

2.1 Isotopes of Chlorine

2.1.1 Stable Isotopes

Chlorine is the second element of the halogen group (group 17 of the periodic table) and is positioned between sulphur and argon in period 3 of this table. Its nucleus consists of 17 protons. It has two stable isotopes as discovered by Aston (1919), ^{35}Cl with 18 neutrons and ^{37}Cl with 20 neutrons. According to the latest report from the IUPAC (Berglund and Wieser 2011) ^{35}Cl is the most common stable isotope with an abundance of 75.76 % of the chlorine, while ^{37}Cl consists of the remaining 24.24 %.

2.1.2 Notation of Stable Isotope Variations and Reference Standard

Variations in chlorine isotope data are reported in the familiar delta notation. The definition for chlorine is:

$$\delta^{37}\text{Cl} = \frac{(^{37}\text{Cl}/^{35}\text{Cl})_{\text{sample}} - (^{37}\text{Cl}/^{35}\text{Cl})_{\text{standard}}}{(^{37}\text{Cl}/^{35}\text{Cl})_{\text{standard}}} \times 1,000 \quad (2.1)$$

Although no standard has been formally defined it was already shown by Kaufmann (1984) that no significant variability was found between

seawater samples from different locations and depths. For that reason he proposed to use ocean water as international standard. As name for this standard he proposed Standard Mean Ocean Chloride (SMOC) which has been in informal use since then by most laboratories working in chlorine isotope geochemistry. The big advantage of the use of ocean chloride as isotope standard is that it can be obtained easily and can be used and exchanged between laboratories without any problem (Kaufmann 1984). Godon et al. (2004) did collect ocean water samples from 15 different locations worldwide, and from three of these locations they collected also a depth profile. No significant variation was observed between all measured samples and from these observations it was concluded that ocean water has an invariant $\delta^{37}\text{Cl}$ of 0.00 ‰ versus SMOC within analytical error, and could thus be used as isotope standard. This study has been confirmed by Liu et al. (2013), who analysed, as part of their study to test a new on-line method to analyse chlorine isotopes with the use of a GasBench to purify chloromethane gas, 10 different seawaters taken from the Chinese coast. The measurements on these samples were all within 0.1 ‰ of their ocean water standard, with an average and standard deviation of 0.00 ± 0.06 ‰.

In two studies it was suggested that variations in ocean water chlorine stable isotopes exist (Shirodkar et al. 2003, 2006). These variations were partly unexplainable, and partly explained as due to evaporation of the upper layer of ocean water. Considering these variations the authors

suggested that it would be advisable to use the ISL354 standard (as developed by Xiao et al. 2002) in stead of ocean chloride as standard for chlorine isotope research. The samples that showed isotope variations in ocean water were measured by a different technique than the samples that indicated no variation (TIMS vs. IRMS) and they were measured in only one laboratory. Considering the fact that the divergent analyses were done in only one laboratory it would be advisable that interlaboratory exchange and measurement of samples between this laboratory and laboratories that analyse by IRMS is organised so that the differences in results between the two techniques can be independently confirmed.

2.1.3 Radioactive Isotopes

Aside from the two stable isotopes 22 radioactive isotopes of chlorine are known. These have mass numbers 28–51, thus containing 11–34 neutrons. The isotopes ^{28}Cl – ^{30}Cl decay by proton decay, and they have extremely low half-lives of less than 30 ns. They are found beyond the so called proton drip-line, which can be considered as the edge of the “stable” radioactive isotopes. The isotopes ^{31}Cl – ^{34}Cl decay primarily by positron or β^+ decay and the isotopes ^{38}Cl – ^{51}Cl decay by electron of β^- decay. All these isotopes have (very) short half-lives, the longest living of these is ^{39}Cl with a half-life of 55.6 min. ^{36}Cl which can decay with both β^- decay to ^{36}Ar and with electron capture to ^{36}S has a much longer half-life of 301,000 years. This cosmogenic isotope is formed by cosmic radiation in the upper atmosphere and is present in environmental chlorine at a ratio of about 7×10^{-13} compared to ^{37}Cl . The relatively long half-life of ^{36}Cl makes it useful for radioactive dating, especially for groundwater samples up to about one million years old.

2.2 Chemistry of Chlorine

As with all halogen elements the most common oxidation state is $-I$ and the most common form of chlorine in nature is the chloride ion (Cl^-).

Negative ions are formed by the addition of electrons to the valence shell by a process called electron affinity. Of all the elements chlorine has the highest electron affinity (349 kJ mol^{-1}), which is even higher than the electron affinity of fluorine. The reason for this is that the fluorine atom is very small and the high electron density in the valence shell compared to chlorine makes it slightly less favourable to add an electron to the shell as compared to chlorine.

Higher oxidation states for chlorine are very well known. They are all strong oxidisers and have different uses as such, mainly as bleaching agents for the lower oxidation states and in pyrotechnics, for example as solid rocket fuel in the higher oxidation states. In these higher oxidation states chlorine is present in the oxyanions hypochlorite (ClO^-), chlorite (ClO_2^-), chlorate (ClO_3^-) and perchlorate (ClO_4^-) where chlorine is in the $+I$, $+III$, $+V$ and $+VII$ oxidation state respectively. Oxidation state $+IV$ is also found in the gas chlorine dioxide, and oxidation state $+VI$ in the compound Cl_2O_6 when in the gaseous state. As can be deduced from the Frost diagram [Frost (1951), Fig. 2.1] in acid solutions only chloride, chlorine and perchlorate are stable as the other forms tend to disproportionate, while in alkaline solutions chloride, hypochlorite, chlorite, chlorate and perchlorate can be stable while chlorine and chlorine dioxide tend to disproportionate.

