Cosmic ray produced Mg^{28}, Si^{31}, S^{38}, Cl^{38}, Cl^{34m} and other short-lived radioisotopes in wet precipitation[1]

By N. BHANDARI, S. G. BHAT, D. P. KHARKAR, S. KRISHNA SWAMY, D. LAL and A. S. TAMHANE, *Tata Institute of Fundamental Research, Bombay-5*

ABSTRACT

The concentrations of seven radioisotopes, expected to be produced in the troposphere by interactions of secondary cosmic rays with atmospheric nuclei, have been measured in "fresh" rain collections. The half-lives of these isotopes range from about half an hour to a day. The procedures developed for rapid, specific and sensitive analyses of these nuclides are discussed.

Detection of two of the isotopes studied, Cl^{39} (half-life: 55 mins.) and Na^{24} (15 hrs.), has been reported earlier by WINSBERG and RÖDEL respectively. Amongst the remaining nuclides, two: S^{38} (2.9 hrs.) and Cl^{38} (37.3 mins.) were independently and almost simultaneously detected by us and PERKINS and his collaborators. Three other isotopes, Cl^{34m} (32 mins.), Si^{31} (2.6 hrs.) and Mg^{28} (21.2 hrs.), detected in the present work have not yet been reported elsewhere.

The nature of cosmic ray secondary particles responsible for the production of these short-lived radionuclides in the troposphere is discussed. Isotope production is found to vary strongly with altitude in the troposphere; it increases by a factor of two every 1.5–2 km depending on the radioisotope under question. This fact combined with the availability of several isotopes of half-lives ranging from about half an hour to a day leads to the possibility of using them as tracers for studying short-term tropospheric processes, e.g. those occurring prior to and during condensation in a precipitating cloud. The implications of the present measurements are discussed.

1. Introduction

Most of the cosmic ray produced radioisotopes detected so far in the atmosphere have half-lives $\geqslant 2$ weeks. They are useful for studying processes which occur on time scales of a few days or more; their studies thus relate to the gross atmospheric circulation and wash-out processes, averaged over such periods of time. Further, since the time scale of mixing within the troposphere is of the order of four weeks, these isotopes provide information essentially on the averaged features of mixing within the bulk troposphere. However, if one wants to study localised and rapidly occurring processes in the atmosphere such as those taking place during and prior to condensations etc., one needs to base the studies on radioactive tracers of much shorter half-life, of the order of a few hours. Several isotopes having half-lives ranging from a few minutes to a day are expected to be produced in cosmic ray interactions in the atmosphere. These are listed in Table 1. Some of these have already been detected.

Two of the short-lived isotopes detected so far are Na^{24} (RÖDEL, 1963) and Cl^{39} (WINSBERG, 1956). Their concentrations have been measured only in a few samples and no attempts were made to use them as meteorological tracers.

We have now detected five other isotopes Mg^{28} (21 hrs), S^{38} (2.9 hrs), Si^{31} (2.6 hrs), Cl^{38} (37 min), and Cl^{34m} (32 min). The results of measurements of the concentrations of these isotopes and of Na^{24} and Cl^{39} in several rain samples collected at Bombay during 1964–65 are presented here. After our work was completed we learnt that PERKINS et al., (1965) had also detected two isotopes, S^{38} and Cl^{38}, independent of our work.

The details of the experimental procedures, the results and their implications are discussed.

TABLE 1. *Short-lived cosmic ray produced radio isotopes* ($20 \ min < \tau_{\frac{1}{2}} < 1 \ day$).

Isotope	Half-life	Principal radiation	Daughter product
$_{12}Mg^{28}$	21.2 h	β^- 0.42 MeV (100 %)	$_{13}Al^{28} \xrightarrow[2.3 \ m]{\beta-} > Si^{28}$ (stable)
$_{11}Na^{24}$	15 h	β^- 1.4 MeV (100 %) γ 1.37 MeV and 2.75 MeV	Mg^{24} (stable)
$_{16}S^{38}$	2.9 h	β^- 1.1 MeV (95 %) 3.0 MeV (5 %) γ 1.88 MeV	$Cl^{38} \xrightarrow[37 \ m]{\beta-} > A^{38}$ (stable)
$_{14}Si^{31}$	2.6 h	β^- 1.47 MeV (100 %)	P^{31} (stable)
$_{9}F^{18}$	1.9 h	β^+ 0.65 MeV	O^{18} (stable)
$_{17}Cl^{39}$	55.5 m	β^- 1.91 MeV (85 %) 2.18 MeV (8 %) 3.45 MeV (7 %) γ 0.25 MeV (43 %) 1.27 and 1.52 MeV	$Ar^{39} \xrightarrow[260 \ y]{\beta-} > K^{39}$ (stable)
$_{17}Cl^{38}$	37.3 m	β^- 1.1 MeV (31 %) 2.78 MeV (16 %) 4.8 MeV (53 %) γ 1.6 MeV (31 %) 2.15 MeV	Ar^{38} (stable)
$_{17}Cl^{34m}$	32 m	β^+ 1.3 MeV (26 %) 2.48 MeV (26 %) 4.5 MeV (47 %) γ 1.2, 2.1 and 3.22 MeV	$Cl^{34} \xrightarrow[1.5 \ sec]{\beta+} > S^{34}$ (stable)
$_{6}C^{11}$	20.4 m	β^+ 0.97 MeV	B^{11} (stable)

