NOTE ON THE FLUORINE CONTENT OF ROCKS AND OCEAN-BOTTOM SAMPLES.[1]

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ABSTRACT. There has been little information about the amounts of fluorine present in rocks, the lack of data being due to the unreliable analytical methods available. The Willard and Winter procedure furnishes an easy and surprisingly accurate method for fluorine determination. This report shows that instead of being a very minor constituent of rocks, fluorine is present in about the same amount as chlorine and must be considered in rock analyses. A tentative average value of about 0.04 per cent is suggested and some indications point to regional concentrations. Ocean-bottom samples contain about the same quantities as the rock. In both rocks and ocean-bottom samples the fluorine varies with the nature of the material.

LECTURES in elementary mineralogy always stress the importance of mineralizers and among these fluorine is given a prominent place. If the student is curious he notices in time that fluorine is not a constituent of most of the rock-forming minerals and indeed is seldom mentioned in analyses of rocks. In such analyses chlorine is frequently reported but fluorine almost never. But if fluorine is an important constituent of magmas one would expect to find it concentrated in rock selvages, in metamorphic rocks, and especially in country rock invaded by magmas. Obsidians, whether conceived as the result of crystallization differentiation or as the result of the remelting of acid rocks by reactivated volatiles, should be rich in this element. The chemist would expect fluorine to be caught and held especially by limestones and shales resulting from weathering.

When, however, one looks through Washington's *Chemical Analyses of Igneous Rocks* he finds the element seldom reported, and Clarke,[2] who estimates chlorine to constitute about 0.07 per cent of the earth's crust, estimates, on very scanty data, fluorine at about one-third the chlorine, i.e. 0.02 per cent. Indeed he omits fluorine from his estimate of the composition

[1] A brief treatment of this subject was presented at the meeting of the International Volcanological Association held in Washington, D. C., September 1939, and has been sent to the Bulletin volcanologique for publication.

[2] Clarke, F. W.: The Data of Geochemistry, U. S. Geol. Surv., Bull. 695, 1920.

of the ocean.[3] Although the analytical record implied that fluorine was usually absent or minimal in rocks, the volcanologists have reported quite otherwise. Incrustations containing this element are frequently reported in the literature. In the most complete study thus far made, Zies[4] found evidence for the exhalation of almost incredible amounts of fluorine from that Alaskan region. We are wholly ignorant of the origin and ultimate destination of the fluorine observed. This ignorance is due to the lack of any reliable method for determining fluorine in small amounts. Not that there has been any lack of methods described in the literature. There are many, and one is tempted to say that each is worse than the other. The majority were never tested beyond taking a known quantity of an alkali fluoride and then keeping after it until the weights came right. In many cases a special providence must have presided over the tests.

In 1933 Willard and Winter[5] published their method for determining fluorine which found immediate favor and has led to more definite information about fluorine than all the preceding efforts. These authors started with the familiar fusion and leaching, and after suitable purification of the leachings volatilized the fluorine as fluosilicic acid, by distilling off at 140° C.[6] Following De Boer and his successors, the authors finally titrated the fluorine with standard thorium nitrate, using alizarine as indicator. This method is reliable and with very careful work capable of surprising accuracy. It is readily capable of an accuracy of ± 0.001 per cent on a two-gram sample of rock in the absence of appreciable amounts of boron. It is able to show small differences in concentration in different parts of the same rock and is easily capable of an accuracy of ± 0.01 per cent without undue precautions. For rock analysis this is a most unusual precision. For this reason we believe that the differences in any one of our series, such as the Little Glass Mountain, Mt. Pelée, and Mauna Loa data, may well be real.

[3] Recent determinations (Thompson, T. G., and Taylor, H. J.: Ind. Eng. Chem., anal. ed. 5, 87-89, 1933) find fluorine to be present in sea water to the extent of about 1 mg. per liter.

[4] Zies, E. G.: The Valley of Ten Thousand Smokes, Nat. Geogr. Soc., Contrib. Tech. Papers, Katmai series No. 4, 79 pp., 1929.

[5] Willard, H. H., and Winter, O. B.: Volumetric method for determination of fluorine, Ind. Eng. Chem., anal. ed., 5, 7-10, 1933.

[6] This reaction and the stability of the fluosilicic acid in the presence of water vapor at low temperatures is not without interest to the geologist.

