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# THE CHEMICAL STATE OF CHLORINE-36 IN NEUTRON-IRRADIATED MINERALS†

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Abstract—The oxidation state assumed upon solution by  ${}^{36}$ Cl formed by thermal neutron irradiation of chlorine-containing minerals was determined. Except for about 0.2 and 0.9 per cent as ClO<sub>3</sub><sup>-</sup> in carnallite and chlorapatite, respectively, all the  ${}^{36}$ Cl radioactivity was found in the chloride state. The  ${}^{36}$ Cl radioactivity in the chloride state in carnallite and chlorapatite was reduced by thermal annealing.

THE discovery that cosmic ray produced secondary neutrons form  ${}^{36}$ Cl in barely detectable amounts in some terrestrial minerals<sup>(1)</sup> has prompted an investigation into the possibilities of natural Szilard-Chalmers enrichment of the specific activity of  ${}^{36}$ Cl. An appreciable percentage of the  ${}^{36}$ Cl activity in an oxidation state other than that normally found for chlorine in a mineral would permit the development of carrier-free separations of the enriched  ${}^{36}$ Cl. However, as described below, the  ${}^{36}$ Cl formed in irradiated chlorine-containing minerals by pile neutron irradiation is almost exclusively in the chloride form when the mineral is placed in solution. Since this is a common oxidation state for the stable chlorine isotopes in each mineral studied, very little isotopic enrichment can be obtained. Although about 0.2 per cent of the  ${}^{36}$ Cl formed in irradiated carnallite, and about 0.9 per cent of that formed in chlorapatite, was found in the ClO<sub>3</sub><sup>-</sup> fraction, the percentages are so small as to be useless for any enrichment purposes.

Mineral	Chlorine*(%)	Origin	Composition
Carnallite	39	Spain	KCl·MgCl <sub>2</sub> ·6H <sub>2</sub> O
Chlorapatite	0.2	Norway	$CaFCa_{4}(PO_{4})_{3}$ with Cl for some F
Halite	54	Kansas	NaCl
Lazurite	0.02	Chile	3NaAlSiO₄·Na₂S with some ·NaCl and ·CaSO.
Mimetite	0.02	Mexico	9PbO·3As <sub>2</sub> O <sub>2</sub> ·PbCl <sub>2</sub>
Nitratite	14	Chile	NaNO <sub>3</sub> (with Cl <sup>-</sup> and ClO <sub>4</sub> <sup>-</sup> )
Scapolite	0.004	Massachusetts	Na <sub>1</sub> Al <sub>3</sub> Si <sub>9</sub> O <sub>24</sub> Cl (with Ca <sub>4</sub> Al <sub>6</sub> Si <sub>6</sub> O <sub>26</sub> )
Scapolite	0.004	Quebec	same as above
Sodalite in Nepheline Svenite	1.0	New Hampshire	3NaAlSiO₄·NaCl
Sylvite with Halite	38	Texas	KCl with NaCl

TABLE 1.—CHLO	RINE-CONTAINING	MINERALS IN	VESTIGATED
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\* By weight as determined by using <sup>36</sup>Cl activity for activation analysis measurement.

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<sup>(1)</sup> R. DAVIS, JR. and O. A. SCHAEFFER, BNL 340 (T-59) (1955). See also O. A. SCHAEFFER, S. O. THOMPSON, and N. L. LARK, J. Geophys. Research 65, 4013 (1960).

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## EXPERIMENTAL

## Irradiation of minerals

Ten chlorine-containing minerals and C.P. sodium chloride were selected for the initial neutron irradiation. The halite sample was obtained from the Department of Geology of the University of Kansas, while the remainder of the minerals were obtained from Ward's Natural Science Establishment, Inc., Rochester, N.Y. The minerals are listed in Table 1, with their place of origin, usual chemical composition, and chlorine content. The chlorine content was determined from the data in Table 2 using the <sup>36</sup>Cl activity as a basis for activation analysis measurement.

