Chlorine Isotopes and their Application to Groundwater Dating at Olkiluoto

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ABSTRACT

The chlorine isotopes ^{36}Cl and ^{37}Cl have been shown to be useful tracers of groundwater, and for investigations of sources of dissolved Cl, mixing of fluids, water-rock interactions in sedimentary environments and in identifying solute sources and transport mechanisms. In addition, the radioactive isotope, ^{36}Cl, is a useful tracer for determining the residence time of groundwater.

This report examines the results of Cl isotopic analysis of groundwaters from as deep as 1000 m at the Olkiluoto site in southwest Finland. Thirty-four samples were analysed for ^{36}Cl/Cl and 29 were analysed for ^{37}Cl (expressed as δ^{37}Cl). The value δ^{37}Cl was found to stabilize at higher salinities and the maximum range of δ^{37}Cl was from about -0.6 to +0.6 ‰. Because of this limited range and the relatively large error margins associated with the δ^{37}Cl measurement, the usefulness of this ratio appears to be limited. Therefore, the main part of this report is largely focused on ^{36}Cl.

Estimation of residence time of ^{36}Cl gives results that support the presence of at least five groundwater types at Olkiluoto. The consistency of ^{36}Cl/Cl ratios in groundwaters of several widely separated, deep locations and different rock compositions, suggests that these deeper groundwaters are in secular equilibrium and, therefore, likely to be older than 1.5 million years.

Keywords: Chlorine isotopes, ^{36}Cl in situ production, groundwater salinity.

KLOORI-ISOTOOPIT JA NIIDEN SOVELTAMINEN OLKILUODON POHJAVEDEN VIIPYMÄN MÄÄRITTÄMISESSÄ

TIIVISTELMÄ

Kloori-isotoopit ^{36}Cl ja ^{37}Cl ovat osoittautuneet käyttökelpoisiksi pohjaveden merkkiaineiksi, joiden avulla voidaan tutkia kloridin alkuperää, vesien sekoittumista, vesikallio vuorovaikutusta sedimenttikiviympäristöissä ja arvioida liuenneiden aineiden alkuperää ja kulkeutumismekanismeja. Lisäksi radioaktiivinen isotooppi ^{36}Cl on käyttökelpoinen tulkittaessa pohjaveden viipymää.

Raportissa tarkastellaan Olkiluodon pohjavesien kloorin isotooppituloksia aina 1000 m syvyyteen saakka. Kaikkiaan ^{36}Cl/Cl on määritetty 34 näytteestä ja δ^{37}Cl 29 näytteestä. δ^{37}Cl:n vaihteluväli on -0.6 — +0.6 ‰, mikä stabiloituu korkeammissa suolapitoisuuksissa. Johtuen δ^{37}Cl:n kapeasta vaihteluvälistä ja siihen nähden suhteellisen suuresta mittaus epätarkkuudesta tulosten käyttökelpoisuus tuntuu rajoitetulta. Tämän vuoksi raportti keskittyy pääasiassa ^{36}Cl-tuloksiin.

Kloori-36 tuloksia hyödyntävät arviot viipymäajoista tukevat vähintään viiden eri pohjavesityypin läsnäolosta Olkiluodossa. Suolaisten pohjavesien ^{36}Cl/Cl suhteiden samankaltaisuus viittaa niiden saavuttaneen sekulaaritasapainon kallioperässä, mikä tarkoittaa näiden syvien pohjavesien suolaisuuden olevan todennäköisesti vähintään 1,5 miljoonaa vuotta vanhaa.

Avainsanat: Kloori-isotoopit, ^{36}Cl in situ tuotanto, pohjaveden suolaisuus.

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1   INTRODUCTION

Chlorine has two principal stable isotopes, ^{35}Cl (75.77%) and ^{37}Cl (24.23%) which make up the main part of elemental chlorine and so occur approximately in the relative proportions of 3:1, respectively. The measured ratio, expressed as δ^{37}Cl, has been found to be invariant in ocean water (Kaufman et al. 1984) but does vary slightly between halites and coexisting groundwaters (Desaulniers et al. 1986). Furthermore, Cl-isotope fractionation has been shown to occur during diffusion in pore fluids in clays.

The other isotopes of Cl are radioactive and short-lived, except for ^{36}Cl, which exists only in trace amounts in the environment, in a ratio of about 7×10^{-13} to 1.0 with the stable isotopes. Chlorine-36 is produced in the atmosphere by spallation of ^{36}Ar during interaction with cosmic ray protons. In the subsurface environment, ^{36}Cl is generated primarily as a result of neutron capture by ^{35}Cl or muon capture by ^{40}Ca. The thermal neutrons for this reaction are produced during spontaneous fission of naturally occurring ^{238}U and by interactions between α particles (from decay of U and Th) and light elements such as Al, Na, O, Mg and Si in surrounding rocks (Florkowski et al. 1988). Chlorine-36 decays to ^{36}S and to ^{36}Ar, with a combined half-life of 308,000 years.

The half-life of this hydrophilic, nonreactive isotope makes it suitable for geologic dating in the range of up to 1.5 million years before present. In addition, large amounts of ^{36}Cl were produced by irradiation of seawater during atmospheric detonation of nuclear weapons, between 1952 and 1958. The residence time of ^{36}Cl in the atmosphere is about 1 week. Thus, ^{36}Cl serves as an event marker of 1950's water in soil and groundwater, and is also useful for dating recharging waters less than 60 years before present.

2   CHLORINE ISOTOPES AS HYDROLOGICAL TRACERS AND INDICATORS OF WATER-ROCK INTERACTION

2.1 ^{37}Cl

Stable Cl isotope ratios (such as ^{37}Cl/^{35}Cl) have been used in hydrological studies to investigate sources of dissolved Cl, mixing of fluids, and water-rock interactions in sedimentary environments (Kaufmann et al. 1992, Eastoe et al. 2001, Zhang et al. 2007). The Cl stable isotopic ratio, when coupled with other geochemical parameters, has been shown to be a useful tool in identifying solute sources and transport mechanisms (Hendry et al. 2000, Godon et al. 2004). Stable Cl isotopes may be fractionated from each other naturally, as a result of partitioning between minerals and aqueous solution. The heavier isotope (^{37}Cl) is preferentially taken up by mineral structures due to the stronger bonding of Cl ion to solid phases relative to aqueous phases (Magenheim et al. 1995). The equilibrium Cl isotope fractionation has been calculated by Schauble et al. (2003) using vibrational spectra and force-field modelling and these authors estimated that silicates were about 2 to 3 ‰ enriched in ^{37}Cl compared to coexisting brines. In laboratory experiments, Eggenkamp et al. (1995) determined a fractionation factor of 1.00026 between halite and the saturated solution. Precipitation and dissolution of evaporite minerals have been identified as the dominant processes for Cl isotope fractionation in sedimentary basins (Eastoe et al. 1999, 2001). Chlorine isotope fractionation measured on the large scale is frequently attributed to processes such as diffusion, ion-filtration and mixing between two different sources. Diffusion occurs as a result of concentration gradients and the isotopes are separated because ^{35}Cl is more mobile than ^{37}Cl. Therefore, the more distant fluids are depleted in ^{37}Cl away from the source. Ion filtration, however, results in an *enrichment* of ^{37}Cl downgradient and occurs when saline water is forced through a charged clay membrane. Mixing is indicated if correlation is found between δ^{37}Cl and Cl concentration (Hendry et al. 2000).