Until we have many more analyses as a basis, the terms high or low fluorine content must be regarded as tentative. But it may help the reader in looking over Table I if we set an arbitrary standard. Thus we select two "normal" rocks, the granite from Stone Mountain, Georgia (No. 60)[7] and the diabase from Granton, New Jersey (No. 71). The granite shows 0.039 per cent fluorine, and the diabase, 0.026 per cent. Both of these rocks would be classed as normal, fresh rocks by the petrologist. The granite shows 0.01 per cent more fluorine than the diabase, as might be expected from the muscovite content. There is a very slight sericitization of the diabase which should make it run a little high. With these figures in mind we may turn to Table I.

TABLE I.

Fluorine Concentration in Various Rocks.

Eruptives.

No.		% F.
1	Obsidian, Coso Mts., Calif. (Cl=0.08%)	0.121
2	Obsidian, Coso Mts. (not same as No. 1)	0.095
3	Obsidian, Coso Mts. (glass surrounding spherulite)	0.094
4	Crystalline kernel of No. 3	0.078
5	Obsidian, Newberry Volcano, Oregon (No. 75, HLW)	0.064
6	Obsidian, Mono Lake, Calif. (Cl=0.13%)	0.062
7	Obsidian, Mt. Morrison Area, Calif. (Cl=0.11%)	0.064
8	Little Glass Mt., Calif. (dense glass) (Cl=0.03%)	0.049
9	Little Glass Mt., Calif., Type 2 (Cl=0.08%)	0.054
10	Little Glass Mt., Calif., Type 3, more vesicles (Cl=0.09%)	0.050
11	Little Glass Mt., Calif., Type 4a (Cl=0.09%)	0.048
11a	Little Glass Mt., Calif., Type 4	0.047
12	Little Glass Mt., Calif., Type 5 (Cl=0.07%)	0.034
13	Little Glass Mt., Calif., Type 6, pumice (Cl=0.07%)	0.035
14	Black glass, Cerro Noagua, New Mexico (Cl=0.06%)	0.062
15	White pitchstone, Cerro Noagua (Cl=0.08%)	0.152
	Average	0.070

[7] Our selection of the Stone Mountain granite as typical has been criticized on the ground that the mass is shot through with veins which contain tourmaline, etc. The block which we have used as a standard is not only normal but free from alteration. The criticism is sound if we can find other normal granites free from such pegmatites and from alteration. At this time we use the Stone Mountain granite as a norm until the work shall have gone far enough to include many other granites. We let the figure stand until we are in position to reach a definite average value. Several other granites have been suggested but thus far all have failed to meet the standard in one detail or another.

Lava Flows.

No.		% F.
16	New Cone, No. 6, Mt. Pelée, Martinique (Cl=0.02%)	0.008
17	Breadcrust, No. 7, Mt. Pelée, Martinique (Cl=0.09%)	0.009
18	Spine, 1902, No. 5, Mt. Pelée, Martinique (Cl=0.02%)	0.008
19	Mauna Loa, summit spatters, 1926 (Cl=0.01%)	0.007
20	Mauna Loa, 1926 flow, 7500′ elevation (Cl=0.01%)	0.009
21	Mt. Erebus, Antarctica, edge of crater, 1908	0.064
22	Lassen Peak, Calif., No. 35	0.023
23	Lassen Peak, Calif., No. 21	0.009
24	Cinder Cone, quartz basalt	0.008
	Average	0.010

Italian Group.

25	Aetna, 1910 flow	0.063
26	Aetna, 1669 flow	0.035
27	Obsidian, Lipari	0.096
28	Stromboli, 1912	0.036
	Average	0.057

29	Iceland, dike selvage, Hawkes No. 391	0.156
30	Iceland, altered dike, Hawkes No. 238	0.338

African Rift Area, N. L. Bowen.

31	No. 253	0.065
32	No. 231	0.141
33	Obsidian, Naivasha	0.685
34	Selvage No. 116	0.204
35	No. 117	0.028
36	Leucite nephrite, No. 120, N. Kivu	0.159
37	Entrance Njarowa Gorge, No. 246	0.414
38	1 km. inside Njarowa Gorge, No. 247	0.279
39	Glass from Eburra, No. 230	0.172
40	No. 248	0.280
41	Quartz trachyte, No. 234	0.225
42	Phonolite, No. 243	0.088
43	Phonolite trachyte, No. 303	0.113
44	Phonolite, No. 235	0.103
45	Phonolite pitchstone	0.149
	Average	0.207

Katmai Area, C. N. Fenner's Collection.

