Chlorine 17

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17-A. Crystal Chemistry

Minerals containing chlorine as a major constituent are chiefly binary and tertiary chlorides, oxychlorides and also borates, sulfates, phosphates and silicates.

The behavior of chlorine is completely non-metallic. In the ground state, the outer electrons of the Cl atom have the configuration $3s^2\,3p^6$. Chlorine occurs in the oxidation states -1, $+1$, $+3$, $+5$, $+7$. In its minerals, chlorine exists as Cl^- exclusively. The ionic radius of Cl^- has been found to be 1.81 Å (Goldschmidt, 1926, see Chapter 12 of Volume I of this handbook); Pauling and Huggins (1934) report a covalent tetrahedral radius of 0.99 Å. The electronegativity of Cl is determined as 3.0 (Pauling, 1960, see Chapter 12 of Volume I of this handbook).

I. Elementary Chlorine

Elementary chlorine is a diatomic gas (Cl—Cl intramolecular: 1.989 Å; Herzberg, 1950). In the crystalline state at $-160°$ C, the Cl_2 molecules are arranged in layers (Collin, SR 1952, 157) with an intramolecular distance of 1.980 Å (Donohue and Goodmann, 1965). There also exists a clathrate structure $Cl_2 \cdot 7\,^2/_3\,H_2O$ (Pauling and Marsh, SR 1952, 376).

The compounds XX'_n where X and X' are different halogen atoms which contain chlorine and iodine, are covered in Section 53-A.

II. Binary and Related Compounds

All elements, except the inert gases, form chlorides and some elements occur in several oxidation states in these compounds. Most chlorides are of ionic character; with the increasing ratio of charge to radius of the metallic ion, the covalency of the bonding increases. A large variety of structures exists due to the different valency, radius and polarizing power of the cations. According to the A—Cl bonds, these structures can be subdivided into framework, layer, chain and molecular structures (Wells, 1962). Table 17-A-1 contains several examples of structure types including data on coordination numbers and coordination polyhedra around chlorine.

$HCl \cdot H_2O$ consists of layers $H_3O^+Cl^-$ (O … Cl: 2.95 Å) (Yoon and Carpenter, SR 1959, 293). In $HCl \cdot 2\,H_2O$, puckered layers of Cl^- are connected by hydrogen bonds of $H_5O_2^+$: O … O: 2.41 Å; O … Cl: 3.04—3.10 Å (Lundgren and Olovsson, 1967a). The structure of $HCl \cdot 3\,H_2O$ may be written as $H_5O_2^+Cl^- \cdot H_2O$ with O … Cl: 3.01—3.13 Å (Lundgren and Olovsson, 1967b).

III. Hydrates of Binary Chlorides

Several of the binary metal chlorides form hydrates which contain different numbers of water molecules per formula unit. A few of these compounds occur in nature. Examples of different types of hydrates of binary chlorides are given in Table 17-A-2.

Table 17-A-1. *Examples of binary chlorides*

Coordination number of chlorine	Structure-type	Compounds, mineral names, interatomic distances	Reference
8	$Cs^{[8]}Cl^{[8]}$	α-NH_4Cl (salmiac)	Havinghurst, Mack and Blake (SB 1913—28, 99), Kuwabara (SR 1959, 295)
		$CsCl^{a}$ Cs-Cl: 3.57 Å	Wyckoff (SB 1913—28, 97)
6	$Na^{[6]}Cl^{[6]}$	NaCl (halite)[b] Na—Cl: 2.82 Å	Bragg and Bragg (SB 1913—28, 103)
		KCl (sylvite) K-Cl: 3.14 Å	Bragg (SB 1913—28, 105)
		AgCl (cerargyrite) Ag-Cl: 2.77 Å	Wilsey (SB 1913—28, 111)
		LiCl, RbCl[c]	Wyckoff (SB 1913—28, 97)
4	α-$Zn^{[4]}S^{[4]}$	CuCl (nantokite)[aa]	Wyckoff and Posnjak (SB 1913—28, 110)
	$Ca^{[8]}F_2^{[4]}$	$SrCl_2$	Mark and Tolksdorf (SB 1913—28, 187)
3 (approx. planar triangular)	$Ca^{[6]}Cl_2^{[3]}$ bb	$CaCl_2$ (hydrophilite)	van Bever and Nieuwenkamp (SB 1933—35, 278)
3 (pyramidal triangular)	$Cd^{[6]}Cl_2^{[3]}$	$MnCl_2$ (scacchite) $FeCl_2$ (lawrencite) $MgCl_2$ (chloromagnesite)	Pauling (SB 1913—28, 774); Bruni and Ferrari (SB 1913—28, 773)
		$NiCl_2$ Ni-Cl: 2.426 Å[cc]	Ferrari, Braibanti, Bigliardi (1963)
	$Cd^{[6]}I_2^{[3]}$	VCl_2	Villadsen (SR 1959, 298)
	$U^{[9]}Cl_3^{[3]}$	$LaCl_3$	Zachariasen (SR 1947—48, 277)
	$Cu^{[4+2]}Cl_2^{[2+1]}$	$CuCl_2$[ab] Cu-Cl: 2.29 Å (4×) 2.98 Å (2×)	Wells (SR 1947—48, 263)
2 (angular)	$Bi^{[6]}I_3^{[2]}$	$FeCl_3$ (molysite) Fe-Cl: 2.39 Å	Wooster (SB 1928—32, 293) Gregory (SR 1951, 151)
	$Cr^{[6]}Cl_3^{[2]}$	$CrCl_3$	Wooster (SB 1928—32, 292)
	$Hg^{[4]}I_2^{[2]}$	γ-$ZnCl_2$[ac] Zn-Cl: 2.27 Å	Brehler (SR 1959, 297)
	α-$Zn^{[4]}Cl_2^{[2]}$	α-$ZnCl_2$[ac] Zn-Cl: 2.34 Å	Brehler (SR 1959, 297)
5/4	$Pb^{[7+2]}Cl^{[5]}Cl^{[4]}$	$PbCl_2$ (cotunnite) Pb-Cl: 2.86—3.08 Å (7×) 3.64 Å (2×)	Braekken and Harang (SB 1928—32, 251) Sahl and Zemann (SR 1961, 324)

Table 17-A-1 (continued)

Coordination number of chlorine	Structure-type	Compounds, mineral names, interatomic distances	Reference
Molecular structures	α-$W^{[6]}Cl_6^{[1]}$	α-WCl_6	Ketelaar and van Oosterhout (SR 1942—44, 159); Smith *et al.* (1968)
	$Sb^{[3]}Cl_3^{[1]}$	$SbCl_3$ Sb-Cl: 2.36 Å (av.) (3×)	Lindquist and Niggli (SR 1956, 240)
	$[Hg_2^{[1]}]Cl_2$	α-Hg_2Cl_2 (calomel)	Hylleras (SB 1913—28, 256)
	$Nb_2^{[6]}Cl_2^{[2]}Cl_8^{[1]}$	$NbCl_5$ Nb-Cl: 2.555 (2×) 2.250 (2×) 2.302 (2×)	Zalkin and Sanos (SR 1958, 237)
		B_8Cl_8 B-Cl: 1.70 Å (av.)	Atoj and Lipscomb (SR 1959, 303) Jacobson and Lipscomb (SR 1959, 303)

[a] Above 460° C, CsCl crystallizes in the NaCl-type (West, SB 1933—35, 231).

[b] NaCl and NaBr form solid solutions (Nickels, Fineman, Wallace, SR 1949, 285)

[c] Under high pressures, RbCl crystallizes in the CsCl-type (Vereščagin and Kabalkina, SR 1957, 215).

[aa] Above 407° C, CuCl crystallizes in the wurtzite-type (Lorenz and Preuer, SR 1956, 237).

[bb] The $CaCl_2$-type is a weakly deformed rutile structure.

[cc] The distance Ni-Cl is shorter than the sum of their ionic radii; Cl-Cl (in the octahedra): 3.85 and 3.48 Å; Cl-Cl (between different octahedra): 3.67 Å.

[ab] Melanothallite has the composition $CuCl_2$ or $Cu(Cl, OH)_2$.

[ac] The distance Zn-Cl is significantly shorter than the sum of their ionic radii, its value is approximately that of the sum of tetrahedral radii.

IV. Complex Chlorides

Many unhydrated and hydrated complex chlorides exist and a few of them form minerals. The complex chlorides can be subdivided according to structural units and a systematic treatment has been given by Wells (1962). Ijdo (1962) has studied the structures and properties of a series of chlorides and complex chlorides of the group b metals. Tables 17-A-3 and 17-A-4 give examples of complex chlorides.

Many of the well known simple and complex halide hydrates can contain hydrogen bonds. A detailed discussion of the relations between chlorine atoms and water molecules and of the probable hydrogen bonding in chloride hydrates of divalent metals has been given by Jensen (1969). He reports distances between 3.07 Å and 3.33 Å for linear and bended O—Cl-hydrogen bridges and values between 3.22 Å and 3.45 Å for bifurcated bridges.

V. Oxychlorides and Related Compounds

There are many compounds containing both oxygen or OH in addition to chlorine and/or different halogen atoms.

Table 17-A-2. *Hydrated binary chlorides*

Compound (mineral name)	Structural formula, interatomic distances etc.	Reference
$\mathrm{ZnCl_2 \cdot 1^1/_3\,H_2O}$	$\mathrm{Zn^{[4,2]}(H_2O)_4\,Zn^{[4]}Cl_3}$ $\mathrm{Zn^{[4]}}$-Cl: 2.24—2.35 Å $\mathrm{Zn^{[4,2]}}$-$\mathrm{OH_2}$: 2.02 Å (4×) ..-$\mathrm{Cl^{a}}$: 2.60 Å (2×)	FOLLNER and BREHLER (1970)
$\mathrm{CuCl_2 \cdot 2\,H_2O}$ (eriochalcite)	$\mathrm{Cu^{[4+2]}Cl_2(H_2O)_2}$ Cu-Cl: 2.27 Å Cu-O: 1.92 Å	PETERSON and LEVY (SR 1957, 397)
$\mathrm{NiCl_2 \cdot 4\,H_2O}$	$\mathrm{[Ni(H_2O)_4]_2NiCl_2}$ Ni-$\mathrm{OH_2}$: 2.13 Å	STROGANOV, KOŽINA, ANDREEV and KOLJADIN (SR 1960, 282)[a]
$\mathrm{FeCl_2 \cdot 4\,H_2O}$	$\mathrm{Fe^{[4,2]}(H_2O)_4Cl_2}$ Fe-Cl: 2.53 Å Fe-$\mathrm{OH_2}$: 2.12 Å, 2.08 Å	PENFOLD and GRIGOR (SR 1959, 299) MEUNIER-PIRET and VAN MEERSSCHE (1971)
$\mathrm{CoCl_2 \cdot 6\,H_2O}$	$\mathrm{[Co^{[4,2]}(H_2O)_4Cl_2] \cdot 2\,H_2O}$	STROGANOV, KOŽINA and ANDREEV (SR 1958, 240) MIZUNO, UKEI and SUGAWARA (SR 1960, 280)[b] EL SAFFAR (SR 1962, 435)
$\mathrm{AlCl_3 \cdot 6\,H_2O}$ (chloroalluminite)	$\mathrm{[Al(H_2O)_6]Cl}$ Al-$\mathrm{OH_2}$: 3.03 Å	BUCHANAM and HARRIS (1968) EL SAFFAR and MULCAHY (1971)
$\mathrm{MgCl_2 \cdot 6\,H_2O}$ (bischofite)	$\mathrm{[Mg^{[6]}(H_2O)_6]Cl_2}$	ANDRESS and GUNDERMANN (SB 1933—35, 489)
$\mathrm{MgCl_2 \cdot 12\,H_2O}$	$\mathrm{[Mg(H_2O)_6]Cl_2^{[6H_2O]}(H_2O)_6}$ Cl-$\mathrm{OH_2}$: 3.17—3.23 Å	SASVÁRI and JEFFREY (1966)

[a] $\mathrm{NiCl_2 \cdot 6\,H_2O}$ is isotypic with $\mathrm{CoCl_2 \cdot 6\,H_2O}$ (STROGANOV, KOŽINA and ANDREEV, SR 1960, 282).

[b] The interatomic distances found in the two investigations are very different.

Oxychlorides and hydroxychlorides have some mineralogical importance. The naturally-occurring compounds of these types are listed by STRUNZ (1970); examples are given in Table 17-A-5.

VI. Chlorites, Chlorates, Perchlorates

Chlorine forms salts of the acids $\mathrm{HClO_2}$, $\mathrm{HClO_3}$ and $\mathrm{HClO_4}$ with several metal ions; examples are given in Table 17-A-6.

Considering the average Cl—O distance in the different $\mathrm{ClO_x^-}$ species, there seems to be a correlation between this distance and the oxidation state of Cl (GILLESPIE, SPARKS and TRUEBLOOD, SR 1959, 458) (see Table 17-A-7).

Perchlorates are known of all electropositive metals. They are often isotypic with the sulfates, permanganates etc.

Table 17-A-3. *Selected examples of complex chlorides*

Compound	Mineral name, interatomic distances	Reference
$K_4[MnCl_6]$	chloromanganokalite[a]	Bellanca (SR 1947—48, 413)
$K_3Na[FeCl_6]$	rinneite[a]	Bellanca (SR 1947—48, 415)
$K_2[FeCl_5OH_2]$	erythrosiderite[a]	Bellanca (SR 1947—48, 419)
$K_2[Pt^{[4\ pl]}Cl_4]$	Pt-Cl: 2.308 Å K-Cl: 3.239 Å	Dickinson (SB 1913—28, 224) Mais *et al.* (1972)
$CsNi^{[6]}Cl_3$[b]	Ni-Cl: 2.43 Å	Tiščenko (SR 1955, 332)
$CsPb^{[6]}Cl_3$[c]	perovskite	Møller (SR 1959, 304)
$Cs_3Tl_2^{[6]}Cl_9$[aa]		Hoard and Goldstein (SR 1933—35, 505)
$Cs_3[CoCl_4]Cl$		Powell and Wells (SR 1935, 498)

[a] Minerals of the same structure type.

[b] In $CsNiCl_3$, chlorine and caesium are forming a hcp; Ni occupies those octahedral holes which are only coordinated by chlorine. A further isotypic substance is, e.g., $CsCrCl_3$ (Seifert and Klatky, SR 1962, 457).

[c] Further isotypic substances are $CsCdCl_3$ and $CsHgCl_3$ (Náray-Szabó, SR 1947—48, 454).

[aa] $Cs_3Tl_2Cl_9$ is built up of a close packing of Cs^+ and Cl^- with Tl^{3+} in certain pairs of adjacent octahedral holes.

Table 17-A-4. *Hydrated complex chlorides*

Compound	Mineral name, interatomic distances	Reference
$K^{[6]}Cl_3Mg(OH_2)_6$	carnallite Cl-K: 3.17—3.33 Å Cl-H_2O: 3.10—3.23 Å	Fischer (1973)
$K[Zn^{[3,1]}Cl_3OH_2]\cdot H_2O$	Zn-Cl: 2.25 Å Cl-H_2O: 3.20—3.40 Å	Süsse and Brehler (SR 1964, 278)
$K[Zn^{[3,1]}Cl_3OH_2]$	Zn-Cl: 2.26 Å Cl-H_2O: 3.11 Å	Brehler and König (1969)
$Na(OH_2)_3[Zn^{[4]}Cl_4]$	Zn-Cl: 2.32 Å (1 ×) Zn-Cl: 2.27 Å (3 ×) Cl-H_2O: 3.26 Å	Brehler (SR 1960, 289) Brehler and Trunz (unpublished)
$[Co(NH_3)_4(H_2O)_2]\ [Tl^{[6]}Cl_6]$	Tl-Cl: 2.54 Å	Linhabo, Manthey and Plieth (SR 1953, 353)

VII. Sulfates, Phosphates, Silicates, etc.

There are some additional minerals (Table 17-A-8) and synthetic compounds containing Cl in its anions. In several of these compounds Cl is able to replace OH partially.

Several additional details about the crystal chemistry of chlorine are given by Wells (1962).

Table 17-A-5. *Selected examples of oxychlorides and related compounds*

Compound	Mineral name, interatomic distances	Reference
BiOCl[a]	bismoclite	Bannister and Hey (SB 1933—35, 370)
PbFCl[a]	matlockite Cl-Pb: 3.07 Å (4×) 3.21 Å (1×)	Nieuwenkamp and Bijvoet (SB 1928—32, 232)
PbOHCl	laurionite	Brasseur (SR 1940—41, 131)
$PbSbO_2Cl$	nadorite	Sillén and Melander (SR 1950, 307)
$Cu_2(OH)_3Cl$	atacamite[b]	Wells (SR 1949, 20)
$Pb_2Cu(OH)_4Cl_2$	diaboleite Cl-Pb: 3.215 Å (2×) 3.430 Å (2×) Cl-Cu: 2.548 Å 2.946 Å	Rouse (1971)
$Pb_{26}Ag_9Cu_{24}Cl_{62}(OH)_{48}$	boleite Cl-Pb: 2.94—3.31 Å Cl-Cu: 2.85—2.91 Å Cl-Ag: 2.52—2.83 Å	Rouse (1973a)
$Pb_4Fe_3O_8Cl$	hematophanite Cl-Pb: 3.29 Å, 3.33 Å	Rouse (1973 b)
$Hg_4O_2Cl_2$	terlinguaite Cl-Hg(I): 3.25 Å Cl-Hg(II): 2.80 Å Cl-Hg(III): 2.57 Å	Šćavničar (SR 1956, 242)
Pb_3O_2Cl	probably identical with mendipite	Vincent and Perrault (1971)

[a] BiOCl bas been found isotypical with PbFCl. In the PbFCl-type, the Cl atoms are on the outer sides of layers $ClPbF_2PbCl$. The Cl atoms have four Pb-neighbors in one layer and a fifth one in the next layer. FeOCl crystallizes similar to PbFCl.

[b] Closely related to atacamite is the other modification of $Cu_2(OH)_3Cl$, paratacamite (atellite) (Frondel, SR 1950, 201).

Table 17-A-6. *Examples of chlorites, chlorates and perchlorates*

Compound	Reference
$NH_4[ClO_2]$[a]	Gillespie, Sparks and Trueblood (SR 1959, 458)
$Ag[ClO_2]$[b]	Curti, Rigandi and Locchi (SR 1957, 355)
$Na[ClO_3]$	Zachariasen (SR 1928—32, 407): Aravindashan (SR 1959, 460)
$NH_4[ClO_3]$	Gillespie, Gantzel and Trueblood (SR 1962, 641)
$K[ClO_4]$[c]	Gottfried and Schusterius (SB 1928—29, 413); Mani (SR 1957, 358)
$Ba(OH_2)_3[ClO_4]_2$	Mani and Ramaseshan (SR 1960, 438)

[a] $HClO_4 \cdot H_2O$ is isotypic with NH_4ClO_4 (Volmer, SB 1928—32, 415; Lee and Carpenter, SR 1959, 461). Proton magnetic resonance confirms the formula $H_3O^+ClO_4^-$ (Kakiuchi, Shono, Komatsu and Kigdshi, SR 1952, 283).

[b] In $AgClO_2$, discrete $AgClO_2$ molecules exist rather than Ag^+ and ClO_2^- ions.

[c] The structure is isotypic with $BaSO_4$, baryte. $KClO_4$ forms a high temperature modification (Hermann and Ilge, SB 1928—32, 411); the high temperature modifications of Na, K, Rb, Cs, NH_4, Tl and Ag perchlorate are isotypical.

Table 17-A-7. *Cl-O distance and O-Cl-O angle in ClO_x^-*

	Cl-O distance (Å)	O-Cl-O angle (°)	Atomic arrangement
ClO_4^-	1.44	109.5	tetrahedral
ClO_3^-	1.46	108	pyramidal
ClO_2^-	1.57	110.5	angular

Table 17-A-8. *Examples of Cl-bearing sulfates, phosphates, silicates, etc.*

Compound	Mineral name	Reference
$KMgCl[SO_4]\cdot 2^3/_4\ H_2O$	kainite	ROBINSON, FANG and OHTA (1972)
$Na_{21}MgCl_3[SO_4]_{10}$	d'ansite	BURZLAFF and HELLNER (SR 1961, 453)
$KNa_{22}Cl[SO_4]_9[CO_3]_2$	hanksite	KATO and SAALFELD (1972)
$Pb_2Na_3Cl[SO_4]_3$	caracolite[a]	SCHNEIDER (1967; 1969)
$Ca_5Cl[PO_4]_3$	chlorine apatite[b]	HENDRICKS and JEFFERSON (SR 1928—32, 458); TABORSZKY (1972)
$Pb_5Cl[PO_4]_3$	pyromorphite	HENDRICKS and JEFFERSON (SR 1928—32, 458) WONDRATSCHEK (1963) FÖRTSCH and WONDRATSCHEK (1965)
$Pb_5Cl[AsO_4]_3$	mimetesite	HENDRICKS and JEFFERSON (SR 1928—32, 458) KEPPLER (1969)
$Al_{12}^{[6]}Al^{[4]}O_4(OH, F)_{18}Cl[Si_5O_{16}]$	zunyite	KAMB (SR 1960, 474)
$Ba_4Ti_4(Ti, Nb, Fe)Cl\ O_{16}[Si_4O_{12}]$	baotite	NEKRAŠOV *et al.* (1969)
$(Mn, Fe)_8(OH)_9Cl[Si_6O_{15}]$	pyrosmalite	KASHAEV (1967)
$Na_8Cl_2[Si_6Al_6O_{24}]$	sodalite[c]	LÖNS and SCHULZ (1967)
$Na_4Cl[Si_8Al_4O_{24}]$	marialite	PAPIKE and ZOLTAI (1965)
β-$Mg_3Cl[B_7O_{13}]$	boracite	ITO, MORIMOTO and SADANAGA (SR 1951, 282)
$Ca_3Na_2Cl[SO_4]_2[B_5O_8(OH)_2]$	heidornite[aa]	BURZLAFF (1967)
$CuCl[B(OH)_4]$	bandylite	FORNASERI (SR 1950, 346); COLLIN (SR 1950, 346)
$Na_2Cl[B(OH)_4]$	teepleite	FORNASERI (SR 1949, 263)
$Fe_2^{3+}H_3[TeO_3]_4Cl$	rodalquilarite	DUSAUSOY and PROTAS (1969)

[a] Caracolite is isotypical with chlorine apatite.

[b] A synopsis of apatite research has been given by McCONNEL (1973). In the apatite-group minerals, Cl is octahedrally coordinated by cations.

[c] Cl is tetrahedrally coordinated by 4 Na with Na-Cl: 2.73 Å.

[aa] In heidornite, Cl is octahedrally coordinated: Cl-Na· 3.02 Å (2×); Cl-Ca: 2.83 Å; Cl-H: 2.27 Å (2×).

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17-B. Isotopes in Nature

There are two stable isotopes of chlorine, ^{35}Cl and ^{37}Cl, their natural abundances being 75.53% and 24.47%, respectively (Boyd *et al.*, 1955). The atomic weight of chlorine is 35.453 (Heath, 1971).

Nine unstable isotopes of chlorine are known: ^{32}Cl, ^{33}Cl, ^{34m}Cl, ^{34}Cl, ^{36}Cl, ^{38}Cl, ^{38m}Cl ^{39}Cl, and ^{40}Cl (Heath, 1971).

I. Stable Isotopes

Several workers have determined the isotopic abundance of ^{35}Cl and ^{37}Cl in geological samples. Baertschi (1953) found no fractionation of these isotopes in Atlantic Ocean water, and Owen and Schaeffer (1955) similarly found no isotopic variation in several rocks and a sample of sodium chloride.

The most extensive work on the natural abundance of the stable isotopes of chlorine was that of Hoering and Parker (1961). These workers determined the isotopic composition of Gulf of Mexico and Pacific Ocean water, oil well brines, chloride minerals including volcanic sublimates, rocks, minerals and stony meteorites (these were all "finds", therefore, much of the chlorine may be of terrestrial origin). From their results, these workers concluded that no large-scale isotopic fractionation occurs in nature.

More recently, Morton and Catanzaro (1964) have determined the chlorine isotope ratio of five Precambrian apatites, including both original high chlorine apatite and metasomatised low chlorine apatite; they found that no isotope fractionation occurs during original emplacement or during subsequent metasomatism.

II. Unstable Isotopes

^{36}Cl has a half-life of 3.1×10^5 years (Heath, 1971) and decays to ^{36}Ar.

The terrestrial distribution of ^{36}Cl was studied by Davis and Schaeffer (1955) and they examined several chlorine-containing materials for the presence of ^{36}Cl, which they considered to be formed essentially from the action of cosmic ray neutrons and neutrons derived from spontaneous fission of uranium. Appreciable amounts of ^{36}Cl were found in a phonolite from an altitude of 3.5 km, but no detectable ^{36}Cl was found in a nepheline sodalite from a low altitude locality. In addition the isotope was not detected in Atlantic Ocean water or in the Great Salt Lake of Utah.

Schaeffer *et al.* (1960) determined the concentration of ^{36}Cl in rain water and other natural waters. These workers concluded that ^{36}Cl production in the atmosphere from cosmic ray interaction with argon, was insufficient to account for all of the observed concentrations of the isotope in natural waters; they suggested that another source of ^{36}Cl resulted from neutron irradiation of sea water by marine nuclear explosions.

Some values for ^{36}Cl in terrestrial materials are given in Table 17-B-1.

Table 17-B-1. *^{36}Cl in terrestrial materials*

Sample	^{36}Cl activity (d.p.m.[a] per gram Cl)	^{36}Cl content (g ^{36}Cl/g Cl[b])	Reference
Pitchblende: Great Bear Lake, M. W. T., Canada	17	2.40×10^{-10}	Jonte (1956)[c]
	4	5.64×10^{-11}	Kuroda *et al.* (1957)
Latite phonolite: Bull Cliff, Cripple Creek, Colorado, U.S.A.	0.12	1.69×10^{-12}	Davies and Schaeffer (1955)
Spring water: Hot Springs National Park, Arkansas, U.S.A.	2.1	2.96×10^{-11}	Jonte (1956)[c]
Petroleum brine (very high in Ra)	1.9	2.68×10^{-11}	Jonte (1956)[c]
Well water: Long Island, U.S.A.	1.02	1.44×10^{-11}	Schaeffer *et al.* (1960)
Stream: Vermont, U.S.A.	0.56	7.90×10^{-12}	Schaeffer *et al.* (1960)
Lake Ronkonkoma: U.S.A.	0.28	3.95×10^{-12}	Schaeffer *et al.* (1960)
Rain water: U.S.A.	0.80—12.2	1.13×10^{-11} to 1.72×10^{-10}	Schaeffer *et al.* (1960)
	[Mean (5) = 5.9]	(Mean 8.32×10^{-11})	

[a] d.p.m. = disintegrations per minute.

[b] assuming 100% counting efficiency.

[c] J. H. Jonte, Ph. D. thesis, University of Arkansas—quoted by Rankama (1963).

Table 17-B-2. *Concentration of radioisotopes ^{34m}Cl, ^{38}Cl, and ^{39}Cl in rain water*

Sample (locality, dates collected, reference)	^{34m}Cl		^{38}Cl		^{39}Cl	
	d.p.m.[a]/liter	atoms/liter[b]	d.p.m.[a]/liter	atoms/liter[b]	d.p.m.[a]/liter	atoms/liter[b]
Bombay, India, 7/8/64—2/8/65,	0.45; 0.9	21; 42	—		2.1—15.7	117—1.257
Bhandari *et al.* (1966)	(Mean (2) = 0.7)	32	(Mean (5) = 13.3)	716	(Mean (12) = 8.2)	657
Richland, Washington,	0.3—1.5	14—69	9—147	484—7,912	15—200	833—16,017
U.S.A., 29/7/64—26/1/67,	(Mean (7) = 0.9)	42	(Mean (10) = 58.8)	3,165	(Mean (10) = 84.2)	6,743
Wogman *et al.* (1968)						

[a] d. p. m. = disintegrations per minute. [b] Assuming 100% counting efficiency.

