

THE OCCURRENCE OF GALLIUM IN MARINE ORGANISMS

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Little is known about the occurrence of gallium in the biosphere. The first recorded instance of its detection in a living organism is due to Cornec (1919), who detected the element in *Laminaria* sp. Vinogradov (1935) suspected its presence in an undetermined gorgonian, but his statement that Zvinden had detected it in human tissue appears to be an erroneous citation (Hutchinson, 1943). Bertrand (1941) detected the element in oysters, and, after chemical concentration, in human urine.

Noddack & Noddack (1940) have determined gallium spectrographically in nine marine organisms. They found concentrations (expressed as parts per million on the dry weight) ranging from 0.1 p.p.m. in *Squalus acanthias* to 0.7 p.p.m. in the body walls of *Asterias rubens* and *Bryssopsis lyrifera*. The average amount recorded (0.4 p.p.m.) corresponds to a concentration factor over sea water of 16,000 (assuming the gallium concentration of 0.025 $\mu\text{g}/\text{l}$. in sea water, found by Burton, Culkin & Riley, 1958). The element has also been detected in *Lycopodium flabelliforme* (0.1 p.p.m.) and *Mitchella repens* (0.1-0.2 p.p.m.) (Hutchinson & Wollack, 1943); in ambergris (Ishiguro, Koga & Matsuo, 1952); in the outer layers of some seeds and fruits, and in several species of beetles (Bergman, Borovik & Borovik-Romanova, 1943; Borovik & Borovik-Romanova, 1944, 1949). From these investigations the concentration of gallium in living organisms appears to be about $n \times 10^{-5}\%$.

The biological role of gallium has been the subject of several investigations. Steinberg (1938, 1939*a, b*; 1941) has found that trace amounts of gallium are necessary for the growth of *Aspergillus niger* and *Lemna minor* in sterile medium. More recent investigations by Bertrand (1954) are, however, at variance with these conclusions. G. A. Riley (1943) has reported that in nutrient deficient culture the growth of the marine diatom, *Nitzschia closterium**, is stimulated by gallium, but that this effect disappeared when nitrate and phosphate were present. No definite conclusions can be drawn from this study since no control experiments were made omitting gallium alone. Hewitt & Bolle-Jones (1952) have found no evidence that gallium is an essential micronutrient for the growth of tomato, lettuce or sugar beet. Bardet, Levaditi, Tchakirian & Vaisman (1931) have studied the distribution of gallium in the organs of rabbits given gallium tartrate in their diet.

* i.e., *Phaeodactylum tricorutum*.

In a review article on the biogeochemistry of aluminium and some other elements of Groups III*a* and III*b* of the Periodic Table, Hutchinson (1943) has pointed out that in many of its properties (gallous and gallic salts, complex cyanides) gallium shows a greater resemblance to iron than to aluminium. He concluded that it might play a part in metabolism similar to iron, but on a restricted scale. Gallium deficiencies are only likely to occur rarely, since few silicate rocks or soils contain less than 5 p.p.m. of the element.

Specific spectrophotometric methods for the determination of gallium in silicates and other minerals have been developed recently (Onishi & Sandell, 1955; Culkin & Riley, 1958). These procedures have sensitivities sufficiently high to allow the estimation of less than 0.1 p.p.m. of gallium using samples weighing less than 5 g. Using a modification of these methods, a study has been made of the distribution of the element in several marine organisms, derived mainly from the Irish Sea and the shores of the Isle of Man. In several of the samples the concentrations of iron, copper and aluminium have also been determined for comparison.