46	Rhyolite, altered old rock, Novarupta	0.017
47	Much altered old rock, A-415	0.015
48	Altered basic inclusion, A-380	0.061
49	Old rock, Falling Mt., corroded by fumaroles	0.007
50	Basic inclusion, Novarupta, A-383	0.010
	Average	0.021

Yellowstone Park, Fenner.

No.		% F.
51	Basalt-rhyolite mixture, No. 537	0.035
52	Basalt-rhyolite mixture, No. 415	0.022
53	Rhyolite, vesicles with tridymite	0.012
	Average	0.023
54	Crystalline striae, Obsidian Cliff	0.122
55	Glass between striae of No. 54 (Cl=0.05%)	0.152
	Average	0.137

Miscellaneous Rocks and Plutonics.

56	Biotite (NLB)	0.214
57	Grünerite, Lockport, N. Y. (NLB)	0.010
58	Hedenbergite	0.000
59	Serpentine, Oregon	0.012
60	Granite, Stone Mt., Georgia (Cl=0.03%)	0.039
61	Marvine laccolite, Henry Mts., Utah (Cl=0.02%)	0.062
62	Baked shale adjacent to No. 61	0.029
Shonkin Sag, Montana:		
63	Shonkinite	0.141
64	Syenite	0.227
65	Coarse transition phase	0.178
66	Shonkinite, dark portion	0.206
67	Shonkinite, light portion	0.054
68	Adinole from beneath the laccolite	0.021
69	Sedimentary splinter caught up into the mass	0.233
70	Basic inclusion, S. Bernardino Mt., Calif.	0.029
71	Diabase, Granton, New Jersey (Cl=0.03%)	0.026
72	Basalt flow, Mt. Morrison Quadrangle, Calif. (Cl=0.01, P_2O_5=0.80%)	0.106

Sedimentaries.

73	Slate, Rochester, New York	0.109
74	Fossiliferous limestone, Maryland	0.023
74a	Fossiliferous limestone, Maryland	0.021
75	Arenaceous shale, New York	0.024
76	Calcareous shale, New York	0.025
77	Shale, Maryland	0.033
78	Argillaceous limestone	0.037
	Average	0.027

The rocks analyzed are listed in Table I and are arranged in arbitrary groups which follow more or less the silica con-

tent. The first group (Nos. 1 to 15) consists of obsidians from the western United States, mostly dense black glasses with few or no phenocrysts. The series from Little Glass Mountain is in order increasingly vesiculated, running all the way from dense glass to pumice.

For the whole group the average fluorine content is 0.07 per cent. If we omit Nos. 8 to 13, which show a decrease of fluorine more or less in the order of vesicularity and in which the last members approach the figure found for fresh lavas, the average fluorine concentration rises to 0.084 per cent. If further we include Nos. 54 and 55 from Yellowstone Park this average reaches F = 0.098 per cent. The actual figures are not important but the tendency is definitely toward a fluorine concentration of 0.100 per cent for obsidians.

The second group of lavas, Nos. 16 to 24, including fresh lavas from both Mt. Pelée and Mauna Loa, shows a surprisingly low fluorine content averaging only 0.010 per cent. This may be compared with Fenner's Katmai material, Nos. 46 to 50, where Zies has reported great quantities of fluorine being evolved. Evidently at the temperatures involved, say about 1000° C., the fluorine escapes readily, if present. This is in line with the behavior of the Little Glass Mountain results.

The Italian group, Nos. 25 to 28, runs comparatively high in fluorine, the average 0.057 per cent suggesting a possible local concentration.

Dr. N. L. Bowen kindly supplied a number of samples from his African Rift collection, Nos. 31 to 45. These run uniformly high with an average of 0.207 per cent and with one, No. 33, a dense black glass taken from a very large mass yielding nearly 0.7 per cent fluorine, the highest we have yet found in any rock. Of passing interest are Nos. 37 and 38. The first was taken from the outer portion of a flow, while the second was from one kilometer inside the mass. This might indicate a concentration in the outer and more rapidly cooled portion of the mass, though a positive statement is surely not warranted.