2. Experimental procedures

As can be seen from Table 1, many of these isotopes have complex decay schemes. They can, therefore, be identified unambiguously inspite of the fact that several isotopes of a particular element are expected to occur simultaneously in a rain-sample, e.g. Cl^{34m}, a positron emitter, can be identified by seeing the coincidence of the annihilation gamma rays in the presence of Cl^{39} and Cl^{38}. Similarly, S^{38} activity can be measured in the presence of a comparable activity due to S^{35} (BHANDARI, 1965) by milking and counting its daughter radioisotope Cl^{38}. Furthermore, the wide differences in their half-lives can be used to estimate separately the concentrations of two isotopes when they have fairly identical decay schemes, e.g. Cl^{39} and Cl^{38}: Good chemical separations are, however, required to avoid contaminations arising from other radionuclides present in rain. The decay rates of some of the important contaminating nuclides expected to be present, e.g. Pb^{214} (27 min) and Bi^{214} (19 min), the daughter radio-

isotopes of radon are similar to those of the cosmic ray produced radionuclides under consideration. The concentrations of radon decay products are several orders of magnitude higher (being ca. 20,000 dpm/litre) as compared to the isotopes under study and therefore a little contamination can seriously interfere. Even the laboratory air has about 0.05 dpm/litre of radon. Any contact with a few litres of air, for instance, while the sample is being filtered under suction, is sufficient to introduce appreciable contamination. Specific chemical procedures, repeated precipitations, processing of samples in "clean" air in the final stages, purification by sublimation/distillation, counting of the milked activity wherever possible, are examples of some of the precautions taken or steps used in the present work. Finally, any procedures devised to this end have to be, however, carried out fairly rapidly since the total contents of these short-lived isotopes are expected to be small, even in fairly large collections of rain-water.

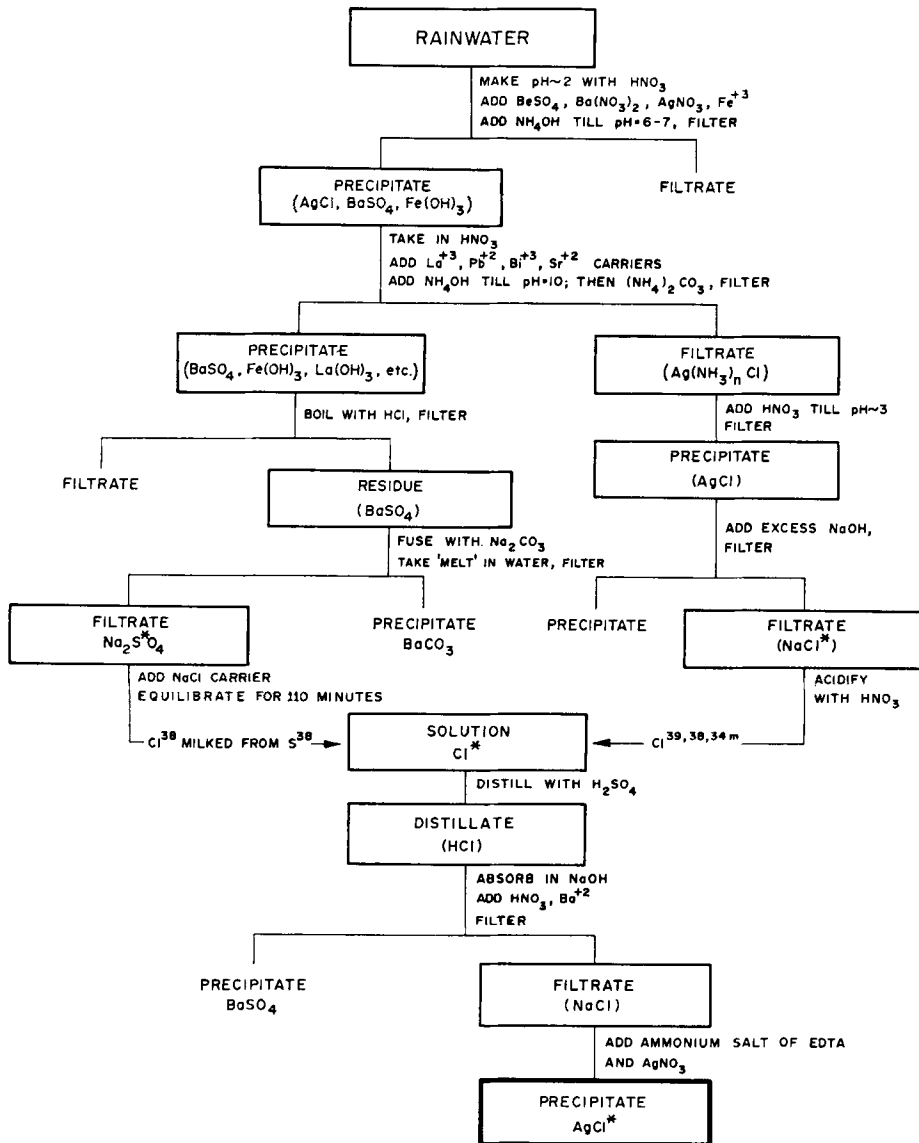Keeping the above factors in mind, we de-

N. BHANDARI et al.

RAINWATER

MAKE pH~2 WITH HNO₃
ADD BeSO₄, Ba(NO₃)₂, AgNO₃, Fe⁺³
ADD NH₄OH TILL pH=6-7, FILTER

PRECIPITATE
(AgCl, BaSO₄, Fe(OH)₃)

FILTRATE

TAKE IN HNO₃
ADD La⁺³, Pb⁺², Bi⁺³, Sr⁺² CARRIERS
ADD NH₄OH TILL pH=10; THEN (NH₄)₂CO₃, FILTER

PRECIPITATE
(BaSO₄, Fe(OH)₃, La(OH)₃, etc.)