^{36}Cl occurs in iron meteorites where it is derived from spallation of the metal due to exposure to cosmic radiation. According to Goel (1964) it can also be derived in large iron meteorites from neutron capture reactions on the lawrencite inclusions within the metal. ^{36}Cl decays to ^{36}Ar and the ^{36}Ar/^{36}Cl ratio in iron meteorites has been used to determine their cosmic ray exposure ages and terrestrial ages (Schaeffer and Heymann, 1965; Vilcsek and Wänke, 1963; see also Honda and Arnold, 1964, and Matsuda *et al.*, 1970).

Cosmic-ray produced ^{36}Cl has been found in lunar samples by several workers (Begemann *et al.*, 1970; Shedlovsky *et al.*, 1970).

The respective half-lives of ^{34m}Cl, ^{38}Cl, and ^{39}Cl are: 32.0 minutes, 37.3 minutes, and 55.5 minutes (Heath, 1971). These three radio-isotopes which are produced in the troposphere by cosmic ray interaction with argon, have been studied in conjunction with their possible use as radioactive tracers for the study of short-term tropospheric processes (Bhandari *et al.*, 1966).

^{39}Cl was first detected in rain water by Winsberg (1956), while ^{38}Cl was first detected in rainwater by Perkins *et al.* (1965) and Bhandari *et al.* (1966); these latter workers also detected ^{34m}Cl.

Bhandari *et al.* (1966) found that the production rate of these radioisotopes of chlorine increases with altitude. Wogman *et al.* (1968) observed that the concentrations of these isotopes varies inversely with precipitation, a fact which helps to explain the large degree of variation shown between the results of various workers (see Table 17-B-2). Engelman and Perkins (1971) stated that ^{39}Cl and ^{38}Cl production rates are such that their equilibrium concentrations are in a ratio of about 1.5:1 in the atmosphere; this ratio can vary markedly during precipitation.

The other radioisotopes of chlorine have very short half-lives; apart from ^{40}Cl with a half-life of 1.4 minutes, the rest have half-lives of less than 2.5 seconds (Heath, 1971). There is no information regarding the occurrence of these isotopes in nature.

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17-C. Abundance in Cosmos, Meteorites, Tektites and Lunar Samples

I. Cosmos

Several values have been proposed for the cosmic abundance of chlorine (Cameron, 1966, 1968) having been derived mainly from analytical data for meteorites. Recently, Lambert *et al.* (1971) have proposed a cosmic abundance of 5.5—5.8 log N(Cl), based on their observed solar abundance and that for the Orion Nebula (Table 17-C-1).

Table 17-C-1. *Extraterrestrial chlorine abundances*

System	Abundance log N (Cl) (where log N (H) = 12.00)	Reference
γ Pegasi	6.25	Aller (1961)
Orion Nebula	~5.8	Lambert *et al.* (1971)
Planetary Nebula	6.9	Aller and Cryzak (1968)
Sun (upper limit)	≦5.5	Lambert *et al.* (1971)
Cosmos	5.5—5.8	Lambert *et al.* (1971)[a]
Cosmos	4.84	Cameron (1968)[b]

[a] Based on Solar and Orion Nebula abundances.

[b] Based essentially on Cc$_1$ meteoritic abundances.

II. Meteorites

a) Stones

The chlorine content of chondritic meteorites varies from less than one ppm to almost 0.1%. In achondrites, the chlorine values are generally comparable with the lowest values for chondrites.

From the values listed in Tables 17-C-2 to 17-C-4, it is apparent that several of the earlier estimates of chlorine abundance in meteorites are much too high (Noddack and Noddack, 1930; Rankama and Sahama, 1950; Salpeter, 1952).

Greenland and Lovering (1965) have analysed "falls" and "finds" from the CL and CH classes. The results given in Table 17-C-5 show that the mean chlorine values for the "finds" of both classes are at least double those of the "falls".

There are marked differences in the chlorine contents of the various classes of chondrites (Table 17-C-6), the values for the carbonaceous and enstatite (Ce$_1$) chondrite classes being generally much greater than those for ordinary chondrites. Chlorine has been classed by Larimer and Anders (1967) as a strongly depleted element in chondritic meteorites.

A major host mineral for chlorine in chondrites is chlorapatite, which has been to found contain 3 to 6% Cl and 0.1 to 0.4% F (Fuchs, 1969; van Schmus and

Table 17-C-2. *Chlorine in carbonaceous and enstatite chondrites*

Class	Meteorite	Number of samples	Cl (ppm)	Method	Reference
Cc_1	Orgueil	1	290	C	Greenland and Lovering (1965)
		1	210	N/R	Reed and Allen (1966)
		3	720	N/R	Goles *et al.* (1967)
	Ivuna	2	280	N/R	Reed and Allen (1966)
		1	750	N/R	Goles *et al.* (1967)
Cc_2	Mighei	1	350	N/R	Reed and Allen (1966)
		2	470	N/R	Goles *et al.* (1967)
	Murray	2	200	N/R	Goles *et al.* (1967)
		1	108	N/R	Quijano-Rico and Wänke (1969)
CHL	Lancé	1	350	C	Greenland and Lovering (1965)
		1	125	N/R	Reed and Allen (1966)
		2	277	N/R	Goles *et al.* (1967)
		1	248	N/R	Quijano-Rico and Wänke (1969)
	Karoonda	1	310	C	Greenland and Lovering (1965)
		1	117	N/R	Reed and Allen (1966)
		1	45	N/R	Quijano-Rico and Wänke (1969)
	Mokoia	1	370	C	Greenland and Lovering (1965)
	Warrenton	1	360	C	Greenland and Lovering (1965)
	Felix	1	270	N/R	Goles *et al.* (1967)
	Grosnaja	1	423	N/R	Quijano-Rico and Wänke (1969)
Ce_1	Abee	2	500	N/R	von Gunten *et al.* (1965)
		1	432	N/R	Reed and Allen (1966)
		1	750	N/R	Goles *et al.* (1967)
		1	994	N/R	Quijano-Rico and Wänke (1969)
	Indarch	1	900	C	Greenland and Lovering (1965)
		2	675	N/R	Reed and Allen (1966)
		1	570	N/R	Goles *et al.* (1967)
Cc_1	St Marks	1	210	C	Greenland and Lovering (1965)
Ce_2	Hvittis	2	222	N/R	von Gunten *et al.* (1965)
		1	250	C	Greenland and Lovering (1965)
		1	323	N/R	Reed and Allen (1966)
		2	144	N/R	Goles *et al.* (1967)
		1	234	N/R	Quijano-Rico and Wänke (1969)
	Khairpur	1	230	C	Greenland and Lovering (1965)
	Pillistfer	1	160	C	Greenland and Lovering (1965)

Ribbe, 1969); meteoritic chlorapatite was first identified by Shannon and Larsen (1925) in the New Concord chondrite. Fuchs (1969) lists the following chondrites in which chlorapatite has been identified: CL class = Ariba, Bruderheim, Harleton, Ness County, New Concord, Shaw and Walters; LL class = Soko-Banja; CHL class = Karoonda. Van Schmus and Ribbe (1969) have identified and analysed chlorapatite in the CH class Djati-Pengilon, the CL class Forksville and the CLL class Manbhoom.

The chlorine content of meteoritic chlorapatite so far analysed is insufficient to balance the formula $Ca_5(PO_4)_3Cl$. Van Schmus and Ribbe (1969) have found small quantities of fluorine in two chondritic meteorites and they assume that small

Table 17-C-3. *Chlorine in ordinary chondrites* (falls only; average values)

Class	Number of samples	Chlorine (range in ppm)	Mean (ppm)	Method	Reference
CH	1		97	N/R	von Gunten *et al.* (1965)
	4	57—170	127	C	Greenland and Lovering (1965)
	2	0.44, 9.05	4.7	N/R	Reed and Allen (1966)
	1		77	N/R	Goles *et al.* (1967)
	23	7—210	82	N/R	Quijano-Rico and Wänke (1969)
CL	4	27—136	93	N/R	von Gunten *et al.* (1965)
	9	92—270	174	C	Greenland and Lovering (1965)
	4	11.1—71	35	N/R	Reed and Allen (1966)
	5	42—124	80	N/R	Goles *et al.* (1967)
	8	27—212	76	N/R	Quijano-Rico and Wänke (1969)
CLL	2	57, 266	162	N/R	von Gunten *et al.* (1965)
	2	89, 230	160	C	Greenland and Lovering (1965)
	2	121, 131	126	N/R	Quijano-Rico and Wänke (1969)
	1		190	N/R	Goles *et al.* (1967)

Table 17-C-4. *Chlorine in achondrites*

Class	Meteorite	ppm Cl (method)	Reference
Ae	Norton County	3.8 (N/R)	von Gunten *et al.* (1965)
Ab	Johnstown	13.0 (N/R)	Quijano-Rico and Wänke (1969)
Aor	Frankfort	14.9 (N/R)	Reed and Jovanovic (1969)
Ap	Moore County	23.8 (N/R)	Reed and Jovanovic (1969)
	Juvinas	18.0 (N/R)	Quijano-Rico and Wänke (1969)
	Pasamonte	8.0 (N/R)	Quijano-Rico and Wänke (1969)
	Stannern	34.5 (N/R)	Quijano-Rico and Wänke (1969)

Table 17-C-5. *Comparison of chlorine content of "falls" and "finds"* (from Greenland and Lovering, 1965; method: C)

Meteorite class	Number of samples	Mean Cl (ppm)	Standard deviation
CL "falls"	11	170	58.4
CL "finds"	20	349.5	211.6
CH "falls"	4	194.9	—
CH "finds"	4	560.5	—

Table 17-C-6. *The relative abundance of chlorine in the various classes of chondrites* (from LARIMER and ANDERS, 1967)

Class	Atoms/10^6 atoms Si	Depletion or enrichment (factor relative to Cc_1 meteorites)
Cc_1	2,000	
Cc_2	2,100	1.1
CHL	1,800	0.93
Ordinary chondrites	41	0.021
Ce_1	3,100	1.6
Ce_2	720	0.37

quantities of the hydroxyl ion are also present. They have, therefore, suggested that the essential composition of meteoritic chlorapatite is represented by: $Ca_5(PO_4)_3^-$ $(Cl_{0.8}F_{0.1}OH_{0.1})$.

Some of the chlorine in stony meteorites is present in a water-soluble phase. Variable amounts of chlorine, ranging from 1.3 to 91% of the total, have been found to be water-soluble (VON GUNTEN *et al.*, 1965; REED and ALLEN, 1966; REED and JOVANOVIC, 1969) (Table 17-C-7); some of this soluble chlorine may be present as the iron chloride lawrencite.

In addition, MEULLER (1953) and STUDIER *et al.* (1965) have found some chlorine in complex organic compounds extracted from carbonaceous chondrites.

b) Irons

BERKEY and FISHER (1967) have investigated the distribution of chlorine in iron meteorites, by analysing different areas of both "falls" and "finds". They have found that both groups show a very pronounced inhomogeneity in their chlorine distribution (Table 17-C-8).

As expected from the pronounced lithophilic nature of chlorine, the element is fractionated away from the metal phase of iron meteorites, occurring mainly in lawrencite, chlorapatite (which has been identified in three iron meteorites, Odessa, Mount Stirling and Weekeroo Station — FUCHS, 1969), and also possibly djerfisherite.

The kamacite phase of iron meteorites was found by BERKEY and FISHER (1967) to have a chlorine content of less than 1 ppm. Further, these workers found that chlorine was concentrated around grain boundaries, having been rejected from the growing minerals. High chlorine was also found in areas surrounding troilite regions.

There is evidence of terrestial contamination resulting in higher chlorine contents of iron meteorites (BERKEY and FISHER, 1967). This is particularly true of the oxidised crust of "finds", which frequently contain several times as much chlorine as the outer regions of "falls". The chlorine content of these outer regions lessens towards the interior of the meteorite and in this way correlates with the oxide content of the metal.

Table 17-C-7. *Leachable chlorine content of stony meteorites*

Meteorite	Class	Total chlorine (ppm)	Water leachable chlorine (% of total)	Reference
Orgueil	Cc_1	210	71	Reed and Allen (1966)
Ivuna	Cc_1	240	35	Reed and Allen (1966)
		320	35	Reed and Allen (1966)
Mighei	Cc_2	350	35	Reed and Allen (1966)
Karoonda	CHL	117	4.1	Reed and Allen (1966)
Lancé	CHL	125	13	Reed and Allen (1966)
Abee	Ce_1	432	49	Reed and Allen (1966)
Indarch	Ce_1	580	75	Reed and Allen (1966)
		770	61	Reed and Allen (1966)
Hvittis	Ce_2	323	20	Reed and Allen (1966)
		222	21	von Gunten *et al.* (1965)
Beoton	CLL	57	7	von Gunten *et al.* (1965)
Dhurmsala	CLL	266	81	von Gunten *et al.* (1965)
Bruderheim	CL	89	6.7	von Gunten *et al.* (1965)
		50	2.4	Reed and Allen (1966)
		2.52	19	Reed and Allen (1966)
		3.5	37	Reed and Allen (1966)
		3.2	82	Reed and Allen (1966)
Harleton	CL	91	1.3	Reed and Allen (1966)
		80	4.8	Reed and Allen (1966)
		96	2.7	Reed and Allen (1966)
Holbrook	CL	21.6	21	Reed and Allen (1966)
Mocs	CL	99	5	von Gunten *et al.* (1965)
		173	3.5	von Gunten *et al.* (1965)
New Concord	CL	31	4.8	Reed and Allen (1966)
		63.7	17	Reed and Allen (1966)
Allegan	CH	10.2	32	Reed and Allen (1966)
		7.9	30	Reed and Allen (1966)
Miller	CH	0.44	82	Reed and Allen (1966)
Pantar (l)[b]	CH	50	19	Reed and Allen (1966)
Pantar (d)[b]	CH	33	39	Reed and Allen (1966)
Pultusk	CH	97	13	von Gunten *et al.* (1965)
Plainview[a]	CH	9.6	33	Reed and Allen (1966)
Norton County	Ae	2.1	10	von Gunten *et al.* (1965)
Frankfort	Aor	14.9	91	Reed and Jovanovic (1969)
Moore County	Ap	26.0	79	Reed and Jovanovic (1969)
		21.5	73	Reed and Jovanovic (1969)

[a] = "find".
[b] (l) and (d) = light and dark portions of meteorite.

III. Tektites

The only data available for the chlorine content of tektites is from the work of Becker and Manuel (1972) (Table 17-C-9). The mean value for five samples of various groups was found to be 2.8 ppm, which is significantly lower than the mean value of 20 ppm quoted by these workers for four analyses of impact glasses.

Table 17-C-8. *Chlorine in iron meteorites* (from BERKEY and FISHER, 1967; Method: N/R)

Meteorite	Class	Description of sample[a]	Cl (ppm)
"Falls"			
Boguslavka	H		0.0109
		i, k	0.0082
Sikote-Alin	H-Ogg		0.0899
			10.7
		i, k	0.365
		i, gb	Mean (2) 13.9
N'Goureyma	O-brecc	s	Mean (3) 5.7
Norfolk	Om	gb	0.052—2.09 Mean (5) 1.02
"Finds"			
Santa Rosa	D	i, k	Mean (3) 0.187
		i, nt	40.5
Tombigbee River	Da	i, k	5 samples < 0.016
		s, svo	0.4—146 Mean (9) 42
Smithonia	H	i	0.474
		i, svo	Mean (3) 1036
		s, vo	Mean (4) 6665
El Burro	H—Ogg	i, k	4 samples < 0.02
		i	Mean (3) 1.69
		s, vo	9.95
		i, gb vo	Mean (3) 20.7

[a] Key: i = internal piece; s = surface piece; k = kamacite; gb = sample with grain boundaries, nt = neighborhood of troilite nodule, vo = visible oxide, svo = slight visible oxide.

Table 17-C-9. *Chlorine in tektites and impact glasses* (from BECKER and MANUEL, 1972; Method: N/R)

Sample	Cl (ppm)
Tektites	
Lee County, Texas	2.8
Australite	4.3
Moldavite	2.1
Philippinite	3.6
Thailand	1.4
Impact Glasses	
Aouelloul	26
Meteor Crater, Arizona	21
Monturaqui	137
Wabar	14

IV. Lunar Samples

Several workers have quoted results for chlorine in lunar samples (Table 17-C-10). Haskin *et al.* (1970) comment that the chlorine content of lunar rocks is distinctly lower than the chlorine content of the breccias and fines. This is supported in the case of Apollo 12 samples by the values of Reed and Jovanovic (1971); however, not all of the analytical data support the contention (Reed and Jovanovic, 1970). Mason and Melso (1970) suggest that chlorine is a depleted element in lunar rocks, having been lost during metamorphism prior to aggregation.

Apatite has been found to occur as a very minor phase in lunar rocks and breccias (Keil *et al.*, 1970). Variable amounts of chlorine have been detected in the apatite; Albee and Chodos (1970) found 1.14% chlorine in one sample of apatite, while less than 0.1% was found in others.

Reed and Jovanovic (1970, 1971) found appreciable quantities of chlorine in lunar samples to be in a water-soluble phase (in most cases more than a third of the total).

Table 17-C-10. *Chlorine in some lunar samples* (Method: N/R)

Sample	Source	Cl (ppm)	Number of samples	Reference
Rock	Apollo 11	13.1	2	Haskin *et al.* (1970)
		12.1	2	Wänke *et al.* (1970)
		14.5	4	Reed and Jovanovic (1970)
		13.1	1	Reed and Jovanovic (1971)
	Apollo 12	6.4	7	Reed and Jovanovic (1971)
		10.1	4	Brunfelt *et al.* (1971a)
Breccia	Apollo 11	65.4	1	Haskin *et al.* (1970)
		16.0	2	Wänke *et al.* (1970)
		12.2	2	Reed and Jovanovic (1970)
	Apollo 12	50.6	1	Reed and Jovanovic (1971)
Fines	Apollo 11	24.1	1	Haskin *et al.* (1970)
		27.1	1	Wänke *et al.* (1970)
		7.3	1	Reed and Jovanovic (1970)
		45.0	1	Reed and Jovanovic (1971)
	Apollo 12	30.9	2	Reed and Jovanovic (1971)
		24.0	1	Brunfelt *et al.* (1971a)
	Apollo 14	47.0	1	Brunfelt *et al.* (1971b)
Apatite (Analysis M)	Apollo 11	1.14%	—	Albee and Chodos (1970)
		0.1%	—	Albee and Chodos (1970)
		<0.1%	—	Albee and Chodos (1970)
		0.34%	—	Keil *et al.* (1970)
	Luna 16	0.06%	—	Albee *et al.* (1972)

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17-D. Abundance in Rock-Forming Minerals; Chlorine Minerals

I. Rock-Forming Minerals

Chlorine forms few independent rock-forming minerals (Table 17-D-1). In sodalite, $Na_4Al_3Si_3O_{12}Cl$, which occurs in silica-undersaturated igneous rocks, the chlorine content may be as high as 7.3%; however, sodalite forms solid solutions with nosean and haüyne (Correns, 1956) and consequently the chlorine content is frequently lower than this.

Another chlorine mineral which occurs in the undersaturated igneous rocks is eudialyte, $Na_6ZrSi_6O_{18}Cl$, the chlorine content of which has been found to range upto 2.2% (Kostetskaya, 1961a).

The mineral scapolite, which occurs in metamorphic and pegmatitic rocks (Shaw, 1960), has two principal end members, chlorine-rich marialite and carbonate-rich meionite (Deer *et al.*, 1963). The chlorine content of scapolite has been shown by Shaw (1960) to range upto 3.3%

Apatite, which is widely distributed in igneous, metamorphic and sedimentary rocks, has a chlorine end member $Ca_5(PO_4)_3Cl$, chlorapatite, which can contain upto 6.8% chlorine. Terrestrial occurrences of chlorapatite appear to be rare, being limited to some hydrothermally formed varieties as at Odegarden, Norway (Morton and Catanzaro, 1964). Apatite found in rocks generally contains less than about 1% chlorine (Kind, 1938; Behne, 1953). An experimental study of the calcium orthophosphate—calcium chloride system and the stability of chlorapatite was performed by Morton (1961).

Halite, NaCl, occurs in evaporite sediments along with other alkali and alkaline earth chlorides. It has also been found in metamorphosed sediments (Engel and Engel, 1953). In addition, crystals of halite have been shown to occur within fluid inclusions in igneous rocks (Stollery *et al.*, 1971; Roedder, 1972).

The chloride ion can substitute for the hydroxyl ion in hydroxysilicate minerals, despite the fairly large difference in the respective ionic radii (OH^- 1.40 Å; Cl^- 1.81 Å) (Correns, 1956; Johns and Huang, 1967). The relatively large ionic radius of chlorine compared with that of fluorine (1.36 Å) make it appear unlikely that these two halogens can readily substitute for one another in minerals (Johns and Huang, 1967). Leelanandam (1969b) found a definite negative correlation between chlorine and fluorine in some hornblendes from charnockites, but suggested the possibility of a vague positive correlation between these two elements in biotites from the same rocks (Leelanandam, 1969a).

Kuroda and Sandell (1953) considered it possible for chlorine to substitute in the O^{2-} position in silicate minerals, but this is considered unlikely by Johns and Huang (1967).

Table 17-D-1. *Chlorine in rock-forming minerals*

Sample, source	Number of samples	Chlorine content %		Reference
		Range	Mean (Method)	
Sodalites, compilation	7	5.56—7.18	6.55	Deer *et al.* (1963)
Sodalite, pegmatite, Norway	1		6.69	Taylor (1967)
Sodalite, phonolite, Kenya	1		5.99	Taylor (1967)
Nosean haüynes, various igneous rocks	11	0.22—1.26	0.61	Taylor (1967)
Scapolites, compilation of "reliable data"	33	0.03—3.30	1.29	Shaw (1960)
Scapolites, Canada	8	0.03—2.30	1.58 (M)	Haughton (1971)
Scapolites, granulite pipes, E. Australia	2		$<$0.02 (M)	Lovering and White (1964)
Scapolites, Nairn (S. Australia)	2	1.8; 2.1	1.95 (M)	Lovering and White (1964)
Eudialytes, nepheline syenites and pegmatites, Lovozero Massif (U.S.S.R.)	27	0.97—1.58	1.36 (W)	Kostetskaya (1961a)
Eudialyte, Lovozero Massif (U.S.S.R.)	1		2.19	Borneman-Starynkevich, quoted by Kostetskaya (1961a)
Eudialytes, Norway		1.44—1.70		
Apatites, igneous rocks	6	0.08—0.96	0.31	Kind, quoted by Correns (1956)
Apatite, Jumilla (Spain)	1		0.563 (W)	Behne (1953)
Apatite, Floitental, Tyrol (Austria)	1		0.053 (W)	Behne (1953)
Apatites, igneous and metasomatic rocks	13	0.25—3.50	1.23	Vasileva (1957)
Micas				
Biotite, granite, Germany	1		0.053 (W)	Behne (1953)
Biotites, granites, Sweden	30	$<$0.005—0.66	0.065 (N/R)	Gillberg (1964)
Biotites, granites, Japan	7	0.002—0.102	0.038 (C)	Sugiura (1968)
Biotites, granites	51	0.008—1.10	0.168 (X)	Haack (1969)
Biotites, granites, Dzhida granitoid complex, W. Transbaykalia (U.S.S.R.)	15	0.11—0.30	0.20 (C)	Kostetskaya and Mordinova (1965)
Biotites, granodiorites, Providencia (Mexico)	20	0.17—0.47	0.33 (M)	Stollery *et al.* (1971)
Biotites, diorites, Dzhida granitoid complex W. Transbaykalia (U.S.S.R.)	10	0.11—0.51	0.22 (C)	Kostetskaya and Mordinova (1965)
Biotites, syenites, Dzhida granitoid complex W. Transbaykalia (U.S.S.R.)	14	0.12—0.33	0.21 (C)	Kostetskaya and Mordinova (1965)
Biotite, gabbro, Sweden	1		0.03 (N/R)	Gillberg (1964)
Biotite, pegmatite, Kondapalli (India)	1		1.96 (M)	Leelanandam (1970)
Biotites, gneisses	34	0.035—0.61	0.191 (X)	Haack (1969)

Table 17-D-1 (continued)

Sample, source	Number of samples	Chlorine content % Range	Chlorine content % Mean (Method)	Reference
Biotite, schist	1		1.11	Lee (1958)
Biotites, charnockites, Kondapalli (India)	10	0.14—0.62	0.33 (M)	Leelanandam (1969a)
Phlogopite	1		0.06 (C)	Kuroda and Sandell (1953)
Phlogopite, kimberlite, S. Africa	1		0.08	Rimsaite (1971)
Phlogopite, eclogite, S. Africa	1		0.05	Rimsaite (1971)
Muscovites, granites, Sweden	2		<0.005 (N/R)	Gillberg (1964)
Lepidolite, Black Hills, S. Dakota (U.S.A.)	1		0.031 (C)	Kuroda and Sandell (1953)
Lepidolite, Africa	1		0.008 (W)	Hoering and Paeker (1961)
Lepidolite, S. Rhodesia	1		0.005 (W)	Hoering and Parker (1961)
Stilpnomelane, Baern, Bohemia (C.S.S.R.)	1		0.043 (C)	Kurdda and Sandell (1953)
Amphiboles				
Hornblendes, granites, Adirondack Mts., New York (U.S.A.)	7	0.26—0.77	0.53	Buddington and Leonard (1953)
Hornblende, Rapakivi granite, Finland	1		0.51	Sahama, quoted by Correns (1956)
Hornblende, diorite, Rhiw, N. Wales (Great Britain)	1		0.099 (C)	Cattermole and Fuge (1969)
Hornblende, andesite, Siebengebirge (Germany)	1		0.021 (W)	Behne (1953)
Hornblende, gabbro, Burlington, Pennsylvania (U.S.A.)	1		0.06	Rosenzweig and Watson, quoted by Correns (1956)
Hornblendes, amphibolites (least altered), N. W. Adirondacks, New York (U.S.A.)	16	0.01—0.13	0.035 (W)	Engel and Engel (1962)
Hornblendes, amphibolites (retrograded), N. W. Adirondacks, New York (U.S.A.)	3	0.02—0.17	0.103 (W)	Engel and Engel (1962)
Hornblendes, gneisses, Adirondacks, New York (U.S.A.)	3	0.03—0.63	0.233 (W)	Buddington (1952)
Hornblendes, ultrabasic charnockites, Kondapalli (India)	4	0.13—0.46	0.315 (M)	Leelanandam (1969b)
Hornblendes, basic charnockites, Kondapalli (India)	5	0.66—1.12	0.824 (M)	Leelanandam (1969b)
Hornblende, skarn, Basttjärn (Sweden)	1		1.42	Magnusson, quoted by Gillberg (1964)
Hornblende, skarn, Långban (Sweden)	1		0.20	Geijer, quoted by Gillberg (1964)
Amphiboles, diorites, Dzhida granitoid complex, W. Transbaykalia (U.S.S.R.)	2	0.21; 0.26	0.235 (C)	Kostetskaya *et al.* (1969)
Amphiboles, syenites, Dzhida granitoid complex W. Transbaykalia (U.S.S.R.)	6	0.10—0.26	0.18 (C)	Kostetskaya *et al.* (1969)