TABLE 2.— <sup>36</sup> Cl radioactivity in different oxidation states ff	ком <sup>as</sup> Cl ( <i>n</i> , γ) in
IRRADIATED MINERALS	

Sample						
			cpm/			
Compound or mineral	Aliquot size (mg)	Solvent	Cl <sup>-</sup> fraction	CIO <sub>3</sub> - fraction	ClO <sub>4</sub> - fraction	mg NaCl carrier
(a) Irradiated for 10	days at 1	5 × 10 <sup>13</sup>	neutrons cm <sup>-2</sup> s	ec <sup>-1</sup> .		
NaCl (C.P.) Carnallite Carnallite Chlorapatite†	7·49 20·3 84·4 79·3	$H_2O$ $H_2O$ $H_2O$ conc.	$\begin{array}{c} 76 \cdot 6  \pm  1 \cdot 4 \\ 123  \pm  2 \\ 416  \pm  7 \cdot 5 \\ 6 \cdot 46  \pm  0 \cdot 12 \end{array}$	$\begin{array}{c} 0.02  \pm  0.04 \\ 0.33  \pm  0.02 \\ 1.32  \pm  0.04 \\ 0.06  \pm  0.01 \end{array}$	$\begin{array}{c} 0.03 \ \pm \ 0.05 \\ 0.02 \ \pm \ 0.01 \\ 0.04 \ \pm \ 0.06 \\ 0.04 \ \pm \ 0.04 \end{array}$	122 126 118 121
Halite Lazurite	, 3∙88 242	HITO3 H2O dilute HCl	$\begin{array}{c} 24.7 \pm 0.5 \\ 2.06 \pm 0.04 \end{array}$	$\begin{array}{c} -0.01 \pm 0.02 \\ -0.1 \pm 0.2 \end{array}$	$\begin{array}{c} 0.00 \ \pm \ 0.02 \\ 0.01 \ \pm \ 0.02 \end{array}$	182 118*
Mimetite	680	conc. HNO <sub>3</sub>	$2.38 \pm 0.04$	$-0.01 \pm 0.01$	$0.00 \pm 0.04$	131
Nitratite† Scapolite (Mass.)	28·4 464	H₂O conc. HNO	$\begin{array}{c} 53 \cdot 2 \ \pm \ 1 \cdot 0 \\ 0 \cdot 33 \ \pm \ 0 \cdot 02 \end{array}$	$\begin{array}{c} 0.01 \ \pm \ 0.02 \\ 0.00 \ \pm \ 0.01 \end{array}$	$\begin{array}{c} -0.01 \ \pm \ 0.02 \\ -0.01 \ \pm \ 0.04 \end{array}$	121 122
Scapolite (Que.)	653	conc.	$0.50 \pm 0.02$	$-0.02 \pm 0.02$	$0.00 \pm 0.05$	116
Sodalite	105	dilute	$19.4 \pm 0.4$	$0.03 \pm 0.03$	$0.00 \pm 0.02$	118*
Sylvite	22.6	H <sub>2</sub> O	148 ± 3	0·01 ± 0·02	$0.02 \pm 0.03$	113
(b) Irradiated for 10	days at 0∙	5 × 10 <sup>11</sup>	neutrons cm <sup>-2</sup> s	ec <sup>-1</sup> .		
KClO <sub>4</sub> (C.P.) NaClO <sub>3</sub> (C.P.) Carnallite Lazurite	86·5 142 109 452	H₂O H₂O H₂O dilute HCl	$\begin{array}{c} 1.90 \ \pm \ 0.04 \\ 4.38 \ \pm \ 0.08 \\ 3.11 \ \pm \ 0.06 \\ 0.20 \ \pm \ 0.01 \end{array}$	$\begin{array}{c} 0.38 \pm 0.03 \\ 0.40 \pm 0.01 \\ 0.13 \pm 0.01 \\ 0.00 \pm 0.01 \end{array}$	$\begin{array}{c} 0.06  \pm  0.01 \\ 0.00  \pm  0.01 \\ 0.00  \pm  0.01 \\ 0.00  \pm  0.01 \\ 0.00  \pm  0.01 \end{array}$	122 125 119 117*
Nitratite Sodalite	186 379	H₂O dilute HCl	$\begin{array}{c} 2 \cdot 10  \pm  0 \cdot 04 \\ 0 \cdot 39  \pm  0 \cdot 01 \end{array}$	$\begin{array}{c} 0.00 \pm 0.01 \\ 0.00 \pm 0.01 \end{array}$	$\begin{array}{c} 0.00 \pm 0.01 \\ 0.00 \pm 0.01 \end{array}$	117 117*
(c) Irradiated for 10	days at 1.	5 × 10 <sup>13</sup> r	eutron cm <sup>-2</sup> sec	c <sup>-1</sup> . and annealed	d 14 days at 200	± 5°C
Carnallite† Chlorapatite†	6·91 111	H₂O conc. HNO <sub>3</sub>	$\begin{array}{r} 34 \cdot 1 \ \pm 1 \cdot 0 \\ 2 \cdot 50 \ \pm \ 0 \cdot 08 \end{array}$	$\begin{array}{c} 0.00 \pm 0.02 \\ 0.02 \pm 0.01 \end{array}$	$\begin{array}{c} 0.00 \pm 0.02 \\ 0.00 \pm 0.02 \end{array}$	125 131

\* NaCl equivalent, actually added as HCl.

