

# STABLE CHLORINE ISOTOPE ABUNDANCES IN APATITES FROM ØDEGÅRDENS VERK, NORWAY

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**A b s t r a c t.**  $^{35}\text{Cl}/^{37}\text{Cl}$  ratios have been determined in five Pre-Cambrian apatites from Ødegårdens verk in South Norway. The apatites selected for analysis were of two principal varieties, namely chlorapatites with wt. % Cl 6.02—6.24 and apatites containing only 1.67 wt. % Cl. The chlorine-poor apatites have obviously been derived by metasomatism of the former group. Three chemical analyses of the apatites are presented. In none of the samples studied was any variation in the stable chlorine isotope abundances detected; the average  $^{35}\text{Cl}/^{37}\text{Cl}$  ratio in the samples being  $3.129 \pm 0.002$ , compared with a reference isotope standard ratio of  $3.128 \pm 0.002$ .

These results compare favourably with those of previous workers and serve to support the thesis that isotopic fractionation of the stable chlorine isotopes is rarely, if ever, effected during normal processes of mineral formation.

## Introduction

Recent studies on Pre-Cambrian apatite-rich veins occurring in the vicinity of Ødegårdens verk in South Norway have revealed a common association of two varieties of apatite (Plate I). It appears that the original chlor-apatite of the veins, which is golden-yellow, transparent and of a sub-vitreous lustre, has been extensively altered, by some subsequent metasomatism, to a yellowish-white, low-chlorine,

Table 1.  
*Chemical analyses of apatites from Ødegården.*  
 Anal. B. Bruun.

	I	II	III
CaO .....	53.81	53.53	55.63
P <sub>2</sub> O <sub>5</sub> .....	40.50	40.30	41.64
Cl .....	6.24	6.02	1.40
H <sub>2</sub> O .....	0.25	0.03	0.57
CO <sub>2</sub> .....	0.08	0.09	0.08
F .....	0.00	0.00	0.00
SiO <sub>2</sub> .....	0.12	0.18	0.35
Na <sub>2</sub> O .....	0.19	0.18	0.03
Fe <sub>2</sub> O <sub>3</sub> .....	0.04	0.11	0.06
	100.86	100.35	99.68
Less O <sub>2</sub> for Cl.....	1.37	1.32	0.30
	99.49	99.03	99.38

I = Chlorapatite occurring as a fresh, unaltered mass in phlogopite, Ceres grube. (Mass spectrogr. sample R.M. 1).

II = Chlorapatite from specimens as shown in plate 1 of this paper, Ceres grube. (Mass spectrogr. sample R.M. 3).

III = Apatite replacing and veining the chlorapatite of II, Ceres grube. (Mass spectrogr. sample R.M. 2).

translucent apatite possessing a silky, bone-like lustre. Preliminary chemical analyses (Table 1) serve to illustrate the chemical differences between the two principal apatite varieties of Ødegården.

The present examination of the isotopic composition of the chlorine in these apatites is intended to augment the data of previous workers and to see whether any significant isotope fractionation has been brought about, either during the initial introduction of the vein components, or during their subsequent metasomatic alteration.

All available data from the previous literature suggest that little or no fractionation of the naturally occurring stable isotopes <sup>35</sup>Cl and <sup>37</sup>Cl is to be expected, as the geochemistry of chlorine is essentially according to the geochemical cycle of that element as proposed by CORRENS (1956). This cycle, being essentially a question of the behaviour of the chloride ion, does not involve any oxidation or reduction reactions which might promote isotopic fractionation; as is

the case with such elements as carbon. However, both RANKAMA (1963) and JENSEN (1953 a and b) suggest that many additional measurements of the isotopic constitution of chlorine are needed to investigate whether fractionation has taken place in certain natural materials such as magmatic or hydrothermal deposits. Furthermore, it is interesting to note that RANKAMA (1963) does comment that isotope-fractionation by solid-state diffusion would be more significant in a trace component of a given mineral such as the heavy-isotope enriched remnant of an element which was formerly present in large quantities.

### Previous Literature on Natural $^{35}\text{Cl}/^{37}\text{Cl}$ Ratios

The atomic weight of chlorine in a chlor-apatite from Ødegården was found to be 35.48 by CURIE (1921). This value agreed closely, within experimental limits to that of 35.46 for chlorine in a standard sodium chloride isolated from sea water. CURIE's results for the Ødegården chlor-apatite were subsequently confirmed by GLEDITSCH and SAMDAHL (1922) and by DORENFELDT (1923).