2.2 ^{36}Cl

Chlorine-36 in surface and groundwater behaves conservatively, in exactly the same manner as stable Cl, and is useful for identifying possible origins of dissolved stable Cl in ancient saline groundwaters extending back to early Quaternary and late Tertiary times (Andrews et al. 1989, Bentley et al. 1986, Andrews and Fontes 1992, Clark and Fritz 1997).

As indicated above, ^{36}Cl in groundwater has three sources: a) cosmic radiation in the upper atmosphere and rain-out, b) spallation of K, Ca, and Ar in soil moisture and minerals and c) subsurface production by neutron activation of stable ^{35}Cl from decay of naturally occurring radioelements (i.e. U, Th) at greater depth in the bedrock. With time, the ^{36}Cl will accumulate and decay until the rate of production equals the rate of decay (i.e. secular equilibrium) and this occurs in a closed system after a period of up to 1.5 million years. Groundwaters with ^{36}Cl values at secular equilibrium with *in situ* ^{36}Cl will therefore have been shielded from atmospheric infiltration and resided in this rock for at least 1.5 million years. To use ^{36}Cl as an age dating tool for groundwater at a site, it is important that Cl in the groundwater is derived from the host rock and is not imported from other locations.

Chlorine-36 is a useful isotopic tracer for determining the residence time of groundwater, identifying mixing of groundwaters and determining the characteristics of water-rock interaction. Interpreting ^{36}Cl data in terms of water residence time* requires understanding the origin of chloride ion dissolved in the water. Groundwater age can be calculated based on measured, initial and secular equilibrium values of the ^{36}Cl/Cl ratio when no sources or sinks of Cl exist in the system (Bentley et al. 1986). However, ^{36}Cl may have been added to the groundwater by processes such as subsurface production, diffusion from pore waters or mixing. Limitations to subsurface neutron production are expected to arise from several rare earth elements (REE), in particular, Gd and Sm. These are considered in section 3.3.

2.3   Methodology

The ratio, ^{37}Cl/Cl, is determined by precipitation of Cl from the groundwater by $AgNO_3$, followed by concentration if necessary, conversion to methyl chloride and then gas-source mass spectrometry for masses 50, 51 and 52.   Results are compared with measurements of Cl in Standard Mean Ocean Chloride (SMOC) which has a designated value of 0 ‰, and is expressed as δ^{37}. Measurements typically have a precision of +/- 0.24 ‰. Chlorine-36 is also determined by precipitation and purification to give $AgNO_3$ but is then analysed for ^{36}Cl by atom counting using Accelerator Mass Spectrometry (AMS). Results are reported as ^{36}Cl/total Cl x 10^{-15}.

Most studies have been concerned with ^{36}Cl dating and ^{37}Cl isotopic fractionation in sedimentary environments and a summary of these references and other Cl-isotopic applications is given in Appendix 1. The study described in this report examines Cl isotopic separation in fractured crystalline rocks in Shield areas. This type of study has been performed on the Stripa granite in Sweden (Andrews et al. 1989, Andrews and Fontes 1992), on the Lac du Bonnet granite in Canada (Gascoyne et al. 1992), and on sites in Sweden and Finland (Smellie et al. 2008, Gascoyne 2001). In a recent paper by Stotler et al. (2009), similar ^{36}Cl levels in the Lupin gold mine in Nunavut, NWT, Canada, were found in Olkiluoto. The reason for this might be the fact that the geological background of Lupin (metasediments) is somewhat similar to that occurring in Olkiluoto,

* Groundwater residence time is sometimes confused with the 'age' of a groundwater. As pointed out by Clark and Fritz (1997): "Only tritium is part of the water molecule and can actually 'date' the water. All other dating methods rely on dissolved constituents whose abundance in water is controlled by physiochemical and biological processes." Groundwater mixing inevitably averages out the age, especially in fractured rock, and various 'dating' methods should be used to derive an "average residence time".

3 RESULTS AND DISCUSSION

3.1 Isotopic data

This report describes the results of ^{36}Cl/Cl and δ^{37}Cl determinations on selected groundwater types and corresponding host rocks at the Olkiluoto site to determine if the data support the various hypotheses proposed for defining the origin of groundwater at the site. The results of recent sampling and analysis of Olkiluoto and other, previously sampled groundwaters, are shown in Table 1 for both ^{36}Cl//Cl and δ^{37}Cl, where possible, and for supporting hydrochemical data. Comparison is made in Table 2 with earlier ^{36}Cl results from Olkiluoto and from other sites such as Simpevarp/Laxemar and Forsmark (both were potential disposal sites in Sweden).

Recently, ^{36}Cl has been measured in selected groundwaters from the Forsmark and Simpewarp/Laxemar sites, in southeastern Sweden (Gascoyne and Gurban 2009). There are only seven ^{36}Cl analyses of each of Laxemar and Forsmark groundwaters from the Swedish database and there are five from Louvat et al. (1999). These are also listed in Table 2 together with values for the Äspö (five samples) and early Olkiluoto (eight samples) sites. Thirty-four analyses are reported in Table 1 for the analysis of ^{36}Cl in Olkiluoto groundwaters and 29 are for δ^{37}Cl.

3. 2 Chemical and isotopic patterns

The relationship between dissolved Cl-isotopic species and Cl, and SO$_4$ is explored using variation diagrams in Figure 1. It is apparent, however, that there is no clear correlation between any of the parameters except that δ^{37}Cl stabilizes at higher salinities, seems to be more negative in SO$_4$-rich groundwaters, and the maximum range of δ^{37}Cl is from about - 0.6 to +0.6 ‰. Because of this limited range and the relatively large error margins associated with the δ^{37}Cl measurement, there appears to be little else (other than the correlations made above) that can be usefully gained from this isotopic ratio. Hence, the following part of this report is largely focused on ^{36}Cl.