 $\dagger$  The assigned error is the statistical counting error, or  $\pm 1.8$  per cent, whichever is greater. The efficiency in (b) is 34 per cent, in (a) and (c), 18 per cent, except for samples marked with  $\dagger$  for which the efficiency was 14 per cent (Plexiglas backing).

Before irradiation, the minerals were crushed into medium fine powders and individually wrapped in aluminium foil. Several grammes of each were then irradiated in the Brookhaven reactor at a flux of  $1.5 \times 10^{13}$  neutrons cm<sup>-2</sup> sec<sup>-1</sup>. for a period of ten days. After irradiation, the samples were allowed to decay for several months, and then transferred to weighing bottles and stored in a desiccator. Those samples with a large chlorine content showed appreciable discoloration from radiation damage.

Additional samples of some of the minerals, as well as C.P. sodium chlorate and potassium perchlorate, were subsequently irradiated for ten days at a flux of approximately  $0.5 \times 10^{11}$  neutrons cm<sup>-2</sup> sec<sup>-1</sup>. in the Argonne CP-5 reactor. These minerals samples showed slight discoloration from irradiation, the sodium chlorate and potassium perchlorate developing a light amber colour.

#### Separation of oxidation states

A portion of each irradiated sample was dissolved in the mildest solvent thought to be capable of taking the chlorine containing compounds into solution, as shown in Table 2. The solution was then filtered and mixed with a carrier solution containing approximately 0.002 mole each of the sodium salts of Cl<sup>-</sup>, ClO<sub>3</sub><sup>-</sup> and ClO<sub>4</sub><sup>-</sup>. No NaCl was added for the samples dissolved in dilute HCl. For samples dissolved in acid, the fitrate was neutralized with 6M NaOH prior to the addition of the carrier solution.

Silver chloride was precipitated from the sample plus carrier solution through the addition of an excess of  $0.5 \text{ M AgNO}_3$  solution, after being made slightly acid with HNO<sub>3</sub>. This silver chloride precipitate was filtered and set aside for purification. More NaCl was added to the filtrate, and this additional AgCl was filtered and discarded, insuring removal of the <sup>36</sup>Cl in the Cl<sup>-</sup> state.

Sulphur dioxide was then bubbled through the filtrate for several minutes, reducing  $ClO_3^-$  to  $Cl^-$ , without chemically affecting  $ClO_4^-$ . Again, AgCl was precipitated through the addition of excess 0.5 M AgNO<sub>3</sub> solution, filtered, and set aside for purification.

The  $\overline{ClO_4}^-$  fraction was isolated by two separate methods. Originally, the filtrate containing the  $ClO_4^-$  carrier was evaporated to a volume of 50 ml, filtered to remove residue, and then further evaporated to about 10 ml. A solution containing 1 gramme of KNO<sub>3</sub> in 3 ml water was then added to the evaporated solution, and cooled slowly to room temperature, and then to 0°C. The crystallized KClO<sub>4</sub> was filtered on glass fibre filter paper, dried at 100°C for 10 min, and, in a test tube over a burner, decomposed to KCl and oxygen. The residue was dissolved, filtered, acidified with nitric acid, and AgCl was precipitated with excess 0.5 M AgNO<sub>3</sub> solution.

Later, a second procedure was developed for the  $ClO_4^-$  fraction. After the filtrate from the chlorate separation was freed from silver ions by standing overnight in ammoniacal solution over magnesium turnings, the perchlorate was precipitated by the addition of tetraphenyl arsonium chloride. The tetraphenyl arsonium perchlorate was filtered, dried at 100°C and then reduced to Cl<sup>-</sup> by a method similar to that suggested by CRUMP and JOHNSON<sup>(2)</sup>. The dry precipitate was placed in a flameignition Parr bomb with an excess of sodium peroxide and the two solids were thoroughly mixed by shaking the closed bomb. The mixture was ignited by heating with a Fischer burner, the heating being stopped when a few ml of water in the recess of the head of the bomb began to boil. After cooling the residue was dissolved, filtered, and the filtrate acidified. Again, a precipitate of AgCl was obtained upon the addition of excess 0.5 M AgNO<sub>3</sub> solution.

