Bromine isotope measurement by MC-ICP-MS in wet plasma conditions

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Cl and Br behave conservatively in porewaters, so their isotopes have been used to trace the origin and fate (circulation pathways) of formation waters in sedimentary rocks and hydrocarbon fields. Numerous studies report $\delta^{37}Cl$ variations in brines [1] [2], but few laboratories worldwide measure $^{81}Br/^{79}Br$ ratios [3-7]. Due to low abundances in geological fluids, high first ionisation energy and purification steps required, relatively large amounts of samples are needed for precise and accurate $\delta^{81}Br$ measurements. Until Zakon et al [8], Br was extracted through silver halide precipitation followed by CH_3Br separation.

We describe a $\delta^{81}Br$ analysis method for solutions (seawater and brines) by MC-ICP-MS in wet plasma conditions, after Br extraction through ion exchange chromatography. The method is robust, for Br amounts in the 1-10 μg range. Reproducibility is $\leq 0.25‰$ (2σ), typically $\leq 0.1‰$.

We extracted Br with NH_4NO_3 from AG 1X4 anion exchange resin. We achieved complete Br recovery and introduced the Br fraction into a MC-ICP-MS (Neptune, Thermo Scientific) through a cyclonic spray chamber. Wet plasma conditions produced higher levels of Ar_2H than gas introduction or desolvation systems. Correcting this ^{81}Br interference was tested in both low- and high-resolution modes. Repeated extraction and analyses of synthetic and natural seawaters proved the robustness of the method.

Measurements of seawater, salts and four HBr solutions with $\delta^{81}Br$ between –1‰ and +2‰ by MC-ICP-MS and IRMS[3] validated the accuracy of our new method.

We analyzed brines from the Paris Basin and North Sea oil fields, and found correlations between $\delta^{81}Br$ and $\delta^{37}Cl$ showing mixing trends and possibly geochemical evolution.

[1] Lavastre et al. (2005) *Geochim. Cosmochim. Acta* [2] Eastoe et al. (2001) *Chem. Geol.* [3] Eggenkamp & Coleman (2000) *Chem. Geol.* [4] Shouakar-Stash et al (2005) *Anal. Chem.* [5] Holmstrand et al. (2010) *R. Com. Mass Spec.* [6] Gelman & Halicz (2011) *Int. J. Mass Spec.* [7] Du et al (2013) *Int. J. Mass Spec.* [8] Zakon et al., 2014, *Anal. Chem.*