The ^{36}Cl/Cl ratio in groundwaters in this study only exceeds 40 x 10^{-15} in a few cases, mainly in the Swedish sites (Table 2). In Olkiluoto samples (Table 1), 2 out of 34 significantly exceed 40 x 10^{-15} and these are for very shallow groundwaters (< 35 m depth). Olkiluoto groundwaters tend to be lower in ^{36}Cl contents when compared with the other areas and this may indicate either that the host rock at Olkiluoto contains less U and Th, or more REE, than the other sites.

The ^{36}Cl/Cl ratios in groundwaters at these sites range from high values (160 x 10^{-15}) for the dilute, near-surface samples, to low values (1.7 x 10^{-15}) for Baltic seawater which has a high ionic Cl concentration (3,660 mg/L). This ^{36}Cl/Cl ratio is close to the detection limit for ^{36}Cl and may be affected by analytical error or to mixing with recent waters as might occur in a groundwater discharge zone or mixing with sea water. In the dilute samples, ^{36}Cl is probably derived mainly from cosmogenic sources and thus this groundwater could be recent and probably < 50 years old. It is also possible that this sample may contain a small quantity of 'bomb pulse' ^{36}Cl, produced by atmospheric nuclear bomb tests in the 1950's and 1960's or, even, from the Chernobyl accident in 1986. The intermediate depth range (250 – 800 m) and deeper (~950 m) brackish to saline Swedish samples have intermediate values of ^{36}Cl/Cl (20 to 48 x 10^{-15}) ratios and this suggests that these are values typical of *in situ* production of ^{36}Cl.

Table 1. *Summary of chemical and isotopic composition of Olkiluoto groundwaters. Samples are graded according to their reliability and representativity in the classes B1 (quantitative), B2 (qualitative), T (temporary changes).*

Sample code	Date	Depth (m)	Class	Water type**	Cl mg/l	SO4 mg/l	TDS mg/l	Na mg/l	Ca mg/l	Mg mg/l	Br mg/l	O-18 o/oo SMOW	H2 o/oo SMOW	Cl-37 o/oo SMOC	Cl-36 *10E-15 SMOC
SEA01, Eteläriutta*_2	10-Sep-02		T	Baltic sea	3050	440.0	5598	1650	89	220.0	8.6	-7.60	-57.30	0.14	0
SEA04, Pitkäkarin kulma_1	9-Sep-02		T	Baltic sea	2910	430.0	5389	1610	85	210.0	8.6	-7.50	-56.50	0.17	0
SEA02, Puskakari_3	10-Sep-02		T	Baltic sea	3010	450.0	5620	1700	90	220.0	8.9	-7.50	-57.40	0.09	0
SEA03, Susikari_1	9-Sep-02		T	Baltic sea	3010	440.0	5630	1730	90	210.0	9.1	-7.60	-57.40	-0.12	0
PR3_1	27-Aug-97	8.28	B1	FB HCO3	30	110.0	798	210	10	3.7	0.1	-10.70			122
KR32_50_1	3-Jan-06	-34.58	B2	FB HCO3	52	28.0	578	118	23	8.7	<0.5	-11.27	-80.30		123
KR30_50_1	1-Aug-05	-39.52	T	FB HCO3	87	55.0	699	158	24	9.7	<0.5	-11.38	-79.20		45
KR39_108_1	22-May-06	-88.18	B2	FB HCO3	331	100.0	1174	267	54	19.0	0.8	-11.32	-79.90	0.080	16
KR1_T76_1	11-Jul-94	-63.31	B2	FB HCO3	413	101.0	1369	324	78	25.0	1.6	-11.10	-78.40		15
KR33_95_1	17-Jan-06	-70.63	B1	FB HCO3	1130	280.0	2675	760	130	42.0	3.8	-10.58	-75.20		3
KR31_143_1	16-Oct-06	-122.35	T1	FB HCO3	869	160.0	1978	519	100	36.0	2.6	-10.72	-76.90		6
KR10_259_1	30-May-05	-249.25	T1	FB HCO3	1400	160.0	2694	751	190	29.0	5.9	-11.29	-83.10		7
KR37_166_1	20-Nov-06	-111.58	T1	FB HCO3	1760	250.0	3408	823	230	88.0	5.7	-10.35	-75.40		4
KR27_124_1	22-Sep-04	-95.16	B2	B SO4	2050	250.0	3806	888	370	89.0	7.6	-13.04	-94.80	-0.62	8