The first accurate measurements of the natural abundance of the stable chlorine isotopes were apparently made by BAINBRIDGE and NIER (1950) who found a composition of  $^{35}\text{Cl}$  75.4 % to  $^{37}\text{Cl}$  24.6 %, producing a calculated  $^{35}\text{Cl}/^{37}\text{Cl}$  Cl ratio of 3.07. This result differs slightly from that of GRAHAM *et al.* (1951) who found a  $^{35}\text{Cl}/^{37}\text{Cl}$  Cl ratio of 3.00 in natural samples.

The work of OWEN and SCHAEFFER (1955) revealed no differences in  $^{35}\text{Cl}/^{37}\text{Cl}$  Cl ratios among 10 samples of igneous, sedimentary and modern marine origin. In the same year BOYD, BROWN and LOUNSBURY (1955) analysed a pure potassium chloride (of unspecified source) and found an isotopic constitution of  $^{35}\text{Cl}$  75.529 % to  $^{37}\text{Cl}$  24.471 %, giving a ratio of 3.0865.

HOERING and PARKER (1961) provided the first series of data for a much wider range (81 samples) of natural materials. In general they observed a distinct lack of variation in the  $^{35}\text{Cl}/^{37}\text{Cl}$  Cl ratios in their samples. They state that chlor-apatite from Snarum (probably Ødegården?), Norway showed a  $\delta^{37}\text{Cl}$  ‰ of  $-0.1 \pm 0.5$ , expressed in terms of parts per thousand difference between the isotopic ratio of that sample and the isotopic ratio of a chlorine isotope reference standard.

Finally SHIELDS, GARNER and DIBELER (1961) found the absolute  $^{35}\text{Cl}/^{37}\text{Cl}$  ratio in certain natural halites and silvites to be rather constant at 3.1272 (+ 0.0079 or - 0.0082).

## METHODS OF PREPARATION AND ANALYSIS

The natural apatite samples selected for analysis were chosen for their coarse grained nature and obvious mineralogical purity. Separation by simple crushing and hand-picking was therefore easier and the material for analysis was obtained free from contamination by other associated chlorine-bearing minerals such as phlogopite, amphiboles and scapolite.

The apatites were immersed in 20 ml of 10 %  $\text{HNO}_3$  and digested in a steam bath overnight. The resulting solutions were filtered and  $\text{AgCl}$  was precipitated by adding 20 ml of 2N  $\text{AgNO}_3$  to the filtrates and allowing the precipitates to settle overnight in total darkness. The  $\text{AgCl}$  was then filtered and dissolved to 15 mg  $\text{Cl}/\text{ml}$  in concentrated  $\text{NH}_4\text{OH}$ .

The samples were then analysed on a mass spectrometer and there appeared to be small (0.25 %) but real differences in the isotopic compositions. However, a brown flocculent precipitate had begun to form in the solutions and the mass spectrometer runs were giving erratic signals. All samples were then filtered and a second  $\text{AgCl}$  precipitation was performed. After this repurification all solutions remained clear; the precision of the mass spectrometric analyses was increased by a factor of 2; and the isotopic differences disappeared.

### Mass Spectrometry

The surface emission mass spectrometer used in this study is a 12-inch radius-of-curvature single focusing instrument with 68-degree analyser tube and 60-degree magnet pole pieces. Triple filament sources of  $1 \times 30$  mils rhenium filaments were used. Each sample filament was loaded by placing on it one drop (0.3 mg  $\text{Cl}$ ) of a 15 mg  $\text{Cl}/\text{ml}$  ammoniacal  $\text{AgCl}$  solution. The drops were dried by the use of heat lamps and electrical currents.

The center filament was operated at approximately 1550° C. Ion currents were measured by means of a vibrating reed electrometer with an expanded scale recorder. The currents were nominally  $5 \times 10^{-13}$  amperes and ratios were measured by varying the magnetic field at constant ion accelerating voltage. Background chlorine signals were always less than  $3 \times 10^{-15}$  amperes and were negligible.

No attempt was made to analyse instrument bias and arrive at absolute ratios. However the standard sample is identical to that used by SHIELDS *et al.* (1961) in their absolute measurements and absolute values for the present results can be obtained by dividing them by 1.00032.

Each sample was run in duplicate. The standard deviation of the average of the duplicate runs is 0.002. The limit of error at the 95 % confidence level is 0.004 for the samples and 0.002 for the standard which was analysed six times.

### Results of Chlorine Isotope Analyses

The results of the isotopic analyses are given in table 2. These illustrate the lack of any measurable variation in the  $^{35}\text{Cl}/^{37}\text{Cl}$  ratios of samples of different chemical composition and location in the area.