## Radiochemical purification

The silver chloride precipitates from the chloride and chlorate fractions were dissolved in 6 M aqueous ammonia and the diammine silver ions were then reduced to metallic silver through the addition of purified magnesium turnings. After standing overnight, the solution was filtered, added to an excess of concentrated sulphuric acid, and distilled. The distillate contained primarily the HCl-water azeotrope but could also have carried the HF-, HBr-, and HI-water azeotropes, if present. Silver chloride was then precipitated in acidic solution and dissolved in ammoniacal solution until constant radioactivity was obtained.

The silver chloride precipitate from the  $ClO_4^-$  fraction was dissolved in 6 M aqueous ammonia, and reprecipitated in acidic solution until constant radioactivity was obtained.

#### Radiochemical assay

Aliquots of purified ammoniacal sample solutions were acidified and collected on weighed glass fibre filter paper. The precipitates were washed with three separate 20 ml portions of absolute ethanol, dried for 10 min at 100°C, weighed, mounted on aluminium or Plexiglas disks, and covered with cellophane tape. The radioactivity of the samples irradiated at the higher flux was determined with an end-window Geiger counter. The measurements on the samples irradiated at the lower flux were

<sup>(2)</sup> L. CRUMP and C. JOHNSON, Analyt. Chem. 27, 1007-8 (1955).

carried out on a 2 in. diameter low-level Geiger counter with a background of 1.0 counts/min, produced by Sharp Laboratories, Inc., La Jolla, California. The Plexiglas backings gave a lower background count than the available aluminium disks.

Corrections of the experimentally determined count rates were made to the activity expected for a precipitate of thickness 11.0 mg/cm<sup>2</sup>. The precipitate thicknesses varied from 1.17 to 28.9 mg/cm<sup>2</sup>, for which the empirically determined thickness correction was never larger than 16 per cent. The correction factors are precise to 1.8 per cent. The standard area of the Cl<sup>-</sup> and ClO<sub>3</sub><sup>-</sup> precipitates was 2.27 cm<sup>2</sup>, while that of the perchlorate precipitates was 3.30 cm.<sup>2</sup> The efficiency of the regular end-window Geiger counter is approximately 18 per cent, while the low-level Geiger counter has an efficiency under our conditions of approximately 34 per cent. The diminution in observed count rates through aluminium absorbers was consistent in each case with the 0.7 MeV.  $\beta$ -ray of <sup>36</sup>Cl.

#### Annealing studies

Possible effects of thermal annealing on the relative radioactivity in the chloride, chlorate, and perchlorate fractions were investigated by holding the irradiated samples of carnallite and chlorapatite at  $200 \pm 5^{\circ}$ C for a period of two weeks. The samples were then dissolved and assayed in the normal manner.

## **RESULTS AND DISCUSSION**

The <sup>36</sup>Cl activity found in each of the three chlorine oxidation states is shown in Table 2. The oxidation state, of course, is that found after solution of the irradiated crystals and does not necessarily imply the oxidation state of the radioactivity prior to solution. The chloride fraction includes through rapid isotopic exchange all <sup>36</sup>Cl in the solution in an oxidation state lower than +5. The listed count rates are the averages of those considered constant for the given fraction.

No <sup>36</sup>Cl radioactivity is found in the oxidized states from any of the minerals except for approximately 0.2 and 0.9 per cent of the total radioactivity as  $ClO_3^-$ , in carnallite and chlorapatite, respectively. Although the percentage in the  $ClO_3^-$  fraction from carnallite is very small, it is reproducible and independent of irradiation time in the range studied, as shown in Table 3. No significant  $ClO_4^-$  radioactivity was found in any of the minerals.

Thermal annealing of the carnallite and chlorapatite samples reduced the already small percentages of  ${}^{36}$ Cl found as ClO<sub>3</sub><sup>-</sup>, as shown in Table 3. The radiation damage discolouration disappeared during the thermal annealing, and the samples resumed their original appearance.