KR41_257_1	18-Dec-07	-234.60	B1	B SO4	2340	130.0	4055	1290	190	33.0	12.2	-12.72	-93.20		10
KR7_282_1	10-Dec-98	-255.56	B2	B SO4	2630	320.0	4761	1200	390	92.0	9.2	-9.90	-75.50	-0.07	
KR19_110_1	30-Aug-05	-100.67	B2	B SO4	2850	410.0	5736	1390	770	120.0	10.0	-9.97	-75.80		8
KR42_308_1	1-Oct-07	-280.59	B2	B SO4	2980	282.0	5293	1330	480	100.0	12.9	-12.12	-88.00		8
KR27_247_1	3-Nov-04	-193.51	B2	B SO4	3400	400.0	6106	1410	510	190.0	15.0	-9.99	-72.20	-0.34	5
KR29_320_1	30-May-05	-293.40	B2	B SO4	3950	370.0	6933	1620	800	110.0	16.0	-10.02	-74.80		5
KR42_175_1	27-Nov-07	-156.69	B2	B SO4	4390	545.0	7862	1920	690	200.0	16.0	-9.84	-72.40		4
KR40_282_1	24-Apr-07	-255.08	B1	B SO4	4430	521.0	7969	1980	670	230.0	15.5	-9.04	-68.30		5
KR4_T132_2	13-Mar-95	-119.58	B1	B SO4	4500	510.0	7992	1870	700	260.0	18.0	-9.50	-72.40		4
KR8_302_1	22-Jul-97	-260.68	B2	B SO4	4770	470.0	8504	2030	1020	130.0	16.0	-9.96	-74.50	-0.36	5
KR47_111_1	21-Jul-08	-88.74	B1	B SO4	4880	516	8658	2420	630	130	17.6	-12.78	-96.6	0.11	7.0
KR47_131_1	23-Sep-08	-105.60	B1	B SO4	5030	437	8665	2180	680	220	15.70	-10.2	-77.8	0.18	9.0
KR13_362_3	6-Mar-06	-293.96	T2	B SO4	2720	86.0	4733	1260	420	28.0	14.4	-11.50	-82.90		12
KR13_362_4	9-Jul-07	-293.96	T2	B SO4	2710	86.9	4708	1240	430	30.0	15.1	-11.39	-82.50		14
KR15_241_1	6-May-03	-231.78	B1	B Cl	2400	1.8	3946	1220	250	21.0	15.0	-13.89	-101.3	0.23	
KR3_243_1	20-Sep-97	-216.14	B1	B Cl	2760	1.4	4569	1445	279	25.0	18.9	-13.13	-96.9	0.46	13
KR3_438_1	27-Nov-98	-390.14	B1	B Cl	2880	11.7	4750	1590	210	9.6	15.0	-12.30		0.44	
KR11_277_1	30-Dec-99	-247.54	B1	B Cl	3080	71	5168	1660	270	37.0	14.0			0.06	
KR39_403_1	27-Mar-06	-344.81	B1	B Cl	3780	13.0	6176	1880	410	18.0	28.1	-12.92	-94.70	0.62	16
KR10_326_2	13-Jun-06	-316.03	T1	B Cl	4770	<1.25	7699	1790	990	58.0	28.9	-12.01	-87.00		15
KR10_324_1	22-Oct-97	-314.03	B1	B Cl	5400	8.3	8723	1930	1240	57.0	37.0	-12.01	-84.90	0.07	12
KR19_455_1	18-Oct-05	-432.62	T1	S	7110	47.0	11653	2470	1800	45.0	45.0	-11.54	-82.50		23
KR27_503_1	30-Dec-04	-391.73	B1	S	7900	<1.25	12687	2540	2100	39.0	57.0	-12.62	-89.60	0.28	16
KR9_470_1	25-Feb-99	-424.90	B1	S	8030	17.1	12957	2810	1950	29.0	56.0	-12.27	-84.50	0.40	
KR5_T446_2	1-Aug-94	-385.56	T1	S	8400	4.2	13526	3020	1940	61.0	56.2				23
KR47_413_1	16-Dec-08	-334.10	B1	S	8820	<0.1	14220	3270	2000	27	57.7	-11.88	-84.90	0.43	16
KR47_708	11-Nov-08	-572.10	B1	S	18800	2.30	30280	6550	4700	8.1	141	-9.26	-54.6	0.50	35
KR9_563_1	30-Jun-97	-507.96	B2	S	11480	1.3	19127	4200	3250	40.0	92.0	-12.02	-80.94	0.26	
KR10_498_1	27-May-99	-487.05	B1	S	13500	1.4	22099	4830	3570	38.0	95.0	-11.20	-77.00	0.46	
KR12_664_1	14-May-02	-632.45	B2	S	23800	5.4	36836	6330	6400	44.0	150.0	-11.07	-67.20	0.32	
KR12_736_1	20-Mar-02	-703.87	B2	S	29200	5.5	46290	7120	9600	35.0	200.0	-10.75	-64.00	0.27	
KR12_741_1	13-Nov-00	-708.31	B1	S	30600	5.1	49483	8300	1020	36.0	204.0	-10.86	-64.26	0.20	
KR29_800_1	4-Apr-05	-742.19	B1	S	32800	<1.25	52197	8850	1000	140.0	260.0	-10.02	-49.00		14
KR4_860_1	20-Jul-98	-817.81	B2	S	43000	1.2	67957	9200	1510	108.0	350.0	-10.09	-49.75	0.09	
KR4_861_1	13-May-97	-818.75	B1	S	43000	<1	69114	9750	1570	110.0	348.0	-10.09	-49.75	0.01	16
KR4_860_2	14-May-02	-817.81	T1	S	45200	8.4	73417	9540	1800	130.0	300.0	-10.07	-50.80	0.37	