Amphiboles, subalkaline syenites, Dzhida granitoid complex W. Transbaykalia (U.S.S.R.)	3	0.16—0.33	0.26 (C)	Kostetskaya *et al.* (1969)
Alkali amphiboles, granites, Nigeria	14	0.01—0.40	0.11 (C)	Borley (1963)
Ferrohastingsites, granites, Nigeria	4	0.66—1.98	1.04 (C)	Borley (1963)
Ferrohastingsite, schist, California (U.S.A.)	1		0.66	Compton (1958)
Other Hydroxysilicates				
Tourmalines, granites and aplites, S. W. England	5	0.038—0.045	0.040 (C)	Fuge and Power (1969a)
Tourmaline, Black Hills, S. Dakota (U.S.A.)	1		0.006 (C)	Kuroda and Sandell (1953)
Topaz	1		0.01 (C)	Kuroda and Sandell (1953)
Pyroxenes				
Pyroxenes, mafic and ultramafic rocks, Japan	3	0.006—0.007	0.007 (C)	Sugiura (1968)
Diallage, gabbro, Harz (Germany)	1		≦0.002 (W)	Behne (1953)
Diallage, Sonoma Co., California (U.S.A.)	1		0.009 (C)	Kuroda and Sandell (1953)
Enstatite	1		0.011 (C)	Kuroda and Sandell (1953)
Hypersthene, Nain, Labrador (Canada)	1		0.022 (C)	Kuroda and Sandell (1953)
Diopside, Hull, Quebec (Canada)	1		0.034 (C)	Kuroda and Sandell (1953)
Feldspars				
Feldspar, granite, Erzgebirge (Germany)	1		0.006 (W)	Behne (1953)
K-feldspar, granite and pegmatite, U.S.A.	3	0.005—0.018	0.012 (C)	Kuroda and Sandell (1953)
Perthite, pegmatite, Montana (U.S.A.)	1		0.058 (C)	Kuroda and Sandell (1953)
Bytownite, Minnesota (U.S.A.)	1		0.005 (C)	Kuroda and Sandell (1953)
Plagioclase, gabbro, Japan	1		0.008 (C)	Sugiura (1968)
Other minerals				
Olivine, basalt, Hawaii	1		0.003 (C)	Iwasaki and Katsura (1964)
Olivine, peridotite, Japan	1		0.001 (C)	Sugiura (1968)
Garnet, eclogite, Japan	1		0.001 (C)	Sugiura (1968)
Spinel, peridotite, Japan	1		0.008 (C)	Sugiura (1968)
Quartz, granite, Erzgebirge (Germany)	1		≦0.002 (W)	Behne (1953)
Quartz (with liquid inclusions)	1		0.003 (C)	Kuroda and Sandell (1953)
Quartzes, granite and pegmatite, Japan	3	0.001—0.003	0.002 (C)	Sugiura (1968)
Calcite, Minnesota (U.S.A.)	1		0.02 (C)	Kuroda and Sandell (1953)
Fluorite, England	1		0.017 (C)	Kuroda and Sandell (1953)
Magnetite, gabbro, Japan	1		0.009 (C)	Sugiura (1968)

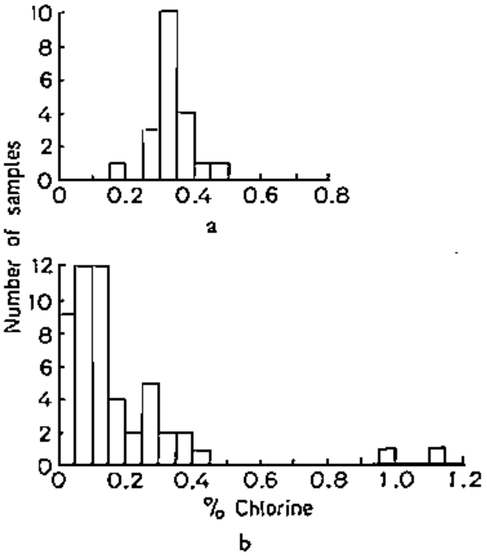

Fig. 17-D-1a and b. Distribution of chlorine in biotites from: a Granodiorites, Providencia Stock, Mexico (from Stollery *et al.*, 1971); b Granites (from Haack, 1969)

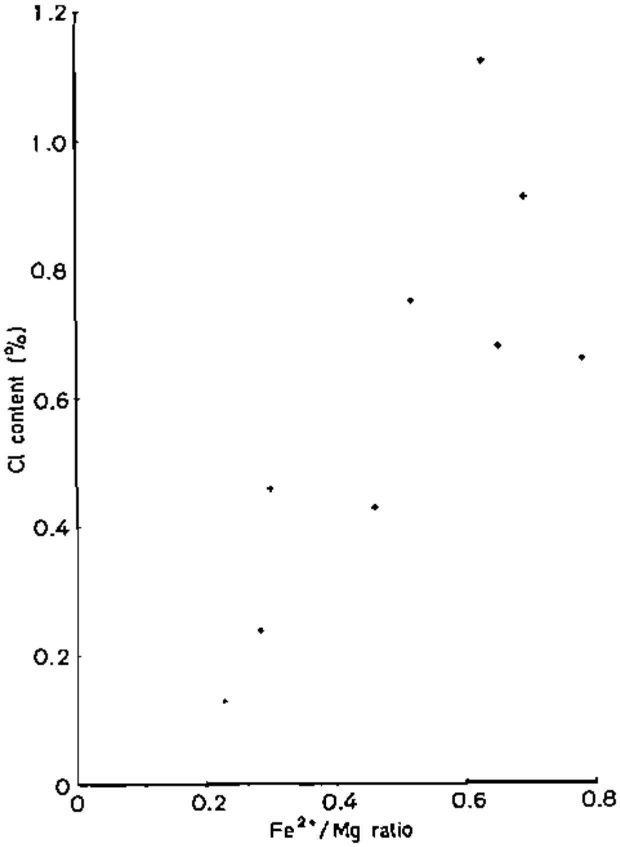

Fig. 17-D-2. Variation of chlorine content with Fe^{2+}/Mg ratio in charnockitic hornblendes, Kondapalli, India (from Leelanandam, 1969b)

Table 17-D-2. *Chlorine in some co-existing minerals, in igneous and metamorphic rocks*

Rock	Cl content of minerals (%)		Analytical method	Reference
	Muscovite	Biotite		
(i) Muscovite and biotite				
Granite	≦0.002	0.065	W	Behne (1953)
Pegmatite	0.005	<0.005	N/R	Gillberg (1964)
Pegmatite	0.005	0.18	N/R	Gillberg (1964)
Pelitic schist	<0.01 (Mean of 22)	0.03 (Mean of 27)	M	Evans (1969)
	Biotite	Amphibole		
(ii) Biotite and amphibole				
Granite	0.065	0.053 (h)	W	Behne (1953)
Granite	0.040	0.10	N/R	Gillberg (1964)
Granite	0.090	0.040	N/R	Gillberg (1964)
Granite	0.070	0.040	N/R	Gillberg (1964)
Granite	0.020	0.010	N/R	Gillberg (1964)
Granite	0.060	0.030	N/R	Gillberg (1964)
Granite	0.010	0.020	N/R	Gillberg (1964)
Charnockite (mafic)	0.53	0.75 (h)	M	Leelanandam (1969c)
Charnockite (mafic)	0.43	0.68 (h)	M	Leelanandam (1969c)
Charnockite (mafic)	0.32	0.66 (h)	M	Leelanandam (1969c)
Charnockite (ultramafic)	0.28	0.46 (h)	M	Leelanandam (1969c)
Charnockite (ultramafic)	0.19	0.24 (h)	M	Leelanandam (1969c)

h = hornblende.

Table 17-D-3. *Chlorine content of felsic minerals in rocks of the Dzhida granitoid complex, W. Transbaykalia (U.S.S.R.)* (from Kostetskaya *et al.*, 1969; method: C)

Rock	Cl content of minerals (ppm)					
	Quartz		Plagioclase		K-feldspar	
	Soluble	Insoluble	Soluble	Insoluble	Soluble	Insoluble
Diorite	35	210	34	18	—	—
Syenite	42	450	48	250	210	460
Syenite	50	270	47	210	40	80
Granite	23	70	20	70	220	90
Granite	12	400	21	420	28	130
Granite	28	80	—	—	20	300

Table 17-D-4. *Chlorine balance of some igneous rocks*

Rock, locality	Minerals	% of mineral in rock	Cl in mineral (%)	Absolute % of Cl contributed to rock	Cl in rock by direct analysis	Analytical method	Reference
Granite, Skearns Co., Minnesota (U.S.A.)	Hornblende (+ biotite)	7	0.18	0.013		C	Kuroda and Sandell (1953)
	Feldspar (mainly K)	80	0.014	0.011			
	Quartz	10	(0.00)	0.00			
				0.024	0.020		
Porphyritic granite, Dzhida complex, W. Transbaykalia (U.S.S.R.)	Biotite	6.8	0.19	0.0129		C	Kostetskaya *et al.* (1969)
	Amphibole	2.4	0.22	0.0052			
	Quartz	19.0	0.0093	0.0017			
	Plagioclase	30.2	0.0090	0.0027			
	Microcline	28.2	0.0110	0.0041			
				0.0266	0.034		
Quartz monzonite, Rockville, Minnesota (U.S.A.)	Microcline	35	0.014	0.005			
	Plagioclase (An 28)	35	0.028	0.010		C	Kuroda and Sandell (1953)
	Biotite	7	0.18	0.013			
	Quartz		0.002	<0.001			
				0.029	0.032		
Syenite, Dzhida complex (U.S.S.R.)	Biotite	5.6	0.240	0.0130		C	Kostetskaya *et al.* (1969)
	Amphibole	2.5	0.330	0.0080			
	Quartz	4.9	0.049	0.0024			
	Plagioclase	36.7	0.025	0.0092			
	Microcline	46.9	0.065	0.0305			
				0.0631	0.055		

The chlorine content of co-existing biotite and amphibole (Table 17-D-2) has been shown to be of similar magnitude (CORRENS ,1956; GILLBERG, 1964; LEELANANDAM, 1969c).

In general the chlorine content of muscovite is low. Where chlorine has been determined in co-existing muscovite and biotite (Table 17-D-2), the latter almost invariably has a far greater chlorine content (BEHNE, 1953; GILLBERG, 1964; EVANS, 1969).

HAACK (1969) found little variation in the chlorine content of biotites from gneisses and granite (Fig. 17-D-1b; see also the data of STOLLERY *et al.*, 1971, Fig. 17-D-1a.)

LEELANANDAM (1969a) suggests that iron-rich charnockitic biotites tend to be enriched in chlorine. The same author (1969b) found a definite increase of chlorine with increasing Fe^{++}/Mg ratio in charnockitic hornblendes (see Fig. 17-D-2).

KOSTETSKAYA *et al.* (1969) found chlorine to be present in all essential minerals of the granitic and syenitic rocks of the Dzhida granitoid complex (Table 17-D-3). Upto one third of the chlorine in the felsic minerals was found to be water-soluble, and is probably present as liquid inclusions. The authors suggested that some of the chlorine in the felsic minerals is contained in microscopic inclusions such as biotite or apatite. Whereas the biotites and amphiboles are enriched in chlorine, one- to two-thirds of the chlorine in the rocks is contributed by the felsic minerals. Similar results were obtained by KURODA and SANDELL (1953) for the chlorine balance of some rocks from North America (Table 17-D-4).

FABER (1941) showed that appreciable quantities of chlorine could be leached from pegmatitic quartzes and feldspars. The total chlorine content of a granitic feldspar sample was found by BEHNE (1953) to be water-soluble. KURODA and SANDELL (1953) found that 12% of the chlorine content of a perthite sample was water-soluble, whereas 50% of the chlorine content of a calcite was soluble. Halite crystals have been found to occur in inclusions of granitic quartzes and feldspars (ROEDDER and COOMBS, 1967; STOLLERY *et al.*, 1971).

Some of the chlorine occurring in hydroxy minerals may also be in a water-soluble state; BEHNE (1953) leached almost 10% of the chlorine from a biotite by boiling with water, and FUGE and POWER (1969a) found that from 0 to 48% (mean 11%) of the total chlorine was leached from 12 samples of tourmaline by boiling with water.

II. Chlorine Minerals

A summary of chlorine minerals is given in Table 17-D-5.

Table 17-D-5. *Chlorine minerals* (compiled mainly from HEY ,1950, and FLEISCHER, 1966)

Mineral	Formula
Halides, oxyhalides etc.	
Halite	$NaCl$
Hydrohalite	$NaCl \cdot 2\,H_2O$
Sylvine (sylvite)	KCl
Sal-ammoniac	NH_4Cl
Carnallite	$KMgCl_3 \cdot 6\,H_2O$

Table 17-D-5 (continued)

Mineral	Formula
Chlormagnesite	$MgCl_2$
Bischofite	$MgCl_2 \cdot 6\ H_2O$
Tachhydrite	$CaMg_2Cl_6 \cdot 12\ H_2O$
Antarcticite	$CaCl_2 \cdot 6\ H_2O$
Gagarinite	$NaCaY(F,Cl)_6$
Koenenite	$Mg_5Al_2Cl_4(OH)_{12} \cdot 2(?)\ H_2O$
Cadwaladerite	$Al(OH)_2Cl \cdot 4\ H_2O$
Chloraluminite	$AlCl_3 \cdot 6\ H_2O$
Zirklerite	$(Fe, Mg, Ca)_9Al_4Cl_{18}(OH)_{12} \cdot 14\ H_2O(?)$
Calomel	Hg_2Cl_2
Terlinguaite	Hg_2ClO
Eglestonite	Hg_4Cl_2O
Mosesite	$Hg_2NCl \cdot H_2O$
Chlorargyrite	$AgCl$
Embolite	$Ag(Cl, Br)$
Iodembolite	$Ag(Cl, Br, I)$
Bideauxite	$Pb_2Ag\ Cl_3\ (F, OH)_2$
Mitscherlichite	$K_2Cu\ Cl_4 \cdot 2\ H_2O$
Nantokite	$CuCl$
Eriochalcite (antofagastite)	$CuCl_2 \cdot 2\ H_2O$
Melanothallite	$CuClOH(?)$
Hydromelanothallite	$CuClOH \cdot {}^1/_2H_2O(?)$
Atacamite	$Cu_2Cl\ (OH)_3$ orthorhomb.
Paratacamite	$Cu_2Cl\ (OH)_3$ hexagon.
Botallackite	$Cu_2Cl\ (OH)_3$
Anthonyite	$Cu\ (OH,Cl)_2 \cdot 3\ H_2O$
Calumetite	$Cu\ (OH, Cl)_2 \cdot 2\ H_2O$
Percylite	$Pb\ Cu\ Cl_2\ (OH)_2$
Cumengéite	$PbCuCl_2(OH)$
Diaboleite	$Pb_2CuCl_2(OH)_4$
Chloroxiphite	$Pb_3Cu\ Cl_2O_2\ (OH)_2$
Pseudoboléite	$Pb_5Cu_4Cl_{10}\ (OH)_8 \cdot 2\ H_2O$
Boléite	$Pb_9Cu_8Ag_3Cl_{21}\ (OH)_{16} \cdot H_2O$
Pseudocotunnite	$3KPbCl_3 \cdot H_2O$
Matlockite	$PbF\ Cl$
Cotunnite	$PbCl_2$
Mendipite	$Pb_3Cl_2O_2$
Laurionite	$PbClOH$ orthorhomb.
Paralaurionite	$PbClOH$ monocl.
Penfieldite	Pb_2Cl_3OH
Fiedlerite	$Pb_3Cl_4(OH)_2$
Blixite	$Pb_2Cl(O,OH)_{2-x}$
Lorettoite	$Pb_7O_6Cl_2$
Hematophanite	$Pb_5Fe_4(Cl,OH)_2O_{10}$
Rinneite	$K_3NaFeCl_6$ (Poss. K_3FeCl_5)
Kremersite	$K\ NH_4FeCl_5 \cdot H_2O$
Erythrosiderite	$K_2FeCl_5 \cdot H_2O$
Douglasite	$K_2FeCl_4 \cdot 2\ H_2O(?)$
Iowaite	$4Mg(OH)_2 \cdot FeOCl \cdot 4\ H_2O$
Lawrencite	$FeCl_2$
Molysite	$FeCl_3$
Unnamed	$FeCl_3 \cdot 6\ H_2O$
Chloromanganokalite	K_4MnCl_6

Table 17-D-5 (continued)

Mineral	Formula
Scacchite	$MnCl_2$
Kempite	$MnCl_2 \cdot 3MnO_2 \cdot 2\,H_2O$
Onoratoite	$Sb_8O_{11}Cl_2$
Nadorite	$PbSbO_2Cl$
Bismoclite	$BiOCl$
Perite	$PbBiO_2Cl$
Borates and carbonates	
Teepleite	$Na_2BO_2Cl \cdot 2\,H_2O$
Boracite	$Mg_6B_{14}O_{26}Cl_2$ (at low temperature: cubic)
α-Boracite	$Mg_6B_{14}O_{26}Cl_2$ (at high temperature: orthorhombic)
Hydrochlorborite	$Ca_4B_8O_{15}Cl_2 \cdot 22\,H_2O$
Hilgardite	$Ca_8(B_6O_{11})_3Cl_4 \cdot 4\,H_2O$ (monocl.)
Parahilgardite	$Ca_8(B_6O_{11})_3Cl_4 \cdot 4\,H_2O$ (tricl.)
Ericaite	$(Fe,Mg,Mn)_3B_7O_{13}Cl$
Bandylite	$CuBO_2Cl \cdot 2\,H_2O$
Wiserite	$Mn_4B_2O_5(OH,Cl)_4$
Chambersite	$Mn_3B_7O_{13}Cl$
Sakhaite	$Ca_{12}Mg_4(CO_3)_4(BO_3)_7Cl(OH)_2 \cdot H_2O$
Northupite	$Na_3Mg(CO_3)_2Cl$
Phosgenite	Pb_2CO_3Cl
Sulfates	
Galeite	$Na_3(SO_4)\,(F,Cl)$ $F:Cl = 4:1$ (hex.: $P\bar{3}1m$) (c_0: 13.94)
Schairerite	$Na_3(SO_4)\,(F,Cl)$ $F:Cl = 4:1$ (hex.: $P\bar{3}1m$) (c_0: 19.19)
Sulphohalite	$Na_6(SO_4)_2ClF$
D'Ansite	$9\,Na_2SO_4 \cdot MgSO_4 \cdot 3\,NaCl$
Kainite	$KMgSO_4Cl \cdot 3\,H_2O$
Caracolite	Na_2PbSO_4ClOH
Trudellite	$Al_{10}(SO_4)_3Cl_{12}(OH)_{12} \cdot 30\,H_2O$
Spangolite	$\sim Cu_6AlSO_4Cl(OH)_{12} \cdot 3\,H_2O$
Arzrunite	$Cu_4Pb_2SO_4Cl_6(OH)_4 \cdot 2\,H_2O$(?)
Kleinite	$Hg_2N(Cl,SO_4) \cdot xH_2O$
Heidornite	$Na_2Ca_3B_5O_8(SO_4)_2Cl(OH)_2$
Tatarskite	$Ca_3Mg(SO_4)(CO_3)Cl_2(OH)_2 \cdot 3^1/_2\,H_2O$
Wherryite	$Pb_4Cu(CO_3)(SO_4)_2(Cl,OH)_2O$
Phosphates, arsenates and vanadates	
Sampleite	$NaCaCu_5(PO_4)_4Cl \cdot 5\,H_2O$
Chlorapatite	$Ca_5(PO_4)_3Cl$
Pyromorphite	$Pb_5(PO_4)_2Cl$
Svabite	$Ca_5(AsO_4)_2(OH,F,Cl)$
Georgiadesite	$Pb_3(AsO_4)Cl_3$
Mimetite	$Pb_5(AsO_4)_3Cl$
Sahlinite	$Pb_{14}(AsO_4)_2O_9Cl_4$
Vanadinite	$Pb_5(VO_4)_2Cl$
Nitrate	
Buttgenbachite	$Cu_{19}Cl_4(NO_3)_2OH_{32} \cdot 2\,H_2O$

Mineral	Formula
Antimonate	
Nadorite	$PbSbO_2Cl$
Arsenites	
Magnussonite	$Mn_5(AsO_3)_3(OH,Cl)$
Finnemanite	$Pb_5(AsO_3)_3Cl$
Heliophyllite	$Pb_3As^{3+}O_{4-n}Cl_{2n+1}$ orthorhomb.
Ekdemite	$Pb_3As^{3+}O_{4-n}Cl_{2n+1}$ tetragon.
Tellurite	
Rhodalquilarite	$Fe_2^{3+}TeO_3(TeO_3H)_3Cl \cdot 0.5\ H_2O$
Acetate	
Calclacite	$CaCl_2 \cdot Ca(CH_3COO)_2 \cdot 10\ H_2O$
Silicates	
Sodalite	$Na_4Al_3Si_3O_{12}Cl$
Eudialyte	$Na_6ZrSi_6O_{18}Cl$
Marialite	$3\ NaAlSi_3O_8 \cdot NaCl$ (end member of scapolite group)
Afghanite	$\sim (Na,Ca,K)_{12}(Si,Al)_{16}O_{34}(Cl,SO_4,CO_3)_4 \cdot 0.6\ H_2O$
Unnamed	$(K,Na)_4Ca_2(Al,Fe)(Si,Al)_8(O,OH,F)_{18} \cdot NaCl$
Tugtupite	$Na_4BeAlSi_4O_{12}Cl$
Barytolamprophyllite	$(Na,K)_6(Ba,Ca,Sr,Mn)_3(Ti,Fe,Mg)_7(Si,Al)_8O_{32}$
Delhayelite	$(Na,K)_4Ca_5Al_6Si_{32}O_{80} \cdot 3(Na,K)_2(Cl_2,F_2,SO_4) \cdot 18\ H_2O$
Zunyite	$Al_{13}Si_5O_{20}(OH,F)_{18}Cl$
Harkerite	$Ca_7(Mg,Al)_5(B,Si)_6(O,OH,Cl)_{24} \cdot 5\ CaCO_3$
Nasonite	$Ca_4Pb_6Si_6O_{21}Cl_2$
Muirite	$Ba_{10}Ca_2MnTiSi_{10}O_{30}(OH,F,Cl)_{10}$
Baotite	$Ba_4(Ti,Nb)_8Si_4O_{28}Cl$
Verplankite	$Ba_2(Mn,Fe,Ti)Si_2O_6(O,OH,Cl,F)_2 \cdot 3\ H_2O$
Traskite	$Ba_9Fe_2Ti_2Si_{12}O_{36}(OH,Cl,F)_6 \cdot 6\ H_2O$
Yoshimuraite	$(Ba,Sr)_2TiMn_2(SiO_4)_2(PO_4,SO_4)(OH,Cl)$
Friedelite	$Mn_8Si_6O_{18}(OH,Cl)_4 \cdot 3\ H_2O$
Pyrosmalite	$(Mn,Fe^{2+})_4Si_3O_7(OH,Cl)_6$
Manganpyrosmalite	$(Mn,Fe^{2+})_8Si_6O_{15}(OH,Cl)_{10}$
Schallerite	$(Mn,Fe)_8AsSi_6(O,OH,Cl)_{26}$
Jagoite	$Pb_{24}Fe_7Si_{27}O_{84}(OH,Cl)_8$
Dashkesanite	chlorine-rich amphibole (7 percent Cl)

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17-E. Abundance and Distribution in Common Igneous Rocks

From the data in Tables 17-E-1 and 17-E-5, it is apparent that there is little correlation between the chlorine and silica contents of plutonic rocks. Johns and Huang (1967) have claimed that there is a clear positive correlation between chlorine and silica in the extrusive rocks, but this is not very apparent from Table 17-E-2.

There is considerable variation of the chlorine content of similar rock types and there does not appear to be a great deal of difference between the equivalent volcanic and plutonic types (see Figs. 17-E-1a to d.)

The alkali-rich magmatic rocks are enriched in chlorine, while the silica under-saturated rocks are enriched to an even greater degree.

Volcanic glasses show marked enrichment in chlorine compared to equivalent crystalline types. Noble *et al.* (1967) found on comparing glassy and crystalline siliceous rocks, that 80% of the original chlorine is likely to have been lost from crystallized volcanic rocks (see Table 17-E-3). In the case of the peralkaline pantellerites and comendites, these differences are even more marked (see Table 17-E-3). Lovering (1966) has shown that almost the total chlorine content of glassy pantellerites is situated in the residual glass. Iwasaki and Katsura (1964) found chlorine to be concentrated in the groundmass of Hawaiian basalts.

In under-saturated rocks such as the phonolites, glassy and crystalline types are similar in chlorine content, due to the retention of chlorine by the precipitation of sodalite (Stormer and Carmichael, 1971).

A possible regional difference in the chlorine content of igneous rocks was suggested by Kuroda and Sandell (1953), with particular reference to the low chlorine values they obtained for Japanese volcanics compared to those of American origin. Iwasaki *et al.* (1957) found no significant difference in the chlorine contents of Japanese volcanics and those of other parts of the world. The volcanic rocks of Hawaii were found by Iwasaki and Katsura (1964) to contain distinctly less chlorine than those of Japan.

Varying amounts of water-soluble chlorine have been found in igneous rocks; some of this chlorine is probably due to contamination by sea water and other fluids (Iwasaki and Katsura, 1964; Yoshida *et al.*, 1971). However, much of the chlorine is likely to be derived from soluble chlorides occurring in the rock within fluid inclusions (see Section 17-D).