Dr. L. Hawkes furnished two specimens from his Icelandic collection, Nos. 28 and 29, where the altered dike shows much more fluorine than the selvage and both show a very high fluorine content.

Dr. C. N. Fenner supplied specimens from Yellowstone Park. These were collected where a basalt had reacted with a later

rhyolite.[8] There was the possibility that fluorine might have been active here and some of it might have been retained. It will be seen that no excessive fluorine remains if any was present.

Continuing the search, we examined several chance specimens in which fluorine might be expected. Thus from the outer region of the Marvine laccolite, Henry Mountains, Utah, we tested No. 61. This would represent the somewhat chilled phase of the intrusion. It does seem a little high in fluorine—0.062 per cent. The baked shale nearby (No. 62) yielded only 0.029 per cent. The Shonkin Sag laccolite, Montana (Nos. 63 to 69) is, of course, a different type of rock and carries more fluorine, the highest being the syenite with 0.227 per cent while the outer mantle, shonkinite, carries least, 0.141 per cent, with the coarse transition material lying in between, 0.178 per cent. A specimen of adinole from beneath the mass gave 0.021 per cent and a sedimentary splinter which had been caught up into the mass of the laccolite near the base and greatly altered gave 0.233 per cent or about the same as the syenite. Dr. H. E. Merwin kindly separated the shonkinite into the dark and light portions where we found that the fluorine was largely in the darker portion.

The writer had the notion that if fluorine is active in the reworking of rocks, as for example by an invading magma, then the partly altered inclusions might catch and hold a slight excess of the element. This is not confirmed by any of the analyses thus far made. A similar guess touching the lithophysae, Nos. 3 and 4, and the crystalline and glassy layers in the Yellowstone Park Obsidian Cliff, Nos. 54 and 55, was, if anything, quite the reverse of the expected.

Dr. C. M. Gilbert supplied an unusual basalt from California. This rock was peculiar in appearance, contained an unusual amount of apatite (P_2O_5 = 0.80 per cent), and for a basalt much fluorine, 0.106 per cent, as compared with the Mauna Loa basalt Nos. 19 and 20.

Since the igneous rocks tested showed much more fluorine than had formerly been supposed, it seemed better to test also a few sedimentaries to see whether they would indicate the fate of fluorine leached out of rocks by weathering. Thus Nos. 74 to 78 show an average fluorine content of 0.027 per cent. Evi-

[8] Fenner, C. N.: Contact relations between rhyolite and basalt on Gardiner River, Bull. Geol. Soc. Am., 49, 1441-1484, 1938.

dently the fluorine is not hiding here. No. 73, a slate, with 0.109 per cent should be followed up further. Many more determinations made on sedimentary rocks will be necessary but it is interesting to compare these with the ocean-bottom samples of Table II.

TABLE II.

Ocean-Bottom Samples.

Collected by the *Carnegie*.

Carnegie Station	Type of sediment	% F
6	terrigenous	0.053
43	globigerina ooze	0.028
44	globigerina ooze	0.033
51	globigerina ooze	0.054
60	globigerina ooze	0.035
62	globigerina ooze	0.033
67	globigerina ooze	0.032
113	terrigenous	0.029
116	terrigenous	0.020
117	red clay	0.033
119	diatom-terrigenous	0.032
127	blue mud	0.072
131	red clay	0.071
132	red clay	0.069
133	red clay	0.071
136	red clay	0.086
137	red clay	0.033
151	red clay	0.114
156	red clay	0.050
157	globigerina ooze	0.010
160	globigerina ooze	0.038
	Average	0.047

From C. S. Piggot's Collection, Atlantic Ocean.

N 39° 13′ W 72° top of core	0.109
Bottom of core, 62″ below top	0.038
Hudson, No. 3	0.035
N 38° 10′ W 73° 50′	0.047
N 37° 26′ W 74° 28′ Maryland Canyon, 700 fathoms	0.039
N 37° 26′ W 74° 28′ Maryland Canyon, 228 fathoms	0.025
Average	0.048

From T. G. Thompson's Alaskan Collection.

B 14683	0.037
B 14684	0.023
B 14685	0.028
B 14686	0.038
B 14688	0.044
B 14690	0.021
B 14691	0.056

The Alaskan group was supplied by Dr. Horace G. Byers of the Bureau of Chemistry and Soils, U. S. Department of Agriculture. All consisted largely of volcanic ash.

