiation with gamma-rays from a ^{60}Co source over a period of two month up to maximum doses of 10 MGy. They observed gas production, mainly CO_2 and H_2 – and noted that contrary to their expectations the organic carbon normalised gas production was significantly elevated in the rock samples in comparison to the kerogen.

As the amount and rate of gas production and its molecular composition is one aspect relevant for subsurface nuclear waste storage, this finding was investigated in more detail in the study presented here for four different clay-rich sedimentary rocks – the Opalinus Clay, a Lower Cretaceous Clay, the Boom Clay, and the Posidonia Shale. Therefore dried rock samples – and in addition dried rock samples with the addition of known amounts of water to mimick the effects of porewater – were irradiated for up to 2 month with gamma radiation by a ^{60}Co source up to total doses of 20 MGy – at a constant temperature of 80°C in gas-tight sealed quartz glass vials. The amounts of the gases – and for CO_2 and the hydrocarbon gases the carbon isotopic composition – were analysed after the end of the experiments by GC, MS and GC-irmMS methods.

The molecular composition of the produced gases changed with increasing total doses, at high doses H_2 and CO_2 clearly dominate for all rocks investigated, but at intermediate doses the relative amounts of CO and CH_4 are elevated. Using its carbon isotopic composition, the main source for CO_2 is the degradation of organic matter by either release of CO_2 from e.g. carboxylic moieties or the total oxidation of released small organic compounds. A small proportion of CO_2 is derived from carbonate by either carbonate decomposition or by dissolution of carbonate by water and release of CO_2. The amount of CO_2 and CO normalised to the organic carbon content of the initial rock sample [μmol/molC_{org}] formed during the irradiation is governed by the initial content of oxygen containing groups in the organic matter as depicted by the correlation with the RockEval oxygen index values. The amount of H_2 [μmol/molC_{org}] formed is not increasing with the hydrogen index, the type II kerogen of the Posidonia shale - and its hydrocarbon irradiation products - seem to act as a sink for hydrogen. The amount of CO_2 is strongly elevated for all rock samples with added water. The amount of CO is significant only in the experiments with dried rock material, but is strongly reduced in irradiation experiments with added water. These findings invoke a mechanism of oxidation of organic carbon (and CO) by radiolysis products of water. The radiolysis of water is producing hydrogen and hydroxy radicals as first products (LaVerne, 2000), molecular hydrogen as analysed here could only evolve by recombination of two hydrogen radicals if the hydroxy radicals are scavenged toward another sink, e.g. the oxidation of carbon towards CO_2. Therefore the amount of (pore)water in the system might govern the amount – and molecular composition of the gases produced – by the radiolysis of water and of the organic matter. This finding could explain the results of Lewan et al. (1991), as the dried rock samples will have contained more residual water e.g. as interlayer water in clay minerals than the kerogen concentrates and hence the radiolysis will result in the higher amounts of H_2 and CO_2 formed as well as the elevated CO_2/CO ratios for the rock samples.

References

DAHL, J., HALLBERG, R. & KAPLAN, I. R. (1988): Effects of irradiation from uranium decay on extractable organic matter in the Alum Shales of Sweden. – Organic Geochemistry, 12(6): 559-571.

LAVERNE, J. A. (2000): OH radicals and oxidizing Products in the gamma radiolysis of water. – Radiation Res. 153: 196-200.

LEWAN, M. D. & BUCHARDT, B. (1989): Irradiation of organic matter by uranium decay in the Alum Shale, Sweden. – Geochimica et Cosmochimica Acta, 53(6): 1307-1322.

LEWAN, M., ULMISHEK, G., HARRISON, W., SCHREINER, F. (1991): Gamma ^{60}Co-irradiation of organic matter in the Phosphoria Retort Shale. – Geochimica et Cosmochimica Acta, 55(4): 1051-1063.