Several workers have noted the high chlorine content of serpentinised ultramafic rocks (see Table 17-E-4). Earley (1958) suggested that the extremely high chlorine contents which he determined in serpentinised dunites, were introduced during serpentinisation by chloride-rich solutions. The chlorine in serpentinised dunite has been shown by Rucklidge (1972) to occur in solid solution in the serpentine, being

Table 17-E-1. *Chlorine in plutonic rocks*

Rock	Number of samples	Chlorine content (ppm)		Reference
		Range	Mean (method)	
Gabbros (U.S.S.R.)	2	140; 260	200	Selivanov (1940)
Gabbros (Germany)	11		80 (W)	Behne (1953)
Gabbros (U.S.A.)	20		210 (C)	Kuroda and Sandell (1953)
Gabbros (U.S.A.)	2	210; 270	240 (W)	Hdering and Parker (1961)
Gabbros (Japan)	2	290; 500	395	Kdkubu (1956)
Gabbros (Japan)	1		70 (C)	Sugiura (1968)
Gabbros (compilation)	53	80—500	186	Johns and Huang (1967)
Essexites (Oslo)	2		650	Barth and Bruun (1945)
Essexites (Czechoslovakia)	3	140—220	177 (X)	Macháček and Shredený (1970)
Theralite (Czechoslovakia)	1		360 (X)	Macháček and Shrebený (1970)
Gabbroic diorites (Japan)	2	100; 150	125 (C)	Kuroda and Sandell (1953)
Gabbroic diorites (California)	4		280 (C)	Kuroda and Sandell (1953)
Diorite (Germany)	1		240 (W)	Behne (1953)
Diorites (U.S.A.)	7		400 (C)	Kuroda and Sandell (1953)
Quartz diorite (Italy)	1		100 (W)	Behne (1953)
Quartz diorite (Japan)	1		70 (C)	Sugiura (1968)
Diorites and quartz diorites (compilation)	25	100—700	335	Johns and Huang (1967)
Granodiorites (U.S.S.R.)	2	300; 790	545	Seliyanov (1940)
Granodiorite (Norway)	1		≦20 (W)	Behne (1953)
Granodiorites and tonalites (Japan)	16	190—580	399	Kokubu (1956)
Granodiorite (Minnesota)	1		200 (W)	Hoering and Parker (1961)
Granodiorites (Mexico)	2	500; 900	700 (W/A)	Stollery *et al.* (1971)
Granodiorite (Japan)	1		90 (C)	Sugiura (1968)
Granodiorites (compilation)	16	20—500	219	Johns and Huang (1967)
Granites (U.S.S.R.)	4	90—400	275	Selivanov (1940)
Granites (Germany)	18		106 (W)	Behne (1953)
Granites (mainly U.S.A.) (includes some granodiorites)	99		220 (C)	Kuroda and Sandell (1953)
Granites (Japan)	4	200—910	418	Kokubu (1956)
Granites (U.S.A.)	3	60—250	160 (W)	Hoering and Parker (1961)

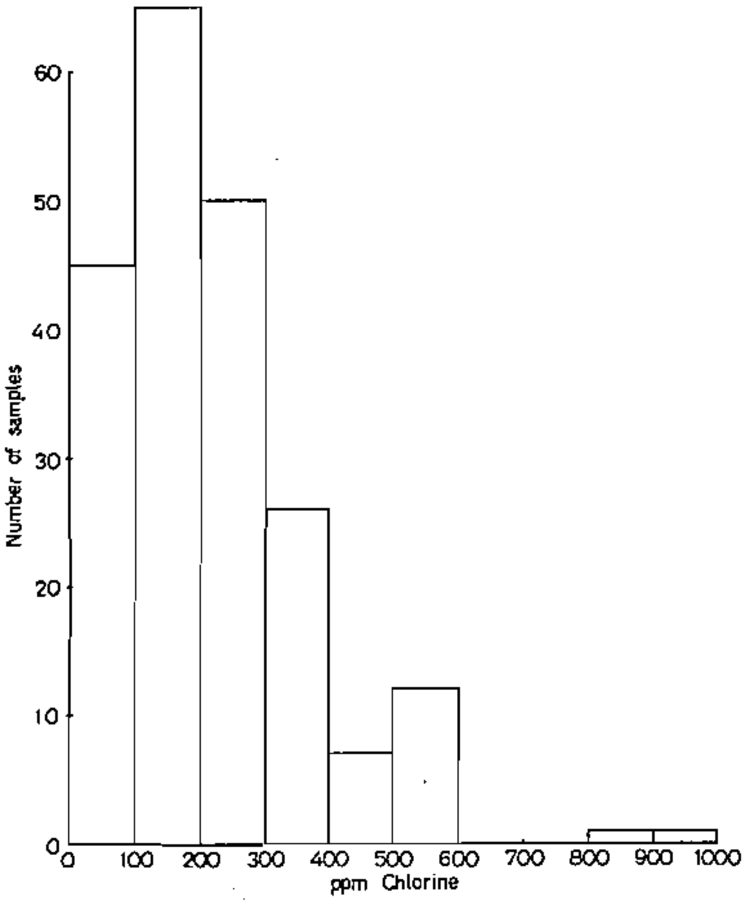
Granites (Japan)	6	10—100	43 (C)	Sugiura (1968)
Granites (S. W. England)	90	75—1,180	507 (C)	Fuge and Power (1969b)
Granites (N. Wales)	36	23—855	195 (C)	Fuge (unpublished)
Granites (compilation)	123	30—500	202	Johns and Huang (1967)
Syenites (U.S.S.R.)	3	10—980	450	Selivanov (1940)
Syenite (Germany)	1		450 (W)	Behne (1953)
Syenites (U.S.A.)	6		550 (C)	Kuroda and Sandell (1953)
Syenites (U.S.A.)	2	90; 160	125 (W)	Hobbing and Parker (1961)
Syenites (Arkansas)	3	100—800	433 (W)	Erickson and Blade (1963)
Syenites (U.S.S.R.)	2	360; 550	455 (C)	Kostetskaya *et al.* (1969)
Syenites, quartz syenites (S. Greenland)	34	200—900	360 (C)	Upton *et al.* (1971)
Syenites (compilation)	40	90—2,000	429	Johns and Huang (1967)
Alkali syenites (Norway)	5		200	Barth and Bruun (1945)
Larvikites (Norway)	4		670	Barth and Bruun (1945)
Nepheline syenites (U.S.S.R.)	2	240; 280	260	Selivanov (1940)
Nepheline syenites (Germany)	22		970 (W)	Behne (1953)
Nepheline syenites (Arkansas)	2	700; 4,600	2,650 (W)	Erickson and Blade (1963)
Nepheline syenites, Lovozero massif (U.S.S.R.)	11	500—3,200	1,000 (W)	Gerasimovskii and Tuzova (1964)
Foyaites, Lovozero massif (U.S.S.R.)	150	1,100—2,900	1,800 (W)	Gerasimovskii and Tuzova (1964)
Foyaites, Lovozero massif (U.S.S.R.)	17	<100—4,000	2,000 (W/C)	Kostetskaya (1961b)
Lujavrites, Lovozero massif (U.S.S.R.)	184	300—2,500	1,480 (W)	Gerasimovskii and Tuzova (1964)
Lujavrites, Lovozero massif (U.S.S.R.)	30	<100—4,200	1,290 (W/C)	Kostetskaya (1961b)
Urtites, Lovozero massif (U.S.S.R.)	86	400—3,200	1,200 (W)	Gerasimovskii and Tuzova (1964)
Urtites, Lovozero massif (U.S.S.R.)	11	<100—12,500	3,337 (W/C)	Kostetskaya (1961b)
Sodalite syenites, Lovozero massif (U.S.S.R.)	7		24,600 (W)	Gerasimovskii and Tuzova (1964)
Sodalite syenites, Lovozero massif (U.S.S.R.)	5	16,000—27,900	23,300 (W)	Kostetskaya (1961b)
Tawites, Lovozero massif (U.S.S.R.)	2		21,900 (W)	Gerasimovskii and Tuzova (1964)
Tawites, Lovozero massif (U.S.S.R.)	2	24,500—31,000	27,500 (W)	Kostetskaya (1961b)
Nepheline syenite types, Kola peninsula (except Lovozero) (U.S.S.R.)	68	<300—5,000	500 (W)	Gerasimovskii and Tuzova (1964)
Nepheline syenites (various localities)	36	0—2,400	600 (W)	Gerasimovskii and Tuzova (1964)

Table 17-E-2. *Chlorine in volcanic rocks*

Rock	Number of samples	Chlorine content (ppm)		Reference
		Range	Mean	
Basalts (U.S.S.R.)	3	120—460	260	Selivanov (1940)
Basalts (mainly U.S.A.)	39		140 (C)	Kurdoa and Sandell (1953)
Basalts (Germany)	2	30; 120	75 (W)	Behne (1953)
Basalts (U.S.A.)	3	100—160	123 (W)	Hoering and Parker (1961)
Basalts (Japan and N. E. China)	84	80—890	230 (C)	Iwasaki *et al.* (1957)
Basalts (Gough Island)	2	600; 900	750	Le Maitre (1962)
Basalts, tholeiitic (Hawaii)	119	60—2,180^a	165 (C)	Iwasaki and Katsura (1964)
		40—250^b	81 (C)	Iwasaki and Katsura (1964)
Basalts, non-tholeiitic, mainly alkali basalts and oceanites, also including some ankaramites, hawaiites, mugarites and basanites (Hawaii)	34	60—670^a	191 (C)	Iwasaki and Katsura (1964)
		40—660^b	134 (C)	Iwasaki and Katsura (1964)
Basalts (Japan)	6	100—450	235 (C)	Sugiura (1968)
Basalts (Japan)	18	32—600	206 (C)	Yoshida *et al.* (1971)
Basalts (Czechoslovakia)	6	60—1,100	543 (X)	Macháček and Shrbený (1970)
Limburgites (Czechoslovakia)	3	600—1,000	810 (X)	Macháček and Shrbený (1970)
Basalts (compilation)	95	30—600	149	Johns and Huang (1967)
Andesites (Japan and U.S.A.)	11	20—370	180 (C)	Kuroda and Sandell (1953)
Andesites (Germany)	2	110; 200	155 (W)	Behne (1953)
Andesite (U.S.A.)	1		140 (W)	Hoering and Parker (1961)
Andesites and dacites (Japan)	82	30—3,900	250 (C)	Iwasaki *et al.* (1957)
Andesites (Japan)	9	80—430	202 (C)	Sugiura *et al.* (1968)
Andesites (Japan)	13	70—620	285 (C)	Yoshida *et al.* (1971)
Andesites (compilation)	17	20—370	166	Johns and Huang (1967)
Dacites and rhyodacites (California)	5	140—510	264 (C)	Kurdoa and Sandell (1953)
Dacite, Colorado (U.S.A.)	1		90 (W)	Hoering and Parker (1961)
Dacites (Japan)	6	30—190	100 (C)	Sugiura (1968)
Dacites (Japan)	4	30—610	188 (C)	Yoshida *et al.* (1971)
Dacites (compilation)	10	90—510	213	Johns and Huang (1967)
Rhyolites and liparites (Japan and U.S.A.)	8		140 (C)	Kurdoa and Sandell (1953)
Liparite (Hungary)	1		20 (W)	Behne (1953)
Rhyolite (Montana)	1		110 (W)	Hoering and Parker (1961)
Rhyolites (Japan)	6	240—690	550 (C)	Iwasaki *et al.* (1957)

Rhyolites and liparites (Japan)	6	30—1,220	598 (C)	Yoshida *et al.* (1971)
Rhyolites and liparites (compilation)	45	20—2,000	328	Johns and Huang (1967)
Glassy rocks (Japan and U.S.A.)	3	310—1,000	587 (C)	Kuroda and Sandell (1953)
Obsidians	4	80—4,560	2,205 (W)	Behne (1953)
Obsidians (Germany)	8		240 (W)	Behne (1953)
Glassy rocks (Japan)	7	90—1,020	517 (C)	Sugiura (1968)
Glassy rocks (Japan)	4	160—800	560 (C)	Yoshida *et al.* (1971)
Obsidians	4	143—760	473 (N/R)	Becker and Manuel (1972)
Obsidians and pumices (compilation)	43		788	Johns and Huang (1967)
Trachyte, Texas (U.S.A.)	1		140 (C)	Kuroda and Sandell (1953)
Trachyte (Germany)	1		<20 (W)	Behne (1953)
Trachyte, Colorado (U.S.A.)	1		130 (W)	Hoering and Parker (1961)
Trachyte, Arkansas (U.S.A.)	1		900 (W)	Erickson and Blade (1963)
Trachytes (Gough Island)	4	200—700	400	Le Maitre (1962)
Trachytes and trachyandesites (Japan)	3	17—100	72 (C)	Yoshida *et al.* (1971)
Trachytes, including alkali trachytes and trachybasalts (Czechoslovakia)	21	<50—1,200	128 (X)	Macháček and Shrbený (1970)
Alkali trachyte (Kenya)	1		800 (X)	Nash *et al.* (1969)
Sodalite trachyte (Arkansas)	1		5,200 (W)	Erickson and Blade (1963)
Sodalite trachytes (Gough Island)	2	1,700; 3,800	2,750	LeMaitre (1962)
Potassium-rich shoshonites, Devon (England)	25	104—8,916	594 (X)	Cosgrove (1972)
Phonolites	4		500 (C)	Kuroda and Sandell (1953)
Phonolites, Bohemia (Č.S.S.R.)	10		160 (W)	Behne (1953)
Phonolite, Colorado (U.S.A.)	1		2,500 (W)	Hoering and Parker (1961)
Phonolites (Kenya)	9	900—4,500	1,910 (X)	Nash *et al.* (1969)
Phonolites, phonolitic trachyte, Arkansas (U.S.A.)	3	4,200—7,100	5,767 (W)	Erickson and Blade (1963)
Phonolites (Czechoslovakia)	2	2,500; 2,600	2,550 (X)	Macháček and Shrbený (1970)
Phonolite, Vesuvius (Italy)	1		1,400 (X)	Savelli (1967)
Phonolites and trachytes (compilation)	29	20—2,500	494	Johns and Huang (1967)
Phonolitic tephrites, Vesuvius (Italy)	17	50—540	166 (X)	Savelli (1967)
Tephrites and basanites (Czechoslovakia)	14	<50—750	226 (X)	Macháček and Shrbený (1970)
Leucite basanites and tephrites, Vesuvius (Italy)	21	1,000—9,400	4,800 (X)	Savelli (1967)
Leucite basanites and tephrites, Vesuvius (Italy)	4		4,600	Stormer and Carmichael (1971)
Nephelinites (Czechoslovakia)	5	50—1,400	548 (X)	Macháček and Shrbený (1970)
Nephelinite (Germany)	1		370 (W)	Behne (1953)
Leucitites (Czechoslovakia)	7	120—720	359 (X)	Macháček and Shrbený (1970)

[a] Total Cl.   [b] H_2O-insoluble Cl.



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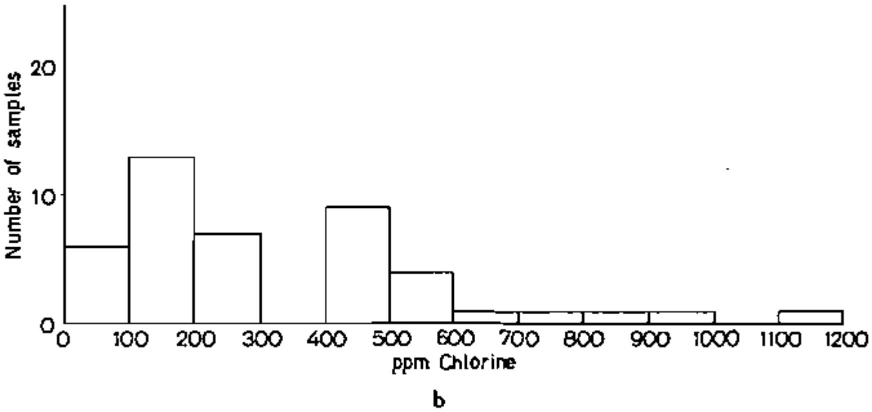
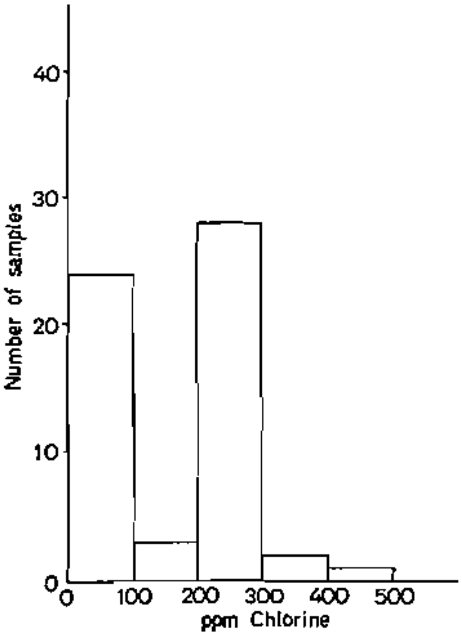


b

Fig. 17-E-1a—d. Distribution of chlorine in: a Granites and granodiorites, b Rhyolites and liparites. c Gabbros. d Basalts (from data of: JOHNS and HUANG, 1967; KOKUBU, 1956; SUGIURA, 1968; YOSHIDA *et al.*, 1971; FUGE, unpublished)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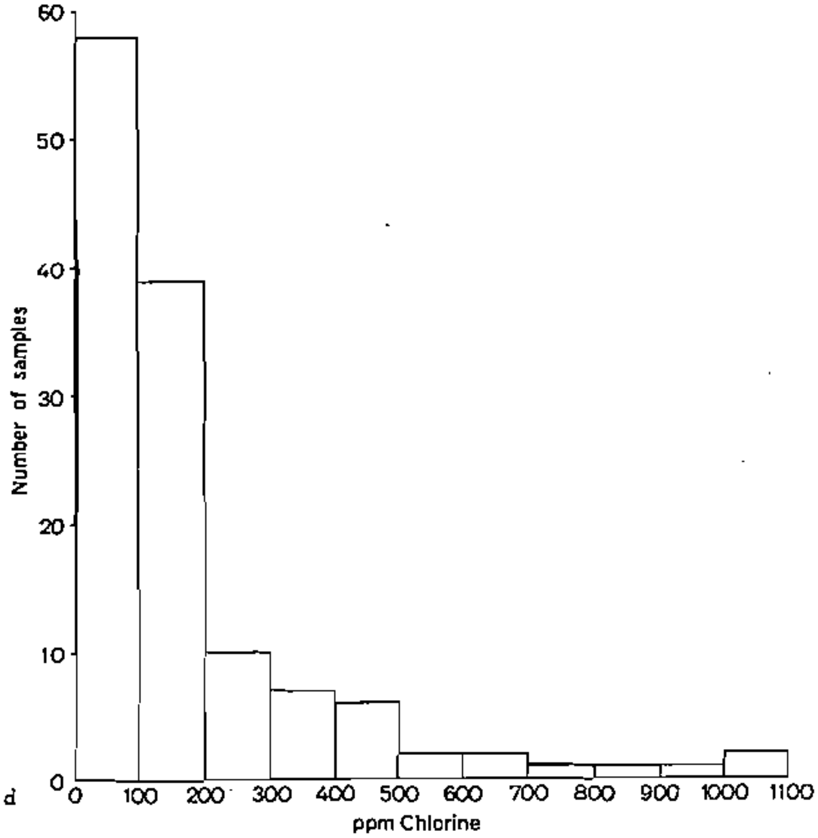
200
300
400
500
ppm Chlorine

c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0
100
200
300
400
500
600
700
800
900
1000
1100
ppm Chlorine

d

Table 17-E-3. *Comparison of chlorine content of glassy and crystalline volcanic rocks and residual glasses*

Sample	Number of samples	Chlorine content (ppm)		Reference
		Range	Mean	
Silicic welded tuffs and lavas, groundmass of hydrated glass (U.S.A.)	47	<100—5,100	990 (W)	Noble *et al.* (1967)
Silicic welded tuffs and lavas, groundmass devitrified (U.S.A.)	67	<100—9,800	396 (W)	Noble *et al.* (1967)
Silicic welded tuffs and lavas, groundmass granophyric crystalline (U.S.A.)	20	<100—1,700	165 (W)	Noble *et al.* (1967)
Silicic welded tuffs and lavas, non-hydrated glass separates	18	500—7,800	1,900 (W)	Noble *et al.* (1967)
Silicic welded tuffs and lavas, hydrated glass separates	5	500—1,700	1,300 (W)	Noble *et al.* (1967)
Glassy liparites (U.S.S.R.)	14	300—2,000	964	Shatkov *et al.* (1970)
Microfelsitic liparites (U.S.S.R.)	5	<100—100	<100	Shatkov *et al.* (1970)
Pantelleritic obsidian (Kenya)	1		3,700 (X)	Nicholls and Carmichael (1969)
Glassy pantellerites (Pantelleria)	2	3,700; 7,600	5,650 (W)	Zeis (1960)
Residual glass from same pantellerites		2,900; 6,900	4,900 (M)	Lovering (1966)
Residual glass from pantelleritic obsidians (Pantelleria)	4	3,100—8,200	6,200	Carmichael (1962)
Porphyritic microcrystalline pantellerite (Pantelleria)	1		400	Carmichael (1962)
Glassy comendites (New Zealand)	2	2,100; 2,200	2,150 (X)	Nicholls and Carmichael (1969)
Residual glass from same comendites		1,700; 2,200	1,950	Nicholls and Carmichael (1969)
Crystalline comendites (New Zealand)	2	100; 300	200 (X)	Nicholls and Carmichael (1969)

Table 17-E-4. *Chlorine in altered and unaltered ultramafic rocks*

Rock	Source	Number of samples	Chlorine content (ppm)		Reference
			Range	Mean	
Dunite	U.S.A. and Newfoundland	5	60—1,000	292 (C)	Kuroda and Sandell (1953)
	U.S.A.	2	140; 170	155 (W)	Hoering and Parker (1961)
	Dun mountain, New Zealand	1		50 (C)	Yoshida *et al.* (1971)
	Inclusion in basalt	1		28 (C)	Stueber *et al.* (1968)
	Alpine intrusions	7	33—184	88 (C)	Stueber *et al.* (1968)
	Compilation	19	28—199	96	Johns and Huang (1967)
Peridotite		1		60 (C)	Kuroda and Sandell (1953)
	New Guinea	1		<10 (C)	Yoshida *et al.* (1971)
	Japan	1		40 (C)	Sugiura (1968)
	Björkedal, Norway	1		40 (W)	Behne (1953)
	Inclusions in basalt	10	7—87	34 (C)	Stueber *et al.* (1968)
	Kimberlite pipes	5	142—299	230 (C)	Stueber *et al.* (1968)
	Kimberlite pipes	8	140—1,000	550 (C)	Greenland (quoted by Stueber *et al.*, 1968)
	Intrusions and sheets	6	65—185	108 (C)	Stueber *et al.* (1968)
	Compilation	19	7—600	156	Johns and Huang (1967)
Pyroxenite	Newfoundland	1		200 (C)	Kuroda and Sandell (1953)
	Magnet Cove, Arkansas (U.S.A.)	2	200; 800	500 (W)	Erickson and Blade (1963)
	Hawaii	1		18 (C)	Stueber *et al.* (1968)
	Russia	1		71 (C)	Stueber *et al.* (1968)
	Compilation	7	18—800	275	Johns and Huang (1967)
Harzburgite	Newfoundland	1		600 (C)	Kuroda and Sandell (1953)
	Montana (U.S.A.)	1		540 (C)	Kuroda and Sandell (1953)
	Red Hill, New Zealand	1		<10 (C)	Yoshida *et al.* (1971)
Bronzitite	Montana (U.S.A.)	1		540 (C)	Kuroda and Sandell (1953)
Eclogite	Kimberlite pipes	5	100—270	160 (C)	Greenland (quoted by Stueber *et al.*, 1968)
	Japan	1		52 (C)	Sugiura (1968)

Table 17-E-4 (continued)

Rock	Source	Number of samples	Chlorine content (ppm)		Reference
			Range	Mean	
Serpentinized dunite	Newfoundland	1		2,400 (C)	KURODA and SANDELL (1953)
	Ontario (Canada)	29	1,100—7,000	2,290 (W)[a]	EARLEY (1958)
	Puerto Rico	4	40—310	150	HESS and OTALORA (1964)
	Quebec (Canada)	3	1,100—1,500	1,233 (W/A)	RUCKLIDGE (1972)
	(10—75% serpentine)	3	139—365	234 (C)	STUEBER *et al.* (1968)
Serpentinized peridotite	Ontario (Canada)	23	300—2,400	654 (W)[a]	EARLEY (1958)
	(10—75% serpentine)	2	187; 214	101 (C)	STUEBER *et al.* (1968)
Serpentinized pyroxenite	Ontario (Canada)	3	280—700	453 (W)[a]	EARLEY (1958)
Serpentinized harzburgite	N. America	1		1,300 (C)	KURODA and SANDELL (1953)
	Puerto Rico	9	40—310	156	HESS and OTALORA (1964)
Serpentinites	U.S.A. and Japan	7	20—520	270 (C)	KURODA and SANDELL (1953)
		17	35—2,870	670 (C)	STUEBER *et al.* (1968)
Suggested average for ultramafic rocks:				85	TUREKIAN and WEDEPOHL (1961)
				50	VINOGRADOV (1962)
Suggested average for unaltered ultramafic rocks:				32	STUEBER *et al.* (1968)

[a] Potentiometric method.

Table 17-E-5. *Chlorine in some "standard" reference rocks*

Sample	Chlorine (ppm)	Method	Reference
Granite G-1	63	C	Huang and Johns (1967)
	50	C	Iwasaki *et al.* (1955)
Granite G-2	192	C	Huang and Johns (1967)
	122	C	Sen Gupta (quoted by Flanagan, 1969)
	99	C	Fuge and Power (1969)
	53	N/R	Johansen and Steinnes (1967)
Granodiorite GSP-1	342	C	Huang and Johns (1967)
	365	C	Sen Gupta (quoted by Flanagan, 1969)
	305	C	Fuge and Power (1969)
	311	N/R	Johansen and Steinnes (1967)
Andesite AGV-1	319	C	Huang and Johns (1967)
	185	C	Sen Gupta (quoted by Flanagan, 1969)
	147	C	Fuge (unpublished)
	115	N/R	Johansen and Steinnes (1967)
Basalt BCR-1	62	C	Huang and Johns (1967)
	120	C	Sen Gupta (quoted by Flanagan, 1969)
	62	C	Cattermole and Fuge (1969)
	58	N/R	Johansen and Steinnes (1967)
Diabase W-1 (Basalt)	187	C	Huang and Johns (1967)
	188	C	Cattermole and Fuge (1969)
	204	N/R	Johansen and Steinnes (1967)
Peridotite PCC-1	74	C	Huang and Johns (1967)
	100	C	Sen Gupta (quoted by Flanagan, 1969)
	85	C	Cattermole and Fuge (1969)
	65	C	Stueber *et al.* (1968)
	66	N/R	Johansen and Steinnes (1967)
Dunite DTS-1	33	C	Huang and Johns (1967)
	20	C	Sen Gupta (quoted by Flanagan, 1969)
	10	C	Cattermole and Fuge (1969)
	9.4	N/R	Johansen and Steinnes (1967)
Nepheline syenite STM-1	431	N/R	Johansen and Steinnes (1967)

almost entirely absent from the olivine; the serpentine contained upto 0.8% chlorine (M).

The effect of serpentinisation on dunite appears to be greater than on other ultramafic rocks.

Stueber *et al.* (1968) propose that as chlorine appears to be easily introduced into ultramafic rocks by secondary alteration, a downward revision of previous estimates of abundance is necessary. They suggest that the chlorine content of unaltered ultramafics is more nearly represented by that of ultramafic inclusions in basalt (mean 32 ppm).

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17-F. Behavior in Magmatogenic Processes (Pegmatites, Gas Transport, Ore Deposition etc.)

I. Behavior during Crystallization and Differentiation

Few studies have been undertaken of the behavior of chlorine during magmatic differentiation. Kuroda and Sandell (1953) found little variation in the chlorine content of the upper and lower zones of differentiated bodies; Greenland and Lovering (1966) showed that the chlorine content of a differentiated Tasmanian tholeiitic dolerite varied between 50 and 120 ppm (W), there being a possible slight enrichment in the final granophyric differentiates (Fig. 17-F-1 a).

