Advances in Isotope Geochemistry

Hans Eggenkamp

The Geochemistry of Stable Chlorine and Bromine Isotopes

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Preface

In 2014, it is 30 years ago that the Ph.D. thesis written by Ronald Kaufmann "Chlorine in Ground Water: Stable Isotope Distribution" was published. This thesis definitely is the landmark publication of all articles, book chapters, conference proceedings, and other papers written on halogen stable isotopes as it, for the very first time, showed that natural chlorine stable isotope variations were clearly, and actually easily, measurable. Earlier papers were published on chlorine (and even bromine) isotopes, but these were published at a very low frequency of less than one paper per year on average. These papers, mostly aimed at the development of analytical methods and experimentally measuring fractionation in the laboratory, showed that, unfortunately, natural variations were too small to be detected. Ronald Kaufmann was the first to develop a method by which it was shown that not only natural variations existed, but also that they showed clear systematics.

Once it was proven that small natural chlorine isotope variations could be measured, it was expected that the number of published studies would rise significantly and quickly. However, it took 10 years until the average number of chlorine isotope publications rose above five per year. Even today, after 30 years, the total number of papers on chlorine and, since the year 2000, bromine isotopes is only about 300, recently averaging at about 20 papers per year.

As a result, it is possible to contain almost the whole combined knowledge on stable chlorine and bromine isotope geochemistry into one small volume in the series "Advances in Isotope Geochemistry". In this volume, I present the development of our knowledge on chlorine and bromine stable isotope geochemistry. The book starts with an introduction on chlorine and bromine, their history, chemistry, and isotope behavior. A large part of the book is filled with the numerous methods that have been developed to analyze chlorine and bromine stable isotope ratios. Striking with this regard is that several methods have been developed within laboratories that presented very little scientific chlorine or bromine isotope work thereafter. It could be questioned what would be the reason for this striking observation.

The book then describes the various processes that fractionate chlorine and bromine isotopes. It is important to realise that chlorine and bromine are predominantly present on earth in the -I oxidation state as chloride and bromide ions, and as a result oxidation–reduction processes that impose large isotope fractionation on other light stable isotope systems are mostly absent.

The range of measured isotope ratios goes rarely beyond 10 ‰, and about 80 % of all chlorine and bromine isotope measurements are between −1 and +1 ‰ of the internationally accepted standard (ocean chloride and ocean bromide). Finally, the book describes the chlorine and bromine isotope variation that has been observed. This includes not only observations on chloride and bromide samples from earth, but also extra-terrestrial material such as meteorites and moon rocks and samples with different oxidation states such as perchlorates and organic molecules.

The number of laboratories that has been involved in chlorine and bromine isotope studies has never been very large. I believe the number has hardly been over 10 worldwide at any one time. It is hoped that the data provided in this book will increase the interest in the study of chlorine and bromine isotopes, and that more laboratories are going to realise the opportunities that investing time and resources in the study of chlorine and bromine isotopes can give a healthy reward. The equipment is present in virtually every isotope laboratory, and with only small adoptions and a small investment every isotope geochemist who wishes can become part of the halogen isotope community.

Hans Eggenkamp

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Part I
Introduction

The Halogen Elements

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Group 17 of the periodic table of the elements (see Table 1.1) consists of the so called halogen elements fluorine, chlorine, bromine, iodine, astatine and the recently discovered element 117 (Organessian et al. 2010), although it is not yet known if this element behaves similar to the other group 17 elements due to possible relativistic effects (see e.g. Pyykkö 2011b). Group 17 elements are characterised by an outer electron shell which contains seven electrons, so that only one electron needs to be added to give it a full noble gas configuration. This property makes that the dominant oxidation state, especially for the lighter elements of this group, is the -I oxidation state and they predominantly form ionogenic compounds. In the earth's surface reservoir chlorine and bromine are most commonly found in aqueous solution in the oceans, as most of their salts are readily soluble in water, and in evaporite deposits while fluorine is most common in some fluoride rich minerals such as fluorite (CaF_2), fluorapatite ($Ca_5(PO_4)_3F$), and cryolite (Na_3AlF_6) as the alkaline earth fluorides (e.g. CaF_2, MgF_2) have a low solubility and precipitate out of waters with significant alkaline earth concentrations. Iodine has a relatively low concentration in seawater as it is efficiently removed from it by certain brown algae which are able to heavily concentrate iodine.

