# The stable isotope geochemistry of the halogens Cl and Br: A review of 15 years development

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It is now 15 years ago that the first study in which significant Cl isotope variations were reported, was presented (Kaufmann *et al.*, 1983). To commemorate this event I am presenting here an overview of the current state of our knowledge on stable Cl (and recently stable Br) isotope geochemistry. As only six references are allowed for this abstract, I am unable to refer to the many contributions in this field, but hope to mention the names of most people working in this field, and the places where the work has been conducted.

Cl and Br are the only halogens with two stable isotopes (fluorine and iodine have only one, astatine has none) so that variations in their ratios can be determined. The two stable Cl isotopes are $^{35}$Cl and $^{37}$Cl, and the $\delta^{37}$Cl is reported relative to 'Standard Mean Ocean Chloride'. The two Br isotopes are $^{79}$Br and $^{81}$Br, and the $\delta^{81}$Br is reported relative to 'Standard Mean Ocean Bromide'. Neither of them is a formal standard, but there are no detectable variations in the isotope compositions of both elements in the oceans.

The first major Cl isotope study, Ronald Kaufmann's doctoral thesis was written in 1984. The thesis included a very good review of the earlier attempts to measure Cl isotope variations, and the development of the method to measure Cl isotope compositions. Kaufmann showed that the Cl isotope composition of seawater is constant. The Cl isotope composition in several natural samples was reported, with emphasis on hydrological systems.

This was the primary work I could rely on when working on my own Ph.D thesis. My thesis was published in 1994 and contained several studies on many different geological environments. In the same year the first extensive studies on rocks, using the TIMS technique were published by Andrew Magenheim.

## Techniques

The two most important analytical techniques used to measure stable Cl isotope compositions are stable isotope ratio gas mass spectrometry (IRMS) and thermal ionisation mass spectrometry (TIMS). The first technique measures the Cl isotope composition of $CH_3Cl$ gas, while the latter measures the isotope composition of $Cs_2Cl^+$ ions. Both techniques have their advantages. IRMS is fast and has a high precision (better than 0.1‰), but needs relatively large samples. Using TIMS, one can analyse very small samples but the data are less precise and sample preparation and measurement is more time consuming. The two techniques have been compared by Jeff Rosenbaum, and he found that results from the two techniques were not significantly different.

IRMS is used by the groups at the University of Arizona in Tucson, AZ, USA (Chris Eastoe, Austin Long), the University of Waterloo in Waterloo, ON, Canada (Shaun Frape, Bob Drimmie), Utrecht University in Utrecht, The Netherlands (Hans Eggenkamp), Reading University in Reading, UK (Hans Eggenkamp, Max Coleman), and Argonne National Laboratory in Argonne, IL, USA (Neil Sturchio, Ben Holt). NTIMS is used by the groups at the Qinghai Institute of Salt Lakes in Xining, China (Xiao YingKai, Liu WeiGuo), San Diego State University in San Diego, CA, USA (Andrew Magenheim), the University of North Carolina in Wilmington, NC, USA (Art Spivack), and the University of Leeds in Leeds, UK (Bob Cliff, Jeff Rosenbaum). Several other laboratories are presently being set up to make Cl isotope measurements.

## Hydrology

Chlorine plays an important role in shallow ground waters. Because it is a conservative element it will mainly be fractionated by physical processes, of which diffusion is an important one. Most published work in the 1980's and early 1990's involved hydrological projects. The groups in Tucson (Ronald Kaufmann, Chris Eastoe and Austin Long) and Waterloo (Shaun Frape, Bob Drimmie, Donald Desaulniers) showed the importance of Cl isotopes in hydrological problems. Amongst others, several studies showed that Cl isotopes could be used as a perfect tracer of diffusion in pore water systems.

## Formation waters

Very large Cl isotope variations were found in deep formation waters from several basins, such as the Texas-Louisiana coast, the North Sea, and the Paris Basin. $\delta^{37}$Cl values down to −5‰ were found in North Sea formation waters. Often it seems that the Cl isotope composition of formation waters result from mixing between several end-member compositions. One end-member is often either seawater or dissolved evaporite (with a $\delta^{37}$Cl close to 0‰). Some of the other(s) sometimes have very depleted $\delta^{37}$Cl values, for which a good explanation does not currently exist.

## Evaporites

Evaporite studies have been made on both ancient and recent salt deposits. Measurements on ancient deposits (by Ronald Kaufmann and Hans Eggenkamp) revealed that no large fractionation (up to 0.5‰) occurs during their formation. The group at the Qinghai Institute of Salt Lakes in Xining have conducted extensive studies on the recent salt deposits in the continental Qaidam Basin in China. They found large variations in the stable Cl isotope composition which were related primarily to the degree of evaporation of the system. The most concentrated brines have $\delta^{37}$Cl values which are more than 2‰ lighter than seawater.

## Rocks

Various MORB's with very low Cl concentrations could be measured by Andrew Magenheim and co-workers in San Diego using TIMS. They were able to detect large variations in MORB's, and concluded that the average $\delta^{37}$Cl in the mantle is approximately +4.7‰. This can be compared with values close to 0‰ for carbonatites which I determined, which could indicate that the mantle is heterogeneous with respect to its Cl isotope composition. Surface rocks can also have very large Cl isotope variations. $\delta^{37}$Cl values of minerals from many different environments range from −4.9‰ (the fumarole sal ammoniac; $NH_4Cl$) to +6.0‰ (the base metal chloride atacamite; $Cu_2(OH)_3Cl$).

## Organic compounds

Recently several methods have been developed by different groups (Waterloo, Argonne, Reading) to measure the Cl isotope composition of organic compounds. Preliminary data from these papers show a large range of $\delta^{37}$Cl values, which, unlike data from inorganic Cl, is not generally limited to values very close to 0‰. They indicate that measurement of Cl isotopes in organic compounds could have very important environmental applications, for example, tracing of (bio)degradation, or identification of the source of organo-chlorine contamination.

## Bromine isotopes

Recently the laboratory in Reading developed a method to measure natural Br isotope compositions, based upon classical methods to separate Cl and Br in samples. Preliminary results show that significant variations do appear in formation water brines, and surprisingly, that a negative correlation between $\delta^{37}$Cl and $\delta^{81}$Br was found. This indicates that different fractionation mechanisms exist for Cl and Br.

## Conclusions

Our knowledge of the Cl isotope distribution in nature has significantly improved over the past 15 years. The primary applications so far have been determining physical processes in sedimentary basins, and looking at the fate of antropogenic organic compounds in the environment. Also, continuing research on the distribution of Cl in the various parts of the earth using Cl isotopes will be important in the near future.

The new method for the measurement of Br isotopes showed very promising results. As Br isotopic characteristics seem different from Cl, it will be useful in the future to measure both Cl and Br isotopes in various systems.

It seems however, that good quantitative explanations of the observed variations can still not be given in many occasions. For this reason it is hoped that many experiments to quantify Cl and Br isotope systematics will be made in the near future, so that finally we will know why we observe the data we actually find in many systems.

## References

Kaufmann, R., Long, A., Bentley, H., and Davis, S. (1983) *Proc. 1983 Meet. Amer. Water Res. Ass. Hydr. Water Res. Ariz. Southwest*, **13**, 85–90.

The full bibliography on stable Cl and Br isotope geochemistry can be accessed at the world-wide-web address: http://www.rdg.ac.uk/~slsegnkm/HalPub.html