Irradiated minerals are not very satisfactory matrices in which to study the actual "hot" atom reactions occurring for the <sup>36</sup>Cl atoms, but the observation of chloride as the predominant oxidation state is consistent with those made for other chlorine isotopes in various inorganic compounds. The radioactivity distribution obtained for NaClO<sub>3</sub> and KClO<sub>4</sub> is shown in Table 4, together with several distributions obtained

Mineral	Irradiation time	(mg) sample	(mg) NaClO <sub>3</sub> carrier	Cl <sup>36</sup> O <sub>3</sub> - (%)
Carnallite	10 days at $1.5 \times 10^{13}$ n cm <sup>-2</sup> sec <sup>-1</sup>	20.3	218	$0.23 \pm 0.02$
Carnallite	10 days at $1.5 \times 10^{13}$ n cm <sup>-1</sup> sec <sup>-1</sup>	84·4	228	$0.23 \pm 0.02$
Carnallite	10 days at $0.5 \times 10^{11}$ n cm <sup>-1</sup> sec <sup>-1</sup>	109	209	$0.24 \pm 0.02$
Carnallite	10 days at $1.5 \times 10^{13}$ n cm <sup>-2</sup> sec <sup>-1</sup> Annealed 14 days at 200 $\pm$ 5°C	6.91	251	$0.00 \pm 0.03$
Chlorapatite	10 days at $1.5 \times 10^{13}$ n cm <sup>-2</sup> sec <sup>-1</sup>	79·3	217	$0.9 \pm 0.2$
Chlorapatite	10 days at 1.5 $ imes$ 10 <sup>13</sup> n cm <sup>-2</sup> sec <sup>-1</sup> Annealed 14 days at 200 $\pm$ 5°C	111	218	$0.6 \pm 0.3$

TABLE 3.—<sup>36</sup>Cl as ClO<sub>3</sub><sup>-</sup> in irradiated carnallite and chlorapatite

previously by other experimenters. The NaClO3 results are quite consistent with those obtained by SHARMAN and MCCALLUM, whose sample had an even heavier neutron and  $\gamma$ -ray exposure than ours.

Compound	Isotope -	Activit	Deference		
		Cl-	ClO <sub>3</sub> -	ClO4	Reference
$\begin{array}{c} \text{KIO}_3 \\ \text{NaCIO}_3 \\ \text{NaCIO}_3 \\ \text{Na}_2 \text{SO}_4 \\ \text{K}_2 \text{S}_2 \text{O}_8 \\ 1 \cdot 0 \text{ M NaCIO}_3 \\ 1 \cdot 0 \text{ M NaCIO}_4 \\ \text{NaCIO}_3 \\ \text{KCIO}_4 \end{array}$	<sup>41</sup> K $(n, \alpha)$ <sup>38</sup> Cl <sup>35</sup> Cl $(n, \gamma)$ <sup>36</sup> Cl <sup>35</sup> Cl $(\gamma, n)$ <sup>34</sup> Cl <sup>34</sup> S $(p, n)$ <sup>34</sup> Cl <sup>34</sup> S $(p, n)$ <sup>34</sup> Cl <sup>37</sup> Cl $(n, \gamma)$ <sup>38</sup> Cl <sup>37</sup> Cl $(n, \gamma)$ <sup>38</sup> Cl <sup>35</sup> Cl $(n, \gamma)$ <sup>36</sup> Cl <sup>35</sup> Cl $(n, \gamma)$ <sup>36</sup> Cl	"Practically All" $86.5 \pm 3.0\%$ $\sim 90\%^{\dagger}$ $13743 \pm 115$ cpm $1047 \pm 24$ cpm $100 \pm 2\%$ $100 \pm 10\%$ $87.6 \pm 0.4\%$ $79.9 \pm 1.5\%$		$ \begin{array}{c}                                     $	(6) (3) (4) (7) (7) (8) (8) (8) This work. This work.

TABLE 4.—OXIDATION STATES OF CHLORINE ISOTOPES IN IRRADIATED COMPOUNDS

\* Reported as chlorine having oxidation state zero to +5.

† Experiments were conducted over a range of conditions; these values are representative.

<sup>(3)</sup> L. J. SHARMAN and K. J. MCCALLUM, J. Chem. Phys. 23, 597 (1955).

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<sup>(8)</sup> W. F. LIBBY, *J. Amer. Chem. Soc.* 62, 1930 (1940).