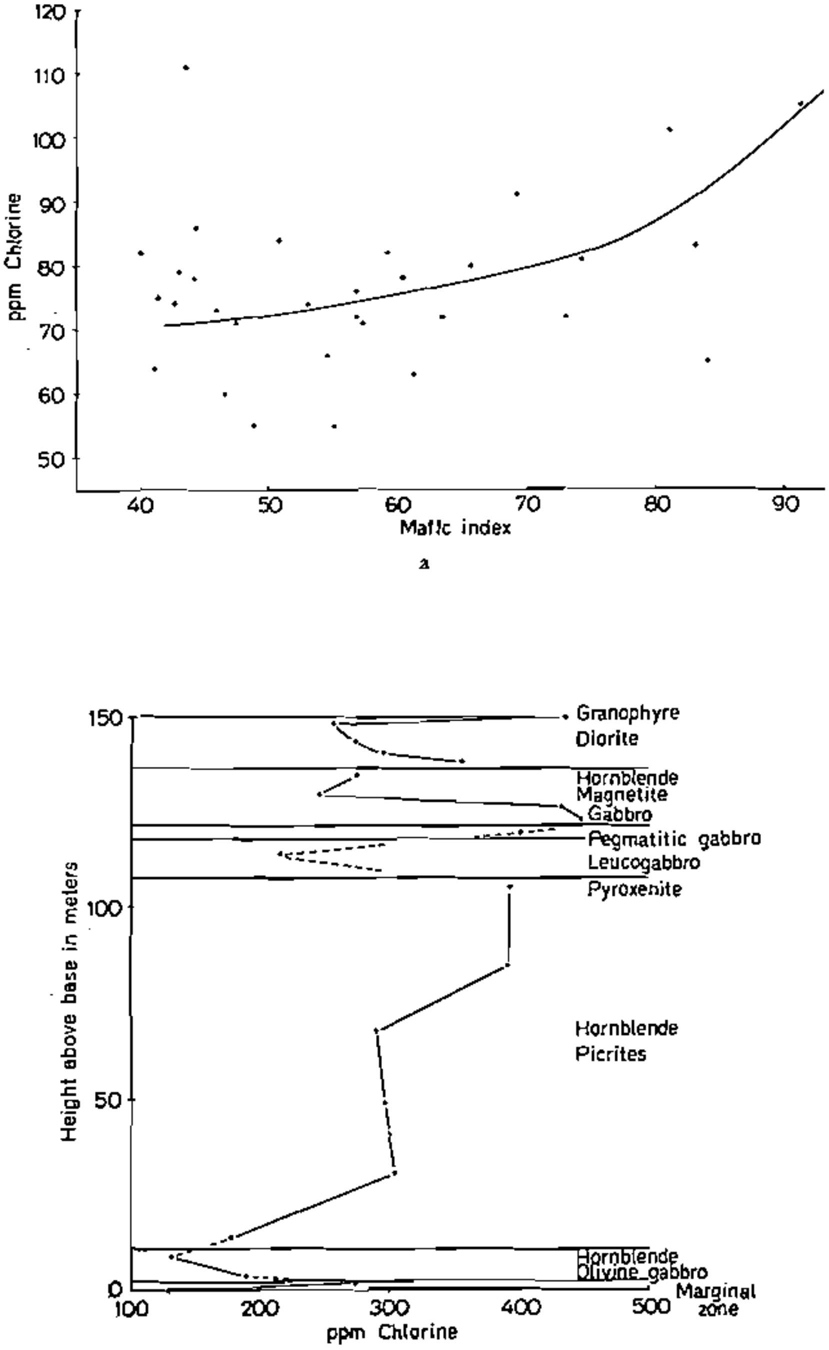
The distribution of chlorine in a differentiated ultramafic to mafic body was studied by Cattermole and Fuge (1969). Their data, summarized in Table 17-F-1 and Fig. 17-F-1 b, show that there is a general enrichment of chlorine with increasing silica content.

Table 17-F-1. *Chlorine in a layered ultramafic to mafic intrusion (Rhiw, N. Wales)* (from data of Cattermole and Fuge, 1969; method: C)

Rock type	Number of samples	SiO_2 (%)	Cl (ppm)
Marginal rock	2	43.1	203
Hornblende olivine gabbro	2	40.5	161
Hornblende picrite (and pyroxenite)	6	39.6	293
Leucogabbro	1	44.5	215
Pegmatitic gabbro	1	42.2	400
Hornblende magnetite gabbro	4	38.1	351
Diorite	4	45.4	283
Granophyre	1	58.6	433

During crystallization, some chlorine enters hydroxyl positions in the lattice of hydroxysilicates and apatite (see section 17-D). However, most of the chlorine is likely to remain in the residual fluids, as has been demonstrated experimentally by Koster van Groos and Wyllie (1969). At extremely high chloride concentrations there is likely to be liquid immiscibility between the silicate and chloride-rich aqueous phases (Delitsyn and Melent'yev, 1968). According to Roedder (1972), some residual magmatic liquids can contain upto 50% by weight of sodium chloride.

Roedder and Coombs (1967) have shown that liquid immiscibility has occurred between the siliceous magma and chlorine-containing phase in granitic blocks from Ascension Island. Immiscibility in the late stages of differentiation of under-saturated magmas, due to high chlorine and other volatiles, has been suggested for the Lovozero alkali massif (Kogarko and Ryabchikov, 1969).



a

b

Fig. 17-F-1a and b. Variation of chlorine content during differentiation of: a Tholeiitic dolerite, Tasmania (from GREENLAND and LOVERING, 1966); b Layered ultramafic/mafic intrusion, Rhiw, N. Wales (from data of CATTERMOLE and FUGE, 1969)

II. Pegmatites; Behavior during Metasomatism

The enrichment of chlorine in the residual magmatic fluids can result in the occurrence of chlorine-rich hydroxysilicate minerals in pegmatites and also in metasomatic deposits such as skarns (Tables 17-F-2 and 17-F-3). In addition scapolite may occur in pegmatites and metasomatised rocks. However, it appears in general that granitic pegmatites are not greatly enriched in chlorine.

The high chlorine content of late stage fluids may greatly affect the crystallized rocks. ORVILLE (1963) showed that chloride-rich fluids assist the movement of alkalis in feldspars. BARSUKOV and KLINTSOVA (1969) have shown that interaction of granite with alkali chloride solutions reproduces such metasomatic effects as albitization, muscovitization and K-feldspathization.

The action of chlorine-rich residual fluids in the Lovozero alkali massif has caused secondary sodalization (KOGARKO and RYABCHIKOV, 1969).

However, many metasomatised and hydrothermally altered granitic rocks particularly greisens (Table 17-F-3) show a marked decrease in chlorine content (FUGE and POWER, 1969b), and STOLLERY *et al.* (1971) have shown that chloritisation of biotites results in lowering of their chlorine contents.

III. Volcanic Gases and Sublimates

Chlorine occurs in volcanic gases primarily as HCl (see Table 17-F-4).

The chlorine content of volcanic gases from Showashinzan volcano, Japan, was shown by SUGIURA *et al.* (1963) to vary greatly with time. BASHARINA (1965) has stated that in common with other volcanic gas components, the chlorine content varies with the composition and stage of cooling of the magma, and a study of volcanic gases in Kamchatka showed that those of a basaltic volcano were richer in chlorine than those of an andesitic volcano.

SUGIURA *et al.* (1963) found that the chlorine content of the volcanic gases of Showashinzan volcano, Japan, decreases as the temperature falls (Fig. 17-F-2a). High temperature gases of Kamchatka were found by BASHARINA (1965) to be enriched in acid gases such as HCl. However, WHITE and and WARING (1963) state that the HCl contents of volcanic gases show little tendency to increase with rising temperature.

The ratio F/Cl in the volcanic gases of Showashinzan (Fig. 17-F-2b) falls rapidly with temperature decrease (SUGIURA *et al.*, 1963). This feature was also observed by BASHARINA (1965) at Kamchatka. YOSHIDA (1963) found that during heating of volcanic rocks, chlorine is volatilised to a greater degree than fluorine.

The HCl content of volcanic gases generally greatly exceeds that of HF (WHITE and WARING, 1963). (The energetics of HCl and its relationship with HF in volcanic emanations is discussed by MUELLER, 1970).

BASHARINA (1965) found that the chlorine content of volcanic gases can greatly influence their metal content, high temperature HCl-rich gases of Kamcharka frequently being enriched in aluminum and iron.

Chlorine is extremely enriched in many volcanic sublimates, Cl^- often being the major anion. Hence ammonium and alkali chlorides are often abundant in volcanic sublimates (WHITE and WARING, 1963). These chlorides together with iron com-

Table 17-F-2. *Chlorine in minerals from pegmatitic and metasomatic rocks*

Sample, source	Number of samples	Chlorine content %		Reference
		Range	Mean	
Apatites, veins, Odegården (Norway)	2	6.02; 6.24	6.13 (W)	Morton and Catanzaro (1964)
Apatite, vein, metasomatically altered, Odegården (Norway)	1		1.40 (W)	Morton and Catanzaro (1964)
Apatite, marble, Ontario (Canada)	1		6.2 (W)	Hounslow and Chao (1970)
Biotite, pegmatite, Kondapalli (India)	1		1.96 (M)	Leelanandam (1970)
Biotites, pegmatites (Japan)	2	0.004; 0.24	0.14 (C)	Sugiura (1968)
Siderophyllite, pegmatite, Brooks Mt. (Alaska)	1		0.24	Gower (1957)
Muscovite, pegmatite, Brazil	1		0.035 (W)	Behne (1953)
Muscovite, pegmatite, Japan	1		0.001 (C)	Sugiura (1968)
Hornblende, skarn, Basttjärn (Sweden)	1		1.42	Magnusson (quoted by Gillberg, 1964)
Hornblende, skarn, Långban (Sweden)	1		0.20	Geijer (quoted by Gillberg, 1964)
Ferrohastingsites, metasomatic magnetite deposits	18	0.81—2.93	1.61	Malinoskii and Kostyuk (1970)
Chlorohastingsites, metasomatic iron-ore deposits	6	0.96—1.69	1.37	Krutov *et al.* (1970)
Dashkesanites, skarn, Dashkesan (U.S.S.R.)	2	5.59; 7.24	6.42	Krutov (1936)
Dashkesanite, skarn, Dashkesan (U.S.S.R.)	1		3.25	Selivanov (1940)
Dashkesanites, skarns, Trans-Baikal (U.S.S.R.)	2	1.42; 2.77	2.10	Novoselova (1961)
Tourmalines, pegmatites, veins and related rocks, S. W. England	17	0.024—0.102	0.045 (C)	Fuge and Power (1969a)
Tourmalines, contact zones, S. W. England	3	0.067—0.078	0.073 (C)	Fuge and Power (1969a)
Tourmalines, hydrothermal, S. W. England	6	0.035—0.071	0.054 (C)	Fuge and Power (1969a)

Table 17-F-3. *Chlorine in some pegmatitic rocks and altered granites*

Sample	Number of samples	Chlorine content (ppm)		Reference
		Range	Mean	
Pegmatites, Japan	2	20; 40	30 (C)	Sugiura (1968)
Pegmatites, S. W. England	6	57—530	383 (C)	Fuge and Power (unpublished)
Topazfels, S. W. England	1		273 (C)	Fuge and Power (unpublished)
Quartz tourmaline rocks, S. W. England	3	171—196	180 (C)	Fuge and Power (unpublished)
Greisens, Germany	24		50 (W)	Behne (1953)
Greisens, S. W. England	5	12—96	40 (C)	Fuge and Power (1969b)
Hydrothermally altered granites, S. W. England	5	80—221	198 (C)	Fuge and Power (1969b)
Kaolinised granites, S. W. England	14	70—381	153 (C)	Fuge and Power (1969b)
Unaltered granites, S. W. England	90	75—1,180	507 (C)	Fuge and Power (1969b)

Table 17-F-4. *HCl content of volcanic gases in volume %* (from compilation of White and Waring, 1963)

Sample source	Temp. (°C)	H_2O concentration	Total "active" gases	HCl as percentage of active gases	Year collected
Showashinzan volcano (Japan)	750	99.25	0.723	5.39	1959
Hypersthene dacite	655	99.48	0.516	8.7	1957
	464	99.10	0.859	1.51	1959
	460	99.24	0.537	10.6	1959
	190	99.72	0.258	4.66	1959
Sheveluch volcano, Kamchatka (U.S.S.R.),	280	n.d.	13.50	1.1	1953
	180	n.d.	1.60	41.0	1953
Andesite	110	n.d.	11.76	2.5	1953
Kliuchevskii volcano, Kamchatka (U.S.S.R.),	170	n.d.	0.06	33	1946
	150	n.d.	0.08	20	1947
Basalt	86	n.d.	0.35	0	1949
	70	n.d.	0.065	31	1946
Ten Thousand Smokes, Katmai volcano, Alaska (U.S.A.)	400	99.97	0.03	87	1917
	300	99.69	0.31	78	1917
Rhyolite ash	100	99.98	0.02	40	1917
White Island (New Zealand) *Hypersthene andesite*	~500	o.d.	85.0	11.5	1927
Mount Hekla (Iceland) *Basalt*	620	o.d.	7.0	11.4	1951

pounds, have also been found to be sublimed from heated volcanic rocks (Yoshioa *et al.*, 1965). In addition several trace elements can occur in these sublimates, including such metals as copper, zinc and lead.

Rubey (1951, 1955) and Kuroda and Sandell (1953) have suggested that much of the chlorine of the oceans has been derived gradually through time from volcanic gas sources (see also Iwasaki *et al.*, 1968).

IV. Hydrothermal Fluids; Ore Transport and Chloride Complexes

Most thermal waters are derived from meteoric water which has subsequently been heated, but small quantities may be of magmatic origin (White *et al.*, 1963). Ellis and Mahon (1964, 1967) have shown by experiment that thermal waters can leach over 50% of the chlorine from volcanic and sedimentary rocks (see Table 17-F-5); such thermal waters (Table 17-F-6), enriched in chlorine, could play a vital role in the transport of metals in solution (Ellis and Mahon, 1967).

Many theories have been advanced to explain the origin of ore bodies (Krauskopf, 1967; Barnes, 1967; and others) The aqueous fluids connected with magmatism have long been thought to be responsible for the deposition of ore bodies related to granitic intrusions (Holland, 1972). For ore deposits related to sedimentary en-

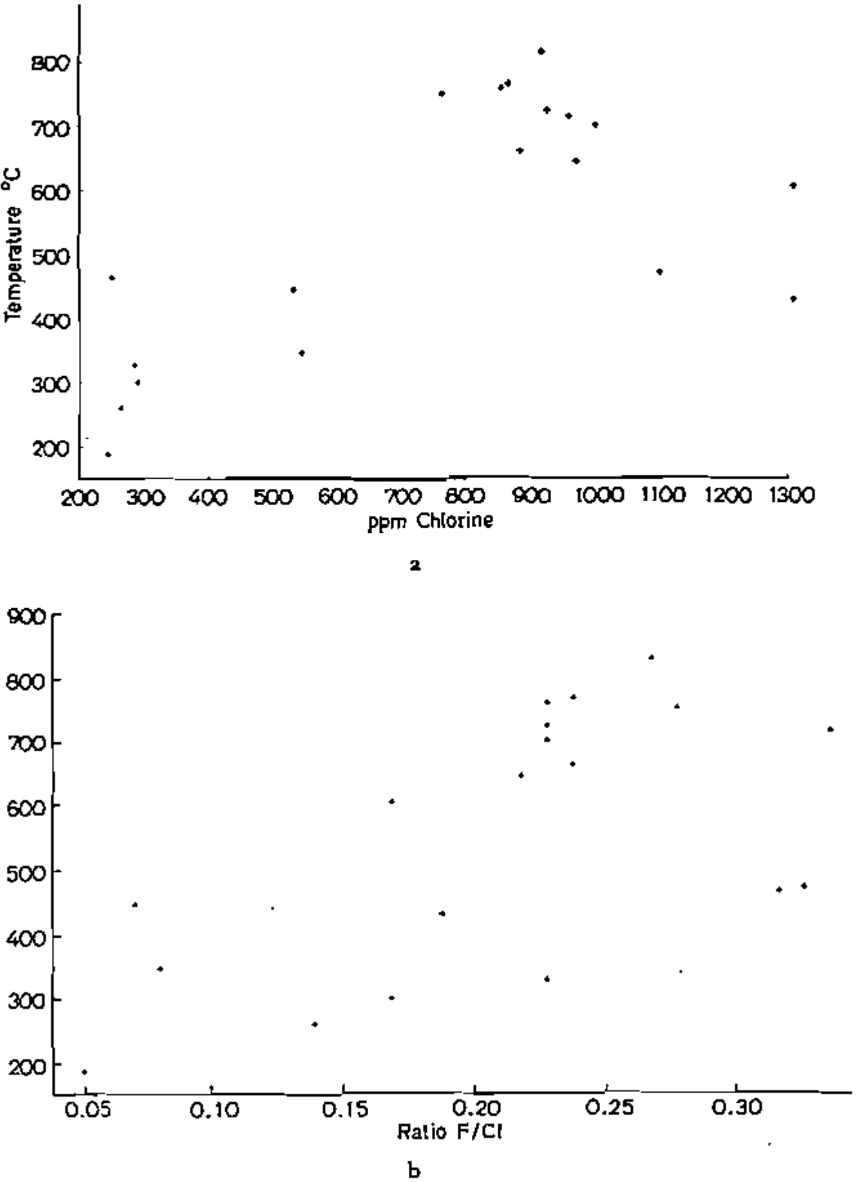


Fig. 17-F-2a and b. Variation with temperature of: a Chlorine, b Fluorine/chlorine ratio, in volcanic gases, Showashinzan volcano, Japan (from SUGIURA *et al.*, 1963; method; W)

vironments, there is no general agreement on the origin of ore-forming solutions (DUNHAM, 1970). At the present time hot metalliferous brines occurring in the Salton Sea, the Red Sea and at Cheleken, U.S.S.R., are precipitating ore minerals (TOOMS, 1970), and it has been suggested that similar sources may account for some mineral deposits of the past (WHITE, 1968; DUNHAM, 1970).

Table 17-F-5. *Maximum quantity of chlorine leached from rocks during reaction for 2 weeks (400° to 600° C; 1,500 bars)* (from Ellis and Mahon, 1967; method: potentiometric)

Rock	Cl content (ppm)	% chlorine leached from rock
Pumice	990	100
Obsidian	900	54
Ignimbrite	600	16
Rhyolite	600	48
Dacite	120	93
Andesite	190	79
Basalt	360	85
Greywacke	12	66

Table 17-F-6. *Chlorine in thermal waters*

Origin	Chloride content (mg/l)	Reference
Average composition, Japanese thermal and mineral springs	1,250	Sugawara (1967)
New Zealand thermal waters associated with volcanicity	280—61,840 Mean (20) 4,280 (W)	Ellis and Mahon (1964)
New Zealand thermal waters in non-volcanic and old volcanic areas	42—16,000 Mean (12) 2,510 (W)	Ellis and Mahon (1964)
Spring and drill hole waters, Tokaanu—Waihi area, New Zealand, associated with andesitic intrusion	7.1—3,255 Mean (64) 1,560	Mahon and Klein (1968)
Geyser waters		White *et al.* (1963)
Yellowstone Park, Wyoming (U.S.A.)	405; 744	
Steamboat springs, Nevada (U.S.A.)	865	
Iceland	63—27,400 Mean (3) 9,200	
Kamchatka	700—1,680 Mean (3) 1,080	
Thermal waters, probably entirely meteoric in origin		White *et al.* (1963)
Bowers, Nevada (U.S.A.)	5.4	
Hot springs, Arkansas (U.S.A.)	2.5	
Kristenes, Iceland	13.0	

Whatever the source of the ore-forming fluids, it appears likely that they are chloride-rich. Roeoder (1967, 1972) has pointed out that the chloride ion is the major anion of many fluid inclusions in ore minerals (see Table 17-F-7). White (1968) has suggested that ore-bearing fluids are likely to be Na—Ca—Cl brines which

Table 17-F-7. *Chlorine content of fluid inclusions from mineral deposits* (from compilation by ROEDDER, 1972)

Mineral	Source	Chloride (ppm of total inclusion fluid)
Sphalerite	Sphalerite-galena, Mississippi Valley-type deposit; Oklahoma (U.S.A.)	124,600
	Replacement deposit, limestone; Santander (Spain)	91,000
	Au-Ag-Cu deposit, volcanic rocks; Japan	63,600
	Pb-Zn-Ag deposit, volcanic rocks; Colorado (U.S.A.)	17,600
	Sphalerite-galena deposit, Mississippi Valley-type deposit?; Cartagena (Spain)	129,600
Galena	Fluorite-sphalerite, vuggy-bedded replacements; Cave-in-Rock district, Illinois (U.S.A.)	115,000
	Sphalerite-galena, Mississippi Valley-type deposit; Mississippi (U.S.A.)	83,000
Barite	Kopet-Dag barite area, Arpaklen deposit (U.S.S.R.)	42,900
	Upper Racha, Georgia, Lesora Section, Chorda (U.S.S.R.)	18,400
	Upper Racha, Georgia, upper Gvalvana, Chorda (U.S.S.R.)	13,400
	Centre of vein, Okureshi deposit; western Georgia (U.S.S.R.)	88,200
	Margin of vein, Okureshi deposit; western Georgia (U.S.S.R.)	88,800
Fluorite	Fluorite-sphalerite, vuggy-bedded replacements; Cave-in-Rock district, Illinois (U.S.A.)	84,000
	Fluorite-sphalerite, vuggy-bedded replacements; Cave-in-Rock district, Illinois (U.S.A.)	78,000
	Hypogene fluorite replacing limestone; Aurakhmat, central Asia	53,000
	Hypogene fluorite replacing limestone; Aurakhmat, central Asia	49,000
	Hypogene fluorite replacing limestone; Aurakhmat, central asia	4,000
Calcite	Iceland spar deposit, pillow lavas, Gonchak, Siberian shield (U.S.S.R.)	83,600
	Iceland spar deposit, pillow lavas, Gonchak, Siberian shield (U.S.S.R.)	158,800
	Iceland spar deposit, pillow lavas, Nidym, Siberian shield (U.S.S.R.)	47,700
	Iceland spar deposit	65,890
Quartz	Antimony—mercury deposit; Pacific region, (U.S.S.R.)	40
	Antimony—mercury deposit; Pacific region, (U.S.S.R.)	660
	Quartz with cinnabar from "concordant type" deposit, central Asian mercury-antimony province, U.S.S.R.	580—620
	Barren quartz vein, rhyolite, Arizona (U.S.A.)	630
	Fluorite-sphalerite, as vuggy-bedded replacements; Cave-in-Rock district, Illinois (U.S.A.)	47,000

he further suggests may be derived from magmatism, connate waters, solution of evaporites followed by reaction with sediments, or by membrane concentration (see Section 17-I).

KILINC and BURNHAM (1972) have shown experimentally that the chlorine of silicate melts is very strongly partitioned towards the aqueous phase; in addition these authors report that previous studies have revealed that base and precious metals are also strongly partitioned in this manner. HOLLAND (1972) has also found that zinc, manganese and probably lead are strongly partitioned into the aqueous phase of silicate melts and that this partitioning is proportional to the square of the chlorine content of the aqueous phase. TOOMS (1970) noted that the metal content of thermal brines appeared to be dependent upon the salinity.

All of these workers favour the theory that the metals of the hydrothermal solutions are present as chloride complexes.

The solubility of ore minerals in pure waters is extremely low (KRAUSKOPF, 1967) and thus it appears reasonable to suppose that ore metals must be transported in the form of complexes (HELGESON, 1964).

HELGESON (1964) demonstrated that the solubility of galena in sodium chloride solutions increases with temperatures upto 350 °C. The same author (1969) has suggested that computed solubilities of many sulfide minerals in 3 molal sodium chloride at pH 5 are more than sufficient at high temperatures to account for hydrothermal deposits. The order of stability for chloride complexes at 25° C as quoted by HELGESON (1964) is:

$$Cu^{++} < Zn^{++} < Pb^{++} < Ag^{+} < Hg^{++}$$

with log K_{298} for the ion pairs being:

$$\sim 0, \quad \sim -2, \quad -1.57, \quad \sim -3.3, \quad -7.3.$$

It has been pointed out by HELGESON that this order corresponds to the sequence of minerals found in many deposits, but that this sequence is not unique to chloride complexes.

From thermodynamic considerations, HELGESON (1969) has shown that there is a high degree of association of metal ion-chloride complexes at high temperature.

Revised manuscript received: March 1973

17-G. Behavior during Weathering

Goldschmidt (1954) assumed that during the process of weathering, all of the chlorine in magmatic rocks would be released.

The behavior of chlorine during weathering of granite was studied by Behne (1953). The results, given in Table 17-G-1, show that there is an increase of chlorine content in the lower weathered layers, the loss of chlorine parallels the bleaching of biotite. The upper layers of the locality St. Andreasberg are higher in chlorine than the fresh granite from Schierke which may be due to local primary differences or secondary accumulation.

Table 17-G-1. *Chlorine content and distribution in a weathering profile of granite* (from Behne, 1953; method: W)

Sample, depth below surface	Cl (ppm)
Fresh granite, Brocken, Schierke (Germany)	270
3—5 m altered granite, St. Andreasberg (Germany)	600
2—3 m altered granite, St Andreasberg (Germany)	670
1—2 m altered granite, St. Andreasberg (Germany)	140
½—1 m altered granite, St. Andreasberg (Germany)	≦20

Table 17-G-2. *Chlorine content of soils* (from Vinogradov, 1959)

Soil type	Horizon	Chlorine (ppm)
Podzol on varved clay	A_2	40
	B	70
Grey forest	A	35
	A_1	30
	B	30
	C	18
		20
Chernozem	A	25
	B	25
	C	90
Brown Forest	A	3.5
Peats		130—650

Sodium chloride can be leached from marine deposited sedimentary rocks to appreciable depths (BILLINGS and WILLIAMS, 1967). NOBLE *et al.* (1967) found that chlorine could be removed from and added to volcanic glasses by the action of ground water.

From their work on Miocene tuffaceous sediments in Gifu Prefecture (Japan), ISHIZUKA *et al.* (1970) found that as the glassy material weathered to clay, the chlorine content decreased (see also OGITA *et al.*, 1967).

Table 17-G-2 lists data on chlorine in soils as being on average less than 50 ppm Cl.

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17-H. Behavior and General Chemistry in Natural Waters

A very large portion of the chlorine released during weathering is easily soluble in water. In natural waters it occurs almost exclusively as the chloride anion and forms no important complexes with other ions (HEM, 1970). It is not adsorbed to any marked degree on mineral surfaces (HEM, 1970) and is concentrated greatly by only a few groups of organisms. Its behavior in natural waters has been described by HEM (1970) as "tame and subdued".

Most of the naturally occurring chlorine in surface run-off is originally marine in origin being derived either from atmospherically transported sodium chloride (see Section 17-I) or from sedimentary rocks and evaporites etc. For this reason chlorine has been described by GOLDSCHMIDT (1954) as a cyclic element.

Revised manuscript received: March 1973

17-I. Abundance in the Atmosphere and in Natural Waters

I. Atmosphere

Chlorine is transported into the atmosphere as sodium chloride from the sea by wave action and bubbles breaking at the surface (WINCHESTER and DUCE, 1967); part of this chlorine is present in a gaseous state and part occurs in the aerosol phase (JUNGE, 1963; DUCE *et al.*, 1965). The gaseous phase may in part be chlorine gas, which may be formed due to reaction of NaCl with ozone (CAUER, 1951), and in part HCl, due to reaction of sodium chloride with sulfuric acid (ERIKSSON, 1960).

The data presented by JUNGE (1963) (see Table 17-I-1) shows that chlorine in the gaseous state may make up over 50% of the total. According to DUCE *et al.* (1965), 50% of atmospheric chlorine over Hawaii is in the gaseous state.

Much of the sodium chloride transported from the sea has a fairly short residence time in the atmosphere, being deposited on the land surface by wet or dry precipitation (see Subsection 17-II-a). However, some of the chloride is transported large distances in the form of aerosols. LOUCKS and WINCHESTER (1970) found that the major portion of the chlorine found in continental aerosols of the U.S.A. is derived from the ocean. WINCHESTER and DUCE (1967) determined the chlorine content of aerosols from three widely differing regions of the U.S.A.; their results are summarized in Table 17-I-1.

Other sources of chlorine in the atmosphere are discussed in Subsection 17-II-a.

II. Natural Waters

a) Rain Water

The greatest source of chlorine in rainfall is the sea. The chloride content of rainfall is far greater near the coast than inland (ERIKSSON, 1952; JUNGE and WERBY, 1958; see Fig. 10-9 in Volume I of this handbook). The chloride contents of inland precipitation do not vary greatly.