FILTRATE
(Ag(NH₃)ₙCl)

BOIL WITH HCl, FILTER

ADD HNO₃ TILL pH~3
FILTER

FILTRATE

RESIDUE
(BaSO₄)

PRECIPITATE
(AgCl)

FUSE WITH Na₂CO₃
TAKE 'MELT' IN WATER, FILTER

ADD EXCESS NaOH,
FILTER

FILTRATE
Na₂S*O₄

PRECIPITATE
BaCO₃

PRECIPITATE

FILTRATE
(NaCl*)

ADD NaCl CARRIER
EQUILIBRATE FOR 110 MINUTES

ACIDIFY
WITH HNO₃

Cl³⁸ MILKED FROM S³⁸ ➔

SOLUTION
Cl*

← Cl³⁹,³⁸,³⁴ᵐ

DISTILL WITH H₂SO₄

DISTILLATE
(HCl)

ABSORB IN NaOH
ADD HNO₃, Ba⁺²
FILTER

PRECIPITATE
BaSO₄

FILTRATE
(NaCl)

ADD AMMONIUM SALT OF EDTA
AND AgNO₃

PRECIPITATE
AgCl*

FIG. 1. The upper half of the diagram shows the various chemical steps used for extracting crude Na₂S*O₄ and NaCl* from rain water. The procedures used for obtaining radiochemically pure chlorine, Cl³⁸ milked from S³⁸ activity present in Na₂S*O₄ and Cl³⁹,³⁸,³⁴ᵐ from NaCl* are shown in the lower half of the diagram.

signed chemical and counting procedures for the detection of all isotopes listed in Table 1, except for F¹⁸ and C¹¹. (The production rate of F¹⁸ is expected to be smaller than that of other isotopes and furthermore two other isotopes of comparable half-life are available; we therefore did not look for F¹⁸. No attempts were likewise made to detect C¹¹; most of its activity is expected to remain in the air as carbon-monoxide and carbondioxide which are not brought down efficiently in rains.) Bearing the fact that isotope studies are useful only if concentrations of two or more are studied simultaneously in a single rain, sequential radiochemical tech-
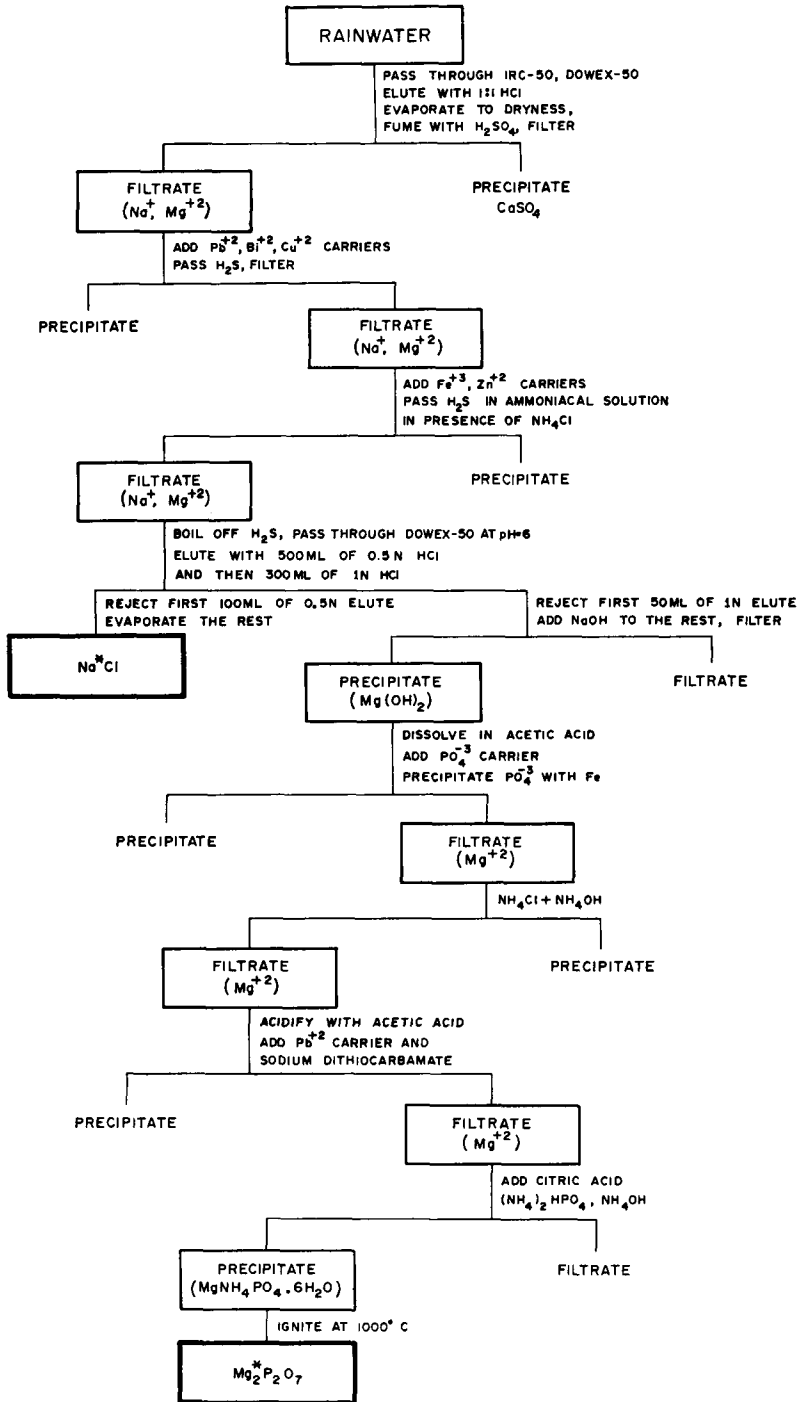
RAINWATER

PASS THROUGH IRC-50, DOWEX-50
ELUTE WITH I:I HCl
EVAPORATE TO DRYNESS,
FUME WITH H_2SO_4, FILTER

FILTRATE
(Na^+, Mg^{+2})

PRECIPITATE
$CaSO_4$

ADD Pb^{+2}, Bi^{+2}, Cu^{+2} CARRIERS
PASS H_2S, FILTER

PRECIPITATE

FILTRATE
(Na^+, Mg^{+2})

ADD Fe^{+3}, Zn^{+2} CARRIERS
PASS H_2S IN AMMONIACAL SOLUTION
IN PRESENCE OF NH_4Cl

FILTRATE
(Na^+, Mg^{+2})

PRECIPITATE

BOIL OFF H_2S, PASS THROUGH DOWEX-50 AT pH=6
ELUTE WITH 500ML OF 0.5N HCl
AND THEN 300ML OF IN HCl

REJECT FIRST 100ML OF 0.5N ELUTE
EVAPORATE THE REST

REJECT FIRST 50ML OF IN ELUTE
ADD NaOH TO THE REST, FILTER

Na^*Cl

PRECIPITATE
($Mg(OH)_2$)

