

Contents

Part I Introduction

1	The Halogen Elements	3
1.1	Discovery of the Halogen Elements	3
1.2	Abundance of the Halogen Elements	7
1.2.1	Abundance in the Solar System and on Earth	7
1.2.2	Distribution and Fluxes of Chlorine and Bromine Between Major Reservoirs on Earth	8
	References	12
2	Chlorine	15
2.1	Isotopes of Chlorine	15
2.1.1	Stable Isotopes	15
2.1.2	Notation of Stable Isotope Variations and Reference Standard	15
2.1.3	Radioactive Isotopes	16
2.2	Chemistry of Chlorine	16
	References	18
3	Bromine	21
3.1	Isotopes of Bromine	21
3.1.1	Stable Isotopes	21
3.1.2	Notation of Stable Isotope Variations and Reference Standard	21
3.1.3	Radioactive Isotopes	21
3.2	Chemistry of Bromine	22
	References	23

Part II Preparation Techniques

4 Preparation Techniques for the Analysis of Stable Chlorine Isotopes	27
4.1 Classical Methods	27
4.1.1 Gravimetric Determination of the Atomic Weight of Chlorine	27
4.1.2 Mass Spectrographic Analyses	28
4.1.3 Early Mass Spectrometric Analyses	28
4.2 General Methods to Analyse Stable Chlorine Isotopes	28
4.2.1 Methods Using Other Gases than Chloromethane in Dual Inlet IRMS	28
4.2.2 Application of Chloromethane in Dual-Inlet IRMS	29
4.2.3 Continuous Flow GC-IRMS	38
4.2.4 N-TIMS	39
4.2.5 P-TIMS	40
4.2.6 SIMS	42
4.2.7 Laser Ablation Multi Collector ICP-MS	42
4.2.8 Measurement of Chlorine Isotopes with Neutron Activation Analysis	43
4.2.9 Measurement of Chlorine Isotopes Using Fast Atom Bombardment Mass Spectrometry	43
4.2.10 Comparisons Between Different Measurement Techniques	43
4.3 Extraction of Chlorine from Silicate Rocks for Isotope Analysis	44
4.3.1 Alkali (NaOH) Fusion Method	44
4.3.2 Hydrogen Fluoride Decomposition Method	45
4.3.3 Pyrohydrolysis Methods	46
4.4 Extraction of Chloride from Non-silicate Rocks	46
4.4.1 Evaporites	47
4.4.2 Carbonatites	47
4.4.3 Other Non-silicate and Non-carbonate Minerals	47
4.5 Chlorine Isotopes in Chlorate and Perchlorate	47
4.5.1 Chlorate	47
4.5.2 Perchlorate	48
4.5.3 Collection of Perchlorate from Natural Samples Containing Low Perchlorate Concentrations	49
4.6 Chlorine Isotopes in Organic Molecules	49
4.6.1 Methods that Apply Reduction of Chlorine to Chloride	50
4.6.2 Measurement of Organochlorine Compounds Using TIMS	52
4.6.3 Techniques to Introduce Organic Molecules into a Mass Spectrometer Directly	53

4.6.4	Analysis of Chlorine Isotopes in Organic Molecules by ICP-MS	53
4.6.5	Analysis of Chlorine Isotopes by Quadrupole Mass Spectrometry	54
4.6.6	Measurement of Chlorine Isotopes in Organic Molecules After High Temperature Conversion	54
4.6.7	A Method for the Measurement of Stable Chlorine Isotopes in Polyvinylchloride.	55
4.7	Extraction of Chlorinated Solvents from (Ground)Water Samples	55
4.8	Extraction of Chloromethane from the Atmosphere for Isotope Analysis	55
4.9	Recapitulation of Analytical Methods	55
	References.	56
5	Preparation Techniques for the Analysis of Stable Bromine Isotopes	61
5.1	Early Attempts to Analyse Bromine Isotopes	61
5.2	Techniques to Separate Bromine from Chlorine in Natural Samples	61
5.3	Analysis of Stable Bromine Isotopes from Inorganic Bromides	62
5.3.1	N-TIMS.	62
5.3.2	P-TIMS	63
5.3.3	Dual Inlet IRMS	64
5.3.4	Continuous Flow GC-IRMS	64
5.3.5	Continuous Flow Analysis After GasBench II Chromatography.	65
5.3.6	ICP-MS	65
5.3.7	Measurement of Bromine Isotopes with Neutron Activation Analyses.	66
5.4	Measurements of Bromine Isotopes in Organic Molecules	66
5.4.1	Measurements by ICP-MS	66
5.4.2	High Temperature Conversion of Organic Molecules	67
5.4.3	Measurement of Bromine Isotope Compositions by Quadrupole Mass Spectrometry	67
5.5	Extraction of Bromomethane from the Atmosphere for Isotope Analysis	67
5.6	Recapitulation and Expectation of the Use of Bromine Isotope Measurements in the Near Future	68
	References.	68

Part III Theoretical and Experimental Estimates of Chlorine and Bromine Isotope Fractionation