METHODS

Determination of gallium in marine organisms and shells

Reagents

- (1) 7.5 N nitric acid.
- (2) Perchloric acid, 60% (w/w).
- (3) Titanous chloride solution, 15% (w/v).
- (4) Di-*iso*-propyl ether. Freshly distilled from sodium hydroxide.
- (5) Hydrochloric acid (6.5 N) containing 1% titanous chloride. Concentrated hydrochloric acid (s.g. 1.16, 325 ml.) was mixed with 33 ml. of 15% titanous chloride solution and diluted to 500 ml.
- (6) Rhodamine B solution. A solution was prepared containing 0.5 g of Rhodamine B in 100 ml. of water. The solution was filtered before use.
- (7) Carbon tetrachloride-chlorobenzene solvent. Carbon tetrachloride (125 ml.) was diluted to 500 ml. with chlorobenzene.
- (8) Standard gallium solution (5 µg/ml.) was prepared by dissolving 0.0438 g of caesium gallium sulphate in water and diluting to 1 l.

Solution of samples of shells (carbonates)

The weighed sample (5–10 g) was placed in a 250 ml. conical flask and 50 ml. of 7.5 N nitric acid was gradually added. After effervescence had ceased, the flask was heated gently on a hot-plate for 30 min, and the nitric acid was then evaporated. The residue was twice evaporated to dryness with 5–10 ml. of hydrochloric acid, to remove the nitrate, and dissolved in 50 ml. of 6.5 N hydrochloric acid containing 1% of titanous chloride.

Solution of samples of marine organisms

The weighed sample (up to 5 g, dried at 110° C) was placed in a 250 ml. conical flask, and 25 ml. of 7.5 N nitric acid was added. The flask was closed with a small funnel and its contents were allowed to digest in the cold until all foaming had

ceased. The nitric acid was then removed by cautious evaporation on the hot plate. Repeated evaporations with 15 ml. portions of concentrated nitric acid were then carried out until all carbonaceous material was removed. The white or pale yellow residue was treated with 2 ml. of 60% (w/w) perchloric acid and fumed to dryness. It was fumed to dryness again after addition of 2 ml. of concentrated sulphuric acid, and dissolved in 50 ml. of 6.5 N hydrochloric acid containing 1% of titanous chloride.

Extraction of gallium

The solution of the sample was transferred to a 250 ml. separating funnel, and, if it was not violet in colour, an excess of 15% titanous chloride was added. Two extractions with 30 ml. portions of di-*iso*-propyl ether were carried out and the combined extracts were evaporated in a beaker on the water bath.

Photometric determination of gallium

The residue in the beaker was dissolved by warming to 70–80° with 5 ml. of 6.5 N hydrochloric acid containing 1% titanous chloride. The cold solution was transferred to a 50 ml. separating funnel containing 8 ml. of chlorobenzene-carbon tetrachloride solvent. The beaker was rinsed with a further 1 ml. of 6.5 N hydrochloric acid and the washings added to the funnel. Rhodamine B solution (0.5 ml.) was added and the separating funnel was shaken mechanically for 10 min. After the two phases had separated, the organic phase was run through a plug of glass wool into a 10 ml. calibrated flask containing 1 ml. of ethyl alcohol. The aqueous phase was washed with a further 1 ml. of the solvent and the washings added to the calibrated flask, which was then filled to the mark with the solvent. The optical density of the solution was measured at 562 $m\mu$ in a 1 cm cell. The reagent blank was determined in the same manner but omitting the sample. The method was calibrated using 1, 2, 4, 6, 8 and 10 μg of gallium. It was found that 5 μg of gallium gave an optical density of 0.565 at 562 $m\mu$ in a 1 cm cell. Recoveries of gallium added to biological samples averaged 98%.

Determination of sulphated ash, iron, aluminium and copper

The dried (110° C) sample (1 g) was weighed into a 25 ml. platinum crucible and allowed to stand for a few hours with *ca.* 5 ml. of concentrated nitric acid and 2 ml. of perchloric acid. The crucible was then carefully heated on a water bath until the nitric acid had evaporated. The evaporation with concentrated nitric acid was repeated until all organic matter had been destroyed. The perchloric acid was then fumed off under an infra-red heater, 2 ml. of concentrated sulphuric acid was added and the heating was continued until no further fumes were evolved. The contents of the crucible were treated with 2 g of powdered ammonium carbonate and heated at 450° C. in a muffle furnace for 30 min. The crucible was allowed to cool in the desiccator and weighed.