Other minor sources of chlorine in precipitation are combustion of coal, human activities such as production of salt by evaporation (some of the high values of chlorine content of rain in continental U.S.A. of Fig. 10-9, in Volume I of this handbook, may be due to this), industrial processes involving chlorine and hydrochloric acid etc., and volcanic emanations (ERIKSSON, 1952). In connection with volcanic sources of chlorine in rain water, ERIKSSON (1952) records upto 247 ppm chlorine in rainfall near Vesuvius, Italy, and 400 ppm chlorine in rainfall near Paricutin, Mexico.

b) Ground Water

The chlorine contents of ground waters associated with specific rock types as quoted by WHITE *et al.* (1963) are given in Table 17-I-2. It is obvious from this

Table 17-I-1. *Chlorine contents of atmosphere, rainwater and snow*

Locality	Number of samples	Concentration of chlorine ($\mu g/m^3$)		Method	Reference
		Aerosol	Gas		
Atmosphere					
Florida, land breeze	6	0.56	0.80	C	Junge (1963)
sea breeze	7	2.39	2.23	C	Junge (1963)
all data	13	1.54	1.57	C	Junge (1963)
Hawaii	10 (14 Gas)	5.09	1.92	C	Junge (1963)
	5	2.58		N/R	Winchester and Duce (1967)
Ipswich, Massachusetts	9		4.40	C	Junge (1963)
Cambridge, Massachusetts	10	2.65		N/R	Winchester and Duce (1967)
Barrow, Alaska	23	0.67		N/R	Winchester and Duce (1967)

Locality	Number of samples	Chlorine content (mg/liter)		Method	Reference
		Range	Mean		
Snow					
Barrow, Alaska	31	0.65—210	36.4	N/R	Duce *et al.* (1966)
Sierra Nevada	28	0.0—2.6	0.6	C	Feth *et al.* (1964)
Czechoslovakia	40		3.9		Valach (quoted by Carpenter (1969)
Rain					
Hawaii	85	0.23—15.6	2.95	N/R	Duce *et al.* (1965)
Japan	300		1.1		Sugawara (1967)
California	56	0.0—23	3.55	C	Whitehead and Feth (1964)
New Zealand, 0.3 miles from sea	2	25.0; 27.3	26.2		Blakemore (1953)
4 miles from sea	2	10.3; 13.1	11.7		Blakemore (1953)
over 4 miles from sea	5	3.7—6.1	5.2		Blakemore (1953)

Table 17-I-2. *The chlorine content of ground water from various rock types* (from compilation of White *et al.*, 1963)

Rock type	Number of samples	Chlorine content	
		Range	Mean
Granites and rhyolites	15	1.2—193	37.5
Gabbros, basalts and ultramafics	16	0.7—75	22.5
Andesites, diorites and syenites	4	0—8.8	4.35
Sandstones, arkoses and greywackes	17	1.5—442	37.3
Siltstones, clays and shales	18	2.0—1,710	209.2
Limestones	14	1.8—112	19.7
Dolomites	6	1.0—17	6.92
Quartzites and marbles	7	0.8—9.9	5.59
Other metamorphics	15	0.4—106	23.2
Unconsolidated sand and gravel	20	1.3—1,820	234.7

Table that waters from fine-grained sedimentary rocks are enriched in chlorine, due probably to the leaching out of sodium chloride from rocks of marine origin (White *et al.*, 1963). The high chlorine content of unconsolidated sands and gravels is likely to be due to many causes, such as leaching from salt deposits and sedimentary rocks, and contamination from such sources as fertilizers and animal and human sewage (White *et al.*, 1963). In connection with the latter sources it is of interest to note that Lahermo (1970) found high chloride values, mean 67.0 mg/liter, for samples from near agricultural settlements in Finland; his values for uncontaminated groundwater were in the range 0.7 to 17.7 mg/liter.

Sugawara (1967) has estimated that of the 5.2 mg/liter of chlorine in Japanese river waters, 0.45 mg is derived from fertilizers (i.e. 8.7%).

The chlorine content of ground water from igneous rocks is generally fairly low, but some samples give very high values (White *et al.*, 1963). Garrels (1967) has suggested that much of the chloride in ground waters in igneous rocks is derived from rain water, small amounts possibly being added from chloride-rich fluid inclusions. Noble *et al.* (1967) have suggested that chlorine can be easily removed from glassy igneous rocks, and it is therefore likely that some may be added to water in this way.

Kolotov and Kolotov (1967) found high chlorine contents in ground waters near alkaline intrusive bodies.

c) River Waters

The chlorine contents of the world's rivers are given in Table 17-I-3; from several studies performed in the U.S.A., it is apparent that much of the chlorine of river waters is derived from sources other than precipitation (Hem, 1970). Human activities, such as the application of chloride-containing fertilizers etc., volcanic gases and thermal springs are likely to be sources. Hutchinson (1968) found that one important source in Maine, U.S.A., was sodium chloride used on road surfaces for de-icing purposes.

A variable amount of the chlorine occurring in river waters is derived from wet or dry precipitation. Baldwin (1971) has shown that 59% of the total chloride carried

Table 17-I-3. *Weighted means of chlorine content of world's rivers* (from LIVINGSTONE, 1963)

	Chlorine content (mg/liter)
N. America	8.0
S. America	4.9[a]
Europe	6.9
Asia	8.7
Africa	12.1
Australia	10.0
World	7.8[a]

[a] GIBBS (1972) has given a modified value of 5.4 for S. American rivers, and 8.1 for the world's rivers.

out of a coastal basin in California is derived from precipitation, but only 19% was derived from wet precipitation. HEM (1970) reports studies where the chloride supplied by precipitation was found to be as low as 1.6%.

SUGAWARA (1967) estimated the average contributions to Japanese river waters (which contain 5.2 mg/liter of chlorine) as follows:

Precipitation: 1.4 mg (26.9%).

Dry fallout: 2.47 mg (47.5%).

Industrial products: 0.90 mg (17.3%) (half from fertilizers and half from sewage etc.)

Thermal and mineral springs: 0.37 mg (7.1%).

Chlorine has been termed a cyclic element, being derived from the sea and carried back to the sea in surface run-off. Whereas a large percentage of the chlorine in rivers is not derived directly from the sea, much of it has been derived indirectly from the sea. Evaporite sediments, brines, sedimentary pore waters etc., some volcanic waters and gases, and even chlorine used for industrial purposes are all derived from the sea. However, small amounts are likely to be added from breakdown of igneous rocks etc.

d) Sea Water

The chloride ion is the major anion in sea water, being present to the extent of 19,353 mg/liter (CULKIN, 1965), while some closed basins such as the Dead Sea can contain as much 208,020 mg/liter (BENTOR, 1969).

It is likely that almost all the chlorine occurring in the oceans has originated from volatiles (RUBEY, 1951). It has been suggested that a large proportion of this chlorine may have been derived from outgassing of the primordial Earth (VINOGRADOV, 1967). Other workers have suggested that much of the chlorine has been derived from volcanic emanations (KURODA and SANDELL, 1953; RUBEY, 1955; see also Section 17-F).

e) Oilfield Brines and Formation Waters

This very important topic can be considered only briefly here. In most oilfield brines and formation waters the chloride ion is the major anion, but in some, the bicarbonate or sulfate anions exceed chloride. Many of these waters have a chloride content which exceeds that of sea water and it appears likely that most waters occurring in sedimentary rocks are derived initially from buried seawater, which is altered to a greater or lesser degree. Chave (1960) has suggested that changes in composition begin almost immediatly after the water has been separated from free circulation with the ocean. The processes which alter the composition of buried sea water have been classified into four categories by Chilingarian and Rieke (1969):

(i) physical (compaction)
(ii) chemical (reaction with rock minerals, organic matter and pore solutions etc.)
(iii) physicochemical (membrane filtration, adsorption etc.)
(iv) biochemical.

The salinity of formation waters increases with depth (i.e. pressure) in porous rocks (von Engelhardt, 1960). von Engelhardt and Gaida (1963) found experimentally that increasing pressure on montmorillonite clays, upto 800 atmospheres, resulted in the removal of NaCl (and $CaCl_2$) from the pore solutions. At higher pressures, upto 3,200 atmospheres, the NaCl content of the pore solutions began to increase again.

The high salinity of some oilfield brines and formation waters is due to the dissolution of evaporites (White *et al.*, 1963; Hitchon *et al.*, 1971).

Clays and shales can act as semi-permeable membranes, due to the electrical properties of clay minerals and, possibly, of kerogen (Berry, 1969). This author has also deduced the following hyperfiltration selectivity sequence for the halogens: $Cl \geqq Br > I > F$ (fluorine showing the greatest tendency to pass through, chlorine the greatest tendency to be retained).

White (1965) has suggested the following relative mobilities of ions through clay membranes:

$$Ca^{++}, SO_4^{=} < Cl^- < NH_4^+, S^{=}, HS^- < Na^+, HCO_3^-, F^-, I^-, H_2O$$

(see also Everdingen, 1968).

A review of diagenetic effects on subsurface waters is given by Chilingarian and Rieke (1969).

It is possible that some chlorine may be lost from waters due to its incorporation in such minerals as chlorite (Johns, 1963). In addition it has been pointed out by Johns (1963) that chlorites of marine origin can contain as much as 1,000 ppm chlorine and slight metamorphism of these chlorites may result in a release of considerable amounts of chlorine into formation waters.

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17-K. Abundance in Common Sediments and Sedimentary Rock Types

From the values quoted in Table 17-K-1, it is apparent that the chlorine content of sediments varies greatly even within rocks of similar type. Most of this variation appears to be due to the soluble chlorine content of the sediments. As very many sedimentary rocks are deposited in a marine environment, it is to be expected that sodium chloride from this environment will modify the original chlorine content of the sediments.

Gulyayeva and Itkina (1962a) and Mun and Bazilevich (1962) showed that the total chlorine content of sediments could be related to the salinity of the environment of deposition. In the case of coals, it has been shown by Gulyayeva and Itkina (1962b) that those laid down in a continental environment have a lower soluble chlorine content than those deposited in shallow marine conditions.

I. Argillaceous Sediments and Sedimentary Rocks

Billings and Williams (1967) found that the water-soluble chlorine content of Alberta shales from bore holes was considerably greater than that for shales occurring at the surface. It has been suggested by Johns and Huang (1967) that the loss of soluble chlorine from marine deposited shales represents the leaching-out of sodium chloride by ground waters.

Behne (1953) found very large chlorine contents in deep-sea sediments; however, this author demonstrated that as much as 100% of this chlorine is in a water-soluble form.

Johns (1963) has obtained some interesting results on the insoluble chlorine content of recently deposited marine and non-marine pelitic material in a coastal region of Texas. The samples were separated into fractions of differing grain sizes. In the 1—2 μ fractions, dominated by clay minerals, the chlorine content was found to increase with increasing salinity, this change parallelling the conversion of montmorillonite to chlorite. The chlorine content increased from about 85 to 200 ppm in response to the mineralogical change. The increase of chlorine (upto 500 ppm) was even more pronounced in the $< 1\,\mu$ fraction, as was the change of montmorillonite to chlorite. In the non-clay mineral fraction, consisting of quartz, K-feldspar and calcite, the chlorine content was constant at about 50 ppm, irrespective of the environmental salinities.

Johns (1963) has explained this increase of chlorine with conversion of montmorillonite to chlorite as being due to the assimilation of chloride ions along with hydroxyl ions into intermediary layers of the chlorite, as magnesium hydroxychloride. In addition, this worker has calculated that chlorites from fresh-water sediments contain about 100 ppm chlorine, while those from marine environments contain upto 1,000 ppm chlorine.

Table 17-K-1. *Chlorine in sedimentary rocks and sediments*

Sample	Number of samples	Chlorine content (ppm)		Method	Reference
		Total	Water-soluble		
		I. *Clastic Sediments*			
Conglomerates, Miura Peninsula (Japan)	6	70—4,500 Mean 1,020	20—4,500 Mean 780	C	Iwasaki *et al.* (1966)
Breccias, Miura Peninsula (Japan)	4	410—1,800 Mean 870	30—1,700 Mean 520	C	Iwasaki *et al.* (1966)
Sandstones and quartzites, Germany	3 (1)	≦20	(1) 5	W	Behne (1953)
Sandstone, Minnesota (U.S.A.)	1	20		C	Kuroda and Sandell (1953)
Sandstones, Miura Peninsula (Japan)	16	180—14,900 Mean 2,135	20—14,900 Mean 1,903	C	Iwasaki *et al.* (1966)
Sandstones, drill holes, 1,100—3,500 meters, W. Turkmenia (U.S.S.R.)	4		127—510 Mean 439		Krasintseva (1964)
Sandstones, Japan	6	10—1,500 Mean 423	5—1,500 Mean 419	C	Ogita *et al.* (1967)
Pyroclastic sandstones and conglomerates. Miura Peninsula (Japan)	5	290—2,500 Mean 894	60—2,500 Mean 672	C	Iwasaki *et al.* (1966)
Tuffaceous sandstones, Kakegawa, Sizuoka (Japan)	7 (6)	30—100 Mean 69	15—50 Mean (6) 25	C	Ogita *et al.* (1967)
Tuffaceous sandstones, Toki, Gifu Pref. (Japan)	13	110—480 Mean 285	0—190 Mean 37	C	Ogita *et al.* (1967)
Quartzites, Wales (Great Britain)	5	200—688 Mean 444		C	Kakar (1971)
Greywackes, composite, Germany	17	100		W	Behne (1953)
Greywackes, Harz (Germany)	2	≦20; 70		W	Behne (1953)
Greywackes, Japan	3	5—55 Mean 28	5—10 Mean 8	C	Ogita *et al.* (1967)

Table 17-K-1 (continued)

Sample	Number of samples	Chlorine content (ppm)		Method	Reference
		Total	Water-soluble		
Greywackes, compilation	25	12—200 Mean 112			Johns and Huang (1967)
Siltstones, drill holes, 1,100—3,500 meters, W. Turkmenia (U.S.S.R.)	5		135—1,791 Mean 729		Krasintseva (1964)
Siltsones, Miura Peninsula (Japan)	47	80—4,100 Mean 530	20—4,100 Mean 396	C	Iwasaki *et al.* (1966)
Siltstones, Wales (Great Britain)	8	151—370 Mean 264		C	Kakar (1971)
Shales, clay and slates, U.S.A.	4	70—230 Mean 128		C	Kuroda and Sandell (1953)
Shales and clays, Germany	17	15—450 Mean 176	≦10—450 Mean 67	W	Behne (1953)
Shales and clays, Pierre Shale, U.S.A.	22	<100—1,300 Mean 170			Tourtelot (1962)
Shale, composite	32	72		C	Huang and Johns (1967)
Shales, surface, Alberta (Canada)	77		7—110 Mean 20	W	Billings and Williams (1967)
Shales, subsurface, Alberta (Canada)	13		45—2,450 Mean 1,386	W	Billings and Williams (1967)
Shales, Wales (Great Britain)	8	215—409 Mean 265		C	Kakar (1971)
Shale, Nagasaki (Japan)	1	760	760	C	Ogita *et al.* (1967)
Slates, Japan	4	0—50 Mean 20	0—20 Mean 6	C	Ogita *et al.* (1967)
Clays, drill boles, 1,100—3,500 meters, W. Turkmenia (U.S.S.R.)	8		102—1,017 Mean 665		Krasintseva (1964)

Clays, Aichi Pref. (Japan)	8	0—45 Mean 12.5	0	C	Ogita *et al.* (1967)
Claystones and argillites, Volga-Ural region (U.S.S.R.)	51	Mean 1,308			Gulyayeva and Itkina (1962a)
Claystones and argillites, organic-rich, marine, Volga-Ural region (U.S.S.R.)	7	Mean 1,100			Gulyayeva and Itkina (1962a)
Argillites, organic-rich, brackish water, Volga-Ural region (U.S.S.R.)	3	Mean 200			Gulyayeva and Itkina (1962a)
Argillites, organic-rich, freshwater, Volga-Ural region (U.S.S.R.)	5	Mean 60			Gulyayeva and Itkina (1962a)
Argillites, low organic matter, freshwater, Volga-Ural region (U.S.S.R.)	6	Mean 3			Gulyayeva and Itkina (1962a)
Argillites, low organic matter, freshwater, China	6	30—790			Gulyayeva and Itkina (1962a)
Marls, organic-rich, Volga-Ural region (U.S.S.R.)	10	Mean 600			Gulyayeva and Itkina (1962a)
Shales and clays, compilation	80	50—450 Mean 103			Johns and Huang (1967)
Muds, lacustrine-freshwater, Central Kazakhstan (U.S.S.R.)	13	1,300—14,600 Mean 6,550			Mun and Bazilevich (1962)
Muds, lacustrine-saline, Central Kazakhstan (U.S.S.R.)	15	8,500—125,800 Mean 44,600			Mun and Bazilevich (1962)
Deep-sea sediments					
Pelagic clays, Atlantic—2 stations, various depths of core	4	14,980—24,900 Mean 19,225	14,900—24,900 Mean 19,060	W	Behne (1953)
Blue mud, Atlantic	1	13,960	13,630	W	Behne (1953)
Pelagic clays, Pacific—2 stations, various depths of core	3	16,900—31,900 Mean 25,880	16,800—31,900 Mean 25,825	W	Behne (1953)

Table 17-K-1 (continued)

Sample	Number of samples	Chlorine content (ppm)		Method	Reference
		Total	Water-soluble		
		II. Biogenic and Chemical Sediments			
Carbonates					
Limestones, Germany	3	50—240 Mean 157	20—110 Mean 69	W	Behne (1953)
Limestone, U.S.S.R.	1	100			Osipova (1959)
Limestones, Japan	6	10—45 Mean 32	10—25 Mean 16	C	Ogita *et al.* (1967)
Chalk, Rügen	2 (1)	220; 2,000	(1) 2,000	W	Behne (1953)
Dolomites, Harz (Germany)	2	610; 880	86; 220	W	Behne (1953)
Dolomites, drill holes, 580—1,047 meters, W. Turkmenia (U.S.S.R.)	15		100—3,970 Mean 907		Krasintseva (1964)
Dolomites—compilation	4	400—880 Mean 659			Johns and Huang (1967)
Siliceous rocks					
Cherts, flints and diatomites, Germany	5	90—330 Mean 178	18—90 Mean 63	W	Behne (1953)
Cherts, Japan	3	10—45 Mean 28	0—5 Mean 3	C	Ogita *et al.* (1967)
Coals					
Coals, continental in origin, U.S.S.R.	13	204—1,157 Mean 435	17—96 Mean 49.5[a]		Gulyayeva and Itkina (1962b)
Coals, near-shore marine origin, U.S.S.R.	6	256—1,995 Mean (5) 955	63—129 Mean 93[a]		Gulyayeva and Itkina (1962b)
Coals, North and Central England	33	Mean 3,255	Mean 3,091	W	Daybell (1967)
Coals, Illinois (U.S.A.)	35	<30—3,600 Mean 994	0—1,900 Mean 426	N/R; W	Gluskoter and Rush (1971)

[a] Leached with very dilute nitric acid.

Undoubtedly, some of the chlorine present in sediments is contained in amphiboles and micas. Clay minerals generally have a low chlorine content, but some comparatively high values have been quoted (Table 17-K-2). BEHNE (1953) found that on shaking up clay minerals with very dilute HCl for extended periods, appreciable quantities of chlorine can be taken up.

WALTERS and WINCHESTER (1971) found that whereas most of the chlorine content of sediments occurs in the water-soluble fraction, not all of the remainder was found to occur within grains (i.e. in the lattices of constituent minerals). A small fraction of insoluble chlorine is bound to the surface of sediment particles.

Table 17-K-2. *Chlorine in clay minerals*

Sample	Chlorine content (ppm)		Method	Reference
	Total	Soluble		
Montmorillonite, Niigata (Japan)	25	0	C	OGITA *et al.* (1967)
Montmorillonite, Niigata (Japan)	10	0	C	OGITA *et al.* (1967)
Montmorillonite, Bavaria (Germany)	30	30	W	BEHNE (1953)
Illite, Illinois (U.S.A.)	30	25	C	OGITA *et al.* (1967)
Illite, Illinois (U.S.A.)	70	70	C	OGITA *et al.* (1967)
Kaolinite, Bavaria (Germany)	290	80	W	BEHNE (1953)
Halloysite, Lawrence County (U.S.A)	350	210	W	BEHNE (1953)

II. Coarse-Grained Clastic Rocks

Very coarse-grained clastic rocks appear to be more enriched in chlorine than are the sandstone-greywacke rocks, which are in general low in insoluble chlorine. OGITA *et al.* (1967) found that in marked contrast to most other sandstones, some tuffaceous sandstones are enriched in insoluble chlorine and showed that this enrichment was correlated with the glass content of the tuffs, high glass contents generally giving high chlorine contents. Weathering of the glassy material to clay resulted in a very marked decrease of the insoluble chlorine content (N.B.: OGITA *et al.* leached their samples with cold water which would result in the extraction of easily soluble chlorine. Reference to the work of NOBLE *et al.* (1967) and Section 17-E would indicate that at least some of the chlorine in the glassy material of tuffs would be soluble. Presumably a more vigorous leach in hot water for extended periods of time is necessary to remove this chlorine).

III. Organic-Rich Sediments and Carbonate Rocks

The data of GULYAYEVA and ITKINA (1962a) appear to show that chlorine, unlike the heavier halogens bromine and iodine, does not appear to be concentrated in organic-rich sediments. However, WALTERS and WINCHESTER (1971) found that 27% of the surface-bound chlorine of sediments can be extracted with organic solvents. In addition, coal samples are generally enriched in chlorine, presumably due in part to its incorporation into plant material which formed the coals. The mode of occurrence of chlorine in coals has been the subject of much discussion; it is possible that greater or lesser amounts of the chlorine occur as inorganic salts, but appreciable quantities may also occur in organic complexes (GLUSKOTER and RUCH, 1971).

Relatively little data are available on the chlorine content of most biogenic and carbonate sediments but it appears that dolomitic limestones may be somewhat enriched in insoluble chlorine. KRASINTSEVA (1964) has also shown that dolomites from deep boreholes can contain appreciable quantities of soluble chlorine.

IV. Evaporites

The composition and origin of evaporites has been the subject of much research; the large amount of data published on these topics has been reviewed by BRAITSCH (1962, English Translation, 1971), STEWART (1963), and BORCHERT and MUIR (1964).

The major elements of marine evaporites are those of seawater, chlorine being the major anion (Table 17-K-3). The minerals found in marine evaporites are essentially chlorides, sulfates, carbonates, fluorides and borates.

Present-day evaporites are accumulating throughout the world in both hemispheres in two belts lying approximately between 15° and 35° from the equator (BORCHERT and MUIR, 1964). Older evaporite deposits are widely distributed, occurring on all the continents. Evaporite deposits are recorded throughout the geological column, the greatest accumulation occurring during the Permian (BRAITSCH, 1971).

It has long been accepted that marine evaporites have been formed by evaporation of sea water bodies with restricted exchange with the open sea together with a low influx of freshwater (BORCHERT and MUIR, 1964), although SHEARMAN (1966) has suggested that many marine evaporites may be diagenetic in origin.

Table 17-K-3. *Some of the chlorine-containing minerals of marine evaporites* (from BRAITSCH, 1971)

Mineral	Chemical formula
Halite	$NaCl$
Hydrohalite	$NaCl \cdot 2\,H_2O$
Sylvite	KCl
Bischofite	$MgCl_2 \cdot 6\,H_2O$
Carnallite	$KMgCl_3 \cdot 6\,H_2O$
Tachhydrite	$CaMg_2Cl_6 \cdot 12\,H_2O$
Chlorocalcite	$KCaCl_3$
D'Ansite	$9\,Na_2SO_4 \cdot MgSO_4 \cdot 3\,NaCl$
Kainite	$KMgSO_4Cl \cdot 3\,H_2O$
Rinneite	$K_3NaFeCl_6$
Douglasite	$K_2FeCl_4 \cdot 2\,H_2O(?)$
Erythrosiderite	$K_2FeCl_5 \cdot H_2O$
Koeoenite	$Mg_5Al_2Cl_4(OH)_{12} \cdot 2(?)\,H_2O$
Zirklerite	$(Fe, Mg, Ca)_9Al_4Cl_{18}(OH)_{12} \cdot 14\,H_2O(?)$
Heidornire	$Na_2Ca_3B_5O_8(SO_4)_2Cl(OH)_2$
Boracite	$Mg_6B_{14}O_{26}Cl_2$
Hilgardite	$Ca_8(B_6O_{11})_3Cl_4 \cdot 4\,H_2O$
Parahilgardite	$Ca_8(B_6O_{11})_3Cl_4 \cdot 4\,H_2O$

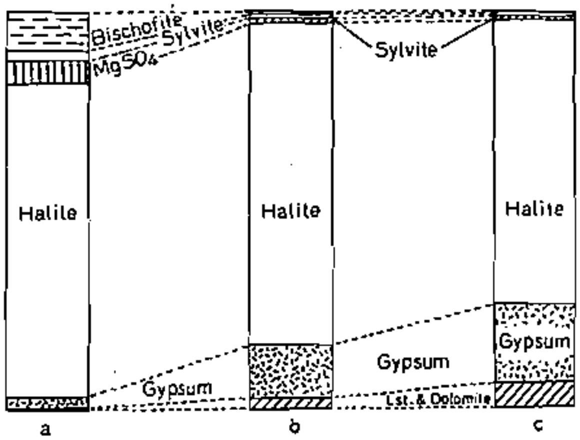

Fig. 17-K-1. Comparative precipitation profiles for evaporites: a experimental evaporation of sea water; b the Zechstein; c average of many other deposits (from BORCHERT and MUIR, 1964) (N.B. In b and c bischofite is absent, being replaced by carnallite)

Halite is the major chloride mineral of evaporite deposits and is the first of the chloride minerals to form, generally occurring with or following the calcium sulfate minerals. The other chlorides occurring in significant amounts are sylvite and carnallite which are more soluble than halite and are consequently precipitated during later stages of evaporation. Bischofite occurs in the final stages of crystallization (see Fig. 17-K-1). In addition to the occurrence of sylvite as a primary mineral of evaporites, many deposits of this mineral are secondary in origin, resulting from solution metamorphism of carnallite (BRAITSCH, 1971). Many of the chloride minerals of evaporites are formed due to solution metamorphism. Hence $CaCl_2$-rich solutions may be important in the formation of secondary tachyhydrite, while rinneite is formed during metamorphism by $FeCl_2$-rich solutions (BRAITSCH, 1971).

The composition of non-marine evaporites is far more varied, but normally the chloride ion is quantitatively less important than the sulfate and carbonate anions.

Detailed accounts of the origin and nature of evaporites are given in the previously cited works.

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17-L. Biogeochemistry

Chlorine as the chloride anion is an essential element for many animal and plant groups including the mammals, insects, angiosperms and possibly algae and bacteria (Table 17-L-1; Bowen, 1966). Chloride is a major anion in mammalian blood and is also concentrated in the hair of mammals (Bowen, 1966). Some coelenterates concentrate chlorine (Vinogradov, 1953).

Table 17-L-1. *Chlorine in plants, animals and animal hard parts and dry tissues* (from compilation of Bowen, 1966)

Sample	Cl (ppm)
Plants	
Brown algae	4,700
Bryophytes	670
Ferns	6,000
Angiosperms	2,000
Bacteria	2,300
Fungi	10,000
Animals	
Coelenterata	90,000
Mollusca	5,000
Echinodermata	7,000
Crustacea	6,000
Insecta	1,200
Pisces	6,000
Mammalia	3,200
Animal hard parts	
Mammal bones (apatite)	3,900
Porifera (SiO_2)	52,000
Corals ($CaCO_3$)	1,700
Molluscs ($CaCO_3$)	35
Red algae ($CaCO_3$)	5,000
Dried mammalian tissues	
Brain	8,000
Heart	6,000
Kidney	9,000
Liver	4,800
Lung	12,000
Muscle	2,800
Skin	11,000
Hair	20,000
Mammalian blood	2,900

Chlorine is taken up by marine and terrestrial plants; SHAW (1962) states that it occurs in all algae and is the major halogen in this group. However, chlorine is not generally concentrated in marine algae with respect to sea water (SHAW, 1962; VINOGRADOV, 1953). From the work of GABRIELLI and MARLETTA (1969) on algae in the Gulf of Trieste, it appears that the Rhodophyceae are richer in chlorine than the Phaeophyceae or Chlorophyceae, but this is not apparent from the values quoted by VINOGRADOV (1953).