In their elemental form group 17 elements form diatomic molecules with a single covalent bond between the atoms. At standard temperature and pressure fluorine and chlorine are gaseous elements, bromine is a liquid and iodine and astatine are solids. No chemical and physical properties are known yet from element 117, although they have been predicted in the past (Seaborg 1968; Fricke et al. 1971; Fricke and Waber 1971). These authors even predicted some properties for the next group 17 element (element 171) which may be so unstable that it will probably never be discovered. The electronegativity of the group 17 elements decreases from fluorine to astatine. Fluorine is the most electronegative element known. As a result fluorine is also one of the strongest oxidising agents that is known. In the same direction the elements also become weaker oxidising agents. Some characteristic chemical and physical properties for the group 17 elements can be found in Table 1.2.

1.1 Discovery of the Halogen Elements

As the group 17 elements are reactive elements they are not normally found as "native" elements in nature. As a consequence they were discovered at a relatively late date. The discovery history of the group 17 elements with stable isotopes is described in detail by Weeks (1942).

The first group 17 element that was discovered was chlorine. It was discovered by Scheele (1774) who, while studying manganese, in the reaction between hydrochloric acid and pyrolusite (MnO_2) noticed that a gas with the odour of warm aqua regia escaped. He was able to detect several of the

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Table 1.1 Characteristics of the group 17 elements

	Group 1	Group 2	Group 3	Group 4	Group 5	Group 6	Group 7	Group 8	Group 9	Group 10	Group 11	Group 12	Group 13	group 14	Group 15	Group 16	Group 17	Group 18
Period 1	1 H 1.0																	2 He 4.0
Period 2	3 Li 7.0	4 Be 9.0											5 B 10.8	6 C 12.0	7 N 14.0	8 O 16.0	9 F 19.0	10 Ne 20.2
Period 3	11 Na 23.0	12 Mg 24.3											13 Al 27.0	14 Si 28.1	15 P 31.0	16 S 32.1	**17 Cl 35.5**	18 Ar 39.9
Period 4	19 K 39.1	20 Ca 40.1	21 Sc 45.0	22 Ti 47.9	23 V 50.9	24 Cr 52.0	25 Mn 54.9	26 Fe 55.8	27 Co 58.9	28 Ni 58.7	29 Cu 63.5	30 Zn 65.4	31 Ga 69.7	32 Ge 72.6	33 As 74.9	34 Se 79.0	**35 Br 79.9**	36 Kr 83.8
Period 5	37 Rb 85.47	38 Sr 87.62	39 Y 88.9	40 Zr 91.2	41 Nb 92.9	42 Mo 96.0	43 Tc (97)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
Period 6	55 Cs 132.9	56 Ba 137.3	La-Lu	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
Period 7	87 Fr (223)	88 Ra (226)	Ac-Lr	104 Rf (267)	105 Db (268)	106 Sg (271)	107 Bh (270)	108 Hs (277)	109 Mt (276)	110 Ds (281)	111 Rg (282)	112 Cn (285)	113 Uut (285)	114 Fl (289)	115 Uup (289)	116 Lv (293)	117 Uus (294)	118 Uuo (294)

Period 6	57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.1	71 Lu 175.0
Period 7	89 Ac (227)	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

Group 17 elements are shown in light grey, chlorine and bromine in darker grey. Within the cells the number at the top is the atomic number, in the middle the symbol and the number at the bottom is the rounded atomic mass after Wieser et al. 2013. For elements without a stable isotope the mass of the longest living isotope according to Wieser et al. 2013 is taken.

properties of this gas, such as its green colour, its solubility in water which produces a weakly acid taste to the water and its bleaching capabilities. However, as in those days all acids were believed to contain oxygen he considered this gas as the oxide obtained from hydrochloric acid, which was then called muriatic acid, and as such failed to recognise it as a new element. In spite of this he still is credited with the discovery of the element. Gay-Lussac and Thénard (1809) tried to remove the oxygen from this gas, but failed to do so. Although they indicated that, because of this observation oxygenated muriatic acid might be a chemical element they did not yet consider it as such as they believed that their observations on it could still be explained more appropriate as it being a compound substance. Finally Davy (1811) after failing to decompose "oxygenated muriatic acid" again realised that it could only be a "simple body" (element) and he proposed the name of (eu)chlorine for it after its bright yellow green colour.