The sulphated ash was treated with 2 ml. of concentrated hydrochloric acid and 15 ml. of water and heated on the water bath; the resultant solution was filtered into a 250 ml. graduated flask. The residue (if any) in the crucible was washed well with hot water and the washings added to the graduated flask. The solution was diluted to volume and used for the spectrophotometric estimation of iron and aluminium as described by Riley (1958), and for copper as described by Riley and Sinhaseni (1958).

OBSERVATIONS

The composition of marine organisms

Gallium, aluminium, iron and copper have been determined in a number of marine plants and animals which were obtained mainly from the Irish Sea off Port Erin and Port St Mary. Unless otherwise stated the analyses were carried out on the whole organism, which had been washed thoroughly with distilled water and dried at 110° C. In addition, the distribution of gallium and copper in certain organs of *Buccinum undatum* L., *Chlamys opercularis* (L.), *Porania pulvillus* (Müll.) and *Pecten maximus* (L.) has been studied. Specimens of *Pecten maximus* were analysed directly after removal from their habitat and also after being allowed to purge themselves in clean sea water for 7 days. The results of the analyses are shown in Tables 1-6.

TABLE 1. OCCURRENCE OF GALLIUM, ALUMINIUM, IRON AND COPPER IN MARINE ALGAE

Organism	Ash (%)	Ga (μg/g)	Cu (μg/g)	Al (μg/g)	Fe (μg/g)	Ga/Al × 10 ⁴	Ga/Fe × 10 ⁴	Ga in ash (μg/g)
CHLOROPHYCEAE								
Codiaceae								
<i>Codium</i> sp.	56.2	0.16	85.5	1336	470	1.2	3.4	0.3
<i>Halimeda gracilis</i>	123	0.05	22.5	143	342	3.5	1.5	0.04
PHAEOPHYCEAE								
Fucaceae								
<i>Ascophyllum nodosum</i>	22.1	0.06	6.2	83.4	61.4	7.2	9.8	0.3
<i>Fucus serratus</i>	30.6	0.03	5.6	101	153.7	3.0	2.0	0.1
<i>F. spiralis</i>	9.2	0.01	15.0	34.4	33.9	2.9	3.0	0.1
<i>F. vesiculosus</i>	24.8	0.03	18.0	51.4	36.4	5.8	8.2	0.1
<i>Pelvetia canaliculata</i>	24.2	0.10	17.9	372	120.8	2.7	8.2	0.4
Laminariaceae								
<i>Laminaria digitata</i>	37.5	0.07	6.2	101	40.9	7.0	17	0.2
RHODOPHYCEAE								
Corallinaceae								
<i>Corallina officinalis</i>	114	0.56	44.7	4420	4680	1.3	1.2	0.5
<i>Lithothamnion</i> sp.	113	0.53	15.7	3570	3420	1.5	1.5	0.5
<i>Lithophyllum</i> sp.	121	0.23	18.1	243	374	1.0	0.6	0.2
Gigartinaeae								
<i>Gigartina stellata</i>	16.7	0.02	32.8	94.8	102	2.1	2.0	0.1
Rhodomelaceae								
<i>Polysiphonia lanosa</i>	24.9	0.19	41	478	493	4.0	2.6	0.8
Rhodymeniaceae								
<i>Rhodymenia palmata</i>	117	0.04	24.4	175	252	2.3	1.6	0.03

The range of gallium concentrations found for the various whole organisms was 0.01-0.96 p.p.m., which is in good agreement with the data for nine marine animals, published by Noddack & Noddack (1940) (0.1-0.7 p.p.m.). Hutchinson (1943) has deduced from the Noddacks' results that gallium is concentrated biologically from sea water to a greater extent than aluminium. This conclusion must be reconsidered in the light of more recent determinations of both aluminium and gallium in sea water. Greenhalgh & Riley (unpublished work) have found aluminium concentrations of *ca.* 10 μg/l. in the