In the freshwater algae, chlorine is often enriched compared to the environment (SHAW, 1962). In terrestrial plants also, chlorine appears to be concentrated relative to the soil solutions (BOWEN, 1966).

From a study of several terrestrial plants, PORTYANKO *et al.* (1970) found that chlorine was concentrated generally in the cortex, mature leaves and peduncle; lowest chlorine contents were found in young leaves, seeds, wood and other young organs.

Chlorine in plants is present mainly as the chloride anion, but some organic chlorine-containing compounds have been found in marine algae (SHAW, 1962) and fungi (BOWEN, 1966). Some of the organochlorine compounds of fungi are antibiotics (BOWEN, 1966).

For chlorine in coals see Table 17-K-1.

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17-M. Abundance in Common Metamorphic Rock Types

The chlorine contents of greisens and metasomatised rocks have been dealt with in Section 17-F; also the chlorine content of minerals from metamorphic rocks are given in Table 17-D-1.

Comparatively few analyses are available for chlorine in metamorphic rocks; some values are quoted in Table 17-M-1. From these values, it appears that chlorine is fairly low in schists, though this is not borne out by the average values quoted by JOHNS and HUANG (1967) (see Table 17-M-2). The data of JOHNS and HUANG also

Table 17-M-1. *Chlorine in metamorphic rocks*

Rock	Chlorine content in ppm (method)	Reference
Phyllite, Morrison County, Minnesota (U.S.A.)	80 (C)	KURODA and SANDELL (1953)
Mica schist, Morrison County, Minnesota (U.S.A.)	80 (C)	KURODA and SANDELL (1953)
Staurolite schist, South Aitkin County, Minnesota (U.S.A.)	70 (C)	KURODA and SANDELL (1953)
Schist	120 (W)	GREENLAND and LOVERING (1965)
Chlorite-carbonate schist, shear zone, Yellowknife (Canada)	trace (W?)	BOYLE (1961)
Carbonate-sericite schist, shear zone, Yellowknife (Canada)	100 (W?)	BOYLE (1961)
Schist, Chichibu, Saitama (Japan)	55 (C)	OGITA *et al.* (1967)
Schist, Chichibu, Saitama (Japan)	15 (C)	OGITA *et al.* (1967)
Schist, Nagatoro (Japan)	10 (C)	OGITA *et al.* (1967)
Schist, Nagatoro (Japan)	10 (C)	OGITA *et al.* (1967)
Schist, Betsi, Ehime (Japan)	85 (C)	OGITA *et al.* (1967)
Schist, Takenuki, Fukushima (Japan)	10 (C)	OGITA *et al.* (1967)
Semi-pelitic schist	47 (C)	HUANG and JOHNS (1967)
Graphite gneiss, Gifu Pref. (Japan)	140 (C)	KURODA and SANDELL (1953)
Hornblende gneiss, Gifu Pref. (Japan)	230 (C)	KURODA and SANDELL (1953)
Migmatite	145 (W)	GREENLAND and LOVERING (1965)
Hornfels	150 (W)	GREENLAND and LOVERING (1965)
Amphibolite, N. W. Adirondacks, New York, (U.S.A.)	400	BUDDINGTON and LEONARD (1962)
Amphibolite, N. W. Adirondacks, New York, (U.S.A.)	300	BUDDINGTON and LEONARD (1962)
Composite, meta-diorite and meta-gabbro-dykes, Yellowknife (Canada)	200 (W?)	BOYLE (1961)

Table 17-M-2. *Mean values for chlorine in metamorphic rocks* (from compilation of JOHNS and HUANG, 1967)

Rock	Number of samples	Chlorine content (ppm)	
		Range	Mean
Schists	68	70—900	354
Gneisses	24	140—1,000	207
Amphibolites	16	100—400	300

show that the chlorine content of amphibolites is fairly constant due, they suggest, to the consistant mineralogy of these rocks.

It has been assumed by JOHNS and HUANG (1967) that chlorine is generally higher in rocks rich in micas and amphiboles. BOYLE (1961) thought that the chlorine of metamorphics in the Yellowknife area of Canada, was likely to be present in apatite and chloride inclusions.

The chlorine content of biotites from gneisses was found by HAACK (1969) to be within the same range as those for granitic rocks. However, some hydroxysilicate minerals from metamorphic rocks are extremely high in chlorine (LEE, 1958). In addition metasomatised rocks such as skarns can contain hydroxy minerals with extremely high chlorine contents, e.g., Dashkesanite.

OSIPOVA (1959) found between 100 and 500 (mean 230) ppm chlorine in seven skarn samples from Tashbulak, U.S.S.R.

FUGE and POWER (1969b) found between 498 and 1,760 (mean 904) ppm in six xenolith samples from the granites of S. W. England.

The chlorine contents of 53 amphibolite-greenschist rocks from the Dalradian of Scotland were found to range between 63 and 430 (mean 130) ppm (X) (VAN DE KAMP, 1970), while 5 pelites from the same series contained 85—210 (mean 129) ppm.

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17-N. Behavior in Metamorphic Reactions

Boyle (1961) found little variation in the chlorine content of progressively metamorphosed rocks of the Yellowknife area; the average chlorine values for each of the three facies types, amphibolite, epidote amphibolite and greenschist, were 300 ppm. Van de Kamp (1970) found only slight variations with metamorphic grade in the chlorine content of greenschist and amphibolite rocks of the Scottish Dalradian.

Only small increases of chlorine content were noted by Floyd and Fuge (1973) on increasing contact metamorphism of basic and intermediate igneous rocks of the Land's End aureole (Table 17-N-1). These authors also noted that the contact metamorphosed basics contained far more chlorine than regionally metamorphosed rocks from the same area; however, it must be borne in mind that the Land's End granite is chlorine-rich (Fuge and Power, 1969a).

During regional metamorphism, chlorine may be mobilised and enter newly forming minerals such as scapolite and chlor-apatite. During progressive metamorphism of amphibolites in the N.W. Adirondacks, New York, the chlorine content of hornblendes decreases (Engel and Engel, 1962).

Release of chlorine from minerals during progressive metamorphism could also result in the accumulation of chlorine in the residual fluids of metamorphism, as is the case during magmatism.

Much of the data regarding the behavior and role of chlorine during metasomatism has been discussed in Section 17-F.

Table 17-N-1. *Chlorine content of some metamorphosed mafic and intermediate igneous rocks from Cornwall, S. W. England*[a] (from Floyd and Fuge, 1973; method: C)

Rock type	Number of samples	Chlorine content (ppm)	
		Range	Mean
Contact metamorphosed			
Actinolite-bearing mafic hornfelses	8	683—1,528	1,207
Hornblende-bearing mafic hornfelses	18	700—2,129	1,355
Hornblende-bearing intermediate hornfelses	9	460—2,090	1,253
Metasomatised			
Anthophyllite-bearing magnesian hornfelses	5	216—360	280
Cummingstonite-bearing magnesian hornfelses	15	240—1,373	945
Calc-silicate-bearing calcareous hornfelses	4	232—1,450	956
Regionally metamorphosed			
Low-grade meta-dolerite-diabase	14	4—288	162

[a] The contact metamorphosed rocks are from the Land's End granite aureole, Peowith peninsula, Cornwall. Regionally metamorphosed rocks are from Cudden Point, S. Cornish coast. (N.B. All of these samples were collected from coastal localities and therefore some of the chlorine found may be due to contamination.)

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17-O. Relationship with Other Elements; Economic Importance

I. Relationship with Other Elements

a) Relationship with Other Halogens

Huang and Johns (1967) found that the ratio Cl/F decreases systematically from basic to acidic rocks. The ratio for ultramafic rocks is generally greater than one.

Fuge and Power (1968) have suggested that during progressive alteration of South-West England granitic rocks, the Cl/F ratio decreases.

Several workers have suggested that the Br/Cl ratio of igneous rocks and volcanic gases is fairly constant (Sugiura, 1968; Yoshida *et al.*, 1971).

b) Relationship with Mineralisation

Ore-forming fluids, whatever their origin, are likely to be enriched in chlorine (see Section 17-F). Stollery *et al.*, (1971) suggest that the chlorine content of intrusive rocks may be used as a possible prospecting tool. Kesler *et al.* (1972) found that high chlorine contents of plutonic rocks correlate with high copper values and that intrusives associated with mineralisation are chlorine-rich (see also Kesler and Van Loon, 1972).

II. Economic Importance

Chlorine has been used extensively for the disinfection of water supplies. It finds wide usage in the manufacture of antiseptics, medicines, dyes, paper products, insecticides, foodstuffs, paints, plastics and several other products. In addition, chlorine is widely used in organic chemistry for the production of such compounds as chloroform and carbon tetrachloride.

According to Hammond (1971) most industrially produced chlorine is used for the manufacture of chlorinated compounds for use in sanitation, disinfectants, pulp bleaching and textile processing.

Common salt has been of great commercial importance since prehistoric times, being an essential ingredient of human and animal diets. In the Ancient world, salt was a very important part of the economy and was even used as money (Encyclopaedia Britannica, 1962).

Sodium chloride is used as a seasoning ingredient of foods and a preservative for meats etc. As well as its culinary uses, salt is important in industry, being used for the production of sodium, chlorine, hydrochloric acid, sodium hydroxide, sodium sulfate and other sodium salts. It also finds uses in the dyeing industry and in the manufacture of soaps, paints and cements (Heilbron, 1950; Borchert and Muir, 1964).

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References: Section 17-A to 17-O

Albee, A. L., Chodos, A. A.: Microprobe investigations on Apollo 11 samples. Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta, Suppl. 1. 2, 135 (1970).

Albee, A. L., Chodos, A. A., Gancarz, A. J., Haines, E. L., Papanastassiou, D. A., Ray, L., Tera, F., Wasserburg, G. J., Wen, T.: Mineralogy, petrology and chemistry of a Luna 16 basaltic fragment, sample B-1. Earth Planet. Sci. Lett. 13, 353 (1972).

Aller, L. H.: The Abundance of the Elements. New York: Interscience 1961.

Aller, L. H., Cryzak, S. J.: In: Osterbrock, D. E., O'Dell, C. R. (eds.): Planetary Nebulae. I. A. U. Symp. 34, 209 (1968).

Baertschi, P.: Über die relativen Unterschiede im $H_2{}^{18}O$-Gehalt natürlicher Wässer. Helv. Chim. Acta 36, 1352 (1953).

Baldwin, A. D.: Contributions of atmospheric chloride in water from selected coastal streams of central California. Water Resour. Res. 7, 1007 (1971).

Barnes, H. L. (ed.): Geochemistry of Hydrothermal Ore Deposits. New York: Holt, Rinehart and Winston 1967.

Barsukov, V. L., Klintsova, A. P.: Experimental modeling of postmagmatic alteration of granites. Geochem. Intern. 6, 310 (1969).

Barth, T. F. W., Bruun, B.: Studies on the igneous rock complex of the Oslo region. IV. Fluorine in the Oslo petrographic province. Skrifter Norske Videnskaps Akad., Oslo, Mat.-Naturv. Kl. 8, 5 (1945).

Basharina, L. A.: Gases of Kamchatka volcanoes. Bull. Volcanol. 28, 95 (1965).

Becker, V. J., Manuel, O. K.: Chlorine, bromine, iodine and uranium in tektites, obsidians and impact glasses. J. Geophys. Res. 77, 6353 (1972).

Begemann, F., Vilcsek, E., Rieder, R., Born, W., Wänke, H.: Cosmic-ray produced radioisotopes in lunar samples from the Sea of Tranquillity (Apollo 11). Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta, Suppl. 1. 2, 1487 (1970).

Behne, W.: Untersuchungen zur Geochemie des Chlor und Brom. Geochim. Cosmochim. Acta 3, 186 (1953).

Bentor, Y. K.: On the evolution of subsurface brines in Israel. Chem. Geol. 4, 83 (1969).

Berkey, E., Fisher, D. E.: The abundance and distribution of chlorine in iron meteorites. Geochim. Cosmochim. Acta 31, 1543 (1967).

Berry, F. A. F.: Relative factors influencing membrane filtration effects in geologic environments. Chem. Geol. 4, 295 (1969).

Bhandari, N., Bhat, S. G., Kharkar, D. P., Krishnaswamy, S., Lal, D., Tamhane, A. S.: Cosmic-ray produced Mg^{28}, Si^{31}, S^{38}, Cl^{38}, Cl^{34m} and other short-lived radioisotopes in wet precipitation. Tellus 18, 504 (1966).

Billings, G. K., Williams, H. H.: Distribution of chlorine in terrestrial rocks — a discussion. Geochim. Cosmochim. Acta 31, 2247 (1967).

Blakemore, L. C.: The chloride content of rain water collected in the Wellington province. New Zealand J. Sci. Technol. 35 B, 193 (1953).

Borchert, H., Muir, R. O.: Salt Deposits: the Origin, Metamorphism and Deformation of Evaporites. Princeton, N.J.,-London: Van Nostrand 1964.

Borley, G. D.: Amphiboles from the younger granites of Nigeria. Part 1. Chemical classification. Mineral. Mag. 33, 358 (1963).

Bowen, H. J. M.: Trace Elements in Biochemistry. London-New York: Academic Press 1966.

Boyd, A. W., Brown, F., Lounsbury, M.: Mass spectrometric study of natural and neutron-irradiated chlorine. Can. J. Phys. 33, 35 (1955).

Boyle, R. W.: The geology, geochemistry and origin of the gold deposits of the Yellowknife District. Geol. Surv. Canada Mem. 310 (1961).

Braitsch, O.: Salt Deposits: Their Origin and Composition. Berlin-Heidelberg-New York: Springer 1971.

Brehler, B., König, B.: Kristallstruktur von Kaliumtrichlorozinkatmonohydrat. Naturwissenschaften 56, 279 (1969).

Brunfelt, A. O., Heier, K. S., Steinnes, E.: Determination of 40 elements in Apollo 12 materials by neutron activation analysis. Proc. Second Lunar Sci. Conf. 2, 1281 (1971a).

Brunfelt, A. O., Heier, K. S., Steinnes, E., Sundvoll, B.: Determination of 36 elements in Apollo 14 bulk fines 14163 by activation analysis. Earth Planet. Sci. Lett. 11, 351 (1971b).

Buchanan, D. R., Harris, P. M.: A neutron and x-ray diffraction investigation of aluminium chloride hexahydrate. Acta Cryst. B 24, 953 (1968).

Buddington, A. F.: Chemical petrology of some metamorphosed Adirondack gabbroic, syenitic and quartz syenitic rocks. Am. J. Sci., Bowen volume, 37 (1952).

Buddington, A. F., Leonard, B. F.: Chemical petrology and mineralogy of hornblendes in Northwest Adirondacks granitic rocks. Am. Mineralogist 38, 891 (1953).

Buddington, A. F., Leonard, B. F.: Regional geology of the St. Lawrence County magnetite district, Northwest Adirondacks, New York. U.S. Geol. Surv. Profess. Paper 376 (1962).

Burzlaff, H.: Struktur des Heidornit Ca$_3$Na$_2$Cl(SO$_4$)$_2$B$_6$O$_8$(OH)$_2$. Neues Jahrb. Mineral. Monatsh. 1967, 157.

Cameron, A. G. W.: Abundances of the elements. In: Clark S. P. (ed.), Handbook of Physical Constants. U.S. Geol. Soc., Mem. 97, 7 (1966).

Cameron, A. G. W.: A new table of abundances of the elements in the solar system. In: Ahrens L. H. (ed.): Origin and Distribution of the Elements. Oxford: Pergamon 1968.

Carmichael, I. S. E.: Pantelleritic liquids and their phenocrysts. Mineral. Mag. 33, 86 (1962).

Carpenter, R.: Factors controlling the marine geochemistry of fluorine. Geochim. Cosmochim. Acta 33, 1153 (1969).

Cattermole, P. J., Fuge, R.: The abundances and distribution of fluorine and chlorine in a layered intrusion at Rhiw, North Wales. Geochim. Cosmochim. Acta 33, 1295 (1969).

Cauer, H.: Some problems of atmospheric chemistry. Compendium Meteorol. 625 (1951).

Chave, K. E.: Evidence on history of seawater from chemistry of deeper subsurface waters of ancient basins. Bull Am. Assoc. Petrol. Geologists 44, 357 (1960).

Chilingarian, G. V., Rieke III, H. H.: Some chemical alterations of subsurface waters during diagenesis. Chem. Geol. 4, 235 (1969).

Compton, R. R.: Significance of amphibole paragenesis in the Bidwell Bar region, California. Am. Mineralogist 43, 890 (1958).

Correns, C. W.: The geochemistry of the halogens. In: Ahrens, L. H. Rankama, K. and Runcorn, S. K. (eds.): Physics and Chemistry of the Earth. 1, 181. London: Pergamon 1956.

Cosgrove, M. E.: The geochemistry of the potassium-rich Permian volcanic rocks of Devonshire England. Contr. Mineral. and Petrol. 36, 155 (1972).

Culkin, F.: The major constituents of sea water. In: Riley, J. P. and Skirrow, G. (eds.): Chemical Oceanography. 1, 121. London: Academic Press 1965.

Davis, R., Schaeffer, O. A.: Chlorine-36 in nature. Ann. N.Y. Acad. Sci. 62, 105 (1955).

Daybell, G. N.: The relationships between sodium and chlorine in some British coals. J. Inst. Fuel 40, 3 (1967).

Deer, W. A., Howie, R. A., Zussman, J.: Rock-forming Minerals. Vols. I-V. London: Longmans 1963.

Delitsyn, L. M., Melent'yev, B. N.: Co-existence of two liquid phases at high temperatures: the system sodium chloride — albite glass. Dokl. Akad. Nauk. SSSR 180, 208 (1968) (English Transl.).

Donohue, J., Goodman, S. H.: Interatomic distances in solid chlorine. Acta Cryst. 18, 568 (1965).

Duce, R. A., Winchester, J. W., van Nahl, T. W.: Iodine, bromine, and chlorine in the Hawaiian marine atmosphere. J. Geophys. Res. 70, 1775 (1965).

Duce, R. A., Winchester, J. W., van Nahl, T. W.: Iodine, bromine and chlorine in winter aerosols and snow from Barrow, Alaska. Tellus 18, 238 (1966).

Dunham, K. C.: Mineralization by deep formation waters: a review. Trans. Sect. B. Inst. Min. Metal. 79, 127 (1970).

Dusausoy, Y., Protas, T.: Détermination et étude de la structure cristalline de la rodalquilarite, chlorotellurite acide de fer. Acta Cryst. B 25, 1551 (1969).

Earley, J. W.: On chlorine in serpentinized dunite. Am. Mineralogist 43, 148 (1958).

Ellis, A. J., Mahon, W. A. J.: Natural hydrothermal systems and experimental hot water/rock interactions. Geochim. Cosmochim. Acta 28, 1323 (1964).

Ellis, A. J., Mahon, W. A. J.: Natural hydrothermal systems and experimental hot water/rock interactions (Part II). Geochim. Cosmochim. Acta 31, 519 (1967).

El Saffar, Z. M., Mulcahy, W.: The water molecules in $AlCl_3 \cdot 6\,H_2O$. Acta Cryst. B 27, 1069 (1971).

Engel, A. E. J., Engel, C. G.: Grenville series in the northwest Adirondack Mountains, New York, Part 1. Bull. Geol. Soc. Am. 64, 1013 (1953).

Engel, A. E. J., Engel, C. G.: Hornblendes formed during progressive metamorphism of amphibolites, northwest Adirondack Mountains, New York. Bull. Geol. Soc. Am. 73, 1499 (1962).

Engelhardt, W. von: Der Porenraum der Sedimente. Berlin-Göttingen-Heidelberg: Springer 1960.

Engelhardt, W. von, Gaida, K. H.: Concentration changes of pore solutions during the compaction of clay sediments. J. Sediment. Petrol. 33, 919 (1963).

Engelman, R. J., Perkins, R. W.: Precipitation processes revealed by cosmogenic radionuclide scavenging. J. Atmos. Sci. 28, 131 (1971).

Eriksson, E.: Composition of atmospheric precipitation. II. Sulphur, chloride, iodine compounds. Tellus 4, 281 (1952).

Eriksson, E.: The yearly circulation of chloride and sulfur in nature; meteorological geochemical and pedological implications. Part II. Tellus 12, 63 (1960).

Erickson, R. L., Blade, L. V.: Geochemistry and petrology of the alkalic igneous complex at Magnet Cove, Arkansas. U.S. Geol. Surv. Profess. Paper 425 (1963).

Evans, B. W.: Chlorine and fluorine in micas of pelitic schists from the sillimanite — orthoclase isograd, Maine. Am. Mineralogist 54, 1209 (1969).

Everdingen, R. O. van: Mobility of main ion species in reverse osmosis and the modification of subsurface brines. Can. J. Ear. Sci. 5, 1253 (1968).

Faber, H.: On the salt-solutions in microscopic cavities in granites. Danmarks Geol. Undersogelse II. Nr. 67 (1941).

Ferrari, A., Braibanti, A., Bigliardi, G.: Refinement of the crystal structure of $NiCl_2$ and of unit-cell parameters of some anhydrous chlorides of divalent metals. Acta Cryst. 16, 846 (1963).

Feth, J. H., Rogers, S. M., Roberson, C. E.: Chemical composition of snow in the northern Sierra Nevada and other areas. U.S. Geol. Surv. Water Supply Paper 1535-I (1964).

Fischer, W.: Die Kristallstruktur des Carnallits $KMgCl_3 \cdot 6H_2O$. Neues Jahrb. Mineral. Monatsh. 1973, 100.

Flanagan, F. J.: U.S. Geological Survey Standards II. First compilation of data for the new U.S.G.S. rocks. Geochim. Cosmochim. Acta 33, 81 (1969).

Fleischer, M.: Index of new mineral names, discredited minerals, and changes of mineralogical nomenclature in volumes 1—50 of "The American Mineralogist." Am. Mineralogist 51, 1248 (1966).

Floyd, P. A., Fuge, R.: Distribution of fluorine and chlorine in some contact and regionally metamorphosed Cornish greenstones. Proc. Ussher Soc. In press (1973).

Förtsch, E., Wondratschek, H.: Zur Kristallchemie der Minerale der Pyromorphit-Gruppe. Naturwissenschaften 52, 182 (1965).

Follner, H., Brehler, B.: Die Kristallstruktur des $ZnCl_2 \cdot 1^1/_3\,H_2O$. Acta Cryst. B 26, 1679 (1970).

Fuchs, L. H.: The phosphate mineralogy of meteorites. In: Millman, P. M. (ed.): Meteorite Research. Dordrecht, Holland: Reidel 1969.

Fuge, R., Power, G. M.: Fluorine and chlorine in some granitic rocks. Proc. Ussher Soc. 2, 43 (1968).

Fuge, R., Power, G. M.: Chlorine in tourmalines from S. W. England. Mineral. Mag. 37, 293 (1969a).

Fuge, R., Power, G. M.: Chlorine and fluorine in granitic rocks from S. W. England. Geochim. Cosmochim. Acta 33, 888 (1969b).

Gabrielli, L. F., Marletta, G. P.: Richerche sulle possibilita'disfruttamento economico delle alghe dell'alto Adriatico. Chloro, bromo e iodio nelle alghe del Golfo di Trieste. Tec. Ital. 34, 427 (1969).

Garrels, R. M.: Genesis of some ground waters from igneous rocks. In: Abelson, P. H.: Researches in Geochemistry, vol. 2, p. 405. New York-London-Sydney: Wiley & Sons 1967.

Geijer, P.: The distribution of halogens in skarn amphiboles in Central Sweden. Arkiv Mineral. Geol. 2, 481 (1960).

Gerasimovskii, V. I., Tuzova, A. M.: Geochemistry of chlorine in nepheline syenites. Geochem. Intern. 1, 855 (1964).

Gibbs, R. J.: Water chemistry of the Amazon river. Geochim. Cosmochim. Acta 36, 1061 (1972).

Gillberg, M.: Halogens and hydroxyl contents of micas and amphiboles in Swedish granitic rocks. Geochim. Cosmochim. Acta 28, 495 (1964).

Gluskoter, H. J., Ruch, R. R.: Chlorine and sodium in Illinois coals as determined by neutron activation analyses. Fuel 50, 65 (1971).

Goel, P. S.: Chlorine-36 produced by neutron capture in meteorites. Nature 203, 1162 (1964).

Goldschmidt, V. M.: Geochemistry. Oxford: Clarendon Press 1954.

Goles, G. G., Greenland, L. P., Jérome, D. Y.: Abundances of chlorine, bromine and iodine in meteorites. Geochim. Cosmochim. Acta 31, 1771 (1967).

Gower, J. A.: X-ray measurement of the iron-magnesium ratio in biotites. Am. J. Sci. 255, 142 (1957).

Greenland, L., Lovering, J. F.: Minor and trace element abundances in chondritic meteorites. Geochim. Cosmochim. Acta 29, 821 (1965).

Greenland, L., Lovering, J. F.: Fractionation of fluorine, chlorine and other trace elements during differentiation of a tholeiitic magma. Geochim. Cosmochim. Acta 30, 963 (1966).

Greenland, L. P.: Ph. D. dissertation, Australian National University (1963).

Gulyayeva, L. A., Itkina, E. S.: Halogens in marine and freshwater sediments. Geochemistry 610 (1962a).

Gulyayeva, L. A., Itkina, E. S.: The halogens and vanadium, nickel and copper in coals. Geochemistry 395 (1962b).

Gunten, H. R. von, Wyttenbach, A., Scherle, W.: Determination of chlorine in stony meteorites by neutron activation analysis. Geochim. Cosmochim. Acta 29, 475 (1965).

Haack, U. K.: Spurenelemente in Biotiten aus Graniten und Gneisen. Contr. Mineral. and Petrol. 22, 83 (1969).

Hammond, C. R.: The elements. In: Weast, R. C. (ed.): Handbook of Chemistry and Physics, 52nd ed. Cleveland, Ohio: The Chemical Rubber Co. Ltd. 1971.

Haskin, L. A., Allen, R. O., Helmke, P. A., Paster, T. P., Anderson, M. R., Korotev, R. L., Zweifel, K. A.: Rare earths and other trace elements in Apollo 11 lunar samples. Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta 34, Suppl. 1. 2, 1213 (1970).

Haughton, D. R.: Plagioclase-scapolite equilibrium. Can. Mineralogist 10, 854 (1971).

Heath, R. L.: Table of isotopes. In: Weast, R. C. (ed.): Handbook of Chemistry and Physics, 52nd, ed. Cleveland, Ohio: The Chemical Rubber Co. 1971.

Hem, J. D.: Study and interpretation of the chemical characteristics of natural water. U.S. Geol. Surv. Water-Supply Paper 1473 (1970).

Heilbron, I. M. (Chief ed.): Thorpe's Dictionary of Applied Chemistry, vol. 10, 4th. ed. London: Longmans 1950.

Helgeson, H. C.: Complexing and Hydrothermal Ore Deposition. Oxford-London-New York-Paris: Pergamon Press 1964.

Helgeson, H. C.: Thermodynamics of hydrothermal systems at elevated temperatures and pressures. Am. J. Sci. 267, 729 (1969).

Herzberg, G.: Molecular Spectra and Molecular Structure I. New York: Van Nostrand 1950.

Hess, H. H., Otalora, G.: Mineralogical and chemical composition of the Mayaguez serpentinite cores. In: Burk, C. A. (ed.): A Study of Serpentinite. National Academy of Sciences — National Research Council Publication 1188 (1964).

Hey, M. H.: An Index of Mineral Species and Varieties Arranged Chemically. London: British Museum (Nat. Hist.) 1950.