FILTRATE

DISSOLVE IN ACETIC ACID
ADD PO_4^{-3} CARRIER
PRECIPITATE PO_4^{-3} WITH Fe

PRECIPITATE

FILTRATE
(Mg^{+2})

$NH_4Cl + NH_4OH$

FILTRATE
(Mg^{+2})

PRECIPITATE

ACIDIFY WITH ACETIC ACID
ADD Pb^{+2} CARRIER AND
SODIUM DITHIOCARBAMATE

PRECIPITATE

FILTRATE
(Mg^{+2})

ADD CITRIC ACID
$(NH_4)_2HPO_4$, NH_4OH

PRECIPITATE
($MgNH_4PO_4 \cdot 6H_2O$)

FILTRATE

IGNITE AT 1000° C

$Mg_2^*P_2O_7$

FIG. 2. A schematic block diagram showing various chemical steps used for the extraction of radio-chemically pure sodium and magnesium.
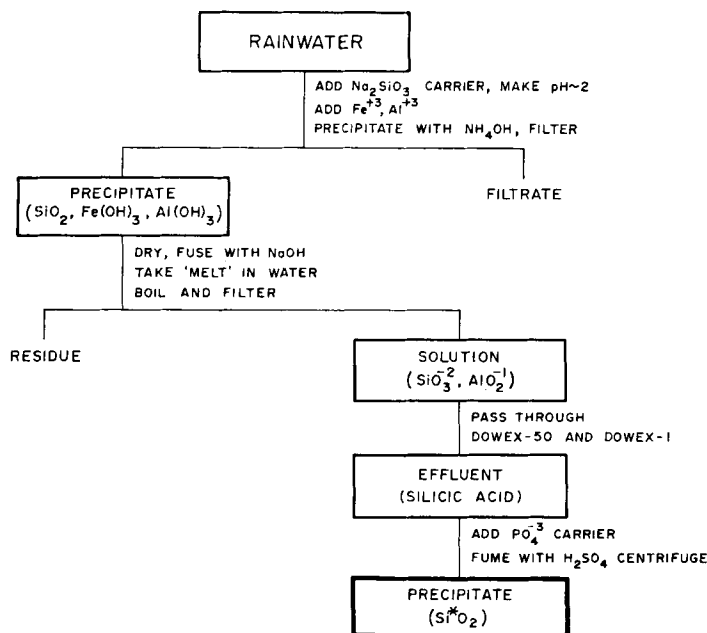
FIG. 3. A schematic block diagram showing various chemical steps used for the extraction of radiochemically pure silicon.

niques for extraction of the isotopes of chlorine, sulphur, silicon, magnesium and sodium from rain water were developed. In a few samples, the radioactivities of the relatively long-lived nuclides, Be^7 and Na^{22} were also measured with a view to obtain additional meteorological information. The chemical and counting techniques adopted for the short-lived nuclides are described below; those for Be^7 and Na^{22} have been discussed elsewhere (BHANDARI, 1965).

2.1. *Chemical procedures*

Rain water was collected on clean polyethylene surfaces which were washed immediately before collection with dilute nitric acid. (This procedure was found necessary to avoid losses due to any possible adsorption[1] of activities on the collecting surfaces.) Four collection systems, providing a total area of 50 m^2 were used in order to obtain sufficient water from a rainburst. The amount of water processed for

[1] At the rain-water pH, several cosmic ray produced radionuclides can get adsorbed on surfaces like cement, concrete, aluminum etc. For example, it was found that during rainy season large amounts of Be^7, about 10^3 d.p.m./m^2, could be obtained on washing the tiled roof.

isotopes Na^{24} and Mg^{28} was of the order of 200 litres, for others 20–50 litres were analysed. As most rain-bursts do not provide such large quantities from our collection area in collection periods of the order of a few minutes, we had to resort to collections over periods of about two hours and fifteen minutes for the analysis of magnesium, sodium and chlorine, sulphur, silicon respectively. In two cases where enough water could be collected in half an hour to permit analyses of Mg^{28}, Na^{24}, the activities of chlorine or sulphur isotopes were also measured. Thus, besides chemical problems, the limitation in obtaining an adequate "collection" did not always permit obtaining simultaneous ratios of several isotopes in a given rain.

The isotopes under consideration were chemically extracted from rain samples following procedures as shown by block-diagrams in Figs. 1, 2 and 3. The activities of chlorine, sulphur, sodium and magnesium were extracted by sequential analyses (Figs. 1 and 2 respectively). The extraction of silicon was carried out singly (Fig. 3).

For obtaining radiochemically pure chlorine, we obtained HCl* by distilling crude NaCl* with H_2SO_4 (Fig. 1). The chlorine was finally

TABLE 2. *Some relevant details on chemical extraction and radiometry.*

Radio-isotope	"Inherent" element present in rain water (p.p.m.)	Carrier added per sample (mg)	Chemical form of the compound counted	Counting mode	Typical detector counting efficiency (ideal) (per cent)
Mg^{28}	0.02–0.5	10	$Mg_2^*P_2O_7$	$\beta-$	33 [a]
Na^{24}	2–5	Nil	Na^*Cl	γ (1.4 MeV)	2.5
S^{38}	0.05–0.1	250	$AgCl^*$	$\beta-$ (Cl^{38})	36
Si^{31}	0.1–1	40	Si^*O_2	$\beta-$	36
Cl^{39}	2–15	Nil	$AgCl^*$ or NH_4Cl^*	i) $\beta-$	36 (i)
				ii) γ (0.25 MeV)	55 (ii)
Cl^{38}	2–15	Nil	$AgCl^*$ or NH_4Cl^*	$\beta-$	36
Cl^{34m}	2–15	Nil	$AgCl^*$	$\beta+$	4

[a] The "effective" counting efficiency is however nearly twice as large because activity of Al^{28} (half-life 2.3 min, $E_{max}(\beta-) = 2.9$ MeV) quickly builds up in secular equilibrium with Mg^{28} (Table 1).

recovered quantitatively as $AgCl^*$ which was counted directly. The details of the procedure are shown in the lower half of Fig. 1. This procedure which was also used for counting the Cl^{38} milked from S^{38} activity ($Na_2S^*O_4$) took about 30 minutes. Overall yields of as high as 60% were occasionally obtained. (In earlier analyses, we obtained NH_4Cl^* and purified by sublimation for counting. The procedure however took longer and was abandoned). For other isotopes, radiochemically pure salts containing the activity were obtained as shown in Figs. 2 and 3 ($Mg_2^*P_2O_7$, Na^*Cl and Si^*O_2 for Mg^{28}, $Na^{24(22)}$, and Si^{31} activities respectively).