*Class codes refer to evaluation report by Pitkänen et al. (2007). FB = fresh/brackish, B = Brackish, S = Saline

Table 2. *Results of previous ^{36}Cl analyses of Forsmark, Simpevarp/Laxemar, Äspö/Laxemar (from Louvat et al. 1999) and Olkiluoto groundwaters (Gascoyne 2001 (ratio values are x 10^{-15}). Data for Olkiluoto are shown by representative drillhole groundwaters and then classified in terms of origin.*

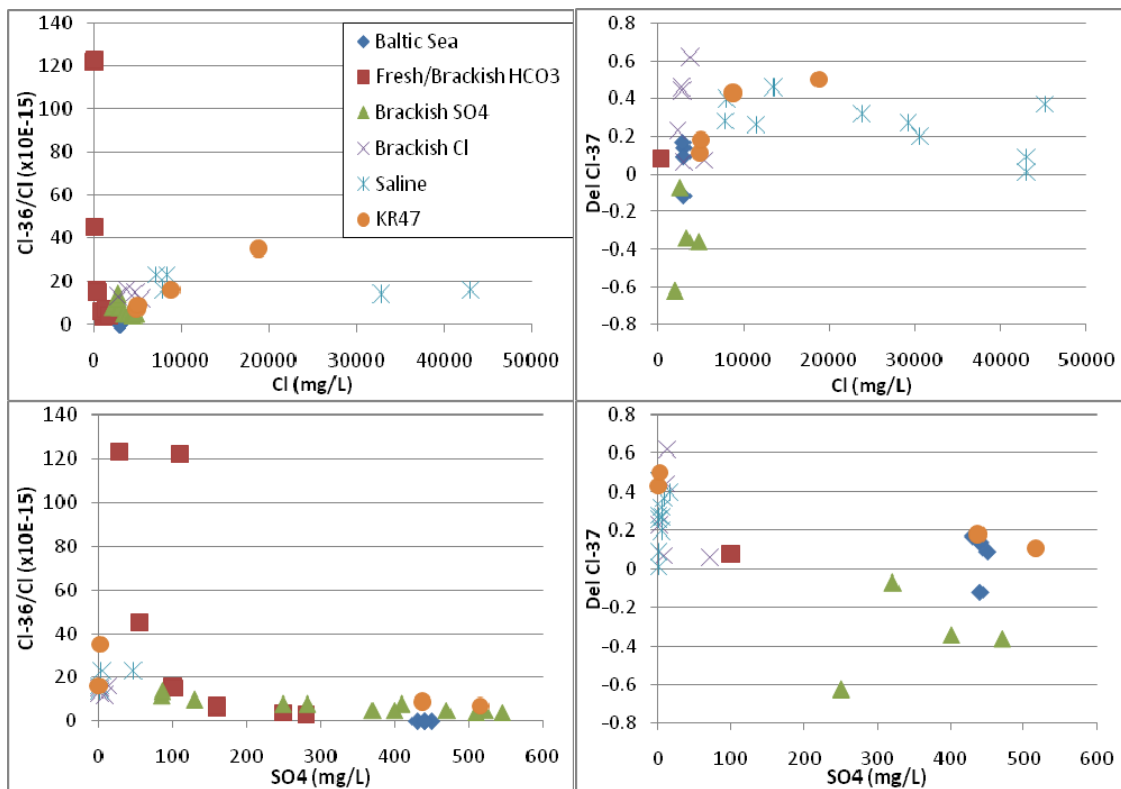| Forsmark				Simpevarp/Laxemar				Äspö/Laxemar				Olkiluoto			
Origin	Depth	Cl	^{36}Cl/Cl	Origin	Depth	Cl	^{36}Cl/Cl	Origin	Depth	Cl	^{36}Cl/Cl	Origin	Depth	Cl	^{36}Cl/Cl
	m	mg/L	x10^{-15}		m	mg/L	x10^{-15}		m	mg/L	x10^{-15}		m	mg/L	x10^{-15}
Baltic Sea		2780	16	Baltic Sea	17	3660	1.7	recharge	0	0.6	45	fresh HCO$_3$	15	30	122
recharge	62	53.4	160	recharge	80	39	76	shallow fresh	226	508	24	brackish HCO$_3$	101	413	15.3
brackish non-marine	832	8160	34	brackish (Litt.)	258	6570	26	brackish (weak Litt.)	314	5340	20	brackish Cl	248	2760	12.9
brackish non-marine	673	7460	36	brackish non-marine	974	7880	48	saline	860	12300	43	brackish SO$_4$ (Litt.)	162	4500	3.5
saline	982	10700	41	saline	970	10499	32	saline	1420	45500	40	brackish SO$_4$ (Litt.)	306	4770	4.6
saline	967	14700	28	saline	958	16800	39					brackish Cl	328	5400	11.9
												saline	494	8400	22.8
												saline	864	43000	16.3

Figure 1. *Variation of Cl isotopic ratios with Cl, and SO$_4$ content of Olkiluoto groundwaters.*

The variations of $^{36}Cl/Cl$ with Cl and SO_4 are shown in Figure 1 for all the data from Olkiluoto. Sulphate concentrations are noticeably variable (ranging from as high as 500 mg/L at depths less than 250 m) and depending on the salinity and depth of the groundwater type (Table 1). Below 250 m, SO_4 decreases dramatically to <10 mg/L. When combined with the earlier data (Table 2), the brackish and deep saline samples have intermediate ratio values that are slightly lower than at the Swedish sites. For instance, Olkiluoto has groundwater $^{36}Cl/Cl$ values of ~3 to 35 x 10^{-15} (Table 1) whereas Swedish values range from 20 to 48 x 10^{-15}. In these waters, no correlation is seen between the $^{36}Cl/Cl$ ratio and groundwater Cl concentrations (Figure 2).

It is notable that KR47_708 has the highest ^{36}Cl ratio (35 x 10^{-15}) in the saline Olkiluoto groundwaters despite the fact that all deep, saline groundwaters should all be in secular equilibrium. This deviates from the common level for saline water (around 20). Although this is only one point on the graph, it does suggest heterogeneity in ^{36}Cl production due to significant variation in U and Th contents and maybe also in shielding by heavy REE contents in rock.

This indicates that the surface-derived ^{36}Cl component either has decayed to very low levels or, more probably, been masked by ^{36}Cl produced *in situ* by (η,γ) reactions with ^{35}Cl present in soluble salts and in pore water in the rock matrix. This effect has been observed in Canadian Shield groundwaters (Gascoyne et al. 1992) where studies of the content of soluble salts have shown that Cl in unaltered grey granite exists as salts in micropores (as fluid inclusions) and as grain boundary deposits, which are accessible to permeating groundwater.

The agreement between the deep saline groundwaters (Figures 2 and 3) and the calculated, secular equilibrium, *in situ* production value (see Section 3.3), is less limited than the brackish non-marine groundwaters but is still within the overall uncertainty of the calculations. Some mixing with other chloride sources may have occurred during drilling and sampling which could explain the observed small deviations from the *in situ* production value.