The average of all ocean-bottom samples is 0.043% F.

In the first group of samples collected by the *Carnegie* we have indicated the nature of the material. The fluorine content of all specimens averages 0.047 per cent. With the exception of No. 6, these are all from the Pacific Ocean. Doctor Piggot's specimens are all from the Atlantic, with an average of 0.048 per cent F. The samples in the Alaskan group are all lower, averaging 0.035 per cent, but these are mostly volcanic ash and their fluorine content agrees with that of pumice (Nos. 12 and 13). The type of bottom is evidently important. Thus globigerina ooze, being largely calcium carbonate, might be expected to hold some excess of fluorine, but obviously calcium fluoride is too soluble in sea water to permit this. On the other hand, the aluminous clays retain larger amounts. The difference between the top and bottom of the core in Piggot's first sample is to be accounted for by such differences in composition.

In Fig. 1 we have plotted geographically the fluorine concentration of the ocean-bottom samples. The fluorine concentration is proportional to the diameter of the circles. With so few data one notes only trends, but some of these are suggestive. It appears, although the data are too few for certainty, that the Atlantic bottom is rather higher in fluorine than the Pacific, whereas there is a notable concentration of fluorine between the west coast of America and the Hawaiian Islands. In view of Zies's[9] observations on the great quantity of fluorine given off by the Alaskan area, and assuming that in the long continuance of Japanese volcanicity similar amounts must have been evolved in that region, we should expect the ocean bottom to have received much of this fluorine and that the samples would show a high content. We anticipated that the concentration would be high all along this northern arc. Instead we find low, or average, fluorine off the Japanese islands and the northern arc, and a notable concentration east of Hawaii. It is possible that this concentration is related to the turn of the ocean currents at this point but no similar richness appears off the South American coast where somewhat similar conditions prevail.

[9] Op. cit.