The second halogen coming to surface was iodine. It was discovered in 1811 by Bernard Courtois who was a producer of saltpetre (KNO_3). Considering that France was a country at war in those days, and saltpetre was used as one of the main gunpowder ingredients, saltpetre was in great demand. Production of saltpetre required Na_2CO_3 which was made from ash prepared from seaweed. Seaweed was burned to isolate the Na_2CO_3, and the ash was washed with water. To destroy the remaining waste sulphuric acid was added. When Courtois added an excess of sulphuric acid accidentally a cloud of a purple vapour rose. It was observed that this vapour condensed on cold surfaces thereby forming dark crystals. He suspected that these crystals might be an at that moment unknown element but he was unable to continue his research because of lack of funding. Courtois supplied the new substance to his friends Charles Bernard Desormes and Nicolas Clément for further analyses after which they presented the discovery to the scientific world (Courtois 1813). The new substance was further investigated by Joseph Louis Gay-Lassac and Humphry Davy who independently concluded that it was a newly discovered element and was subsequently called "iode" after the purple colour of iodine vapour by Gay-Lassac. Davy also discovered the chemical similarities between this newly discovered element and chlorine which he studied a few years earlier (Gay-Lussac 1813a, b, 1814; Davy 1813, 1814a).

Bromine has been discovered independently by Antoine Jérôme Balard and Karl Löwich in 1825/1826. Because Balard was the first to publish on his observations (Balard 1826) he is credited with the discovery of this element although Löwich might have prepared it a little earlier (Löwich 1827, 1828) than Balard. Balard discovered bromine when he extracted iodine from seaweed. During this process he distilled a substance from which he discovered that it has properties that were intermediate between chlorine and iodine. He tried to prove that this substance was iodine chloride (ICl) but failed in this process. He concluded that the substance was an element that he called muride. However, this was renamed bromide as the name proposed by Balard did not get approval by the French Academy of Sciences and it was renamed bromine after its "bad odour". Löwich discovered bromine when he oxidized salty springwater with elementary chlorine. He found a red liquid that he showed to his professor (Leopold Gmelin). Gmelin asked Löwich to produce some more of the substance so that it could be studied in more detail. While he was working on this task Balard's discovery was made public, indicating the same properties as the red liquid discovered by Löwich.

Due to its extremely reactive behaviour the discovery of fluorine was delayed for a very long time. Hydrogen fluoride was already described for the first time in 1768 (Marggraf 1768) and the results of these experiments were confirmed by Scheele three years later (Scheele 1771). As in that period it was believed that all acids contain oxygen it was concluded that hydrofluoric acid should also contain oxygen. However. Davy (1814b) showed that this was not the case. It was Ampère (1816) who realised that hydrofluoric acid must be a compound between hydrogen and an, at that moment, unknown element. Searching for the pure element was a very delicate task. Considering the fact that fluorine is the most

Table 1.2 Characteristics of the group 17 elements

Colour	F Light yellow	Cl Yellow green	Br Red brown	I Black	At	E117	E171
Atomic number	9	17	35	53	85	117	171
Atomic weight	18.9984032 (5)	[35.446;35.457]	[79.901; 79.907]	126.90447 (3)	[210][a]	[294][b], [313][c]	[500][c]
Stable isotopes	19 (100 %)	35 (75.76 %), 37 (24.24 %)	79 (50.69 %), 81 (49.31 %)	127 (100 %)			
Melting point (°C)	−219.62	−101.5	−7.3	113.7	302	350 − 550	
Boiling point (°C)	−118.12	−34.04	59	184.3	337	610	
Electronegativity (pauling)	3.98	3.16	2.96	2.66	2.2		
Oxidation states	−I	−I, 0, + I, + III, + IV, +V, (+VI), +VII	−I, 0, + I, + III, + V, (+VII)	−I, 0, +I, +III, +V, +VII	−I, 0, +I, +III, +V, (+VII)	+I, +III	+I, +III, +V
Oxidation potential ($2X^- \leftrightarrow X_2 + 2e^-$, V)	+3.05	+1.36	+1.07	+0.54	+0.36	+0.25 − +0.5	
Ionic radius (X^-, pm)	119	167	182	206			
Year of discovery	1810, 1886	1774	1826	1811	1939	2010	Not discovered

Most data in this table are taken from data available at the WebElements internet site (http://www.webelements.com) authored by Dr Mark J Winter. Data from elements 117 en 171 are mostly taken from Seaborg (1968), Fricke and Waber (1971) and Fricke et al. (1971). The redox potential from astatine is taken from Champion et al. (2010), the atomic weights of the known elements are taken from Wieser et al. (2013) and their isotopic compositions from Berglund and Wieser (2011)

[a] Isotope with longest half life

[b] Isotope with longest known half life

[c] Undiscovered isotope with the longest expected half life