3.3   In situ production of ^{36}Cl

Calculation of *in situ* ^{36}Cl concentration is a complex undertaking, requiring proprietary codes, and it is not always possible to complete because of the lack of data. Calculations were made several years ago for the Olkiluoto site (Table 3) by J. Fabryka-Martin of the Los Alamos National Laboratory, New Mexico, and were reported by Gascoyne (2001).
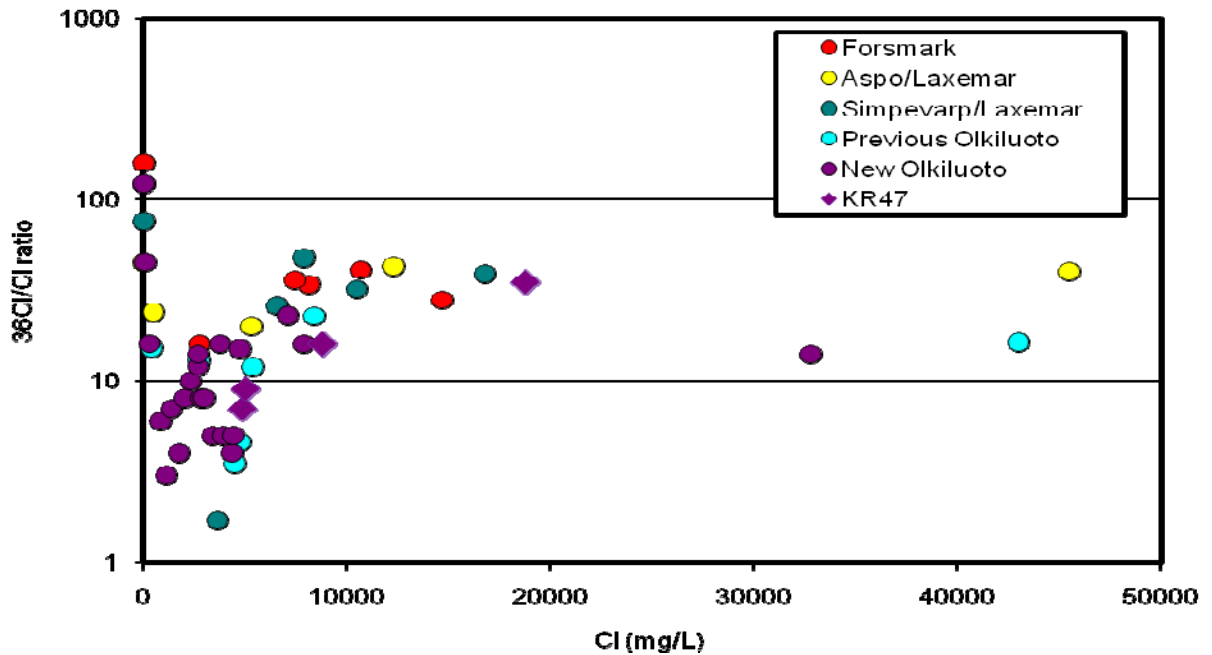
Figure 2. *Variation of $^{36}Cl/Cl$ with increasing Cl concentration for Swedish and Finnish sites. New data from Olkiluoto since Gascoyne (2001) is shown in purple. OL-KR47 is a drillhole specifically drilled under the Baltic sea.*
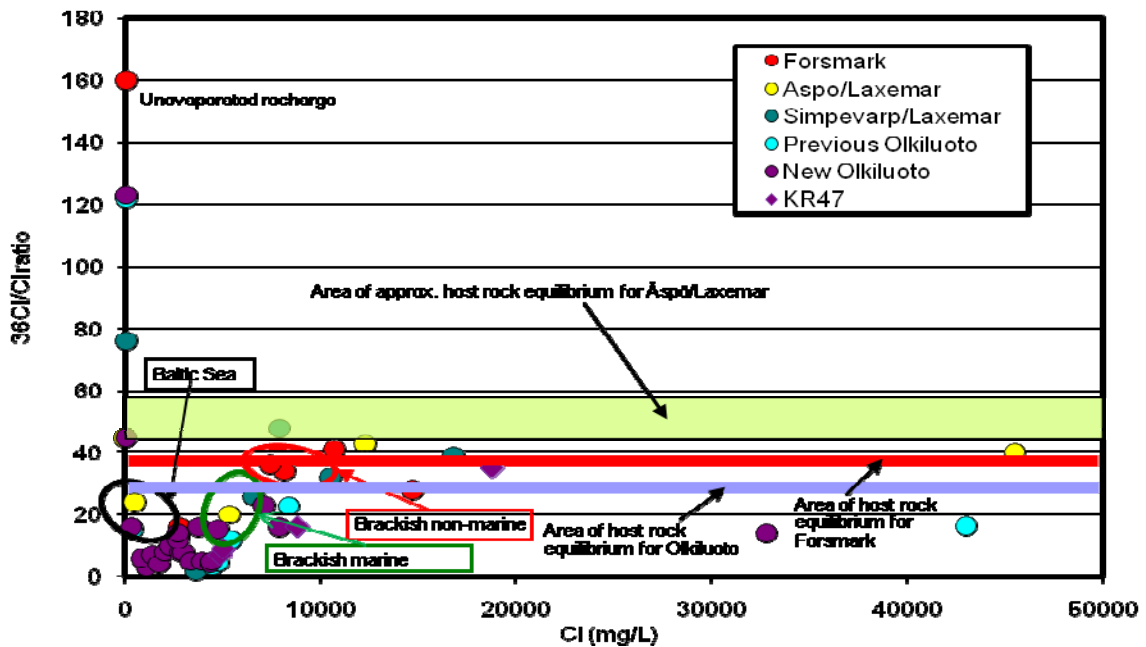

Figure 3. *Variations of $^{36}Cl/Cl$ versus Cl (from Gascoyne & Gurban 2009). In red are the Forsmark samples, in yellow are Laxemar+Simpevarp data, in green the Äspö/Laxemar data from Louvat et al, (1999), in light blue the Olkiluoto data and in purple the new Olkiluoto data. OL-KR47 is a drillhole specifically drilled under the Baltic sea.*

To calculate the *in situ* [36]Cl production rate at a site and, hence, the equilibrium [36]Cl/Cl ratio of associated groundwaters, the neutron production rate and initial neutron energy spectrum must be estimated from the U and Th contents of the rock (J. Fabryka-Martin, pers. comm.). The neutron flux and, consequently, the production rate of [36]Cl, is then calculated using a Monte Carlo neutron transport code for the average elemental composition of the rock types at the site. Rock composition data, rock porosity, bulk density and rare earth concentrations (particularly gadolinium (Gd) and samarium (Sm)), are essential parameters in the calculation of neutron production rate and flux. Gadolinium is important because it has a very large thermal neutron cross-section and is able to stop most of the neutron flux despite its normally low (ppm level) concentration in crystalline rocks. The results of neutron calculations performed for Olkiluoto rock types are shown in Table 3. Although the rock types and elemental compositions are different to those of Laxemar (or even Forsmark), the variation in [36]Cl/Cl values is not large ($25 - 35 \times 10^{-15}$) except for one test which has a high HREE content and gives a ratio of $\sim 10 \times 10^{-15}$ (Table 3).

An alternative explanation for the deviation between mixing and in situ production is that the rocks in which these waters originally resided might have slightly different U, Th, K, Gd, Sm, etc. concentrations and thus have a slightly different neutron flux and [36]Cl *in situ* production rate.

4 IMPLICATIONS FOR GROUNDWATER ORIGINS

The origins of Olkiluoto groundwaters have been considered over the last 20 years (Lampen & Snellman 1993, Pitkänen et al. 1996, Posiva 2005). Recently, the origins have been detailed and clarified by the use of comprehensive geochemical and isotopic data sets for over 40 boreholes (Posiva 2009). At least six groundwater types are now proposed, three from recently infiltrated waters and three 'relic' (old) waters (Posiva 2008). The recent waters originate from three periods: meteoric recharge in the last ~ 2500 years, sea water (from the Gulf of Bothnia) and water from the Korvensuo reservoir (river water). The relic water is derived from the Littorina Sea (2500-8500 years), cold-climate recharge (>10,000 years, probably glacial meltwater) and saline water (originally hydrothermal, possibly of brine composition, and of Phanerozoic age).