TABLE 2. OCCURRENCE OF GALLIUM, ALUMINIUM, IRON AND COPPER IN MARINE ANIMALS

Organism	Ash (%)	Ga ($\mu\text{g/g}$)	Cu ($\mu\text{g/g}$)	Al ($\mu\text{g/g}$)	Fe ($\mu\text{g/g}$)	Ga/Al $\times 10^4$	Ga/Fe $\times 10^4$	Ga in ash ($\mu\text{g/g}$)
PROTOZOA								
Foraminifera								
<i>Ramulina</i> sp.	116	0.18	111	973	1148	1.9	1.6	0.2
PORIFERA								
<i>Halichondria panicea</i>	88.7	0.93	59.5	3700	4040	2.5	2.3	1.1
COELENTERATA								
<i>Alcyonium digitatum</i>	69.0	0.05	61.5	435	438	1.2	1.1	0.1
CRUSTACEA								
Cirripedia								
<i>Balanus balanoides</i>	120	0.07	28.7	240	146	2.9	4.8	0.05
Decapoda								
<i>Cancer pagurus</i>	79.0	0.03	35.0	166	157	1.8	1.9	0.04
<i>Corystes cassioe-lanus</i>	71.6	0.36	—	1041	1045	3.5	3.4	0.5
MOLLUSCA								
(Shells only)								
Lamellibranchia								
<i>Mytilus edulis</i>	—	0.010	2.1	38	41	2.6	2.4	0.01
<i>Pecten maximus</i>	—	0.008	6.0	81	118	1.0	0.7	0.01
<i>Chlamys opercularis</i>	—	0.069	3.8	174	239	4.0	2.8	0.07
Gastropoda								
<i>Buccinum undatum</i>	—	0.036	1.6	76	85	4.7	4.2	0.04
<i>Littorina littorea</i>	—	0.011	5.2	32	45	3.4	2.4	0.01
<i>Gibbula umbilicalis</i>	—	0.014	7.9	48	51	2.9	2.7	0.01
MOLLUSCA								
(Soft parts)								
Lamellibranchia								
<i>Mytilus edulis</i>	15.8	0.16	53.7	465	325	3.4	4.9	1.0
<i>Pecten maximus</i>				See Table VI.				
<i>Chlamys opercularis</i>	15.7	0.05	37.1	186	1093	2.7	0.5	0.3
Gastropoda								
<i>Buccinum undatum</i>	8.8	0.007	53.5	198	86	0.35	0.8	0.08
<i>Littorina littorea</i>	12.9	0.06	50.2	198	171	3.0	3.5	0.5
<i>L. littoralis</i>	9.0	0.05	102	238	229	2.1	2.2	0.5
<i>Patella vulgata</i>	17.7	0.04	—	346	1415	1.2	0.3	0.2
ECHINODERMATA								
Asteroidea								
<i>Asterias rubens</i>	49.2	0.10	34.7	159	332	6.3	3.0	0.2
<i>Henricia sanguinolenta</i>	70.5	0.05	20.4	652	925	0.8	0.5	0.1
<i>Luidia ciliaris</i>	42.6	0.03	59.0	152	149	2.0	2.0	0.1
<i>Marthasterias glacialis</i>	64.5	0.02	37.7	142	186	1.4	1.1	0.03
<i>Porania pulvillus</i>	65.2	0.11	90.0	365	457	3.0	2.4	0.2
<i>Stichastrella rosea</i>	88.5	0.10	35.0	263	271	3.8	3.7	0.1
Echinoidea								
<i>Echinus esculentus</i>	111	0.03	76.0	597	597	5.0	5.0	0.03
<i>Spatangus purpureus</i>								
Whole organism	122	0.35	36.9	1830	1700	1.9	2.1	0.3
— gut								
Gut + contents	124	3.7	31.6	16,480	14,800	2.2	2.5	3.0
Ophiuroidea								
<i>Ophiocoma nigra</i>	105	0.09	29.5	894	1600	1.0	0.6	0.1

