Methane-halide reactions in shield waters, inferred from $\delta^{13}C$ and $\delta^{2}H$ of methane and $\delta^{81}Br$ and $\delta^{37}Cl$ of dissolved ions

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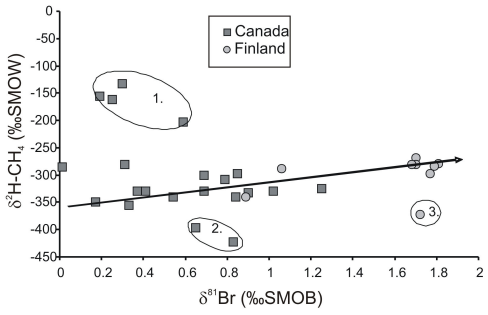
Previous works have characterized the methane isotopic composition at fifteen sites in the Fennoscandian and Canadian Shields [1,2]. Methanes were of both biogenic and abiogenic origin. Eighty water samples from twenty-four different sites in the Fennoscandian and Canadian shields were analyzed for $\delta^{81}Br$ and $\delta^{37}Cl$ isotopic signatures. The $\delta^{81}Br$ values obtained ranged from +0.01‰ to +2.04‰ relative to SMOB and the $\delta^{37}Cl$ ranged from -0.78‰ to +1.03‰ relative to SMOC.

Comparison of the stable isotopic composition of dissolved halides with the associated methane generally shows an increasing trend (see Figure, error for bromine is the size of the data point, error for hydrogen is 1/10 the data point). This suggests paleofluids in shield environments contained quantities of CH_3Br and CH_3Cl, the primary natural components of halogen radicals contributing to ozone depletion in the atmosphere. Sources of methyl halides in these deep groundwaters likely include pyrolysis of methane and subsequent reactions of HCl or HBr in hydrothermal fluids or low-mid temperature metamorphism. C1-C2 and C2-C3 geothermometry suggest these reactions occurred between 200 and 300°C. Deviations from the trend at three sites indicate other origins and/or processes.



References

[1] Sherwood-Lollar B., Frape S.K., Weise S.M., Fritz P., Macko S.A., and Welhan J.A. (1993) *Geochimica et Cosmochimica Acta.* **57,** 5087-5097.

[2] Sherwood-Lollar B., Frape S.K., Fritz P., Macko S.A., Welhan J.A., Blomqvist R., and Lahermo P.W. (1993) *Geochimica et Cosmochimica Acta* **57,** 5073-5085.