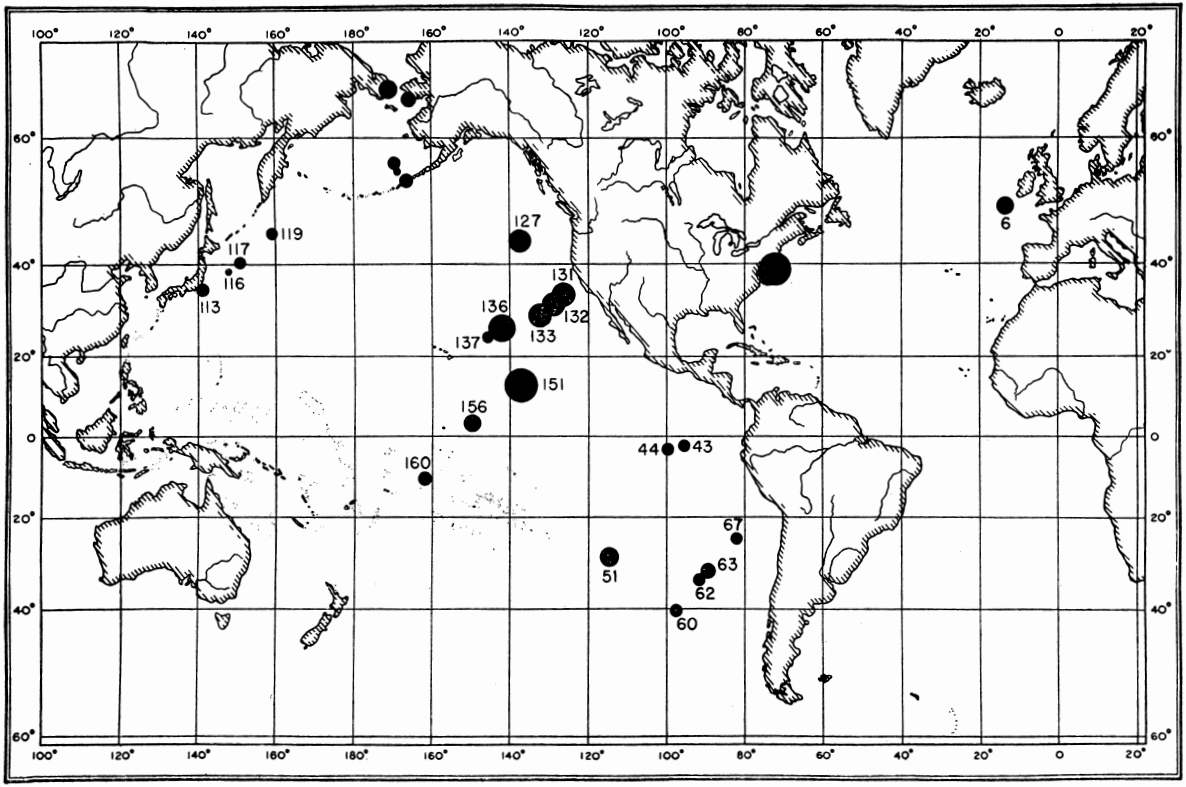

Fig. 1. Fluorine content of ocean-bottom samples. Fluorine concentration proportional to diameter of circles. Numbers refer to *Carnegie* stations.

SUMMARY.

One definite fact has been established. Fluorine is not an insignificant constituent of the Earth's crust, as had been supposed. It is evidently present in quantities as great as, and sometimes greater than, chlorine, and this poses a question for which there is at present no satisfying answer. The question is: What becomes of this fluorine? Zies has discussed this matter and summarized the answers thus far. It is true that great deposits of fluorine as well as of chlorine exist, but it is far from clear how the fluorine that is being released all over the Earth finds its way into such deposits. The ocean-bottom data shed some light on this, as do the few sedimentary rocks tested. Since 1933 much work has been done and is being done on the fluorine content of inland waters, and this work indicates again the spotty character of such concentrations in various geological formations. As this work continues we shall be able to trace the vagaries of this elusive element. It seems to the writer that when account is taken of all the known loci of fluorine there still remains a large amount unaccounted for, or else the chlorine present in the outer portions of the Earth did not all derive from the rocks.

To the geologist our data may be interesting but the characteristics of fluorine as a chemical agent point that interest. Here is an element about whose migrations we are as yet little informed. Chemically it is indeed active, but the readiness with which it forms transient compounds and the ease with which it will at times escape from such compounds unpredictably, are irritating. In the presence of organic matter and sometimes with only moisture and a little heat it may volatilize. The low temperature at which fluosilicic acid volatilizes with steam has been noted, so that fluorine may have been present or even of crucial importance in some metamorphic reactions and then have disappeared from the area. We know that at the temperatures of magmas fluorine increases the fluidity of the magma notably and yet although much fluorine has been evolved at Katmai relatively little of it remains.

Either as SiF_4 or as fluosilicic acid, fluorine may deposit silica at one point or another and then pass on, a phenomenon observed with disgust by any analyst who has tried to study the element in the laboratory. One might say that often it leaves a trail of silica behind it wherever it goes and even in its most firmly bound condition may elude one either by volatiliza-

tion or going colloidal. We are as yet ignorant of definite criteria by which its former presence can be established.

A great many more analyses will be necessary before any certainty can adhere to such inferences as we may draw from the above data. As we have emphasized throughout, the best we can do is to indicate trends only. It is believed, however, that we have covered enough ground to show the need of further study and to indicate directions along which such tests may be profitable.

In a tentative way we may assume that about 0.04 per cent F. is characteristic of plutonic rocks. The lavas examined tend toward about 0.01 per cent even where large amounts of fluorine are known to have been exhaled. Next in order of concentration fall the sedimentaries, while the greatest average concentration seems to lie with the obsidians. Certain regions seem to show local concentrations, as do the alkaline rocks, but more data are needed on this point.

We tried plotting fluorine against other rock-forming elements but without success. It did not, as had been suggested, increase in proportion to phosphorus. In fact, our data showed no definite relationships except a dubious one with potassium. All questions remain open but it is hoped that our data will encourage others to take note of the presence or absence of this element now that adequate methods are available.

The writer is indebted as always to his colleagues for material and help: in particular to Drs. H. E. Merwin and E. G. Zies; to Dr. C. S. Piggot for several ocean-bottom specimens; to Dr. J. A. Fleming for the *Carnegie* collection; and to Dr. Horace Byers for specimens from the Aleutian-Behring Sea area. It is planned to continue the work until a reasonable body of data has accumulated, and it is hoped that others who are prepared to do so will also gather such information as may come their way.

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