Table 3. *Data table for analyses of Olkiluoto core samples.*

	Base case (8.8 ppm Gd, Sm)			Low HREE (3 ppm)			High HREE (60 ppm)		
	Mica gneiss	Tonalite	Migmatite	Mica gneiss	Tonalite	Migmatite	Mica gneiss	Tonalite	Migmatite
Porosity, %	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
ppm U	4.5	3.8	7.8	4.5	3.8	7.8	4.5	3.8	7.8
ppm Th	13.2	11.8	4.9	13.2	11.8	4.9	13.2	11.8	4.9
Yield, n/g/yr/ppm U (= X)	1.128	1.176	1.049	1.128	1.176	1.049	1.128	1.176	1.049
Yield, n/g/yr/ppm Th (= Y)	0.523	0.540	0.481	0.523	0.540	0.481	0.523	0.540	0.481
Total yield, n/g/yr	13.901	12.081	13.867	13.901	12.081	13.867	13.901	12.081	13.867
Thermal cross-section, cm2/g	0.0072	0.0072	0.00645	0.00598	0.00599	0.00523	0.018	0.018	0.0172
Thermal flux, n/cm2/yr	1931	1678	2150	2325	2017	2651	772	671	806
Equilibrium 36Cl/Cl x 1E-15	28	24	31	34	29	38	11	10	12

	Base case (0.1% porosity)			High porosity (1% porosity)			Very high porosity (10% porosity)		
	Mica gneiss	Tonalite	Migmatite	Mica gneiss	Tonalite	Migmatite	Mica gneiss	Tonalite	Migmatite
Porosity, %	0.1	0.1	0.1	1	1	1	10	10	10
ppm U	4.5	3.8	7.8	4.5	3.8	7.8	4.5	3.8	7.8
ppm Th	13.2	11.8	4.9	13.2	11.8	4.9	13.2	11.8	4.9
Yield, n/g/yr/ppm U (= X)	1.128	1.176	1.049	1.128	1.176	1.049	1.128	1.176	1.049
Yield, n/g/yr/ppm Th (= Y)	0.523	0.540	0.481	0.523	0.540	0.481	0.523	0.540	0.481
Total yield, n/g/yr	13.901	12.081	13.867	13.901	12.081	13.867	13.901	12.081	13.867
Thermal cross-section, cm2/g	0.0072	0.0072	0.00645	0.00727	0.00728	0.00652	0.00805	0.00805	0.0073
Thermal flux, n/cm2/yr	1931	1678	2150	1912	1659	2127	1727	1501	1900
Equilibrium 36Cl/Cl x 1E-15	28	24	31	28	24	31	25	22	28

Baltic Sea water and the brackish marine (Littorina) groundwater behave in an interesting manner. Both types have ^{36}Cl/Cl ratios below those of secular equilibrium with granitic rocks and far below those of fresh meteoric recharge (Figure 3). If recharge was the dominant water source for these sea waters, then they would have a higher ^{36}Cl/Cl ratio. In contrast, the low ratios measured indicate that most of the chloride dissolved in the Littorina and the Baltic Sea has resided in the bedrock over long periods of time and therefore has been shielded from the atmosphere. The Littorina groundwater has a lower ratio than the Baltic Sea water and this indicates that its dissolved Cl content must have undergone additional shielding from atmospheric input and/or mixing with low ^{36}Cl groundwater from the bedrock. This is consistent with an overall older 'age' of this water type, but not old enough to receive a significant quantity of subsurface-produced ^{36}Cl. This provides further evidence for the argument that these (brackish marine) waters are derived from the Littorina Sea (Gascoyne 2001).

In addition, the consistency of ^{36}Cl/Cl ratios in Olkiluoto groundwaters of several widely separated, deep locations and different rock compositions, suggests that these deeper groundwaters are in secular equilibrium and, therefore, likely to be older than 1.5 million years. For the brackish to saline non-marine groundwaters it would require about 1.5 Ma to produce the measured ^{36}Cl concentration *in situ*. This is in accordance with the ^{36}Cl data for the deep saline groundwaters from both the Forsmark and Laxemar sites in Sweden, where secular equilibrium appears to have been achieved. It further provides strong evidence that at these depths, the average groundwater residence time is of the order of 1.5 Ma or greater.

5   SUMMARY AND CONCLUSIONS

In summary, the following can be noted:

1. ^{37}Cl has a range of variation from about 1 ‰ (from -0.6 to + 0.6 ‰) in Olkiluoto groundwater but it shows no clear relationship with other parameters except for the stable values seen in high salinity groundwaters (about +0.0 to +0.4 ‰)

2. Olkiluoto deep groundwaters have slightly lower values of ^{36}Cl/Cl than other (Swedish) sites. This may be due to lower U & Th concentrations in Olkiluoto bedrock, thus causing lower neutron flux and ^{36}Cl production rates or, alternatively, to rock composition, porosity, bulk density and rare earth concentration (Gd) and (Sm), essential in calculation of neutron production rate and flux.

3. Calculations and flux modeling show that although the rock types and elemental compositions are different to those of Laxemar (or even Forsmark), the variation in ^{36}Cl/Cl values is not large (25 - 35 x 10^{-15}) except for one calculation which has a high REE content and gives a ratio of ~10 x 10^{-15}.

4. For Swedish sites, ^{36}Cl in deep groundwaters is 20 – 48 x 10^{-15} which may indicate that this is the approximate *in situ* production rate for ^{36}Cl at these sites.

5. Neutron flux calculations using chemical data and U and Th concentrations are in close agreement with the measured values of ^{36}Cl in the rock.

6. The consistency of ^{36}Cl/Cl ratios for several widely separated locations and different rock compositions suggests that these groundwaters are in secular equilibrium and, therefore likely to be older than 1.5 million years.

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Appendix : Summary of literature showing presence and significance of ^{36}Cl in various rock and groundwater types.