TABLE 3. DISTRIBUTION OF GALLIUM, ALUMINIUM, IRON AND COPPER IN *CHLAMYS OPERCULARIS*

Organ	Ash (%)	Ga ($\mu\text{g/g}$)	Cu ($\mu\text{g/g}$)	Al ($\mu\text{g/g}$)	Fe ($\mu\text{g/g}$)	Ga/Al $\times 10^4$	Ga/Fe $\times 10^4$	Ga in ash ($\mu\text{g/g}$)
Shell	—	0.07	3.8	174	239	4.0	2.9	0.07
Muscle	6.5	0.06	47.9	773	52.8	0.8	1.1	1.0
Gonad	10.4	0.06	—	—	—	—	—	0.6
Mantle and viscera	21.6	0.55	1150	3420	2720	1.6	2.0	2.5

TABLE 4. DISTRIBUTION OF GALLIUM AND COPPER IN *BUCCINUM UNDATUM*

	Mantle	Operculum	Digestive gland	Digestive tract	Mucous gland	Foot	Female ducts	Male ducts
Sulphated ash (%)	5.0	3.7	4.1	5.7	20.4	4.1	3.3	5.9
Ga ($\mu\text{g/g}$)	<0.01	<0.01	0.014	<0.01	<0.01	<0.01	<0.01	—
Cu ($\mu\text{g/g}$)	33.4	25.7	80.4	29.2	26.9	2.5	13.7	28.8
Ga in ash ($\mu\text{g/g}$)	<0.2	<0.3	0.28	<0.2	<0.05	<0.25	<0.3	—
	Renal organ	Female gonads	Ctenidium	Heart				
Sulphated ash (%)	10.0	2.1	10.9	5.4				
Ga ($\mu\text{g/g}$)	—	—	—	—				
Cu ($\mu\text{g/g}$)	30.0	27.7	50.3	87.0				
Ga in ash ($\mu\text{g/g}$)	—	—	—	—				

TABLE 5. DISTRIBUTION OF GALLIUM IN *PORANIA PULVILLUS*

	Skin	Digestive gland	Stomach + oral region	Skin from aboral region
Sulphated ash (%)	—	11.3	95	60.4
Ga ($\mu\text{g/g}$)	0.5	0.02	0.20	0.09
Ga in ash ($\mu\text{g/g}$)	—	0.18	0.21	0.15

TABLE 6. DISTRIBUTION OF GALLIUM, ALUMINIUM, IRON AND COPPER IN *PECTEN MAXIMUS*

Unpurged	Full gonad	Spent gonad	Striped muscle	Unstriped muscle	Mantle	Digestive gland	Gonad + gut	Mantle + gut + digestive gland
Sulphated ash (%)	10.7	3.2	6.0	4.7	13.3	7.2	12.6	13.9
Ga ($\mu\text{g/g}$)	<0.01	0.009	<0.01	<0.01	<0.01	0.79	0.29	0.30
Al ($\mu\text{g/g}$)	—	—	86.6	—	161	454	833	842
Fe ($\mu\text{g/g}$)	—	—	167	—	189	841	1552	766
Cu ($\mu\text{g/g}$)	—	25.2	4.0	—	—	153	—	50.8
Ga in ash ($\mu\text{g/g}$)	<0.1	0.28	<0.2	<0.2	<0.1	11.0	2.3	2.2
Purged	Gills	Male gonad	Female gonad	Striped muscle	Gut + digestive gland	Mantle		
Sulphated ash (%)	25.0	3.0	10.2	12.7	10.9	9.4		
Ga ($\mu\text{g/g}$)	0.14	0.034	<0.01	<0.01	0.011	0.01		
Cu ($\mu\text{g/g}$)	6.3	11.3	26.6	7.5	70.9	10.2		
Ga in ash ($\mu\text{g/g}$)	0.56	1.1	<0.1	<0.1	1.0	<0.1		