Rain-water contained sufficient amounts of dissolved chloride and sodium and no carrier was added for extraction of these elements. The chemical efficiency of chlorine was based on potentiometric titrations with a calomel and silver electrode against a "standard" solution of $AgNO_3$. For S^{38} analyses, we added 1 gm of Na_2SO_4, an amount which is considerably larger than that internally present in 25–50 litres of rain water. The chemical efficiency for extraction of sulphur was based on the amount of $BaCO_3$ recovered (Fig. 1). Cl^{38} was then milked after an addition of 200 mg equivalent AgCl. The inherent Na^+ content was determined by the flame-photometric method. For magnesium, a carrier of ca. 50 mg equivalent $Mg_2P_2O_7$ was added. The inherent Mg^{++} content was determined spectrophotometrically. For Si^{31} estimations, we added ca 175 mg equivalent of Na_2SiO_3 in each case. The typical amount of carriers inherently present and other relevant details are summarised in Table 2.

2.2. Radiometric techniques

The radioactivities of the extracted salts were measured on either of the three low-level beta, gamma, or gamma–gamma counting systems, depending on which was more satisfactory and specific for the isotope in question. The beta counters used are identical to those designed by LAL & SCHINK (1960). Rectangular counters, having active dimensions of 3.9 × 1.4 cm were employed. The counters permitted mounting of two source holders, each having a source area of 4.1 cm^2. The background and the counting efficiency for a typical counter were 7 c.p.h. and 36% (for K^{40} β-radiation) respectively. A well crystal (NaI (Tl)) of dimensions 5.1 × 4.4 cm (well size: 1.6 × 3.8 cm) was used for γ-counting. The crystal was surrounded successively by mercury (2 cm), lead (10 cm) and steel (10 cm) to suppress the background. Pulses were recorded on a 400 channel RIDL analyser (Model 34-112B). Background counting rates in the 0.25, and 0.51 MeV photopeak were 2.2 and 1.5 c.p.m. respectively. The details of the gamma–gamma system employed in the present work are described by AMIN et al. (1966). Two sodium iodide crystals (NaI(Tl) of diameter 6.4 cm and thickness 3.8 cm were operated in anticoincidence with a guard counter. The 0.51 MeV photopeak pulses
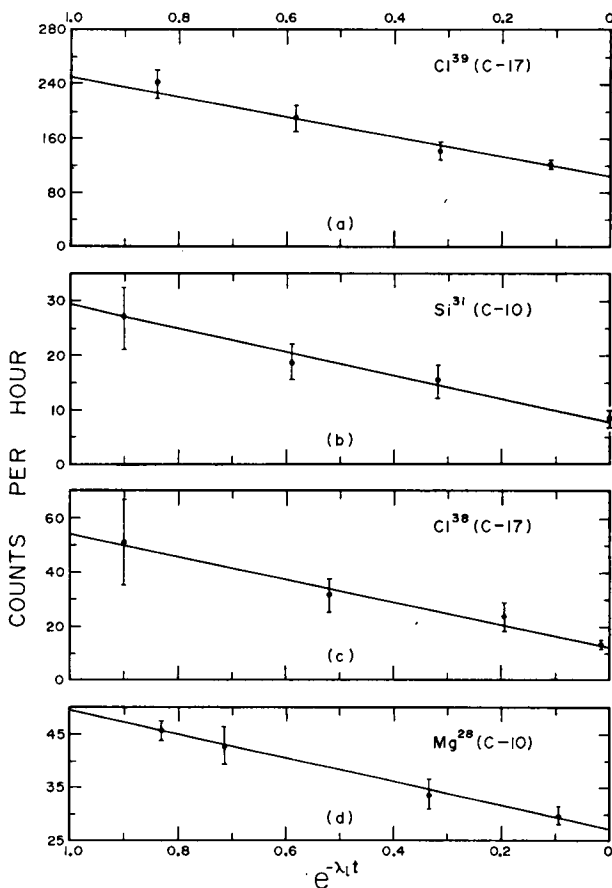
FIG. 4. Typical decay curves of Cl^{39}, Si^{31}, Cl^{38} (milked from S^{38}) and Mg^{28} activities. Observed gross counting rates are plotted versus $(e^{-\lambda_i t})$.

(460–560 KeV) from one counter were put in prompt coincidence with the pulses from the other counter. The coincidence spectrum was recorded by the 400 channel RIDL analyser. The background in the 0.51 MeV photopeak was 2 c.p.h.

The details of the mode of counting of individual activities are summarised in Table 2, in which are also listed the ideal counting efficiencies (i.e. those for a weightless source).

The identity of the isotopes analysed was conveniently checked by following their decay. Typical decay curves observed for Cl^{39}, Si^{31}, Cl^{38} (milked from S^{38}) and Mg^{28} are shown in Fig. 4. This procedure could not be adopted for the case of Cl^{38} whose activity had to be inferred from the decay curve of the combined[1]

Cl^{39}, Cl^{38} activities, using the Biller's plot method (BILLER, 1953). Here we entirely relied on the radiochemical purity of the sample.

3. Results and discussions

The results of measurements of concentrations of short-lived activities in rain water samples analysed during 1964–65 are presented in Tables 3 and 4. In Table 3 are listed the results of measurements for those isotopes for which at least three rain samples were analysed. Table 4 lists the rest of the measurements,

---

[1] A correction has also to be applied for Cl^{34m} present. However, as its concentration is found to be an order of magnitude lower than that of Cl^{39} or Cl^{38}, the correction is small.