Hitchon, B., Billings, G. K., Klovan, J. E.: Geochemistry and origin of formation waters in the western Canada sedimentary basin — III. Factors controlling chemical composition. Geochim. Cosmochim. Acta 35, 567 (1971).

Hoering, T. C., Parker, P. L.: The geochemistry of the stable isotopes of chlorine. Geochim. Cosmochim. Acta **23**, 186 (1961).

Holland, H. D.: Granites, solutions, and base metal deposits. Econ. Geol. 67, 281 (1972).

Honda, M., Arnold, J. R.: Effects of cosmic rays on meteorites. Science 143, 203 (1964).

Hounslow, A. W., Chao, G. Y.: Monoclinic chlorapatite from Ontario. Can. Mineralogist 10, 253 (1970).

Huang, W. H., Johns, W. D.: The chlorine and fluorine contents of geochemical standards. Geochim. Cosmochim. Acta 31, 597 (1967).

Hutchinson, F. E.: Concentration of nine inorganic ions in Maine rivers. Res. Life Sci. 15, 8 (1968).

Ijdo, D. J. W.: Het gedrag van de chloriden der overgangselementen bij complexvorming met caesiumchloride. N. V. Uitgeverij W. P. Van Stockum & Zoon, 'S Gravenhage 1962.

Ishizuka, T., Nakai, N., Oana, S.: Senkrechte Veränderung der Bor- und Chlorgehalte von miozänischem Sediment in Toki, Gifu — Ken Japan. J. Geol. Soc. Japan 76, 23 (1970).

Iwasaki, B., Katsura, T.: The chlorine content of Hawaiian lavas. Bull. Chem. Soc. Jap. 37, 1827 (1964).

Iwasaki, B., Kitayama, K., Katsura, T.: The chlorine and fluorine contents of Tertiary sediments on the Miura Peninsula. Bull. Chem. Soc. Japan 39, 1462 (1966).

Iwasaki, I., Katsura, T., Ozawa, T., Yoshida, M., Iwasaki, B.: Chlorine content of volcanic rocks and migration of chlorine from the mantle to the surface of the earth. In: Knopoff, L., Drake, C. L., and Hart, P. J. (eds.): The Crust and Upper Mantle of the Pacific Area. Geophysical Monograph 12. Washington: American Geophysical Union 1968.

Iwasaki, I., Katsura, T., Sakato, N.: The determination of chlorine in volcanic rocks. Nippon Kagaku Zasshi 76, 1116 (1955).

Iwasaki, I., Katsura, T., Sakato, N., Hirayama, M.: Geochemical investigations of volcanoes in Japan. XLI Chlorine in volcanic rocks. Nippon Kagaku Zasshi **78**, 164 (1957).

Jensen, S. J.: Hydrater af nogle divalente metallers chlorider. Diss. Univ. Århus (1969).

Johansen, O., Steinnes, E.: Determination of chlorine in U.S.G.S. standard rocks by neutron activation analysis. Geochim. Cosmochim. Acta **31**, 1107 (1967).

Johns, W. D.: Die Verteilung von Chlor in rezenten marinen und nichtmarinen Sedimenten. Fortschr. Geol. Rheinland Westfalen 10, 215 (1963).

Johns, W. D., Huang, W. H.: Distribution of chlorine in terrestrial rocks. Geochim. Cosmochim. Acta **31**, 35 (1967).

Jonte, J. H.: Ph.D. dissertation, University of Arkansas (1956).

Junge, C. E.: Recent investigations in air chemistry. Tellus 8, 127 (1956).

Junge, C. E.: Chemical analysis of aerosol particles and of gas traces on the island of Hawaii. Tellus 9, 528 (1957).

Junge, C. E.: Air Chemistry and Radioactivity. New York-London: Academic Press 1963.

Junge, C. E., Werby, R. T.: The concentration of chloride, sodium, potassium, calcium, and sulfate in rain water over the United States. J. Meteorol. 15, 417 (1958).

Kakar, S. K.: Ph.D. dissertation, University of Wales (1971).

Kashaev, A. A.: The crystal structure of pyrosmalite. [Russian.] Kristallografiya **12**, 1062 (1967). English translation in Soviet Phys. Cryst. **12**, 923 (1968).

Kato, K., Saalfeld, H.: The crystal structure of hanksite, $KNa_{22}[Cl(CO_3)_2(SO_4)_9]$, and its relation to the K_2SO_4 I structure type. Acta Cryst. **B 28**, 3614 (1972).

Keil, K., Bunch, T. E., Prinz, M.: Mineralogy and composition of Apollo 11 lunar samples. Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta Suppl. 1. **2**, 561 (1970).

Keppler, U.: Zum Modifikationswechsel Chlor-haltiger Apatite. Neues Jahrb. Mineral. Monatsh. 1969, 64.

Kesler, S. E., Loon, J. C. van, Moore, C. H.: Relation between Cl and F (water-extractable) and economic mineral potential of igneous rocks (abstract). Bull. Can. Inst. Mining Metall. 65, 45 (1972).

Kilinc, I. A., Burnham, C. W.: Partitioning of chloride between a silicate melt and coexisting aqueous phase from 2 to 8 kilobars. Econ. Geol. 67, 231 (1972).

Kino, A.: Der magmatische Apatit, seine chemische Zusammensetzung und seine physikalischen Eigenschaften. Chem. Erde **12**, 50 (1938).

Kogarko, L. N., Ryabchikov, I. D.: Differentiation of alkali magmas rich in volatiles. Geochem. Intern. 6, 1113 (1969).

Kokubu, N.: Fluorine in rocks. Mem. Fac. Sci. Kyushu Univ., Ser. C **2**, 95 (1956).

Kolotov, A. B., Kolotov, B. A.: Hydrogeochemistry of certain elements on the weathering of intrusions in the Far East. Dokl. Akad. Nauk. SSSR 177, 230 (1967) (English Transl.).

Koster van Groos, A. F., Wyllie, P. J.: Melting relationships in the system $NaAlSi_3O_8$—$NaCl$—H_2O at 1 kilobar pressure with petrological applications. J. Geol. 77, 581 (1969).

Kostetskaya, E. V.: Chlorine content in the eudialytes of the Lovozero Massif. Geochemistry 1099 (1961a).

Kostetskaya, E. V.: Some regularities of distribution of chlorine in the nepheline syenites of the Lovozero Massif. Geochemistry 988 (1961b).

Kostetskaya, E. V., Markova, M. E., Petrova, Z. I.: Distribution of chlorine in rocks and minerals of the Paleozoic Dzhida granitoid complex (Western Transbaykalia). Geochem. Intern. 6, 172 (1969).

Kostetskaya, E. V., Mordvinova, V. I.: The distribution of fluorine and chlorine in biotites from the rocka of the Dzhida complex of Paleozoic granitoids (Western Transbaykalia). Geochem. Intern. **2**, 927 (1965).

Krasintseva, V. V.: Geochemistry of chlorine and bromine. Geochem. Intern. 1, 78 (1964).

Krauskopf, K. B.: Source rocks for metal-bearing fluids. In: Barnes, H. L. (ed.): Geochemistry of Hydrothermal Ore Deposits. New York: Holt, Rinehart and Winston 1967.

Krutov, G. A.: A new chlorine mineral of the hastingsite group. Bull. Acad. Sci. U.R.S.S., Cl. Sci. Mat. Nat. Sér. Géol. 341 (1936).

Krutov, G. A., Vinogradova, R. A., Kiseleva, I. A.: (Chlorine-containing minerals and some genetic questions of metasomatic magnetite deposits of the Mul'ga Burluksk and Krasnokamsk group of eastern Siberia.) Mosk. Univ. Geol. **31** (1970) [Russian].

Kuroda, P. K., Edwards, R. R., Robinson, B. L., Jonte, J. H., Goolsby, C.: Chlorine-36 in pitchblende. Geochim. Cosmochim. Acta 6, 35 (1954).

Kuroda, P. K., Sandell, E. B.: Chlorine in igneous rocks. Bull. Geol. Soc. Am. 64, 879 (1953).

Lahermo, P.: Chemical geology of ground and surface waters in Finnish Lapland. Bull. Comm. Geol. Finlande **242**, (1970).

Lambert, D. L., Mallia, E. A., Brault, J.: On the abundance of chlorine in the sun. Solar Phys. 19, 289 (1971).

Larimer, J. W., Anders, E.: Chemical fractionations in meteorites. II. Abundance patterns and their interpretation. Geochim. Cosmochim. Acta 31, 1239 (1967).

Lee, D. E.: A chlorine-rich biotite from Lemhi County, Idaho, Am. Mineralogist 43, 107 (1958).

Leelanandam, C.: H_2O^+, F and Cl in the charnockitic biotites from Kondapalli, India. Neues Jahrb. Mineral. Monatsh. 461 (1969a).

Leelanandam, C.: Fluorine and chlorine in the charnockitic hornblendes from Kondapalli, India. Neues Jahrb. Mineral. Monatsh. 379 (1969b).

Leelanandam, C.: Electron microprobe analyses of chlorine in hornblendes and biotites from the charnockitic rocks of Kondapalli, India. Mineral. Mag. 37, 362 (1969c).

Leelanandam, C.: A chlorine-rich biotite from Kondapalli, Andhra Pradesh, India. Am. Mineralogist 55, 1353 (1970).

Le Maitre, R. W.: Petrology of volcanic rocks Gough Island, South Atlantic. Bull. Geol. Soc. Am. 73, 1309 (1962).

Livingstone, D. A.: Chemical composition of rivers and lakes. In: Fleischer, M. (ed.): Data of Geochemistry, 6th ed. U.S. Geol. Surv. Profess. Paper 440-G (1963).

Löns, J., Schulz, H.: Strukturverfeinerung von Sodalith, $Na_8Si_6Al_6O_{24}Cl_2$. Acta Cryst. 23, 434 (1967).

Loon, J. C. van, Kesler, S. E., Moore, C. M.: Analysis of water-extractable chloride in rocks by use of a selective ion electrode. Handbook — Fourth International Geochemical Exploration Symposium, London, 429—434 (1972).

Loucks, R. H., Winchester, J. W.: Pollution contributions to the atmospheric inventory of chlorine and bromine in aerosols over continental U.S.A. In: Hemphill, D. D. (ed.): Trace Substances in Environmental Health 3, 233. Proc. Univ. Mo. Annu. Conf. 3rd. 1969, 1970.

Lovering, J. F.: Electron microprobe analyses of chlorine in two pantellerites. J. Petrol. 7, 65 (1966).

Lovering, J. F., White, A. J. R.: The significance of primary scapolite in granulite inclusions from deep-seated pipes. J. Petrol. 5, 195 (1964).

Lundgren, J.-O., Olovsson, I.: Hydrogen bond studies. XV. The crystal structure of hydrogen chloride dihydrate. Acta Cryst. 23, 966 (1967a).

Lundgren, J. O., Olovsson, I.: Hydrogen bond studies. XVI. The crystal structure of hydrogen chloride trihydrate. Acta Cryst. 23, 971 (1967b).

Macháček, V., Shrbený, O.: Beryllium and chlorine in the volcanic rocks of the České Středohoří Mts. Vestn. Ústřed. Ústavu Geol. 45, 321 (1970).

Magnusson, N.H.: Lyusnarsbergs malmtrakt. Sveriges Geol. Undersok. Arsbiok Ser. Ca. Avhandl. Uppsat 30 (1940).

Mahon, W. A. J., Klyen, L. E.: Chemistry of the Tokaanu — Waihi hydrothermal area. New Zealand J. Sci. 11, 140 (1968).

Mais, R. H. B., Owston, P. G., Wood, A. M.: The crystal structure of K_2PtCl_4 and K_2PdCl_4: with estimates of the factors affecting accuracy. Acta Cryst. B 28, 393 (1972).

Malinoskii, I. Y., Kostyuk, E. A.: (Chlorine in amphiboles). Geol. Geofiz. 44 (1970) [Russian].

Mason, B., Melso, W. G.: The Lunar Rocks. New York: Wiley-Interscience 1970.

Matsuda, H., Horie, K., Honda, M.: ^{36}Cl in iron meteorites. Geochem. J. 4, 83 (1970).

McConnell, D.: Apatite. Its Crystal Chemistry, Mineralogy, Utilization, and Geologic and Biologic Occurrences. Wien-New York: Springer 1973.

Meuller, G.: The properties and theory of genesis of the carbonaceous complex within the Cold Bokevelt meteorite. Geochim. Cosmochim. Acta 4, 1 (1953).

Meunier-Piret, J., Van Meerssche, M.: Nouvelle détermination de la structure du chlorure de fer(II)tétrahydrate. Acta Cryst. B 27, 2329 (1971).

Morton, R. D.: Synthetic chlorapatites and equilibria in the system calcium orthophosphate — calcium chloride. Norsk Geol. Tidsskr. 41, 223 (1961).

Morton, R. D., Catanzaro, E. J.: Stable chlorine isotope abundances in apatites from Ødegårdens Verk, Norway. Norsk. Geol. Tidsskr. 44, 307 (1964).

Mueller, R. F.: Energetica of HCl and HF in volcanic emanations. Geochim. Cosmochim. Acta 34, 737 (1970).

Mun, A. I., Bazilevich, Z. A.: Distribution of bromine in lacustrine bottom muds. Geochemistry 199 (1962).

Nash, W. P., Carmichael, I. S. E., Johnson, R. W.: The mineralogy and petrology of Mount Suswa, Kenya. J. Petrol. 10, 409 (1969).

Nekrasov, Yu. V., Ponomarev, V. I., Simonov, V. I., Kheiker, D. M.: Refinement of the atomic structure of baotite and the isomorphic relationships in this mineral. [Russian.] Kristallografiya 14, 602 (1969). English translation in Soviet. Phys. Cryst. 14, 508 (1970).

Nicholls, J., Carmichael, I. S. E.: Peralkaline acid liquids: a petrological study. Contrib. Mineral. and Petrol. 20, 268 (1969).

Noble, D. C., Smith, V. C., Peck, L. C.: Loss of halogens from crystallized and glassy silicic volcanic rocks. Geochim. Cosmochim. Acta 31, 215 (1967).

Noddack, I., Noddack, W.: Die Häufigkeiten der chemischen Elemente. Naturwissenschaften 18, 757 (1930).

Novoselova, L. N.: Amphibole of the hastingsite — dashkesanite series from the Akatvev deposit (East Transbaikal). Mem. All — Union Min. Soc. 90, 225 (1961).

Ogita, H., Nakai, N., Oana, S.: Chlorine in sedimentary rocks. Geochem. J. 1, 139 (1967).

Orville, P. M.: Alkali ion exchange between vapour and feldspar phases. Am. J. Sci. 261, 201 (1963).

Osipova, G. A.: Migration of components during the formation of skarns at the Tashbulak deposit. Geochemistry 33 (1959).

Owen, H. R., Schaeffer, O. A.: The isotope abundances of chlorine from various sources. J. Am. Chem. Soc. 77, 898 (1955).

Papike, J. J., Zoltai, T.: The crystal structure of a marialite scapolite. Am. Mineralogist 50, 641 (1965).

Pauling, L.: Die Natur der Chemischen Bindung. Weinheim: Verlag Chemie 1964.

Pauling, L., Huggins, M. L.: Covalent radii of atoms and interatomic distances in crystals containing electron-pair bonds. Z. Krist. 87, 205 (1934).

Perkins, R. W., Thomas, C. W., Hill, M. W., Nielson, J. M.: Chlorine-38 and sulphur-38 produced by cosmic radiation. Nature 205, 790 (1965).

Portyanko, V. F., Kostina, A. E., Dulova, M. K., Portyanko, V. V.: (Distribution of chlorine and iodine in plants.) Fiziol. Rast. 17, 169 (1970) (In Russian).

Quijano-Rico, M., Wänke, H.: Determination of boron, lithium and chlorine in meteorites. In: Millman, P. M. (ed.): Meteorite Research. Dordrecht, Holland: Reidel 1969.

Rankama, K.: Progress in Isotope Geology. New York: Interscience 1963.

Rankama, K., Sahama, T. G.: Geochemistry. Chicago: Chicago Univ. Press 1950.

Reed, G. W., Allen, R. O.: Halogens in chondrites. Geochim. Cosmochim. Acta 30, 779 (1966).

Reed, G. W., Jovanovic, S.: Some halogen measurements on achondrites. Earth Planet. Sci. Lett. 6, 316 (1969).

Reed, G. W., Jovanovic, S.: Halogens, mercury, lithium and osmium in Apollo 11 samples. Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta, 1. Suppl. 2, 1487 (1970).

Reed, G. W., Jovanovic, S.: The halogens and other trace elements in Apollo 12 samples and the implications of halides, platinum metals, and mercury on surfaces. Proc. Second Lunar Sci. Conf. 2, 1261 (1971).

Rimsaite, J.: Distribution of major and minor constituents between mica and host ultrabasic rocks and between zoned mica and zoned spinel. Contrib. Mineral. and Petrol. 33, 259 (1971).

Robinson, P., Fang, J. H., Ohya, Y.: The crystal structure of kainite. Am. Mineralogist 57, 1325 (1972).

Roedder, E.: Fluid inclusions as samples of ore fluids. In: Barnes, H.L. (ed.): Geochemistry of Hydrothermal Ore Deposits. New York: Holt, Rinehart and Winston 1967.

Roedder, E.: Composition of fluid inclusions. In: Fleischer, M. (ed.): Data of Geochemistry, 6th ed., U.S. Geol. Surv. Profess. Paper 440-JJ (1972.)

Roedder, E., Coombs, D. S.: Immiscibility in granitic melts, indicated by fluid inclusions in ejected granitic blocks from Ascension Island. J. Petrol. 8, 417 (1967).

Rosenzweig, A., Watson, E.: Some hornblendes from south eastern Pennsylvania and Delaware. Am. Mineralogist 39, 581 (1945).

Rouse, R. C.: The crystal chemistry of diaboleite. Z. Krist. 134, 69 (1971).

Rouse, R. C.: The crystal structure of boleite — a mineral containing silver atom clusters. J. Solid State Chem. 6, 86 (1973a).

Rouse, R. C.: Hematophanite, a derivative of the perovskite structure. Mineral. Mag. 39, 49 (1973b).

Rubey, W. W.: Geologic history of sea water. Bull. Geol. Soc. Am. 62, 1111 (1951).

Rubey, W. W.: Development of the hydrosphere and atmosphere with special reference to probable composition of the early atmosphere. In: Poldervaart, A. (ed.): Crust of the Earth. Geol. Soc. Am. Spec. Paper 62, 631 (1955).

Rucklidge, J.: Chlorine in partially serpentinized dunite. Econ. Geol. 67, 38 (1972).

Sahama, T. G.: Rapakivi amphibole from Uuksunjoki, Salmi area. Bull. Comm. Geol. Finlande 140 (1947).

Salpeter, E.: Spektroskopische Chlorbestimmung in Steinmeteoriten. Richerche Spectroscopische Specola Vaticana 2/I (1952).

Sasvari, K., Jeffrey, G. A.: The crystal structure of magnesium chloride dodecahydrate, $MgCl_2 \cdot 12H_2O$. Acta Cryst. 20, 875 (1966).

Savelli, C.: The problem of rock assimilation by Somma — Vesuvius magma. I. Composition of Somma and Vesuvius lavas. Contrib. Mineral. Petrol. 16, 328 (1967).

Schaeffer, O. A., Heymann, D.: Comparison of ^{36}Cl—^{36}Ar and ^{39}Ar—^{38}Ar cosmic ray exposure ages of dated fall iron meteorites. J. Geophys. Res. 70, 1473 (1965).

Schaeffer, O. A., Thompson, S. O., Lark, N. L.: Chlorine-36 radioactivity in rain. J. Geophys. Res. 65, 4013 (1960).

Schneider, W.: Caracolit, das $Na_3Pb_2(SO_4)_3Cl$ mit Apatitstruktur. Neues Jahrb. Mineral. Monatsh. 1967, 284.

Schneider, W.: Bestimmung einer Überstruktur am Caracolit. Neues Jahrb. Mineral. Monatsh. 1969, 58.

Selivanov, L. S.: Chlorine and bromine in massive crystalline rocks. Dokl. Akad. Nauk, SSSR 28, 809 (1940) (English Transl.).

Shannon, E. V., Larsen, E. S.: Merrillite and chlorapatite from stony meteorites. Am. J. Sci. 9, 250 (1925).

Shatkov, G. A., Shatkova, L. N., Gushchin, Ye. N.: The distribution of uranium, thorium, fluorine, chlorine, molybdenum and niobium in liparites and acid volcanic glasses. Geochem. Intern. 7, 1051 (1970).

Shaw, D. M.: The geochemistry of scapolite. I. Previous work and general mineralogy. J. Petrol. 1, 218 (1960).

Shaw, T. I.: In: Lewin, R. A. (ed.): Physiology and Biochemistry of Algae. New York: Academic Press 1962.

Shearman, D. J.: Origin of marine evaporites by diagenesis. Trans. Inst. Min. and Metall. Sect. B. 75, 208 (1966).

Shedlovsky, J. P., Honda, M., Reedy, R. C., Evans, J. C., Lal, D., Lindstrom, R. M., Delany, A. C., Arnold, J. R., Loosli, H. H., Fruchter, J. S., Finkel, R. C.: Pattern of bombardment-produced radionuclides in rock 10017 and in lunar soil. Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta, Suppl. 1. 2, 1503 (1970).

Smith, D. K., Landingham, R. L., Smith, G. S., Johnson, Q.: The crystal structure of WCl_6. Acta Cryst. B 24, 1563 (1968).

Stueber, A. M., Huang, W. H., Johns, W. D.: Chlorine and fluorine abundances in ultramafic rocks. Geochim. Cosmochim. Acta 32, 353 (1968).

Stewart, F. H.: Marine Evaporites. In: Fleischer, M. (ed.): Data of Geochemistry, 6th ed. U.S. Geol. Surv. Profess. Paper 440-Y (1963).

Stollery, G., Borcsik, M., Holland, H. D.: Chlorine in intrusives: a possible prospecting tool. Econ. Geol. 66, 361 (1971).

Stormer, J. C., Carmichael, I. S. E.: The free energy of sodalite and the behavior of chloride, fluoride and sulfate in silicate magmas. Am. Mineralogist 56, 292 (1971).

Strunz, H.: Mineralogische Tabellen. Leipzig: Akademische Verlagsgesellschaft 1970.

Studier, M. H., Hayatsu, R., Anders, E.: Organic compounds in carbonaceous chondrites. Science 149, 1455 (1965).

Sugawara, K.: Migration of elements through phases of the hydrosphere and atmosphere. In: Vinogradov, A. P. (ed.): Chemistry of the Earth's Crust, 501. Jerusalem: Israel Program for Scientific Translations 1967.

Sugiura, T.: Bromine to chlorine ratios in igneous rocks. Bull. Chem. Soc. Japan 41, 1133 (1968).

SUGIURA, T., MIZUTANI, Y., OANA, S.: Fluorine, chlorine, bromine and iodine in volcanic gases. J. Earth Sci. Nagoya Univ. 11, 272 (1963).

TABORSZKY, F. K.: Das Problem der Cl-Apatite. Lithos 5, 315 (1972).

TAKÉUCHI, Y., KAWADA, I., SADANAGA, R.: The crystal structure and polytypes of manganpyrosmalite. Acta Cryst. 16, A16 (1963).

TAYLOR, D.: The sodalite group of minerals. Contrib. Mineral. and Petrol. 16, 172 (1967).

TOOMS, J. S.: Review of knowledge of metalliferous brines and related deposits. Trans. Inst. Min. Metall. Sect. B. 79, 116 (1970).

TOURTELOT, H. A.: Preliminary investigation of the geological setting and chemical composition of the Pierre Shale Great Plains region. U.S. Geol. Surv. Profess. Paper 390 (1962).

TUREKIAN, K. K., WEDEPOHL, K. H.: Distribution of the elements in some major units of the Earth's crust. Bull. Geol. Soc. Am. 72, 175 (1961).

UPTON, B. G. J., THOMAS, J. E., MACDONALD, R.: Chemical variation within three alkali complexes in south Greenland. Lithos 4, 163 (1971).

VALACH, R.: Fluoride und Chloride in Niederschlägen von Böhmen. Studia Geophys. Geodaet. Cesk. Akad. Ved. 11, 241 (1967).

VAN DE KAMP, P. C.: The green beds of the Scottish Dalradian Series: Geochemistry, origin and metamorphism of mafic sediments. J. Geol. 78, 281 (1970).

VAN SCHMUS, W. R., RIBBE, P. H.: Composition of phosphate minerals in ordinary chondrites. Geochim. Cosmochim. Acta 33, 637 (1969).

VASILEVA, Z. V.: Fluorine, chlorine and hydroxyl in apatites. Geochemistry 825 (1957).

VILCSEK, E., WÄNKE, H.: Cosmic-ray exposure ages and terrestrial ages of stone and iron meteorites derived from Cl^{36} and Ar^{39} measurements. I.A.E.A. Vienna 381 (1963).

VINCENT, H., PERRAULT, G.: Structure cristalline de l'oxychlorure de plomb synthétique $Pb_3O_2Cl_2$. Bull. Soc. Franc. Mineral. Crist. 94, 323 (1971).

VINOGRADOV, A. P.: The Elementary Chemical Composition of Marine Organisms. New Haven: Sears Foundation for Marine Research 1953.

VINOGRADOV, A. P.: The Geochemistry of Rare and Dispersed Chemical Elements in Soils, 2nd ed. New York: Consultants Bureau 1959.

VINOGRADOV, A. P.: Average contents of chemical elements in the principal types of igneous rocks of the Earth's crust. Geochemistry 641 (1962).

VINOGRADOV, A. P.: Gas regime of the Earth. In: VINOGRADOV, A. P. (ed.): Chemistry of the Earth's Crust. Jerusalem: Israel Program for Scientific Translations 1967.

WALTERS, L. J., WINCHESTER, J. W.: Neutron activation analysis of sediments for halogens using the Szilard — Chalmers reactions. Anal. Chem. 43, 1020 (1971).

WÄNKE, H., BEGEMANN, F., VILSEK, E., RIEDER, R., TESCHKE, F., BORN, W., QUIJANO-RICO, M., VOSHAGE, H., WLOTSKA, F.: Major and trace elements and cosmic-ray produced radioisotopes in Lunar samples. Science 167, 523 (1970).

WELLS, A. F.: Structural Inorganic Chemistry. Oxford: Clarendon Press 1962.

WHITE, D. E.: Saline waters of sedimentary rocks. In: YOUNG, A., and GALLEY, J. E. (eds.): Fluids in Subsurface Environments — a Symposium. Am. Assoc. Petrol. Geologists, Mem. 4, 342 (1965).

WHITE, D. E.: Environment of generation of some base-metal ore deposits. Econ. Geol. 63, 301 (1968).

WHITE, D. E., HEM, J. D., WARING, G. A.: Chemical composition of sub-surface waters. In: FLEISCHER, M. (ed.): Data of Geochemistry, 6th ed. U.S. Geol. Surv. Profess Paper 440-F (1963).

WHITE, D. E., WARING, G. A.: Volcanic emanations. In: FLEISCHER, M. (ed.): Data of Geochemistry, 6th ed. U.S. Geol. Surv. Profess. Paper 440-K (1963).

WHITEHEAD, H. C., FETH, J. H.: Chemical composition of rain, dry fallout and bulk precipitation at Menlo Park, California, 1957—1959. J. Geophys. Res. 69, 3319 (1964).

WINCHESTER, J. W., DUCE, R. A.: The global distribution of iodine, bromine and chlorine in marine aerosols. Naturwissenschaften 54, 110 (1967).

WINSBERG, L.: The production of chlorine-39 in the lower atmosphere by cosmic radiation. Geochim. Cosmochim. Acta 9, 183 (1956).