Irish Sea and English Channel; Monaghan, Simons & Taggart (1953) have detected similar amounts in the Atlantic Ocean and in the waters of the Gulf of Mexico. These amounts are approximately two orders of magnitude less than earlier work had indicated (cf. Richards, 1957). Assuming an aluminium content of $10 \mu\text{g/l.}$ and a gallium content of $0.025 \mu\text{g/l.}$ (Burton, Culkin & Riley, 1958), the Ga:Al ratio in sea water is 25×10^{-4} . The average Ga:Al ratio in the lithosphere is *ca.* 2×10^{-4} , which shows that sea water is enriched approximately tenfold in gallium relative to aluminium compared with the lithosphere.

The average value of the Ga:Al ratio for the marine organisms examined in this paper was $2-3 \times 10^{-4}$, which is very similar to the average ratio for the lithosphere (*ca.* 2×10^{-4}). Since the majority of the specimens examined were either bottom-living or from shallow water it seems very probable that most of their aluminium and gallium was derived from the bottom muds rather than from the sea water itself. The actual range found for the Ga:Al ratio is small ($1-7 \times 10^{-4}$). This suggests that there is no significant biological separation of gallium from aluminium in the specimens examined, if allowance is made for variations in the Ga and Al contents of the muds in the various localities in which they lived.

The iron content of the organisms is generally similar to their aluminium content, but the Ga:Fe ratio shows rather greater variations than the Ga:Al ratio. The variation in the iron concentration is probably related to its role as an essential trace element in biological systems.

There is apparently no relationship between species and their contents of gallium, iron, aluminium or copper. The low concentrations of these elements found in the calcareous shells of molluscs suggests that the mechanism by which the calcium of sea water is converted into calcium carbonate is quite selective for calcium. The gallium contents of the shells are similar to those of carbonate rocks (Culkin & Riley, unpublished). All four elements are concentrated in the digestive glands and viscera of the molluscs, but it seems probable that the gallium, aluminium and iron contents of these organisms are associated with ingested detritus. This is confirmed by the low concentrations of these elements present in the gut and digestive glands of *Pecten maximus* specimens, which had been allowed to purge themselves in filtered sea water for 7 days. The copper contents of the purged and unpurged specimens were similar, and it is probable that the copper in them is mainly adsorbed on to the mucous surfaces.

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SUMMARY

A spectrophotometric method has been developed for the determination of submicrogram amounts of gallium in biological materials. Using this procedure a study has been made of the occurrence of gallium in a number of marine plants and animals (dried at 110° C). Data are also presented for the concentrations of iron, aluminium and copper in the same samples.

The gallium content of the samples ranged from *ca.* 0.01 to 0.96 p.p.m. The Ga:Al ratio varied from $1-7 \times 10^{-4}$ (average $2-3 \times 10^{-4}$), which compares well with the average Ga:Al ratio of the lithosphere, and contrasts with the ratio of 25×10^{-4} for sea water. It seems likely that the organisms examined derived their gallium, aluminium and iron from the bottom muds rather than from the sea water. There is no evidence of selective uptake of gallium in preference to aluminium. Iron and aluminium were generally present in roughly equal amounts.

The distribution of gallium in the various organs of *Pecten maximus*, *Buccinum undatum*, *Chlamys opercularis* and *Porania pulvillus*, has been investigated. Most of the tissues of these molluscs contain less than 0.07 p.p.m. of gallium, but the viscera and digestive organs contain higher concentrations, presumably contained in ingested inorganic material. The average gallium content of carbonate shells is 0.02 p.p.m.

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