# Halogen isotopes: now and then

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## Then – the distant & more recent history

Direct study of stable isotopes began with Aston's Nobel prize winning mass spectra in 1919, including $^{35}Cl$ & $^{37}Cl$ [1]. Urey calculated equilibrium isotope fractionations of Cl, Br & I in the 1930s & 40s. Despite predictions of large effects for Cl (e.g. $ClO_4^-$:$Cl^-$ ~80‰ at 25°C), natural materials gave no differences greater than analytical precision until the mid 1980s. Kaufmann et al. used $CH_3Cl$ & + ion mass spec, got ±0.24‰ & saw ±~1‰ around the seawater standard (SMOC). Even so, the small variations showed evaporation processes to form salt deposits obey a Rayleigh distillation model, though the solid-solute fractionation is very small.

Later, oilfield brine Cl gave the first large variation from SMOC, ≤ -4‰, showing oil-zone & aquifer water were very different. $\delta^{81}Br$ in the same samples showed smaller variation & anticorrelation with Cl: not yet explained. Aqueous diffusion kinetic fractionation also gives big differences in both lab & natural samples for Cl & Br. This allowed testing stability of groundwater flow for possible radwaste sites. Microbial $ClO_4^-$ reduction to $Cl^-$ shows massive fractionation, ~-15‰, & gauges extent of contaminated site bioremediation.

Cosmogenic radioisotopes $^{129}I$ & $^{36}Cl$ decay slowly & can help date waters but need correction for *in situ* production underground & care to avoid anthropogenic (bomb) inputs.

## Now - and the possible future

Extensive chemical pre-processing probably inhibited more Br isotope work but recently ICPMS methods, coupled with ion-exchange help, & also give much increased sensitivity. Similar approaches allowed analysis of small amounts of chlorinated solvents after GC separation.

Measuring small amounts of Cl very precisely has raised the possibility, still controversial, that the Earth's mantle is isotopically different from the bulk Earth. This is important in understanding planetary distribution of volatiles including water in the early solar system & habitability of exoplanets. Cl in lunar basalts also indicates water is absent in the Moon. Some Martian meteorite Cl isotope compositions show effects of surface interactions while primary values are similar to Earth's mantle. Rover analyses of Mars sediments show extremely large variations (to -60‰), which vary systematically with stratigraphic height, not yet explained too.

Clearly, halogen isotopes still have a lot to teach us.

[1] Aston (1920) *Nature* **105** 617-619 ***& all that followed***.
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