6	Fractionation	73
	References	74
7	Theoretical and Experimental Fractionation Studies of Chloride and Bromide Isotopes	75
7.1	Diffusion	75
7.1.1	Diffusion of Chloride and Bromide in Aqueous Solutions	75
7.1.2	Diffusion in Molten Salts	82
7.2	Ion Filtration/Ion Exclusion	83
7.2.1	Theory	83
7.2.2	Experimental	84
7.3	Fractionation During Ion-Exchange Chromatography of Chloride	84
7.4	Salt Precipitation	85
7.4.1	Experimental Determination of the Chlorine Isotope Fractionation During Precipitation of Salt Minerals	86
7.4.2	Theoretical Isotope Fractionation Between Chlorides in Different Phases	87
7.5	Volcanic Systems	87
7.5.1	Chlorine Isotope Fractionation Between $\text{HCl}_{(\text{g})}$ and $\text{Cl}_{(\text{aq})}^-$	88
7.5.2	Chloride Isotope Fractionation During Ammonium Chloride Formation	88
7.5.3	Kinetic Fractionation Due to Hydrogen Chloride Escaping from an Acid Solution	88
7.6	High Temperature Equilibrium Fractionation in Rocks	89
7.7	Fractionation Due to Acid Displacement in Aerosols	89
7.7.1	Observations of Chlorine Isotope Variation on Aerosols	89
7.7.2	Experimental Determination on Hydrogen Chloride Escape in the Reaction of Sodium Chloride with Sulphuric Acid	90
7.8	Equilibrium Fractionation in Systems with Lesser Geologic Relevance	90
7.8.1	Equilibrium Fractionation Between Chloride and Hexchloroplatinate	90
7.8.2	Equilibrium Between Hydrogen Chloride Gas and Chlorides Dissolved in Glacial Acetic Acid	90
	References	91

8 Theoretical and Experimental Fractionation Between Species with Different Oxidation States	95
8.1 Theoretical Fractionation Between Chlorine and Bromine Species with Different Oxidation States	95
8.2 Experimental Determination of Isotope Fractionation Between Species with Different Oxidation States	96
8.2.1 Experimental Determination of Isotope Fractionation Between HX and X ₂ (X = Cl, Br)	96
8.2.2 Experimental Determination of Equilibrium Chlorine Isotope Fractionation Between Hypochlorous Acid (ClOH _{aq}) and Chloride (Cl _{aq} ⁻)	97
8.3 Microbial Reduction of Perchlorates	97
References	98
9 Isotope Fractionation Related to Organochlorine and Organobromine Compounds	101
9.1 Early Experimental Determination of Chlorine Isotope Fractionation	101
9.2 Theoretical Estimates on Chlorine Isotope Fractionation Between Organochlorine Molecules and Chloride	103
9.3 Modern Experimental Determination of Chlorine Isotope Fractionation in Organic Compounds	103
9.3.1 Chemical Fractionation Studies	104
9.3.2 Thermal Decomposition of 1,2-Dichloroethane in Air	104
9.3.3 Chlorine Isotope Fractionation Induced by Microbial Activity	105
9.3.4 Kinetic Fractionation of Organochlorine Compounds in the Environment	107
9.4 Isotope Fractionation of Bromine in Organic Compounds	109
References	110
Part IV Natural Chlorine and Bromine Isotope Variations	
10 Natural Variations of Stable Chlorine and Bromine Isotopes on Earth	115
10.1 The Hydrosphere	115
10.1.1 Oceans	116
10.1.2 Sediment Pore Water	118
10.1.3 Evaporites	127
10.1.4 Indications for the Existence of Larger Bromine Than Chlorine Isotope Variations During the Phanerozoic	129

10.2 The Mantle and Rocks Derived from It and Their Isotope Variation	130
10.2.1 The Chlorine Isotope Composition of the Mantle	130
10.2.2 Mantle Metasomatism	133
10.2.3 Chlorine Isotopes in Volcanic Systems	133
10.2.4 Oceanic Crust.	134
10.2.5 Chlorine Isotope Variations in Deep Sea Pore Waters and Their Relation to Serpentinites.	135
10.3 Continental Magmatic Rocks	137
10.4 Chlorine Isotopes in Fluid Inclusions.	137
10.5 Atmosphere	138
10.5.1 Chlorine	139
10.5.2 Bromine	139
References	139
11 Chlorine Isotope Characteristics of Extraterrestrial Material	145
11.1 Meteorites (Chondrites)	145
11.2 Moon	146
11.3 Mars	147
References	147
12 Isotope Variations of Perchlorates in the Environment	149
12.1 Introduction	149
12.2 Chlorine and Oxygen Stable Isotope Composition of Perchlorates	150
12.2.1 Natural Perchlorate	150
12.2.2 Synthetic Perchlorate	150
12.3 Isotopic Compositions of Perchlorates as Natural Tracers for Its Origin.	150
References	151
13 Isotope Variations of Organochlorine and Organobromine Compounds in Natural Environments	153
13.1 Introduction	153
13.2 Chlorine	153
13.2.1 Studies on the Dispersion of Chlorinated Solvents in Ground Waters	153
13.2.2 The Use of Chlorine Isotopes to Test the (Anthropogenic) Origin of a Chlorinated Compound	156
13.3 Bromine Isotopes in Naturally Occurring Organic Compounds	157
References	157

**Part V Historical Overview and Future Development
of Halogen Isotope Geochemistry**

14 Halogen Isotope Studies in Historical Perspective and Future Outlook	161
References.	167