TABLE 3. *Observed concentrations of radioisotopes in rainwater.*

Code number	Date of collection	Concentration (dpm/litre)				
		Mg^{28}	Na^{24}	S^{38}	Si^{31}	Cl^{39}
R-1	7.8.64	—	—	5.7	—	10.6
R-2	12.8.64	—	—	2.1	—	5.5
R-3	8.9.64	—	—	6.3	—	15.7
R-4	18.9.64	—	—	2.5	(0.4)	9.0
R-5	18.9.64	—	—	—	(0.13)	—
R-6	20.9.64	0.06	—	—	—	—
R-7	21.9.64	—	—	—	(0.1)	—
R-8	24.9.64	—	—	2.1	—	15.7
R-9	24.9.64	—	—	—	(0.1)	—
R-10	24.9.64	0.045	—	—	—	—
R-11	1.10.64	—	—	—	—	—
R-12	1.10.64	—	—	2.9	0.18	—
C-5	15.6.65	—	—	0.7	(0.02)	3.8
C-7	26.6.65	—	—	—	(0.03)	—
C-9	1.7.65	—	—	5.5	—	—
C-10	2.7.65	0.012	0.03	2.8	0.16	—
C-11	9.7.65	—	—	—	(0.03)	—
C-12	15.7.65	—	0.1	7.4	—	—
C-13	15.7.65	—	—	0.5	—	(2.1)
C-14	19.7.65	—	0.28	—	—	—
C-15	21.7.65	—	—	—	—	12.0
C-16	27.7.65	—	—	1.5	—	6.2
C-17	27.7.65	—	—	1.3	—	12.3
C-18	29.7.65	—	—	1.5	—	(2.6)
C-21	2.8.65	—	—	0.16	—	(3.6)

including the activity ratios of Cl^{39}/Cl^{38} in some rains. The latter samples have not been listed in Table 3, because in these cases the absolute concentrations were not determined; the chemical efficiency for the extraction of AgCl* was not estimated.

The statistical errors due to counting are 25% or less for all samples listed in Tables 3 and 4, except for those placed within paranthesis. For these, the errors may be as much

as about a factor of two. The errors in the case of Cl^{39}/Cl^{38} ratios may be 30–40% as the results are based on the application of Biller's plot method with the small signals observed. Systematic errors of 25–30% should in addition be considered due to errors in calibration of the counters, particularly for the γ-system. Thus though several rain samples could be analysed satisfactorily for the contents of the short-lived species studied, we have been left with a fair

TABLE 4. *Results of measurements of activities in rain water.*

Cl^{34m}	Isotope concentration (dpm/litre)[a]			Cl^{39}/Cl^{38} (activity ratio)[a]
	Cl^{38}	Be^7	Na^{22}	
0.45 (C-15, 21.7.65)	10.2 (C-16, 27.7.65)	32 (C-18, 29.7.65)	0.012 (C-16, 27.7.65)	0.4 (R-13, 18.9.64)
				0.5 (R-14, 20.9.64)
0.9 (C-17, 27.7.65)		50 (C-21, 2.8.65)	0.026 (C-12, 15.7.65)	0.8 (R-15, 23.9.64)
				0.8 (R-16, 1.10.64)
				0.6 (C-16, 27.7.65)

[a] The code number and the date of collection of the rain sample are given within the paranthesis. In all samples with "C" code numbers, other radioisotopes have been analysed (see Table 3).

amount of less quantitative data for one or two isotopes in many cases. The reasons for this arise mainly from the necessity of carrying out the elaborate specific chemical extraction steps in the short time available in such work. Nevertheless, sufficiently reliable numbers for two or more isotopes exist for several rains. We will now discuss the results and their implications.

The average concentration values in rains of the seven isotopes studied are listed in Table 5. A comparison is also made for the four isotopes, Na^{24}, S^{38}, Cl^{39} and Cl^{38} with the data reported in literature. Significant disagreements seem to be present in the case of Cl^{39} and Cl^{38}. The larger values obtained by PERKINS *et al.* (1965) cannot be explained as due to latitude effect which can at most account for a factor of two (BHANDARI & LAL, 1965). If the disagreement is taken seriously, i.e. barring the small statistics on the number of samples in the case of PERKINS *et al.* (1963), presence of some contaminating radionuclide in their case seems to be a likely explanation. Their chemical procedures did not aim for such a high degree of radiochemical purification as in the present work.

TABLE 5. *Average concentrations of short-lived activities in rainwater.*

Figures in paranthesis denote the number of samples on which the result is based.

Isotope	Concentration (dpm/litre)	
	Present work	Others
Mg^{28}	0.04 (3)	—
Na^{24}	0.14 (3)	0.23 (3)[a]
S^{38}	2.9 (15)	6.0 (3)[b]
Si^{31}	0.13 (9)	—
Cl^{39}	8.2 (12)	62 (6)[b]
Cl^{38}	13.3 (5)[c]	54 (6)[b]
Cl^{34m}	0.7 (2)	—

[a] RÖDEL (1963).
[b] PERKINS *et al.* (1965).
[c] Based on the mean activity ratio of Cl^{39}/Cl^{38} (Table 4) and the average concentration of Cl^{39}. Absolute Cl^{38} concentration was determined to be 10.2 dpm/litre in one sample, C-16.