Author(s)	Title	Journal	Year
Argento, D.C., et al.	Chlorine-36 in seawater	Nucl Instr and Meth in Phys Res B 268:1226-1228	2010
Balderer, W., et al.	Application of the chlorine-36 method for the delineation of groundwater infiltration of large river systems: example of the Danube River in western Hungary (Szigetkoz area)	Environmental Geology 46:755-762	2004
Beasley, T.M., et al.	Cl-36 in the Snake River Plain aquifer at the Idaho National Engineering Laboratory: Origin and implications	Groundwater 31-2:302-310	1993
Beasley, T.M., et al.	Cl-36 releases from the Savannah river site nuclear fuel reprocessing facilities	Groundwater 30-4:539-548	1992
Bouchaou, l., Michelot, J.L.	Application of multiple isotopic and geochemical tracers for investigation of recharge, salinization, and residence time of water in the Souss–Massa aquifer, southwest of Morocco	J Hydrology 352:267-287	2008
Cameron, E.M., et al.	Atacamite in the oxide zone of copper deposits in northern Chile: involvement of deep formation waters?	Miner Deposita 42:205-218	2007
Campbell, K., et al.	Chlorine-36 data at Yucca Mountain: statistical tests of conceptual models for unsaturated-zone flow	J Contam Hydrology 62-63:43-61	2003
Cecil, L., et al.	Use of chlorine-36 to determine regional-scale aquifer dispersivity, eastern Snake River Plain aquifer, Idaho/USA	Nucl Instr and Meth Phys Res 172:679-687	2000
Chmiel, G., et al.	Control of ^{36}Cl production in carbonaceous shales by phosphate minerals	Geochimica et Cosmochimica Acta 67-13:2377-2395	2003
Cresswell, R.G., et al.	A first estimate of ground water ages for the deep aquifer of the Kathmandu Basin, Nepal, using the radioisotope chlorine-36	Groundwater 39-3:449-457	2001
Daëron, M., et al.	Constraints on the post 25-ka slip rate of the Yammoûneh fault (Lebanon) using in situ cosmogenic ^{36}Cl dating of offset limestone-clast fans	Earth and Planetary Science Letters 227:105-119	2004
Davis, S.N., et al.	Chlorine-36, bromide, and the origin of spring water	Chemical Geology 179:3-16	2001
Davis, S.N., et al.	Chlorine-36 in ground water containing low chloride concentrations	Groundwater 38-6:912-921	2000
Davis, S.N., et al.	Chlorine-36 in groundwater of the United States: empirical data	Hydrogeology 1:217-227	2003
Endo, S., et al.	Radioactivity in atomic-bomb samples from exposure to environmental neutrons	Health Physics 93-6:689-695	2007
Fréchou,C., Degros, J-P.	Measurement of 36Cl in nuclear wastes and effluents: Validation of a radiochemical protocol with an in-house reference sample	J Radioanalytical and Nucl Chem 263-2:333-339	2005
Green, J.R., et al.	Chlorine-36 and cesium-137 in ice-core samples from mid-latitude glacial sites in the Northern Hemisphere	Nucl Instr and Meth Phys Res B 172:812-816	2000
Green, J.R., et al.	A high resolution record of chlorine-36 nuclear-weapons-tests fallout from Central Asia	Nucl Instr and Meth Phys Res 223-226:854-857	2004
Guendouz, A., Michelot, J.L.	Chlorine-36 dating of deep groundwater from northern Sahara	J Hydrology 328:572-580	2006
Guerin, M.	Tritium and 36Cl as constraints on fast fracture flow and percolation flux in the unsaturated zone at Yucca Mountain	J Contam Hydrol 51:257-288	2001
Hu, Q.H., et al.	Assessing field-scale migration of radionuclides at the Nevada Test Site: ''mobile'' species	J Environ Radioactivity 99:1617-1630	2008

Jiang, S.S., et al.	Determination of Cl-36 in the groundwaters and ores around a uranium deposit	Nucl Instr and Meth Phys Res B 92;1-4:385-388	1994
Kulongoski, J.T., et al.	Helium-4 characteristics of groundwaters from Central Australia: Comparative chronology with chlorine-36 and carbon-14 dating techniques	J Hydrology 348:176-194	2008
N Laturnus, F., Matucha, M.	Chloride e a precursor in the formation of volatile organochlorines by forest plants?	J Environ Radioactivity 99:119-125	2008
Lehmann, B.E., et al.	A comparison of groundwater dating with ^{81}Kr, ^{36}Cl and ^{4}He in four wells of the Great Artesian Basin, Australia	Earth and Planetary Science Letters 211:237-250	2003
Levy, S.S., et al.	Chlorine-36 investigations of groundwater infiltration in the exploratory studies facility at Yucca Mountain, Nevada	Materials Research Society Conference Proc 465:901-908	1997
Lu, G.P., et al.	Implications of halide leaching on Cl-36 studies at Yucca Mountain, Nevada	Water Resources Research 39-12:1361	2003
Matucha, M., et al.	A chlorine-36 and carbon-14 study of the role of chlorine in the forest ecosystem	J Label Compd Radiopharm 50:437-439	2007
Matucha, M., et al.	Determination of trichloroacetic acid in environmental studies using carbon 14 and chlorine 36	Chemosphere 63:1924-1932	2005
Moran, J.E., Rose, T.P.	A chlorine-36 study of regional groundwater flow and vertical transport in southern Nevada	Environmental Geology 43:592-605	2003
Nagashima, et al.	Chlorine-36 in granite samples from the Hiroshima A-bomb site	Nucl Instr and Meth Phys Res B 223-224:782-787	2004
Palumbo, L., et al.	Slip history of the Magnola fault (Apennines, Central Italy) from ^{36}Cl surface exposure dating: evidence for strong earthquakes over the Holocene	Earth and Planetary Science Letters 225:163-176	2004
Phillips, F.M.	Environmental tracers for water-movement in desert soils of the American Southwest	Soil Science Society of America 58-1:15-24	1994
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Purdy, CB., et al	Aquia aquifer dissolved Cl- and Cl-36/Cl: Implications for flow velocities	Water Resources Research 32-5:1163-1171	1996
Rodriguez, M., et al.	Radiochemical analysis of chlorine-36	Czech Journal of Physics 56:D211-D217	2006
Seki, R., et al.	Isotopic ratios of Cl-36/Cl in Japanese surface soil	Nucl Instr and Meth Phys Res B 259:486-490	2007
Shaw, G., et al.	Radionuclide transport above a near-surface water table: IV. Soil migration and crop uptake of chlorine-36 and technetium-99, 1990 to 1993	J Environ Qual 33: 2272-2280	2004
Sheppard, S.C., et al.	Chlorine-36 in nuclear waste disposal-I. Assessment results for used fuel with comparison to 1291 and 14C	Waste Management 16-7:607-614	1996
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Sturchio, N.C., et al.	Chlorine-36 as a Tracer of Perchlorate Origin	Environ Sci Technol 43:6934-6938	2009
Veizer, J.	Celestial Climate Driver: A perspective from four billion years of the carbon cycle	Geoscience Canada 32-1:13-28	2005
Wagner, G., et al.	Chlorine-36 evidence for the Mono Lake event in the Summit GRIP ice core	Earth and Planetary Science Letters 181:1-6	2000
Zhu, C., et al.	Late Pleistocene and Holocene groundwater recharge from the chloride mass balance method and chlorine-36 data	Water Resources Research 39-7:1182	2003