The reduction potentials used in this figure were taken from www.webelements.com. Well known is the hypochlorite ion which, in the form of sodium hypochlorite is commonly used as a bleaching agent. It is the strongest oxidiser of all chlorine oxyanions and it is a very unstable ion that only exists in solutions. When water is removed from a sodium hypochlorite solution it converts to a mixture of sodium chloride and sodium chlorate. It is a very effective oxidizer used to kill germs while cleaning. It is also used, mainly in the form of calcium hypochlorite as “chlorine” in swimming pools.

Chlorite is mainly used for the generation of chlorine dioxide which is also used as a bleaching agent. Sodium chlorite itself was used in the past as a chlorinating agent for the disinfection of

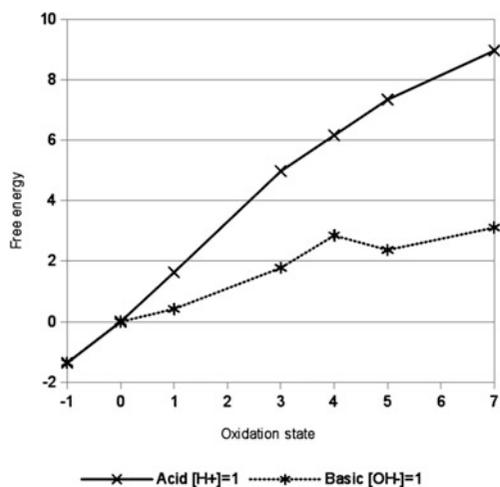


Fig. 2.1 Frost diagram of the chlorine species showing the relative stability of these species in acid and basic solutions

drinking water, as it, contrary to chlorine did not produce trihalomethanes organic contaminants. Since 2009 it is however phased out in the European Union.

Chlorates are mainly used as herbicides and oxidants in explosives and rock fuel. Little is known about its occurrence on earth but it appears to be associated with perchlorate occurrences (Rao et al. 2010) which are very well known from the Atacama desert in Chile (Ericksen 1981) and also from more recent studies in the United States (Rajagopalan et al. 2006; Parker et al. 2008) and Antarctica (Kounaves et al. 2010). As these studies indicate that chlorate is almost always associated with perchlorate it is also likely that chlorate is present at the Phoenix landing site on Mars (Hanley et al. 2012) where perchlorate was detected. Chlorate salts have very strong freezing point depression capabilities and the eutectic point of magnesium chlorate dissolved in water is only 204 K ($-66\text{ }^{\circ}\text{C}$). As a result it is theoretically possible that liquid water on Mars is present as concentrated chlorate solutions (Hanley et al. 2012). Chlorate is also common in municipal drinking water as a result of chlorination of with chlorine dioxide. Concentration in drinking water can be as high as 3.2–7.0 mg/L (Michael et al. 1981) and the WHO (2005) has proposed a provisional guideline

value of 0.7 mg/L. This guideline value is designated as provisional because use of chlorine dioxide as a disinfectant may result in the chlorate guideline value being exceeded, and difficulties in meeting the guideline value should never be a reason for compromising adequate disinfection according to the WHO (2005). One study is known in which chlorine isotope ratios of chlorate compounds have been measured. Ader et al. (2001) analysed the chlorine isotope composition of several man made chlorates and found that $\delta^{37}\text{Cl}$ values in commercially produced sodium and potassium chlorates are $+0.2$ to $+0.3\text{ }_{\text{‰}}$ versus SMOC.

Perchlorates do have comparable applications as chlorates. Unlike chlorates however there is considerable more knowledge on the occurrence and distribution of perchlorates on earth. It is at present generally well known that it is much more widely distributed than was assumed in the past. Perchlorate is produced naturally by atmospheric oxidation of chlorine species with ozone (e.g. Kang et al. 2008) and due to the solubility of most perchlorate salts it is mostly concentrated in the driest regions on the earth. Perchlorates are also manufactured industrially by electrolysis of sodium chloride brines. The annual production is in the order of 10^7 kg year^{-1} (Dasgupta et al. 2006). Its isotopic behaviour is by now fairly well established. Following preliminary studies by Ader et al. (2001) it is now possible to determine various sources of perchlorate by its chlorine and oxygen isotopes (e.g. Sturchio et al. 2011) and it has also been possible to determine the isotope effects of microbial perchlorate reduction (Ader et al. 2008).

Chlorine is also present in organic compounds. Although minor amounts of organochlorine compounds are known to be from natural origins larger amounts are produced annually in industrial processes. Analyses of the chlorine isotopic composition of organochlorine compounds potentially found in geologic environments started with the development of several methods using dual inlet techniques in the 1990s (Van Warmerdam et al. 1995; Holt et al. 1997; Jendrzewski et al. 1997; Beneteau et al. 1999). During the early years of the 21st century

techniques were developed using continuous flow techniques (Shouakar-Stash et al. 2003; Wassenaar and Koehler 2004) and with ICP-MS (Van Acker et al. 2006). More recently also techniques were developed where these isotopes are measured directly on whole molecules and fragments of them using isotope ratio mass spectrometry (e.g. Shouakar-Stash et al. 2006) and quadrupole mass spectrometry (Jin et al. 2011; Bernstein et al. 2011).

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