An examination of the results presented in Tables 3 and 4 shows that: (i) Absolute isotope concentrations vary largely between rains, the variations being as large as a factor of 30. In contrast, for the case of long-lived isotopes,
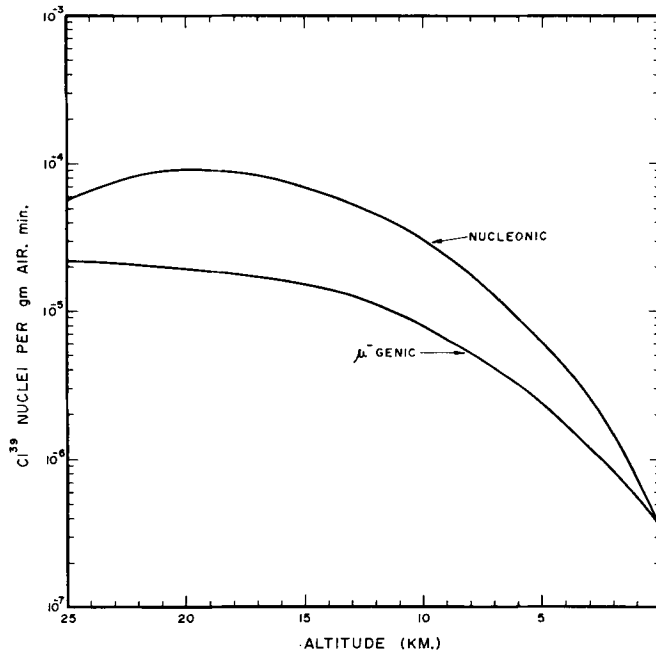

FIG. 5. Calculated rates of production of Cl^{39} due to secondary cosmic ray nucleons and mu-mesons at $\lambda = 20°$ are shown as a function of altitude.

e.g. Be[7], the corresponding variations are much less, factors of 7 (BHANDARI, 1965). (ii) The ratios of isotope concentrations also varies from rain to rain; these variations are however usually much smaller than in absolute concentrations.

To consider the implications of these results, it becomes necessary to consider the production mechanisms of the isotopes under question. The production rate of Cl^{39} due to spallation of atmospheric argon by nucleons (LAL & PETERS, 1962) and negative muon capture in argon (WINSBERG, 1956) have been discussed. The results are presented in Fig. 5 which shows the expected altitude variation in the rate of production of Cl^{39} (nuclei/gm·air·min). In the troposphere, one should also consider the production of isotopes by electromagnetic interactions, mainly due to photons. This effect has been estimated and found to be unimportant compared to the total production by nucleons and muons for all the isotopes studied (BHANDARI & LAL, 1965). The production of Mg^{28}, Na^{24}, Si^{31} and Cl^{34m} does not occur to any appreciable extent by negative mu-capture, as the excitation energy of the target nucleus is not sufficient, being less than 20 MeV. The relative production of S^{38} and Cl^{38} by nucleons and by muons will be essentially similar to the case of Cl^{39} (Fig. 5); absolute rates will, however, be smaller.

From these discussions, it becomes clear that for isotopes with $\Delta A > 4$ ($\Delta A = 40 -$ mass number of isotope), one needs to consider only the nucleon spallation process for their production. For others, variable contributions are expected from negative mu-capture—the highest being for the case of Cl^{39}. At altitudes from where precipitations normally occur, the isotope production increases by a factor of two every 1.5–2 km depending on the radioisotope under question.

For isotopes of half-lives of few hours or less, one may normally expect a secular equilibrium (with local production) to exist in the troposphere. A similar situation may also be expected for the long-lived isotopes Mg^{28} and Na^{24}, unless the vertical mixing occurs on time scales short compared to their half-lives. Since to a first approximation[1] the concentrations

[1] Some fluctuations are expected to arise due to the differences, if any, in the amount of air cleansed per gram of water from rain to rain.
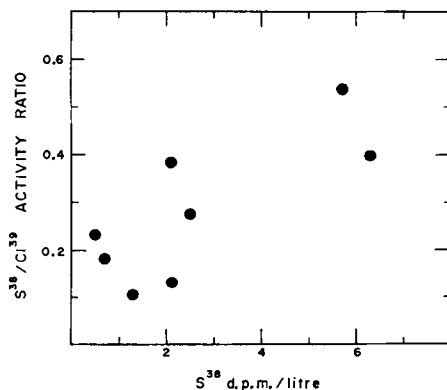

FIG. 6. Observed ratios of S^{38} and Cl^{39} activities are plotted against S^{38} concentrations in individual rains.

in rain are indicative of concentrations in air, one would expect that isotope concentrations in rain be confined to variations in production rate at the precipitating altitude. However, as the observed absolute variations are considerably greater than those expected from changes in the precipitating level (Fig. 5), the data indicate that immediately prior to condensation, appreciable up or down draughts must occur. A more informative study of this can be made from investigations of the changes in the ratios of isotopes. The expectations for any significant air motions occurring prior to condensation are briefly sketched below, on the assumption that before such motions occur all short-lived activities exist in a state of near secular equilibrium with their production.

If air moves down from a high level (where the production rates are also high), in its new environments, the ratio of activities of a *long-lived* and a *short-lived* isotope will at first increase with time due to the preferential decay of the short-lived isotope. (Eventually, the ratio will return to the secular equilibrium value, of course.) On the other hand, if air moves up and mixes with some higher level air which already has attained a secular equilibrium, the ratio will still remain around the secular value. (In the extreme case, however, when ground level air moves to higher levels in the troposphere without undergoing mixing, values lower than the secular equilibrium ratio by factors up to the ratio of their half-lives can be expected.) Thus, on the basis of this simplified

picture, one would expect the activity ratio of a long-lived and a short-lived isotope to be either equal to or higher than the secular equilibrium ratio, the latter situation arising primarily as a result of down movements of air; upward motions not being amenable by the ratio method of study. The distribution of ratios could then be taken as indicative of the time scales involved between the down-draught of air and the removal of activities from it. The available data on S^{38} and Cl^{39} activities permit us to study such "delays" if they occur.

The measured activity ratios, S^{38}/Cl^{39}, range from 0.1–0.5 (Fig. 6). If the model discussed above is applicable one would expect to find a general correlation between the ratios and the absolute activities, since the high ratios should be due to descent of higher level air and thus have relatively higher S^{38} activities. The data clearly support this model and permit us to estimate the magnitude of time delays. The ratio, S^{38}/Cl^{39}, is expected to increase due to decay, by a factor of two every 80 minutes, and delays of up to 3 hr are therefore indicated by the data as S^{38}/Cl^{39} activity ratios vary over a factor of five.