It seems that no fractionation of the  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  isotopes has taken place, either during the initial phase of vein injection or during the subsequent phase of metasomatism which involved a partial

Table 2.  
 *$^{35}\text{Cl}/^{37}\text{Cl}$  ratios in apatite from Odegården.*

Sample no.	$^{35}\text{Cl}/^{37}\text{Cl}$	Mineral composition
R.M. 1	$3.129 \pm 0.004$	Chlor-apatite
R.M. 2	$3.128 \pm 0.004$	Low-chlorine apatite
R.M. 3	$3.130 \pm 0.004$	Chlor-apatite
R.M. 4	$3.129 \pm 0.004$	Chlor-apatite
R.M. 5	$3.129 \pm 0.004$	Mixture*
Reference standard	$3.128 \pm 0.002$	

The error statement represents the limit of error at the 95 % confidence level.

\* This sample is a mass of chlor-apatite which is extensively replaced by minute veins of secondary low-chlorine apatite.

removal of the chlorine from the apatite lattice and its replacement by other suitable ions (e.g. OH).

This lack of isotopic ratio variation in our samples is probably in accordance with RANKAMA's (1963) observation that stable-isotope fractionation becomes insignificant or non-existent at temperatures in the range 700° C to 1000° C. It has long been agreed that the apatite-rich veins of Ødegården exhibit a mineral paragenesis which suggests a relatively high temperature origin, well above 700° C. Also the removal of chlorine from chlorapatite and its substitution by other ions e.g. OH seems, on the basis of cursory studies, to require quite high temperatures at normal pressure. On the basis of that knowledge one would therefore anticipate the lack of variation of isotopic ratios encountered.

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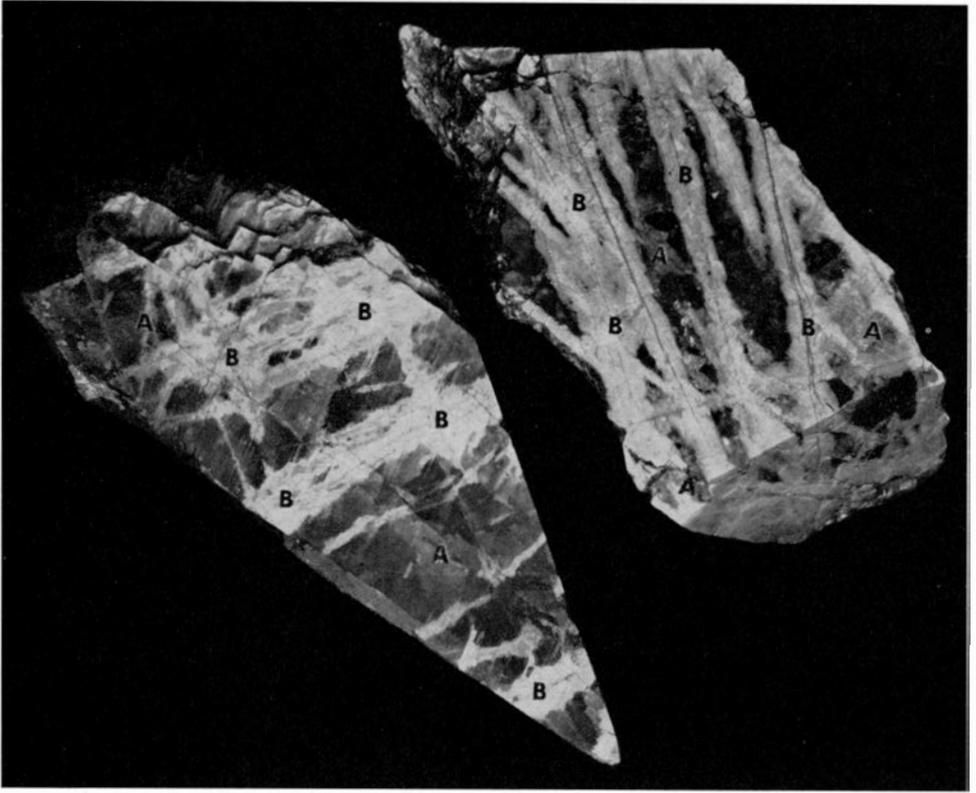
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Apatite specimens from small working on east side of ski-jump by Ceres mine, Ødegården. (2x natural size). Both show the typical veining and partial replacement of chlor-apatite (dark grey, A) by the low chlorine apatite (light grey, B).