There exist two other mechanisms which may give rise to the observed variations in the S^{38}/Cl^{39} ratios. One of these may be the less efficient (and hence variable) removal of one isotope compared to the other in the rainout process. Such a situation may hold for the pair of isotopes under consideration. Atmospheric Cl^{39} should exist mainly as attached to aerosols. The isotope S^{38}, may exist as S^*O_2 over sufficiently long periods of time before attachment onto aerosols. It is possible that the chief mechanism for the removal of S^{38} is its direct incorporation in the cloud droplets as S^*O_2 (JUNGE & RYAN, 1958; GAMBELL & FISHER, 1964). Our present knowledge on the time scales of attachment and the chemical behaviour of various radioactive species is very limited. A study of the short-lived isotopes investigated in the present work should, in principle, give

answers in this direction. As an illustration, if the isotopes get attached to aerosols soon after their formation, the relative concentrations of isotopes of identical half-life, e.g. S^{38} and Si^{31} should not differ from rain to rain. In the present work the number of S^{38}/Si^{31} ratios measured is too small to draw any conclusions. However, the two accurate ratios determined are 16 and 17 and are thus not inconsistent with the behaviour expected for their rapid and efficient incorporation in cloud droplets.

Alternatively, the observed variations in the ratio of S^{38}/Cl^{39} could arise if the activities spend a considerable time in the cloud after their incorporation in the rain drops. Such a mechanism seems necessary to explain the ratios Bi^{214}/Pb^{214} estimated by BHANDARI & RAMA (1963). They found that in about 20% of the rains, Bi^{214} was not in equilibrium with its parent, Pb^{214} indicating delays of 30 min or more between the removal of radioactivity in the cloud and its arrival at ground.

Thus we see that the study of two groups of short-lived radioisotopes, those produced by cosmic rays and those arising in the decay of radon, shows a great promise for the understanding of the processes occurring prior to and during condensation of moisutre in a precipitating cloud. The data available already indicate that rain drops spend a considerable time in the cloud before precipitation occurs.

Acknowledgements

REFERENCES

AMIN, B. S., KHARKAR, D. P., and LAL, D., 1966, Cosmogenic Be^{10} and Al^{26} in marine sediments. Deep Sea Res. In Press.

BHANDARI, N., and RAMA, 1963, Study of atmospheric washout processes by means of radon decay products. *Jour. Geophys. Res.*, 68, pp. 3823–3826.

BHANDARI, N., 1965, Ph.D. Thesis, University of Bombay.

BHANDARI, N., and LAL, D., 1965, Production of radioisotopes on the earth by cosmic ray muons and photons. Presented at the Cosmic Ray Conference held at London, September 6–16, 1965.

BILLER, W., 1953, Characteristics of Bismuth fission induced by 340 MeV protons (Thesis), UCRL-2067. University of California, Berkeley.

GAMBELL, A. W., and FISHER, D. W., 1964, Occurrence of sulphate and nitrate in rainfall. *Jour. Geophys. Res.*, 69, p. 4203.

JUNGE, C. E., and RYAN, T. G., 1958, Study of SO_2 in solution and its role in atmospheric chemistry. *Quart. J. Roy. Meteorol. Soc.*, 84, p. 46.

LAL, D., and SCHINK, D. R., 1960, *Rev. Sci. Instr.*, 31, pp. 395–398.

LAL, D., and PETERS, B., 1962, Cosmic Ray produced isotopes and their application to problems in geophysics. *Progress in Elementary Particle and Cosmic Ray Physics*, ed. J. G. WILSON and S. A. WOUTHUYSEN (North Holland Publishing Co., Amsterdam) 6, pp. 3–74.

PERKINS, R. W., THOMAS, C. W., HILL, M. W., and NIELSEN, J. M., 1965, Chlorine-38 and Sulfur-38 produced by cosmic radiation. *Nature*, 205, p. 790.

RÖDEL, W., 1963, Sodium-24 produced by cosmic radiation. *Nature*, 200, pp. 999–1000.

WINSBERG, L., 1956, The production of Chlorine-39 in the lower atmosphere by cosmic radiation. *Geochim. et Cosmochim. Acta*, 9, pp. 183–189.

СОДЕРЖАНИЕ В ДОЖДЕ Mg^{28}, Si^{31}, Si^{38}, Cl^{38}, Cl^{34}, ОБРАЗОВАВШИХСЯ ПОД ДЕЙСТВИЕМ КОСМИЧЕСКИХ ЛУЧЕЙ, А ТАКЖЕ ДРУГИХ КОРОТКОЖИВУЩИХ РАДИОАКТИВНЫХ ИЗОТОПОВ

В «свежих» пробах дождевой воды измерялись концентрации семи радиоактивных изотопов, которые вероятно образуются при взаимодействии вторичных космических лучей с ядрами атомов тропосферы. Периоды полураспада этих изотопов лежат между получасом и одними сутками. Обсуждается методика, разработанная для быстрых чувствительных и специфических анализов этих ядер.

Обнаружение двух из этих изотопов: Cl^{39} (период полураспада 55 мин) и Na^{24} (период полураспада 15 час.) доложили раньше Winsberg и Rodel соответственно. Содержание в осадках S^{38} (2,9 часа) i Cl^{38} (37,3 мин) было обнаружено независимо и почти одновременно нами и Perkin'ом со своими сотрудниками. Обнаружение оставшихся трех изотопов: Cl^{34} (32 мин), Si^{31} (2,6 ч) и Mg^{28} публикуется впервые в этой работе.

Обсуждается природа вторичных частиц в космических лучах, производящих эти коротко-живущие радиоактивные ядра. Найдено, что количество образующихся в тропосфере изотопов существенно зависит от высоты; оно увеличивается вдвое через каждые 1,5–2 км в зависимости от вида изотопа. Этот факт совместно с наличием изотопов с различным периодом полураспада от получаса до суток позволяет использовать их для изучения коротковременных тропосферных процессов, например процессов, происходящих до и во время конденсации в дождевых облаках. Обсуждается также приложения полученных данных.